NHC–silicon(I) dimer : key to unlock catalytic capability of low-valent silicon complexes

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**NHC–SILICON(I) DIMER: KEY TO UNLOCK CATALYTIC
CAPABILITY OF LOW-VALENT SILICON COMPLEXES**

LEONG BI XIANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2021

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LEONG BI XIANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Bi-Xiang LEONG

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I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 4 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as first author with or without equal contribution.

Chapter 1 is published as Chan, Y.-C. Chan,[‡] B.-X. Leong,[‡] Y. Li, M.-C. Yang, Y. Li, M.-D. Su* and C.-W. So.* A Dimeric NHC–Silicon Monotelluride: Synthesis, Isomerization, and Reactivity. *Angewandte Chemie International Edition* **56**, 11565-11569 (2017). DOI: [10.1002/anie.201705168](https://doi.org/10.1002/anie.201705168).

[‡] Denotes first author with equal contribution.

The contributions of the co-authors are as follows:

- Assoc. Prof. Dr. C.-W. So outlined the initial project direction and prepared the manuscript drafts. Dr. Y.-C. Chan and I edited and revised the manuscript drafts. Dr. Y. Li commented on the final manuscript draft.
- I co-designed the study with Assoc. Prof. Dr. C.-W. So and Dr. Y.-C. Chan.
- Dr. Y.-C. Chan optimized the synthesis of compounds **1.13-I** and **1.17**.
- Dr. Y.-C. Chan designed the synthesis route to compound **1.32**. I synthesized compounds **1.31**, **1.33**, **1.34-Te** and **1.34-S**.
- I proposed and proved the reaction mechanism experimentally.
- All laboratory syntheses, analyses and characterization methods were conducted by Dr. Y.-C. Chan (compound **1.32**) and me (compounds **1.31**, **1.33**, **1.34-Te** and **1.34-S**) at the Division of Chemistry and Biological Chemistry.
- Dr. Y. Li provided X-ray crystallographic analyses and data.
- M.-C. Yang and Prof. Dr. M.-D. Su performed DFT computation.

Chapter 2 is published as Y. Li,[‡] Y.-C. Chan,[‡] B.-X. Leong,[‡] Y. Li, E. Richards,^{*} I. Purushothaman, S. De, P. Parameswaran^{*} and C.-W. So.^{*} Trapping a Silicon(I) Radical with Carbenes: A Cationic cAAC-Silicon(I) Radical and an NHC–Parent-Silyliumylidene Cation. *Angewandte Chemie International Edition* **56**, 7573-7578 (2017). DOI: [10.1002/anie.201702760](https://doi.org/10.1002/anie.201702760).

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- Assoc. Prof. Dr. C.-W. So outlined the initial project direction and prepared the manuscript drafts. Dr. Y. Li, Dr Y.-C. Chan Dr. E. Richards, I. Purushothaman, Dr. S. De, Prof. Dr. P. Parameswaran and I edited and revised the manuscript drafts.
- I co-designed the study with Assoc. Prof. Dr. C.-W. So, Dr. Y.-C. Chan and Dr. Y. Li.
- Dr. Y.-C. Chan designed the synthesis route to compound **2.20**. I prepared compound **2.20** for characterization and reactivity study. I synthesized compound **2.21**. Dr. Y. Li synthesized compound **2.22**.
- All laboratory syntheses, analyses and characterization methods were conducted by Dr. Y. Li (compound **2.22**) and me (compounds **2.20** and **2.21**) at the Division of Chemistry and Biological Chemistry.
- Dr. E. Richards provided EPR analyses and data.
- Dr. Y. Li provided X-ray crystallographic analyses and data.
- I. Purushothaman, Dr. S. De and Prof. Dr. P. Parameswaran performed DFT computation.

Chapter 3 is published as B.-X. Leong, J. Lee, Y. Li, M.-C. Yang, C.-K. Siu,* M.-D. Su* and C.-W. So.* A Versatile NHC–Parent Silyliumylidene Cation for Catalytic Chemo- and Regioselective Hydroboration. *Journal of American Chemical Society* **141**, 17629-17636 (2019); B.-X. Leong,[‡] Y.-C. Teo,[‡] C. Condamines, M.-C. Yang, M.-D. Su,* C.-W. So.* A NHC–Silyliumylidene Cation for Catalytic *N*-Formylation of Amines Using Carbon Dioxide. *ACS Catalysis* **10**, 14824-14833 (2020). DOI: [10.1021/jacs.9b06714](https://doi.org/10.1021/jacs.9b06714) and [10.1021/acscatal.0c03795](https://doi.org/10.1021/acscatal.0c03795), respectively.

[‡] Denotes first author with equal contribution.

The contributions of the co-authors for the **first paper** are as follows:

- Assoc. Prof. Dr. C.-W. So outlined the initial project direction and prepared the manuscript drafts. J. Lee and I edited and revised the manuscript drafts.
- I co-designed the study with Assoc. Prof. Dr. C.-W. So and Dr. Y. Li.
- I prepared compound **2.20**. Dr. Y. Li explored the catalytic ability of compound **2.20** in hydroboration of aldehyde, ketone and pyridine derivatives. I examined the feasibility of **2.20**-catalyzed hydroboration of carbon dioxide.
- I performed optimization of carbon dioxide and aldehyde. Dr. Y. Li and J. Lee performed optimization of aldehyde, ketone, and pyridine.
- I performed **2.20**-catalyzed hydroboration of CO₂. Dr. Y. Li, J. Lee and I performed catalysis for aldehyde, ketone, and pyridine derivatives using compound **2.20**. I performed **3.28**-catalyzed hydroboration of CO₂, aldehydes, ketones, and pyridines.
- I designed and performed isolation methods for the resultant borate esters and *N*-boryl-1,4-dihydropyridine derivatives.
- Assoc. Prof. Dr. C.-W. So and I proposed the reaction mechanism.
- I carried out all mechanism studies experimentally, inclusive of stepwise reactions, blank reactions and the catalytic feasibility using I_{Me}.
- I synthesized compound **3.29**.
- All laboratory work, analyses and characterization methods were conducted by Dr. Y. Li, J. Lee and me at the Division of Chemistry and Biological Chemistry.
- Prof. Dr. C.-K. Siu, M.-C. Yang and Prof. Dr. M.-D. Su performed DFT computation.

The contributions of the co-authors for the **second paper** are as follows:

- I proposed the initial project direction. Assoc. Prof. Dr. C.-W. So prepared the manuscript drafts. Y.-C. Teo and I edited and revised the manuscript drafts.
- I co-designed the study with Assoc. Prof. Dr. C.-W. So.
- I prepared compound **2.20** and explored the feasibility of **2.20**-catalyzed *N*-formylation of amine using carbon dioxide.
- Y.-C. Teo and I performed optimization for catalytic *N*-formylation.
- Y.-C. Teo performed catalysis at 40 and 90 °C whereas C. Condamines contributed to the catalysis performed at 60 °C.
- I designed the isolation methods and Y.-C. Teo carried out the isolation of the resultant *N*-formylated amines.
- I isolated suitable crystals of compound **3.31m**, **3.31p** and **3.31w** for X-ray crystallographic analysis.
- Y.-C. Teo performed gram scale reaction and *d*-labeling reactions.
- Assoc. Prof. Dr. C.-W. So proposed the reaction mechanism.
- I performed mechanism studies experimentally, inclusive of stepwise reactions, blank reactions and catalytic hydrosilylation of CO₂. Y.-C. Teo performed stepwise hydrosilylation of carbon dioxide before subsequent addition of amine.
- All laboratory work, analyses and characterization methods were conducted by Y. C. Teo, C. Condamines and me at the Division of Chemistry and Biological Chemistry.
- M.-C. Yang and Prof. Dr. M.-D. Su performed DFT computation.

29th December 2020

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Date

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Bi-Xiang LEONG

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Signing off,

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ABSTRACT

This dissertation generally narrates the reactivity of *N*-heterocyclic carbene (NHC)–silicon(I) dimer as building block for construction of various low-valent silicon complexes and their application in catalysis.

Chapter 1 describes the reactivity of dimeric NHC–silicon(I) iodide $[\text{I}_{\text{Ar}}\text{Si}(\text{I})]_2$ (**1.13-I**, $\text{I}_{\text{Ar}} = :\text{C}\{\text{N}(\text{Ar})\text{CH}\}_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) and its reduced form of dimeric NHC–disilicon(0) complex $[(\text{I}_{\text{Ar}})\text{Si}=\text{Si}(\text{I}_{\text{Ar}})]$ (**1.17**) with elemental tellurium. The reaction of the NHC–disilicon(0) complex **1.17** with four equivalents of elemental Te in toluene for four weeks proceeded through the formation of the first dimeric NHC–silicon monotelluride $[(\text{I}_{\text{Ar}})\text{Si}=\text{Te}]_2$ (**1.31**), its isomeric complex $[(\text{I}_{\text{Ar}})\text{Si}(\mu\text{-Te})\text{Si}(\text{I}_{\text{Ar}})=\text{Te}]$ (**1.32**) and the NHC–disilicon tritelluride complex $[\{(\text{I}_{\text{Ar}})\text{Si}(=\text{Te})\}_2\text{Te}]$ (**1.34-Te**), to form the dimeric NHC–silicon ditelluride $[(\text{I}_{\text{Ar}})\text{Si}(=\text{Te})(\mu\text{-Te})]_2$ (**1.33**). The reaction is further supported when the reaction is subjected to stepwise addition of elemental Te, in agreement with theoretical mechanistic studies for the formation of **1.33**. Further, compound **1.32** reacted with one equivalents of elemental S in toluene to form the first NHC–disilicon sulfur ditelluride complex $[\{(\text{I}_{\text{Ar}})\text{Si}(=\text{Te})\}_2\text{S}]$ (**1.34-S**). Finally, the reaction of compound **1.13-I** with 2 equivalents of elemental Te furnished a dimeric NHC–silicon(III) iodo(μ -telluride) radical $[\text{I}_{\text{Ar}}(\text{I})(\mu\text{-Te})\text{Si}^\bullet]_2$ (**1.35**), exhibits both a major singlet biradical and minor triplet spin states in a single molecule.

Chapter 2 documents the interaction of complex **1.13-I** with less steric NHC I_{Me} ($I_{Me} = :C\{N(Me)CMe\}_2$). Treatment of **1.13-I** with 4 equivalents of I_{Me} proceeded through the formation of a silicon(I) radical intermediate, afforded $[(I_{Me})_2SiH]^+I^-$ (**2.20**) comprising the first NHC–parent–silyliumylidene cation. Its further reaction with fluorobenzene afforded the $C_{Ar}-H$ bond activation product $[1-F-2-I_{Me}-C_6H_4]^+I^-$ (**2.21**). Subsequently, the trapping of a silicon(I) radical with *N*-heterocyclic carbenes is described. The reaction of the cyclic (alkyl)(amino) carbene $[cAAC_{Me}]$ ($cAAC_{Me} = :C(CMe_2)_2(CH_2)NAr$) with H_2SiI_2 in a 3:1 molar ratio in DME afforded a mixture of the separated ion pair $[(cAAC_{Me})_2Si:]^+I^-$ (**2.22**), which features a cationic $cAAC$ –silicon(I) radical, and $[cAAC_{Me}-H]^+I^-$. The isolation of **2.22** confirmed the reaction mechanism for the formation of **2.20** and **2.21**.

An insight to the practical utility of our work is presented in **Chapter 3**, in which we introduce first use of a silicon(II) complex, NHC–parent–silyliumylidene cation complex **2.20** as a versatile catalyst in organic synthesis. Complex **2.20** (loading: 10 mol %) was shown to act as an efficient catalyst (reaction time: 0.08 h, yield: 94%, TOF = 113.2 h⁻¹; reaction time: 0.17 h, yield: 98%, TOF = 58.7 h⁻¹) for the selective reduction of CO₂ with pinacolborane (HBpin) to form the primarily reduced formoxyborane [pinBOC(=O)H]. The activity is better than the currently available base-metal catalysts used for this reaction. In addition, complex **2.20**-catalyzed chemo- and regioselective hydroboration of carbonyl compounds and pyridine derivatives afforded borate esters and *N*-boryl-1,4-dihydropyridine derivatives with quantitative conversions, respectively. Mechanistic studies show that the silicon(II) center in complex **2.20** activated the substrates and then mediated the catalytic hydroboration. In addition, complex **2.20** was slightly converted into the NHC–borylsilyliumylidene complex [(Ime)₂SiBpin]I (**3.28**) in the catalysis, which was also able to mediate the catalytic hydroboration. The catalytic capability of complex **2.20** could further extended to *N*-formylation of primary and secondary amines to afford quantitative yields of *N*-formamides with high selectivity. Mechanistic studies showed that complex **2.20** sequentially activates CO₂, PhSiH₃, and amines, which proceeds via a dihydrogen elimination mechanism, to form formamides, siloxanes, and dihydrogen gas.

Chapter 4 explores the catalytic capability of complex **1.13-I** in hydroboration of CO₂, with its efficiency increased with an increment in BH₃ additive. The final reactivity probed the reaction of complex **1.13-I** with borane BH₃.THF to feature the first unsymmetric silicon(I) complex containing a silicon(I) hydride moiety, NHC/BH₃-stabilized hydridosilicon(I)-iodosilicon(I) complex [I_{Ar}Si(BH₃)(H)–Si(BH₃)(I)I_{Ar}] (**4.13**). Complex **4.13** exhibited similar activity as **1.13-I** in the presence of BH₃ additive (20 and 45 mol %), which was a pre-catalyst to mediate CO₂ hydroboration via Si⁰/Si^{II} species. An extension of work covered chemo- and regioselective catalytic *N*-formylation of primary and secondary amines to afford the respective high yields of *N*-formamides, along with its catalytic hydroboration of aldehyde and ketone derivatives to yield borate esters.

Chapter 5 offers an overview on the recent advances of main group p-block (Group 13 – 15) complexes in cheaper, greener, and sustainable metal-free organic transformations. The common strategies involved in activation of unsaturated substrates can be categorized as such, (i) Lewis acid (LA) and/or Lewis base (LB) mechanism, (ii) E–H σ -bond metathesis, (iii) multiply bonded heavier main group element and (iv) filled and vacant coordination site. Next, we summarize the focal point of this thesis, along with its implication on the scientific and industry communities. Lastly, we describe the future aspiration, opportunities, and outlook in designing robust, newer generation of main group-derived application in sustainable organic synthesis in chemical industry.

TABLE OF CONTENT

ACKNOWLEDGEMENTS	i
ABSTRACT.....	iii
TABLE OF CONTENT	vii
LIST OF CHARTS	x
LIST OF SCHEMES	xii
LIST OF TABLES	xv
LIST OF FIGURES	xviii
LIST OF ABBREVIATIONS AND SYMBOLS.....	xxviii
LIST OF SYNTHESIZED COMPOUNDS	xxxix
Chapter 1: N-Heterocyclic Carbene-stabilized Silicon(0/I) Complexes and Their Reactivity toward Chalcogen.....	1
1.1 Introduction.....	1
1.2 Results and Discussion	9
1.2.1 Optimizing the Synthesis of NHC–Silicon(I) Dimer (1.13-I)	9
1.2.2 Synthesis of NHC–Silicon(0) Dimer (1.17)	13
1.2.3 Reactivity of NHC–Silicon(0) Dimer (1.17) toward Chalcogen	17
1.2.4 Reactivity of NHC–stabilized Silicon(I) Dimer (1.13-I) toward Tellurium	27
1.3 Conclusion	32
1.4 Experimental	33
1.4.1 Optimized Synthesis of NHC–Silicon(I) Dimer (1.13-I) and Reduction of NHC–Silicon(0) Dimer (1.17)	34
1.4.2 Reactivity of NHC–stabilized Silicon(0) Dimer (1.17) toward Chalcogen	35
1.4.3 Reactivity of NHC–Silicon(I) Dimer (1.13-I) toward Tellurium	39
1.5 Appendices.....	40
1.5.1 NMR Spectra	40
1.5.2 UV-Visible Spectra of Compounds 1.32 – 1.33 and 1.35	56
1.5.3 Crystallographic Data of All Structures	58
1.5.4 Theoretical Studies	60
1.6 References.....	126
Chapter 2: A Parent NHC-stabilized Silyliumylidene Cation.....	130
2.1 Introduction.....	130
2.2 Results and Discussion	137
2.2.1 Synthesis of a Parent NHC–Silyliumylidene Cation (2.20)	137

2.3	Conclusion	149
2.4	Experimental	150
2.4.1	Synthesis of a Parent NHC–Silyliumylidene Cation (2.20) and cAAC-Silicon(I) Cation (2.22)	151
2.5	Appendices.....	157
2.5.1	NMR Spectra	157
2.5.2	UV-Visible Spectrum of a Parent NHC–Silyliumylidene Cation (2.20) and cAAC-Silicon(I) Cation (2.22)	161
2.5.3	Crystallographic Data of All Structures	162
2.5.4	Theoretical Studies	165
2.6	References.....	182
Chapter 3: A Parent NHC–Silyliumylidene Cation in Catalysis		186
3.1	Introduction.....	186
3.2	Results and Discussion	196
3.2.1	A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of CO ₂	196
3.2.2	A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic <i>N</i> -formylation of Amines	204
3.2.3	A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of Aldehyde, Ketone and Pyridine Derivatives	217
3.3	Conclusion	224
3.4	Experimental	225
3.4.1	A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of CO ₂	226
3.4.2	A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic <i>N</i> -formylation of Amines	234
3.4.3	A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of Aldehyde, Ketone and Pyridine Derivatives	256
3.5	Appendices.....	273
3.5.1	NMR Spectra	273
3.5.2	Crystallographic Data of All Structures	384
3.5.3	Theoretical Studies	388
3.6	References.....	451
Chapter 4: A Lewis Acid and Base-Stabilized Silicon(I) Hydride and Its Application in Catalysis.....		457
4.1	Introduction.....	457
4.2	Results and Discussion	461
4.2.1	Dimeric NHC-Silicon(I) Iodide (1.13-I) in Catalytic Hydroboration of CO ₂	461
4.2.2	Synthesis of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13)	463
4.2.3	Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of CO ₂ and <i>N</i> -formylation	465
4.2.4	Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of Aldehyde and Ketone Derivatives	478
4.3	Conclusion	481
4.4	Experimental	482
4.4.1	Dimeric NHC-Silicon(I) Iodide (1.13-I) in Catalytic Hydroboration of CO ₂	483
4.4.2	Synthesis of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13)	485
4.4.3	Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of CO ₂ and <i>N</i> -formylation	486

4.4.4	Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of Aldehyde and Ketone Derivatives	500
4.5	Appendices.....	511
4.5.1	NMR Spectra	511
4.5.2	Crystallographic Data of All Structures	561
4.6	References.....	563
 Chapter 5: Renaissance of p-block Elements: From Organoreagents to Efficient Catalysts..... 566		
5.1	Main Group Elements as Transition Metals: Towards Catalysis.....	566
5.1.1	Lewis Acid Mechanism	568
5.1.2	Frustrated Lewis Pair Mechanism	569
5.1.3	Main Group Element Hydride Mechanism	572
5.1.4	Multiply Bonded Heavier Main Group Element	581
5.1.5	Filled and Vacant Coordination Site	585
5.2	Research Implication: Now and Then	595
5.3	Conclusion and Outlook.....	602
5.4	References.....	603

LIST OF CHARTS

Chart 1. 1	Schematic representation of a silylene.....	1
Chart 1. 2	Selected examples of silylenes.	2
Chart 1. 3	Examples of silicon-based alkyne analogues, disilynes.....	3
Chart 1. 4	Selected orbital interactions in linear D_{2h} and trans-bent C_{2h} $RE\equiv ER$ model.....	4
Chart 1. 5	Bonding model in (a) linear alkyne and (b) heavy homonuclear tetryne and its constitutional isomer silicon(I) dimer.	5
Chart 1. 6	Isolated base-stabilized silicon(I) dimers.....	6
Chart 1. 7	Base-stabilized silicon(0) dimers.....	7
Chart 1. 8	Multi-reactive sites of compound 1.13-I	8
Chart 1. 9	Reactivity of NHC-stabilized silicon(I) dimer 1.13-I	9
Chart 1. 10	Reactivity of NHC-stabilized silicon(I) dimer 1.13-I	10
Chart 1. 11	Reactivity of NHC-stabilized silicon(0) dimer 1.17	14
Chart 1. 12	Reactivity of Lewis base-stabilized mono- and disilicon(0) towards chalcogen.....	15
Chart 2. 1	Selected examples of silylium ions.....	131
Chart 2. 2	Selected examples of silylium ion-catalyzed reactions.	131
Chart 2. 3	Schematic representation of a free (left) and donor-stabilized silyliumylidene ions (center and right).	132
Chart 2. 4	Selected examples of base-stabilized silyliumylidenes.	134
Chart 2. 5	Bonding model in silicon(I) dimer and its constitutional isomer silicon(I) radical (center) and silicon(I) radical ion pair (right).	135
Chart 2. 6	Correlation between silicon(I) radical cation and silyliumylidene ion.	136
Chart 3. 1	Bonding model for the interaction of H_2 with (a) transition metal, (b) multiply bonded heavier main group element, (c) frustrated Lewis pair (d) singlet tetrylene.	187
Chart 3. 2	Mechanism for H_2 activation using heavier main group alkyne analogue.....	188
Chart 3. 3	Low-valent main group complexes in activation of H_2 ; (a) digermynes, (b) frustrated Lewis pair and (c) silylenes.	189
Chart 3. 4	Examples of silylene-mediated oxidative addition of small molecules.	190
Chart 3. 5	Generic catalytic cycle for transition metal (left) and main group element (right).....	191
Chart 3. 6	Reversible complexation of small molecules by silylenes.....	193
Chart 3. 7	Selected catalytic reactions mediated by heavier main group complexes.	194
Chart 3. 8	Examples of catalysts in hydroboration of CO_2	196
Chart 3. 9	Organocatalytic C–N bond formation using CO_2	205
Chart 3. 10	Selected recent advances in hydroboration of carbonyl derivatives.	217
Chart 3. 11	Recent advances in hydroboration of pyridine and quinoline derivatives.	218
Chart 4. 1	Low-oxidation state silicon complexes in catalysis.....	458
Chart 4. 2	Examples of palladium(I) dimer pre-catalysts.....	460
Chart 5. 1	Activation modes of main group complexes in catalysis.....	566
Chart 5. 2	Single site borenium ions in catalytic Diels-Alder and 1,3-dipolar cycloaddition reactions.	568
Chart 5. 3	FLP catalysts.....	569

Chart 5. 4 Single site Group 13 catalysts for hydroboration reactions.	573
Chart 5. 5 Group 14 element hydride 5.11 in catalysis.....	575
Chart 5. 6 Selected examples of DAP hydride 5.12 in catalysis.	578
Chart 5. 7 NHPs 5.13 - and 5.14 -catalyzed hydroboration of pyridine derivatives.....	579
Chart 5. 8 Multiply bonded Group 13 catalysts.....	582
Chart 5. 9 Single site heavier Group 14 catalysts.....	587
Chart 5. 10 Methoxystannalyne 5.23 -catalyze dehydrocoupling of amines.....	588
Chart 5. 11 Proazaphosphatranes catalyst 5.25 in hydroboration and functionalization of CO ₂	590
Chart 5. 12 Selected examples of DAP and DAAs pre-catalysts.	592
Chart 5. 13 Phosphetanes 5.34 -catalyze Wittig reaction.	593
Chart 5. 14 Selected examples of phosphetanes in catalysis.	594
Chart 5. 15 Versatility of silicon(II) cation 2.20 (this work).	596
Chart 5. 16 Versatility of asymmetrical silicon(I) dimer 4.13 (this work).	597
Chart 5. 17 Catalytic reactions mediated by NHC–germanium(II) cation 5.38	598
Chart 5. 18 Heavier Group 14 element(II) cation 5.39 – 5.40 in organosilicon chemistry.	601

LIST OF SCHEMES

Scheme 1. 1 Optimized synthesis of NHC–stabilized silicon(I) dimer 1.13-I	11
Scheme 1. 2 Synthesis of NHC–stabilized silicon(0) dimer 1.17	13
Scheme 1. 3 Synthesis of compounds 1.31 – 1.33 . The formation of compound 1.33 through the NHC–disilicon tritelluride intermediate 1.34-Te is also shown.	18
Scheme 1. 4 Free energy profile (kcal/mol) for the formation of compounds 1.31 – 1.33 at M06-2X/def2-SVP level of theory.	22
Scheme 1. 5 Synthesis of compounds 1.34-S, 1.34-Te and 1.33	25
Scheme 1. 6 Synthesis of 1.35	27
Scheme 2. 1 Syntheses of compounds 2.20 and 2.21 . The proposed mechanism for the formation of 2.20 through the silicon(I) radical intermediate 2.20a is also shown.	137
Scheme 2. 2 Proposed mechanism for the formation of compound 2.21	140
Scheme 2. 3 Synthesis of 2.22	142
Scheme 2. 4 Proposed mechanism of 2.22	143
Scheme S2. 1 Schematic representation of a) in phase (++) donation of the I _{Me} carbene σ lone pair orbitals into the vacant p-orbital on Si and b) the out of phase (+-) donation to the other vacant p-orbital on Si. The in phase (++) combination of lone pairs donates two electrons to the p _y -orbital of Si and the out of phase (+-) combination of lone pairs donates two electrons to the p _x -orbital of Si.	169
Scheme S2. 2 Schematic representation of a) in phase (++) donation of the cAAC _{Me} σ lone pair orbitals into the vacant p-orbital on Si and b) the out of phase (+-) donation to the other vacant p-orbital on Si. The in phase (++) combination of lone pairs donates two electrons to the p _y -orbital of Si and the out of phase (+-) combination of lone pairs donates two electrons to the p _x -orbital of Si.	169
Scheme 3. 1 2.20 -catalyzed reduction of CO ₂ . (All the catalytic trials were repeated in triplicate) .	197
Scheme 3. 2 Synthesis of compound 3.28	199
Scheme 3. 3 Calculated Gibbs free energies (ΔG _{rel}) for the reaction of 2.20 , CO ₂ and HBpin at 24 °C (M06-2X/def2-TZVP). Int and TS stands for intermediate and transition state..	200
Scheme 3. 4 Calculated Gibbs free energies (ΔG _{rel}) via 3.28 at 24 °C (M06-2X/def2-TZVP).	202
Scheme 3. 5 DFT calculations for catalytic <i>N</i> -formylation of amines with CO ₂ and PhSiH ₃	212
Scheme 3. 6 Deuterium-labelling study using <i>d</i> ₁₁ -piperidine (<i>D</i> , 98%).	213
Scheme 3. 7 Scrambling reaction with <i>d</i> ₁₁ -piperidine (<i>D</i> , 98%) and piperidine in 1:1 ratio.	214
Scheme 3. 8 2.20 -catalyzed hydrosilylation of CO ₂	214
Scheme 3. 9 DFT calculations for catalytic hydrosilylation of CO ₂	215
Scheme S3. 1 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, CO ₂ , HBpin, Int, I _{Me} and TS stand for compound, carbon dioxide, pinacolborane, intermediate, [·C{N(Me)C(Me)} ₂] and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states and compounds	

2.20 and 3.28 are at M06-2X/def2-TZVP level of theory. No transition state was found between compound 2.20 and Int3.2, which indicates that the reaction from Cpd2.20 to Int3.2 should have a pretty low barrier, which is not easy to find out, or a non-barrier process.....	395
Scheme S3. 2 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, CO ₂ , HBpin, Int and TS stand for compound, carbon dioxide, pinacolborane, intermediate and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states and compounds 2.20 and 3.27a are at M06-2X/def2-TZVP level of theory.	396
Scheme S3. 3 Mechanism for the reaction of compound 2.20 with CO ₂ and HBpin to afford compound 3.27a with the regeneration of compound 2.20.....	397
Scheme S3. 4 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, CO ₂ , Int and TS stand for compound, carbon dioxide, intermediate and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states, compounds 2.20 and 3.27a are at M06-2X/def2-TZVP level of theory.	398
Scheme S3. 5 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, Int and TS stand for compound, intermediate and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states and compounds 2.20 and 3.27a are at M06-2X/def2-TZVP level of theory.	399
Scheme S3. 6 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 25 °C and 1 atm for catalytic <i>N</i> -formylation reaction. The abbreviations Cpd, der., Int and TS stand for compound, derivative, intermediate and transition state, respectively. Geometrical coordinates of the compound 2.20, PhSiH ₃ , compound 3.30u, amine derivative, intermediates, transition states, H ₂ , formamide 3.31u and (PhSiH ₂) ₂ O are at M06-2X/def2-TZVP level of theory.	431
Scheme S3. 7 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 25 °C and 1 atm for catalytic hydrosilylation of CO ₂ . The abbreviations Cpd, Int and TS stand for compound, intermediate and transition state, respectively. Geometrical coordinates of the compound 2.20, PhSiH ₃ , intermediates, transition states and PhH ₂ SiOC(O)H are at M06-2X/def2-TZVP level of theory.	432
Scheme 4. 1 Synthesis of 4.13.....	463
Scheme 4. 2 4.13-catalysed reduction of CO ₂	465
Scheme 4. 3 DFT calculations for 4.13-catalyzed hydroboration of CO ₂	467
Scheme 4. 4 Deuterium-labelling study using d ₁₁ -piperidine 4.16b-D (<i>D</i> , 98%).....	475
Scheme 4. 5 Proposed mechanism for complex 4.13-catalyzed <i>N</i> -formylation of amine.....	476
Scheme 5. 1 Mechanism for phosphine-borane 5.4-catalyzed hydroboration of CO ₂	570
Scheme 5. 2 Mechanism for diazaborinium 5.6-catalyzed <i>N</i> -formylation of amines.	571
Scheme 5. 3 Mechanism for aluminum hydride 5.9-catalyzed hydroboration of CO ₂	574
Scheme 5. 4 Mechanism for aluminum hydride 5.8-catalyzed cyanosilylation of carbonyl derivatives.	574
Scheme 5. 5 Mechanism for germanium(II) 5.11-catalyzed catalytic reduction of CO ₂	576
Scheme 5. 6 Mechanism for neutral tetrylene E-H 5.11-catalyzed hydroboration of carbonyl derivatives.	576
Scheme 5. 7 Mechanism for DAP hydride 5.12-catalyzed <i>N</i> -formylation of amines using CO ₂	578
Scheme 5. 8 Mechanism for NHPs 5.13-catalyzed hydroboration of pyridine derivatives.....	580
Scheme 5. 9 Mechanism for dialumene 5.15-Si-catalyzed hydroboration of CO ₂	583

Scheme 5. 10 Digermynes 5.17 -catalyzed cyclotrimerization of terminal arylacetylenes.....	584
Scheme 5. 11 Single site silicon(II) cation 5.18 in controlled degradation of oligoethers.	585
Scheme 5. 12 Mechanism for germa-acylium cation 5.19 -catalyzed C–N bond formation using CO ₂ with secondary amine.....	586
Scheme 5. 13 Mechanism for neutral tetrylenes 5.20 - and 5.21 -catalyzed hydroboration of carbonyl derivatives.	588
Scheme 5. 14 Mechanism for intramolecular tetrylenes 5.24 -catalyzed hydroboration of carbonyl derivatives.	589
Scheme 5. 15 Mechanism for proazaphosphatranes 5.25 -catalyzed <i>N</i> -methylation of CO ₂	591
Scheme 5. 16 Phosphine 5.26 catalyst in transfer hydrogenation of diphenylhydrazine.	592
Scheme 5. 17 Mechanism for germanium(II) cation 5.38 -catalyzed hydroboration of aldehydes....	599
Scheme 5. 18 Mechanism for germanium(II) cation 5.38 -catalyzed in C–N bond formation using CO ₂	600
Scheme 5. 19 Mechanism for heavier Group 14 element(II) cation 5.39 – 5.40 in organosilicon chemistry.....	601

LIST OF TABLES

Table S1. 1 Crystallographic data of 1.31 – 1.35	59
Table S1. 2 Occupancies and Second-Order Perturbation Energies, ΔE_{ij} (kcal/mol), derived from NBO Analysis for Compounds 1.31 – 1.33 at M06-2X/def2-SVP Level of Theory	69
Table S1. 3 EDA-NOCV results of chemical bonding in compounds 1.31 – 1.33 at M06-2X/DZP level of theory.	72
Table S1. 4 Optimized cartesian coordinates of compound 1.17	74
Table S1. 5 Optimized cartesian coordinates of Int1.1	77
Table S1. 6 Optimized cartesian coordinates of TS1.1	80
Table S1. 7 Optimized cartesian coordinates of Int1.2	83
Table S1. 8 Optimized cartesian coordinates of PRC	86
Table S1. 9 Optimized cartesian coordinates of TS1.2	90
Table S1. 10 Optimized cartesian coordinates of Int1.3	93
Table S1. 11 Optimized cartesian coordinates of TS1.3	96
Table S1. 12 Optimized cartesian coordinates of compound 1.31	99
Table S1. 13 Optimized cartesian coordinates of TS1.4	103
Table S1. 14 Optimized cartesian coordinates of compound 1.32	106
Table S1. 15 Optimized cartesian coordinates of Int1.4	109
Table S1. 16 Optimized cartesian coordinates of TS1.5	112
Table S1. 17 Optimized cartesian coordinates of Int1.5	116
Table S1. 18 Optimized cartesian coordinates of compound 1.33	119
Table S1. 19 Mulliken charge (q) and spin density (s) on the selected atoms of singlet and triplet 1.35 at the BP86/def2-SVP level of theory.	124
 Table 2. 1 Spin Hamiltonian parameters for compound 2.22	 145
 Table S2. 1 Crystallographic data of compounds 2.20, 2.21 and 2.22 (C ₆ H ₅ F)	 164
Table S2. 2 Charge distribution given by the Natural Bond Orbital Analysis for 2.20, 2.20a and 2.22 at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	167
Table S2. 3 Selected Wiberg bond orders and bond occupancies given by the Natural Population Analysis for 2.20, 2.20a and 2.22 at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	168
Table S2. 4 NBO spin densities given by the Natural Population Analysis for 2.20a and 2.22 at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	168
Table S2. 5 EDA-NOCV results of Si-C1 and Si-C2 bonds of 2.20 , Si-C1 and Si-C2 bonds of 2.20a , and Si-C1 and Si-C21 bonds of 2.22 at the BP86/TZ2P level of theory.	170
Table S2. 6 Optimized cartesian coordinates of compound 2.20	174
Table S2. 7 Optimized cartesian coordinates of compound 2.20a	175
Table S2. 8 Optimized cartesian coordinates of compound 2.22 (C1)	176
Table S2. 9 Optimized cartesian coordinates of cAAC _{Me}	179
Table S2. 10 Optimized cartesian coordinates of I _{PrMe}	181

Table 3. 1 Optimization of <i>N</i> -formylation of amines with CO ₂ and PhSiH ₃	206
Table 3. 2 Scope of Primary Amine Substrates.....	207
Table 3. 3 Scope of Secondary Amine Substrates.....	210
Table 3. 4 <i>N</i> -formylation of amines via silylformates resulting in low yields of 3.31	216
Table 3. 5 Scope of Aldehyde Substrates.....	220
Table 3. 6 Scope of Ketone Substrates.....	221
Table 3. 7 Scope of Pyridine Substrates.....	222
Table S3. 1 Catalytic table for hydroboration of CO ₂ using HBpin.....	231
Table S3. 2 Catalytic table for hydroboration of CO ₂ using HBpin in C ₆ D ₆ containing O ₂ and/or H ₂ O.	232
Table S3. 3 Catalytic table for hydroboration of CO ₂ using BH ₃ ·SMe ₂	233
Table S3. 4 Catalytic table for hydroboration of CO ₂ using HBcat.	233
Table S3. 5 Catalytic table for <i>N</i> -formylation of amines using CO ₂	235
Table S3. 6 Catalytic table for the stepwise <i>N</i> -formylation of amines using CO ₂ via silylformate intermediates.....	239
Table S3. 7 Catalytic table for <i>N</i> -formylation of primary amines using phenylsilane. Isolated yields are shown in parentheses.....	250
Table S3. 8 Catalytic table for <i>N</i> -formylation of secondary amines using phenylsilane. Isolated yields are shown in parentheses.....	253
Table S3. 9 Catalytic table for hydroboration of aldehyde derivatives using HBpin. Isolated yields are shown in parentheses.....	264
Table S3. 10 Catalytic table for hydroboration of ketone derivatives using HBpin. Isolated yields are shown in parentheses.	267
Table S3. 11 Catalytic table for hydroboration of pyridine derivatives using HBpin. Isolated yields are shown in parentheses.....	269
Table S3. 12 Catalytic table for hydroboration of aldehyde derivatives using HBpin.....	271
Table S3. 13 Catalytic table for hydroboration of ketone derivatives using HBpin.	271
Table S3. 14 Catalytic table for hydroboration of pyridine derivatives using HBpin.....	272
Table S3. 15 Crystallographic data of 3.29 , 3.31m , 3.31p and 3.31w	387
Table S3. 16 The theoretical calculated ²⁹ Si NMR chemical shift (ppm) in solution (C ₆ D ₆) using TMS as the reference at B3LYP/6-311++G(2df,2pd)//B3LYP/6-31G** level of theory.	392
Table S3. 17 Natural Bond Order (NBO) of Int3.1 at M06-2X/def2-TZVP level of theory.	394
Table S3. 18 Optimized cartesian coordinates of compound 2.20	400
Table S3. 19 Optimized cartesian coordinates of HBpin	401
Table S3. 20 Optimized cartesian coordinates of Int3.1	402
Table S3. 21 Optimized cartesian coordinates of Int3.2	403
Table S3. 22 Optimized cartesian coordinates of I _{Me}	404
Table S3. 23 Optimized cartesian coordinates of Int3.3v	405
Table S3. 24 Optimized cartesian coordinates of [I _{Me} -H]I	406
Table S3. 25 Optimized cartesian coordinates of Int3.4	407
Table S3. 26 Optimized cartesian coordinates of compound 3.28	409
Table S3. 27 Optimized cartesian coordinates of compound 3.28	410
Table S3. 28 Optimized cartesian coordinates of TS3.1	412
Table S3. 29 Optimized cartesian coordinates of TS3.2	414
Table S3. 30 Optimized cartesian coordinates of TS3.3	416
Table S3. 31 Optimized cartesian coordinates of compound 3.27a	418
Table S3. 32 Optimized cartesian coordinates of TS3.4	419

Table S3. 33 Optimized cartesian coordinates of TS3.5	421
Table S3. 34 Optimized cartesian coordinates of Int3.5	422
Table S3. 35 Optimized cartesian coordinates of Int3.6	424
Table S3. 36 Optimized cartesian coordinates of TS3.6	426
Table S3. 37 Optimized cartesian coordinates of compound 2.20	433
Table S3. 38 Optimized cartesian coordinates of Int3.1	434
Table S3. 39 Optimized cartesian coordinates of PhSiH₃	435
Table S3. 40 Optimized cartesian coordinates of compound 3.30u	436
Table S3. 41 Optimized cartesian coordinates of TS3.7	437
Table S3. 42 Optimized cartesian coordinates of Int3.7	439
Table S3. 43 Optimized cartesian coordinates of TS3.8	441
Table S3. 44 Optimized cartesian coordinates of Int3.8	443
Table S3. 45 Optimized cartesian coordinates of TS3.9	445
Table S3. 46 Optimized cartesian coordinates of compound 3.31u	446
Table S3. 47 Optimized cartesian coordinates of (PhSiH₂)₂O	447
Table S3. 48 Optimized cartesian coordinates of TS3.10	448
Table S3. 49 Optimized cartesian coordinates of PhH₂SiOC(O)H	450
Table 4. 1 Catalytic table for hydroboration of CO₂ using HBpin	462
Table 4. 2 Catalytic table for <i>N</i> -formylation of amines using CO₂	468
Table 4. 3 Scope of Primary Amine Substrates	470
Table 4. 4 Selected literature catalysts used for <i>N</i> -formylation of primary amines	472
Table 4. 5 Scope of Secondary Amine Substrates	473
Table 4. 6 Selected literature catalysts used for <i>N</i> -formylation of secondary amines	474
Table 4. 7 Scope of Aldehyde Substrates	479
Table 4. 8 Scope of Ketone Substrates	480
Table S4. 1 Catalytic table for hydroboration of CO₂ using HBpin	484
Table S4. 2 Catalytic table for hydroboration of CO₂ using HBpin	487
Table S4. 3 Catalytic table for hydroboration of CO₂ using BH₃·SMe₂	487
Table S4. 4 Catalytic table for <i>N</i> -formylation of amines using CO₂	489
Table S4. 5 Catalytic table for <i>N</i> -formylation of primary amines using HBpin	496
Table S4. 6 Catalytic table for <i>N</i> -formylation of secondary amines using HBpin	498
Table S4. 7 Catalytic table for hydroboration of aldehyde derivatives using HBpin	506
Table S4. 8 Catalytic table for hydroboration of ketone derivatives using HBpin	509
Table S4. 9 Crystallographic data of 4.13	562

LIST OF FIGURES

Figure 1. 1 Molecular structure of 1.31	19
Figure 1. 2 Molecular structure of 1.32	20
Figure 1. 3 Molecular structure of 1.33	21
Figure 1. 4 Molecular structures of 1.34-S and 1.34-Te	26
Figure 1. 5 Molecular structures of 1.35	28
Figure 1. 6 EPR spectra of 1.35 in (a) 0.1 mM in toluene, (b) 5 mM in toluene, (c) 50 mM in toluene, (d) solid state, from 298 K (top) to 115 K (bottom).....	29
Figure 1. 7 CW EPR (X-band) spectra of 1.35 in toluene:THF solution at (a) 298 K and (b) 115 K. 29	
Figure 1. 8 Schematic representation of Ψ_2 and Ψ_3 orbitals in open shell singlet 1.35	31
Figure S1. 1 ^1H NMR spectrum of a mixture of 1.17 (1), 1.31 (2) and 1.32 (3) (in C_6D_6).....	40
Figure S1. 2 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound 1.31 (in C_6D_6).....	41
Figure S1. 3 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of compound 1.31 (in C_6D_6).	41
Figure S1. 4 ^1H NMR spectrum of compound 1.32 at room temperature (in C_6D_6).....	42
Figure S1. 5 ^1H NMR spectrum of compound 1.32 at -80°C (in d_8 -toluene).....	42
Figure S1. 6 Variable-temperature (from -85 to 24°C) ^1H NMR spectra of compound 1.32 (in d_8 -toluene).	43
Figure S1. 7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 1.32 at room temperature (in C_6D_6).....	43
Figure S1. 8 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound 1.32 at room temperature (in C_6D_6).	44
Figure S1. 9 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of compound 1.32 at room temperature (in C_6D_6).....	44
Figure S1. 10 ^1H NMR spectrum of compound 1.33 at room temperature (in C_6D_6).....	45
Figure S1. 11 Variable-temperature ^1H NMR spectra of compound 1.33 (in d_8 -toluene). (a) $-70 - 24^\circ\text{C}$; (b) $25 - 75^\circ\text{C}$	46
Figure S1. 12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 1.33 at room temperature (in C_6D_6).....	47
Figure S1. 13 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound 1.33 at room temperature (in C_6D_6).....	47
Figure S1. 14 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of compound 1.33 at room temperature (in C_6D_6).....	48
Figure S1. 15 ^1H NMR spectrum of a mixture of 1.33 (4), 1.34-S (5-S) and 1.34-Te (5-Te) (in C_6D_6).	48
Figure S1. 16 The decomposition of 1.34-Te (5-Te) after 1 day (in C_6D_6).	49
Figure S1. 17 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of 1.34-S (in C_6D_6).	49
Figure S1. 18 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of compound 1.34-S (in C_6D_6).	50
Figure S1. 19 ^1H NMR spectrum of the residue in C_6D_6 showing a mixture of 1.33 (4), 1.34-S (5-S) and 1.34-Te (5-Te).....	50
Figure S1. 20 The reaction of 1.17 (1) with four equivalents of tellurium in d_8 -THF monitored by ^1H NMR spectroscopy to afford 1.31 (2), 1.32 (3) and 1.33 (4). 1.34-Te is not observed.	51
Figure S1. 21 The reaction of 1.17 with four equivalents of tellurium in toluene monitored by NMR spectroscopy, (a) Full ^1H NMR spectrum; (b) imidazole region in the ^1H NMR spectrum.	52
Figure S1. 22 ^1H NMR spectrum of 1.35 (in C_6D_6).....	53
Figure S1. 23 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1.35 (in C_6D_6).....	53
Figure S1. 24 ^{29}Si NMR spectrum of 1.35 (in C_6D_6).	54
Figure S1. 25 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of 1.35 (in C_6D_6).	54

Figure S1. 26 Variable-temperature ^1H NMR spectra of compound 1.35 in d_8 -THF.	55
Figure S1. 27 UV-Visible spectrum of compound 1.32	56
Figure S1. 28 UV-Visible spectrum of compound 1.33	56
Figure S1. 29 UV-Visible spectrum of compound 1.35	57
Figure S1. 30 Optimized geometries of the minimal and transition states for the formation of compounds 1.31 – 1.33 at M06-2X/def2-SVP level of theory.	61
Figure S1. 31 Molecular orbitals of compound 1.17 , Int1.2 , compound 1.32 , Int1.5 and Te atom at M06-2X/def2-SVP level of theory.	63
Figure S1. 32 NLMOs of compound 1.31 at M06-2X/def2-SVP level of theory.	64
Figure S1. 33 NLMOs of compound 1.32 at M06-2X/def2-SVP level of theory.	65
Figure S1. 34 NLMOs of compound 1.33 at M06-2X/def2-SVP level of theory.	66
Figure S1. 35 Wiberg bond index and natural charge population of compound 1.31 at M06-2X/def2- SVP level of theory.	67
Figure S1. 36 Wiberg bond index and natural charge population of compound 1.32 at M06-2X/def2- SVP level of theory.	67
Figure S1. 37 Wiberg bond index and natural charge population of compound 1.33 at M06-2X/def2- SVP level of theory.	68
Figure S1. 38 Leading resonance structures according to NRT analyses of models 1.31 ^{Me} – 1.33 ^{Me} at M06-2X/def2-SVP level of theory.	71
Figure S1. 39 Relaxed potential energy surface scan for the reaction of the first Te atom with compound 1.17 at M06-2X/def2-SVP level of theory.	72
Figure S1. 40 Relaxed potential energy surface scan for the direct reaction of Int1.1 with the second tellurium atom at M06-2X/def2-SVP level of theory.	73
Figure S1. 41 Important geometrical parameters of 1.35 (a) X-ray crystal structure (b) BP86/def2- SVP optimized geometry in triplet electronic state and (c) BP86/def2-SVP optimized geometry in singlet electronic state.	123
Figure S1. 42 A schematic representation of the four important frontier orbitals and the electronic configuration considered for the CASSCF (6,6)/def2-SVP calculations of the ground state singlet (S_0), doubly excited singlet state (S_2) and first triplet excited state (T_1) on the crystal structure geometry of 1.35	125
Figure S1. 43 Schematic representation Lewis structure of 1.35 in singlet (left) and triplet (right) electronic state.	125
 Figure 2. 1 X-ray crystal structure of 2.20	138
Figure 2. 2 Plot of a) singly occupied molecular orbital (SOMO), b) lone pair on Si (HOMO-1) (isosurface value 0.03) and c) spin density calculated by natural population analysis (isosurface value 0.008) of 2.20a at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	141
Figure 2. 3 Molecular structure of 2.22	144
Figure 2. 4 CW EPR (X-band) spectra of 2.22 in toluene/THF solution recorded at a) 298 K and b) 115 K. The corresponding simulations are shown in a' and b'.	145
Figure 2. 5 Plots of a) the SOMO, b) the lone pair on the Si atom (HOMO-1; isosurface value 0.03), and c) the spin density calculated by natural population analysis (isosurface value 0.008) of 2.22 at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	146
 Figure S2. 1 The ^{29}Si NMR spectrum of the mother liquor showing the absence of Si-containing by- product.	152

Figure S2. 2 The mass spectrum of the mother liquid showing the formation of a THF-based ring-opening polymerization product.	154
Figure S2. 3 LC-MS spectrum of the reaction mixture showing a peak at m/z 47 corresponding to a [MeOMe] ⁺ fragment.....	155
Figure S2. 4 (a) ¹ H NMR spectrum of 2.20 (<i>d</i> ₅ -pyridine) and (b) ¹ H NMR spectrum of [SiD]- 2.20 (<i>d</i> ₅ -pyridine).....	157
Figure S2. 5 (a) ²⁹ Si NMR spectrum of 2.20 (<i>d</i> ₅ -pyridine) and (b) ²⁹ Si NMR spectrum of [SiD]- 2.20 (<i>d</i> ₅ -pyridine).....	158
Figure S2. 6 ²⁹ Si{ ¹ H} NMR spectrum of 2.20 (<i>d</i> ₅ -pyridine).....	159
Figure S2. 7 ¹ H NMR spectrum of the NMR-tube reaction of 2.20 and MeOH in C ₆ D ₆	159
Figure S2. 8 ²⁹ Si NMR spectrum of the NMR-tube reaction of 2.20 and MeOH in C ₆ D ₆	160
Figure S2. 9 ¹ H NMR spectrum of a mixture of 2.21 and [I _{Me} -H] ⁺ I ⁻ in the prolonged crystallization of compound 2.20 in fluorobenzene (<i>d</i> ₅ -pyridine).....	160
Figure S2. 10 UV-visible spectrum of 2.20 (fluorobenzene).....	161
Figure S2. 11 UV-visible spectrum of 2.22 (THF).....	161
Figure S2. 12 Molecular structure of 2.21	162
Figure S2. 13 Molecular structure of [I _{Me} -H] ⁺ I ⁻	163
Figure S2. 14 Molecular structure of [cAAC _{Me} -H] ⁺ I ⁻	163
Figure S2. 15 Optimized geometries and important geometrical parameters of 2.20 , 2.20a and 2.22 at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	166
Figure S2. 16 Plot of highest occupied molecular orbital (HOMO) of 2.20 at the M06/def2-TZVPP//BP86/def2-SVP level of theory.	166
Figure S2. 17 NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots and orbital stabilization energies ΔE for Si–C1 and Si–C2 bonds of 2.20 at the BP86/TZ2P level of theory.....	171
Figure S2. 18 NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots and orbital stabilization energies ΔE of Si–C1 and Si–C2 bonds of 2.20a at the BP86/TZ2P level of theory.	172
Figure S2. 19 NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots and orbital stabilization energies ΔE for Si–C1 and Si–C2 bonds of 2.22 at the BP86/TZ2P level of theory.....	173
Figure S3. 1 ¹ H NMR spectrum of compound 3.28 (in C ₆ D ₆).	273
Figure S3. 2 ¹¹ B NMR spectrum of compound 3.28 (in C ₆ D ₆).	274
Figure S3. 3 ¹¹ B{ ¹ H} NMR spectrum of compound 3.28 (in C ₆ D ₆).	274
Figure S3. 4 ²⁹ Si NMR spectrum of compound 3.28 (in C ₆ D ₆).	275
Figure S3. 5 ²⁹ Si{ ¹ H} NMR spectrum of compound 3.28 (in C ₆ D ₆), (a) before flattening the baseline, (b) after flattening the baseline, (c) focus view.....	277
Figure S3. 6 ESI-MS of 3.28	278
Figure S3. 7 ¹ H NMR spectrum of compound [(I _{Me}) ₂ Bpin]I (in CDCl ₃).	278
Figure S3. 8 ¹¹ B NMR spectrum of compound [(I _{Me}) ₂ Bpin]I (in CDCl ₃).	279
Figure S3. 9 ¹¹ B{ ¹ H} NMR spectrum of compound [(I _{Me}) ₂ Bpin]I (in CDCl ₃).	279
Figure S3. 10 ²⁹ Si{ ¹ H} NMR spectrum of compound Int3.1 (in <i>d</i> ₅ -pyridine).....	280
Figure S3. 11 ¹ H NMR spectra of the reaction of CO ₂ with HBpin catalyzed by 2.20 (10 mol %, in C ₆ D ₆), at (a) 24 °C, (b) 60°C and (c) 90 °C.	283
Figure S3. 12 NMR spectra of the resultant reaction of CO ₂ with HBpin catalyzed by 2.20 (10 mol %, in C ₆ D ₆), (a) ¹ H, (b) ¹¹ B, (c) ¹¹ B{ ¹ H} and (d) ¹³ C{ ¹ H}.	285

Figure S3. 13 NMR spectra of the reaction of CO ₂ with HBpin catalyzed by 3.28 (2.5 mol %, 90 °C, in C ₆ D ₆), (a) ¹ H and (b) ¹¹ B{ ¹ H}.....	287
Figure S3. 14 ¹ H NMR of the reaction of CO ₂ with BH ₃ ·SMe ₂ catalyzed by 2.20 (10 mol %, in C ₆ D ₆), at (a) 60 °C and (b) 90 °C.....	288
Figure S3. 15 NMR spectra of the resultant reaction of CO ₂ with BH ₃ ·SMe ₂ catalyzed by 2.20 (10 mol %, in C ₆ D ₆), (a) ¹ H, (b) ¹¹ B, (c) ¹¹ B{ ¹ H}.	290
Figure S3. 16 NMR spectra of the resultant reaction of CO ₂ with HBcat catalyzed by 2.20 (10 mol %, in C ₆ D ₆), (a) ¹ H, (b) ¹¹ B, (c) ¹¹ B{ ¹ H}.	292
Figure S3. 17 ¹ H NMR spectrum of resultant compound 3.31b (in C ₆ D ₆).	293
Figure S3. 18 ¹ H NMR spectrum of isolated compound 3.31b (in C ₆ D ₆).....	293
Figure S3. 19 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31b (in CDCl ₃).	294
Figure S3. 20 ¹ H NMR spectrum of isolated compound 3.31c (in CDCl ₃).....	294
Figure S3. 21 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31c (in CDCl ₃).....	295
Figure S3. 22 ¹ H NMR spectrum of resultant compound 3.31d (in C ₆ D ₆).	295
Figure S3. 23 ¹ H NMR spectrum of isolated compound 3.31d (in CDCl ₃).	296
Figure S3. 24 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31d (in CDCl ₃).	296
Figure S3. 25 ¹ H NMR spectrum of isolated compound 3.31e (in CDCl ₃).....	297
Figure S3. 26 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31e (in CDCl ₃).....	297
Figure S3. 27 ¹ H NMR spectrum of isolated compound 3.31f (in CDCl ₃).	298
Figure S3. 28 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31f (in CDCl ₃).	298
Figure S3. 29 ¹ H NMR spectrum of isolated compound 3.31g (in CDCl ₃).	299
Figure S3. 30 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31g (in CDCl ₃).	299
Figure S3. 31 ¹ H NMR spectrum of resultant compound 3.31h (in C ₆ D ₆).	300
Figure S3. 32 ¹ H NMR spectrum of isolated compound 3.31h (in CDCl ₃).	300
Figure S3. 33 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31h (in CDCl ₃).	301
Figure S3. 34 ¹ H NMR spectrum of isolated compound 3.31k (in CDCl ₃).	302
Figure S3. 35 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31k (in CDCl ₃).	302
Figure S3. 36 ¹ H NMR spectrum of isolated compound 3.31m (in CDCl ₃).	303
Figure S3. 37 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31m (in CDCl ₃).	303
Figure S3. 38 ¹ H NMR spectrum of isolated compound 3.31n (in CDCl ₃).	304
Figure S3. 39 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31n (in CDCl ₃).	304
Figure S3. 40 ¹ H NMR spectrum of resultant compound 3.31p (in C ₆ D ₆).	305
Figure S3. 41 ¹ H NMR spectrum of isolated compound 3.31p (in CDCl ₃).	305
Figure S3. 42 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31p (in CDCl ₃).	306
Figure S3. 43 ¹ H NMR spectrum of isolated compound 3.31r (in CDCl ₃).....	307
Figure S3. 44 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31r (in CDCl ₃).....	307
Figure S3. 45 ¹ H NMR spectrum of isolated compound 3.31s (in CDCl ₃).....	308
Figure S3. 46 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31s (in CDCl ₃).....	308
Figure S3. 47 ¹ H NMR spectrum of isolated compound 3.31t (in CDCl ₃).	309
Figure S3. 48 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31t (in CDCl ₃).	309
Figure S3. 49 ¹ H NMR spectrum of resultant compound 3.31u (in C ₆ D ₆).	310
Figure S3. 50 ¹ H NMR spectrum of isolated compound 3.31u (in CDCl ₃).	310
Figure S3. 51 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31u (in CDCl ₃).	311
Figure S3. 52 ¹ H NMR spectrum of isolated compound 3.31v (in CDCl ₃).	312
Figure S3. 53 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31v (in CDCl ₃).	312
Figure S3. 54 ¹ H NMR spectrum of resultant compound 3.31w (in C ₆ D ₆).....	313
Figure S3. 55 ¹ H NMR spectrum of isolated compound 3.31w (in CDCl ₃).	313
Figure S3. 56 ¹³ C{ ¹ H} NMR spectrum of isolated compound 3.31w (in CDCl ₃).	314

Figure S3. 57 ^1H NMR spectrum of isolated compound 3.31x (in CDCl_3).	315
Figure S3. 58 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.31x (in CDCl_3).	315
Figure S3. 59 ^1H NMR spectrum of resultant compound 3.33a (in C_6D_6).	316
Figure S3. 60 ^1H NMR spectrum of isolated compound 3.33a (in CDCl_3).	316
Figure S3. 61 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33a (in CDCl_3).	317
Figure S3. 62 ^1H NMR spectrum of isolated compound 3.33b (in CDCl_3).	318
Figure S3. 63 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33b (in CDCl_3).	318
Figure S3. 64 ^1H NMR spectrum of resultant compound 3.33c (in C_6D_6).	319
Figure S3. 65 ^1H NMR spectrum of isolated compound 3.33c (in CDCl_3).	319
Figure S3. 66 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33c (in CDCl_3).	320
Figure S3. 67 ^1H NMR spectrum of isolated compound 3.33e (in CDCl_3).	321
Figure S3. 68 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33e (in C_6D_6).	321
Figure S3. 69 ^1H NMR spectrum of isolated compound 3.33f (in C_6D_6).	322
Figure S3. 70 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33f (in C_6D_6).	322
Figure S3. 71 ^1H NMR spectrum of isolated compound 3.33g (in CDCl_3).	323
Figure S3. 72 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33g (in CDCl_3).	323
Figure S3. 73 ^1H NMR spectrum of resultant compound 3.33h (in C_6D_6).	324
Figure S3. 74 ^1H NMR spectrum of isolated compound 3.33h (in CDCl_3).	324
Figure S3. 75 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33h (in CDCl_3).	325
Figure S3. 76 ^1H NMR spectrum of resultant compound 3.33k (in C_6D_6).	326
Figure S3. 77 ^1H NMR spectrum of isolated compound 3.33k (in CDCl_3).	326
Figure S3. 78 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33k (in CDCl_3).	327
Figure S3. 79 ^1H NMR spectrum of resultant compound 3.33m (in C_6D_6).	328
Figure S3. 80 ^1H NMR spectrum of isolated compound 3.33m (in CDCl_3).	328
Figure S3. 81 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.33m (in CDCl_3).	329
Figure S3. 82 ^1H NMR spectra of the resultant deuterium-labelling study of catalytic <i>N</i> -formylation using <i>d</i> ₁₁ -piperidine 3.32g-D , catalyzed by 2.20 (5 mol %, 60 °C, 1 hour, in C_6D_6), (a) full spectrum, (b) enlarged spectrum.	330
Figure S3. 83 ^1H NMR spectra of the resultant catalytic <i>N</i> -formylation using piperidine 3.32g and <i>d</i> ₁₁ -piperidine 3.32g-D in 1:1 ratio, catalyzed by 2.20 (5 mol %, 60 °C, 1 hour, in C_6D_6), (a) full spectrum, (b) enlarged spectrum.	331
Figure S3. 84 ^1H NMR spectra of the resultant reaction between PhSiH_3 and <i>d</i> ₁₁ -piperidine 3.32g-D , both in the presence and absence of 2.20 (24, 60 and 90 °C, 24 hours, in C_6D_6), (a) full spectrum, (b) enlarged spectrum.	332
Figure S3. 85 NMR spectra of the resultant hydrosilylation of CO_2 catalyzed by 2.20 (10 mol %, 90 °C, 1 hour, in C_6D_6), (a) ^1H , (b) $^{13}\text{C}\{^1\text{H}\}$ and (c) ^{29}Si	334
Figure S3. 86 Timeline study of hydrosilylation of CO_2 catalyzed by 2.20 (10 mol %, in C_6D_6), monitored by ^1H NMR spectroscopy.	335
Figure S3. 87 Stepwise hydroboration of benzaldehyde 3.41a catalyzed by 3.28 (5 mol %, 24 °C, in C_6D_6), monitored by ^1H NMR spectroscopy, (a) first step: addition of HBpin to 2.20 to afford 3.28 and (b) second step: addition of benzaldehyde 3.41a	336
Figure S3. 88 Timeline study of hydroboration of benzaldehyde 3.41a catalyzed by 2.20 (10 mol %, 24 °C, in C_6D_6), monitored by ^1H NMR spectroscopy.	337
Figure S3. 89 Timeline study of hydroboration of 3-methyl-2-butanone 3.43e catalyzed by 2.20 (10 mol %, 90 °C, in C_6D_6), monitored by ^1H NMR spectroscopy.	338
Figure S3. 90 Timeline study of hydroboration of quinoline 3.45d catalyzed by 2.20 (10 mol %, 90 °C, in C_6D_6), monitored by ^1H NMR spectroscopy.	339

Figure S3. 91 Timeline study of hydroboration of benzaldehyde 3.41a catalyzed by 3.28 (2.5 mol %, 24 °C, in C ₆ D ₆), monitored by ¹ H NMR spectroscopy.....	340
Figure S3. 92 Timeline study of hydroboration of 1,4-dioxaspiro[4.5]decan-8-one 3.43d catalyzed by 3.28 (5 mol %, 90 °C, in C ₆ D ₆), monitored by ¹ H NMR spectroscopy.....	341
Figure S3. 93 Timeline study of hydroboration of pyridine 3.45a catalyzed by 3.28 (3 mol %, 90 °C, in C ₆ D ₆), monitored by ¹ H NMR spectroscopy.....	342
Figure S3. 94 ¹ H NMR spectrum of compound 3.42a (in C ₆ D ₆), (a) crude solution and (b) isolated compound.....	343
Figure S3. 95 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42a (in C ₆ D ₆), (a) crude solution and (b) isolated compound.	344
Figure S3. 96 ¹ H NMR spectrum of compound 3.42b (in C ₆ D ₆).	345
Figure S3. 97 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42b (in C ₆ D ₆).	345
Figure S3. 98 ¹ H NMR spectrum of compound 3.42c (in C ₆ D ₆).	346
Figure S3. 99 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42c (in C ₆ D ₆).	346
Figure S3. 100 ¹ H NMR spectrum of compound 3.42d (in C ₆ D ₆).	347
Figure S3. 101 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42d (in C ₆ D ₆).	347
Figure S3. 102 ¹ H NMR spectrum of compound 3.42e (in C ₆ D ₆), (a) crude solution and (b) isolated compound.....	348
Figure S3. 103 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42e (in C ₆ D ₆), (a) crude solution and (b) isolated compound.	349
Figure S3. 104 ¹ H NMR spectrum of compound 3.42f (in C ₆ D ₆).	350
Figure S3. 105 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42f (in C ₆ D ₆).	350
Figure S3. 106 ¹ H NMR spectrum of isolated compound 3.42g (in C ₆ D ₆), (a) crude solution and (b) isolated compound.	351
Figure S3. 107 ¹¹ B{ ¹ H} NMR spectrum of isolated compound 3.42g (in C ₆ D ₆), (a) crude solution and (b) isolated compound.....	352
Figure S3. 108 ¹ H NMR spectrum of compound 3.42h (in C ₆ D ₆).	353
Figure S3. 109 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42h (in C ₆ D ₆).	353
Figure S3. 110 ¹ H NMR spectrum of compound 3.42k (in C ₆ D ₆).	354
Figure S3. 111 ¹³ C NMR spectrum of compound 3.42k (in C ₆ D ₆).	354
Figure S3. 112 ¹ H NMR spectrum of compound 3.42m (in C ₆ D ₆).	355
Figure S3. 113 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42m (in C ₆ D ₆).	355
Figure S3. 114 ¹ H NMR spectrum of compound 3.42n (in C ₆ D ₆).	356
Figure S3. 115 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42n (in C ₆ D ₆).	356
Figure S3. 116 ¹ H NMR spectrum of compound 3.42p (in C ₆ D ₆).	357
Figure S3. 117 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42p (in C ₆ D ₆).	357
Figure S3. 118 ¹ H NMR spectrum of compound 3.42q (in C ₆ D ₆).	358
Figure S3. 119 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42q (in C ₆ D ₆).	358
Figure S3. 120 ¹ H NMR spectrum of compound 3.42r (in C ₆ D ₆).	359
Figure S3. 121 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42r (in C ₆ D ₆).	359
Figure S3. 122 ¹ H NMR spectrum of compound 3.42s (in C ₆ D ₆).	360
Figure S3. 123 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42s (in C ₆ D ₆).	360
Figure S3. 124 ¹ H NMR spectrum of compound 3.42t (in C ₆ D ₆).	361
Figure S3. 125 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42t (in C ₆ D ₆).	361
Figure S3. 126 ¹ H NMR spectrum of compound 3.42u (in C ₆ D ₆).	362
Figure S3. 127 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42u (in C ₆ D ₆).	362
Figure S3. 128 ¹ H NMR spectrum of compound 3.42v (in C ₆ D ₆).	363
Figure S3. 129 ¹¹ B{ ¹ H} NMR spectrum of compound 3.42v (in C ₆ D ₆).	363

Figure S3. 130 ^1H NMR spectrum of isolated compound 3.44a (in C_6D_6), (a) crude solution and (b) isolated compound.	364
Figure S3. 131 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.44a (in C_6D_6), (a) crude solution and (b) isolated compound.	365
Figure S3. 132 ^1H NMR spectrum of compound 3.44b (in C_6D_6).	366
Figure S3. 133 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44b (in C_6D_6).	366
Figure S3. 134 ^1H NMR spectrum of compound 3.44c (in C_6D_6).	367
Figure S3. 135 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44c (in C_6D_6).	367
Figure S3. 136 ^1H NMR spectrum of compound 3.44d (in C_6D_6).	368
Figure S3. 137 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44d (in C_6D_6).	368
Figure S3. 138 ^1H NMR spectrum of compound 3.44e (in C_6D_6), (a) crude solution and (b) isolated compound.	369
Figure S3. 139 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44e (in C_6D_6), (a) crude solution and (b) isolated compound.	370
Figure S3. 140 ^1H NMR spectrum of compound 3.44f (in C_6D_6), (a) crude solution and (b) isolated compound.	371
Figure S3. 141 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44f (in C_6D_6), (a) crude solution and (b) isolated compound.	372
Figure S3. 142 ^1H NMR spectrum of compound 3.44g (in C_6D_6).	373
Figure S3. 143 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44g (in C_6D_6).	373
Figure S3. 144 ^1H NMR spectrum of isolated compound 3.44h (in C_6D_6), (a) crude solution and (b) isolated compound.	374
Figure S3. 145 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.44h (in C_6D_6), (a) crude solution and (b) isolated compound.	375
Figure S3. 146 ^1H NMR spectrum of compound 3.44k (in C_6D_6).	376
Figure S3. 147 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.44k (in C_6D_6).	376
Figure S3. 148 ^1H NMR spectrum of compound 3.46a (in C_6D_6).	377
Figure S3. 149 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.46a (in C_6D_6).	377
Figure S3. 150 ^1H NMR spectrum of compound 3.46b (in C_6D_6).	378
Figure S3. 151 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.46b (in C_6D_6).	378
Figure S3. 152 ^1H NMR spectrum of isolated compound 3.46c (in C_6D_6), (a) crude solution and (b) isolated compound.	379
Figure S3. 153 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.46c (in C_6D_6), (a) crude solution and (b) isolated compound.	380
Figure S3. 154 ^1H NMR spectrum of isolated compound 3.46d (in C_6D_6), (a) crude solution and (b) isolated compound.	381
Figure S3. 155 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound 3.46d (in C_6D_6), (a) crude solution and (b) isolated compound.	382
Figure S3. 156 ^1H NMR spectrum of compound 3.46e (in C_6D_6).	383
Figure S3. 157 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 3.46e (in C_6D_6).	383
Figure S3. 158 Molecular structure of $[(\text{I}_{\text{Me}})_2\text{Bpin}]\text{I}$ and $[\text{I}_{\text{Me}}-\text{H}]\text{I}$ (3.29).	384
Figure S3. 159 Molecular structure of 3.31m	385
Figure S3. 160 Molecular structure of 3.31p	385
Figure S3. 161 Molecular structure of 3.31w	386
Figure S3. 162 Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory.	389
Figure S3. 163 Orbital interaction diagram of compound 2.20 and CO_2 at M06-2X/def2-TZVP level of theory.	393

Figure S3. 164 Molecular orbitals of compound 2.20 , CO ₂ and Int3.1 at M06-2X/def2-TZVP level of theory.	394
Figure S3. 165 Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory.	428
Figure 4. 1 Molecular structure of 4.13	464
Figure S4. 1 ¹ H NMR spectrum of compound 4.13 (in <i>d</i> ₈ -THF).	511
Figure S4. 2 ¹ H NMR spectrum of compound 4.13 (in C ₆ D ₆).	512
Figure S4. 3 ¹¹ B NMR spectrum of compound 4.13 (in <i>d</i> ₈ -THF).	512
Figure S4. 4 ¹¹ B{ ¹ H} NMR spectrum of compound 4.13 (in <i>d</i> ₈ -THF).	513
Figure S4. 5 ¹³ C NMR spectrum of compound 4.13 (in <i>d</i> ₈ -THF).	514
Figure S4. 6 ²⁹ Si NMR spectrum of compound 4.13 (in <i>d</i> ₈ -THF).	515
Figure S4. 7 IR spectrum of compound 4.13	515
Figure S4. 8 ¹ H NMR spectra of the reaction of CO ₂ with HBpin (in C ₆ D ₆), catalyzed by 4.13 (10 mol %), (a) 90 °C and (b) 110 °C.	517
Figure S4. 9 ¹ H NMR spectra of the resultant reaction of CO ₂ with HBpin (in C ₆ D ₆), catalyzed by 4.13 (10 mol %), (a) ¹ H, (b) ¹¹ B, (c) ¹¹ B{ ¹ H} and (d) ¹³ C{ ¹ H}.	519
Figure S4. 10 ¹ H NMR spectrum of attempted isolation of compound 4.15a (in CDCl ₃).	520
Figure S4. 11 ¹ H NMR spectrum of attempted isolation of compound 4.15b (in CDCl ₃).	521
Figure S4. 12 ¹ H NMR spectrum of attempted isolation of compound 4.15c (in CDCl ₃).	521
Figure S4. 13 ¹ H NMR spectrum of attempted isolation of compound 4.15d (in CDCl ₃).	522
Figure S4. 14 ¹ H NMR spectrum of attempted isolation of compound 4.15e (in CDCl ₃).	522
Figure S4. 15 ¹ H NMR spectrum of attempted isolation of compound 4.15h (in CDCl ₃).	523
Figure S4. 16 ¹ H NMR spectrum of attempted isolation of compound 4.15k (in CDCl ₃).	523
Figure S4. 17 ¹ H NMR spectrum of attempted isolation of compound 4.15m (in CDCl ₃).	524
Figure S4. 18 ¹ H NMR spectrum of compound resultant 4.15n (in C ₆ D ₆).	524
Figure S4. 19 ¹ H NMR spectrum of attempted isolation of compound 4.15n (in CDCl ₃).	525
Figure S4. 20 ¹ H NMR spectrum of attempted isolation of compound 4.15p (in CDCl ₃).	525
Figure S4. 21 ¹ H NMR spectrum of attempted isolation of compound 4.15q (in CDCl ₃).	526
Figure S4. 22 ¹ H NMR spectrum of attempted isolation of compound 4.15r (in CDCl ₃).	526
Figure S4. 23 ¹ H NMR spectrum of attempted isolation of compound 4.15s (in CDCl ₃).	527
Figure S4. 24 ¹ H NMR spectrum of attempted isolation of compound 4.17a (in CDCl ₃).	527
Figure S4. 25 ¹ H NMR spectrum of resultant compound 4.17b (in C ₆ D ₆).	528
Figure S4. 26 ¹ H NMR spectrum of resultant compound 4.17c (in C ₆ D ₆).	528
Figure S4. 27 ¹ H NMR spectrum of resultant compound 4.17d (in C ₆ D ₆).	529
Figure S4. 28 ¹ H NMR spectrum of resultant compound 4.17e (in C ₆ D ₆).	529
Figure S4. 29 Enlarged ¹ H NMR spectrum of the resultant reaction of amines, CO ₂ and HBpin catalyzed by 4.13 (3 mol %, 40 °C, 24 hour, in C ₆ D ₆). H ₂ gas was found in all catalyses.	530
Figure S4. 30 Enlarged ¹ H NMR spectrum of the resultant reaction of <i>d</i> ₁₁ -piperidine, CO ₂ and HBpin catalyzed by 4.13 (3 mol %, 40 °C, 24 hour, in C ₆ D ₆).	530
Figure S4. 31 Stepwise hydroboration of benzaldehyde 4.18a catalyzed by 4.13 (10 mol%, 60 °C, in C ₆ D ₆) monitored by ¹ H NMR spectroscopy, (a1) first step: addition of benzaldehyde, 1 day, ¹ H, (a2) first step: addition of benzaldehyde, 1 day, ¹¹ B{ ¹ H} and (b) second step: addition of HBpin.	532

Figure S4. 32 Stepwise hydroboration of benzaldehyde 4.18a catalyzed by 4.13 (in C ₆ D ₆) at 60°C, monitored by ¹ H NMR spectroscopy, (a) first step: addition of HBpin and (b) second step: addition of benzaldehyde.	534
Figure S4. 33 Stepwise hydroboration of benzaldehyde 4.18a catalyzed by 4.13 (in C ₆ D ₆) at 60°C, monitored by ¹ H NMR spectroscopy, (a) first step: addition of 2 equiv. of HBpin, 3h and (b) second step: addition of benzaldehyde.	536
Figure S4. 34 ¹ H NMR spectrum of isolated compound 4.19a (in C ₆ D ₆).....	537
Figure S4. 35 ¹¹ B NMR spectrum of isolated compound 4.19a (in C ₆ D ₆).....	537
Figure S4. 36 ¹ H NMR spectrum of isolated compound 4.19b (in C ₆ D ₆).....	538
Figure S4. 37 ¹¹ B NMR spectrum of isolated compound 4.19b (in C ₆ D ₆).....	538
Figure S4. 38 ¹ H NMR spectrum of isolated compound 4.19c (in C ₆ D ₆).....	539
Figure S4. 39 ¹¹ B NMR spectrum of isolated compound 4.19c (in C ₆ D ₆).....	539
Figure S4. 40. ¹ H NMR spectrum of isolated compound 4.19d (in C ₆ D ₆).....	540
Figure S4. 41 ¹¹ B NMR spectrum of isolated compound 4.19d (in C ₆ D ₆).....	540
Figure S4. 42 ¹ H NMR spectrum of isolated compound 4.19e (in C ₆ D ₆).....	541
Figure S4. 43 ¹¹ B NMR spectrum of isolated compound 4.19e (in C ₆ D ₆).....	541
Figure S4. 44 ¹ H NMR spectrum of isolated compound 4.19f (in C ₆ D ₆).	542
Figure S4. 45 ¹¹ B NMR spectrum of isolated compound 4.19f (in C ₆ D ₆).	542
Figure S4. 46 ¹ H NMR spectrum of isolated compound 4.19g (in C ₆ D ₆).....	543
Figure S4. 47 ¹¹ B NMR spectrum of isolated compound 4.19g (in C ₆ D ₆).....	543
Figure S4. 48 ¹ H NMR spectrum of isolated compound 4.19h (in C ₆ D ₆).....	544
Figure S4. 49 ¹¹ B NMR spectrum of isolated compound 4.19h (in C ₆ D ₆).....	544
Figure S4. 50 ¹ H NMR spectrum of isolated compound 4.19k (in C ₆ D ₆).....	545
Figure S4. 51 ¹¹ B NMR spectrum of isolated compound 4.19k (in C ₆ D ₆).....	545
Figure S4. 52 ¹ H NMR spectrum of isolated compound 4.19m (in C ₆ D ₆).....	546
Figure S4. 53 ¹¹ B NMR spectrum of isolated compound 4.19m (in C ₆ D ₆).	546
Figure S4. 54 ¹ H NMR spectrum of isolated compound 4.19n (in C ₆ D ₆).....	547
Figure S4. 55 ¹¹ B NMR spectrum of isolated compound 4.19n (in C ₆ D ₆).....	547
Figure S4. 56 ¹ H NMR spectrum of isolated compound 4.19p (in C ₆ D ₆).....	548
Figure S4. 57 ¹¹ B NMR spectrum of isolated compound 4.19p (in C ₆ D ₆).....	548
Figure S4. 58 ¹ H NMR spectrum of isolated compound 4.19q (in C ₆ D ₆).....	549
Figure S4. 59 ¹¹ B NMR spectrum of isolated compound 4.19q (in C ₆ D ₆).....	549
Figure S4. 60 ¹ H NMR spectrum of isolated compound 4.19r (in C ₆ D ₆).....	550
Figure S4. 61 ¹¹ B NMR spectrum of isolated compound 4.19r (in C ₆ D ₆).....	550
Figure S4. 62 ¹ H NMR spectrum of isolated compound 4.19s (in C ₆ D ₆).	551
Figure S4. 63 ¹¹ B NMR spectrum of isolated compound 4.19s (in C ₆ D ₆).	551
Figure S4. 64 ¹ H NMR spectrum of isolated compound 4.19t (in C ₆ D ₆).	552
Figure S4. 65 ¹¹ B NMR spectrum of isolated compound 4.19t (in C ₆ D ₆).	552
Figure S4. 66 ¹ H NMR spectrum of isolated compound 4.19u (in C ₆ D ₆).....	553
Figure S4. 67 ¹¹ B NMR spectrum of isolated compound 4.19u (in C ₆ D ₆).....	553
Figure S4. 68 ¹ H NMR spectrum of isolated compound 4.19v (in C ₆ D ₆).....	554
Figure S4. 69 ¹¹ B NMR spectrum of isolated compound 4.19v (in C ₆ D ₆).....	554
Figure S4. 70 ¹ H NMR spectrum of isolated compound 4.19w (in C ₆ D ₆).....	555
Figure S4. 71 ¹¹ B NMR spectrum of isolated compound 4.19w (in C ₆ D ₆).....	555
Figure S4. 72 ¹ H NMR spectrum of isolated compound 4.21a (in C ₆ D ₆).....	556
Figure S4. 73 ¹¹ B NMR spectrum of isolated compound 4.21a (in C ₆ D ₆).....	556
Figure S4. 74 ¹ H NMR spectrum of isolated compound 4.21b (in C ₆ D ₆).....	557
Figure S4. 75 ¹¹ B NMR spectrum of isolated compound 4.21b (in C ₆ D ₆).....	557

Figure S4. 76 ^1H NMR spectrum of resultant compound 4.21c (in C_6D_6).....	558
Figure S4. 77 ^{11}B NMR spectrum of resultant compound 4.21c (in C_6D_6).....	558
Figure S4. 78 ^1H NMR spectrum of resultant compound 4.21d (in C_6D_6).	559
Figure S4. 79 ^{11}B NMR spectrum of resultant compound 4.21d (in C_6D_6).	559
Figure S4. 80 ^1H NMR spectrum of isolated compound 4.21e (in C_6D_6).....	560
Figure S4. 81 ^{11}B NMR spectrum of isolated compound 4.21e (in C_6D_6).....	560

LIST OF ABBREVIATIONS AND SYMBOLS

9-BBN	9-borabicyclo[3.3.1]nonane
Ar	2,6- <i>i</i> Pr ₂ C ₆ H ₃
br	broad
<i>ca</i>	<i>circa</i>
Cat	catalyst
calcd.	calculated
Ch	chalcogen
cm ⁻¹	wavenumber
cpd	compound
CW	continuous wave
d	doublet
<i>d</i>	density
D	deuterated
DAAs	1,3,2-diazaarsole
DAP	1,3,2-diazaphopholenes
dec.	decomposed
DFT	density functional theory
DMAP	4-dimethylaminopyridine
E	main group element, tetrel
EA	ethyl acetate
EDA	energy decomposition analysis
EPR	electron paramagnetic resonance
ESI	electron spray ionization
equiv.	equivalent(s)
eV	electron volt
FLP	frustrated Lewis pair(s)
PhF	fluorobenzene
g	gram(s)
G	Gibbs free energy
GIAO	gauge invariant atomic orbital
h	hour(s)
HBcat	catecholborane
HBpin	pinacolborane
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrometry
Hz/MHz	hertz/megahertz
I _{Ar}	:C{N(Ar)CH} ₂
I _{Me}	:C{N(Me)C(Me)} ₂
int	intermediate

<i>i</i> Pr	isopropyl
IR	infrared
IS	Internal standard
<i>J</i>	coupling constant
K	Kelvin
kcal	kilocalory
kJ	kilojoule
L	ligand
LA	Lewis acid
LB	Lewis base
LP	lone pair
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	molar (mol dm ⁻³)
m.p.	melting point
Me	methyl
Mes	mesityl
mL	millilitre(s)
μL	microlitre(s)
mmol/mol	millimole(s)/mole(s)
MG	main group
MO	molecular orbital
MS	mass spectroscopy
NBO	natural bond orbital
NHC	<i>N</i> -heterocyclic carbene
NHP	<i>N</i> -heterocyclic phosphine
NHSi	<i>N</i> -heterocyclic silylene
NMR	nuclear magnetic resonance
NOCV	natural orbit for chemical valence
NPA	natural population analysis
NRT	natural resonance theory
pdt	product
Ph	phenyl
Pn	pnictogen
ppm	parts per million
PRC	pre-reaction complex
q	quartet
R	σ-bonded substituent
rt	room temperature
s	singlet
sept	septet
sm	starting material
t	triplet

<i>t</i> Bu	<i>tert</i> -butyl
THF	tetrahydrofuran
TM	transition metal
TOF	turnover frequency
TON	turnover number
TS	transition state
UV/Vis	Ultraviolet-Visible
V	volume
<i>vs</i>	versus
WBI	Wiberg Bond Index
%	percentage
Å	angstrom(s)
°	degree(s)
°C	degree(s) Celcius
α	alpha
β	beta
δ	chemical shift
Δ	delta
η	‘eta’ (hapticity)
γ	gamma
λ_{max}	wavenumber at maximum absorption
ε	molar absorptivity
μ	‘mu’ (bridging)
ψ	orbital
π	pi
σ	sigma

LIST OF SYNTHESIZED COMPOUNDS

Formula	Numbering	Page	Structure
$C_{54}H_{72}N_4Si_2Te_2$	1.31	18
$C_{54}H_{72}N_4Si_2Te_2$	1.32	18
$C_{54}H_{72}N_4Si_2Te_4$	1.33	18
$C_{54}H_{72}N_4S_8Si_2$	1.34-S	25
$C_{54}H_{72}N_4Si_2Te_2$	1.34-Te	25
$C_{78}H_{92}F_4I_2N_4Si_2Te_2$	1.35	27
$C_{14}H_{25}IN_4Si$	2.20	137

Formula	Numbering	Page	Structure
$C_{13}H_{16}FIN_2$	2.21	137
$C_{23.50}H_{42.50}BI_{1.50}N_5O_2$	3.29	384
$C_{13}H_{19}NO$	3.31m	385
$C_8H_9NO_2$	3.31p	385
C_8H_8ClNO	3.31w	386
$C_{54}H_{79}B_2IN_4Si_2$	4.13	463

Chapter 1:

***N*-Heterocyclic Carbene-stabilized Silicon(0/I) Complexes and Their Reactivity toward Chalcogen[†]**

1.1 Introduction

Being the second element after oxygen (*ca* 45.5%) in terms of abundance on the Earth's crust, silicon (*ca* 27.2%) mostly revolves around compounds whereby the silicon atom is in its tetravalent state, for instance polysilicon, silicates, silica and organosilicon compounds.^[1] Remarkably, for the past three decades, the chemistry of silicon has shown extraordinary progress in low-valent silicon complexes ranging from +2^[2], +1^[3] to even 0^[4].^[3e,5] The isolation of low-valent silicon species which was once thought to be impossible to obtain was structurally presented by West in the mid-1990s.^[2a] The first *N*-heterocyclic silylene (NHSi) **1.1** (:Si{N(*t*Bu)CH}₂, Chart 1.2) provides a visual evidence on its composition in the form of [L₂Si:] (L = donor ligand, Chart 1.1). The silicon atom comprises of an unoccupied p-orbital and a non-bonding electron pair (Chart 1.1). To summarize, the divalent silicon centre can be both electron pair donor and acceptor, are both Lewis basic and Lewis acid properties in a single molecule, termed as ambiphilic.

Chart 1. 1 Schematic representation of a silylene.

[†] Portions of this chapter are adapted with permission from Y.-C. Chan, B.-X. Leong, Y. Li, M.-C. Yang, Y. Li, M.-D. Su, C.-W. So, *Angew. Chem. Int. Ed.* **2017**, 56, 11565-11569. Copyright 2020 Wiley-VCH GmbH.

Chart 1. 2 Selected examples of silylenes.^[2a-i]

Their relentless spotlight in this chemistry is largely associated to their intriguing electronic structures and reactivities comparable to that of transition metals, especially activation of enthalpically strong bonds (H₂, H₂O, N₂, C≡O, CO₂, O₂, NH₃, C₂H₄, etc.).^[6] Notable remark goes to the isolable acyclic silylene **1.7**, which features a small energy gap of 103.7 kJ/mol between the singlet-triplet first state, easily activates H₂ under ambient conditions to deliver addition product **1.7-H₂**.^[2g] According to the DFT calculation performed by Szilvási on the parameters that constitute of a transition metal ligand, which are the σ-donor and/or π-acceptor capability, steric effect and ligand-to-metal transfer criterions, silylenes are far superior ancillary ligands as compared to the conventional carbenes and phosphines in transition metal mediated C–Y bond formations (Y = B, C, N and O), in addition to catalyzing reduction reaction of C=C and C=O bonds.^[7] Additionally, since silylenes are Lewis ambiphilic, a slight chemical modifications on the ligands will effect in a vastly different chemical behaviour, making it a versatile ligand. One recent example would be the catalyst silylene–platinum(0) complex, generated from the coordination of silylene **1.4** (Chart 1.2) with Karstedt’s catalyst, revealed as an impressive catalytic intermediate for hydrosilylation of terminal alkenes in comparison with the lighter carbene ligand analogues.^[7g] Therefore, it is not surprising that a significant number of “bottleable” silylenes such as cyclic silylenes (**1.1** – **1.5**, Chart 1.2)^[2a-e] and acyclic silylenes (**1.6** to **1.9**, Chart 1.2)^[2f-i] were synthesized with their reactivity extensively studied.

Having said that the divalent silylenes seem to be stable enough to be “bottleable”, they do not obey the octet rule since the divalent silicon atom is designated with six valence electrons. Therefore, these species, albeit termed as “bottleable”, are generally air- and moisture-sensitive, often stored under inert conditions as they could easily dimerize to form silicon(II) complexes, namely disilenes or more commonly, oligomerize into silicon(IV)-containing polymeric structures, comprising of Si–Si single bonds. Therefore, such stable silylene species are often stabilized by manipulation of one or a concoction of strategies: (i) sterically encumbering ligands and/or (ii) σ -acceptor and/or π -donor substituents (i.e., amino, phosphino and boryloxy substituents) to overcome the kinetic and thermodynamic instability, respectively.

1.10, Sekiguchi 2004

1.11, Sekiguchi 2010

1.12, Tokitoh 2008

Chart 1. 3 Examples of silicon-based alkyne analogues, disilynes.^[3a-c]

The realization that the pivotal step in the development of low-valent silicon depends on sufficient steric protection from dimerization while preserving the core structure from over-reduction, has facilitated the advancement into the multiply-bonded main group chemistry, i.e., heavy congeners of alkene ($>E=E<$, $E = \text{Si, Ge, Sn}$) and alkyne ($R-E\equiv E-R$, $R = \sigma$ -bonded substituent).^[5b-d] In turn, multiply-bonded silicon chemistry has garnered tremendous interest due to its unique structures and bonding.^[2k,3a-c,5d] However, intervening years between the first disilene^[2k] ($\text{Mes}_2\text{Si}=\text{SiMes}_2$, $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) in the early 1980s to the eventual first disilynes^[3a] (**1.10**, Chart 1.3) in 2004 has clearly illustrate the daunting challenges faced by simply reducing the formal oxidation states at the dimeric silicon atom from +2 to +1. Consequently, isolation of such mono-valent species is restricted to only a handful of examples (Chart 1.3).

Essentially pioneered Sekiguchi, the first isolable disilyne (**1.10**, Chart 1.3), features a true $\text{Si}\equiv\text{Si}$ triple bond has sparked a milestone in this chemistry. Disilyne **1.10** could be synthesized by reduction of a sterically bulky 1,1,2,2-tetrabromodisilane $\text{R}^1(\text{Br})_2\text{Si}-\text{Si}(\text{Br})_2\text{R}^1$ ($\text{R}^1 = \text{Si}(i\text{Pr})\{\text{CH}(\text{SiMe}_3)_2\}_2$).^[3a] In essence, the generic blueprint in isolating low-valent silicon species such as disilynes requires sterically encumbered ligands (i.e., bulky silyl and terphenyl ligands) and dehalogenation from the disilicon precursor, demonstrated in the latter series of disilynes (**1.11** – **1.12**, Chart 1.3), along with their utility in catalysis and small molecule activations.^[3b,3c,8]

Chart 1. 4 Selected orbital interactions in linear D_{2h} and trans-bent C_{2h} $\text{RE}\equiv\text{ER}$ model.

Generally, the bond lengths of the triply-bonded Si≡Si moiety of the mono-valent disilynes **1.10** – **1.12** ranges from 2.0569 – 2.108 Å, are significantly shortened from the common doubly-bonded Si=Si (*ca* 2.14 – 2.30 Å) in disilenes and the typical singly-bonded Si–Si (2.37 Å) found in silanes, indicative of the triply interaction within the Si≡Si fragment in **1.10** – **1.12** (Chart 1.3).^[5d] Contrary to their lighter congeners that constitute of a linear triply-bonded C≡C, disilynes **1.10** – **1.12** (Chart 1.3) exhibit a planar, yet *trans*-bent core geometry about the triply-bonded Si≡Si fragments (133.0 – 138.8°) with substantial deviation from linearity (dihedral angle: 164.1° for **1.12**).^[3a-c] From the computation point of view, such deviation arises from the mixing of in-plane $\pi_{(\text{Si-Si})}$ and anti-bonding $\sigma^*_{(\text{Si-Si})}$ orbitals that are of the same symmetry in C_{2h} point group (Chart 1.4).^[5c,9] In addition, such mixing is possible since the separation between the π -orbital and σ^* -orbital is estimated at half or less than that of the carbon congeners. The π - σ^* mixing ensuing the aggregation of electron density of non-bonding characteristic at the silicon centre, resulting in bending or *trans*-bent phenomena at these silicon centres caused by interelectronic repulsion. Particularly, the resultant LUMO is expected to be low-lying in energy.

Chart 1.5 Bonding model in (a) linear alkyne and (b) heavy homonuclear tetrelyne and its constitutional isomer silicon(I) dimer.

One would expect a disilyne complex constitutes a combination of a π -bond and two donor-acceptor interactions within the two silicon centers (Chart 1.5b, left).^[5c,9] To elaborate, consider each of the silicon atom as sp -hybridized, whereby one unpaired electron forms a σ -interaction between R–Si. The π -bond is derived from interaction between the remaining unpaired electron in the sp -hybridized orbital with another silicon atom. Finally, the two donor-acceptor bonds involve the bonding between the stereoactive electron pair from the p-orbital at the two silicon atoms into the unoccupied p-orbital of another silicon center.

Interestingly, when the *trans*-bent angle of a disilyne (Chart 1.5b, left) approaches 90° or incorporation of strongly σ -donating donor ligands (NHCs, imines and phosphines)^[3d-h,4] at the silicon centres, induces structure resembling highly polarized 1,2-diylidic structures with non-bonding nature of lone pair and a long Si–Si bond (Chart 1.5b, right).^[5c,9] In short, each of the silicon element retains an electron pair, an unoccupied p-orbital stabilized by donor ligand, a σ -interaction between Si–R and lastly a Si–Si π -bond.

Henceforth, low-oxidation state silicon chemistry has established a vigorous domain of study with increasing focus towards novel complexes comprises of mono-valent dinuclear silicon centers within a molecule (**1.13** – **1.16**, Chart 1.6).^[3d-h] Their fascinating electronic properties allow them being powerful reagents for the transformation of small molecules (i.e., Br₂, PhC≡CH, [Li][B(C₆F₅)₄] and thiolate), unsaturated substrates (CO₂, PhC≡CH and 1,2-C₂H₄X₂; X = Cl, Br, I), etc..^[3e,3h,5n,10] Notably, bis-silylene **1.16** (Chart 1.6) features the only silicon(I) dimer template capable of non-metal mediated reduction of CO₂ to CO at room temperature.^[3h] Our group has also explored the reactivity of **1.14** (Chart 1.6) with varying amount of phenylacetylene (1 – 2 equivalents) to furnish the unprecedented *cis*-1,2-disilylenylethene [*cis*-R²Si{C(Ph)=C(H)}SiR²] (R² = {PhNC(*t*Bu)}) and singlet delocalized biradicaloid [R²Si(μ₂-C₂Ph₂)₂SiR²].^[10c] Furthermore, they function as fundamental units for the assembly of complex compounds^[11] and serve as excellent transition metal ligand in catalytic transformations^[12], which have been extensively investigated by our group.^[10c,11-12]

Chart 1. 6 Isolated base-stabilized silicon(I) dimers.^[3d-h]

It was then discovered that the *N*-heterocyclic carbenes (NHCs) ligands are efficient Lewis bases (LB) in the kinetic and thermodynamic stabilization of exceedingly labile low-oxidation state silicon complexes.^[13] Robinson first utilize NHC as a synthetic strategy for [L $\ddot{\text{Si}}$ – $\ddot{\text{Si}}$ L] species via the reduction of I_{Ar}SiCl₄ (I_{Ar} = :C{N(Ar)CH}₂, Ar = 2,6-*i*PrC₆H₃) using KC₈ to afford bis-silylene **1.13-Cl** (Chart 1.6).^[4] Both X-ray crystallography and theoretical studies elucidated that the imperative extremely σ -donor property of the NHC as the main stabilization of the reactive :Si–Si: fragment. Replacing the halide substituents with iodide furnishes the same frameworks **1.13-Br** and **1.13-I** (Chart 1.6).^[3e] Another notable example is the development of a new class of silylene by Roesky and extension work by Jones, whereby the amidinato silicon(I) dimer **1.14** – **1.15** (Chart 1.6) features a template with four-membered ring enclosing each of the silicon(I) atom, preserving :Si–Si: moiety from the reduction of their corresponding silicon(IV) trichloride.^[3f,3g] Similar dehalogenation/reduction protocol was implemented with amido-phosphine backbone to access the resultant silicon(I) dimer **1.16** (Chart 1.6).^[3h]

The bond length of Si–Si moiety in the silicon(I) dimer **1.13** – **1.16** ranges from 2.385 – 2.393 Å, which are significantly elongated from the average singly-bonded Si–Si (2.37 Å) found in silanes and the classical doubly-bonded Si=Si (*ca* 2.14 – 2.29 Å) in disilenes, characteristic of feeble interaction within the Si–Si fragment in **1.10** – **1.12**.^[5d] Therefore, silicon(I) dimer conforms to the bonding mode of the singly-bonded derivative of disilyne as shown in Chart 1.5b (right). As expected, the reactivity of these compounds predominates on the HOMO, which is the stereoactive lone pair.^[3e,3h,5n,10-11,14]

Chart 1. 7 Base-stabilized silicon(0) dimers.^[4,15]

Another class of silicon species to be reckoned with belongs to the diatomic zero-valent silicon complexes. Clothed with the accumulated wisdom on stabilization techniques of low-valent silicon species, Roesky adopted the strongly σ -donating and sterically shielding I_{Ar} to encapsulate the Si=Si fragment in compound **1.17** (Chart 1.7) via simple dehalogenation reaction from $I_{Ar}SiCl_4$.^[4] The NHC-stabilized silicon(0) dimer **1.17** comprises of :Si=Si: moiety and features a doubly-bonded Si=Si (2.2294(1) Å) comparable to typical disilenes.^[4,5d] The two I_{Ar} ligands are in parallel arrangement and are bound almost orthogonally to the core Si=Si fragment (93.37(5) °), showing predominantly p-character for the Si–ligand bonding interactions and prevailing non-bonding s-type electron pair on the silicon element. Consequently, the silicon center is in mono-valent state.^[4] Not long ago, a cyclic (alkyl)(amino)carbenes (cAACs)-stabilized silicon(0) dimer **1.18** was unveiled using similar strategy (Chart 1.7).^[15]

Chart 1. 8 Multi-reactive sites of compound **1.13-I**.^[3e]

Given phenomenal achievements in developing various low-valent silicon compounds, reactivity of the dimeric silicon(I) and silicon(0) species is rather bland as compared to their silicon(II) variant. The underwhelming response has galvanized us to showcase its well-deserving limelight, particularly for the case of **1.13** and **1.17**. Compound **1.13-I** is an embodiment of a flexible yet worthwhile synthetic synthon with its displaceable halide and ligand functionalities as compared to its sister compounds in Chart 1.6 (Chart 1.8), raises the playing field for infinite exciting reactivities yet to unravel—the centrepiece of this thesis.

1.2 Results and Discussion

1.2.1 Optimizing the Synthesis of NHC–Silicon(I) Dimer (1.13-I)

Granted with the passing years since the identification of the NHC–stabilized silicon(I) dimer **1.13-Cl** in 2008, the chemistry of NHC–stabilized silicon(I) dimer **1.13** were minimally explored by Robinson and Filippou (Chart 1.9).^[3e,5n] In this context, we are excited to explore its potential as the multi-reactive site synthon for exotic transformations.

Chart 1. 9 Reactivity of NHC–stabilized silicon(I) dimer **1.13-I**.^[3e,5n]

In spite of success by Robinson, the yield of **1.13-Cl** entailed was undesirable (6.1%) and it co-crystallized with the dimeric NHC-stabilized silicon(0) **1.17** (Chart 1.10).^[4] While Fillippou has actualized an array of pure dimeric NHC-stabilized silicon(I) halides **1.13**, accessible via the oxidation of NHC-stabilized silicon(0) $[\text{I}_{\text{Ar}}\text{Si}]_2$ with 1,2-dihaloethanes in relatively high yield, however, the addition of the 1,2-dihaloethanes require high precision and slow addition at low temperature, else it undergoes further oxidation to form silicon(II) halides $[\text{I}_{\text{Ar}}(\text{I})_2\text{Si}]$ (Chart 1.10).^[3e] Moreover, the precursor $[\text{I}_{\text{Ar}}\text{Si}]_2$ **1.17** involves multi-step synthesis and the yield is less than desirable (6.1%), which hampers the further exploration of its reactivity (Chart 1.10). Consequently, the reactivity of the NHC-stabilized silicon(I) halides remains scarce. Therefore, it is imperative to reassess the reaction conditions to tailor an improved synthetic protocol of **1.13-I** with favorable yield.

Chart 1. 10 Reactivity of NHC-stabilized silicon(I) dimer **1.13-I**.^[3d-h,4,16]

As portrayed in Chart 1.10, reduction of halogenated precursors is an inevitable event to procure silicon(I) dimers. However, using harsh reducing agents such as the classical KC_8 and lithium accompany with the risk of over-reduction, in which the intended low-valent center is in the further reduced state and deposits itself in an undesirable elemental form. Consequently, poor yield is expected. Amongst the reducing reagents, β -diketiminato-stabilized Mg(I) dimer $[\{(\text{Nacnac}_{\text{Mes}})\text{Mg}\}_2]$ ($\text{Nacnac}_{\text{Mes}} = [\{\text{N}(\text{Mes})\text{CMe}\}_2\text{CH}]$, $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) effected the best yield of the corresponding bulky amidinato silicon(I) dimer **1.15** (91%), though overshadowed by its lengthy and laborious synthetic routes (Chart 1.10),^[16] pales in comparison to the classical reducing agents, which are much straightforward and efficient. Except for the method described by Filippou, the silicon(I) dimers are obtained from their respective silicon(IV) trihalides in a single step reduction.

With much consideration, we prescribed an improved synthesis route for **1.13-I** by incorporating the methodologies developed by Robinson and Filippou. Instead of using $\text{I}_{\text{Ar}}\text{SiCl}_4$ precursor, we engage the direct reduction of the heavier analogue $[\text{I}_{\text{Ar}}\text{SiI}_3]^+\text{I}^-$ ^[17] with three equivalents of KC_8 at room temperature in toluene (Scheme 1.1). In contrast to the indirect synthetic method disclosed by Fillipou^[3e] our methodology offers a simpler synthetic step and a better overall reaction yield.

Scheme 1. 1 Optimized synthesis of NHC-stabilized silicon(I) dimer **1.13-I**.

The NHC-stabilized tetraiodosilane $[\text{I}_{\text{Ar}}\text{SiI}_3]^+\text{I}^-$ can be easily achieved in quantitative yield from the overnight reaction of NHC I_{Ar} with silicon(IV) iodide at room temperature in toluene (Scheme 1.1).^[17] Upon stirring the resultant $[\text{I}_{\text{Ar}}\text{SiI}_3]\text{I}$ with three equivalents of KC_8 for three days under ambient conditions, the expected crystal of **1.13-I** was obtained from toluene under reduced pressure. Its identity was characterized by X-ray and NMR spectroscopy, is agreeable to reported literature.^[3e] Despite the mediocre yield of 33%, it translates to about six- and two-fold improvement from that of Robinson and Filippou, respectively. Herein, with this improved formulation at hand, we divulge into the reactivity of **1.13-I**.

1.2.2 Synthesis of NHC–Silicon(0) Dimer (**1.17**)

Reduction of NHC–stabilized silicon(I) dimer **1.13-I** was successfully performed using KC_8 at ambient temperature to afford the corresponding NHC–stabilized silicon(0) **1.17** after 16 hours (Scheme 1.2). Upon work up, the moisture- and air-sensitive red crystalline **1.17**, obtained in 92% yield, was subjected to X-ray crystallography and NMR spectrometry analyses, which its structure corresponds to the reported literature.^[4] Unfortunately, the overall attainable yield is limited to 30% from the precursor $[\text{I}_{\text{Ar}}\text{SiI}_3]^+\text{I}^-$, is only slim improvement from Robinson's protocol. Nevertheless, it is sufficient to be an alternative synthetic method to access compound **1.17**.

Scheme 1. 2 Synthesis of NHC–stabilized silicon(0) dimer **1.17**.^[4]

Amongst diverse transformation of NHC–stabilized silicon(0) dimer **1.17** with various substrates and transition metal complexes (Chart 1.11),^[5e-m] the reaction of NHC–stabilized silicon(0) **1.17** with oxygen caught our attention. Herein, we are delighted to indulge the scope of complex **1.17** towards heavier chalcogen (Ch = S, Se and Te).

Very recently, dimeric NHC–silicon dichalcogenide complexes were isolated from NHC–disilicon(0) complexes. Robinson et al. reported the NHC–disilicon trioxide [$\{(I_{Ar})Si(=O)\}_2O$] (**1.20**, Chart 1.12) and dimeric NHC–silicon dioxide complexes [$(I_{Ar})Si(=O)(\mu-O)_2$] (**1.21**) by the reaction of the NHC–disilicon(0) complex **1.17** with three equivalents of N_2O and two equivalents of molecular oxygen (O_2), respectively (Chart 1.12).^[51] However, the conversion of compound **1.21** into **1.20** is inaccessible by an oxidation, instead decomposition of **1.21** was found. Similarly, Roesky et al. isolated the heavier analogue, dimeric cAAC–silicon disulfide and diselenide complexes [$(cAAC_{Me})Si(=Ch)(\mu-Ch)_2$] (**1.22**, $Ch = S, Se$; $cAAC_{Me} = :C(CMe_2)_2(CH_2)N_{Ar}$, Chart 1.12), but the key intermediates, NHC–silicon monochalcogenides were not observed in the reactions.^[22]

Chart 1. 12 Reactivity of Lewis base-stabilized mono- and disilicon(0) towards chalcogen.^[51,22-24]

Driess et al. utilized another class of NHC–silicon(0) complex, the (bis-NHC)–monosilicon(0) complex (bis-NHC: $H_2C[NC(H)=C(H)N(Ar)]C:$) to isolate the (bis-NHC)– $GaCl_3$ -stabilized silicon monoselenide and disulfide donor–acceptor complexes, as well as the (bis-NHC)–silicon ditelluride complex (**1.23** – **1.26**, Chart 1.12).^[23] Moreover, they showed that the (bis-NHC)– $GaCl_3$ -stabilized silicon monoselenide complex **1.24** further underwent an oxidation to form the corresponding monomeric silicon diselenide complex (**1.25**, Chart 1.12).^[23a] Furthermore, Baceiredo and Kato et al. isolated a monomeric SiO_2 complex using a different donor–acceptor strategy (**1.27**, Chart 1.12).^[24]

On the basis of the above-mentioned examples, we are interested in isolating a molecular silicon monotelluride SiTe with the aid of an *N*-heterocyclic carbene. Moreover, it is anticipated that a NHC–disilicon(0) complex **1.17** undergoes a different and complex reaction mechanism toward chalcogenation in comparison with a (bis-NHC)monosilicon(0) complex, which could result in the formation of fruitful molecular binary silicon chalcogenides and even unknown ternary silicon heterodichalcogenides, such as a molecular disilicon tritelluride and disilicon sulfur ditelluride.

In the next section, we report how tellurium atoms interact with a :Si=Si: moiety, which results in the formation of a dimeric silicon monotelluride comprising Si=Te double bonds in the form of an adduct with NHCs. We also report its isomerization and further oxidation to form a NHC–disilicon tritelluride and dimeric NHC–silicon ditelluride complex, as well as a remarkable NHC–disilicon sulfur ditelluride complex.

1.2.3 Reactivity of NHC–Silicon(0) Dimer (**1.17**) toward Chalcogen

First, the reaction of the NHC–disilicon(0) complex $[(\text{I}_{\text{Ar}})\text{Si}=\text{Si}(\text{I}_{\text{Ar}})]$ (**1.17**) with four equivalents of elemental tellurium in toluene was monitored by ^1H NMR spectroscopy (see Section 1.5.1, Figure S1.21). After 3 days of the reaction, the ^1H NMR spectrum showed a mixture of unreacted compound **1.17**, the dimeric NHC–silicon monotelluride $[(\text{I}_{\text{Ar}})\text{Si}=\text{Te}]_2$ (**1.31**, Scheme 1.3) and its isomeric complex $[(\text{I}_{\text{Ar}})\text{Si}(\mu\text{-Te})\text{Si}(\text{I}_{\text{Ar}})=\text{Te}]$ (**1.32**) in a ratio of 1:1:0.08 on the basis of HC=CH proton integration of I_{Ar} ligands at δ 6.20 (**1.31**) and 6.18, 6.28 ppm (**1.32**). After 5 days, the ^1H NMR spectrum illustrated that compound **1.17** was completely transformed into compounds **1.31** and **1.32** in a ratio of 0.2:1. After 10 days, compound **1.32** was the only product present in the reaction mixture. These observations suggest that compound **1.31** is an intermediate and undergoes an isomerization to form a mixed-valent Si_2Te ring in compound **1.32**. It further reacted with elemental tellurium. After 16 days, trace amount of the NHC–disilicon tritelluride complex $[\{(\text{I}_{\text{Ar}})\text{Si}(=\text{Te})\}_2\text{Te}]$ (**1.34-Te**) and dimeric NHC–silicon ditelluride $[(\text{I}_{\text{Ar}})\text{Si}(=\text{Te})(\mu\text{-Te})]_2$ (**1.33**) were formed in a **1.32**: **1.34-Te**: **1.33** ratio of 1:0.05:0.2 on the basis of HC=CH proton integration of I_{Ar} ligands at δ 6.18, 6.28 (**1.32**), 6.23 ppm (**1.34-Te**) and 6.18, 6.21 ppm (**1.33**). After one month, the reaction was completed and only compound **1.33** was found. When the same reaction was performed in d_8 -THF, it was completed in 3.5 h and only compound **1.33** was afforded as the sole product (Figure S1.20). Owing to the fast reaction rate, it is anticipated that the isolation of intermediates is difficult using THF as solvent.

Scheme 1.3 Synthesis of compounds **1.31** – **1.33**. The formation of compound **1.33** through the NHC–disilicon tritelluride intermediate **1.34-Te** is also shown.

In this context, compound **1.17** was reacted with two equivalents of elemental tellurium in toluene at room temperature for three days.^[25] After workup, orange crystals of **1.31** (major product) and red crystals of **1.32** (minor product) were afforded from its concentrated fluorobenzene solution. An attempt to separate compounds **1.31** and **1.32** by recrystallization failed. Furthermore, prolonged crystallization led to the disappearance of orange crystals of **1.31** and only red crystals of **1.32** were afforded. Moreover, when the same reaction was performed for ten days, only dark red, block-like crystals of **1.32** were isolated (yield: 49.4 %) from the reaction mixture. Furthermore, compound **1.17** reacted with four equivalents of elemental tellurium in toluene for four weeks. After workup, red crystals of **1.33** were isolated (yield: 31.8 %) from its concentrated fluorobenzene solution. An attempt to isolate **1.34-Te** from the reaction of **1.17** with Te in various conditions failed, but it was unexpectedly afforded using another method (see below, Scheme 1.4).

Crystals of compounds **1.31** – **1.33** are air- and moisture-sensitive and stable in an inert atmosphere of argon gas. They are soluble in THF and fluorobenzene, but compounds **1.31** and **1.32** slowly decomposed in solution to form compound **1.33** and a black precipitate. They were characterized by NMR spectroscopy and X-ray crystallography.

Figure 1. 1 Molecular structure of **1.31** (ellipsoids set at 30 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si1A 2.343(14), Si1–Te1 2.246(7), C1–Si1 1.926(13), C1–N1 1.348(15), C1–N2 1.383(15); C1–Si1–Si1A 106.8(10), C1–Si1–Te1 119.5(10), Si1A–Si1–Te1 127.8(5), N1–C1–N2 104.5(11).

The ^1H NMR spectrum of **1.31** shows one set of signals due to the I_{Ar} ligands. Its ^{29}Si ($\delta = -107$ ppm) and ^{125}Te ($\delta = -1413$ ppm) chemical shifts are in high field region, which are similar to those of base-stabilized four-coordinate silanetellones such as the amidinato silanetellone $[\text{PhC}\{\text{N}(t\text{Bu})\}_2\text{Si}(=\text{Te})\{\text{N}(\text{SiMe}_3)_2\}]$ (^{29}Si : $\delta = -47.6$; ^{125}Te : -1093 ppm)^[26] and NHC-stabilized *N*-heterocyclic silanetellone $[\{\text{N}(\text{Ar})\text{C}(\text{CH}_2)\text{C}(\text{H})\text{C}(\text{Me})\text{N}(\text{Ar})\}\text{Si}(\text{I}_{\text{PrMe}})=\text{Te}]$ (^{29}Si : $\delta = -49.6$; ^{125}Te : -982.5 ppm; $\text{I}_{\text{PrMe}} = :\text{C}\{\text{N}(i\text{Pr})\text{C}(\text{Me})\}_2$).^[27] These indicate the Si=Te double bonds in **1.31** are highly polar.

The molecular structure of **1.31** (Figure 1.1) shows that the Si1–Si2 bond (2.343(14) Å) is the longest yet reported for a Si=Si double bond (2.144 – 2.2890(14) Å)^[28] because compound **1.31** is strongly *trans*-bent (24.1°) and twisted (angle between C1–Si1–Si1A–C1A and Te1–Si1–Si1A–Te1A least-squares planes: 27.7°), along with pyramidalization at two silicon atoms (354.1°). In contrast, the Si1–Te1 bond (2.246(7) Å) is the shortest yet reported for a Si=Te double bond (three-coordinate Si=Te: 2.3210(6) Å,^[29] four-coordinate base-stabilized Si=Te: 2.3720(15) – 2.383(2) Å).^[27,30] It is also slightly shorter than that in the parent silanetellone $\text{H}_2\text{Si}=\text{Te}$ (2.28 Å).^[31] The C1–Si1 bond (1.926(13) Å) is comparable with that of **1.17** (1.9271(15) Å).^[4]

Figure 1. 2 Molecular structure of **1.32** (ellipsoids set at 30 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.330(11), Si1–Te1 2.387(7), Si1–Te2 2.530(8), Si2–Te2 2.641(8), C1–Si1 1.97(2), C28–Si2 1.98(2), C1–N1 1.37(2), C1–N2 1.382(19), C28–N3 1.36(2), C28–N4 1.38(2); C1–Si1–Te2 98.6(5), C28–Si2–Si1 98.5(6), C28–Si2–Te2 100.6(7), Si1–Te2–Si2 53.5(2), Si1–Si2–Te2 60.8(3), Si2–Si1–Te2 65.7(3), Te1–Si1–Te2 123.1(3).

The ^1H NMR spectrum of **1.32** displays two sets of signals assignable to two different I_{Ar} ligand environments. At room temperature, two ^{29}Si NMR signals at $\delta = -110$ and -126 ppm (in C_6D_6) correspond to the three- and four-coordinate silicon atoms, respectively, which are upfield shifted in comparison with ^{29}Si NMR signals of the Si_2E ($\text{E}=\text{O}$, Te) three-membered rings in the NHC–disilicon trioxide [$\{(\text{I}_{\text{Ar}})\text{Si}(=\text{O})\}_2\text{O}$] (**1.21**, $\delta = -49.1$ ppm, Chart 1.12)^[51] and the disilatelluriranes [$\{\text{Mes}_2\text{Si}\}_2\text{Te}$] ($\delta = -90.3$ ppm)^[32] and [$\{(t\text{Bu}_3\text{Si})(\text{Ph})\text{Si}\}_2\text{Te}$] ($\delta = -81.1$ ppm).^[33] At -80°C , the nearly identical chemical shifts ($\delta -109$ and -131 ppm, in d_8 -toluene) suggest that the interconversion between **1.31** and **1.32** was not taken place in solution. The ^{125}Te NMR signals of **1.32** at $\delta = -1035$ (bridging) and -1083 ppm (terminal) are in the high field region, which are similar to the terminal Te signal of **1.31** ($\delta = -1413$ ppm) and bridging Te signal of [$\{\text{Mes}_2\text{Si}\}_2\text{Te}$] ($\delta = -783.8$ ppm)^[32] and [$\{(t\text{Bu}_3\text{Si})(\text{Ph})\text{Si}\}_2\text{Te}$] ($\delta = -1285$ ppm).^[33]

The molecular structure of **1.32** (Figure 1.2) comprises two different Si environments. The Si1 and Si2 atoms adopt a tetrahedral and distorted trigonal pyramidal geometry, respectively. The sum of the bond angles around the Si2 atom (259.9°) suggests the presence of a stereoactive lone pair on the Si2 atom. The three-membered Si₂Te ring features unequal Si–Te bond lengths (2.530(8), 2.641(8) Å), owing to the different coordination environment at the Si1 and Si2 atoms. The Si1–Si2 (2.330(11) Å) and Si1–Te2 bond lengths (2.530(8) Å) are similar to the Si₂Te rings in the disilatelluriranes [{Mes₂Si}₂Te] (Si–Si: 2.337(4); Si–Te: 2.523(3), 2.524(3) Å)^[32] and [{(*t*Bu₃Si)(Ph)Si}₂Te] (Si–Si: 2.343(8) Å; Si–Te: 2.532(5), 2.536(6) Å).^[33] The Si1–Te1 bond length (2.387(7) Å) is longer than that of **1.31**, but is comparable with that of the NHC-stabilized *N*-heterocyclic silanetellone (2.383(2) Å),^[27] indicating a considerable double bond character. The Si–C bonds (1.97(2), 1.98(2) Å) are the longest in comparison with those of **1.31** and **1.33** (1.959(7) Å).

Figure 1. 3 Molecular structure of **1.33** (30% ellipsoids probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Te1 2.390(2), Si1–Te2 2.517(2), C1–Si1 1.959(7), C1–N1 1.373(9), C1–N2 1.356(10); C1–Si1–Te1 106.3(2), C1–Si1–Te2 108.2(2), C1–Si1–Te2A 109.4(2), N1–C1–N2 105.3(6), Te1–Si1–Te2 118.18(8), Te1–Si1–Te2A 117.37(8), Te2–Si1–Te2A 96.94(7).

The ^1H NMR spectrum of **1.33** displays two sets of signals corresponding to I_{Ar} ligands, which are inconsistent with the solid-state structure. Hence, variable-temperature ^1H NMR spectroscopy was performed and only one set of signals for I_{Ar} ligands was observed at $75\text{ }^\circ\text{C}$, which suggests that the restricted rotation of I_{Ar} ligands was relaxed at high temperature. The ^{29}Si NMR signal ($\delta = -166\text{ ppm}$) is upfield shifted in comparison with the lighter analogue, dimeric NHC–silicon dioxide $[(\text{I}_{\text{Ar}})\text{Si}(=\text{O})(\mu\text{-O})]_2$ (**1.20**, $\delta = -76.3\text{ ppm}$, Chart 1.12).^[51] The ^{125}Te NMR signals for the terminal ($\delta = -941\text{ ppm}$) and bridging Te ($\delta = -587\text{ ppm}$) atoms are in high field region, which are similar to those of **1.32**. The molecular structure of **1.33** (Figure 1.3) is isostructural to the lighter analogue $[(\text{I}_{\text{Ar}})\text{Si}(=\text{O})(\mu\text{-O})]_2$ (**1.20**, Chart 1.12),^[51] along with the terminal Si1–Te1 ($2.390(2)\text{ \AA}$) and bridging Si1–Te2 ($2.517(2)\text{ \AA}$) bonds being comparable with those in **1.32**, respectively.

Scheme 1. 4 Free energy profile (kcal/mol) for the formation of compounds **1.31** – **1.33**. The abbreviations Int, TS, and PRC stand for intermediate, transition state, and pre-reaction complex, respectively. Geometrical coordinates of the reactants, intermediates, transition states, and compounds **1.31** – **1.33** are at M06-2X/def2-SVP level of theory. $i\text{PrNHC} = \text{I}_{\text{Ar}}$.

DFT studies for the reaction mechanism (Scheme 1.4) are in line with experimental results. Compound **1.17** reacts with the first Te atom by overlapping the LUMO of the Te atom (Figure S1.31f) with the HOMO-2 (lone pair orbital on the Si atom; Figure S1.31b) of **1.17** to form **Int1.1**, comprising a :Si=Si=Te skeleton ($\Delta G_{1.17+2\text{Te} \rightarrow \text{Int1.1}} = -88.2$ kcal/mol). **Int1.1** isomerizes through **TS1.1** (free energy barrier: 18.3 kcal/mol) leading to the formation of a three-membered :Si₂Te ring in **Int1.2** ($\Delta G_{1.17+2\text{Te} \rightarrow \text{Int1.2}} = -94.4$ kcal/mol). It then reacts without barrier with the second Te atom by overlapping the LUMO of the Te atom with the HOMO of **Int1.2** (Figure S1.31c) through a pre-reaction-complex (**PRC**) ($\Delta G_{1.17+2\text{Te} \rightarrow \text{PRC}} = -117.3$ kcal/mol) and **TS1.2** (4.8 kcal/mol above **PRC**) to form a :Si(μ -Te)₂Si: ring in **Int1.3** ($\Delta G_{1.17+2\text{Te} \rightarrow \text{Int1.3}} = -177.0$ kcal/mol). **Int1.3** isomerizes and proceeds through **TS1.3** (free energy barrier: 27.0 kcal/mol) by interacting two sp hybrid and p-orbitals of the Si atoms to form the Si-Si σ and π orbitals in **1.31** ($\Delta G_{1.17+2\text{Te} \rightarrow 1.31} = -166.4$ kcal/mol), respectively. Alternatively, **Int1.1** can also directly react with the second Te atom to form **1.31**. The relaxed potential energy surface scan at M06-2X/def2-SVP (Figure S1.40) suggests that the reaction is exothermic and the direct reaction of **Int1.1** with the second Te atom is a barrierless process, similar to the reaction of compound **1.17** with the first Te atom (Figure S1.39). Compound **1.31** further isomerizes through **TS1.4** (free energy barrier: 33.8 kcal/mol) by the overlapping of p-orbitals between the Si and Te atoms to form compound **1.32** ($\Delta G_{1.17+2\text{Te} \rightarrow 1.32} = -180.8$ kcal/mol). It reacts without barrier with the third Te atom by interacting the lone-pair electrons of the Si (HOMO; Figure S1.31d) and Te atoms (LUMO; Figure S1.31f) to give **Int1.4 (1.34-Te)**, comprising a Te=Si(μ -Te)Si=Te skeleton ($\Delta G_{1.17+2\text{Te} \rightarrow \text{Int1.4}} = -254.1$ kcal/mol). Subsequent isomerization of **Int1.4 (1.34-Te)** by overlapping the p-orbitals between the Si and Te atoms, along with cleavage of the Si-Si bond (free energy barrier: 30.8 kcal/mol), lead to the formation of a TeSi(μ -Te)₂Si: four-membered ring in **Int1.5** ($\Delta G_{1.17+2\text{Te} \rightarrow \text{Int1.5}} = -260.1$ kcal/mol). **Int1.5** further undergoes a barrierless oxidation with the fourth Te atom to furnish the formation of **1.33** ($\Delta G_{1.17+2\text{Te} \rightarrow 1.33} = -344.4$ kcal/mol). It appears that the theoretical reaction mechanism is not in line with experimental results, as the reaction of **1.32** with Te required 15 days for the complete conversion into **1.33**. The long reaction time is due to the very poor solubility of tellurium metal in toluene. It is noteworthy that the reaction of **1.17** with Te in THF was complete in 3.5 h to form **1.33**, which is consistent with the theoretical reaction mechanism.

The nature of bonding in **1.31** – **1.33** was further probed by DFT studies at the M06-2X/def2-SVP level of theory. The natural bond orbital (NBO) analysis shows that the Si–Si bond in **1.31** consists of a sp^2 -hybridized σ bond (36.7 % s, 62.8 % p, 0.5 % d) and a p-type π bond (5.3 % s, 94.4 % p, 0.3 % d). Accordingly, the Wiberg bond index (WBI) of 1.433 suggests that the Si–Si bond in **1.31** possesses considerable double bond character. Furthermore, compound **1.32** comprises a polarized Si–Si σ bond ($\sigma_{SiSi} = 57.4\%$ Si_{four-coord} + 47.6 % Si_{three-coord}) with WBI of 0.912. There is no bonding between the Si atoms in compound **1.33** (calculated Si...Si distance: 3.362 Å). All bridging and terminal Si–Te σ bonds in **1.31** – **1.33** are polarized towards the Te atoms (NPA charge, **1.31**: +0.26 for Si, -0.59 for Te_{terminal}; **1.32**: +0.10, +0.36 for Si, -0.39 for Te_{bridge}, -0.62 for Te_{terminal}; **1.33**: +0.46 for Si, -0.19 for Te_{bridge}, -0.57 for Te_{terminal}). Moreover, there are two degenerate lone-pair orbitals (p-orbitals) for each terminal Te atom in **1.31** – **1.33**. They form negative hyperconjugation with the σ^* orbitals around the Si atoms (the sum of second order perturbation stabilizing energies, **1.31**: 39.24 kcal/mol; **1.32**: 42.67 kcal/mol; **1.33**: 92.72 kcal/mol), which result in shortening the terminal Si–Te bonds. Accordingly, the WBIs of the Si–Te_{terminal} bonds in **1.31** (1.303), **1.32** (1.318) and **1.33** (1.325) are significantly larger than those of the Si–Te_{bridge} bonds in **1.32** (0.838) and **1.33** (0.911), suggesting a considerable double-bond character for the Si–Te_{terminal} bonds. All Si–C_{carbene} bonds are polarized toward the C_{carbene} atoms (**1.31**: 75.9 % C + 24.1 % Si; **1.32**: 76.1 % C + 23.9 % Si; **1.33**: 75.8 % C + 24.2 % Si), while the corresponding heterolytic bond dissociation energies are 64.1, 50.9, and 53.3 kcal/mol for compounds **1.31** – **1.33**, respectively. Moreover, the WBI of Si–C_{carbene} bonds in **1.31** – **1.33** are 0.686, 0.645, and 0.622, respectively. In the EDA-NOCV analysis, the energies contribution of C_{carbene}–Si bonds in **1.31** – **1.33** from the electrostatic interaction (**1.31**: 54.6; **1.32**: 55.2; **1.33**: 55.3 %) are slightly greater than that from the orbital interaction (**1.31**: 45.4; **1.32**: 44.8; **1.33**: 44.7 %). Furthermore, the Si–C_{carbene} orbital interactions are majorly formed by the donation of a lone pair of electrons from the C_{carbene} to Si atoms (**1.31**: $\Delta E = -101$ kcal/mol, 64.0 %; **1.32**: $\Delta E = -89.1$ kcal/mol, 65.7 %; **1.33**: $\Delta E = -92.0$ kcal/mol, 67.1 % of the total covalent interaction).

On the basis of experimental and theoretical results (Figure S1.38), the Si=Te bonds in **1.31** – **1.33** are dominated by the high polarity of the Si–Te linkage(s) and by the negative hyperconjugation between the lone pairs at the terminal tellurium atom(s) and the σ^* orbitals around the silicon atom(s). A similar bonding situation can also be found in the Si=Te bond of the NHC–heavier silatelluroaldehyde [(I_{Me})Ter*Si(=Te)H] (Ter*=2,6-bis(2,4,6-triisopropylphenyl)phenyl).^[34]

Scheme 1.5 Synthesis of compounds **1.34-S**, **1.34-Te** and **1.33**.

Following complete characterization of **1.31** – **1.33**, the reactivity of **1.32** was preliminarily investigated. It reacted with one equivalent of elemental sulfur S in toluene at room temperature to form a mixture of the NHC–disilicon sulfide ditelluride complex [(I_{Ar})Si(=Te)]₂S (**1.34-S**, Scheme 1.5), NHC–disilicon tritelluride complex [(I_{Ar})Si(=Te)]₂Te (**1.34-Te**), **1.33** and a black precipitate. After work-up, compounds **1.34-S** and **1.34-Te** were co-crystallized in a ratio of 4:1 as red block-like crystals. An attempt to separate them by recrystallization failed. Similar results were found when the reaction was performed at -78 °C. The reaction mechanism is unknown as yet. It is proposed that compound **1.32** reacts with elemental sulfur to form **1.34-S**, while it also simultaneously undergoes a disproportionation to form **1.34-Te**, **1.33** and tellurium in the reaction. **1.34-S** is the first molecular ternary silicon heterodichalcogenide comprising two different chalcogens in the form of an adduct with NHC. To the best of our knowledge, bulk ternary silicon heterodichalcogenides are still unknown. The red co-crystals were analyzed by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum supports the presence of a mixture of **1.34-S** and **1.34-Te** in an approximate ratio of 6:1 on the basis of HC=CH proton integration of I_{Ar} ligands (**1.34-S**: δ = 6.28, **1.34-Te**: 6.23 ppm). Furthermore, the HC=CH proton chemical shift of **1.34-Te** is in line with ¹H NMR spectroscopy of the above-mentioned mechanistic studies for the formation of **1.33**, showing that **1.34-Te** is an intermediate in the reaction. It is noteworthy that **1.34-Te** is unstable in solution and decomposed in C₆D₆ after a

day (Figures S1.15 and S1.16). In this context, its ^{29}Si and ^{125}Te NMR signals cannot be obtained. The ^{29}Si and ^{125}Te NMR signals (^{29}Si : $\delta = -114$; ^{125}Te : -1060 ppm) for **1.34-S** are in high field region similar to those of **1.32**. The X-ray crystal structures of **1.34-S** and **1.34-Te** (Figure 1.4) are isostructural to that of the NHC–disilicon trioxide complex $[(\text{I}_{\text{Ar}})\text{Si}(=\text{O})_2\text{O}]$ **1.21** (Chart 1.12).^[51] The Si1–Si2 (2.336(5) Å), Si1–S1 (2.141(11) Å), and Si2–S1 (2.117(9) Å) bonds in **1.34-S** are comparable with those of the Si_2S three-membered ring in the disilathiirane $[\{\text{Mes}_2\text{Si}\}_2\text{S}]$ (Si–Si: 2.289(2); Si–S: 2.161(2), 2.162(2) Å).^[35] The bridging Si–Te2 bond lengths (2.531(11), 2.562(10) Å) in **1.34-Te** are comparable with those of **1.32**.

Figure 1. 4 Molecular structures of **1.34-S** and **1.34-Te** (ellipsoids set at 30 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1.34-S**: Si1–Si2 2.336(5), Si1–Te1 2.371(3), Si2–Te2 2.355(4), C1–Si1 1.926(12), C2–Si2 1.933(12), Si1–S1 2.141(11), Si2–S1 2.117(9); S1–Si1–Si2 56.2(3), Si1–S1–Si2 66.6(3), S1–Si2–Si1 57.2(4). **1.34-Te**: Si1–Te3 2.531(11), Si2–Te3 2.562(10); Si1–Te3–Si2 54.6(2), Te3–Si1–Si2 63.4(3), Te3–Si2–Si1 62.0(3).

1.2.4 Reactivity of NHC–stabilized Silicon(I) Dimer (1.13-I) toward Tellurium

Following the successful isolation of the dimeric NHC–silicon monotelluride **1.31**, we were interested in synthesizing another example of monotelluride species via the oxidation of **1.13-I** with tellurium. However, the treatment of **1.13-I** with two equivalents of elemental tellurium did not afford the expected $[\text{I}_{\text{Ar}}(\text{I})\text{Si}(=\text{Te})]_2$, instead the formation of first dimeric NHC–stabilized silicon(III) iodo(μ -telluride) radical $[\text{I}_{\text{Ar}}(\text{I})(\mu\text{-Te})\text{Si}^\bullet]_2$ (**1.35**, Scheme 1.6) was observed. The reaction was conducted in toluene for 5 days under light sensitive and ambient conditions. Upon work up, red crystals of **1.35** were afforded in 16% yield from its concentrated fluorobenzene solution. The poor yield is attributed to its inherent poor solubility in most organic solvents.

Scheme 1. 6 Synthesis of **1.35**.

Crystals of complex **1.35** are moisture- and air-sensitive. It is bottleable for months under inert atmosphere of argon gas. Compound **1.35** is partially soluble in THF, benzene and fluorobenzene, but it decomposes in solution over time to form compound **1.13-I** and a black precipitate. The identity of **1.35** was affirmed using NMR spectroscopy and X-ray crystallography.

The ^1H NMR spectrum of **1.35** indicates one set of signals due to the I_{Ar} ligands. Its ^{29}Si ($\delta = -9.76$ ppm) chemical shifts is extremely downfield shifted as compared to its structural isomers dimeric NHC–silicon ditelluride $[(\text{I}_{\text{Ar}})\text{Si}(=\text{Te})(\mu\text{-Te})]_2$ (**1.33**, $\delta = -166$ ppm). However, it is comparable to the bulky silyl-stabilized silicon(III) dimer $[\text{R}^5\{\mu\text{-N}(\text{Ar}^1)\}\text{Si}^\bullet]_2$ ($\delta = 19.4$ ppm; $\text{R}^5 = \text{Si}i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$, $\text{Ar}^1 = 3,5\text{-Me}_2\text{C}_6\text{H}_3$)^[36] and amidinato-stabilized silicon(III) radical dimer $[\text{R}^2\{\mu\text{-CN}(\text{Ar})\}\text{Si}^\bullet]_2$ ($\delta = -39.9$ ppm)^[11c] It is also comparable to the biradical $(\text{cAAC}_{\text{Me}}^\bullet)_2\text{SiCl}_2$ ($\delta = 4.13$ ppm)^[37]. The $^{125}\text{Te}\{^1\text{H}\}$ NMR signal for the bridging Te in **1.35**

($\delta = -318$ ppm) is unexpectedly low field in comparison with bridging Te found in $[(\text{I}_{\text{Ar}})\text{Si}(\mu\text{-Te})\text{Si}(\text{I}_{\text{Ar}})=\text{Te}]$ **1.32** ($\delta = -1035$ ppm) and **1.33** ($\delta = -587$ ppm). In addition, solid state $^{125}\text{Te}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy did not result in any fruitful signal.

Figure 1. 5 Molecular structures of **1.35** (ellipsoids set at 30 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-Te1 2.5237(18), Si1-Te1 2.5195 (18), Si1-I1 2.3848(18); Si1-Te1-Si1 84.04(6), Te1-Si1-Te1 95.96(3), Te1-Si1-I1 106.02(7), Te1-Si1-I1 119.34(8).

The molecular structure of **1.35** features an almost planar centrosymmetric four-membered Si_2Te_2 ring (Figure 1.5a, Figure S1.41) with a distorted tetrahedral geometry on each of the silicon center. Further, the of $\text{Si1}\cdots\text{Si1}$ bond length in the Si_2Te_2 ring is 3.376 Å, substantially longer than average Si–Si bond (2.37 Å) in silanes^[5d], precursor **1.13-I** (2.3909 (9) Å)^[3e] and amidinato-stabilized silicon(III) radical dimer analogues ($\text{Si}\cdots\text{Si} = 2.6380(9)$ and 2.553(2) Å)^[11c,36]. Compound **1.35** shows bridging Si1–Te2 bond length (2.5195(18) and 2.5237(18) Å) comparable to **1.33** (2.517(2) Å) and slightly shorter than those in **1.32** (2.530(8) Å), indicative of a single bond Si–Te character. In this context, we postulate that compound **1.35** is a biradical species in which each of the silicon atom bears a radical center.

Figure 1. 6 EPR spectra of **1.35** in (a) 0.1 mM in toluene, (b) 5 mM in toluene, (c) 50 mM in toluene, (d) solid state, from 298 K (top) to 115 K (bottom).

Figure 1. 7 CW EPR (X-band) spectra of **1.35** in toluene:THF solution at (a) 298 K and (b) 115 K.

In order to elucidate the biradical nature of compound **1.35**, a variable-temperature ^1H NMR spectroscopy was performed (Figure S1.26). The intensity of signals in ^1H NMR of **1.35** reduces along with lower temperature and the disappearance of signal was observed at $-90\text{ }^\circ\text{C}$. EPR spectroscopy was conducted from 298 to 115 K in both toluene solution and solid state (Figure 1.6), which revealed a weak signal at ambient temperature and the signal intensifies as the temperature is lowered to 115 K (Figure 1.6). In addition, the signals intensified as the concentration of **1.35** increases (Figure 1.6a – c). The continuous wave (CW) EPR spectrum of **1.35** (in toluene:THF mixture, $T = 298\text{ K}$ (Figure 1.7a), and 115 K (Figure 1.7b)) suggests a three-line hyperfine multiplet pattern with $a_{\text{iso}} \sim 13\text{ G}$ was observed, suggestive of electron spin density ($\sim 2\%$) localised on a single ^{14}N nucleus. Upon inspection of molecular structure of **1.35** (Figure 1.5), it is unclear as to the origin of this hyperfine coupling. By factoring the EPR, NMR and X-ray analyses into consideration, we hypothesized that compound **1.35** is a biradical complex, exhibiting predominantly singlet and minor triplet attributes, similar to the $(\text{cAAC}_{\text{Me}}\bullet)_2\text{SiCl}_2$ ($\delta = 4.13\text{ ppm}$)^[37].

Theoretical study for the optimized geometry **1.35** displayed a large variation in the Si–I bond lengths in both optimized geometries of triplet and singlet state as compared to the X-ray crystal structure (Figure S1.41). Therefore, single point calculation on the X-ray crystal structure of **1.35** were carried out at the BP86/def2-SVP and CASSCF(6,6)/def2-SVP level of theory. The atomic spin density at the BP86/def2-SVP level of theory of the singlet **1.35** calculations using X-ray crystal structure indicate concentration of α -spin on the C and N atoms of one of the I_{Ar} and concentration of β -spin on the C and N atoms of another I_{Ar} (Table S1.19). Thus, the atomic spin density analysis shows the open shell singlet configuration of **1.35**.

The antibonding combination of the electron pair on Te and I centers is represented by Ψ_1 , which is doubly filled in all the three electronic states (Figure S1.42). The Ψ_2 and Ψ_3 represent the bonding and antibonding combination of the $\text{C}=\text{N}\pi^*$ orbital on the two NHCs coordinated to the Si-atoms. The singlet ground state CASSCF(6,6) calculations using def2-SVP basis set predicts almost equal contribution from S_0 ($\Psi_1^2\Psi_2^2\Psi_3^0\Psi_4^0$, 47%) and S_2 ($\Psi_1^2\Psi_2^0\Psi_3^2\Psi_4^0$, 52%), while no contribution to the singlet electronic state from the open shell singlet S_1 ($\Psi_1^2\Psi_2^\alpha\Psi_3^\beta\Psi_4^0$) is obtained. The triplet $\Psi_1^2\Psi_2^\alpha\Psi_3^\alpha\Psi_4^0$ configuration on the other hand shows 99% contribution to the T_1 electronic state. The triplet energy state is computed as 13.8 kcal/mol higher than that of singlet state.

Figure 1. 8 Schematic representation of Ψ_2 and Ψ_3 orbitals in open shell singlet **1.35**. The CASSCF (6,6)/def2-SVP calculation, indicating major contribution from the C=N π^* orbitals and slight contribution from Si-I σ^* orbitals.

In S_0 state, Ψ_2 molecular orbital is doubly filled. This means that each I_{Ar} are in their triplet state. One electron of each I_{Ar} is used for the formation electron sharing bond with Si atom and other electron is in their antibonding p^* -MO. Here, the linear combination of p^* -MO of both I_{Ar} are bonding type (Figure 1.8, left). In S_2 state, Ψ_3 molecular orbital is doubly filled. This also means that each I_{Ar} are in their triplet state. One electron of each I_{Ar} is used for the formation electron sharing bond with Si-atom and other electron is in their antibonding p^* -MO. Here, the linear combination of p^* -MO of NHCs are antibonding type (Figure 1.18, right). As per CASSCF calculation, the contribution of S_0 state is 47% and that of S_2 state is 52%. Hence the actual ground state can be considered as the superposition of two states viz., S_0 and S_2 . The bonding in **1.35** can be schematically represented as shown in Figure S1.43.

Nonetheless, a single molecular system that contains both singlet and triplet biradical attributes is rare and its reactivity is a worthy area of research. The biradical analysis of **1.35** is currently under study and its findings will be documented in due time.

1.3 Conclusion

The optimized synthesis of NHC-stabilized silicon(I) dimer **1.13-I** ($I_{Ar} = 2,6\text{-}i\text{PrC}_6\text{H}_3$) was described by the reaction of NHC-silicon(IV) tetraiodide $[I_{Ar}\text{SiI}_3]^+\text{I}^-$ with three equivalents of KC_8 . I_{Ar} could be obtained quantitatively by the adduct formation between I_{Ar} and silicon(IV) tetraiodide. Next, the reduction of **1.13-I** with two equivalents of KC_8 delivered the successful isolation of NHC-stabilized silicon(0) dimer **1.17**. The NHC-disilicon(0) complex **1.17** underwent an oxidation with elemental tellurium to form the first dimeric NHC-silicon monotelluride complex **1.31**. It isomerized to form the more stable form **1.32**. **1.32** was further oxidized with elemental tellurium, which proceeded through the NHC-disilicon tritelluride complex **1.34-Te**, to form the dimeric NHC-silicon ditelluride complex **1.33**. The reactions are in line with DFT studies of reaction mechanism that compounds **1.31**, **1.32**, and **1.34-Te** are intermediates for the formation of **1.33**. Moreover, experimental and theoretical studies conclusively show that the terminal $\text{Si}=\text{Te}$ bonds in compounds **1.31** – **1.33** comprise considerable double bond character with high polarity. Furthermore, the NHC-disilicon ditelluride isomer **1.32** can react with one equivalent of elemental sulfur to form the first NHC-disilicon sulfide ditelluride **1.34-S**, which illustrates that **1.32** can serve as a valuable building block to construct ternary silicon heterodichalcogenides. To further elucidate the reactivity with chalcogen, **1.13-I** was reacted with two equivalents of elemental tellurium to afford dimeric NHC-stabilized silicon iodotelluride radical **1.35**, exhibits both a major singlet biradical and minor triplet spin states in a single molecule.

1.4 Experimental

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. THF and toluene were dried over and distilled from Na/K alloy prior to use. *d*₆-benzene, *d*₈-toluene and *d*₈-THF were dried and distilled over K metal prior to use. Te and S₈ powder were purchased from Sigma Aldrich and used without further purification. The ¹H, ¹³C{¹H}, ²⁹Si{¹H} and ¹²⁵Te{¹H} NMR spectra were recorded on a JEOL ECA 400, Bruker AV300, Bruker AV400, Bruker AV500 and Bruker BBFOII spectrometer. The NMR spectra were recorded in *d*₆-benzene, *d*₈-toluene or *d*₈-THF, and the chemical shifts are relative to SiMe₄ for ¹H, ¹³C{¹H}, ²⁹Si{¹H}, and Ph₂Te for ¹²⁵Te{¹H}, respectively. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

1.4.1 Optimized Synthesis of NHC–Silicon(I) Dimer (1.13-I) and Reduction of NHC–Silicon(0) Dimer (1.17)

Synthesis of $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$ (1.13-I). To a 100 mL Schlenk flask with $\text{I}_{\text{Ar}}\text{SiI}_4$ ^[17] (3.42 g, 3.70 mmol) and KC_8 (1.55 g, 11.47 mmol), toluene (50 mL) was added to the mixture at room temperature. The greenish yellow mixture was stirred at room temperature for 48 hours. A dark red mixture was formed. After filtration and concentration of the filtrate, compound $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$ **1.13-I** was obtained as red crystals. X-ray quality crystals can be grown either from diethyl ether or toluene. Yield: 0.66 g (33%). ^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 0.95 (d, 12H, $\text{CH}(\text{CH}_3)_2$), 0.99 (d, 12H, $\text{CH}(\text{CH}_3)_2$), 1.43 (br, 12H, $\text{CH}(\text{CH}_3)_2$), 1.73 (br, 12H, $\text{CH}(\text{CH}_3)_2$), 3.23 (br, 8H, $\text{CH}(\text{CH}_3)_2$), 6.30 (s, 4H, NCH), 6.98-7.25 (m, 12H, Ar). ^1H NMR (395.9 MHz, -50 °C, d_8 -THF, ppm): δ 0.84 (b, 6H, $\text{CH}(\text{CH}_3)_2$), 0.95 (b, 6H, $\text{CH}(\text{CH}_3)_2$), 1.06 (b, 12H, $\text{CH}(\text{CH}_3)_2$), 1.12 (b, 6H, $\text{CH}(\text{CH}_3)_2$), 1.29 (b, 6H, $\text{CH}(\text{CH}_3)_2$), 1.36 (b, 6H, $\text{CH}(\text{CH}_3)_2$), 1.57 (b, 6H, $\text{CH}(\text{CH}_3)_2$), 2.37 (b, 2H, $\text{CH}(\text{CH}_3)_2$), 2.86 (b, 2H, $\text{CH}(\text{CH}_3)_2$), 3.25 (b, 2H, $\text{CH}(\text{CH}_3)_2$), 3.34 (b, 2H, $\text{CH}(\text{CH}_3)_2$), 6.91 (s, 2H, NCH), 7.11 (s, 2H, NCH), 7.19-7.32 (m, 12H, Ar). $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, 24 °C, d_8 -THF, ppm): δ = 20.2. The ^1H and ^{29}Si data agrees with the literature values.^[3e]

Synthesis of $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$ (1.17). To a 100 mL Schlenk flask with $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$ **1.13-I** (3.26 g, 3.00 mmol) and KC_8 (0.81 g, 6.00 mmol), THF (50 mL) was added to the mixture at room temperature. The red mixture was stirred at room temperature for 12 hours. A dark red mixture was formed. After filtration and concentration of the filtrate, compound **1.17** was obtained as red crystals. X-ray quality crystals can be grown either from diethyl ether or THF. Yield: 2.30 g (92%). ^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 1.10 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 3.13 (m, 8H, $\text{CH}(\text{CH}_3)_2$), 6.59 (s, 4H, NCH), 7.01 – 7.03 (d, 8H, Ar-*H*), 7.18 – 7.25 (t, 4H, Ar-*H*). $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, 24 °C, C_6D_6 , ppm): δ = 224.5. The ^1H and ^{29}Si data agrees with the literature values.^[4]

1.4.2 Reactivity of NHC-stabilized Silicon(0) Dimer (1.17) toward Chalcogen

Synthesis of 1.31. To a 100 mL Schlenk flask with **1.17** (167 mg, 0.2 mmol) and Te (51.0 mg, 0.4 mmol), toluene (30 mL) was added to the mixture at room temperature. The dark red solution was stirred at room temperature for three days. A red mixture was formed. After filtration and concentration of the filtrate, compound **1.31** was isolated as orange crystals. X-ray quality crystals were grown from fluorobenzene. Several attempts to isolate pure **1.31** by recrystallization failed. Hence, the chemical yield, melting point, and elemental analysis of **1.31** cannot be obtained. By reference to the NMR spectra of pure **1.17** and **1.32**, the NMR resonances of **1.31** were identified in the NMR spectra of the mixture of **1.17**, **1.31** and **1.32**. ^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 0.99 (d, 7 Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.38 (d, 7 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.56 (d, 6 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.67 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 2.98 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 6.20 (s, 4H, NCH). The aromatic region in the ^1H NMR spectrum cannot be determined due to the overlapping of signals with compounds **1.17** and **1.32**. $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, 24 °C, C_6D_6 , ppm): δ = -107. $^{125}\text{Te}\{^1\text{H}\}$ NMR (124.9 MHz, 24 °C, C_6D_6 , ppm): δ = -1413.

Synthesis of 1.32. To a 100 mL Schlenk flask with **1.17** (106 mg, 0.127 mmol) and Te (34.2 mg, 0.268 mmol), toluene (30 mL) was added to the mixture at room temperature. The dark red mixture was stirred at room temperature for ten days. A dark red mixture was formed. After filtration and concentration of the filtrate, compound **1.32** was isolated as dark red, block-like crystal. Yield: 68.4 mg (49.4%). Mp: 213.0 °C. Calcd for $\text{C}_{54}\text{H}_{72}\text{N}_4\text{Si}_2\text{Te}_2 \cdot \text{C}_7\text{H}_8$: C, 62.05; H, 6.83; N, 4.75. Anal. Found: C, 62.15; H, 6.91; N, 4.89. ^1H NMR (400.13 MHz, 24 °C, C_6D_6 , ppm): δ = 0.89 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.93 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.97 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.98 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.45 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.50 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.55 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.60 (d, 8 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 2.82-2.89 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.95-3.08 (m and br., 4H, $\text{CH}(\text{CH}_3)_2$), 3.40 (br., 2H, $\text{CH}(\text{CH}_3)_2$), 6.18 (s, 2H, NCH), 6.28 (s, 2H, NCH), 7.04-7.14 (m, 7H, Ar), 7.20-7.28 (m, 5H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.55 MHz, 24 °C, C_6D_6 , ppm): δ = 23.4, 23.6, 24.1, 24.8, 25.9, 26.0 ($\text{CH}(\text{CH}_3)_2$), 28.8, 29.1, 29.3 ($\text{CH}(\text{CH}_3)_2$), 123.7, 124.0 (NCH), 124.5, 124.6, 124.7, 124.8, 125.7, 129.3, 130.3, 130.9, 135.3, 136.3, 145.9, 146.0, 146.3, 146.5, 146.8 (Ar), 154.1, 167.6 (NCN). $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz,

24 °C, C₆D₆, ppm): δ = -110.0, -125.9. ¹²⁵Te{¹H} NMR (124.9 MHz, 24 °C, C₆D₆, ppm): δ = -1035, -1083. UV-Vis (toluene): $\lambda_{\text{max}}(\epsilon)$ = 301 (34600 L mol⁻¹cm⁻¹) and 466 (7680 L mol⁻¹cm⁻¹) nm.

Synthesis of 1.33. To a 100 mL Schlenk flask with **1.17** (167 mg, 0.200 mmol) and Te (102 mg, 0.800 mmol), toluene (30 mL) was added to the mixture at room temperature. The dark red solution was stirred at room temperature for 30 days. A brown mixture was formed. All volatiles were removed under reduced pressure. The residue was extracted with fluorobenzene (30ml). After filtration and concentration of the filtrate, compound **1.33** was isolated as red crystals. X-ray quality crystals were grown from fluorobenzene or 1,2-difluorobenzene. Yield: 84 mg (31.8%). Mp: 134.2 °C. Calcd for C₅₄H₇₂N₄Si₂Te₄·C₇H₈: C, 51.02; H, 5.62; N, 3.90. Anal. Found: C, 51.20; H, 6.38; N, 3.83. ¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 0.87-0.97 (m, 30H, CH(CH₃)₂), 1.65 (t, 7 Hz, 12H, CH(CH₃)₂), 1.79 (d, 6 Hz, 6H, CH(CH₃)₂), 2.87-2.95 (m, 4H, CH(CH₃)₂), 3.64 (m, 7 Hz, 2H, CH(CH₃)₂), 3.78 (m, 7 Hz, 2H, CH(CH₃)₂), 6.18 (d, 2 Hz, 2H, NCH), 6.21 (d, 2 Hz, 2H, NCH), 6.96 -7.02 (m, 4H, Ar), 7.05 -7.09 (m, 2H, Ar), 7.24 -7.28 (m, 4H, Ar), 7.38-7.42 (m, 2H, Ar). ¹³C{¹H} NMR (99.5 MHz, 24 °C, C₆D₆, ppm): δ = 24.0, 24.4, 24.6, 25.0, 25.2, 25.6, 25.9, 26.1 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 29.0 (CH(CH₃)₂), 29.7 (CH(CH₃)₂), 123.9 (NCH), 124.5 (NCH), 124.8, 125.0, 125.3, 125.8, 130.5, 131.1, 135.8, 141.8, 146.0, 146.2 (Ar), 146.6, 147.0 (NCN). ²⁹Si{¹H} NMR (78.65 MHz, 24 °C, C₆D₆, ppm): δ = -166.4. ¹²⁵Te{¹H} NMR (124.9 MHz, 24 °C, C₆D₆, ppm): δ = -587, -941. UV-Vis (toluene): $\lambda_{\text{max}}(\epsilon)$ = 291 (35600) and 353 (17200 L³mol⁻¹cm⁻¹) nm.

Synthesis of 1.34. To a 100 mL Schlenk flask with **1.32** (218 mg, 0.200 mmol) and S₈ (6.41 mg, 0.025 mmol), toluene (30 mL) was added to the mixture at room temperature. The dark red solution turned to dark orange red with a black precipitate after 1 hour. The resulting mixture was allowed to stir for 1 day. A dark orange red solution with a black precipitate were observed. Volatiles were removed under reduced pressure. The residue was extracted with fluorobenzene (30 mL). After filtration and concentration of the filtrate, compounds **1.34-S** and **1.34-Te** were co-crystallized as red block-like crystals after a month, along with the formation of significant amount of black metal. The ¹H NMR spectrum of the residue is a mixture of **1.34-S**, **1.34-Te** and **1.33** (Figure S1.19). X-ray crystallography showed that the ratio of **1.34-S** and **1.34-Te** is 4:1. In addition, NMR spectroscopy also supported the presence of a mixture of **1.34-S** and **1.34-Te** in the ratio of 17:3 on the basis of imidazole proton integration (**1.34-S**: δ 6.28; **1.34-Te**: 6.23 ppm, Figure S1.15). Several attempts to isolate pure **1.34-S** and **1.34-Te** by recrystallization failed. Hence, the chemical yield, elemental analysis and melting point of **1.34-S** and **1.34-Te** cannot be determined.

¹H NMR of **1.34-S** (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 0.92 (br, 6H, CH(CH₃)₂), 0.95 (s, 6H, CH(CH₃)₂), 0.96 (s, 6H, CH(CH₃)₂), 0.98 (br, 6H, CH(CH₃)₂), 1.49 (d, 6 Hz, 6H, CH(CH₃)₂), 1.56 (d, 6 Hz, 6H, CH(CH₃)₂), 1.74 (d, 7 Hz, 6H, CH(CH₃)₂), 1.80 (t, 6H, CH(CH₃)₂), 3.08 (m, 2H, CH(CH₃)₂), 3.16 – 3.33 (m, 4H, CH(CH₃)₂), 3.46 (m, 2H, CH(CH₃)₂), 6.29 (d, 4 Hz, 4H, NCH). The aromatic region in the ¹H NMR spectrum cannot be determined due to the overlapping of signals with compound **1.34-Te**. ²⁹Si{¹H} NMR of **1.34-S** (78.65 MHz, 24 °C, C₆D₆, ppm): δ = -114.0. ¹²⁵Te{¹H} NMR of **1.34-S** (124.9 MHz, 24 °C, C₆D₆, ppm): δ = -1060.

¹H NMR of **1.34-Te** (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 0.92 (br, 12H, CH(CH₃)₂), 1.00 (s, 6H, CH(CH₃)₂), 1.52 (s, 6H, CH(CH₃)₂), 1.61 (d, 6 Hz, 6H, CH(CH₃)₂), 1.63 (d, 6 Hz, 6H, CH(CH₃)₂), 1.70 (d, 6H, CH(CH₃)₂), 1.80 (t, 6H, CH(CH₃)₂), 3.16 – 3.33 (m, 8H, CH(CH₃)₂), 6.23 (s, 4H, NCH). The aromatic region in the ¹H NMR spectrum cannot be determined due to the overlapping of signals with compound **1.34-S**. Compound **1.34-Te** is unstable in solution. It decomposed in solution such as C₆D₆ after 1 day (Figure S1.16). In this context, ²⁹Si and ¹²⁵Te NMR signals cannot be obtained.

Study of solvent influence in the reaction of compound **1.17** with Te

(a) THF

To a J-Young NMR tube with **1.17** (11.0 mg, 0.10 mmol) and Te (51.0 mg, 0.40 mmol), *d*₈-THF (0.4 mL) was added to the mixture at room temperature. The reaction was monitored by the *CH*(CH₃)₂ proton chemical shift in a regular interval (Figure S1.20). At 0 min, only an intense dark red solution of **1.17** (δ = 2.92 ppm) was observed. After 30 mins, **2** (δ = 2.50, 2.79 ppm) and **3** (δ = 2.67, 2.90, 3.19 ppm) were formed and the ratio of **1.17** : **1.31** : **1.32** is 4 : 3.4 : 1.2. At 45 mins, a dark orange red mixture of **1.17**, **1.31** and **1.32** was detected in the ratio of 0.8 : 3.4 : 4. After 1.5 hours, only **1.17** was fully consumed. **1.32** was further reacted with Te to form **1.33** (δ = 2.79, 3.44, 3.54 ppm). The ratio of **1.31** : **1.32** : **1.33** is 2.3 : 4 : 0.5. After 2 hours, **1.31** was completely isomerized, along with increasing amount of **1.33**. The ratio of **1.32** : **1.33** was 2 : 1. After 3.5 hours, an orange solution of **1.33** was afforded as the sole product.

(b) Toluene

To a 100 mL Schlenk flask with **1.17** (167 mg, 0.200 mmol) and Te (102 mg, 0.800 mmol), toluene (30 mL) was added to the mixture at room temperature. The reaction was monitored by the imidazole proton chemical shift in a regular interval (Figure S1.21). On day 3, **1.17** was 50% consumed (δ = 6.58 ppm) to form **1.31** (δ = 6.20 ppm), which started to isomerize to form **1.32** (δ = 6.18, 6.28 ppm). The ratio of **1.17** : **1.31** : **1.32** is 4 : 4 : 0.3. On day 5, **1.17** was fully consumed. In addition, **1.31** was almost consumed, along with **1.32** as the major product. The ratio of **1.31** : **1.32** was 0.7 : 4. On day 7, **1.32** was the sole compound in the reaction mixture for nine days. On day 16, trace amount of **1.34-Te** (δ = 6.23 ppm) and **1.33** (δ = 6.18, 6.21 ppm) were observed in the **1.32** : **1.34-Te** : **1.33** ratio of 4 : 0.2 : 0.7. On day 27, the ratio of **1.32** : **1.34-Te** : **1.33** is 2 : 0.9 : 4. The NMR studies show that the isolation of **1.34-Te** from the reaction mixture is a synthetic challenge.

1.4.3 Reactivity of NHC–Silicon(I) Dimer (1.13-I) toward Tellurium

Synthesis of $[\text{IAr(I)}(\mu\text{-Te})\text{Si}^\bullet]_2$ (1.35). To a 100 mL Schlenk flask with $[\text{IAr(I)Si:}]_2$ **1.13-I** (217 mg, 0.20 mmol) and elemental tellurium (0.51 g, 0.40 mmol), THF (50 mL) was added to the mixture at room temperature. The red mixture was stirred at room temperature in the absence of light for 5 days. A dark red mixture was formed. The crude mixture was then dried and extracted with fluorobenzene. After filtration and concentration of the filtrate, compound **1.35** was obtained as red crystals. Yield: 432 mg (16%). ^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 0.90 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 1.79 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 3.35 (m, 8H, $\text{CH}(\text{CH}_3)_2$), 6.21 (s, 4H, NCH), 7.00 (d, 8H, Ar-H), 7.11 – 7.13 (m, 4H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 24 °C, C_6D_6 , ppm): δ = 24.4, 26.3 ($\text{CH}(\text{CH}_3)_2$), 29.8 ($\text{CH}(\text{CH}_3)_2$), 124.3 (NCH), 125.4 (NCH), 127.4, 127.9, 131.6133.5 (Ar), 147.0 (NCN). ^{29}Si NMR (78.65 MHz, 24 °C, C_6D_6 , ppm): δ -9.76. $^{125}\text{Te}\{^1\text{H}\}$ (124.9 MHz, 24 °C, C_6D_6 , ppm): δ = -318. HRMS (ESI): m/z calcd for $\text{C}_{54}\text{H}_{73}\text{N}_4\text{Si}_2\text{Te}_2\text{I}_2$ 1347.1588; found: 1347.1600. UV-Vis (benzene): $\lambda_{\text{max}}(\epsilon)$ = 292 and 373 nm.

1.5 Appendices

1.5.1 NMR Spectra

Reactivity of NHC–Silicon(0) Dimer (1.17) toward Chalcogen

Figure S1. 1 ^1H NMR spectrum of a mixture of **1.17**, **1.31** and **1.32** (**3**) (in C_6D_6).

Figure S1. 2 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **1.31** (in C_6D_6).

Figure S1. 3 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of compound **1.31** (in C_6D_6).

Figure S1. 4 ¹H NMR spectrum of compound **1.32** at room temperature (in C₆D₆).

Figure S1. 5 ¹H NMR spectrum of compound **1.32** at -80 °C (in d₈-toluene).

Figure S1. 6 Variable-temperature (from -85 to 24 °C) ^1H NMR spectra of compound **1.32** (in d_8 -toluene).

Figure S1. 7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1.32** at room temperature (in C_6D_6).

Figure S1. 8 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **1.32** at room temperature (in C_6D_6).

Figure S1. 9 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of compound **1.32** at room temperature (in C_6D_6).

Figure S1. ^1H NMR spectrum of compound **1.33** at room temperature (in C_6D_6).

(a)

(b)

Figure S1. 11 Variable-temperature ^1H NMR spectra of compound **1.33** (in d_8 -toluene). (a) - 70 – 24 °C; (b) 25 – 75 °C.

Figure S1. 12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1.33** at room temperature (in C_6D_6).

Figure S1. 13 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **1.33** at room temperature (in C_6D_6).

Figure S1. 16 The decomposition of **1.34-Te** (**5-Te**) after 1 day (in C₆D₆).

Figure S1. 17 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1.34-S** (in C_6D_6).

Figure S1. 20 The reaction of **1.17(1)** with four equivalents of tellurium in *d*₈-THF monitored by ¹H NMR spectroscopy to afford **1.31** (**2**), **1.32** (**3**) and **1.33** (**4**). **1.34-Te** is not observed.

Figure S1. 21 The reaction of **1.17** with four equivalents of tellurium in toluene monitored by NMR spectroscopy, (a) Full ^1H NMR spectrum; (b) imidazole region in the ^1H NMR spectrum.

Reactivity of NHC–Silicon(I) Dimer (1.13-I) toward Chalcogen

Figure S1. 22 ¹H NMR spectrum of 1.35 (in C₆D₆).

Figure S1. 23 ¹³C{¹H} NMR spectrum of 1.35 (in C₆D₆). * denotes solvent residue *n*-hexane.

Figure S1. 24 ^{29}Si NMR spectrum of **1.35** (in C_6D_6).

Figure S1. 25 $^{125}\text{Te}\{^1\text{H}\}$ NMR spectrum of **1.35** (in C_6D_6).

Figure S1. 26 Variable-temperature ^1H NMR spectra of compound **1.35** in d_8 -toluene.

1.5.2 UV-Visible Spectra of Compounds 1.32 – 1.33 and 1.35

Figure S1. 27 UV-Visible spectrum of compound **1.32**.

Figure S1. 28 UV-Visible spectrum of compound **1.33**.

Figure S1. 29 UV-Visible spectrum of compound **1.35**.

1.5.3 Crystallographic Data of All Structures

The X-ray diffraction intensity data were measured at temperature setting indicated in Table S1.1 with a Bruker APEX II diffractometer equipped with a CCD detector, employing Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) for compound **1.31** and **1.33**, and Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) for compound **1.32**, **1.34** and **1.35**, with the SMART suite of programs.^[38] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.^[39] Structural solution and refinement were carried out with the SHELXTL suite of programs.^[40] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC-1547061 (**1.31**), 1547060 (**1.32**), 1547062 (**1.33**), 1547063 (**1.34**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. 1 Crystallographic data of **1.31 – 1.35**.

	1.31	1.32	1.33	1.34	1.35
Formula	C ₅₄ H ₇₂ N ₄ Si ₂ Te ₂	C ₅₄ H ₇₂ N ₄ Si ₂ Te ₂	C ₅₄ H ₇₂ N ₄ Si ₂ Te ₄	C ₅₄ H ₇₂ N ₄ S _{0.8} Si ₂ Te _{2.2}	C ₇₈ H ₉₂ F ₄ I ₂ N ₄ Si ₂ Te ₂
Temperature (K)	103(2)	153(2)	133(2)	100(2)	153(2)
Fw	1088.53	1088.53	1343.73	1139.70	1276.73
Color	Orange	Red	Red	Red	Red
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Triclinic
Space group	<i>P 1 21/n1</i>	<i>P 4 3212</i>	<i>P 1 21/n1</i>	<i>P 1 211</i>	<i>P -1</i>
<i>a</i> (Å)	12.6169(5)	15.635(3)	11.4172(2)	12.3953(13)	10.8075(5)
<i>b</i> (Å)	15.0658(3)	15.635(3)	17.7479(5)	15.8016(15)	12.3698(6)
<i>c</i> (Å)	14.6026(4)	28.984(6)	14.2160(3)	14.8705(14)	16.0147(7)
α (deg)	90	90	90	90	108.763(3)
β (deg)	103.794(2)	90	99.5152(17)	108.267(3)	90.551(3)
γ (deg)	90	90	90	90	111.319(3)
<i>V</i> (Å³)	2695.66(14)	7085(3)	2840.97(11)	2765.8(5)	1868.92(16)
<i>Z</i>	2	4	2	2	1
<i>d</i>_{calcd} (g cm⁻³)	1.341	1.021	1.571	1.368	1.534
μ (mm⁻¹)	9.240	0.886	16.722	1.268	1.639
<i>F</i>(000)	1112	2224	1320	1158	862
crystal size (mm)	0.02 x 0.04 x 0.06	0.38 x 0.40 x 0.42	0.01 x 0.02 x 0.10	0.04 x 0.20 x 0.22	0.06 x 0.12 x 0.14
θ range (deg)	4.17 to 66.61	1.48 to 25.68	4.02 to 66.63	2.27 to 27.22	2.71 to 31.14
Index range	-14 ≤ <i>h</i> ≤ 14, -17 ≤ <i>k</i> ≤ 17, -17 ≤ <i>l</i> ≤ 17	-18 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 13, -35 ≤ <i>l</i> ≤ 35	-13 ≤ <i>h</i> ≤ 13, -21 ≤ <i>k</i> ≤ 20, -16 ≤ <i>l</i> ≤ 11	-15 ≤ <i>h</i> ≤ 15, -20 ≤ <i>k</i> ≤ 19, -19 ≤ <i>l</i> ≤ 19	-15 ≤ <i>h</i> ≤ 15 -17 ≤ <i>k</i> ≤ 17 -23 ≤ <i>l</i> ≤ 23
no. of rflns collected	19374	54973	15831	66340	55107
no. of indep rflns	4725	6733	4956	11843	11944
<i>R</i>1, <i>wR</i>2 (<i>I</i> > 2(σ))	0.0687, 0.1596	0.0860, 0.2269	0.0532, 0.1202	0.0624, 0.1429	0.0674, 0.1400
<i>R</i>1, <i>wR</i>2 (all data)	0.1399, 0.2050	0.1834, 0.2972	0.0788, 0.1348	0.1190, 0.1805	0.1709, 0.1841
Goodness of fit, <i>F</i>²	1.028	1.064	0.991	1.073	1.029
no. of data/ restraints/params	4725 / 1527 / 576	6733 / 1356 / 527	4956 / 0 / 297	11843 / 7 / 596	11944 / 357 / 483
Largest diff peaks and hole, eÅ⁻³	0.878 to -1.470	1.051 to -0.521	1.446 to -0.773	1.621 to -1.818	1.567 to -1.653

1.5.4 Theoretical Studies

Reactivity of NHC–Silicon(0) Dimer (1.17) toward Chalcogen

In the present work, geometry optimizations were fully performed without any symmetry restriction by using M06-2X/def2-SVP level of theory. The vibrational frequency calculations were performed to establish the nature of stationary points. The local minima were confirmed by zero imaginary frequencies, and transition states were characterized by an imaginary frequency. The energies in the reaction profiles for the mechanistic study are ΔG values at 298.15 K and 1 atm. Wiberg bond indices, natural localized molecular orbitals and partial charges were obtained by using NBO 5.9 as implemented in Gaussian 09.^[41] The bonding analysis by energy decomposition analysis combined with the natural orbitals for chemical valence (EDA-NOCV) method was carried out at M06-2X/DZP level of theory with ADF 2016 program package. The relativistic effect was taken into consideration by applying the scalar zero-order regular approximation (ZORA). The interaction energy and its decomposition terms are obtained from single-point calculation with M06-2X/DZP basis set from the Gaussian 09 optimized geometry at M06-2X/def2-SVP level of theory.

Figure S1. 30 Optimized geometries of the minimal and transition states for the formation of compounds **1.31** – **1.33** at M06-2X/def2-SVP level of theory.

Figure S1.30 (continued). Optimized geometries of the minimal and transition states for the formation of compounds 1.31 – 1.33 at M06-2X/def2-SVP level of theory.

Figure S1. 31 Molecular orbitals of compound **1.17**, **Int1.2**, compound **1.32**, **Int1.5** and Te atom at M06-2X/def2-SVP level of theory.

Figure S1. 32 NLMOs of compound **1.31** at M06-2X/def2-SVP level of theory: a) Si-Si σ -bonding orbital; b) Si-Si π -bonding orbital; c) Si-C σ -bonding orbital; d) Si-Te_{terminal} σ -bonding orbital; e,f) one of the two degenerate lone-pair orbitals of the Te_{terminal} atom.

Figure S1. 33 NLMOs of compound **1.32** at M06-2X/def2-SVP level of theory: a) Si–Si σ -bonding orbital; b) Si–C σ -bonding orbital; c) Si–Te_{bridging} σ -bonding orbital; d) Si–Te_{terminal} σ -bonding orbital; e,f) one of the two degenerate lone-pair orbitals of the Te_{terminal} atom.

a

Si-C σ -bonding orbital

75.8 % C + 24.2 % Si

C: 44.4% s + 55.6% p

Si: 21.8% s + 77.5% p + 0.7% d

c

Si-Te_{terminal} σ -bonding orbital

50.5 % Si + 49.5 % Te

Si: 33.6% s + 65.9% p + 0.5% d

Te: 15.0% s + 84.5% p + 0.5% d

b

Si-Te_{bridging} σ -bonding orbital

43.0 % Si + 57.0 % Te

Si: 22.4% s + 76.9% p + 0.7% d

Te: 12.7% s + 86.7% p + 0.6% d

d

Lone-pair orbitals of the Te_{terminal}

Te: 0.1% s + 99.8% p + 0.1% d

Figure S1. 34 NLMOs of compound **1.33** at M06-2X/def2-SVP level of theory: a) Si-C σ -bonding orbital; b) Si-Te_{bridging} σ -bonding orbital; c) Si-Te_{terminal} σ -bonding orbital; d) lone-pair orbital of the Te_{terminal} atom.

Figure S1. 35 Wiberg bond index and natural charge population of compound **1.31** at M06-2X/def2-SVP level of theory.

Figure S1. 36 Wiberg bond index and natural charge population of compound **1.32** at M06-2X/def2-SVP level of theory.

Figure S1. 37 Wiberg bond index and natural charge population of compound **1.33** at M06-2X/def2-SVP level of theory.

The negative hyperconjugation from the Te lone pairs to the σ^* orbitals around Si atoms

Table S1. 2 Occupancies and Second-Order Perturbation Energies, ΔE_{ij} (kcal/mol), derived from NBO Analysis for Compounds **1.31** – **1.33** at M06-2X/def2-SVP Level of Theory.

$\text{iPrNHC} = :\text{C}\{\text{N}(\text{Ar})\text{C}(\text{H})\}_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$.

Compounds	1.31	1.32	1.33
occ. of LPs(Te)	1.85	1.85	1.81
	1.78	1.80	1.79
occ. of $\sigma^*(\text{iPrNHC-Si})$	0.11	0.16	0.19
occ. of $\sigma^*(\text{Si-Si})$	0.14	0.08	---
occ. of $\sigma^*(\text{Si-Te})$	---	0.17	0.13
			0.14
$\Delta E_{ij}\{\text{LPs}(\text{Te}) \rightarrow \sigma^*(\text{iPrNHC-Si})\}$	12.56	15.92	14.99
$\Delta E_{ij}\{\text{LPs}(\text{Te}) \rightarrow \sigma^*(\text{Si-Si})\}$	7.06	6.49	---
$\Delta E_{ij}\{\text{LPs}(\text{Te}) \rightarrow \sigma^*(\text{Si-Te})\}$	---	20.26	31.37

As shown in the Table S1.2, the second order perturbation stabilizing energies (ΔE_{ij}) for the interaction between Te(5p) and $\sigma^*(\text{Si-Te})$ are the largest. Take compound **1.32** as an example, the order of stabilizing energy is $\Delta E_{ij}\{\text{LPs}(\text{Te}) \rightarrow \sigma^*(\text{Si-Te})\} = 20.26 \text{ kcal/mol} > \Delta E_{ij}\{\text{LPs}(\text{Te}) \rightarrow \sigma^*(\text{iPrNHC-Si})\} = 15.92 \text{ kcal/mol} > \Delta E_{ij}\{\text{LPs}(\text{Te}) \rightarrow \sigma^*(\text{Si-Si})\} = 6.49 \text{ kcal/mol}$ ($\text{iPrNHC} = :\text{C}\{\text{N}(\text{Ar})\text{C}(\text{H})\}_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$). Therefore, the sum of ΔE_{ij} for each $\text{Te}_{\text{terminal}}$ atom for compound **1.31** is 19.62 kcal/mol; for compound **1.32** is 42.67 kcal/mol; for compound **1.33** is 46.36 kcal/mol and thus the total sum for compound **1.31** is 19.62×2 (2 $\text{Te}_{\text{terminal}}$ atoms) = 39.24 kcal/mol; for compound **1.32** is 42.67×1 (1 $\text{Te}_{\text{terminal}}$ atom) = 42.67 kcal/mol; for compound **1.33** is 46.36×2 (2 $\text{Te}_{\text{terminal}}$ atoms) = 92.72 kcal/mol.

The natural resonance theory (NRT) analyses for compounds **1.31** – **1.33** failed despite many attempts. To the best of our knowledge, large system (> 100 atoms) is a significant challenge for NRT. As such, the NRT calculations at M06-2X/def2-SVP were performed on smaller model systems that the very large 2,6-*i*Pr₂C₆H₃ groups at the NHC ligands are replaced by methyl groups. At the same time, the frozen optimizations were also executed. That is to say that all coordinates except substituted groups are fixed at their positions from the previous optimization of the full systems. The NRT results for models **1.31**^{Me} – **1.33**^{Me} are shown in Figure S1.32. Take model **1.32**^{Me} as an example, the weighting of possible resonance structures identifies the structure **1.32**^{Me}**A** including two Si–Te single bonds as a dominating resonance structure. The canonical representations including a Si=Te double bond **1.32**^{Me}**B**, **1.32**^{Me}**C** and **1.32**^{Me}**D** are typical Lewis representations for negative hyperconjugation. They correspond to LPs(Te) → σ^{*}(Si–Te), LPs(Te) → σ^{*}(ⁱPrNHC–Si) and LPs(Te) → σ^{*}(Si–Si), respectively. According to NBO analysis (Table S1.2), it can be seen that the stabilizing energy term is the largest for the interaction between Te(5p) and σ^{*}(Si–Te). This is in agreement with the largest contribution of resonance structure **1.32**^{Me}**B** (7.99%) in comparison with that of **1.32**^{Me}**C** (3.76%) and **1.32**^{Me}**D** (3.23%). Moreover, NRT calculations for model **1.33**^{Me} show that the contribution of resonance structure **1.33**^{Me}**B** (21.84%) is larger than that of **1.33**^{Me}**C** (7.28%) which matches to LPs(Te) → σ^{*}(Si–Te) and LPs(Te) → σ^{*}(ⁱPrNHC–Si), respectively. Furthermore, the NRT results for model **1.31**^{Me} show that the contribution of resonance structure **1.31**^{Me}**B** (22.51%) is larger than that of **1.31**^{Me}**C** (9.40%).

Figure S1. 38 Leading resonance structures according to NRT analyses of models **1.31^{Me}** – **1.33^{Me}** at M06-2X/def2-SVP level of theory

Table S1. 3 EDA-NOCV results of chemical bonding in compounds **1.31** – **1.33** at M06-2X/DZP level of theory. $i\text{PrNHC} = :\text{C}\{\text{N}(\text{Ar})\text{C}(\text{H})\}_2$, Ar = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$.

EDA-NOCV results of chemical bonding in Cpd.2-4 at M06-2X/DZP. Fragments are $i\text{PrNHC}(\text{A})$ and $\text{Si}_2\text{Te}_2i\text{PrNHC}(\text{B})/\text{Si}_2\text{Te}_2i\text{PrNHC}(\text{B})/\text{Si}_2\text{Te}_4i\text{PrNHC}(\text{B})$, respectively. Both fragments are in singlet(S) electronic state. All energy values are in kcal/mol.			
Fragments	$i\text{PrNHC}(\text{A})$ and $\text{Si}_2\text{Te}_2i\text{PrNHC}(\text{B})$ in 1.31	$i\text{PrNHC}(\text{A})$ and $\text{Si}_2\text{Te}_2i\text{PrNHC}(\text{B})$ in 1.32	$i\text{PrNHC}(\text{A})$ and $\text{Si}_2\text{Te}_4i\text{PrNHC}(\text{B})$ in 1.33
ΔE_{int}	-95.8	-79.7	-81.7
ΔE_{Pauli}	251.4	223.3	225.1
$\Delta E_{\text{elstat}}^{(b)}$	-189.6(54.6%)	-167.4(55.2%)	-169.5(55.3%)
$\Delta E_{\text{orb}}^{(b)}$	-157.6(45.4%)	-135.6(44.8%)	-137.2(44.7%)
$\Delta E_1^{(c)}$	-100.9(64.0%)	-89.1(65.7%)	-92.0(67.1%)
$\Delta E_2^{(c)}$	-15.1(9.6%)	-12.3(9.1%)	-13.8(10.1%)
$\Delta E_3^{(c)}$	-11.7(7.4%)	-7.9(5.8%)	-5.8(4.2%)
$\Delta E_4^{(c)}$	-4.1(2.6%)	-4.1(3.0%)	-3.7(2.7%)
$\Delta E_5^{(c)}$	-2.9(1.8%)	-2.2(1.6%)	-2.0(1.5%)
$\Delta E_6^{(c)}$	---	-2.2(1.6%)	-3.2(2.3%)
$\Delta E_{\text{rest}}^{(c)}$	-17.1(10.9%)	-14.1(10.4%)	-13.0(9.5%)

^(a) Optimized structures at M06-2X/def2-SVP level of theory ^(b) The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$ ^(c) The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb} .

The relaxed potential energy surface scan at M06-2X/def2-SVP level of theory

Figure S1. 39 Relaxed potential energy surface scan for the reaction of the first Te atom with compound **1.17** at M06-2X/def2-SVP level of theory

Figure S1. 40 Relaxed potential energy surface scan for the direct reaction of **Int1.1** with the second tellurium atom at M06-2X/def2-SVP level of theory

The relaxed potential energy surface scan for the direct reaction of **Int1.1** with the second tellurium atom at M06-2X/def2-SVP is shown in Figure S1.34. It can be seen that the reaction is exothermic and there is no obvious bump on the surface, suggesting that the direct reaction of **Int1.1** with the second tellurium atom is a barrierless process like the reaction of compound **1.17** with the first tellurium atom (Figure S1.33). Therefore, the direct reaction of **Int1.1** with the second tellurium atom is possible and can be the second option to afford compound **1.31**.

Table S1. 4 Optimized cartesian coordinates of compound **1.17**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.197026	0.001849	-0.697828
6	3.832393	0.697105	-2.107042
1	4.452866	1.422901	-2.623208
6	3.818039	-0.658101	-2.140587
1	4.426833	-1.370162	-2.689026
6	2.638306	-2.437640	-0.870066
6	1.638654	-3.213220	-1.481086
6	0.800899	-2.663732	-2.618985
1	0.731617	-1.574894	-2.481075
6	-0.627771	-3.198924	-2.614576
1	-1.228886	-2.656151	-3.359010
1	-1.093835	-3.047998	-1.629579
1	-0.668617	-4.270551	-2.868754
6	1.493802	-2.939547	-3.959119
1	2.500524	-2.497267	-3.994213
1	0.907016	-2.515704	-4.787467
1	1.595042	-4.023190	-4.127408
6	1.495796	-4.535091	-1.049601
1	0.715761	-5.158752	-1.487934
6	2.332902	-5.066654	-0.071772
1	2.206261	-6.102677	0.247899
6	3.327670	-4.282474	0.499656
1	3.977208	-4.704576	1.269145
6	3.498010	-2.947681	0.117898
6	4.567511	-2.105185	0.793033
1	4.635635	-1.145324	0.261184
6	4.182813	-1.800747	2.244407
1	3.231945	-1.246772	2.288664
1	4.966050	-1.197189	2.728244
1	4.067840	-2.732985	2.820288
6	5.945484	-2.767145	0.706862
1	5.975738	-3.706071	1.279954
1	6.713711	-2.099763	1.124331
1	6.215445	-2.997365	-0.334228
6	2.664042	2.438603	-0.776700
6	1.740005	3.265546	-1.435521
6	0.920449	2.756322	-2.605303
1	0.838022	1.664320	-2.497541

6	-0.503917	3.303427	-2.599155
1	-1.097291	2.803439	-3.378900
1	-0.533236	4.385991	-2.802181
1	-0.985313	3.109837	-1.629210
6	1.630955	3.065267	-3.928190
1	1.741726	4.152745	-4.063104
1	1.051014	2.671366	-4.775907
1	2.634910	2.617281	-3.965184
6	1.638113	4.590734	-1.001340
1	0.922849	5.258546	-1.483294
6	2.438520	5.071027	0.031841
1	2.351484	6.112169	0.347839
6	3.337039	4.225783	0.672608
1	3.947007	4.604873	1.495303
6	3.457887	2.885340	0.293150
6	4.416088	1.973918	1.041259
1	4.300086	0.955934	0.642275
6	4.065935	1.910581	2.530479
1	4.763688	1.243573	3.058084
1	3.045090	1.522435	2.663853
1	4.131895	2.904099	3.001184
6	5.869940	2.401332	0.820195
1	6.122331	2.424079	-0.250240
1	6.556451	1.702938	1.321965
1	6.051365	3.406485	1.231417
7	2.819182	-1.068256	-1.273119
7	2.839064	1.082991	-1.222766
14	0.855127	0.008535	0.719229
6	-2.197034	0.002102	0.697845
6	-3.818201	-0.657573	2.140555
1	-4.427117	-1.369533	2.688995
6	-3.832334	0.697634	2.107000
1	-4.452695	1.423539	2.623145
6	-2.663698	2.438938	0.776682
6	-1.739627	3.265812	1.435544
6	-0.920138	2.756528	2.605354
1	-0.837822	1.664520	2.497607
6	0.504277	3.303502	2.599189
1	1.097665	2.803411	3.378866
1	0.985594	3.109914	1.629211
1	0.533704	4.386059	2.802245
6	-1.630631	3.065547	3.928225
1	-2.634621	2.617632	3.965206
1	-1.050731	2.671606	4.775949

1	-1.741330	4.153032	4.063136
6	-1.637613	4.590988	1.001354
1	-0.922293	5.258730	1.483325
6	-2.437934	5.071342	-0.031867
1	-2.350802	6.112475	-0.347867
6	-3.336494	4.226163	-0.672661
1	-3.946398	4.605287	-1.495391
6	-3.457469	2.885732	-0.293187
6	-4.415676	1.974369	-1.041346
1	-4.299695	0.956369	-0.642407
6	-4.065455	1.911086	-2.530555
1	-3.044637	1.522868	-2.663907
1	-4.763212	1.244138	-3.058229
1	-4.131364	2.904641	-3.001205
6	-5.869531	2.401776	-0.820325
1	-6.050998	3.406901	-1.231603
1	-6.556017	1.703341	-1.322076
1	-6.121932	2.424550	0.250106
6	-2.638663	-2.437298	0.870090
6	-1.639152	-3.213011	1.481167
6	-0.801342	-2.663616	2.619071
1	-0.731883	-1.574793	2.481128
6	0.627239	-3.199048	2.614751
1	1.228404	-2.656351	3.359200
1	0.667898	-4.270678	2.868945
1	1.093380	-3.048200	1.629774
6	-1.494376	-2.939257	3.959180
1	-1.595807	-4.022875	4.127517
1	-0.907587	-2.515470	4.787556
1	-2.501033	-2.496816	3.994162
6	-1.496483	-4.534920	1.049744
1	-0.716580	-5.158708	1.488132
6	-2.333624	-5.066379	0.071886
1	-2.207130	-6.102433	-0.247743
6	-3.328243	-4.282065	-0.499621
1	-3.977814	-4.704095	-1.269118
6	-3.498410	-2.947244	-0.117898
6	-4.567747	-2.104606	-0.793120
1	-4.635954	-1.144829	-0.261121
6	-4.182753	-1.799907	-2.244359
1	-4.965943	-1.196312	-2.728230
1	-3.231930	-1.245831	-2.288365
1	-4.067636	-2.732036	-2.820386
6	-5.945748	-2.766549	-0.707417

1	-6.216013	-2.996935	0.333553
1	-6.713846	-2.099088	-1.124996
1	-5.975843	-3.705377	-1.280678
7	-2.838899	1.083353	1.222758
7	-2.819383	-1.067894	1.273125
14	-0.855007	0.008603	-0.719043

Table S1. 5 Optimized cartesian coordinates of **Int1.1**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.077041	-1.155436	0.503398
6	3.287971	-2.763863	1.527996
1	3.535016	-3.776360	1.831486
6	3.912984	-1.580160	1.747305
1	4.833810	-1.345206	2.269000
6	3.509063	0.790990	1.076940
6	4.132804	1.261000	-0.091588
6	4.460609	2.618129	-0.149489
1	4.945070	3.013760	-1.043793
6	4.180328	3.465796	0.915989
1	4.437293	4.524893	0.852360
6	3.578533	2.968735	2.067432
1	3.362769	3.644806	2.894930
6	3.228779	1.619054	2.180621
6	2.616453	1.087752	3.468343
1	1.921403	0.275873	3.196446
6	3.702550	0.534290	4.403812
1	4.419605	1.329249	4.661231
1	4.265271	-0.297383	3.964039
1	3.245746	0.171943	5.336334
6	1.813268	2.141707	4.230716
1	1.246531	1.652529	5.035444
1	1.085152	2.646080	3.583880
1	2.476260	2.890162	4.693791
6	4.519067	0.341824	-1.239549
1	3.954365	-0.595142	-1.136432
6	6.010638	-0.002704	-1.154764
1	6.625033	0.906438	-1.246159
1	6.295420	-0.691709	-1.964106
1	6.255922	-0.478966	-0.193794
6	4.152796	0.926956	-2.603684

1	3.091436	1.215076	-2.621502
1	4.323592	0.178974	-3.392771
1	4.763495	1.810623	-2.847401
6	1.299060	-3.504645	0.243446
6	0.119761	-3.819078	0.941419
6	-0.655269	-4.869648	0.441812
1	-1.577779	-5.141272	0.955485
6	-0.271050	-5.569947	-0.698855
1	-0.889643	-6.391126	-1.065400
6	0.884964	-5.214016	-1.384156
1	1.164859	-5.752124	-2.292341
6	1.692701	-4.165191	-0.931006
6	2.931051	-3.766961	-1.716914
1	3.400490	-2.912041	-1.207594
6	3.956968	-4.903264	-1.752935
1	4.248173	-5.211719	-0.738200
1	4.862834	-4.586803	-2.290800
1	3.550870	-5.786555	-2.269345
6	2.557101	-3.301769	-3.127874
1	2.109941	-4.121915	-3.711106
1	3.453211	-2.955891	-3.665241
1	1.835875	-2.472117	-3.079672
6	-0.281819	-3.080709	2.205499
1	0.129907	-2.061180	2.149339
6	-1.794568	-2.928283	2.340127
1	-2.022118	-2.269732	3.189826
1	-2.294986	-3.895815	2.507485
1	-2.219716	-2.456196	1.441270
6	0.315144	-3.763950	3.441630
1	0.056921	-3.193312	4.345584
1	1.411798	-3.831827	3.383775
1	-0.082989	-4.785248	3.550017
7	2.166585	-2.483530	0.770328
7	3.149469	-0.603960	1.132974
6	-1.913328	1.133333	-0.791034
6	-3.854343	1.514314	-1.858031
1	-4.880724	1.319307	-2.150638
6	-2.985250	2.489071	-2.229811
1	-3.097956	3.337309	-2.896739
6	-0.562958	2.927881	-1.847091
6	-0.080978	3.841554	-0.898736
6	1.141357	4.461034	-1.172669
1	1.558829	5.162514	-0.449631
6	1.836037	4.186960	-2.346037

1	2.790726	4.679857	-2.539116
6	1.324485	3.283483	-3.271908
1	1.883766	3.072931	-4.185093
6	0.117587	2.618979	-3.037358
6	-0.422186	1.628228	-4.059055
1	-1.175306	1.000232	-3.558003
6	-1.110938	2.369720	-5.212299
1	-0.381982	2.995920	-5.749564
1	-1.915980	3.028805	-4.858620
1	-1.541912	1.655143	-5.929380
6	0.655021	0.687555	-4.604659
1	1.401424	1.231074	-5.203926
1	0.192605	-0.063442	-5.263017
1	1.169445	0.163086	-3.786538
6	-0.863454	4.174597	0.357910
1	-1.469655	3.298542	0.631582
6	-1.817402	5.344972	0.091612
1	-1.254160	6.248019	-0.191436
1	-2.404372	5.572074	0.993549
1	-2.519349	5.115969	-0.724463
6	0.045657	4.452746	1.552322
1	0.800412	3.658288	1.649979
1	-0.550701	4.466152	2.475912
1	0.559519	5.423344	1.461269
6	-3.692955	-0.580699	-0.524074
6	-3.309744	-1.726622	-1.247830
6	-3.844872	-2.950613	-0.836983
1	-3.564779	-3.860842	-1.368737
6	-4.726651	-3.020938	0.237293
1	-5.133523	-3.986277	0.543660
6	-5.081836	-1.870350	0.932686
1	-5.762317	-1.941913	1.781549
6	-4.570631	-0.619088	0.571123
6	-4.998079	0.637924	1.309014
1	-4.188554	1.375855	1.195445
6	-6.288459	1.206644	0.703673
1	-6.176857	1.455072	-0.360640
1	-6.586797	2.122122	1.235284
1	-7.107860	0.476578	0.793152
6	-5.182806	0.403254	2.808384
1	-6.079650	-0.200766	3.017630
1	-5.309673	1.368662	3.319197
1	-4.300351	-0.092423	3.235548
6	-2.418732	-1.649668	-2.477938

1	-1.781581	-0.759437	-2.380464
6	-1.462280	-2.833503	-2.596963
1	-1.990152	-3.774864	-2.817565
1	-0.882506	-2.954925	-1.670644
1	-0.750335	-2.652075	-3.416672
6	-3.269328	-1.496310	-3.745213
1	-2.621411	-1.403825	-4.630444
1	-3.915585	-0.607152	-3.701486
1	-3.915896	-2.376598	-3.885223
7	-3.178875	0.690788	-0.978763
7	-1.796355	2.229383	-1.577732
14	0.959879	-0.370292	-0.886498
14	-0.581850	0.400387	0.440350
52	-1.357596	0.847316	2.672590

Table S1. 6 Optimized cartesian coordinates of **TS1.1**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.146674	-0.575942	0.552288
6	-4.060471	-0.311872	1.711320
1	-5.029258	0.118279	1.942287
6	-3.350029	-1.298135	2.311858
1	-3.567913	-1.914066	3.177963
6	-1.233541	-2.511984	1.857424
6	-1.187633	-3.629025	0.994813
6	-0.274783	-4.639145	1.303633
1	-0.193224	-5.508362	0.652224
6	0.531472	-4.561020	2.436007
1	1.231938	-5.367868	2.659624
6	0.439173	-3.465727	3.282418
1	1.074014	-3.412823	4.168504
6	-0.435340	-2.407272	3.007109
6	-0.503037	-1.227744	3.963142
1	-1.051345	-0.410795	3.470766
6	-1.241839	-1.627124	5.247504
1	-0.695014	-2.421988	5.778696
1	-2.256207	-2.002361	5.046010
1	-1.325385	-0.762862	5.922231
6	0.884868	-0.677399	4.300834
1	0.780004	0.238757	4.898938
1	1.429899	-0.405942	3.385834

1	1.479380	-1.401028	4.881373
6	-2.105946	-3.758712	-0.214081
1	-2.105089	-2.788152	-0.739215
6	-3.549154	-4.071811	0.203457
1	-3.588595	-5.035404	0.734354
1	-4.192052	-4.145748	-0.687422
1	-3.976186	-3.301458	0.860255
6	-1.630539	-4.795619	-1.228962
1	-0.582678	-4.626807	-1.509783
1	-2.246660	-4.733651	-2.137934
1	-1.727170	-5.819187	-0.834935
6	-3.824903	0.983573	-0.406048
6	-3.879353	2.370464	-0.190927
6	-4.365278	3.161316	-1.239750
1	-4.409498	4.243114	-1.109896
6	-4.794512	2.596847	-2.434605
1	-5.162531	3.237394	-3.237646
6	-4.780941	1.215067	-2.597640
1	-5.155153	0.774611	-3.523368
6	-4.310955	0.378628	-1.583783
6	-4.437783	-1.128488	-1.737126
1	-3.829977	-1.607131	-0.959236
6	-5.893846	-1.548729	-1.497395
1	-6.232438	-1.251614	-0.493720
1	-6.001869	-2.639925	-1.588197
1	-6.561742	-1.076423	-2.233976
6	-3.930690	-1.634159	-3.087573
1	-4.581093	-1.305770	-3.912987
1	-3.919675	-2.735606	-3.095932
1	-2.909460	-1.274659	-3.276430
6	-3.535156	3.008784	1.141822
1	-2.895549	2.308635	1.697412
6	-2.751416	4.312734	0.991670
1	-2.455019	4.676377	1.986925
1	-3.360614	5.101019	0.521701
1	-1.828829	4.160720	0.414148
6	-4.824651	3.253863	1.938247
1	-4.588738	3.678488	2.925057
1	-5.398454	2.328434	2.093246
1	-5.480221	3.962582	1.407978
7	-3.320209	0.103680	0.621068
7	-2.190027	-1.466536	1.576468
6	2.215196	0.338990	-0.868395
6	3.833990	1.282307	-2.132331

1	4.426895	2.099738	-2.529495
6	3.847222	-0.046651	-2.391402
1	4.475328	-0.645020	-3.042719
6	2.685702	-2.038374	-1.495443
6	3.345646	-2.698124	-0.443087
6	3.205429	-4.086356	-0.363432
1	3.697008	-4.625897	0.448522
6	2.465202	-4.787894	-1.308596
1	2.379337	-5.873779	-1.237695
6	1.834423	-4.109272	-2.347465
1	1.263005	-4.669742	-3.088673
6	1.913194	-2.717538	-2.453177
6	1.231852	-1.987531	-3.599979
1	1.057522	-0.950233	-3.272504
6	2.137172	-1.960949	-4.838212
1	2.337120	-2.986714	-5.185018
1	3.102739	-1.480876	-4.630785
1	1.652199	-1.409535	-5.657204
6	-0.130479	-2.585332	-3.954012
1	-0.034954	-3.589408	-4.395529
1	-0.633975	-1.946847	-4.694463
1	-0.778341	-2.645274	-3.067359
6	4.236338	-1.973578	0.551375
1	4.096623	-0.893120	0.410151
6	5.712019	-2.293507	0.286806
1	5.910865	-3.366447	0.436099
1	6.352192	-1.729794	0.981269
1	6.010743	-2.036312	-0.739717
6	3.854001	-2.290634	1.999058
1	2.803559	-2.024115	2.191083
1	4.491151	-1.719105	2.690488
1	3.988758	-3.359794	2.227391
6	2.517239	2.831520	-0.741573
6	1.614181	3.587108	-1.497288
6	1.359938	4.896123	-1.075544
1	0.655924	5.513451	-1.636661
6	1.972282	5.409372	0.060815
1	1.760587	6.431481	0.378542
6	2.824834	4.612761	0.820685
1	3.257571	5.011613	1.738405
6	3.106301	3.300133	0.443992
6	4.001273	2.415310	1.295791
1	3.557660	1.406644	1.267925
6	5.425400	2.364701	0.725219

1	5.474655	1.833895	-0.234774
1	6.104079	1.854894	1.426113
1	5.798176	3.389292	0.567641
6	4.032194	2.825463	2.767272
1	4.611777	3.747357	2.927296
1	4.523148	2.034910	3.353554
1	3.009257	2.963663	3.146613
6	0.857871	3.003671	-2.678431
1	1.061389	1.922701	-2.710800
6	-0.653327	3.151262	-2.476962
1	-0.966617	4.206893	-2.503346
1	-0.946448	2.728478	-1.501141
1	-1.199982	2.619252	-3.270497
6	1.326194	3.610087	-4.004389
1	0.782629	3.160974	-4.848998
1	2.402511	3.446308	-4.162641
1	1.144941	4.696183	-4.022987
7	2.842072	1.501854	-1.194067
7	2.848774	-0.613954	-1.619001
14	-0.854234	-0.405136	-0.922344
14	0.890470	-0.069675	0.480208
52	0.085420	1.984441	1.684884

Table S1. 7 Optimized cartesian coordinates of **Int1.2**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.132448	-1.031964	0.489198
6	-4.159791	-1.478436	1.384343
1	-5.235065	-1.391691	1.497983
6	-3.252125	-2.262174	2.016005
1	-3.367052	-3.011595	2.792136
6	-0.824610	-2.718643	1.767339
6	-0.333140	-3.659487	0.838125
6	0.844194	-4.328154	1.175890
1	1.279693	-5.042956	0.478860
6	1.480767	-4.095739	2.394292
1	2.399460	-4.634071	2.634943
6	0.959915	-3.177937	3.294450
1	1.475287	-2.992959	4.238444
6	-0.197852	-2.451106	2.992023
6	-0.723791	-1.415149	3.972560

1	-1.418057	-0.757255	3.427730
6	-1.476550	-2.091659	5.125155
1	-0.801537	-2.754396	5.689111
1	-2.319596	-2.702267	4.771502
1	-1.871242	-1.336947	5.821265
6	0.393204	-0.522283	4.519624
1	-0.044740	0.312440	5.086139
1	0.994076	-0.103120	3.699643
1	1.056801	-1.077454	5.201171
6	-1.039670	-3.926178	-0.487475
1	-1.188686	-2.944291	-0.972839
6	-2.413143	-4.587416	-0.304001
1	-2.301295	-5.556357	0.206971
1	-2.869308	-4.774065	-1.288203
1	-3.115900	-3.974379	0.273225
6	-0.213691	-4.779504	-1.445860
1	0.785285	-4.356611	-1.606700
1	-0.722602	-4.838598	-2.419090
1	-0.101954	-5.807155	-1.065451
6	-4.080524	0.145691	-0.504226
6	-4.493767	1.421494	-0.085675
6	-5.081093	2.254027	-1.043954
1	-5.404189	3.254412	-0.752643
6	-5.251240	1.831212	-2.357165
1	-5.705197	2.500619	-3.089714
6	-4.845641	0.555999	-2.739166
1	-4.989252	0.229351	-3.770477
6	-4.252133	-0.313879	-1.822162
6	-3.861113	-1.717983	-2.251447
1	-3.188721	-2.134556	-1.489202
6	-5.102411	-2.615749	-2.310182
1	-5.605583	-2.665131	-1.332806
1	-4.828605	-3.639099	-2.608071
1	-5.826415	-2.228197	-3.043633
6	-3.095148	-1.728622	-3.575062
1	-3.744632	-1.465101	-4.424030
1	-2.691917	-2.734877	-3.769648
1	-2.256557	-1.018375	-3.534470
6	-4.365691	1.885368	1.354509
1	-3.582095	1.277672	1.832210
6	-3.937400	3.350616	1.465425
1	-3.676680	3.581959	2.508552
1	-4.750388	4.031968	1.169483
1	-3.055878	3.559701	0.842918

6	-5.687447	1.668634	2.103389
1	-5.590885	1.985568	3.152253
1	-6.002276	0.615708	2.093835
1	-6.492343	2.259820	1.639202
7	-3.461805	-0.743320	0.445269
7	-2.023363	-1.996073	1.435886
6	2.220500	0.764050	-0.684255
6	3.526964	2.109256	-1.956619
1	3.878580	3.057529	-2.350748
6	3.955426	0.838972	-2.148751
1	4.753784	0.428276	-2.758452
6	3.309256	-1.390805	-1.305098
6	4.050720	-1.944059	-0.246013
6	4.258436	-3.325179	-0.261463
1	4.828810	-3.789614	0.544834
6	3.768265	-4.112183	-1.300425
1	3.958908	-5.187028	-1.304678
6	3.039593	-3.534523	-2.334890
1	2.663435	-4.160951	-3.146396
6	2.774348	-2.160969	-2.348602
6	1.981036	-1.538649	-3.486415
1	1.734902	-0.503874	-3.203548
6	2.822578	-1.500254	-4.767424
1	3.082493	-2.520309	-5.090754
1	3.761315	-0.947194	-4.618927
1	2.264638	-1.015740	-5.581964
6	0.654462	-2.260343	-3.727448
1	0.809736	-3.303929	-4.043282
1	0.091920	-1.750424	-4.523352
1	0.033454	-2.253252	-2.819402
6	4.672724	-1.082132	0.839499
1	4.175890	-0.102251	0.816029
6	6.163062	-0.866532	0.552090
1	6.706903	-1.823691	0.572606
1	6.608494	-0.203555	1.308911
1	6.318699	-0.410905	-0.437378
6	4.443669	-1.653747	2.238464
1	3.368034	-1.803036	2.412086
1	4.823233	-0.951257	2.995303
1	4.970266	-2.610359	2.382455
6	1.881193	3.256135	-0.550090
6	0.798420	3.834084	-1.229989
6	0.298977	5.037739	-0.728868
1	-0.549002	5.513428	-1.223572

6	0.841621	5.617947	0.414234
1	0.425480	6.550202	0.799914
6	1.903574	5.009966	1.074348
1	2.312598	5.466601	1.978123
6	2.452551	3.815265	0.600559
6	3.602747	3.158493	1.346443
1	3.859869	2.222541	0.828718
6	4.849627	4.048664	1.329675
1	5.158138	4.284349	0.300409
1	5.687672	3.546574	1.835827
1	4.662745	4.999781	1.851267
6	3.197729	2.786934	2.776242
1	2.966277	3.686189	3.368045
1	4.020606	2.255607	3.278575
1	2.310235	2.137232	2.774215
6	0.175263	3.173217	-2.447542
1	0.422957	2.100508	-2.404563
6	-1.351551	3.271804	-2.456131
1	-1.691357	4.303399	-2.639809
1	-1.770826	2.915935	-1.502963
1	-1.759849	2.636986	-3.256581
6	0.769015	3.750003	-3.738678
1	0.326139	3.260377	-4.618831
1	1.859282	3.611985	-3.783731
1	0.562938	4.829647	-3.807208
7	2.468633	2.046983	-1.066172
7	3.149834	0.034703	-1.366039
14	-0.844565	-0.046009	-0.683389
14	1.134698	-0.162738	0.704187
52	-0.603491	1.682772	1.273685

Table S1. 8 Optimized cartesian coordinates of **PRC**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	0.372485	2.438170	0.523464
6	0.126880	4.451328	1.539502
1	-0.383668	5.378809	1.778192
6	1.332389	3.962937	1.912467
1	2.112109	4.370253	2.547480
6	2.612140	1.900260	1.462337
6	2.623643	0.979173	2.577664

6	1.448527	0.922638	3.539462
1	0.547088	1.218661	2.979221
6	1.188212	-0.477572	4.087009
1	1.004485	-1.190378	3.271877
1	0.296026	-0.460649	4.728966
1	2.026351	-0.840966	4.701706
6	1.653485	1.911586	4.695522
1	0.771432	1.918954	5.352695
1	1.818036	2.937779	4.341252
1	2.528732	1.617502	5.295600
6	3.753060	0.234146	2.776745
1	3.814634	-0.454608	3.619589
6	4.885633	0.335477	1.905124
1	5.845592	-0.058494	2.236495
6	4.844583	1.254577	0.807097
1	5.776485	1.575558	0.340241
6	3.665951	2.061451	0.598198
6	3.672225	3.078336	-0.524779
1	2.646549	3.459097	-0.632666
6	4.067967	2.453912	-1.864298
1	5.106048	2.087131	-1.853700
1	3.981489	3.208997	-2.659560
1	3.405864	1.609871	-2.105111
6	4.581318	4.259897	-0.163800
1	4.261691	4.743351	0.770979
1	4.558818	5.012084	-0.965446
1	5.626026	3.935365	-0.039076
6	-1.750956	3.762943	0.142558
6	-2.881820	3.356182	0.869202
6	-2.760956	2.527955	2.138220
1	-1.788024	2.011885	2.102340
6	-2.786571	3.419104	3.386067
1	-3.739551	3.967889	3.446663
1	-1.971340	4.157144	3.379868
1	-2.686055	2.808517	4.296130
6	-3.824850	1.431752	2.227673
1	-3.589762	0.754453	3.062404
1	-3.842971	0.831444	1.305634
1	-4.828047	1.849765	2.407826
6	-4.130081	3.704578	0.352783
1	-5.032880	3.401290	0.884616
6	-4.238929	4.394201	-0.852335
1	-5.225329	4.643362	-1.247158
6	-3.099153	4.750704	-1.564209

1	-3.196367	5.270795	-2.519590
6	-1.824794	4.445841	-1.076530
6	-0.588544	4.822093	-1.875613
1	0.291149	4.412826	-1.356857
6	-0.425328	6.343559	-1.946733
1	-1.281408	6.806094	-2.461824
1	0.486246	6.609888	-2.502266
1	-0.359145	6.786889	-0.941975
6	-0.615093	4.192946	-3.271462
1	-1.452715	4.584033	-3.869414
1	-0.716357	3.099843	-3.202454
1	0.317555	4.423292	-3.808276
7	1.459039	2.732461	1.296929
7	-0.449240	3.509255	0.704786
14	0.469740	0.935859	-0.792651
52	-2.063758	0.713541	-1.365115
6	-0.957353	-2.238359	-0.386930
6	-0.812388	-4.177682	-1.546946
1	-0.329637	-4.914700	-2.180764
6	-2.024318	-4.160180	-0.948116
1	-2.833712	-4.882230	-0.942123
6	-3.228565	-2.656747	0.593914
6	-4.419565	-2.216210	-0.005222
6	-4.571891	-2.056740	-1.508579
1	-3.564053	-1.941909	-1.937059
6	-5.376373	-0.809142	-1.886452
1	-5.014300	0.080942	-1.352931
1	-5.281732	-0.619739	-2.965524
1	-6.447649	-0.941038	-1.668156
6	-5.234237	-3.298811	-2.120404
1	-5.333846	-3.180972	-3.209570
1	-4.661033	-4.216329	-1.930407
1	-6.241246	-3.441868	-1.698342
6	-5.506410	-1.959528	0.839206
1	-6.443924	-1.605735	0.408103
6	-5.407144	-2.139147	2.212681
1	-6.264969	-1.925782	2.852660
6	-4.216599	-2.590931	2.776556
1	-4.153499	-2.731149	3.855918
6	-3.103170	-2.863977	1.980677
6	-1.826125	-3.413464	2.595489
1	-0.985354	-3.099031	1.961311
6	-1.555107	-2.846982	3.987304
1	-2.266833	-3.232271	4.733480

1	-0.545856	-3.132897	4.320191
1	-1.614568	-1.749176	3.968677
6	-1.853282	-4.946920	2.617283
1	-1.986948	-5.364680	1.608476
1	-0.911170	-5.342808	3.027501
1	-2.680715	-5.310483	3.246271
6	1.220108	-2.858104	-1.562873
6	1.547337	-2.160475	-2.736785
6	0.490397	-1.420834	-3.533678
1	-0.264113	-1.049830	-2.822799
6	-0.220870	-2.365628	-4.510591
1	0.492646	-2.779586	-5.240847
1	-0.709229	-3.204218	-3.994248
1	-0.998430	-1.814735	-5.060079
6	1.041247	-0.206890	-4.279324
1	0.202080	0.400881	-4.648129
1	1.644491	0.426340	-3.613299
1	1.650382	-0.501404	-5.149178
6	2.874821	-2.224632	-3.171498
1	3.167680	-1.683095	-4.071422
6	3.818523	-2.989141	-2.489606
1	4.841140	-3.054457	-2.866235
6	3.465297	-3.666156	-1.322085
1	4.217916	-4.251365	-0.792888
6	2.159279	-3.598546	-0.823211
6	1.779466	-4.248421	0.498437
1	0.742438	-4.611929	0.412193
6	2.652954	-5.446315	0.866043
1	3.679751	-5.134094	1.108829
1	2.245196	-5.942805	1.758147
1	2.699707	-6.184208	0.052056
6	1.807557	-3.196667	1.615848
1	2.837813	-2.848815	1.789969
1	1.214084	-2.309338	1.345931
1	1.410747	-3.617157	2.553870
7	-2.096992	-2.977208	-0.241378
7	-0.166754	-3.003923	-1.185896
14	-0.867935	-0.489414	0.622529
52	4.545301	-0.902381	-0.136773

Table S1. 9 Optimized cartesian coordinates of **TS1.2**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.898338	0.286646	0.357495
6	4.562350	1.404023	1.413982
1	5.154076	2.273384	1.682400
6	4.658337	0.101047	1.771449
1	5.352058	-0.422962	2.421134
6	3.430533	-1.978328	1.304894
6	2.579365	-2.410900	2.337656
6	1.763695	-1.422532	3.156910
1	1.520675	-0.577334	2.490716
6	0.428855	-2.005367	3.618735
1	-0.112545	-2.447997	2.769988
1	-0.194489	-1.206488	4.045802
1	0.564602	-2.771615	4.398377
6	2.554031	-0.887452	4.357279
1	1.939931	-0.175312	4.928865
1	3.473314	-0.368488	4.052705
1	2.834380	-1.713195	5.029881
6	2.479936	-3.785992	2.547121
1	1.822677	-4.163205	3.330640
6	3.171538	-4.686659	1.739765
1	3.069795	-5.759058	1.913858
6	3.969183	-4.227847	0.699670
1	4.488667	-4.941831	0.057681
6	4.118515	-2.856806	0.460271
6	4.998058	-2.374517	-0.680833
1	4.855582	-1.288639	-0.789334
6	4.585065	-3.013921	-2.008947
1	4.772088	-4.098695	-2.008258
1	5.161688	-2.573762	-2.835768
1	3.517210	-2.842005	-2.207357
6	6.477169	-2.628409	-0.372159
1	6.786336	-2.121466	0.553861
1	7.112262	-2.263147	-1.192675
1	6.669998	-3.705020	-0.246305
6	3.039957	2.770687	0.042885
6	2.127726	3.515782	0.809316
6	1.540418	2.965676	2.098720
1	1.552144	1.866049	2.019855

6	2.385172	3.375754	3.312088
1	2.406128	4.472648	3.407439
1	3.422698	3.022369	3.232955
1	1.955611	2.960420	4.236018
6	0.082845	3.374827	2.301788
1	-0.349189	2.812858	3.143526
1	-0.518900	3.159395	1.405016
1	-0.011816	4.446473	2.540337
6	1.754136	4.767399	0.319433
1	1.037703	5.371047	0.877987
6	2.247861	5.235452	-0.896168
1	1.931400	6.210770	-1.269950
6	3.125311	4.460214	-1.644837
1	3.491269	4.830748	-2.604351
6	3.544428	3.205791	-1.188350
6	4.505449	2.368870	-2.015202
1	4.540859	1.358332	-1.580166
6	5.919206	2.957541	-1.958682
1	5.932813	3.977420	-2.373129
1	6.617808	2.342055	-2.544530
1	6.290386	3.010668	-0.924504
6	4.020488	2.216037	-3.458717
1	4.042327	3.177302	-3.994604
1	2.993928	1.822173	-3.486627
1	4.670192	1.515175	-4.002992
7	3.627256	-0.562358	1.132734
7	3.476834	1.502412	0.563973
14	1.879110	-0.251480	-1.289794
52	0.025680	1.576387	-1.403492
6	-2.812699	0.000626	-0.202420
6	-4.908251	-0.558781	-0.837225
1	-5.672461	-1.203985	-1.259450
6	-4.965895	0.689034	-0.315524
1	-5.796185	1.369770	-0.159702
6	-3.385138	2.242254	0.761289
6	-3.175133	3.421761	0.024786
6	-3.185047	3.440734	-1.495355
1	-2.876911	2.441140	-1.841776
6	-2.201620	4.459524	-2.077832
1	-1.209210	4.376007	-1.612114
1	-2.085360	4.285352	-3.157204
1	-2.571103	5.488855	-1.948707
6	-4.595845	3.722347	-2.030164
1	-4.587026	3.740235	-3.129884

1	-5.322159	2.962166	-1.713420
1	-4.952035	4.701687	-1.674241
6	-3.010336	4.606424	0.750307
1	-2.841807	5.541232	0.214744
6	-3.060263	4.610739	2.140456
1	-2.934226	5.548417	2.684465
6	-3.259982	3.425456	2.840503
1	-3.288993	3.439682	3.931512
6	-3.424052	2.212746	2.166269
6	-3.690121	0.935593	2.946801
1	-3.592204	0.083702	2.257967
6	-2.659636	0.725586	4.057483
1	-2.732201	1.504668	4.831873
1	-2.824141	-0.246004	4.547309
1	-1.645353	0.731305	3.631964
6	-5.120459	0.930722	3.497490
1	-5.861430	1.037164	2.691427
1	-5.324031	-0.010847	4.029127
1	-5.270365	1.760854	4.204938
6	-3.196074	-2.266916	-1.244852
6	-2.606068	-2.361557	-2.515163
6	-2.258041	-1.118905	-3.314625
1	-1.922378	-0.357681	-2.593150
6	-3.476630	-0.571173	-4.067026
1	-3.839486	-1.304678	-4.804332
1	-4.310090	-0.330418	-3.391029
1	-3.203880	0.348904	-4.605334
6	-1.085604	-1.331102	-4.268885
1	-0.760982	-0.358288	-4.665485
1	-0.232332	-1.780505	-3.739915
1	-1.358354	-1.970472	-5.124024
6	-2.317793	-3.643656	-2.987310
1	-1.844034	-3.760981	-3.961741
6	-2.589683	-4.768486	-2.216109
1	-2.344879	-5.760384	-2.599347
6	-3.157644	-4.639372	-0.952477
1	-3.352217	-5.532360	-0.358419
6	-3.480653	-3.380044	-0.438221
6	-4.039127	-3.221202	0.968986
1	-4.710253	-2.347704	0.973533
6	-4.860573	-4.424663	1.430926
1	-4.223001	-5.305224	1.599276
1	-5.354845	-4.195826	2.385845
1	-5.633586	-4.696023	0.697540

6	-2.904297	-2.934793	1.960951
1	-2.185726	-3.769120	1.968864
1	-2.343953	-2.024669	1.696700
1	-3.302425	-2.806446	2.979696
7	-3.677261	1.019183	0.057493
7	-3.586649	-0.964116	-0.760751
14	-0.927237	0.088489	0.524759
52	0.090872	-3.250464	-0.399611

Table S1. 10 Optimized cartesian coordinates of **Int1.3**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.882838	0.193285	0.362245
6	4.536725	1.309171	1.436064
1	5.121085	2.179454	1.717322
6	4.643048	0.002101	1.775191
1	5.340457	-0.525354	2.418103
6	3.432700	-2.080429	1.278095
6	2.584187	-2.534484	2.303796
6	1.759740	-1.564482	3.136112
1	1.510405	-0.711968	2.481677
6	0.429304	-2.164662	3.588329
1	-0.107710	-2.599661	2.732876
1	-0.200928	-1.377012	4.026012
1	0.570625	-2.940716	4.357207
6	2.544616	-1.039981	4.344705
1	1.924209	-0.341026	4.925677
1	3.459893	-0.509278	4.048406
1	2.831114	-1.872829	5.005858
6	2.495821	-3.913164	2.493722
1	1.840978	-4.306763	3.271181
6	3.195477	-4.796658	1.674418
1	3.102353	-5.872205	1.833248
6	3.990260	-4.316699	0.641702
1	4.516131	-5.017277	-0.009787
6	4.128587	-2.941239	0.421837
6	5.005163	-2.435711	-0.711465
1	4.853908	-1.349608	-0.804763
6	4.598583	-3.059637	-2.048887
1	4.794470	-4.142749	-2.063330
1	5.172317	-2.603147	-2.868834

1	3.529534	-2.893658	-2.245914
6	6.486028	-2.681856	-0.404932
1	6.790222	-2.185540	0.528462
1	7.118836	-2.299864	-1.219574
1	6.687543	-3.758527	-0.294102
6	3.004417	2.682596	0.082886
6	2.085448	3.409316	0.858852
6	1.501521	2.836270	2.139773
1	1.522308	1.738000	2.045399
6	2.341823	3.236046	3.359653
1	2.353725	4.331618	3.470505
1	3.382274	2.892297	3.276572
1	1.914858	2.804206	4.277197
6	0.040473	3.230598	2.347145
1	-0.387694	2.653284	3.180432
1	-0.558699	3.022953	1.446820
1	-0.063158	4.297958	2.600709
6	1.702068	4.664638	0.386320
1	0.980231	5.254465	0.952628
6	2.193021	5.153835	-0.822057
1	1.868925	6.131721	-1.182344
6	3.077441	4.396441	-1.580723
1	3.441203	4.783471	-2.534544
6	3.506399	3.139157	-1.141578
6	4.474960	2.321876	-1.979208
1	4.518248	1.305615	-1.558450
6	5.883806	2.921212	-1.912971
1	5.889438	3.946922	-2.312960
1	6.587934	2.319789	-2.506755
1	6.253627	2.962750	-0.877776
6	3.992538	2.185500	-3.425220
1	4.006988	3.154387	-3.947457
1	2.969258	1.783702	-3.459713
1	4.648431	1.497725	-3.978690
7	3.617990	-0.660609	1.126144
7	3.451190	1.410694	0.586447
14	1.869497	-0.329816	-1.293495
52	0.001283	1.484283	-1.383218
6	-2.825174	-0.131410	-0.207349
6	-4.915521	-0.698881	-0.852079
1	-5.674057	-1.344272	-1.284136
6	-4.983826	0.540926	-0.312867
1	-5.819792	1.212591	-0.148276
6	-3.416773	2.091630	0.787348

6	-3.215771	3.283100	0.067785
6	-3.224499	3.323468	-1.451946
1	-2.907894	2.331418	-1.812141
6	-2.248922	4.358381	-2.018997
1	-1.256274	4.276397	-1.553515
1	-2.130290	4.200432	-3.100604
1	-2.626924	5.382734	-1.875718
6	-4.637081	3.601083	-1.984131
1	-4.627438	3.634578	-3.083480
1	-5.357433	2.830598	-1.678878
1	-5.001581	4.572355	-1.614770
6	-3.061306	4.458700	0.810127
1	-2.899955	5.402326	0.287986
6	-3.112493	4.442965	2.200147
1	-2.994607	5.373861	2.757469
6	-3.303130	3.246319	2.883187
1	-3.333219	3.244891	3.974259
6	-3.456684	2.041957	2.191732
6	-3.712989	0.751774	2.953885
1	-3.607501	-0.089472	2.253188
6	-2.681801	0.534514	4.062518
1	-2.761417	1.301959	4.847759
1	-2.838787	-0.445210	4.538410
1	-1.667223	0.554525	3.638134
6	-5.143724	0.727445	3.503024
1	-5.884829	0.839213	2.697805
1	-5.340059	-0.223172	4.021108
1	-5.301037	1.546247	4.221974
6	-3.189075	-2.387051	-1.282080
6	-2.597194	-2.458914	-2.553011
6	-2.258635	-1.202291	-3.334498
1	-1.929845	-0.448622	-2.602011
6	-3.480999	-0.653949	-4.080304
1	-3.837194	-1.379902	-4.828256
1	-4.316995	-0.429582	-3.401806
1	-3.215307	0.275838	-4.605293
6	-1.083661	-1.391405	-4.290490
1	-0.766656	-0.410467	-4.672989
1	-0.227210	-1.841256	-3.767068
1	-1.350420	-2.020834	-5.154844
6	-2.298029	-3.731818	-3.042929
1	-1.822467	-3.831492	-4.018446
6	-2.561392	-4.869615	-2.287960
1	-2.308147	-5.853967	-2.684923

6	-3.131504	-4.763009	-1.023198
1	-3.319292	-5.665860	-0.442004
6	-3.465253	-3.513751	-0.491532
6	-4.026248	-3.379372	0.917220
1	-4.704498	-2.511534	0.933432
6	-4.838233	-4.595906	1.361300
1	-4.193630	-5.473523	1.517834
1	-5.335201	-4.384627	2.318862
1	-5.608354	-4.863179	0.623384
6	-2.894673	-3.097753	1.914262
1	-2.169311	-3.926214	1.911109
1	-2.341557	-2.179442	1.663448
1	-3.294736	-2.987067	2.934320
7	-3.698265	0.876281	0.066060
7	-3.590716	-1.094453	-0.780019
14	-0.941135	-0.038440	0.522879
52	0.241312	-2.158750	-0.424517

Table S1. 11 Optimized cartesian coordinates of **TS1.3**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.416118	0.095660	-0.868475
6	3.433294	0.880199	-2.708759
1	3.800670	1.640884	-3.388749
6	3.608434	-0.465260	-2.694445
1	4.137525	-1.129251	-3.369484
6	3.030236	-2.282738	-1.071055
6	2.065280	-3.207014	-1.502544
6	0.980620	-2.817397	-2.491078
1	0.763637	-1.746335	-2.348397
6	-0.321876	-3.569641	-2.237809
1	-1.119326	-3.165339	-2.876350
1	-0.634323	-3.450134	-1.190470
1	-0.224600	-4.644912	-2.456686
6	1.454334	-3.014045	-3.936423
1	2.370624	-2.446311	-4.152065
1	0.673490	-2.675145	-4.632040
1	1.661003	-4.077434	-4.133483
6	2.154113	-4.505364	-0.989277
1	1.418563	-5.251231	-1.289161
6	3.150221	-4.850798	-0.080032

1	3.194411	-5.866750	0.315514
6	4.081847	-3.907623	0.339001
1	4.850400	-4.189449	1.058715
6	4.043901	-2.596813	-0.145945
6	5.097654	-1.586382	0.273679
1	4.680864	-0.577782	0.129968
6	5.478253	-1.714311	1.749067
1	4.584227	-1.696816	2.388336
1	6.124007	-0.873621	2.042123
1	6.039270	-2.641374	1.942191
6	6.335005	-1.715544	-0.625264
1	6.780109	-2.716855	-0.519187
1	7.094582	-0.970308	-0.347441
1	6.084143	-1.567968	-1.685865
6	2.504396	2.595740	-1.198728
6	1.540826	3.352823	-1.888167
6	0.584988	2.761329	-2.911633
1	0.486679	1.681950	-2.711616
6	-0.813971	3.381584	-2.810432
1	-1.525778	2.760605	-3.370951
1	-0.831566	4.395234	-3.240080
1	-1.164038	3.439007	-1.767136
6	1.107014	2.929709	-4.345023
1	1.228914	3.996664	-4.587530
1	0.387256	2.493213	-5.052558
1	2.074313	2.435068	-4.503465
6	1.476761	4.722389	-1.601382
1	0.743130	5.338350	-2.121262
6	2.310933	5.300018	-0.654331
1	2.235729	6.367352	-0.440760
6	3.233024	4.518098	0.034621
1	3.871435	4.979427	0.786818
6	3.369167	3.153002	-0.232211
6	4.455185	2.342717	0.460387
1	4.021152	1.364408	0.713124
6	4.900603	2.954731	1.787646
1	5.529771	2.232255	2.326930
1	4.038640	3.185290	2.429120
1	5.495858	3.868847	1.637321
6	5.677705	2.137189	-0.445502
1	5.443453	1.582397	-1.363948
1	6.449190	1.569116	0.097276
1	6.111032	3.107758	-0.733120
7	2.973645	-0.925822	-1.560266

7	2.708775	1.211558	-1.575217
14	1.142905	-0.397930	0.594998
52	2.077924	0.441306	2.634154
6	-2.339545	-0.087622	0.882216
6	-3.079051	-1.014836	2.790290
1	-3.316821	-1.824960	3.470202
6	-3.323679	0.318329	2.869237
1	-3.801869	0.918404	3.636297
6	-3.111642	2.212306	1.234485
6	-2.165838	3.215899	1.495251
6	-0.904167	2.935068	2.289909
1	-0.639964	1.872729	2.159054
6	0.286935	3.752391	1.797915
1	1.192910	3.442441	2.337504
1	0.459576	3.588690	0.723263
1	0.147283	4.830944	1.972718
6	-1.144834	3.172004	3.785827
1	-1.972531	2.557557	4.169328
1	-0.238443	2.913955	4.352801
1	-1.391440	4.228188	3.976683
6	-2.445399	4.492257	0.995479
1	-1.731828	5.298934	1.161293
6	-3.605799	4.742589	0.268427
1	-3.795998	5.745528	-0.116867
6	-4.519428	3.723160	0.020744
1	-5.420652	3.932642	-0.556813
6	-4.292153	2.430655	0.499198
6	-5.317247	1.328894	0.284678
1	-4.802124	0.362640	0.380247
6	-5.958061	1.357364	-1.102702
1	-5.194608	1.378432	-1.891832
1	-6.569260	0.452970	-1.244471
1	-6.626067	2.223842	-1.223711
6	-6.391020	1.402764	1.379427
1	-6.922000	2.365715	1.326622
1	-7.128825	0.596351	1.255659
1	-5.953135	1.313860	2.384186
6	-2.282016	-2.602279	1.071561
6	-1.241684	-3.382268	1.607268
6	-0.250289	-2.866528	2.637152
1	-0.222246	-1.767905	2.573040
6	1.169533	-3.386884	2.388143
1	1.878806	-2.813896	3.001755
1	1.260210	-4.450490	2.660743

1	1.467617	-3.272037	1.333670
6	-0.680414	-3.240858	4.062331
1	-0.747088	-4.334421	4.171909
1	0.061030	-2.863935	4.781642
1	-1.655021	-2.815824	4.333362
6	-1.153584	-4.715019	1.182312
1	-0.355427	-5.344224	1.576983
6	-2.063289	-5.245855	0.278010
1	-1.976370	-6.287323	-0.035692
6	-3.084161	-4.450958	-0.232946
1	-3.787927	-4.874997	-0.947902
6	-3.228702	-3.116953	0.156091
6	-4.405188	-2.298622	-0.356515
1	-4.035190	-1.284282	-0.564479
6	-4.969097	-2.819739	-1.677773
1	-5.670455	-2.079169	-2.088340
1	-4.173593	-2.966861	-2.420699
1	-5.519974	-3.763871	-1.543185
6	-5.528971	-2.218778	0.687243
1	-5.212869	-1.720734	1.614389
1	-6.376999	-1.648624	0.276371
1	-5.889378	-3.226682	0.944310
7	-2.872909	0.862332	1.686045
7	-2.488398	-1.252517	1.559369
14	-1.296785	0.607950	-0.705476
52	-2.275211	-0.264690	-2.706141

Table S1. 12 Optimized cartesian coordinates of compound **1.31**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.238697	-0.003398	0.973797
6	-3.597775	0.609317	2.645253
1	-4.160549	1.298820	3.266232
6	-3.468984	-0.743176	2.690204
1	-3.894650	-1.480670	3.362660
6	-2.526471	-2.478750	1.181768
6	-1.472549	-3.288031	1.634659
6	-0.452961	-2.803196	2.644625
1	-0.363132	-1.711483	2.548842
6	0.934564	-3.396160	2.406656
1	1.663598	-2.889091	3.053715

1	1.252645	-3.248319	1.362066
1	0.963334	-4.473886	2.633135
6	-0.929754	-3.095441	4.072623
1	-1.906430	-2.633349	4.279487
1	-0.204954	-2.693568	4.795598
1	-1.027321	-4.179756	4.238660
6	-1.431210	-4.606481	1.166917
1	-0.616808	-5.256513	1.486344
6	-2.401917	-5.095057	0.300884
1	-2.344440	-6.124797	-0.056102
6	-3.445730	-4.275687	-0.113870
1	-4.206998	-4.669016	-0.788324
6	-3.538181	-2.951502	0.322699
6	-4.753515	-2.117352	-0.049969
1	-4.486819	-1.056727	0.060997
6	-5.209374	-2.319125	-1.495272
1	-4.372829	-2.186966	-2.194290
1	-5.983985	-1.577357	-1.742501
1	-5.654830	-3.315171	-1.642237
6	-5.909817	-2.423245	0.913375
1	-6.202412	-3.481386	0.830362
1	-6.787303	-1.805956	0.669130
1	-5.639762	-2.232653	1.961355
6	-2.854857	2.409436	1.084972
6	-1.935984	3.327925	1.617425
6	-0.880723	2.927581	2.630102
1	-0.705112	1.844375	2.537873
6	0.459241	3.608888	2.357007
1	1.214135	3.230899	3.059126
1	0.399197	4.702417	2.473957
1	0.811923	3.376539	1.340268
6	-1.361510	3.207218	4.058201
1	-1.521064	4.286224	4.211624
1	-0.608623	2.859987	4.780547
1	-2.308151	2.692193	4.279620
6	-2.036389	4.655526	1.185268
1	-1.341661	5.396301	1.581556
6	-2.996507	5.039142	0.257878
1	-3.058149	6.080366	-0.063136
6	-3.863392	4.095921	-0.284798
1	-4.586593	4.403372	-1.039685
6	-3.811895	2.756307	0.108963
6	-4.753069	1.734590	-0.510101
1	-4.202970	0.784370	-0.565159

6	-5.132086	2.074391	-1.950979
1	-5.646912	1.215091	-2.404449
1	-4.235659	2.278158	-2.553111
1	-5.813844	2.937393	-2.005208
6	-6.013800	1.530149	0.338294
1	-5.783925	1.181139	1.354670
1	-6.667619	0.780718	-0.133601
1	-6.579171	2.471505	0.420470
7	-2.646515	-1.107181	1.643073
7	-2.848661	1.043331	1.571742
14	-0.975985	0.219453	-0.478752
52	-1.982508	-0.251094	-2.603660
6	2.238641	0.003472	-0.973856
6	3.598026	-0.609294	-2.645056
1	4.160834	-1.298821	-3.265978
6	3.469256	0.743197	-2.690059
1	3.895046	1.480664	-3.362469
6	2.526606	2.478831	-1.181835
6	1.472596	3.288039	-1.634665
6	0.452857	2.803065	-2.644419
1	0.363020	1.711373	-2.548432
6	-0.934620	3.396092	-2.406297
1	-1.663779	2.888968	-3.053177
1	-1.252528	3.248345	-1.361638
1	-0.963409	4.473797	-2.632867
6	0.929447	3.095031	-4.072533
1	1.906087	2.632883	-4.279433
1	0.204547	2.692996	-4.795317
1	1.026987	4.179312	-4.238816
6	1.431284	4.606531	-1.167051
1	0.616818	5.256508	-1.486420
6	2.402092	5.095222	-0.301190
1	2.344648	6.125005	0.055680
6	3.445958	4.275909	0.113536
1	4.207294	4.669315	0.787868
6	3.538388	2.951680	-0.322910
6	4.753733	2.117565	0.049824
1	4.487065	1.056940	-0.061217
6	5.209436	2.319287	1.495180
1	4.372870	2.186886	2.194123
1	5.984184	1.577659	1.742395
1	5.654669	3.315410	1.642279
6	5.910139	2.423562	-0.913358
1	6.202706	3.481698	-0.830203

1	6.787603	1.806267	-0.669050
1	5.640228	2.233064	-1.961388
6	2.854861	-2.409376	-1.084870
6	1.936018	-3.327866	-1.617393
6	0.880853	-2.927504	-2.630164
1	0.705072	-1.844340	-2.537742
6	-0.459063	-3.609075	-2.357434
1	-1.213909	-3.231067	-3.059595
1	-0.398823	-4.702566	-2.474591
1	-0.811962	-3.376999	-1.340712
6	1.361898	-3.206764	-4.058249
1	1.521479	-4.285725	-4.211944
1	0.609122	-2.859338	-4.780617
1	2.308571	-2.691669	-4.279386
6	2.036453	-4.655469	-1.185265
1	1.341768	-5.396271	-1.581579
6	2.996567	-5.039096	-0.257867
1	3.058227	-6.080337	0.063087
6	3.863417	-4.095883	0.284865
1	4.586602	-4.403338	1.039771
6	3.811866	-2.756247	-0.108834
6	4.752980	-1.734525	0.510331
1	4.202978	-0.784239	0.565176
6	5.131698	-2.074230	1.951307
1	5.646430	-1.214911	2.404853
1	4.235157	-2.277983	2.553266
1	5.813463	-2.937215	2.005706
6	6.013890	-1.530297	-0.337852
1	5.784192	-1.181519	-1.354349
1	6.667655	-0.780795	0.134001
1	6.579239	-2.471692	-0.419753
7	2.646643	1.107238	-1.643066
7	2.848724	-1.043272	-1.571658
14	0.975791	-0.219360	0.478566
52	1.982266	0.250835	2.603605

Table S1. 13 Optimized cartesian coordinates of **TS1.4**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.163149	0.210999	1.026754
6	3.994008	-0.155030	2.270259
1	4.972656	-0.569088	2.491227
6	3.179220	0.665932	2.977971
1	3.296836	1.133914	3.949056
6	1.072897	1.879251	2.557007
6	1.104830	3.111403	1.871452
6	0.134069	4.054577	2.211843
1	0.098163	5.006850	1.682946
6	-0.785161	3.800608	3.227185
1	-1.532410	4.553941	3.483162
6	-0.755489	2.596783	3.916446
1	-1.482031	2.408290	4.707227
6	0.165200	1.594413	3.587971
6	0.141909	0.273694	4.337968
1	0.618078	-0.494461	3.706735
6	0.905549	0.381923	5.664543
1	0.434397	1.131648	6.319497
1	1.956482	0.673813	5.531218
1	0.889239	-0.585856	6.186050
6	-1.284815	-0.208885	4.609421
1	-1.255541	-1.249990	4.958622
1	-1.886769	-0.197763	3.690172
1	-1.779631	0.402192	5.381437
6	2.192134	3.449082	0.859648
1	2.429346	2.544048	0.278540
6	3.470648	3.887187	1.588373
1	3.278035	4.801163	2.170925
1	4.269893	4.102184	0.862492
1	3.838507	3.115044	2.279555
6	1.768221	4.510986	-0.149740
1	0.810877	4.247671	-0.617919
1	2.530580	4.596661	-0.937714
1	1.666074	5.502072	0.319254
6	4.115880	-1.011954	-0.013171
6	3.960334	-2.377505	-0.288697
6	4.753718	-2.910149	-1.306972
1	4.652385	-3.964413	-1.564399

6	5.648998	-2.110526	-2.012115
1	6.253738	-2.546815	-2.808744
6	5.773443	-0.758651	-1.713891
1	6.470879	-0.140409	-2.282422
6	5.004984	-0.175509	-0.702950
6	5.142169	1.310949	-0.410856
1	4.421396	1.581173	0.374277
6	6.537830	1.640477	0.127879
1	6.767427	1.054936	1.030481
1	6.610884	2.708780	0.382217
1	7.312041	1.418652	-0.622378
6	4.803089	2.160693	-1.639632
1	5.522054	1.986044	-2.454536
1	4.845435	3.231282	-1.383631
1	3.798307	1.920262	-2.018732
6	2.949889	-3.209135	0.471247
1	2.066570	-2.573805	0.649188
6	2.461138	-4.424665	-0.308379
1	1.573112	-4.830296	0.200657
1	3.226690	-5.215801	-0.360879
1	2.175719	-4.147675	-1.332995
6	3.475270	-3.640486	1.844509
1	2.679371	-4.174642	2.383633
1	3.770407	-2.782270	2.465336
1	4.346135	-4.306365	1.736001
7	3.366207	-0.409606	1.071463
7	2.066327	0.891606	2.198675
6	-2.301827	0.185853	-0.966922
6	-3.850930	-0.490316	-2.451566
1	-4.515690	-1.203116	-2.928779
6	-3.637768	0.829661	-2.668592
1	-4.082566	1.525732	-3.371822
6	-2.416718	2.623390	-1.490026
6	-3.167792	3.249535	-0.477324
6	-2.929614	4.606375	-0.244440
1	-3.490508	5.120301	0.538586
6	-2.013859	5.314157	-1.016625
1	-1.850396	6.377042	-0.829696
6	-1.316886	4.676166	-2.037580
1	-0.610072	5.244743	-2.643717
6	-1.491697	3.311662	-2.292294
6	-0.752537	2.634178	-3.432323
1	-0.720510	1.554440	-3.219375
6	-1.498309	2.848894	-4.755879

1	-1.538902	3.920736	-5.005766
1	-2.530734	2.475058	-4.714822
1	-0.980667	2.324247	-5.571995
6	0.695058	3.107765	-3.565920
1	0.752892	4.153357	-3.907791
1	1.219105	2.481860	-4.302094
1	1.238540	3.012242	-2.615816
6	-4.278527	2.539037	0.281074
1	-4.212399	1.461607	0.075993
6	-5.640712	3.014784	-0.239659
1	-5.771401	4.093060	-0.059556
1	-6.456059	2.481320	0.270844
1	-5.738797	2.838433	-1.321125
6	-4.169084	2.714964	1.796060
1	-3.184125	2.383747	2.155152
1	-4.942972	2.114963	2.298612
1	-4.320522	3.764491	2.093830
6	-3.136146	-2.208004	-0.867933
6	-2.550151	-3.244767	-1.602725
6	-2.824618	-4.554160	-1.196289
1	-2.377356	-5.386295	-1.742734
6	-3.639496	-4.805373	-0.101088
1	-3.839305	-5.833752	0.203764
6	-4.171516	-3.750634	0.633999
1	-4.769341	-3.963109	1.520250
6	-3.930382	-2.426255	0.271463
6	-4.508914	-1.279947	1.085174
1	-3.803282	-0.438263	1.017467
6	-5.855828	-0.815803	0.518930
1	-5.771290	-0.491005	-0.529543
1	-6.248423	0.029230	1.106272
1	-6.592017	-1.633202	0.562219
6	-4.617006	-1.612737	2.573413
1	-5.426142	-2.332364	2.772578
1	-4.844230	-0.698839	3.142605
1	-3.666836	-2.030493	2.940691
6	-1.623682	-2.991540	-2.777591
1	-1.395546	-1.914978	-2.817483
6	-0.293146	-3.711321	-2.555172
1	-0.413396	-4.805437	-2.597786
1	0.113451	-3.447258	-1.568321
1	0.436101	-3.413861	-3.323231
6	-2.268174	-3.397963	-4.105714
1	-1.579934	-3.199890	-4.940479

1	-3.201265	-2.846607	-4.295661
1	-2.507848	-4.472682	-4.109469
7	-3.039247	-0.864338	-1.396481
7	-2.691395	1.231224	-1.746908
14	0.788900	0.120541	-0.379524
14	-1.228088	0.460373	0.674228
52	1.634635	-0.383931	-2.518018
52	-0.619339	-2.868872	1.986449

Table S1. 14 Optimized cartesian coordinates of compound **1.32**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.203488	0.705533	-0.911378
6	-4.156158	0.910958	-2.007392
1	-5.206581	0.719934	-2.201506
6	-3.252745	1.703124	-2.634336
1	-3.347413	2.373789	-3.481370
6	-0.905689	2.375461	-2.251606
6	-0.562563	3.431538	-1.380766
6	0.574835	4.172995	-1.706252
1	0.901659	4.977536	-1.049085
6	1.308285	3.901131	-2.860217
1	2.192476	4.497845	-3.091520
6	0.926504	2.873173	-3.708465
1	1.514572	2.661407	-4.602659
6	-0.184297	2.072879	-3.415763
6	-0.553390	0.929343	-4.347025
1	-1.212075	0.242165	-3.794383
6	-1.294097	1.447271	-5.586197
1	-0.651505	2.134730	-6.157986
1	-2.213789	1.991458	-5.330004
1	-1.567045	0.610060	-6.245405
6	0.676695	0.121975	-4.773866
1	0.358167	-0.807967	-5.266916
1	1.292273	-0.144966	-3.903460
1	1.296445	0.683397	-5.490117
6	-1.386205	3.757592	-0.137805
1	-1.508408	2.820723	0.435698
6	-2.782538	4.293162	-0.486210
1	-2.698240	5.201176	-1.103214
1	-3.316222	4.559607	0.438481

1	-3.406119	3.568001	-1.024352
6	-0.693740	4.755646	0.785103
1	0.315883	4.422337	1.055109
1	-1.274951	4.865792	1.711567
1	-0.622042	5.749191	0.314856
6	-4.211846	-0.497718	0.013266
6	-4.352357	-1.866586	-0.245420
6	-5.070379	-2.621725	0.687485
1	-5.191131	-3.694060	0.527670
6	-5.629538	-2.025432	1.810536
1	-6.182792	-2.632727	2.528556
6	-5.483661	-0.658361	2.029784
1	-5.916493	-0.208651	2.923501
6	-4.765591	0.138383	1.138571
6	-4.613183	1.633105	1.374438
1	-3.667410	1.946060	0.904648
6	-5.763484	2.403178	0.711015
1	-5.805422	2.234154	-0.374334
1	-5.653472	3.484747	0.880931
1	-6.727080	2.086229	1.139052
6	-4.514796	2.001667	2.854663
1	-5.475508	1.857285	3.372645
1	-4.249656	3.065335	2.952463
1	-3.739947	1.402827	3.353566
6	-3.799045	-2.515568	-1.500888
1	-3.033920	-1.846265	-1.922151
6	-3.116512	-3.852739	-1.208366
1	-2.578303	-4.201446	-2.102155
1	-3.848286	-4.628911	-0.935483
1	-2.387675	-3.752169	-0.391863
6	-4.908512	-2.687845	-2.545700
1	-4.504442	-3.140236	-3.463441
1	-5.369339	-1.725596	-2.813325
1	-5.703577	-3.344442	-2.159736
7	-3.503709	0.324141	-0.942372
7	-2.068014	1.582904	-1.936340
6	2.360640	-0.356675	0.718303
6	3.761107	-1.480709	2.084403
1	4.275462	-2.355535	2.468470
6	3.810960	-0.176891	2.443633
1	4.384237	0.340212	3.205882
6	2.965880	1.938032	1.513415
6	3.807526	2.530487	0.551193
6	3.879068	3.925041	0.526821

1	4.518125	4.413219	-0.211486
6	3.182696	4.693932	1.454812
1	3.268744	5.781868	1.435431
6	2.389425	4.078250	2.416071
1	1.854903	4.687902	3.146368
6	2.245302	2.686258	2.457714
6	1.388575	2.036570	3.528584
1	1.173822	1.002796	3.217834
6	2.136256	2.000303	4.866802
1	2.348111	3.020509	5.224419
1	3.095107	1.467634	4.789232
1	1.526439	1.489867	5.626198
6	0.036235	2.730400	3.689284
1	0.143148	3.764293	4.055435
1	-0.578819	2.172145	4.409057
1	-0.516245	2.732926	2.739503
6	4.708257	1.719051	-0.366348
1	4.399736	0.666252	-0.316660
6	6.155636	1.792136	0.136961
1	6.524988	2.829024	0.114102
1	6.815159	1.179634	-0.495706
1	6.237451	1.427199	1.171736
6	4.603622	2.151884	-1.829494
1	3.558262	2.116514	-2.170223
1	5.199789	1.476683	-2.462582
1	4.995556	3.170642	-1.977198
6	2.710549	-2.842393	0.346788
6	1.982109	-3.845932	0.999388
6	1.923916	-5.100818	0.383401
1	1.362545	-5.903167	0.864828
6	2.543334	-5.331113	-0.837114
1	2.475510	-6.314001	-1.306206
6	3.237457	-4.305258	-1.473640
1	3.699090	-4.492470	-2.443022
6	3.344098	-3.040315	-0.894657
6	4.109406	-1.927884	-1.593341
1	3.581610	-0.984811	-1.388484
6	5.534165	-1.803472	-1.040962
1	5.537279	-1.604081	0.041346
1	6.067336	-0.978472	-1.539006
1	6.097126	-2.732903	-1.218052
6	4.123651	-2.073265	-3.114242
1	4.753686	-2.914415	-3.442104
1	4.532735	-1.159237	-3.568951

1	3.106078	-2.224879	-3.503582
6	1.235617	-3.612410	2.301391
1	1.201343	-2.529392	2.496949
6	-0.218295	-4.078269	2.192978
1	-0.285776	-5.172157	2.081398
1	-0.713264	-3.593607	1.339331
1	-0.771372	-3.787694	3.097130
6	1.938636	-4.302348	3.475843
1	1.396351	-4.104559	4.411927
1	2.974236	-3.954133	3.602706
1	1.970127	-5.392717	3.323784
7	2.883209	-1.574083	1.018352
7	2.958069	0.498387	1.592561
14	-0.767474	-0.062768	0.205923
14	1.314817	0.363218	-0.817263
52	-1.420257	-0.519514	2.464194
52	-0.034376	-1.808093	-1.499423

Table S1. 15 Optimized cartesian coordinates of **Int1.4**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.458187	-0.988856	-0.461386
6	4.517268	-1.670351	-1.063714
1	5.600510	-1.623674	-1.104696
6	3.625754	-2.536343	-1.598575
1	3.754438	-3.437869	-2.187958
6	1.257031	-2.956662	-1.604321
6	0.732148	-3.848107	-0.650076
6	-0.084270	-4.873890	-1.124162
1	-0.523966	-5.578270	-0.419677
6	-0.373305	-4.997036	-2.480536
1	-1.013221	-5.810465	-2.825441
6	0.105975	-4.061087	-3.385035
1	-0.170251	-4.132432	-4.438366
6	0.934889	-3.015266	-2.967257
6	1.420255	-1.992947	-3.981469
1	1.896009	-1.165371	-3.432474
6	2.444419	-2.589867	-4.952972
1	2.007767	-3.439222	-5.500598
1	3.347246	-2.949773	-4.438762
1	2.754993	-1.835455	-5.690678

6	0.230921	-1.404050	-4.748734
1	0.553278	-0.527233	-5.329864
1	-0.566549	-1.093368	-4.058358
1	-0.187544	-2.139672	-5.453386
6	1.000971	-3.670850	0.837416
1	0.932560	-2.586411	1.031715
6	2.397536	-4.145206	1.259163
1	2.506863	-5.224563	1.071090
1	2.542468	-3.970418	2.337077
1	3.207543	-3.624833	0.727440
6	-0.065992	-4.339438	1.701623
1	-1.075864	-4.019040	1.403285
1	0.085899	-4.065824	2.755271
1	-0.003590	-5.436903	1.637323
6	4.492980	0.317956	0.333072
6	4.803988	1.475339	-0.387261
6	5.585272	2.438273	0.258938
1	5.840044	3.360114	-0.266614
6	6.027097	2.239451	1.560459
1	6.632377	3.003275	2.050993
6	5.688241	1.077986	2.251599
1	6.018211	0.952149	3.282876
6	4.906480	0.089147	1.655326
6	4.494476	-1.159534	2.419397
1	3.515272	-1.477799	2.023189
6	5.497143	-2.302083	2.211667
1	5.594494	-2.584744	1.154096
1	5.181392	-3.195954	2.770252
1	6.492309	-2.004056	2.576446
6	4.303000	-0.891476	3.912142
1	5.265789	-0.728133	4.420200
1	3.825645	-1.760564	4.388501
1	3.663698	-0.010701	4.068593
6	4.310617	1.709956	-1.803894
1	3.557362	0.942126	-2.040763
6	3.612158	3.065881	-1.919455
1	3.124085	3.162812	-2.900662
1	4.326993	3.896588	-1.814312
1	2.847007	3.165328	-1.136369
6	5.453009	1.575128	-2.815577
1	5.079596	1.727917	-3.838752
1	5.921771	0.581011	-2.766009
1	6.235071	2.325573	-2.622222
7	3.789058	-0.740723	-0.356107

7	2.370164	-2.111959	-1.216229
6	-2.191880	0.895096	0.724910
6	-3.204472	2.641835	1.705350
1	-3.566880	3.661253	1.780196
6	-3.298256	1.588003	2.550781
1	-3.751326	1.490191	3.531372
6	-2.878755	-0.827430	2.457093
6	-4.077158	-1.499975	2.141350
6	-4.270587	-2.759365	2.712599
1	-5.175872	-3.318583	2.475802
6	-3.330267	-3.311874	3.576899
1	-3.505197	-4.296977	4.012895
6	-2.176302	-2.608224	3.895399
1	-1.455686	-3.038436	4.592200
6	-1.923475	-1.348219	3.342597
6	-0.711976	-0.547105	3.767849
1	-0.507196	0.202617	2.991991
6	-0.999100	0.211636	5.068373
1	-1.173607	-0.489922	5.899626
1	-1.885943	0.855519	4.978627
1	-0.140885	0.851430	5.321989
6	0.554506	-1.385961	3.915026
1	0.474540	-2.121097	4.731915
1	1.402206	-0.721511	4.129764
1	0.785887	-1.921767	2.982410
6	-5.165498	-0.886254	1.272521
1	-4.679597	-0.189227	0.573083
6	-6.176246	-0.107585	2.128388
1	-6.654600	-0.782568	2.854763
1	-6.963803	0.317519	1.488045
1	-5.715671	0.717272	2.686522
6	-5.919900	-1.922053	0.436438
1	-5.227409	-2.594588	-0.084789
1	-6.534752	-1.409524	-0.318316
1	-6.601880	-2.519746	1.061017
6	-2.454208	3.038361	-0.595338
6	-1.644416	4.182896	-0.551991
6	-1.640904	5.009876	-1.680677
1	-1.017571	5.905258	-1.680255
6	-2.393566	4.696785	-2.803793
1	-2.362733	5.345464	-3.680646
6	-3.193928	3.557900	-2.812126
1	-3.786658	3.324231	-3.696253
6	-3.261111	2.712254	-1.703586

6	-4.224833	1.537162	-1.696039
1	-3.769510	0.711789	-1.133202
6	-5.529886	1.927128	-0.989953
1	-5.355522	2.241210	0.050854
1	-6.221604	1.070717	-0.972976
1	-6.022580	2.757922	-1.518723
6	-4.505013	0.967476	-3.084226
1	-5.124613	1.644345	-3.693046
1	-5.042773	0.014193	-2.980760
1	-3.568610	0.757976	-3.621264
6	-0.783876	4.550852	0.643981
1	-0.723031	3.677365	1.310250
6	0.648611	4.881024	0.220808
1	0.693012	5.816396	-0.359015
1	1.066846	4.064709	-0.382732
1	1.284901	4.996825	1.109710
6	-1.390961	5.728515	1.416098
1	-0.772597	5.967708	2.293618
1	-2.412814	5.522514	1.766415
1	-1.437103	6.625139	0.778228
7	-2.539264	2.197436	0.581211
7	-2.703777	0.513120	1.924741
14	1.056295	0.242436	0.182608
14	-1.137866	-0.277383	-0.466287
52	1.692651	1.709797	1.970715
52	0.218234	1.250579	-2.014984
52	-2.495252	-2.059579	-1.270464

Table S1. 16 Optimized cartesian coordinates of **TS1.5**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-3.075143	-0.561587	-0.441069
6	-5.279426	-0.563651	-0.825957
1	-6.298627	-0.196673	-0.767586
6	-4.745048	-1.639150	-1.461975
1	-5.198115	-2.424675	-2.058378
6	-2.490168	-2.652747	-1.669801
6	-1.994087	-2.572043	-2.979678
6	-2.261794	-1.378754	-3.880606
1	-2.549961	-0.529640	-3.240557
6	-1.005454	-0.960719	-4.648514

1	-0.130897	-0.922216	-3.984077
1	-1.149063	0.034480	-5.094048
1	-0.790129	-1.663663	-5.468222
6	-3.417044	-1.668439	-4.846596
1	-3.597339	-0.803502	-5.502172
1	-4.353440	-1.893042	-4.314957
1	-3.175204	-2.534954	-5.480900
6	-1.225648	-3.645737	-3.432411
1	-0.805240	-3.614642	-4.438150
6	-0.959438	-4.732034	-2.607539
1	-0.340750	-5.551466	-2.975382
6	-1.440750	-4.762738	-1.303092
1	-1.190623	-5.604835	-0.656927
6	-2.218612	-3.718368	-0.798280
6	-2.757029	-3.766555	0.621868
1	-2.985324	-2.737016	0.938457
6	-1.718829	-4.300050	1.609618
1	-1.563709	-5.383315	1.488520
1	-2.057499	-4.123781	2.641190
1	-0.756293	-3.786046	1.471232
6	-4.055969	-4.578834	0.679991
1	-4.831893	-4.152751	0.026091
1	-4.449324	-4.603853	1.707353
1	-3.875624	-5.615715	0.356864
6	-4.386183	1.302750	0.570696
6	-4.282604	2.532789	-0.103860
6	-4.098352	2.615957	-1.611661
1	-3.541778	1.721664	-1.934687
6	-5.464391	2.613051	-2.312369
1	-6.050116	3.494683	-2.009521
1	-6.054751	1.719021	-2.069659
1	-5.332939	2.645974	-3.403692
6	-3.291536	3.835680	-2.056284
1	-3.073527	3.758620	-3.131061
1	-2.333132	3.902904	-1.523711
1	-3.853328	4.769404	-1.900626
6	-4.428235	3.692396	0.663741
1	-4.344259	4.666976	0.182550
6	-4.666446	3.618970	2.031771
1	-4.767285	4.536462	2.613856
6	-4.774688	2.384917	2.665521
1	-4.958524	2.346142	3.739072
6	-4.642928	1.192412	1.948722
6	-4.817257	-0.154285	2.632189

1	-4.164220	-0.875097	2.115064
6	-6.270816	-0.634869	2.518042
1	-6.949309	0.085217	3.000624
1	-6.389938	-1.606338	3.019843
1	-6.592517	-0.754760	1.474892
6	-4.393312	-0.135110	4.100388
1	-5.115115	0.417841	4.721200
1	-3.399210	0.316476	4.221063
1	-4.349303	-1.163961	4.485043
7	-3.388904	-1.612970	-1.218455
7	-4.236699	0.089202	-0.201520
14	-1.303782	-0.000121	0.144226
52	-0.955606	-0.481837	2.396808
52	-0.375962	1.387174	-1.550828
6	2.898022	0.734637	0.359317
6	4.363859	0.998657	2.058449
1	5.128648	0.683598	2.760600
6	3.786382	2.201574	1.834739
1	3.940811	3.169258	2.299792
6	2.314146	3.164055	0.118027
6	1.155257	3.762342	0.644792
6	0.469321	3.224961	1.889528
1	0.641899	2.136646	1.913785
6	-1.043371	3.455223	1.887878
1	-1.496706	3.176872	0.925565
1	-1.510827	2.836026	2.668161
1	-1.293641	4.507796	2.100072
6	1.062754	3.833770	3.167728
1	0.507641	3.471923	4.045924
1	2.116984	3.567688	3.312055
1	0.985514	4.931964	3.139864
6	0.655182	4.887100	-0.015388
1	-0.247761	5.366963	0.362951
6	1.273738	5.380391	-1.159858
1	0.856930	6.249223	-1.672344
6	2.425041	4.774828	-1.650368
1	2.913290	5.180939	-2.537861
6	2.982982	3.661237	-1.013176
6	4.313959	3.104824	-1.491435
1	4.471964	2.128690	-1.013761
6	4.348798	2.866656	-3.001369
1	4.239615	3.804282	-3.566752
1	5.314728	2.423774	-3.287638
1	3.549884	2.173230	-3.301630

6	5.454470	4.025285	-1.040088
1	5.429547	4.184709	0.047943
1	6.428901	3.586627	-1.302018
1	5.378618	5.009679	-1.527722
6	4.320217	-1.241715	1.087266
6	3.885042	-2.165947	2.049002
6	2.758583	-1.853887	3.018030
1	2.179342	-1.020340	2.589206
6	3.297487	-1.427963	4.389404
1	3.915554	-2.228448	4.825689
1	3.913217	-0.519476	4.330144
1	2.464811	-1.223963	5.079225
6	1.798762	-3.035097	3.173684
1	0.909030	-2.719867	3.739261
1	1.469109	-3.400012	2.190102
1	2.265046	-3.864798	3.728370
6	4.500408	-3.419451	2.057514
1	4.180826	-4.164820	2.786784
6	5.484568	-3.743109	1.130510
1	5.944106	-4.732710	1.147591
6	5.873554	-2.815272	0.170970
1	6.635374	-3.085236	-0.560725
6	5.307038	-1.538686	0.134474
6	5.780171	-0.513350	-0.881940
1	4.935375	0.154492	-1.105404
6	6.907963	0.347570	-0.300257
1	7.776930	-0.280181	-0.047577
1	7.231702	1.106973	-1.028806
1	6.590132	0.869975	0.614958
6	6.179594	-1.132079	-2.219384
1	7.124414	-1.692604	-2.155478
1	5.390809	-1.808328	-2.578431
1	6.321456	-0.337948	-2.966766
7	2.885791	2.025942	0.799859
7	3.811706	0.112357	1.151885
14	2.189176	0.005456	-1.404038
52	1.495218	-2.276333	-0.827791

Table S1. 17 Optimized cartesian coordinates of **Int1.5**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.898937	0.000065	0.408983
6	-5.011747	-0.677284	0.772182
1	-5.808685	-1.398328	0.918509
6	-5.011726	0.677448	0.772239
1	-5.808640	1.398507	0.918624
6	-3.330690	2.472466	0.593405
6	-2.929831	3.020239	1.828232
6	-2.865307	2.185666	3.100278
1	-2.550793	1.171104	2.806740
6	-1.836063	2.700059	4.106923
1	-0.856054	2.846940	3.633760
1	-1.718569	1.966571	4.917423
1	-2.161579	3.645958	4.566604
6	-4.241199	2.102319	3.776938
1	-4.177391	1.498389	4.694314
1	-5.004594	1.649608	3.131000
1	-4.585820	3.109816	4.056369
6	-2.602666	4.377108	1.843113
1	-2.267845	4.837263	2.772454
6	-2.667124	5.143158	0.682324
1	-2.388887	6.197801	0.714664
6	-3.082354	4.574830	-0.515651
1	-3.133654	5.187565	-1.416180
6	-3.439934	3.223554	-0.587031
6	-4.000799	2.638535	-1.872051
1	-3.815396	1.553578	-1.860725
6	-3.316334	3.191852	-3.120887
1	-3.592315	4.242219	-3.304551
1	-3.625524	2.606994	-3.999072
1	-2.225044	3.111351	-3.035878
6	-5.514259	2.883338	-1.947361
1	-6.053494	2.427855	-1.104962
1	-5.920716	2.458860	-2.877176
1	-5.731021	3.962852	-1.940235
6	-3.330761	-2.472338	0.593202
6	-2.929947	-3.020229	1.827991
6	-2.865545	-2.185794	3.100132
1	-2.551142	-1.171159	2.806727

6	-4.241476	-2.102687	3.776742
1	-4.585979	-3.110257	4.056055
1	-5.004901	-1.650016	3.130812
1	-4.177788	-1.498836	4.694179
6	-1.836292	-2.700199	4.106764
1	-1.718913	-1.966795	4.917357
1	-0.856247	-2.846927	3.633631
1	-2.161737	-3.646184	4.566317
6	-2.602763	-4.377095	1.842754
1	-2.267970	-4.837333	2.772065
6	-2.667181	-5.143035	0.681892
1	-2.388931	-6.197678	0.714138
6	-3.082406	-4.574604	-0.516037
1	-3.133694	-5.187258	-1.416622
6	-3.439998	-3.223325	-0.587300
6	-4.000896	-2.638210	-1.872261
1	-3.815477	-1.553256	-1.860865
6	-5.514363	-2.882983	-1.947532
1	-5.731142	-3.962495	-1.940462
1	-5.920845	-2.458446	-2.877309
1	-6.053565	-2.427542	-1.105090
6	-3.316494	-3.191458	-3.121162
1	-3.592533	-4.241798	-3.304896
1	-2.225198	-3.111017	-3.036183
1	-3.625688	-2.606520	-3.999292
7	-3.707871	1.076630	0.562966
7	-3.707906	-1.076490	0.562875
14	-1.027335	0.000062	-0.248525
52	-1.227766	0.000082	-2.643205
52	0.227742	-1.875518	0.874564
6	3.055362	-0.000062	-0.316286
6	4.785492	0.676738	-1.603036
1	5.436009	1.399828	-2.084247
6	4.785432	-0.677095	-1.602993
1	5.435876	-1.400273	-2.084170
6	3.512029	-2.466233	-0.498806
6	2.691108	-3.249548	-1.331338
6	1.894220	-2.637389	-2.471898
1	1.530433	-1.655273	-2.122674
6	0.656991	-3.457813	-2.830527
1	0.050592	-3.675750	-1.937640
1	0.036682	-2.876459	-3.526650
1	0.927361	-4.406498	-3.321899
6	2.743224	-2.416346	-3.730016

1	2.122190	-1.960774	-4.515257
1	3.594386	-1.745788	-3.553774
1	3.132291	-3.374569	-4.109026
6	2.602191	-4.610298	-1.030709
1	1.968557	-5.250793	-1.643253
6	3.279066	-5.155788	0.057417
1	3.186046	-6.221255	0.274104
6	4.058329	-4.349173	0.876506
1	4.575113	-4.784613	1.733565
6	4.196389	-2.981977	0.612011
6	5.093271	-2.127168	1.493387
1	4.909010	-1.071175	1.249273
6	4.771385	-2.300592	2.978905
1	4.998511	-3.320291	3.325250
1	5.376060	-1.604183	3.578583
1	3.710665	-2.087903	3.175730
6	6.569293	-2.422249	1.203883
1	6.814132	-2.241397	0.146912
1	7.218949	-1.784058	1.821457
1	6.807990	-3.473203	1.429548
6	3.512301	2.466035	-0.498859
6	2.691383	3.249445	-1.331305
6	1.894380	2.637389	-2.471840
1	1.530494	1.655312	-2.122612
6	2.743323	2.416247	-3.729983
1	3.132466	3.374428	-4.109024
1	3.594430	1.745615	-3.553757
1	2.122222	1.960718	-4.515196
6	0.657239	3.457960	-2.830437
1	0.036848	2.876683	-3.526551
1	0.050877	3.675970	-1.937541
1	0.927712	4.406614	-3.321812
6	2.602607	4.610193	-1.030629
1	1.968987	5.250762	-1.643110
6	3.279610	5.155592	0.057464
1	3.186694	6.221061	0.274193
6	4.058883	4.348890	0.876458
1	4.575779	4.784262	1.733484
6	4.196813	2.981692	0.611904
6	5.093748	2.126796	1.493144
1	4.909503	1.070825	1.248919
6	6.569749	2.421927	1.203589
1	6.808441	3.472868	1.429320
1	7.219444	1.783700	1.821082

1	6.814539	2.241159	0.146591
6	4.771944	2.300065	2.978699
1	4.999043	3.319744	3.325121
1	3.711248	2.087304	3.175567
1	5.376690	1.603629	3.578274
7	3.714397	-1.075032	-0.823859
7	3.714493	1.074816	-0.823926
14	1.982550	0.000031	1.376934
52	0.227806	1.875625	0.874519

Table S1. 18 Optimized cartesian coordinates of compound **1.33**
M06-2X/def2-SVP

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	3.096751	0.009790	-0.482260
6	5.024022	-0.641046	-1.433416
1	5.735677	-1.351644	-1.840861
6	5.049497	0.711351	-1.344403
1	5.790495	1.440860	-1.654483
6	3.432068	2.480254	-0.787993
6	2.835364	2.949274	-1.973913
6	2.651389	2.068925	-3.200641
1	2.723197	1.018032	-2.882201
6	1.284533	2.238373	-3.866273
1	0.463277	2.085892	-3.152405
1	1.168858	1.495819	-4.670136
1	1.177284	3.233668	-4.324148
6	3.778300	2.332235	-4.208603
1	3.674341	1.672240	-5.082374
1	4.772444	2.165250	-3.769079
1	3.738462	3.374544	-4.561003
6	2.439821	4.287473	-2.001684
1	1.961758	4.685323	-2.897604
6	2.623114	5.109809	-0.894022
1	2.289009	6.147990	-0.929049
6	3.234442	4.619301	0.254478
1	3.386320	5.279095	1.109316
6	3.671876	3.292167	0.329648
6	4.453899	2.797566	1.531722
1	4.356583	1.703170	1.575414
6	3.919953	3.343223	2.855076
1	4.117342	4.421379	2.961715

1	4.414056	2.827248	3.690736
1	2.840363	3.160248	2.949780
6	5.938797	3.142678	1.358880
1	6.356815	2.699884	0.442640
1	6.519468	2.766529	2.213794
1	6.079898	4.233106	1.299054
6	3.404087	-2.439247	-0.978114
6	2.609718	-2.846516	-2.070407
6	2.067106	-1.858841	-3.097563
1	1.772728	-0.948908	-2.546167
6	3.123663	-1.479333	-4.144336
1	3.438672	-2.371277	-4.707694
1	4.018750	-1.018934	-3.704573
1	2.696091	-0.759997	-4.859313
6	0.808786	-2.358174	-3.805871
1	0.377258	-1.542922	-4.403005
1	0.040750	-2.674616	-3.085685
1	1.034261	-3.193899	-4.486786
6	2.310378	-4.206896	-2.155712
1	1.686613	-4.566020	-2.973250
6	2.767888	-5.107737	-1.196490
1	2.513394	-6.165195	-1.283947
6	3.531804	-4.667722	-0.123965
1	3.874228	-5.380721	0.626976
6	3.872947	-3.316390	0.010004
6	4.753722	-2.857010	1.159525
1	4.613041	-1.772306	1.284569
6	6.230236	-3.131305	0.847346
1	6.401059	-4.209512	0.703353
1	6.865153	-2.792347	1.678904
1	6.563038	-2.615425	-0.064545
6	4.357395	-3.506928	2.485973
1	4.605852	-4.579620	2.503028
1	3.283641	-3.379700	2.679590
1	4.902408	-3.024272	3.309949
7	3.854525	1.096710	-0.774546
7	3.812586	-1.052821	-0.917198
14	1.522071	-0.035169	0.712994
52	2.393980	-0.179741	2.930915
52	-0.045384	-1.895875	0.007740
6	-3.096881	-0.009725	0.482158
6	-5.024189	0.641307	1.433103
1	-5.735795	1.351982	1.840505
6	-5.049843	-0.711081	1.343974

1	-5.790969	-1.440505	1.653947
6	-3.432337	-2.480077	0.787936
6	-2.835949	-2.948890	1.974090
6	-2.652433	-2.068351	3.200747
1	-2.724850	-1.017527	2.882243
6	-1.285472	-2.236909	3.866384
1	-0.464276	-2.083377	3.152667
1	-1.170540	-1.494670	4.670654
1	-1.177354	-3.232332	4.323774
6	-3.779228	-2.332199	4.208689
1	-3.675852	-1.671866	5.082277
1	-4.773445	-2.166085	3.768995
1	-3.738664	-3.374373	4.561408
6	-2.440332	-4.287061	2.002169
1	-1.962564	-4.684762	2.898316
6	-2.623210	-5.109547	0.894552
1	-2.289012	-6.147690	0.929803
6	-3.234229	-4.619237	-0.254202
1	-3.385754	-5.279145	-1.109014
6	-3.671747	-3.292148	-0.329677
6	-4.453487	-2.797747	-1.532012
1	-4.355872	-1.703390	-1.576048
6	-3.919565	-3.344014	-2.855122
1	-4.117220	-4.422160	-2.961385
1	-4.413490	-2.828236	-3.691010
1	-2.839926	-3.161347	-2.949806
6	-5.938484	-3.142448	-1.359208
1	-6.356522	-2.699259	-0.443170
1	-6.518968	-2.766462	-2.214322
1	-6.079827	-4.232825	-1.299030
6	-3.403983	2.439319	0.978016
6	-2.609733	2.846378	2.070466
6	-2.067375	1.858460	3.097525
1	-1.773007	0.948602	2.545981
6	-3.124163	1.478893	4.144040
1	-3.439193	2.370782	4.707476
1	-4.019213	1.018640	3.704036
1	-2.696802	0.759410	4.858995
6	-0.809084	2.357491	3.806102
1	-0.377692	1.542036	4.403062
1	-0.040941	2.674031	3.086064
1	-1.034531	3.193063	4.487211
6	-2.310275	4.206715	2.155982
1	-1.686619	4.565688	2.973669

6	-2.767515	5.107708	1.196772
1	-2.512934	6.165131	1.284400
6	-3.531239	4.667879	0.124033
1	-3.873429	5.380983	-0.626918
6	-3.872501	3.316595	-0.010139
6	-4.752985	2.857414	-1.159967
1	-4.612584	1.772665	-1.284923
6	-6.229534	3.132130	-0.848346
1	-6.400140	4.210395	-0.704526
1	-6.864243	2.793246	-1.680092
1	-6.562769	2.616427	0.063490
6	-4.355938	3.507149	-2.486292
1	-4.603926	4.579948	-2.503454
1	-3.282171	3.379458	-2.679534
1	-4.900854	3.024699	-3.310452
7	-3.854850	-1.096560	0.774235
7	-3.812656	1.052956	0.916997
14	-1.522049	0.035048	-0.712906
52	-2.393859	0.179384	-2.930876
52	0.045316	1.895768	-0.007510

Reactivity of NHC–Silicon(I) Dimer (1.13-I) toward Chalcogen

Figure S1. 41 Important geometrical parameters of **1.35** (a) X-ray crystal structure (b) BP86/def2-SVP optimized geometry in triplet electronic state and (c) BP86/def2-SVP optimized geometry in singlet electronic state. The hydrogen atoms on the Ar group are omitted for clarity.

Table S1. 19 Mulliken charge (q) and spin density (s) on the selected atoms of singlet and triplet **1.35** at the BP86/def2-SVP level of theory.

Atom No.	Singlet		Triplet	
	Charge (q)	Spin density (s)	Charge (q)	Spin density (s)
Te1	-0.151	-0.002	-0.197	0.190
Te2	-0.167	0.017	-0.212	0.189
Si1	0.104	0.054	0.117	0.290
Si2	0.123	-0.055	0.135	0.294
I1	-0.170	-0.036	-0.162	0.098
I2	-0.174	0.028	-0.163	0.098
C1	0.030	0.173	0.033	0.209
C2	0.019	-0.177	0.023	0.209
N1	-0.182	0.066	-0.184	0.065
N2	-0.166	0.061	-0.164	0.059
N3	-0.166	-0.062	-0.164	0.060
N4	-0.182	-0.067	-0.181	0.065

Figure S1. 42 A schematic representation of the four important frontier orbitals and the electronic configuration considered for the CASSCF (6,6)/def2-SVP calculations of the ground state singlet (S_0), doubly excited singlet state (S_2) and first triplet excited state (T_1) on the crystal structure geometry of **1.35**. The relative energies at the same level of theory is given below each electronic state.

Figure S1. 43 Schematic representation Lewis structure of **1.35** in singlet (left) and triplet (right) electronic state.

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Chapter 2:

A Parent NHC-stabilized Silyliumylidene Cation[※]

2.1 Introduction

Silylium ions $[\text{R}^1_3\text{Si}]^+$ (R^1 = alkyl and aryl) are highly reactive and incredibly robust Lewis acids, attributable to its electronic sextet and an unoccupied p-orbital at the silicon atoms.^[1] As such, these cationic trivalent silicon species are inherently labile, indubitably originate from the immense electrophilicity at the silicon center. This could be explained by the more polarizable, more electropositive silicon as compared to the lighter carbon atom. More importantly, larger size of the silicon atom effects the poorer orbital interaction between the silicon atom and the substituents, which results in longer Si–R bond (R = σ -bonded substituents).^[2] Consequently, the large positive charge on the silicon center reduces stabilization from π -conjugation and hyperconjugation, resulted in a far superior Lewis acid than the carbenium ion analog $[\text{R}_3\text{C}]^+$.^[2] Therefore, silylium ions can easily react with nearly all available nucleophiles (σ -, π - and n -donor). However, with a thoughtful design of a weakly coordinating anions (WCAs), donor free solvent and extreme steric congestion from the substituents, an isolable silylium ions is beyond a laboratory curiosity (Chart 2.1).^[3] Further, the silylium ions is incredibly electron-deficient with its omnipresence in Lewis acid catalysis and C–F bond activation (Chart 2.2).^[4]

[※] Portions of this chapter are adapted with permission from Y. Li, Y.-C. Chan, B.-X. Leong, Y. Li, E. Richards, I. Purushothaman, S. De, P. Parameswaran, C.-W. So, *Angew. Chem. Int. Ed.* **2017**, 56, 7573-7578. Copyright 2020 Wiley-VCH GmbH.

Chart 2. 1 Selected examples of silylium ions.^[3]

(a) C–H arylation

(b) Friedels-Craft C–H silylation

(c) Diels-Alder cycloaddition

Chart 2. 2 Selected examples of silylium ion-catalyzed reactions.^[4]

Silyliumylidene ions $[\text{HSi:}]^+$ (Chart 2.3, left) depicts the most fundamental unit of polyatomic low-valent silicon moiety. The electronic structure features a stereoactive electron pair, two unoccupied p-orbitals as well as a positive charge at the silicon atom (Chart 2.3, left). Accordingly, the cationic divalent silicon(II) is truly intriguing as it features the best blend of Lewis ambiphilic silylene and a potent Lewis acidic silylium ion in monoatomic silicon center, amongst the most reactive silicon species. As expected, the study of silyliumylidene ions is considered as part of the principal themes in contemporary silicon chemistry. However, the synthesis of isolable and highly reactive parent silyliumylidene ion species remained challenging since it is only noticeable as a labile intermediate in gas phase under mass spectrometric^[5] and astrochemical process^[6].

Chart 2. 3 Schematic representation of a free (left) and donor-stabilized silyliumylidene ions (center and right).

Nonetheless, silyliumylidene ions represent a promising yet unexploited class of low-valent silicon with paramount importance as basic building blocks to construct novel organosilicon and low-valent silicon compounds.^[7] Similar to the silylium ion and silylene archetypes, in addition the strong electronic resemblance of the silyliumylidenes with the transition metal complexes that manifests an open coordination site and a stereo-active lone pair of electrons with a small energy separation, one can envisage silyliumylidene ion as a robust contender in transition metal-like reactivity including small molecule activation and catalysis, or even as efficient transition metal ligand in catalysis. The capability of low-valent silicon species in demonstrating transition metal-like reactivity will be further entailed in Chapter 3. Unfortunately, a structural motif of mono-coordinated cationic silicon(II) species in the condensed phase remained unknown until the year 2020, whereby Hinz presented the only example of bulky carbazolyl skeleton of mono-substituted silyliumylidene separated ion

pair **2.9** (Chart 2.4), owing to the agostic interaction of the cationic silicon(II) center with the flanking aryl substituents for additional stabilization.^[8]

The landmark discovery of the first *N*-heterocyclic silylene (NHSi) [$\text{:Si}\{\text{N}(t\text{Bu})\text{CH}\}_2$] by West around the mid-1990s marked a significant milestone in introducing the notion of kinetic and/or thermodynamic stabilizations as the key elements in stable isolable low-valent silicon species.^[9] Evidently, computation studies performed by Müller on mono-coordinated silyliumylidene complexes stabilized by substituent R^2 ($\text{R}^2 = \text{R}^1$, amino and halogen) illustrate the sp-type HOMO (singlet ground state lone pair) and two low-lying degenerate p-type LUMOs, primarily found on the silicon atom with a singlet-triplet energy separation of $\Delta E_{\text{ST}} = 142 - 452 \text{ kJ/mol}$, in agreement with the composition $[\text{R}-\text{Si:}]^+$ (Chart 2.3, left).^[2] Further, the two degenerate LUMOs could be stabilized by Lewis base donors (L), whereas the electron-donating substituents R^1 can further reinforce the thermodynamic stability of the highly electrophilic cationic silicon(II) moiety (Chart 2.3, center and right).^[2] Therefore, playing the right balance between the inert solvent, lower temperature settings, and suitable substituents and/or donor ligands, persistent silyliumylidene cations can be isolated in the form of salts.

To circumvent the labile mono-coordinated silyliumylidene ions, sterically encumbered electron donor motif was necessitated to prepare series of silyliumylidene salts **2.10** – **2.19** (Chart 2.4).^[8,10] A decade since the breakthrough by West, Jutzi presented the first silyliumylidene salt, inclusive of a nido-cluster type cation $[(\eta^5\text{-C}_5\text{Me}_5)\text{Si}]^+$ (**2.10**, Chart 2.4).^[10a] The stability of compound **2.10** is largely benefited by the π -delocalization of the C_5Me_5 framework and a WCA borate $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.^[10a] Driess documents the isolation of silyliumylidene cation **2.11** and **2.12** using β -diketiminato ligand and bis(iminophosphorane) donor ligand, respectively (Chart 2.4).^[10b,10c] The reactions proceeded by using the ligand scaffold and $\text{I}_{\text{Ar}}-\text{SiCl}_2$ ($\text{I}_{\text{Ar}} = \text{:C}\{\text{N}(\text{Ar})\text{CH}\}_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) to induce ligand exchange and halide displacement. To date, compounds **2.11** and **2.12** are the only examples of divalent silyliumylidene ions. Taking advantage of the well-established *N*-heterocyclic carbenes (NHCs) as excellent Lewis-bases in taming highly reactive silicon species in its exotic oxidation states (+2, +1 and 0),^[11] several groups have utilized various NHCs such as chelating bis-NHC $[\text{:CN}(\text{Ar})\text{C}(\text{H})\text{C}-\mu\text{]}_2\text{CH}_2$, cAAC_{Me} ($\text{cAAC}_{\text{Me}} = \text{:C}(\text{CMe}_2)_2(\text{CH}_2)\text{NAr}$), I_{Ar} and $\text{I}_{i\text{Pr}}$ ($\text{I}_{i\text{Pr}} = \text{:C}\{\text{N}(i\text{Pr})\text{CH}\}_2$) as the ligand template to furnish the recent silyliumylidenes **2.13** – **2.18**

(Chart 2.4).^[10d-h] Another striking example includes the amidinato-stabilized silyliumylidene salt **2.19**, obtained through oxidation of dimeric amidinato–silicon(I) complex $[L^1Si:]_2$ ($L^1 = PhC\{N(tBu)\}_2$) with trimethylsilyl-4-dimethylaminopyridinium triflate $[4-NMe_2C_5H_4NSiMe_3]OTf$ (Chart 2.4).^[10i]

Chart 2. 4 Selected examples of base-stabilized silyliumylidenes.^[8,10]

Despite the successive isolations of stable silyliumylidene ions, majority of them are three co-ordinates and demand severe stabilization by up to two Lewis bases. As such, the much-anticipated great synthetic potential of these species are much restricted by the stabilization imposed. Predictably, the reactivities of heavily stabilized silyliumylidene ion are limited to stoichiometric syntheses. For example, reductive dehalogenation, salt metathesis, simple oxidation of small molecules (N_2O , CO_2 , H_2O and $\text{PhC}\equiv\text{CH}$) and silylene-like coordination to transition metal.^[12] Across all the literature silyliumylidenes, only compound **2.10** (Chart 2.4) poses the highest potential with extended reactivity in the synthesis of various asymmetrical silylenes and regrettably, the sole example to exhibit catalytic feature in degradation of oligoether to dioxane and mono-ethers.^[13] Hitherto, the reactivity demonstrated is closely related to the silylene counterpart and do not attest to the catalytic aspect of a silyliumylidene ion. These circumstances command for preparation of a new isolable yet highly reactive silyliumylidene which can perform catalytic transformations.

Chart 2. 5 Bonding model in silicon(I) dimer and its constitutional isomer silicon(I) radical (center) and silicon(I) radical ion pair (right).

In Chapter 1, we illustrated the bonding model of a silicon(I) dimer $[\text{L}(\text{R})\text{Si}]_2$ (Chart 2.5, left), constitutes a vacant p-orbital for ligand coordination, a long singly-bonded Si–Si and a stereoactive electron pair located at each of the silicon center. From another standpoint, these species can be regarded as two equivalents of silicon(I) radicals $[\text{L}(\text{R})\text{Si}:\cdot]$, arise from the homoleptic splitting of the Si–Si single bond (Chart 2.5, center). The resultant fleeting intermediate contains an electron pair, an unoccupied p-orbital and a radical at the silicon atom, is unprecedented and extremely unstable. When one or more sterically hindered donor ligands

are employed, the silicon(I) radical would assume a new structure, a separated ion pair silicon(I) radical $[(L)Si:\bullet]^+[R]^-$ (Chart 2.5, right).^[1,14] Lastly, $H^\bullet$ abstraction would effect in the formation of a new silyliumylidene separated ion pair (Chart 2.6), which our group has demonstrated in a similar reaction via a transient amidinato-stabilized silylene radical intermediate.^[10i] Conversely, silyliumylidene ion could displace its $H^\bullet$ to furnish a cationic silicon(I) radical. Since silyl radicals are extremely reactive species,^[14] the cationic silicon(I) radical remained obscure.

Chart 2. 6 Correlation between silicon(I) radical cation and silyliumylidene ion.

We envisioned that silyliumylidene could be a befitting catalyst candidate since its oxidation will generate the extremely unstable silylium cation intermediate, in turn favor the subsequent elimination reaction. Such process is reminiscent of oxidative addition/reductive elimination in typical catalytic cycle mediated by transition metals. In contrast, oxidation of silylene only leads to the highly stable form silane, hence elimination reaction is not plausible. As described in Chapter 1, we discussed the multi-reactive site of a silicon(I) dimer $[I_{Ar}(I)Si:]_2$, which includes bearing a long cleavable Si–Si linkage, in addition to displaceable ligands and halides. Herein, in this chapter, we will introduce a synthetic protocol presenting homonuclear cleavage of $[I_{Ar}(I)Si:]_2$ using a less steric I_{Me} ($I_{Me} = :C\{N(Me)C(Me)\}_2$), inducing ligand and halide displacement to generate a transient silicon(I) radical cation intermediate (Chart 2.5), which then abstract a $H^\bullet$ from solvent to generate the first NHC-stabilized parent silyliumylidene (Chart 2.6). Likewise, to confirm the correlation shown in Chart 2.6, an opposite reaction of a transient silyliumylidene to displace $H^\bullet$ will be unveiled using a similar model. After which, the catalytic potential of a silyliumylidene in various transition metal-free chemo- and regioselective catalyses will be outlined in Chapter 3.

2.2 Results and Discussion

2.2.1 Synthesis of a Parent NHC–Silyliumylidene Cation (2.20)

We investigated the cleavage of the Si–Si bond in a silicon(I) dimer with NHCs to generate an NHC–silicon(I) radical intermediate, which then rearranges to form an NHC–parent silyliumylidene cation complex. After *numerous attempts*,^[15] the reaction of the NHC–iodosilicon(I) dimer $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$ (**1.13-I**)^[16] with four equivalents of I_{Me} in toluene afforded the first NHC–parent silyliumylidene iodide $[(\text{I}_{\text{Me}})_2\text{SiH}]^+\text{I}^-$ (**2.20**, Scheme 2.1). It is proposed that the I_{Me} ligands displace the I_{Ar} ligands and iodide ions in $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$, along with homoleptic cleavage of the Si–Si bond, to afford the separated ion pair with a cationic NHC–silicon(I) radical intermediate $[(\text{I}_{\text{Me}})_2\text{Si:}\cdot]^+\text{I}^-$ (**2.20a**), which then abstracts a $\text{H}\cdot$ radical from toluene to form compound **2.20** (Scheme 2.1). The reaction of $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$ and I_{Me} was also performed in d_8 -toluene to afford the deuterated derivative $[(\text{I}_{\text{Me}})_2\text{Si-D}]^+\text{I}^-$ (**[SiD]-2.20**), which confirms that toluene is the $\text{H}\cdot$ source (see Section 2.5.1, Figure S2.4b)

Scheme 2. 1 Syntheses of compounds **2.20** and **2.21**. The proposed mechanism for the formation of **2.20** through the silicon(I) radical intermediate **2.20a** is also shown.

Orange crystals of compound **2.20** were isolated from a concentrated solution in fluorobenzene after two hours (see below). They are quite stable under an inert atmosphere for two months, but they are highly unstable in solution. They instantaneously decompose in THF and CHCl_3 and slowly decompose in fluorobenzene and pyridine over three days. The ^1H NMR spectrum shows one set of resonances that is due to the I_{Me} ligands and another one arising from the Si-H proton ($\delta = 9.73$ ppm). The latter is downfield-shifted in comparison with that in the NHC-hydridosilylene complexes $[\text{I}_{\text{Me}}-\text{SiH}(\text{Si}t\text{Bu}_3)]$ ($\delta = 3.17$ ppm) and $[\text{I}_{\text{Me}}-\text{SiH}(\text{Ter})]$ ($\text{Ter} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$, $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $\delta = 4.00$ ppm) owing to the presence of an electron-withdrawing cationic Si^{II} center.^[17] The ^{29}Si NMR signal of compound **2.20** ($\delta = -77.9$ ppm, $J_{\text{Si-H}} = 283$ Hz) is an intermediate value between that of the NHC-iodosilyliumylidene iodide **2.14** ($\delta = 55.3$ ppm, Chart 2.4)^[10f] and $[\text{I}_{\text{Me}}-\text{SiH}(\text{Si}t\text{Bu}_3)]$ ($\delta = -137.8$ ppm).^[17b] The Si-H chemical shift is further evidenced by its disappearance when compound **2.20** reacted with MeOH in C_6D_6 to afford a mixture of hydrogen gas, $\text{Si}(\text{OMe})_4$, and I_{Me} -containing compounds (Scheme 2.1 and Figure S2.7).

Figure 2. 1 X-ray crystal structure of **2.20** (30% ellipsoids probability). Hydrogen atoms except the H1 atom are omitted for clarity. The calculated geometrical parameters at the BP86/def2-SVP level of theory are given in square brackets. Selected bond lengths (Å) and angles (°): Si1-H1 1.455 [1.529], Si1-C1 1.932(3) [1.977], Si1-C8 1.931(3) [1.949]; C1-Si1-C8 96.63(12) [100.7], C1-Si1-H1 100.07 [96.0], C8-Si1-H1 95.49 [94.6].

The X-ray crystal structure of compound **2.20** shows a separated ion pair with a Si...I distance (10.013 Å) that is longer than the sum of their van der Waals radii (ca. 4.08 Å; Figure 2.1). The Si atom adopts a trigonal-pyramidal geometry. The sum of the bond angles at the Si atom (292.19°) indicates the presence of a stereoactive lone pair at the silicon atom. The Si–C bond lengths of 1.932(3) and 1.931(3) Å are intermediate values between those in the NHC–iodosilyliumylidene iodide **2.14** (1.947(2), 1.967(2) Å) and the NHC–silicon(II) dication [(I_{Me})₃Si]²⁺ (1.917(3) – 1.909(3) Å).^[17a] The hydrogen atom bound to the Si1 atom was located in the electron difference map and refined isotropically to the expected Si–H bond length of 1.455 Å.^[18]

The bonding analysis of **2.20** shows that its HOMO is a lone-pair orbital on the Si atom with 58.6% s-character (Figure S2.17). The EDA-NOCV analysis suggests that the best bonding description is the donor-acceptor interaction between the Si⁺(H) and two I_{Me} moieties. The Si–C_{NHC} bonds have almost equal contribution from covalent (ΔE_{orb} = 51.7%) and electrostatic interaction. The energy for the donor-acceptor interaction between two I_{Me} ligands and Si⁺(H) fragment is -185.2 kcal/mol.

Thus, on the basis of the experimental and theoretical results, compound **2.20** is a separated ion pair of the NHC–parent silyliumylidene complex, which has one lone-pair orbital on the Si atom and two donor–acceptor σ-bonds between the Si⁺(H) and two I_{Me} moieties.

When the recrystallization of compound **2.20** in fluorobenzene was prolonged, orange crystals of compound **2.20** cannot be isolated. Instead [I_{Me}–H]⁺I[–] (Figure S2.13) and yellow crystals of [1-F-2-I_{Me}–C₆H₄]⁺I[–] (**2.21**, Scheme 2.1, Figure S2.12) were obtained. These results show that compound **2.20** further reacts with fluorobenzene. As such, the reaction of the NHC–iodosilicon(I) dimer [I_{Ar}(I)Si:]₂ and I_{Me} was performed in fluorobenzene, which directly afforded a mixture of [I_{Me}–H]⁺I[–] and **2.21** (Scheme 2.1). Although the mechanism for the formation of compound **2.21** is unknown as yet, the reaction appears to proceed through an electrophilic aromatic substitution at the *ortho* position of fluorobenzene with compound **2.20** (Scheme 2.2).

Scheme 2. 2 Proposed mechanism for the formation of compound **2.21**.

In support of the feasibility of the intermediate **2.20a** and its high reactivity to abstract a $\text{H}^\bullet$ radical from toluene to form **2.20** using deuterium-labelling experiment (Figure S2.4b), DFT calculations of **2.20a** were performed (Figure 2.2, Figure S2.15). The DFT calculations indicate that the SOMO of **2.20a** is a majorly π -type p-orbital localized on the Si-center and the contribution from the C–N π^* -MO of I_{Me} (Figure 2.2). Accordingly, the group charge analysis indicates a low positive charge on the Si center (0.42 e) in **2.20a**. Moreover, the C–N bond lengths in **2.20a** (average 1.372 Å) is almost the same as that in un-coordinated I_{Me} (1.376 Å). The HOMO-1 is a lone pair orbital on the Si-center (Figure 2.2b, % of α and β -type s-orbital = 79.2 and 75.9). The localization of the unpaired electron on the Si-center (0.72 e) is also indicated by the natural spin density plot (Figure 2.2c).

The EDA-NOCV analysis performed on **2.20a** suggests that the best bonding pattern is the donor-acceptor interaction between the $[\text{:Si}^\bullet]^+$ (^2P ; $3s^23p_x^03p_y^03p_z^1$) and two I_{Me} moieties (Table S2.5). The Si–C_{NHC} bonds have almost equal contribution from the covalent interaction ($\Delta E_{\text{orb}} = 52.4\%$) and the electrostatic interaction. The major contribution to the covalent interaction is the σ -donation from I_{Me} ligands to the $[\text{:Si}^\bullet]^+$ centre (Figure S2.18, Scheme S2.1; $\Delta E_{\sigma(++)} + \Delta E_{\sigma(+-)} = -195.6$ kcal/mol). The energy corresponds to the π -back donation from the unpaired electron present in the π -type p-orbital on the $[\text{:Si}^\bullet]^+$ centre to one of the C–N π^* -MO of I_{Me} in **2.20a** was found to be at $\Delta E_{\pi} = -28.1$ kcal/mol. The bonding in **2.20a** comprises

two donor-acceptor σ -bonds with two I_{Me} ligands, $\text{C}_{\text{NHC}} \rightarrow [\text{:Si}^\bullet]^+ \leftarrow \text{C}_{\text{NHC}}$. This retains one singly occupied π -type p-orbital and one σ -type lone pair on the Si-centre. The poor back donation from the π -type p-orbital on the Si-atom to the C–N π^* -MO of I_{Me} might be responsible for its high reactivity towards abstraction of a $\text{H}^\bullet$ radical from the solvent to form **2.20**.

Figure 2. 2 Plot of a) singly occupied molecular orbital (SOMO), b) lone pair on Si (HOMO-1) (isosurface value 0.03) and c) spin density calculated by natural population analysis (isosurface value 0.008) of **2.20a** at the M06/def2-TZVPP//BP86/def2-SVP level of theory. Eigen values in eV are given in parentheses.

The formation of compound **2.20** summarises the cleavage of the Si–Si bond in a silicon(I) dimer with NHCs to generate an unstable NHC–silicon(I) radical cation intermediate $\{\text{:Si}^\bullet\}^+$, which then abstracts a $\text{H}^\bullet$ radical from solvent to form a stable NHC–parent silyliumylidene cation complex comprising of a $\{\text{:SiH}\}^+$ fragment. This encounter inspired us towards an opposite idea, namely if there is an unstable NHC–parent silyliumylidene intermediate “ $\{\text{:SiH}\}^+$ ” that displaces a $\text{H}^\bullet$ radical with ethereal solvents to form a stable NHC–silicon(I) radical cation $\{\text{:Si}^\bullet\}^+$. As such, the feasibility of a base-stabilized cAAC–silicon(I) radical cation (cAAC = cyclic (alkyl)(amino) carbene) and its reactivity toward solvents were studied.^[19]

Scheme 2. 3 Synthesis of **2.22**.

The reaction of the cAAC [cAAC_{Me}]^[20] with H₂SiI₂ in a 2:1 molar ratio in THF initially gave a purple mixture, which then turned into a white suspension within a few minutes. This observation prompted us to employ a higher 3:1 molar ratio of cAAC_{Me}/H₂SiI₂ in the reaction in THF, which afforded a sustainable dark purple-red suspension, and then a colorless crystalline solid of [cAAC_{Me}-H]⁺I⁻ (Figure S2.14) was gradually formed. After filtration of [cAAC_{Me}-H]⁺I⁻, the separated ion pair [(cAAC_{Me})₂Si•]⁺I⁻ (**2.22**) featuring a cationic cAAC–silicon(I) radical complex was isolated as purple crystals in 5 % yield (Scheme 2.3).^[20] In addition, the 2,3-disiladiiodobutadiene derivative [cAAC_{Me}=Si(I)]₂ was not observed in this reaction.^[22] In the second experiment, when the solvent was changed to Et₂O, the reaction of cAAC_{Me} and H₂SiI₂ in a 3:1 molar ratio afforded a mixture of crystals of **2.22** (a few pieces of crystals), [cAAC_{Me}-H]⁺I⁻ (major product), and [cAAC_{Me}=Si(I)]₂ (major product, 22 % yield).^[22] These results show that **2.22** is formed in Et₂O, but is unstable and dimerizes to form [cAAC_{Me}=Si(I)]₂.^[22] In the third experiment, when toluene was used as the solvent for the reaction of cAAC_{Me} and H₂SiI₂ in a 3:1 molar ratio, **2.22** was not afforded; instead a mixture of the cAAC-silicon(0) complex [(cAAC_{Me})₂Si] (32 % yield) and [cAAC_{Me}-H]⁺I⁻ as the sole products was afforded.^[20] In the last experiment, cAAC_{Me} was reacted with H₂SiI₂ in a 3:1 molar ratio in dimethoxyethane (DME) to afford **2.22** in high yield (62%). Similarly, [cAAC_{Me}=Si(I)]₂ was not observed.^[22] Using a higher 4:1 molar ratio of cAAC_{Me} and H₂SiI₂ in

DME did not improve the yield of **2.22**. These results illustrate that compound **2.22** cannot be formed in non-ethereal solvents because cAAC_{Me} undergoes a double dehydroiodination.

The following mechanism for the formation of stable and isolable **2.22** is proposed (Scheme 2.4). Two molecules of cAAC_{Me} simultaneously undergo dehydroiodination and coordination with H₂SiI₂ to form [cAAC_{Me}-H]⁺I⁻ and a cAAC-iodosilylene intermediate, “(cAAC_{Me})Si(I)H”. Subsequently, the latter reacts with another molecule of cAAC_{Me}, along with displacement of the I⁻ anion, to form a cAAC-parent-silyliumylidene iodide intermediate, “{(cAAC_{Me})₂SiH}⁺I⁻”. This intermediate displaces a H[•] radical by reacting with ethereal solvents to form **2.22**, in which the resulting Si^I radical is stabilized by one cAAC_{Me} ligand (see below).^[23] On the basis of the experimental results, the displacement of a H[•] radical is favored in DME as DME is able to undergo radical reactions via homoleptic cleavage of the central C-C bond in CH₃OCH₂-CH₂OCH₃.^[24] This mechanism is further supported by the following facts: 1) The yield did not improve when cAAC_{Me} and H₂SiI₂ were reacted in a 4:1 molar ratio, indicating that cAAC_{Me} cannot abstract a H[•] radical from the {(cAAC_{Me})₂SiH}⁺I⁻ intermediate. 2) H₂ gas was not observed in the abovementioned reactions. 3) Results derived from the formation and reactivity of compound **2.20** (see above).

Scheme 2. 4 Proposed mechanism of **2.22**.

Compound **2.22** is the first example of a separated ion pair of a base-stabilized silicon(I) radical, following a previous report on the only example of a neutral germanium(I) radical, $[\text{HC}\{\text{C}(t\text{Bu})\text{N}(\text{Ar})\}_2\text{Ge:}]^\cdot$.^[25] Purple crystals of complex **2.22** are air- and moisture-sensitive but stable under an inert atmosphere for one month. They are soluble in THF and DME, but only marginally soluble in toluene.

Figure 2. 3 Molecular structure of **2.22**. Ellipsoids set at 30 % probability. Solvent molecule and hydrogen atoms are omitted for clarity. The calculated geometrical parameters at the BP86/def2-SVP level of theory are given in square brackets. Selected bond lengths [Å] and angles [°]: C1–N1 1.319(4) [1.345], C1–Si1 1.896(4) [1.945], C21–N2 1.332(4) [1.352], C21–Si1 1.867(3) [1.930]; N1–C1–C2 109.9(3) [109.0], C2–C1–Si1 134.0(2) [130.6], N1–C1–Si1 115.9(3) [115.6], N2–C21–C22 109.1(3) [108.9], C22–C21–Si1 127.0(2) [136.9], N2–C21–Si1 120.5(3) [113.9], C1–Si1–C21 122.96(15) [115.4].

The X-ray crystal structure of **2.22** (Figure 2.3) shows that the Si1 atom adopts a bent geometry, and is coordinated to the C1 and C21 atoms of cAAC_{Me}. The Si1 atom lies on the same plane as the N1-C1-C2 skeleton while it is displaced from the N2-C21-C22 least-squares plane by 0.564 Å. The cAAC_{Me} rings are tilted with respect to each other (C1-N1-C21-N2=133.37°). The C1-Si1-C21 bond angle (122.96(15)°) is significantly wider than that of the cAAC–silicon(0) complex [(cAAC_{Me})₂Si] (117.70(8)°).^[19] The two C–Si1 bonds do not have the same lengths (C1–Si1 1.896(4) Å, C21–Si1 1.867(3) Å) but both are slightly longer than the donor–acceptor Si–C double bonds in [(cAAC_{Me})₂Si] (1.8411(18), 1.8417(17) Å).^[20] They are comparable to the donor–acceptor Si–C_{cAAC} single bond in the NHC–cAAC–iodosilyliumylidene iodide [cAAC_{Me}(SiI)I_{PrMe}]⁺I[–] (I_{PrMe} = :C{N(*i*Pr)CMe}₂, 1.878(5) Å).^[10e] Simultaneously, the C1–N1 (1.319(4) Å) and C21–N2 bonds (1.332(4) Å) are shorter than those of the C_{cAAC}-centered radical [cAAC_{Me}[•]–Si(Cl)₂–cAAC_{Me}[•]] (1.395(2)–1.3994(19) Å)^[26] and the cAAC–silicon(0) complex [(cAAC_{Me})₂Si] (1.378(2) Å).^[20]

Figure 2. 4 CW EPR (X-band) spectra of **2.22** in toluene/THF solution recorded at a) 298 K and b) 115 K. The corresponding simulations are shown in a' and b'.

Table 2. 1 Spin Hamiltonian parameters for compound **2.22**.

<i>g</i>_{iso}			
Expt		2.0037	
DFT^a		2.0078	
<i>a</i>_{iso}/ MHz	¹⁴ N1	¹⁴ N2	²⁹ Si
Expt^b	-	10.67	212.00
DFT	5.52	11.32	102.00

^a ±0.0001, ^b ± 5 MHz

A purple solution of **2.22** in 1:1 toluene/THF solvent was characterized by continuous wave (CW) EPR spectroscopy. The 298 K EPR spectrum (Figure 2.4a) shows a three-line hyperfine multiplet pattern with $a(^{14}\text{N})_{\text{iso}}=18.5$ MHz, suggestive of about 1 % s-orbital electron spin density localized on a single ^{14}N nucleus. This characteristic splitting pattern suggests that the radical delocalizes to one of the cAAC ligands only, which is consistent with the calculated spin densities of **2.22** (see below). In addition, the 115 K EPR spectrum (Figure 2.4b) shows an intense signal at $B \approx 336$ mT, which has some evidence for a small degree of anisotropy. Although the ^{14}N hyperfine coupling is only poorly resolved in the frozen-solution spectrum, a pair of weak satellite features can be observed with $a(^{29}\text{Si}) \approx 212$ MHz, which likely arises from coupling to the low-abundant nuclear-spin-active ^{29}Si nuclei, consistent with about 5 % s-orbital electron spin density localized on the silicon nucleus. The experimental spin-Hamiltonian parameters for **2.22** are listed in Table 2.1, and are in good agreement with DFT-calculated hyperfine coupling values based on the crystal structure, performed in ORCA 3.0.3^[27] using the hybrid PBE0 functional and a basis set consisting of EPR-II on C, H, and N^[28] and def2-TZVP on Si.^[29] The deviation of the ^{29}Si EPR data arises from some disorder in the frozen solution, which is not reflected in the crystal structure from which the DFT output was calculated. In this context, the EPR spectroscopic data suggest that **2.22** is a separated ion pair of a base-stabilized silicon(I) radical complex with the unpaired electron localized in a p-orbital on the Si atom.

Figure 2. 5 Plots of a) the SOMO, b) the lone pair on the Si atom (HOMO-1; isosurface value 0.03), and c) the spin density calculated by natural population analysis (isosurface value 0.008) of **2.22** at the M06/def2-TZVPP//BP86/def2-SVP level of theory. Eigenvalues in eV are given in parentheses.

In support of the experimental observations, DFT calculations of **2.22** were performed at the M06/def2-TZVPP//BP86/def2-SVP level of theory (Figure S2.15). The MO analysis indicates that the SOMO is mainly a π -type p-orbital localized on the Si atom with little back-donation to the C–N π^* -MO of one of the cAAC_{Me} fragments (Figure 2.5a). In addition, the orientations of the two cAAC_{Me} rings prevent simultaneous back-donation of the unpaired electron on the Si atom into two C–N π^* -MOs of the cAAC_{Me} ligands. Accordingly, in the calculations, one cAAC_{Me} ligand has a longer C21–N2 bond (1.352 Å) and a shorter C21–Si1 bond (1.930 Å) than the other cAAC_{Me} ligand (calculated C1–N1 1.345 Å, C1–Si1 1.945 Å). In addition, the EDA-NOCV analysis (Table S2.5 and Figure S2.19) shows that the energy corresponding to the π -back donation from the unpaired electron on the $[\text{Si}^\bullet]^+$ moiety to one C–N π^* -MO in $[(\text{cAAC}_{\text{Me}})_2\text{Si}]^+\text{I}^-$ **2.22** ($\Delta E_\pi = -38.1$ kcal/mol) is more than that in I_{Me} ($\Delta E_\pi = -28.1$ kcal/mol). Accordingly, the group charge analysis indicates a higher positive charge on the Si atom (0.83 e) in **2.22** than that in **2.20a** (0.43 e). This corroborates well with the poor π -acidity of I_{Me} as compared to cAAC.^[16,30] This back-donation is also consistent with the lower occupancy of the π -type p-orbital on the Si atom (0.67 e, Table S3). The HOMO-1 is a σ -type lone-pair orbital (Figure 2.5b) on the Si atom with greater s-character (α - and β -type s-orbitals from NBO analysis: 77.3 and 73.2 %) is similar to **2.20a**. In this context, these results indicate that the unpaired electron in **2.22** (0.52 e; Figure 2.5 and Table S2.4) is less active than that in **2.20a** (0.74 e; Figure 2.2 and Table S2.4), which accounts for the instability of **2.20a** and the abstraction of a H $^\bullet$ radical from toluene to form **2.20**.

The plot of the natural spin density also corroborates well with the MO and geometrical data that the unpaired electron is mainly localized on the Si atom (0.52 e) with a little delocalization to one of the cAAC_{Me} ligands (Figure 2.5c and Table S2.4). This is in line with the EPR spectroscopic data.

The nature of the bonding interaction between the $[\text{Si}]^+$ ($^2\text{P}; 3s^2 3p_x^0 3p_y^0 3p_z^1$) and cAAC_{Me} fragments in **2.22** was further analyzed by the EDA-NOCV approach (Table S2.5). In the $\text{Si}-\text{C}_{\text{cAAC}_{\text{Me}}}$ bonds, the covalent interaction ($\Delta E_{\text{orb}}=55.8\%$) has a higher energy contribution than the electrostatic interaction, in which the energy corresponding to σ -donation from the cAAC_{Me} ligands to the $[\text{Si}]^+$ center (Figure S2.19 and Scheme S2.2; $\Delta E_{\sigma(++)} + \Delta E_{\sigma(+-)} = -221.6$ kcal/mol) is significantly higher than that of the π -back-donation from the unpaired electron in the π -type p-orbital on the $[\text{Si}]^+$ center to one of the C–N π^* -MOs of the cAAC_{Me} ligands ($\Delta E_{\pi} = -38.1$ kcal/mol).

Thus, on the basis of these experimental and theoretical results, compound **2.22** is a separated ion pair featuring a cationic cAAC -silicon(I) radical complex with two donor–acceptor σ -bonds between the $[\text{Si}]^+$ ($^2\text{P}; 3s^2 3p_x^0 3p_y^0 3p_z^1$) and cAAC_{Me} moieties, one σ -type lone-pair orbital, and one unpaired electron on the p-type orbital on the Si center.

The mechanism for the formation of **2.22** was also studied. It is proposed that the cAAC –parent-silyliumylidene intermediate “ $\{(\text{cAAC}_{\text{Me}})_2\text{SiH}\}^+\text{I}^-$ ” is the key intermediate in the reaction of cAAC_{Me} and H_2SiI_2 , which displaces a $\text{H}^\bullet$ radical with ethereal solvents to form **2.22**. Thus, the formation of **2.22** supports our hypothesis for the reaction of $[\text{I}_{\text{Ar}}(\text{I})\text{Si}:]_2$ with I_{Me} that the intermediate $\text{Si}^\bullet$ can react with toluene to form **2.20**.

2.3 Conclusion

The first NHC–parent silyliumylidene iodide $[(\text{I}_{\text{Me}})_2\text{SiH}]^+\text{I}^-$ (**2.20**) has been prepared by a simple procedure, with the treatment of $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$ (**1.13-I**) with four equivalents of I_{Me} . The transient intermediate silicon(I) radical ion $[(\text{I}_{\text{Me}})_2\text{Si}:\bullet]^+\text{I}^-$ (**2.20a**) has a lone pair of electrons and a radical on the silicon centre. From a computation standpoint, the radical is highly unstable. Therefore, it undergoes $\text{H}^\bullet$ radical abstraction from the solvent to form compound **2.20**. Notably, complex **2.20** exhibit transition-metal-like reactivity in functionalizing the ortho- $\text{C}_{\text{Ar}}\text{--H}$ bond of fluorobenzene, leading to C–C bond formation of $[\text{1-F-2-I}_{\text{Me}}\text{--C}_6\text{H}_4]^+\text{I}^-$ (**2.21**). The feasibility of the $[(\text{I}_{\text{Me}})_2\text{SiH}]^+\text{I}^-$ intermediate is supported by the isolation of the first separated ion pair of cAAC-silicon(I) radical $[(\text{cAAC}_{\text{Me}})_2\text{Si}:\bullet]^+\text{I}^-$ (**2.22**). The reactivity of compound **2.20** toward solvents evidence our hypothesis that the reactive Si–H bond in the intermediate “ $\{(\text{cAAC}_{\text{Me}})_2\text{SiH}\}^+\text{I}^-$ ” can react with DME to form the stable compound $[(\text{cAAC}_{\text{Me}})_2\text{Si}:\bullet]^+\text{I}^-$ (**2.22**).

2.4 Experimental

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. THF and toluene were dried over and distilled from Na/K alloy prior to use. Fluorobenzene was dried over and distilled from CaH₂ prior to use. H₂SiI₂ was purchased from Sigma Aldrich and used directly. I_{Ar}SiI₄,^[10f] I_{Me} (:C{N(Me)CMe}₂)^[31] and cAAC_{Me}^[32] were prepared according to the literature procedures. [I_{Ar}(I)Si:]₂ was prepared by a new method, which is different from literature procedures (See Chapter 1, Section 1.4.1).^[16] *d*-Chloroform, *d*₆-benzene, *d*₅-pyridine and *d*₈-toluene were dried and distilled over K metal prior to use. The NMR spectra were recorded on a JEOL ECA 400 spectrometer and Bruker 400 spectrometer. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected. IR spectra were recorded on a Bruker Tensor 27 instrument at room temperature. EPR spectra were recorded at 298 K on an X-band *Bruker EMX* spectrometer operating at 100 kHz field modulation, 10 mW microwave power and fitted with a high sensitivity cavity (ER 4119HS). The *g* values were determined using a DPPH standard, and are accurate to ±0.0001. EPR computer simulations were performed using the Easyspin^[33] toolbox for Matlab.

2.4.1 Synthesis of a Parent NHC–Silyliumylidene Cation (**2.20**) and cAAC-Silicon(I) Cation (**2.22**)

Syntheses of 2.20. Toluene (30 mL) was added to a mixture of $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$ (0.31 g, 0.29 mmol) and I_{Me} (0.15 g, 1.2 mmol) at room temperature. The red solution was stirred at room temperature for 12 hours. An orange-red precipitate was formed and filtered, which was then washed with hot toluene at 60 °C (2 x 20 mL) and dried under vacuum. Orange powder of **2.20** was afforded. X-ray quality crystals of **2.20** were isolated from its concentrated fluorobenzene at room temperature within 2 hours. The mother liquor must then be immediately filtered and orange crystals of **2.20** were dried completely under vacuum. Yield: 0.41 g (72%, based on $[\text{I}_{\text{Ar}}(\text{I})\text{Si}]_2$). Mp: 189 °C (dec.). Elemental analysis calcd for $\text{C}_{14}\text{H}_{25}\text{N}_4\text{SiI}$: C, 41.58; H, 6.23; N, 13.86. Anal. Found: C, 41.01; H, 6.80; N, 13.25. ^1H NMR (395.9 MHz, 25 °C, d_5 -pyridine, ppm): δ = 1.93 (s, 12H, $\text{N}(\text{CH}_3)$), 3.71 (s, 12H, $\text{C}(\text{CH}_3)$), 9.73 (s, 1H, Si-H). ^{29}Si NMR (160.5 MHz, 25 °C, d_5 -pyridine, ppm): δ = -77.9 ($^1J_{\text{SiH}}$ = 283 Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (160.5 MHz, 25 °C, d_5 -pyridine, ppm): δ = -77.5. UV/vis (fluorobenzene): $\lambda_{\text{max}}(\epsilon)$ = 480 ($2.1 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$), 370 ($1.7 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$), 283 ($4.5 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$) nm. IR (Nujol/ cm^{-1}): 2680, 2610, 1910(w), 1643, 1577, 1261(s), 1099(s), 1019(s), 864, 800(s), 720, 688, 497(s).

Syntheses of 2.21. When the recrystallization of compound **2.20** in fluorobenzene was prolonged, $[\text{I}_{\text{Me}}-\text{H}]^+\text{I}^-$ and yellow crystals of $[\text{1-F-2-I}_{\text{Me}}-\text{C}_6\text{H}_4]^+\text{I}^-$ (**2.21**) were afforded. For **2.21**: ^1H NMR (500 MHz, 25 °C, d_5 -pyridine, ppm): δ = 7.36 – 7.34 (m, 2H, Ar-H, overlapped with I_{Ar}), 7.26 (t, $^1J_{\text{HH}}$ = 7.5 Hz, 1H, Ar-H), 7.16 (t, $^1J_{\text{HH}}$ = 6.9 Hz, 1H, Ar-H), 3.84 (s, 6H, NMe), 2.14 (s, 6H, CMe). ^1H NMR (400 MHz, 25 °C, CDCl_3 , ppm): δ = 8.25 (m, 1H, ArH), 7.98 (m, 1H, ArH), 7.45 (m, 1H, ArH), 7.15 (m, 1H, ArH), 4.10 (s, 3H, CMe), 4.03 (s, 3H, NMe), 2.43 (s, 3H, CMe), 2.36 (s, 3H, CMe). ^{19}F NMR (79 MHz, 25 °C, CDCl_3 , ppm): δ = -49. The structure of $[\text{I}_{\text{Me}}-\text{H}]^+\text{I}^-$ was confirmed by X-ray crystallography (see Figure S2.13).

Alternate synthesis of 2.21. Fluorobenzene (30 mL) was added to a mixture of $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$ (0.31 g, 0.29 mmol) and I_{Me} (0.15 g, 1.22 mmol) at room temperature. The resulting red solution was stirred at room temperature for 12 hours. Orange-red precipitate of **2.20** was formed and collected by filtration. Yield: 0.38 g (67%, based on $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$). The orange filtrate was then concentrated to afford a mixture of yellow crystals of **2.21** and colorless crystals of $[\text{I}_{\text{Me}}\text{-H}]^+\text{I}^-$.

Study of reactivity of 2.20 with fluorobenzene

In a 100 mL Schlenk flask, fluorobenzene (20 mL) was added to an orange powder of **2.20** (0.2 g, 0.5 mmol) at room temperature. The reaction suspension was stirred at room temperature for 24 hours to afford a mixture of yellow powder of **2.20**, colorless crystals of $[\text{I}_{\text{Me}}\text{-H}]^+\text{I}^-$ and a small amount of unknown white solid. The first two compounds were characterized by ^1H NMR spectroscopy, which shows the same spectroscopic data as mentioned above. The white solid is highly insoluble in any polar or nonpolar solvents, such as THF, toluene, PhF, CH_2Cl_2 and pyridine. The ^{29}Si NMR spectrum of the mother liquor does not show any signal (Figure S2.1). This implies that the white solid may be some unidentified Si-containing complexes.

Figure S2. 1 The ^{29}Si NMR spectrum of the mother liquor showing the absence of Si-containing by-product.

Synthesis of $[(\text{I}_{\text{Me}})_2\text{Si}(\text{D})]^+\text{I}^-$ ($[\text{SiD}]\text{-2.20}$). d_8 -toluene (10 mL) was added to a mixture of $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$ (0.10 g, 0.1 mmol) and I_{Me} (0.05 g, 0.4 mmol) at room temperature. The red solution was stirred at room temperature for 12 hours. An orange precipitate was formed and filtered, which was then washed with hot d_8 -toluene (50 °C, 2 x 5 mL) to remove the I_{Ar} and dried under vacuum. Orange powder of **2.20(Si-D)** was afforded. Yield: 0.12 g (71%, based on $[\text{I}_{\text{Ar}}(\text{I})\text{Si:}]_2$). ^1H NMR (395.9 MHz, 25 °C, d_5 -pyridine, ppm): δ = 1.93 (s, 12H, $\text{N}(\text{CH}_3)$), 3.71 (s, 12H, $\text{C}(\text{CH}_3)$). No Si-H signal at 9.73 ppm is observed. ^{29}Si NMR (160.5 MHz, 25 °C, d_5 -pyridine, ppm): δ = -77.3 (s). No Si-H coupling is observed.

Reaction of 2.20 with MeOH. In a J-Young NMR tube, absolute MeOH (3 mg, 0.10 mmol) was added dropwise via a micro-syringe to the C₆D₆ suspension of **2.20** (40 mg, 0.10 mmol). A gas evolution was observed and slight yellow solution was afforded in 10 minutes. The ¹H NMR spectrum (Figure S2.7) of the reaction mixture shows a singlet at $\delta = 4.47$ ppm attributable to H₂ gas, along with a mess of singlets corresponding to unknown I_{Me}-containing compounds. The ²⁹Si NMR spectrum (Figure S2.8) shows a singlet at -78 ppm for Si(OMe)₄, which is identical to the reported data.^[34]

Synthesis of 2.22. H₂SiI₂ (0.28 g, 1.00 mmol) was added rapidly to a THF solution of cAAC_{Me} (1.32 g, 3.00 mmol) at room temperature. A purple-red suspension was afforded immediately, along with the formation of a colorless crystalline solid. The reaction mixture was stirred for 1 hour and dried under vacuum to remove all volatiles. The residue was extracted with 10 mL of fluorobenzene. The insoluble colorless crystalline solid (see below) was filtered and the filtrate was concentrated to afford purple-red crystals of **2.22** at 0 °C. Yield: 0.036 g (5% based on H₂SiI₂). Mp: 176 °C. Elemental analysis calcd for C₄₀H₆₂SiN₂I: C, 66.18; H, 8.61; N, 3.86. Anal. Found: C, 65.89; H, 8.11; N, 3.09. UV/vis (THF): $\lambda_{\text{max}}(\epsilon) = 497 (1.9 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1})$, 358 ($0.12 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$) nm. The mother liquor was filtered and its further concentration did not yield any crystals of **2.22**. The mass spectrum of the mother liquid shows the formation of a THF-based ring-opening polymerization product (Figure S2.2).

Figure S2. 2 The mass spectrum of the mother liquid showing the formation of a THF-based ring-opening polymerization product.

The insoluble colorless crystalline solid is $[\text{cAAC}_{\text{Me}}\text{-H}]^+\text{I}^-$ salt, which is confirmed by ^1H NMR and X-ray crystallography (Figure S2.14). ^1H NMR data for $[\text{cAAC}_{\text{Me}}\text{-H}]^+\text{I}^-$ (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz, ppm): δ 10.89 (s, 1H, $\text{C}_{\text{carbene}}\text{-H}$), 7.52 (m, 3H, ArH), 7.35 (m, 2H, ArH), 2.65 (sept, 2H, CHMe_2 , $^3J_{\text{HH}} = 8$ Hz), 2.43 (s, 2H, $\text{-CH}_2\text{-}$), 1.84 (s, 6H, NCMe_2), 1.56 (s, 6H, CMe_2), 1.35 (d, 6H, CHMe_2 , $^3J_{\text{HH}} = 8$ Hz), 1.30 (d, 6H, CHMe_2 , $^3J_{\text{HH}} = 8$ Hz).

Alternative synthesis of 2.22: H_2SiI_2 (0.28 g, 1.00 mmol) was added rapidly to a DME solution of cAAC_{Me} (1.32 g, 3.00 mmol) at room temperature. A purple-red suspension was afforded immediately along with the formation of a colorless crystalline solid of $[\text{cAAC}_{\text{Me}}\text{-H}]^+\text{I}^-$. The reaction mixture was stirred for 1 hour at room temperature. The reaction mixture was then filtered. The filtrate was further concentrated to give purple-red crystals of **2.22**. Yield: 0.45 g (62% based on H_2SiI_2). The colorless crystalline solid of $[\text{cAAC}_{\text{Me}}\text{-H}]^+\text{I}^-$ was dried and weighed. Yield: 0.13 g (65%), which is in agreement with the yield calculated by the production of **2.22** (62%). The reaction mixture was also analyzed by LC-MS spectrometry to show a peak at m/z 47 corresponding to a $[\text{MeOMe}]^+$ fragment (Figure S2.3; THF as diluting solvent).

Figure S2. 3 LC-MS spectrum of the reaction mixture showing a peak at m/z 47 corresponding to a $[\text{MeOMe}]^+$ fragment.

Reaction of 2.22 with LiNiPr_2 : Toluene was added to a mixture of **2.22** (0.14 g, 0.20 mmol) and LiNiPr_2 (0.026 g, 0.25 mmol) at room temperature to afford a purple-blue suspension. The reaction mixture was stirred for 12 hours and dried under vacuum to get a blue solid of the cAAC-silicon(0) complex $[(\text{cAAC}_{\text{Me}})_2\text{Si}]$, which was confirmed by ^1H NMR spectroscopy and X-ray crystallography.^[20] Yield: 0.09 g (76%, based on **2.22**).

Study of the solvent influence in the reaction of cAAC_{Me} and H₂SiI₂:

(a) Toluene

H₂SiI₂ (0.28 g, 1.00 mmol) was added rapidly to a toluene solution of cAAC_{Me} (1.32 g, 3.00 mmol) at room temperature. A brown suspension was formed immediately. The reaction mixture was stirred for 4 h and then filtered. The color of the filtrate turned to intense blue in 24 hours. The solution was dried under vacuum and the residue was extracted with *n*-hexane. After filtration and concentration of the filtrate to give blue crystals of the cAAC-silicon(0) complex [(cAAC_{Me})₂Si], which is confirmed by the ¹H NMR spectrum and X-ray crystallography.^[20] Yield: 0.19 g (32%, based on H₂SiI₂).

(b) Et₂O

H₂SiI₂ (0.28 g, 1.00 mmol) was added rapidly to an Et₂O suspension of cAAC_{Me} (1.32 g, 3.00 mmol) at room temperature. A brown-red suspension was formed with deposition of a white powder of [cAAC_{Me}-H]⁺I⁻ and small pink crystalline solid of **2.22**. The reaction mixture was stirred for 4 hours and then filtered. The filtrate was concentrated under vacuum to 1/2 of its original volume to give orange crystals of the 2,3-disiladiiodobutadiene derivative [cAAC_{Me}=Si(I)]₂, which is confirmed by ¹H NMR spectroscopy and X-ray crystallography.^[10e] Yield: 0.097 g (22%, based on H₂SiI₂).

2.5 Appendices

2.5.1 NMR Spectra

#The singlet peak at 9.73 ppm corresponds to the proton of Si-H in compound **2.20**.

*No peak at 9.73 ppm is observed.

Figure S2. 4 (a) ^1H NMR spectrum of **2.20** (d_5 -pyridine)[#] and (b) ^1H NMR spectrum of [SiD]-**2.20** (d_5 -pyridine).

A Si–H coupling is observed.

*No Si–H coupling is observed.

Figure S2. 5 (a) ^{29}Si NMR spectrum of **2.20** (d_5 -pyridine) and (b) ^{29}Si NMR spectrum of [SiD]-**2.20** (d_5 -pyridine).

Figure S2. 6 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2.20** (d_5 -pyridine).

Figure S2. 7 ^1H NMR spectrum of the NMR-tube reaction of **2.20** and MeOH in C_6D_6 .

Figure S2. 8 ^{29}Si NMR spectrum of the NMR-tube reaction of **2.20** and MeOH in C_6D_6 .

Figure S2. 9 ^1H NMR spectrum of a mixture of **2.21** and $[\text{IMe-H}]^+\text{I}^-$ in the prolonged crystallization of compound **2.20** in fluorobenzene (d_5 -pyridine).

2.5.2 UV-Visible Spectrum of a Parent NHC–Silyliumylidene Cation (2.20) and cAAC-Silicon(I) Cation (2.22)

Figure S2. 10 UV-visible spectrum of **2.20** (fluorobenzene).

Figure S2. 11 UV-visible spectrum of **2.22** (THF).

2.5.3 Crystallographic Data of All Structures

The crystals of compounds **2.20** and **2.21** and **2.22**(C₆H₅F), were mounted onto quartz fibers. The X-ray diffraction intensity data were measured at 103 K with a Bruker APEX II diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073$ Å) for compound **2.20** and **2.22**, and Cu K α radiation ($\lambda = 1.541778$ Å) for compound **2.21**, with the SMART suite of programs.^[35] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.^[36] Structural solution and refinement were carried out with the SHELXTL suite of programs.^[37] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC-1537739 (**2.20**), CCDC-1537741 (**2.21**), CCDC-1537740 (**2.22**), CCDC-1537742 [cAAC_{Me}-H]⁺I⁻ and CCDC-1537743 [I_{Me}-H]⁺I⁻ contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Figure S2. 12 Molecular structure of **2.21** (30% ellipsoids probability). Hydrogen atoms are omitted for clarity.

Figure S2. 13 Molecular structure of $[\text{Ime-H}]^+\text{I}^-$ (30% ellipsoids probability). Solvent molecule and hydrogen atoms except $\text{C}_{\text{NHC}}\text{-H}$ are omitted for clarity.

Figure S2. 14 Molecular structure of $[\text{cAAC}_{\text{Me}}\text{-H}]^+\text{I}^-$ (30% ellipsoids probability). Hydrogen atoms except $\text{C}_{\text{Carbene}}\text{-H}$ are omitted for clarity.

Table S2. 1 Crystallographic data of compounds **2.20**, **2.21** and **2.22**(C₆H₅F).

	2.20	2.21	2.22 (C₆H₅F)
Formula	C ₁₄ H ₂₅ IN ₄ Si	C ₁₃ H ₁₆ FIN ₂	C ₄₆ H ₆₇ FIN ₂ Si
Fw	404.37	346.18	822.00
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P 1 21/c1</i>	<i>P 1 21/c1</i>	<i>P 1 21/c1</i>
<i>a</i> (Å)	11.7342(10)	11.8320(11)	15.8396(13)
<i>b</i> (Å)	11.7245(10)	14.5440(11)	17.4035(13)
<i>c</i> (Å)	13.2182(10)	8.4814(9)	16.2945(15)
<i>α</i> (deg)	90	90	90
<i>β</i> (deg)	92.512(2)	110.090(7)	103.024(5)
<i>γ</i> (deg)	90	90	90
<i>V</i> (Å³)	1816.8(3)	1370.7(2)	4376.3(6)
<i>Z</i>	4	4	4
<i>d</i>_{calcd} (g cm⁻³)	1.478	1.678	1.248
<i>μ</i> (mm⁻¹)	1.826	18.304	0.795
<i>F</i>(000)	816	680	1732
crystal size (mm)	0.060 x 0.120 x 0.180	0.020 x 0.020 x 0.040	0.220 x 0.400 x 0.420
<i>θ</i> range (deg)	2.37 to 31.08	3.04 to 66.72	2.34 to 26.23
Index range	-17 ≤ <i>h</i> ≤ 17	-14 ≤ <i>h</i> ≤ 13	-19 ≤ <i>h</i> ≤ 19
	17 ≤ <i>k</i> ≤ 17	-17 ≤ <i>k</i> ≤ 17	-21 ≤ <i>k</i> ≤ 21
	-19 ≤ <i>l</i> ≤ 19	-10 ≤ <i>l</i> ≤ 9	-19 ≤ <i>l</i> ≤ 20
no. of rflns collected	45534	11109	66729
no. of indep rflns	5802	2385	9132
<i>R</i>1, <i>wR</i>2 (<i>I</i> > 2(<i>σ</i>))	0.0392, 0.0680	0.0764, 0.2089	0.0596, 0.1468
<i>R</i>1, <i>wR</i>2 (all data)	0.0716, 0.0783	0.0903, 0.2328	0.0752, 0.1620
Goodness of fit, <i>F</i>²	1.030	1.138	1.088
no. of data/restraints/params	5802 / 1 / 196	2385 / 0 / 159	9132 / 306 / 516
Largest diff peaks and hole, eÅ⁻³	1.531, -1.400	2.748, -1.755	2.301, -2.370

2.5.4 Theoretical Studies

All the geometries were optimized using the DFT functional BP86^[38] with the def2-SVP basis set^[39] using the Gaussian09 program package.^[40] The single-point calculations of optimized geometries were done at the M06^[41]/def2-TZVPP^[42] level of theory, and the energies were corrected by adding the zero-point energies from the BP86/def2-SVP level of theory. The molecular orbital (MO) and natural bond order (NBO)^[43-44] analyses were performed at the same level of theory. Energy decomposition analysis of all the structures was performed at the BP86/TZ2P level of theory using the ADF 2013.01 program^[45] on the optimized geometries at the BP86/def2-SVP level of theory. The core electrons were treated by the frozen-core approximations, and scalar relativistic effects were incorporated using zeroth-order regular approximation (ZORA).^[46] Bonding studies were performed using EDA-NOCV analysis. Energy decomposition analysis (EDA)^[47] gives the instantaneous interaction energy (ΔE_{int}) between two fragments in the frozen geometry of the compound. With the help of this method it is possible to partition the instantaneous interaction energy into three chemically meaningful terms: electrostatic interaction (ΔE_{elstat}), Pauli's repulsion (ΔE_{Pauli}), and orbital interactions (ΔE_{orb}).

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

Different bonding possibilities between the fragments of interest can be considered. The electronic state that leads to lowest ΔE_{orb} is considered as the best bonding description. EDA-NOCV analysis^[48] is an extension of EDA analysis in which ΔE_{orb} term is decomposed into the contributions from different natural orbitals of chemical valence (NOCV). The EDA-NOCV scheme gives insight into the orbital interactions by providing the energy contributions for each specific orbital interaction between fragments to the total bond energy.

Figure S2. 15 Optimized geometries and important geometrical parameters of **2.20**, **2.20a** and **2.22** at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

HOMO (-8.32)

Figure S2. 16 Plot of highest occupied molecular orbital (HOMO) of **2.20** at the M06/def2-TZVPP//BP86/def2-SVP level of theory. The eigenvalues (in eV) are given in parenthesis.

Table S2. 2 Charge distribution given by the Natural Bond Orbital Analysis for **2.20**, **2.20a** and **2.22** at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

2.20		2.20a		2.22	
Atom	Charge	Atom	Charge	Atom	Charge
Si	0.424	Si	0.425	Si	0.832
H1	-0.188	C1	0.023	C1	-0.110
C1	0.096	C2	0.023	N1	-0.401
C8	0.122	N1	-0.335	C21	-0.056
SiH	0.236	N2	-0.342	N2	-0.402
		N3	-0.335	cAAC-1	0.054
		N4	-0.342	cAAC-2	0.114

Theoretical studies of **2.20a**

The DFT calculations indicate that the SOMO of **2.20a** is a majorly π -type p-orbital localized on the Si-center (Figure 2.2) and the contribution from the C–N π^* -MO of I_{Me} . Accordingly, the group charge analysis indicates a lower positive charge on the Si center (0.42 e) in **2.20a** as compared to that in **2.22** (0.83 e). This corroborates well with the poor π -acidity of I_{Me} as compared to cAAC.^[30] Moreover, the C–N bond lengths in **2.20a** (average 1.372 Å) is almost the same as that in un-coordinated I_{Me} (1.376 Å). The HOMO-1 is a lone pair orbital on the Si-center (Figure 2.2b, % of α and β -type s-orbital = 79.2 and 75.9), similar to that in **2.22**. The localization of the unpaired electron on the Si-center (0.72 e) is also indicated by the natural spin density plot (Figure 2.2c).

The EDA-NOCV analysis performed on **2.20a** suggests that the best bonding pattern is the donor-acceptor interaction between the $[:Si^\bullet]^+$ ($2P; 3s^2 3p_x^0 3p_y^0 3p_z^1$) and two I_{Me} moieties (Table S2.5). The Si–C $_{I_{Me}}$ bonds have almost equal contribution from the covalent interaction ($\Delta E_{orb} = 52.4\%$) and the electrostatic interaction. The major contribution to the covalent interaction is the σ -donation from I_{Me} ligands to the $[:Si^\bullet]^+$ centre (Figure S2.18, Scheme S2.1; $\Delta E_{\sigma(++)} + \Delta E_{\sigma(+-)} = -195.6$ kcal/mol), which is less than that in **2.22** ($\Delta E_{\sigma(++)} + \Delta E_{\sigma(+-)} = -221.6$ kcal/mol). The energy corresponds to the π -back donation from the unpaired electron present in the π -type p-orbital on the $[:Si^\bullet]^+$ centre to one of the C–N π^* -MO of I_{Me} is also less in **2.20a** ($\Delta E_\pi = -28.1$ kcal/mol) as compared to that in **2.22** ($\Delta E_\pi = -38.1$ kcal/mol). The bonding in **2.20a** comprises two donor-acceptor σ -bonds with two I_{Me} ligands, $C_{I_{Me}} \rightarrow [:Si^\bullet]^+ \leftarrow C_{I_{Me}}$. This retains one singly occupied π -type p-orbital and one σ -type lone pair on the Si-centre. The poor back donation from the π -type p-orbital on the Si-atom to the C–N π^* -MO of I_{Me} might be responsible for its high reactivity towards abstraction of a $H^\bullet$ radical from the solvent to form **2.20**.

Table S2. 3 Selected Wiberg bond orders and bond occupancies given by the Natural Population Analysis for **2.20**, **2.20a** and **2.22** at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

2.20			2.20a			2.22		
	Wiberg bond index	Bond occupancy		Wiberg bond index	Bond occupancy		Wiberg bond index	Bond occupancy
Si-C1	0.835	1.951	C1-Si	0.795	1.94	C1-Si	0.780	1.936
Si-C2	0.755	1.950	C2-Si	0.795	1.94	C21-Si	0.799	1.768
Si-H	0.891	1.939	C1-N1	1.236	1.98 (σ) 1.88 (π)	C1-N1	1.396	1.982 (σ)
LP Si		1.818	C2-N3	1.236	1.98 (σ) 1.88 (π)			1.947 (π)
			C1-N2	1.222	1.98	C21-N2	1.443	1.982 (σ) 1.95 (π)
			C2-N4	1.222	1.98	LP1 Si		1.797
			LP1 Si		1.90	LP2 Si		0.673
			LP2 Si		0.74	C-N π^*		0.39

Table S2. 4 NBO spin densities given by the Natural Population Analysis for **2.20a** and **2.22** at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

2.20a		2.22	
Atom	Spin	Atom	Spin
Si	0.74	Si	0.52
C1	0.01	C1	0.18
C2	0.01	N1	0.16
N1	0.05	C21	0.03
N2	0.06	N2	0.04
N3	0.05		
N4	0.06		

a)

b)

Scheme S2. 1 Schematic representation of a) in phase (++) donation of the I_{Me} carbene σ lone pair orbitals into the vacant p-orbital on Si and b) the out of phase (+-) donation to the other vacant p-orbital on Si. The in phase (++) combination of lone pairs donates two electrons to the p_y -orbital of Si and the out of phase (+-) combination of lone pairs donates two electrons to the p_x -orbital of Si.

a)

b)

Scheme S2. 2 Schematic representation of a) in phase (++) donation of the $cAAC_{Me}$ σ lone pair orbitals into the vacant p-orbital on Si and b) the out of phase (+-) donation to the other vacant p-orbital on Si. The in phase (++) combination of lone pairs donates two electrons to the p_y -orbital of Si and the out of phase (+-) combination of lone pairs donates two electrons to the p_x -orbital of Si.

Table S2. 5 EDA-NOCV results of Si-C1 and Si-C2 bonds of **2.20**, Si-C1 and Si-C2 bonds of **2.20a**, and Si-C1 and Si-C21 bonds of **2.22** at the BP86/TZ2P level of theory. Energies are in kcal/mol.

Interacting fragments	2.20		2.20a		2.22	
	Si ⁺ H + (NHC) ₂	SiH + (NHC) ₂ ⁺	[Si•] ⁺ (s ² p _x ⁰ p _y ⁰ p _z ¹) + (NHC) ₂	Si (s ² p _x ¹ p _y ⁰ p _z ¹) + (NHC) ₂ ⁺	[Si•] ⁺ (s ² p _x ⁰ p _y ⁰ p _z ¹) + (cAAC) ₂	Si (s ² p _x ¹ p _y ⁰ p _z ¹) + (cAAC) ₂ ⁺
ΔE_{int}	-203.8	-142.0	-206.2	-139.4	-209.0	-137.8
ΔE_{Pauli}	312.9	394.9	312.5	398.4	371.4	481.7
$\Delta E_{\text{elstat}}^{\text{a}}$	-249.7 (48.3%)	-246.9 (46.0%)	246.8 (47.6%)	-249.2 (46.3%)	-256.4 (44.2%)	-292.9 (47.3%)
$\Delta E_{\text{orb}}^{\text{a}}$	-267.0 (51.7%)	-290.0 (54.0%)	-271.9 (52.4%)	-288.6 (53.7%)	-324.0 (55.8%)	-326.7 (52.7%)
$\Delta E_{\sigma(++)}^{\text{b}}$	-133.8 (50.1%)	149.0 (51.4%)	-132.0 (48.5%)	101.6 (35.2%)	-147.1 (45.4%)	-139.0 (42.5%)
$\Delta E_{\sigma(+)}^{\text{b}}$	-65.6 (24.6%)	107.9 (37.2%)	-63.6 (23.4%)	145.9 (50.6%)	-74.5 (23.0%)	-129.6 (39.7%)
$\Delta E_{\pi}^{\text{b}}$	-21.3 (8.0%)	17.0 (5.9)	-28.1 (10.3%)	21.2 (7.3%)	-38.1 (11.8%)	-34.7 (10.6%)
$\Delta E_{\text{rest}}^{\text{b,c}}$	46.3 (17.3%)	16.1 (5.6%)	-48.2 (17.7%)	19.9 (6.9%)	-64.3 (19.8%)	-23.4 (7.2%)
ΔE_{prep}	18.6		21.6		27.9	
$-\mathbf{D_e}$	-185.2		-184.6		-181.1	

^aValues in parenthesis give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. ^bValues in parenthesis give the percentage contribution to orbital interaction ΔE_{orb} . ^c $\Delta E_{\text{rest}} = \Delta E_{\text{orb}} - (\Delta E_{\sigma(++)} + \Delta E_{\sigma(+)} + \Delta E_{\pi})$.

Figure S2. 17 NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots and orbital stabilization energies ΔE for Si-C1 and Si-C2 bonds of **2.20** at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho$ is from red $\rightarrow$ blue. Isosurface value for NOCV pair orbitals is 0.03 and that for deformation density is 0.003.

Figure S2. 18 NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots and orbital stabilization energies ΔE of Si–C1 and Si–C2 bonds of **2.20a** at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho$ is from red $\rightarrow$ blue. Isosurface value for NOCV pair orbitals is 0.03 and that for deformation density is 0.003.

Figure S2. 19 NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots and orbital stabilization energies ΔE for Si–C1 and Si–C21 bonds of **2.22** at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho$ is from red $\rightarrow$ blue. Isosurface value for NOCV pair orbitals is 0.03 and that for deformation density is 0.003.

Optimized Cartesian coordinates and total energies (in a.u.) including zero-point energy correction of all the calculated molecules at the BP86/def2-SVP level of theory (E₁) and total energy at M06/def2-TZVPP level of theory including zero-point energy correction from the BP86/def2-SVP level of theory (E₂) using G09 program package. Symmetry of the structures is mentioned in the parenthesis. The number of imaginary frequencies is abbreviated as Nimag.

Table S2. 6 Optimized cartesian coordinates of compound **2.20**

M06/def2-TZVPP//BP86/def2-SVP

E₁ = -1055.870392 a.u.

E₂ = -1056.187579 a.u.

Nimag = nil

	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
	14	-0.032109000	-0.050496000	1.841837000
	6	-1.510834000	0.004930000	0.573185000
	6	-3.639242000	-0.169298000	-0.242853000
	6	-3.051924000	0.929355000	-0.842973000
	6	-2.925450000	-1.863289000	1.487546000
	1	-3.558760000	-2.605311000	0.966570000
	1	-3.435723000	-1.543917000	2.419910000
	1	-1.960180000	-2.330433000	1.758023000
	6	-5.011399000	-0.740714000	-0.394928000
	1	-5.604844000	-0.129743000	-1.100511000
	1	-5.561187000	-0.760715000	0.569889000
	1	-4.993266000	-1.778720000	-0.791304000
	6	-3.595829000	1.890490000	-1.849540000
	1	-4.617255000	1.590281000	-2.149444000
	1	-2.977163000	1.925511000	-2.771378000
	1	-3.663110000	2.925246000	-1.449427000
	6	-0.795527000	2.069766000	-0.623314000
	1	-0.241537000	2.325798000	0.304113000
	1	-1.327399000	2.971815000	-0.976466000
	1	-0.072468000	1.752017000	-1.402469000
	6	1.507702000	-0.162622000	0.606534000
	6	3.098290000	-0.804567000	-0.901471000
	6	3.609580000	0.262373000	-0.179527000
	6	0.955241000	-2.118803000	-0.873951000
	1	0.013318000	-2.092335000	-0.299301000
	1	1.447929000	-3.099393000	-0.719534000
	1	0.735060000	-1.992910000	-1.952806000
	6	3.701237000	-1.615984000	-2.001347000

1	4.715889000	-1.247415000	-2.241891000
1	3.098840000	-1.566080000	-2.933298000
1	3.794246000	-2.687232000	-1.722574000
6	4.934292000	0.948003000	-0.260088000
1	5.554081000	0.496515000	-1.056979000
1	5.501640000	0.862890000	0.691038000
1	4.830822000	2.029724000	-0.489362000
6	2.785688000	1.712092000	1.704772000
1	1.866923000	1.769093000	2.321553000
1	2.950562000	2.677465000	1.186267000
1	3.652875000	1.501866000	2.361243000
7	-2.675336000	-0.720901000	0.612581000
7	-1.756070000	1.018154000	-0.318070000
7	1.816951000	-1.040405000	-0.398798000
7	2.618149000	0.631676000	0.730671000
1	-0.096587000	-1.557125000	2.095468000

Table S2. 7 Optimized cartesian coordinates of compound **2.20a**

M06/def2-TZVPP//BP86/def2-SVP

E1 = -1055.257853 a.u.

E2 = -1055.571441 a.u.

Nimag = nil

Atomic		Coordinates (Angstroms)		
Number		X	Y	Z
6	-1.487888000	0.576429000	0.066652000	
6	-3.670795000	-0.078066000	-0.158209000	
6	-5.070999000	-0.034748000	-0.676035000	
1	-5.110282000	-0.152015000	-1.780114000	
1	-5.574610000	0.923288000	-0.426472000	
1	-5.672203000	-0.850959000	-0.233888000	
6	-3.066863000	-0.937557000	0.744648000	
6	-3.623836000	-2.097296000	1.503830000	
1	-4.674731000	-2.279352000	1.210891000	
1	-3.613959000	-1.920492000	2.601119000	
1	-3.056817000	-3.032848000	1.312225000	
7	-2.689753000	0.832817000	-0.554087000	
7	-1.739318000	-0.514603000	0.867907000	
14	0.000006000	1.834036000	-0.000023000	
6	1.487907000	0.576437000	-0.066669000	
6	3.670849000	-0.077986000	0.158056000	
6	5.071023000	-0.034708000	0.675975000	

1	5.110321000	-0.153522000	1.779897000
1	5.574155000	0.923928000	0.427799000
1	5.672653000	-0.849990000	0.232693000
6	3.066867000	-0.937580000	-0.744673000
6	3.623753000	-2.097452000	-1.503713000
1	4.675031000	-2.278756000	-1.211685000
1	3.612728000	-1.921305000	-2.601093000
1	3.057418000	-3.033205000	-1.311018000
7	2.689814000	0.832873000	0.553971000
7	1.739301000	-0.514678000	-0.867856000
6	-2.929191000	1.924698000	-1.496036000
1	-1.972340000	2.453576000	-1.676307000
1	-3.313326000	1.529482000	-2.457442000
1	-3.662732000	2.643675000	-1.079517000
6	-0.782936000	-1.116867000	1.789689000
1	-0.399176000	-2.082967000	1.401736000
1	0.063658000	-0.419830000	1.929093000
1	-1.265026000	-1.295655000	2.770257000
6	0.782876000	-1.117001000	-1.789547000
1	-0.063732000	-0.419974000	-1.928919000
1	1.264943000	-1.295833000	-2.770114000
1	0.399113000	-2.083097000	-1.401570000
6	2.929234000	1.924674000	1.496021000
1	3.312837000	1.529348000	2.457600000
1	3.663201000	2.643385000	1.079802000
1	1.972493000	2.453903000	1.675879000

Table S2. 8 Optimized cartesian coordinates of compound **2.22** (C1)

M06/def2-TZVPP//BP86/def2-SVP

E1 = -1958.125986

E2 = -1958.756962

Nimag = nil

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.510412000	-1.168742000	0.583131000
6	1.690455000	-2.438037000	1.436912000
6	0.527578000	-2.675714000	2.417232000
1	0.425453000	-1.832810000	3.127550000
1	0.712508000	-3.598084000	3.006529000
1	-0.438140000	-2.794882000	1.889799000
6	1.862282000	-3.672097000	0.512032000

1	0.952622000	-3.864962000	-0.086344000
1	2.057688000	-4.573599000	1.129231000
1	2.705710000	-3.556520000	-0.196095000
6	3.006579000	-2.145092000	2.213824000
1	2.756404000	-1.707290000	3.202479000
1	3.594036000	-3.065428000	2.403276000
6	3.806432000	-1.112852000	1.391732000
6	4.862666000	-1.748228000	0.465960000
1	5.359898000	-0.979777000	-0.157389000
1	4.443976000	-2.525851000	-0.199266000
1	5.642621000	-2.224136000	1.093638000
6	4.514180000	-0.087795000	2.288877000
1	4.987153000	0.721623000	1.698161000
1	5.317795000	-0.609464000	2.847074000
1	3.829616000	0.360928000	3.031856000
6	2.900609000	0.742636000	-0.197815000
6	3.327983000	0.645914000	-1.558550000
6	3.386223000	-0.663180000	-2.353137000
1	3.208260000	-1.501050000	-1.649556000
6	4.750827000	-0.898958000	-3.034330000
1	4.948565000	-0.145360000	-3.824467000
1	4.770409000	-1.894698000	-3.523822000
1	5.594754000	-0.856017000	-2.316989000
6	2.251289000	-0.702466000	-3.401323000
1	1.260552000	-0.544184000	-2.923214000
1	2.235985000	-1.680473000	-3.926412000
1	2.382158000	0.089998000	-4.167634000
6	3.639399000	1.843921000	-2.234613000
1	3.976458000	1.795332000	-3.281691000
6	3.522152000	3.091205000	-1.611078000
1	3.781200000	4.010329000	-2.159434000
6	3.053421000	3.166185000	-0.294301000
1	2.930262000	4.153016000	0.178214000
6	2.727970000	2.009294000	0.443141000
6	2.134484000	2.194459000	1.844540000
1	2.033097000	1.191606000	2.309346000
6	3.022290000	3.062399000	2.763280000
1	4.066712000	2.696957000	2.817344000
1	2.610018000	3.077033000	3.793496000
1	3.057497000	4.115508000	2.415051000
6	0.716188000	2.802471000	1.759300000
1	0.742057000	3.820052000	1.316493000
1	0.269583000	2.886898000	2.771585000
1	0.040690000	2.181613000	1.133588000

6	-1.585641000	-1.298829000	-0.480069000
6	-1.879401000	-2.645036000	-1.181351000
6	-1.921302000	-3.819699000	-0.167903000
1	-0.923716000	-4.039170000	0.253430000
1	-2.271009000	-4.734485000	-0.689629000
1	-2.609335000	-3.632281000	0.679288000
6	-0.847638000	-2.962986000	-2.284825000
1	-0.806164000	-2.159186000	-3.047452000
1	-1.127066000	-3.906589000	-2.798879000
1	0.172396000	-3.096272000	-1.872112000
6	-3.285673000	-2.405496000	-1.800862000
1	-3.169828000	-2.049679000	-2.846078000
1	-3.893274000	-3.331392000	-1.835346000
6	-3.965285000	-1.301523000	-0.969149000
6	-4.856388000	-0.397467000	-1.826590000
1	-5.219904000	0.483568000	-1.261139000
1	-5.744273000	-0.982273000	-2.141471000
1	-4.343640000	-0.053402000	-2.742454000
6	-4.811581000	-1.841250000	0.201096000
1	-4.239168000	-2.494200000	0.886004000
1	-5.653856000	-2.433668000	-0.209443000
1	-5.245106000	-1.009838000	0.789716000
6	-2.813398000	0.772499000	0.126405000
6	-2.747650000	1.896735000	-0.763400000
6	-2.404846000	1.821694000	-2.257894000
1	-2.321942000	0.750557000	-2.539892000
6	-1.035389000	2.478976000	-2.552363000
1	-1.056928000	3.565835000	-2.327438000
1	-0.782923000	2.367097000	-3.627494000
1	-0.223888000	2.015783000	-1.956579000
6	-3.482352000	2.483385000	-3.148934000
1	-3.490880000	3.584797000	-3.014462000
1	-4.505908000	2.118508000	-2.937157000
1	-3.263042000	2.292016000	-4.219802000
6	-2.960642000	3.177607000	-0.214398000
1	-2.912674000	4.054407000	-0.878359000
6	-3.234361000	3.364147000	1.145414000
1	-3.418769000	4.375559000	1.539861000
6	-3.253699000	2.259439000	2.002573000
1	-3.442115000	2.413775000	3.076321000
6	-3.031278000	0.949466000	1.528148000
6	-2.976946000	-0.177977000	2.563433000
1	-2.835205000	-1.137229000	2.025537000
6	-1.754814000	0.014991000	3.489637000

1	-0.815302000	0.100920000	2.906206000
1	-1.656731000	-0.839347000	4.191295000
1	-1.854841000	0.936683000	4.099847000
6	-4.264646000	-0.286453000	3.408377000
1	-4.411454000	0.612045000	4.042949000
1	-4.207185000	-1.160723000	4.089494000
1	-5.173344000	-0.401327000	2.784661000
7	2.673868000	-0.479811000	0.569700000
7	-2.719929000	-0.577853000	-0.424105000
14	0.065069000	-0.279887000	-0.335996000

Table S2. 9 Optimized cartesian coordinates of cAAC_{Me}

M06/def2-TZVPP//BP86/def2-SVP

E1 = -834.417069 a.u.

E2 = -834.695637 a.u.

Nimag = nil

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.341222000	-0.084835000	-1.033234000
6	-2.800085000	-0.189025000	-0.585475000
6	-2.760115000	-0.484414000	0.953671000
1	-3.541255000	0.068270000	1.515265000
1	-2.940715000	-1.565624000	1.130248000
6	-1.340174000	-0.111031000	1.440596000
6	-3.503519000	-1.316557000	-1.369807000
1	-3.480966000	-1.107301000	-2.458572000
1	-4.564327000	-1.414860000	-1.051480000
1	-3.004703000	-2.294850000	-1.206123000
6	-3.489215000	1.159411000	-0.912377000
1	-3.033489000	2.006321000	-0.358719000
1	-4.566475000	1.116501000	-0.642591000
1	-3.407841000	1.386167000	-1.994769000
6	-1.283847000	1.261742000	2.136678000
1	-1.802869000	1.200603000	3.116035000
1	-1.780980000	2.053403000	1.542503000
1	-0.237215000	1.572504000	2.332654000
6	-0.724503000	-1.161575000	2.377050000
1	-1.281497000	-1.168052000	3.337284000
1	0.336584000	-0.932971000	2.606627000
1	-0.780046000	-2.182847000	1.952724000
6	0.841690000	0.039211000	0.001312000

6	1.464953000	1.317769000	-0.053915000
6	0.669458000	2.601392000	-0.298949000
1	-0.379491000	2.410636000	-0.002996000
6	1.167713000	3.811474000	0.512332000
1	1.210322000	3.593211000	1.599936000
1	0.489935000	4.678314000	0.364937000
1	2.180643000	4.139624000	0.196447000
6	0.646895000	2.902362000	-1.816002000
1	1.672915000	3.079990000	-2.203405000
1	0.039669000	3.808713000	-2.027010000
1	0.205657000	2.048919000	-2.370693000
6	2.875038000	1.367425000	-0.026827000
1	3.379744000	2.345553000	-0.060922000
6	3.645175000	0.198139000	0.018621000
1	4.744737000	0.260895000	0.049661000
6	3.012715000	-1.051887000	-0.019035000
1	3.624619000	-1.966763000	-0.046603000
6	1.606836000	-1.161231000	-0.044187000
6	0.958020000	-2.528275000	-0.272064000
1	-0.101256000	-2.456527000	0.044536000
6	0.939435000	-2.834809000	-1.788066000
1	0.392706000	-2.040141000	-2.336372000
1	0.437551000	-3.806257000	-1.985795000
1	1.971493000	-2.893659000	-2.195185000
6	1.607320000	-3.670904000	0.529732000
1	2.646877000	-3.876646000	0.197332000
1	1.034579000	-4.611720000	0.390582000
1	1.639905000	-3.447867000	1.616556000
7	-0.608604000	-0.055690000	0.063943000

Table S2. 10 Optimized cartesian coordinates of I_{PrMe}

M06/def2-TZVPP//BP86/def2-SVP

E1 = -382.977843 a.u.

E2 = -383.109514 a.u.

Nimag = nil

Atomic		Coordinates (Angstroms)		
Number		X	Y	Z
6	-0.000035000	-1.581391000	0.000000000	
6	-0.690443000	0.641466000	-0.000171000	
6	0.690502000	0.641433000	-0.000022000	
6	-2.444652000	-1.176681000	-0.000079000	
1	-2.992620000	-0.827289000	-0.901406000	
1	-2.992986000	-0.825791000	0.900439000	
1	-2.418020000	-2.281902000	0.000869000	
6	-1.670311000	1.771233000	0.000245000	
1	-1.143305000	2.745833000	-0.003716000	
1	-2.329915000	1.755884000	0.896007000	
1	-2.335431000	1.751524000	-0.891283000	
6	1.670356000	1.771222000	-0.000169000	
1	1.143283000	2.745789000	-0.004427000	
1	2.335215000	1.751193000	-0.891884000	
1	2.330181000	1.756303000	0.895432000	
6	2.444633000	-1.176723000	0.000158000	
1	2.418031000	-2.281935000	0.000428000	
1	2.992790000	-0.826277000	0.900945000	
1	2.992697000	-0.826881000	-0.900937000	
7	-1.067202000	-0.712815000	-0.000122000	
7	1.067171000	-0.712871000	0.000089000	

2.6 References

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Chapter 3:

A Parent NHC–Silyliumylidene Cation in Catalysis[‡]

3.1 Introduction

The main group elements, particularly p-block elements, represent the most common category of elements on the Earth's crust. Their prevalent availability, abundance, low toxicity and diversity find themselves in a myriad aspect of chemical application, ranging from economic, industrial, and environmental importance. Following the final quarter before the turn of the millennium has witnessed remarkable development in the main group chemistry.^[1] The prestige seminal work by Power in the year 2010 titled “Main-group Elements as Transition Metals” revealed the fundamentally distinctive electronic properties of the well-established p-block carbon and its heavier analogues (Si, Ge and Sn), latter drew closer resemblance to the transition metals and its dominance in small molecule activations (i.e., H₂, CO₂, NH₃ and C₂H₄).^[2]

Prior to the 1980s, the valence s- and p-orbitals of the main group complexes were assumed as either fully filled or empty with large energy separation. These qualities are deemed less attractive and fashionable in the scientific research since they do not possess energetically accessible open shell, which are unique to transition metal species.^[2] Therefore, the differences among the main group complexes were concealed with the stoichiometry, property and chemical reactivity. In contrast, the transition metals have partially filled d-orbitals that are close in energy (≤ 4 eV), remained popular for decades for their diverse reactivity.^[2]

[‡] Portions of this chapter are adapted with permission from B.-X. Leong, J. Lee, Y. Li, M.-C. Yang, C.-K. Siu, M.-D. Su, C.-W. So, *J. Am. Chem. Soc.* **2019**, *141*, 17629-17636; B.-X. Leong, Y.-C. Teo, C. Condamines, M.-C. Yang, M.-D. Su, C.-W. So, *ACS Catal.* **2020**, *10*, 14824-14833. Copyright 2020 American Chemical Society.

With much delight, such dilemma was surmounted by forcing the heavier main group elements into isolable exotic states that embody both low-oxidation (0, I and II) and coordination states within a single molecule, notably with the recent endeavors displaying much richness and utility akin to the transition metals.^[3] Whilst possessing a modest energy gap between the frontier orbitals of the low-valent complexes, comprising of an unoccupied p-orbital and a stereoactive electron pair around the central tetrel atom, they exhibit transition metal-like reactivity towards small molecules and enthalpically strong bonds at ambient temperature.^[3a-d] This in turn, trigger the burgeoning of the main group chemistry, particularly in the area of activation of small molecule and as promising candidate for environmentally benign and metal-free alternative in catalytic organic synthesis.^[3] One spectacular model was demonstrated by Power in 2005, featuring the heavier alkyne analogue, digermynes $\text{Ar}^1\text{Ge}\equiv\text{GeAr}^1$ (**3.1**, $\text{Ar}^1 = 2,6-(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$) for the cleavage of H_2 at ambient temperature to give a range of oxidative addition products, **3.1-H_n** ($n = 2 - 4$, Chart 3.2).^[4] Theoretical studies illuminated the key cooperative interaction that effected the splitting of H–H bond lied in the interaction of the electron density from the HOMO(σ) of H_2 to the LUMO(n^+) of the germanium complex, concomitant with the interaction of electron density from the latter HOMO(π) into the LUMO(σ^*) of H_2 (Chart 3.2, Chart 3.1b).^[4] Such mechanism is reminiscent of the oxidative addition reaction of H_2 mediated by transition metal complexes (Chart 3.1a), is the first indication of low-oxidation state heavier main group elements could participate in transition metal chemistry.

Chart 3. 1 Bonding model for the interaction of H_2 with (a) transition metal, (b) multiply bonded heavier main group element, (c) frustrated Lewis pair (d) singlet tetrelene.

Chart 3. 2 Mechanism for H_2 activation using heavier main group alkyne analogue.^[4]

Following that, various low-oxidation state main group species **3.2** – **3.8** have similarly activate H_2 under mild conditions (Chart 3.3 – 3.4).^[5] Similitude to structural **3.1**, Jones documented amino-substituted digermynes **3.2** – **3.3** with H_2 to afford hydrogenated products, comprising mixed-valent $\text{Ge}^{\text{II}}\text{--Ge}^{\text{IV}}$ species **3.2-H₂** and digermene **3.3-H₂** respectively (Chart 3.3a).^[5a,5b] Another notable mention was portrayed by Stephan, using Lewis acid-base strategy, known as frustrated Lewis pairs (FLPs) **3.4** (Chart 3.3b). The FLP possesses both stereo-active donor and acceptor orbitals, which is an emulation of the frontier orbitals found in transition metal compounds, to reversibly activate H_2 (Chart 3.1b).^[5c] On the other hand, stable singlet tetrylenes (i.e., carbenes, silylenes and germylenes), characteristic of an unoccupied p-orbital and a stereoactive electron pair with modest energy separation, have witnessed reliable reactivity in transition metal chemistry (Chart 3.1c). For example, Bertrand observed oxidative addition of H_2 using cyclic and acyclic alkyl(amino)carbenes.^[5d] Another essential clue driven the facile activation of H_2 is the relation of obtuse angle of the divalent tetrylenes as the inverse function to the resultant HOMO-LUMO gap, of which smaller HOMO-LUMO gap will allow cleavage of H_2 . In comparison with Power's acyclic silylene $[\text{Si}\{\text{S}(2,6\text{-}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{-C}_6\text{H}_3)\}_2]$ (**3.15**, S-Si-S angle: $90.52(2)^\circ$, $\Delta\text{HOMO-LUMO}$: 4.3 eV, Chart 3.6) which is inert towards H_2 ,^[5e] larger obtuse angle in acyclic silylenes **3.5** ($109.7(1)^\circ$, 2.00 eV) and **3.6** ($116.91(5)^\circ$, 1.991 eV) readily hydrogenated at room temperature to furnish the corresponding

silanes **3.5-H₂** and **3.6-H₂** (Chart 3.3c),^[5f,5g] is further supported by theoretical studies.^[6] The last strategy involves the synergistic intramolecular Si^{II}/B^{III} **3.7** acting in FLP fashion in the splitting of H₂, affording silane borane **3.7-H₂** (Chart 3.3c).^[5h]

Chart 3. 3 Low-valent main group complexes in activation of H₂; (a) digermynes, (b) frustrated Lewis pair and (c) silylenes.^[5]

Chart 3. 4 Examples of silylene-mediated oxidative addition of small molecules.^[8-11]

Strikingly, low-valent silicon complexes such as the divalent silylenes (described in Chapter 1) and silyliumylidene cations $[\text{RSi:}]^+$ ($\text{R} = \sigma$ -bonded substituent, described in Chapter 2) were exceptional in activating other enthalpically strong bonds and organic substrates.^[7] For instance, Inoue demonstrated the sole precedence of a highly reactive acyclic *N*-heterocyclic imino-stabilized silylene **3.8** that could reversibly undergo intramolecular C=C insertion of the ligand backbone and form the “masked” silylene **3.8'**, subsequently activates small molecules, for example H_2 , CO_2 and ethylene to access the corresponding oxidative addition products (Chart 3.4).^[8] The β -diketiminato silylene **3.9** could perform oxidative addition of NH_3 and $\text{C}_\text{Ar}\text{H}$ to form silanes **3.9-NH₃** and **3.9-Ar**, respectively (Chart 3.4).^[9] Additionally, Driess' mixed-valent disiloxane $\text{Si}^{\text{IV}}/\text{Si}^{\text{II}}$ **3.10**, achieved from the reaction of **3.9** and H_2O , similarly exhibit reactivity towards small molecules (Chart 3.4).^[10] Moreover, silyliumylidene cations $[\text{RSi:}]^+$ and hydridosilylenes $[\text{R(H)Si:}]$ can show transition metal-like reactivity in the area of small molecule activation.^[7a] To elaborate, Inoue et al. showed that the *N*-heterocyclic carbene (NHC)–arylsilyliumylidene cation **3.11** can reduce CO_2 to form CO and activate the C–H bond of phenylacetylene (Chart 3.4).^[11]

Chart 3. 5 Generic catalytic cycle for transition metal (left) and main group element (right).^[3e]

The above-mentioned phenomenal milestone symbolizes the first key step of a typical catalytic cycle—oxidative addition, a chemistry known to be exclusively dominated by transition metals (Chart 3.5a).^[3e] From a transition metal complex's perspective, the resultant intermediate $\text{TM}^{(n+2)+}$ (TM = transition metal) is highly unstable and easily reacts with another small molecule (Chart 3.5b) to afford a *cis*-complex (Chart 3.5c). Finally, in order to effect a turnover, the reductive elimination of the product is necessitated, concomitant with the regeneration of the active catalyst TM^{n+} (Chart 3.5d). To summarize, a generic catalytic cycle often involves one or more of the basic reactions—oxidative addition, insertion, and reductive elimination.^[3e]

Till date, there is no comparable reactions with silicon(II) complex was known. Inevitably, transition metals remained as the preferred choice of element across the periodic table for catalysis, attributed to their intrinsic flexibility to manipulate various oxidation states to accept electrons from substrates and vice-versa, dependent on the nature of the reaction. As expected, they can react strongly with small molecules, namely H_2 , CO_2 , ammonia, olefins and related molecules for catalytic transformations under mild conditions.^[2] On the contrary, oxidative addition of these silicon(II) species only leads to the thermodynamic stable products such as silane derivatives, consequently, render elimination reaction implausible and impeding catalytic use. To illustrate, computation studies performed by the group of Bertrand depicted the addition of the respective H_2 and NH_3 with model cyclic and acyclic mono(amino)carbenes are favorably exothermic (for $\text{H}_2 = -180.0 - -211.8 \text{ kJ/mol}$ and $\text{NH}_3 = -139.3 - -161.9 \text{ kJ/mol}$), in agreement with the irreversibility observed experimentally.^[5d] Evidently, H_2 activation by silylene **3.5** to product **3.5-H₂** (Chart 3.3) was calculated to be exceedingly exergonic ($\Delta G = -122.2 \text{ kJ/mol}$), which hamper the reverse pathway from product **3.5-H₂** to silylene **3.5**.^[5f] In addition, reactivity of silyliumylidene **3.11** towards phenylacetylene proceeded with large thermodynamic stability of $\Delta G = -47.0 \text{ kcal/mol}$ (Chart 3.4).^[11] Nonetheless, silicon-based complexes are still of interest as benign alternative to precious metal and transition metal catalysts, owing to their distinctive non-toxicity and high abundance.

Henceforth, it is of paramount importance to design a catalytic cycle reminiscent that of transition metal complexes, in which certain fundamental challenges must be addressed: (i) ligand design for isolable yet reactive silicon(II) complexes with an open coordination site (Chart 3.5e); (ii) capable of small molecule activations (Chart 3.5f) and (iii) elimination of desired product (Chart 3.5g), accompanied with regeneration of the active catalyst (Chart 3.5e).^[3e]

Chart 3. 6 Reversible complexation of small molecules by silylenes.^[12-14]

Alternately, reversible binding of small molecules could potentially circumvent the exceedingly challenging reductive elimination, is common in transition metal- and FLP-based catalysis, resulting in transfer and/or elimination of the functionalised product. Such process is attainable for silicon(II) complexes. The precedence was led by Kato, in which they reported the base-stabilized (amido)(hydrido)silylenes **3.12** – **3.14** underwent the reversible oxidative addition of Si^{IV}–H and P^{III}–H bonds at room temperature (Chart 3.6),^[12] in addition to the uncatalyzed insertion of the Si^{II}–H bonds with unsaturated C–Y bonds (Y = C, N, O, etc.).^[13] Likewise, Power demonstrated the reversible complexation of ethylene using acyclic silylene

3.15 and **3.16** to achieve **3.15-C₂H₄** and **3.16-C₂H₄**, respectively (Chart 3.6).^[14] Using variable-temperature ¹H NMR spectroscopy to perform Van't Hoff analysis, the same group found the energy required for association of ethylene gas with **3.16** was at $\Delta G_{\text{assn}} = -24.9(2.5)$ kJ mol⁻¹ (vs model :Si(SPh)₂, $\Delta G_{\text{assn}} = -24$ kJ mol⁻¹), thus enabled the reverse reaction at ambient temperature.^[14]

Catalysts

Chart 3. 7 Selected catalytic reactions mediated by heavier main group complexes.^[16-17,19]

The aforementioned findings are indicative of silicon(II) species have the inclination to rival transition metal chemistry as promising metal-free catalyst, with some precedence observed among the heavier main group congeners.^[2,3e,15] First, it was elucidated by Jones that germylene **3.17** and stannylene **3.18** (Chart 3.7) are efficient transition metal-like catalysts in mediating the hydroboration of unsaturated compounds, due to their far more reactive E^{II}-H bonds in comparison with classical E^{IV}-H bonds.^[16] In addition, the two-coordinate Ge^{II} and Sn^{II} centers preserve their Lewis ambiphilic characters, which enable the σ -bond metathesis, oxidative addition, and reductive elimination processes in the catalyses. Furthermore, Power et al. used the methoxystannylene precatalyst **3.19** to catalytically dehydrocouple amine-borane adducts (Chart 3.7).^[17]

Similarly, silicon(II) complexes are well-established for their Lewis amphiphilicity; a tweak in chemical modifications on the ligands will induce a vastly different chemical behaviour, making it a versatile catalyst candidate. Unfortunately, catalytic organic transformations mediated by silicon(II) compounds surprisingly remain unexplored. It could be possibly due to the supporting ligands in a silicon(II) compound, which impart kinetic and thermodynamic stabilization effects on the highly reactive silicon center to prevent oligomerization into polymeric structures.^[18] As a consequence, its Lewis ambiphilic character is not pronounced and the high catalytic potential of a silicon(II) compound is suppressed. To the best of our knowledge, only one precedence of silicon(II) compounds shows catalytic capability, whereby Jutzi et al. used the cyclopentadienyl silyliumylidene cation **3.20** to catalyze the controlled degradation of oligo(ethylene glycol) diethers (Chart 3.7).^[19] In this context, it is imperative to develop a strategy to activate the catalytic ability of stable silicon(II) compounds, which would greatly advance sustainable catalysis.

In Chapter 2, we described the synthesis of an NHC–parent silyliumylidene cation complex, [(I_{Me})₂SiH]I (**2.20**, see below, Scheme 3.1, I_{Me} = :C{N(Me)C(Me)}₂),^[20] and its transition metal-like reactivity in functionalizing the *ortho*-C–H bond of fluorobenzene.^[20] Considering the chemistry of the above-mentioned base-stabilized silyliumylidene cations and hydridosilylenes, it is anticipated that **2.20** could be a promising candidate to catalyze organic reactions due to its dual functionality: Si^{II} cation and reactive Si^{II}–H bond. Additionally, in contrast to the neutral silylene motif, oxidative addition of cationic silyliumylidene would generate the extremely unstable silylium cation intermediate, subsequently favors reductive elimination, concomitant with the regeneration of silyliumylidene catalyst, reminiscent of catalytic cycle in Chart 3.5.

In this context, we were highly interested in investigating its catalytic capability. Herein, we report the first low-oxidation state group 14 element catalytic system NHC–parent silyliumylidene cation to promote chemo- and regioselective hydroboration of carbon dioxide, carbonyl compounds, and pyridine derivatives. Further, the NHC–silyliumylidene cation complex **2.20** is extended to catalyze metal-free chemoselective *N*-formylation of amines with carbon dioxide to selectively deliver *N*-formamides.

3.2 Results and Discussion

3.2.1 A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of CO₂

The relentless rise of atmospheric carbon dioxide (CO₂) as a consequence of global change in climate landscape, initiates the immense focus in the field of catalytic conversion of CO₂ as a cheap C₁ feedstock for their functionalized reduced form, i.e., methanol, methane, formaldehyde and formic acid.^[21] These synthetic building blocks will then be converted into useful chemicals and as fuel source.^[22] Such transformations has been mostly explored by employing transition metal complexes as catalysts in the past decades.^[22] Despite their high performance, such complexes have become an increasingly unpopular choice for catalysis mainly because of the cost efficiency, toxicity and the exhaustible source. In sharp contrast, main group compounds are gaining popularity since the past seven years for its catalytic ability in the reduction of CO₂ to methanol equivalents with borane as the hydrogen source.^[23]

Chart 3. 8 Examples of catalysts in hydroboration of CO₂.^[16b,24]

Scheme 3. 1 **2.20**-catalyzed reduction of CO_2 . (All the catalytic trials were repeated in triplicate)

However, catalytic hydroboration of CO_2 is limited to only a handful of catalysts, often are metal- and transition metal-based (Chart 3.8).^[16b,24] Herein, the catalytic ability of the NHC–parent silyliumylidene cation complex **2.20**^[20] toward hydroboration of CO_2 with pinacolborane (HBpin) was first examined, considering that non-metal compounds have been rarely used as homogeneous catalysts for such reactions; the obtained turnover frequencies (TOF) and selectivity are often low, leading to a mixture of methoxyborane [pinBOMe] (**3.27b**) and diborate ether [(pinB)₂O] (**3.27c**). To begin with, there was no reaction between CO_2 and borane (HBpin, $\text{BH}_3\cdot\text{SMe}_2$, HBcat) in C_6D_6 at 90 °C. However, in the presence of **2.20** (10 mol %), the reduction of CO_2 with HBpin in C_6D_6 at 90 °C was extremely clean, resulting in the formation of the formoxyborane [pinBOC(O)H] (**3.27a**, reaction time: 0.08 h, yield: 94%, TOF = 113.2 h^{-1} ; reaction time: 0.17 h, yield: 98%, TOF = 58.7 h^{-1} ; Scheme 3.1; see Section 3.4.1, Table S3.1), along with a trace amount of the diborate ether **3.27c** (yield: <2%). No other identifiable boron-containing products such as methoxyborane **3.27b** were found in the reaction mixture when increasing the reaction time or temperature. Moreover, complex **2.20** (10 mol %) was able to catalyze the reduction of CO_2 under air and/or in wet

C₆D₆ to afford **3.27a** and **3.27c**, but the yield of **3.27a** decreased (Table S3.2). It is because HBpin decomposed in these reaction conditions to give **3.27c**, and hence the yield of the latter increased. When the amount of complex **2.20** decreased (5 mol %), the catalytic hydroboration was incomplete (90% conversion, Table S3.1) in 0.5 h, but the selectivity was still observed. It is noteworthy that complex **2.20** is the first non-metal catalytic system that selectively delivers the primarily reduced formoxyborane **3.27a**. Complex **2.20** is one of the very few examples that catalyze the selective reduction of CO₂, including the main-group and transition metal catalysts, namely, an amine-lithium borohydride **3.21** (TOF = 10 h⁻¹, Chart 3.8),^[24a] a NHC-copper **3.22** (yield: 85%, TOF = 0.35 h⁻¹, Chart 3.8),^[24b] and a PSiP-pincer-palladium complex **3.23** (yield: 93%, TOF = 1550 h⁻¹, Chart 3.8).^[24c] Moreover, **2.20** exceeds the base-metal catalysts, **3.21** and **3.22**, in terms of both reaction time and TOF. Furthermore, the TOF of the hydroboration of CO₂ with HBpin far surpasses the TOF values of the activated non-transition-metal catalysts (TOF = 0.07 – 2.5 h⁻¹) and even the non-metal catalysts (TOF = 0.40 – 14.5 h⁻¹).^[24d,24e,25]

When more potent [BH₃·SMe₂] was used instead of HBpin, 10 mol % of complex **2.20** catalyzed the reduction of CO₂ with >99% conversion to form a mixture of the borate esters [B(OMe)₃] (**3.27d**) and [BO(OMe)₃] (**3.27e**) in a ratio of 1:4 in 0.5 h (TOF = 19.8 h⁻¹, Scheme 3.1, Table S3.3), but selectivity cannot be achieved.

On the other hand, the **2.20**-catalyzed reduction of CO₂ with catecholborane (HBcat) slowly proceeded (24 h, >99% conversion, TOF = 0.34 h⁻¹, Table S3.4) to afford a mixture of diborate ether [(catB)₂O] (major product, yield: 70%) and methoxyborane [catBOMe] (minor product, yield: 12%). In comparison with other examples, the above-mentioned NHC-copper complex **3.22** (Chart 3.8) did not catalyze the selective reduction of CO₂ with HBcat,^[24b] whereas the (amido)(hydrido)stannylenes **3.18** (Chart 3.8) outperformed **2.20** using HBcat to non-selectively reduce CO₂ into [(catB)OMe] and [(catB)₂O] (TOF = 1188 h⁻¹, yield of each compound was not reported).^[26]

Scheme 3. 2 Synthesis of compound **3.28**.

Upon completing the catalytic hydroboration of CO₂ with HBpin, a weak singlet at ca. δ 0.9 ppm, in addition to the signal of **3.27a**, was observed in ¹¹B (see section 1.5.1, Figure S3.12b) and ¹¹B{¹H} NMR spectroscopy. These indicate that a new boron compound, which does not have any H atom on the boron atom, was formed in the catalysis. To clarify these phenomena, complex **2.20** was treated with excess HBpin in C₆D₆ at 60 °C for 5 min, whereby the same ¹¹B NMR signal at δ = 0.92 ppm (singlet) was observed, indicating formation of the new boron compound. The reaction was further analyzed by ¹H and ²⁹Si NMR spectroscopy. The ¹H NMR spectrum shows a set of signals due to methyl protons of I_{Me} and Bpin. The ²⁹Si NMR spectrum displays a singlet at δ = -93.0 ppm (²⁹Si{¹H} NMR: δ = -95.6 ppm, singlet; Figures S3.4 and S3.5), which is an intermediate value between that of **2.20** (δ = -77.9 ppm, ¹J_{Si-H} = 283 Hz) and the NHC–hydridosilylene complex [I_{Me}–:SiH(Si^tBu₃)] (δ = -137.8 ppm).^[20,27] The upfield Si NMR signal corresponds to a Si^{II} cationic center, and there is no hydrogen atom on the Si center. On the basis of NMR spectroscopic data, the new boron compound formed in the reaction is an NHC–borylsilyliumylidene complex [(I_{Me})₂SiBpin]I (**3.28**, Scheme 3.2). Its composition is also supported by the theoretical ²⁹Si NMR value (δ = -94.0 ppm, B3LYP/6-311⁺⁺G(2df,2pd)//B3LYP/6-31G**, Table S3.16) and HRMS. After workup, complex **3.28** was isolated as a colorless solid (yield: ca. 30% for 5 min reaction time). Compound **3.28** is highly unstable in solution, and hence obtaining suitable single crystals for X-ray crystallography is still in progress. In this context, its structure was simulated by density functional theory (DFT) calculations (Figure S3.162). Complex **3.28** easily decomposed in toluene and ethereal solvents to form a white insoluble precipitate, which comprises a mixture of an NHC–boronium cation [(I_{Me})₂Bpin]I (¹¹B NMR: δ = 2.37 ppm), an imidazolium salt [I_{Me}–H]I (**3.29**, Figure S3.158), and unidentified products. However, they are inactive in any catalytic hydroboration.

In supporting complex **3.28** that is involved in the catalysis, it was used to catalyze the hydroboration of carbon dioxide with HBpin, whereby selective reduction of CO₂ was achieved to obtain **3.27a** (2.5 mol %; time: 0.17 h, yield: 94%, TOF = 227 h⁻¹, Table S3.1).

These results brought up a question of whether complex **2.20** or **3.28** is a genuine catalyst in the hydroboration of CO₂.

Scheme 3. 3 Calculated Gibbs free energies (ΔG_{rel}) for the reaction of **2.20**, CO₂ and HBpin at 24 °C (M06-2X/def2-TZVP). Int and TS stands for intermediate and transition state. For the detailed mechanism with arrow pushing, see Scheme S3.3.

Considering that the conversion of complex **2.20** into complex **3.28** is slight (see above), it is suggested that complex **2.20** could prefer to react with CO₂ instead of HBpin in the first step of the catalysis. To gain insight, complex **2.20** was used to react with CO₂ in C₅D₅N at -40 °C, whereby the ²⁹Si NMR signal ($\delta = -68.9$ ppm, ¹J_{Si-H} = 202 Hz, -40 °C, Figure S3.10) is downfield shifted in comparison with that of **2.20**, indicating that the Si lone pair electrons interact with CO₂ to form **Int3.1** (Scheme 3.3). The Si-H coupling constant, as well as the absence of signal for the formate, -C(O)H, moiety in the ¹H NMR spectrum, indicates that CO₂ did not insert into the Si-H bond in **2.20** during the catalysis.^[28] When a stoichiometric amount of HBpin was subsequently added to the reaction mixture, compound **3.27a** was afforded, along with regeneration of complex **2.20**. Notably, the reaction of complex **2.20** and

CO₂ was found to be reversible upon the removal of CO₂ and volatiles of the reaction mixture *in vacuo* at room temperature. As a result, complex **2.20** does not resemble the (amido)(hydrido)germylene **3.17** (Chart 3.8) and –stannylene **3.18** (Chart 3.8) to catalyze hydroboration through the σ -E-H bond metathesis mechanism (E = Ge, Sn).^[26,29]

DFT calculations were then performed (Scheme 3.3). It was found that complex **2.20** is capable of mediating the catalysis, whereby the Si lone pair electrons interact with CO₂ to form **Int3.1** ($\Delta G = -3.1$ kcal/mol). The HOMO-3 of **Int3.1** shows that the Si lone pair orbital interacts with the π^* orbital of CO₂ (Figure S3.162). Accordingly, the NBO analysis shows that the Si–C_{CO2} bond results from the overlap of a $sp^{2.14}$ hybrid on Si with a $sp^{2.59}$ hybrid on C (Table S3.17). In the formation of **Int3.1**, the natural charge of the Si atom increases from 0.44 (compound **2.20**) to 1.02 (**Int3.1**), while that of the C_{CO2} atom decreases from 1.03 (**2.20**) to 0.54 (**Int3.1**). Subsequently, the H–B bond of HBpin inserts into the C=O bond via a low kinetic barrier (**TS3.1**; $\Delta G_{\text{Int3.1} \rightarrow \text{TS3.1}} = 10.6$ kcal/mol at 24 °C, Scheme S3.2), which results in the formation of the formoxyborane **3.27a** and regeneration of **2.20** ($\Delta G = -8.5$ kcal/mol). In other words, the Si lone pair of electrons in complex **2.20** is Lewis basic enough to activate CO₂ for subsequent hydroboration, whereas the Si–H bond is not sufficiently hydridic to activate CO₂. The mechanism is in contrast to the σ -E-H bond metathesis mechanism (E = main-group element) in main-group-element-catalyzed hydroboration.^[25] Moreover, the interaction of the Si lone pair in **2.20** with **3.27a** is endergonic ($\Delta G = 7.0$ kcal/mol, Scheme S3.5), whereas that with CO₂ is exergonic (Scheme 3.3). This suggests that complex **2.20** does not prefer to further react with **3.27a** after a catalytic cycle, while it chooses to react with CO₂ again and achieves the selective reduction.

DFT calculations also support that the catalytic hydroboration of CO₂ via complex **3.28** is feasible ($\Delta G = -1.1$ kcal/mol; M06-2X/def2-TZVP, Scheme 3.4, Scheme S3.1); especially complex **3.28** catalyzes the hydroboration of CO₂ via a lower kinetic barrier ($\Delta G_{\text{3.28} \rightarrow \text{TS3.4}} = 5.0$ kcal/mol) in comparison with the mechanism via **TS3.1**. It is consistent with experimental results that the activity of **3.28** in terms of TOF is much higher than that of **2.20** (Table S3.1). However, the kinetic barrier for the formation of **3.28** is relatively high ($\Delta G_{\text{2.20} \rightarrow \text{3.28}} = 15.2$ kcal/mol), which suggests that the mechanism via **TS3.1** should be more dominant than that via **3.28** and **TS3.4** in the catalysis.

Scheme 3. 4 Calculated Gibbs free energies (ΔG_{rel}) via **3.28** at 24 °C (M06-2X/def2-TZVP).

Inoue et al. reported that the NHC–arylsilyliumylidene cation [RSi(I_{Me})₂]Cl (**3.11**) with sterically hindered substituent 2,6-Mes₂C₆H₃ (R = Ar_{Mes}) reacted with CO₂ at room temperature to afford the NHC–arylsilaacylium **3.11-O** (Chart 3.4).^[30] In contrast, when the Ar_{Mes} substituent was replaced by a lesser sterically hindered substituent, 2,4,6-*i*Pr₃C₆H₂ (R = Tipp), only insoluble amorphous precipitates were formed in the reaction at room temperature. Considering the steric environment of complex **2.20** and the catalytic conditions, it is anticipated that the complex **2.20**-catalyzed reduction of CO₂ with HBpin via an NHC–parent silaacylium intermediate is not possible. To support this hypothesis, the reaction of **2.20** with CO₂ was studied by DFT calculations. The kinetic barrier and free energy for the formation of an NHC–parent silaacylium intermediate [(I_{Me})₂Si(=O)H]I (kinetic barrier: ΔG = 13.4 kcal/mol, Scheme S3.4) are energetically less favorable in comparison with those for the formation of formoxyborane **3.27a** (Scheme 3.3).

The presence of I_{Me} in complex **2.20** also brought up a question of whether I_{Me} dissociates from complex **2.20** and then catalyzes the hydroboration of CO_2 . As such, 0.1 mol % of I_{Me} , which presumes a small amount of the NHC ligand is dissociated during the catalysis, was used to mediate the reduction of CO_2 with HBpin in C_6D_6 at 90 °C for 0.25 h, resulting in non-selective catalysis (19% conversion, Table S3.1) to afford a mixture of [pinBOC(O)H] (**3.27a**), [pinBOMe] (**3.27b**), and [(pinB)₂O] (**3.27c**). In comparison with the catalytic results mediated by **2.20**, it is suggested that I_{Me} did not dissociate and was not involved in the hydroboration of CO_2 .

Theoretical studies and experimental results show that complex **2.20** is the first stable silicon(II) species undergoing catalytically selective hydroboration with CO_2 . Interestingly, the proposed mechanism is very similar to a recent report of the PNP–pincer ligand-iron(II) hydride complex-catalyzed hydroboration of alkynes, whereby the iron(II) hydride complex $[L^1FeH]$ ($L^1 = 2,5$ -bis(phosphinomethyl)pyrrolide) can convert into the corresponding iron(II) boryl complex $[L^1FeBpin]$ in the catalysis, along with both complexes being capable of catalyzing the hydroboration.^[31]

3.2.2 A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic *N*-formylation of Amines

Catalytic conversion of carbon dioxide (CO₂) into value-added chemicals and fuels has attracted much attention due to the increasing amount of anthropogenic CO₂ in the atmosphere and its corresponding climatic problems.^[21a] Considering that C–N bonds are commonly found in agrochemicals and pharmaceuticals,^[32] investigation of catalytic C–N bond formation using CO₂ as C₁ building block becomes indispensable. Consequently, a large number of precious transition metal catalysts have been developed to overcome the high thermodynamic stability of CO₂ for such catalyses.^[33] However, harsh conditions such as high pressure of CO₂ and long reaction time were required. Organocatalysis then emerged and was established as an alternative strategy, where N-heterocyclic carbenes (NHCs),^[34] superbases,^[35] and ionic liquids,^[33d,36] were used as catalysts to promote a range of C–N bond forming reactions between amines and CO₂.^[37] Mechanistic studies show that organocatalysts activate amines [R₂NH] (R = substituent) to form a [catalyst–H][R₂N] complex, which consequently reacts with CO₂ to form a carbamate salt in the form of [catalyst–H][R₂NCOO] (Chart 3.9).^[35c,38] The carbamate anion subsequently acts as a nucleophile to reduce CO₂ in the presence of silane or borane derivatives, affording formamides, *N*-methyamines, and/or amins with the selectivity dependent upon reaction temperature, CO₂ pressure, and type of solvent and amines.^[35c,35d,36e,36f,38a,38e] In addition, organocatalytic C–N cyclization reactions using CO₂ were feasible in the synthesis of quinazoline-2,4-diones^[39] and oxazolidinones.^[40] Recently, a different catalytic platform was developed by employing main-group element compounds as catalysts. These main group elements are considered as sustainable alternatives to precious transition metal species due to their high abundance and relatively low toxicity. A handful of examples were reported, whereby carbodicarbene,^[41] proazaphosphatrane,^[42] 1,3,2-diazaphospholene,^[43] and NHC–germaacylium cations^[44] undergo different mechanisms to mediate catalytic *N*-amination using CO₂. These results prompted us to search for other main group element compounds that could promote more efficient catalytic C–N bond formation using CO₂ via new reaction pathways.

Chart 3. 9 Organocatalytic C–N bond formation using CO_2 .^[37a]

Among main group elements, silylene compounds could be a good option due to their unique properties: the presence of a lone pair of electrons and a vacant p-orbital on the silicon(II) atom of a silylene. These electronic properties enable them to possess both electrophilic and nucleophilic characters, leading to Lewis ambiphilicity. In this context, they can display reactivity similar to transition metal complexes in the area of small molecules and enthalpically strong bond activation,^[15b,45] thus showing possible application in catalyzing organic reactions.^[46] To prove this concept, various silylene compounds have been shown to separately undergo CO_2 activation^[45m-p] and ammonia, amine, and hydrazine N–H bond activation.^[15b,45e-l] However, there is still no example capable of stoichiometrically or catalytically activating both CO_2 and a N–H bond simultaneously, resulting in C–N bond formation. In addition, other coupling reactions between two small molecules mediated by a silylene compound are currently unknown. This aroused our interest to investigate the catalytic capability of a silicon(II) compound in C–N bond formation. Herein, we report the NHC–silyliumylidene cation complex **2.20**-catalyzed N -formylation of amines and CO_2 to selectively afford N -formamides.

Optimization was first performed using diisopropylamine **3.32b** (Table 3.1, see Section 3.4.2, Table S3.5). The NHC–silyliumylidene cation complex **2.20**^[20] (10 mol %) was unable to catalyze the reaction of **3.32b** with CO₂ in the absence of a hydride source at 60 °C. Subsequently, three equivalents of hydride reagent (HBpin, Ph₃SiH, Ph₂SiH₂, PhSiH₃) was added into the reaction mixture to afford the *N*-formamide **3.33b**, demonstrating that complex **2.20** can mediate *N*-formylation regardless of the type of hydride source used (entries 2 – 5). Among the hydride reagents, PhSiH₃ showed the best activity in terms of TOF (entry 5). The catalytic loading of **2.20** (entries 5, 9, and 12), molar ratio of PhSiH₃ (entries 10 – 12), and reaction temperature (entries 5 – 8) were then modulated, where complex **2.20** showed the best performance in catalytic *N*-formylation under 5 mol % catalytic loading, reaction temperature of 60 °C, and two equivalents of PhSiH₃ (entry 11).

Table 3. 1 Optimization of *N*-formylation of amines with CO₂ and PhSiH₃.^a

Reaction scheme: **3.32b** + CO₂ $\xrightarrow[\text{C}_6\text{D}_6, \text{Temperature (T), Time (t)}]{\text{Catalyst } \mathbf{2.20} \text{ (X mol \%), H}^+ \text{ source}}$ **3.33b**

Entry	X	H ⁺ source (eq.)	T (°C)	t (h)	Yield (%)	TON	TOF (h ⁻¹)
1	10	None	60	96	0	0.0	0.0
2	10	HBpin (3)	60	1	68	6.8	6.8
3	10	Ph ₃ SiH (3)	60	96	30	3.0	0.03
4	10	Ph ₂ SiH ₂ (3)	60	1	43	4.3	4.3
5	10	PhSiH ₃ (3)	60	1	91	9.1	9.1
6	10	PhSiH ₃ (3)	24	3	95	9.5	3.2
7	10	PhSiH ₃ (3)	40	1	75	7.5	7.5
8	10	PhSiH ₃ (3)	90	1	71	7.1	7.1
9	1	PhSiH ₃ (3)	60	1	84	8.4	8.4
10	5	PhSiH ₃ (1)	60	1	54	10.8	10.8
11 ^b	5	PhSiH ₃ (2)	60	1	90	18.0	18.0
12	5	PhSiH ₃ (3)	60	1	88	17.6	17.6

^aReaction conditions: Amine **3.32b** (0.10 mmol), required amount of silane, C₆D₆ (0.5 mL), catalytic amount of complex **2.20** and CO₂ (*ca.* 50.0 mg). Catalyst loading is relative to amine. The yield was obtained by ¹H NMR using the –CH₂ protons of cyclohexane as an internal standard. TON and TOF are assigned to the number of hydride transferred. All the catalytic trials were repeated in triplicate. ^bOptimized conditions.

Table 3. 2 Scope of Primary Amine Substrates.^a

^aReaction conditions: Primary amine (0.10 mmol), 2 equiv. of PhSiH₃ (0.20 mmol), catalyst **2.20** (5 mol %), C₆D₆ (0.50 mL), CO₂ (ca. 50.0 mg). Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard, on the basis of the consumption of the amine. The identity of the product was confirmed as RHNC(=O)H. Isolated yields were reported in parenthesis. All the catalytic trials were repeated in triplicate. ^bReaction performed at 40 °C. ^cMono- and diformylation was observed in 3:2 ratio.

The catalytic reaction of primary amines with CO₂ and PhSiH₃ was then investigated (Table 3.2, Table S3.7) using the optimized conditions (Table 3.1, entry 11). First, isopropylamine **3.30a** did not undergo catalytic *N*-formylation under any conditions. Second, complex **2.20** (5 mol %) was found to be capable of catalyzing *N*-formylation of less sterically hindered aliphatic amines, namely, 2-methoxyethan-1-amine **3.30b** and *n*-butylamine **3.30c** to form the corresponding *N*-formamides (yield for **3.31b** and **3.31c**: >99%; TOF = 20.0 h⁻¹). The olefinic functionality in prop-2-yn-1-amine **3.30d** remained intact during the catalysis, showing the possibility of chemoselective *N*-formylation. Third, >99% yield was achieved for the *N*-formylation of aromatic aniline **3.30e** (TOF = 10.0 h⁻¹). Its derivatives with electron-donating, electron-withdrawing, and sterically hindered substituents were well tolerated (**3.30f** – **3.30t**). Fourth, benzylamine **3.30u** underwent catalytic *N*-formylation to form **3.30u** with >99% conversion (TOF: 6.7 h⁻¹). However, when electron-donating and electron-withdrawing groups were introduced at the ortho and para positions of **3.30u**, complex **2.20** was less active in these reactions (TOF = 4.1 – 6.1 h⁻¹). Fifth, diformylated products were not observed in most reactions. Only the *N*-formylation of **3.30k** afforded mono- and diformylated products in a 3:2 ratio. In these catalyses, the activity of complex **2.20** in terms of TOF and product yield are better than the *N*-heterocyclic carbene (NHC), I_{Ar} (:C{N(Ar)CH}₂, Ar = 2,6-*i*Pr₂C₆H₃). Examples of I_{Ar}, **3.30e**: yield = 35%, TOF = 0.3 h⁻¹; **3.30m**: 47%, 0.4 h⁻¹; **3.30n**: 86%, 0.7 h⁻¹; **3.30q**: 0%; **3.30u**: 85%, 0.7 h⁻¹).^[34b] When the Ar substituent is replaced by Mes (2,4,6-Me₃C₆H₂), I_{Mes} (:C{N(Mes)CH}₂) can only mediate the reaction of amines with CO₂ and Ph₂SiH₂ to solely form *N*-methyamines.^[34a] Another NHC, namely, thiazolium carbene (:C{N(Bn)CH=C(H)S}, Bn = CH₂Ph), was capable of catalyzing both *N*-formylation and *N*-methylation of amines with polymethylhydrosiloxane and CO₂ depending on the reaction temperature, but its activity (example of thiazolium carbene: **3.30e**: yield = 53%, TOF = 0.4 h⁻¹) is slower than **2.20**.^[34c] Sixth, the activity of **2.20** is better than superbases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD (examples of TBD, **3.30e**: yield = 24%, TOF = 0.2 h⁻¹)^[35a] and *N*-butyl-*N'*,*N''*,*N'''*,*N''''*-tetramethylguanidine, BTMG (examples of BTMG, **3.30e**: yield = 95%, TOF = 4.3 h⁻¹; **3.30u**: mixture of products).^[35c] In particular, complex **2.20** exhibits better activity in comparison with ionic liquids, for example, 1-butyl-3-methylimidazolium chloride [BMIm]Cl (examples of [BMIm]Cl, **3.30e**: yield = 76%, TOF = 0.15 h⁻¹; **3.30u**: 60%, 0.12 h⁻¹),^[36a] glycine betaine (**3.30c**: 85%, 4.5 h⁻¹; **3.30m**: 43%, 4.5 h⁻¹; **3.30u**: 81%, 4.5 h⁻¹),^[36e] and lecithin (**3.30c**: 89%, 1.7 h⁻¹; **3.30m**: no reaction; **3.30u**: 84%,

1.7 h⁻¹).^[36h] Lastly, the formation of *N*-formamides in the catalyses was further confirmed by X-ray crystallography of **3.31m**, **3.31p**, and **3.31w** (Figures S3.159 – S3.161). Moreover, it is noteworthy that the abovementioned NHC,^[34c] superbases,^[35b,35c] and ionic liquids^[36f,36g] mediated both catalytic *N*-formylation and *N*-methylation of amines and CO₂. However, complex **2.20** can only selectively mediate *N*-formylation regardless of reaction conditions. In other words, the *N*-formamides formed in the catalyses (Tables 3.2 and 3.3) did not undergo further reduction to form *N*-methyamines.

The catalytic reaction of secondary amines with CO₂ and PhSiH₃ was further investigated (Table 3.3, Table S3.8). First, 5 mol % **2.20** was able to catalyze the *N*-formylation of aliphatic secondary amines, namely, diethylamine (**3.32a**) and diisopropylamine (**3.32b**), to afford the corresponding *N*-formamides in high yield. Selective *N*-formylation was observed for the product **3.33c**, where the olefinic functionality in *N*-methylprop-2-yn-1-amine **3.32c** remained intact during the catalysis. In particular, the activity of **2.20** toward sterically hindered **3.32f** is much higher than that of the superbase DBU (yield = 54%, TOF = 0.1 h⁻¹)^[35b] and ionic liquids [BMIm]Cl (69%, 0.14 h⁻¹)^[36a] and glycine betaine (77%, 0.8 h⁻¹).^[36e] Second, less activity was found in aromatic *N*-methylaniline **3.32e** (95%, 6.3 h⁻¹), but the TOF of **2.20** is still higher than those of NHC, I_{Ar} (>99%, 0.8 h⁻¹),^[34b] superbase, TBD (40%, 0.16 h⁻¹),^[35a] and ionic liquid, [BMIm]Cl (95%, 0.19 h⁻¹).^[36a] Third, excellent yields (85 to >99%) and high activity (TOF: 20.0 h⁻¹) were found in the **2.20**-catalyzed *N*-formylation of cyclic amines such as piperidine **3.32g**, morpholine **3.32h**, indoline **3.32k**, and 1,2,3,4-tetrahydroquinoline **3.32m**. >99% yield and high activity (TOF: 6.7 – 10 h⁻¹) were also achieved for the *N*-formylation of *N*-heterocycles, namely, dimethylpyrazole **3.32n**, imidazole **3.32p**, and benzimidazole **3.32q**. The catalytic activity outperformed that of NHC catalysts found in the literature.^[34b] Notably, complex **2.20** shows better selectivity in comparison with other main-group element compounds, where 1,3,2-diazaphospholene unselectively catalyzes *N*-formylation of secondary amines leading to a mixture of *N*-formylated and *N*-methylated products.^[43] It is noteworthy that complex **2.20** is capable of showing selective *N*-formylation of both primary and secondary amines.

Table 3. 3 Scope of Secondary Amine Substrates.^a

<div><div>CO_2 + </div><div>Catalyst 2.20 (5 mol %) 2 equiv. PhSiH₃ C₆D₆, 60 °C</div><div> </div></div> <th data-kind="ghost"></th> <th data-kind="ghost"></th> <th data-kind="ghost"></th> <th data-kind="ghost"></th>							
3.32	3.33
3.33a	3.33b	3.33c	3.33d^c
>99 (46) %, 40.0 h ⁻¹	85 (72) %, 17.0 h ⁻¹	>99 (70) %, 20.0 h ⁻¹	0 %
3.33e^b	3.33f^d	3.33g	3.33h
95 (95) %, 6.3 h ⁻¹	>99 (99) %, 20.0 h ⁻¹	>99 (69) %, 20.0 h ⁻¹	>99 (70) %, 20.0 h ⁻¹
3.33k^b	3.33m^b	3.33n^c	3.33p
>99 (90) %, 20.0 h ⁻¹	>99 (97) %, 20.0 h ⁻¹	>99 %, 20.0 h ⁻¹	>99 %, 10.0 h ⁻¹
3.33q	3.33r^c		
>99 %, 6.7 h ⁻¹	>99 %, 20.0 h ⁻¹						

^aReaction conditions: Secondary amine (0.10 mmol), 2 equiv. of PhSiH₃ (0.20 mmol), catalyst **2.20** (5 mol %), C₆D₆ (0.50 mL), CO₂ (ca. 50.0 mg). Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard on the basis of the consumption of the amine. The identity of the product was confirmed as RHNC(=O)H. Isolated yields were reported in parenthesis. ^bReaction performed at 40 °C. ^cReaction performed at 90 °C. ^dReaction was also performed in 1 g scale, leading to full conversion, under the same reaction conditions.

In order to shed some light into the practical utility of our catalytic protocol using complex **2.20**, a gram-scale reaction was carried out. Under the standard reaction conditions, dibenzylamine **3.32f** was fully converted to **3.33f** (yield: >99%, TOF: 20.0 h⁻¹) as the sole product. In other words, both selectivity and yield were preserved upon upscaling of our catalytic protocol.

Upon completing the above catalytic *N*-formylation of amines, a weak singlet at $\delta = \sim 4.5$ ppm was observed (Figures S3.17, S3.22, S3.31, S3.40, S3.49, S3.54, S3.59, S3.64, S3.73, S3.76, and S3.79), which is attributable to H₂ gas. To clarify these phenomena, *N*-methylaniline **3.32e** was treated with PhSiH₃ in C₆D₆ at room temperature or 60 °C, whereby no reaction occurred. This demonstrates that the N–H proton of **3.32e** and Si–H hydride of PhSiH₃ did not react to form H₂ and the silylamine [Ph(Me)NSiH₂Ph] in C₆D₆ in the absence of complex **2.20**. This result is consistent with the recent findings, where a catalyst is essential for the dehydrocoupling of silanes and amines to form silylamines and H₂.^[47] Moreover, there was no reaction between complexes **2.20** and **3.32e**, which demonstrates that the Si–H bond in complex **2.20** did not react with the N–H proton of **3.32e** in C₆D₆ to form H₂ and the amidosilyliumylidene cation [(Ime)₂SiN(Me)Ph]⁺I⁻. In this context, complex **2.20** behaves differently from other organocatalysts, which activate amine (R₂NH) to form [catalyst–H][R₂N] (Chart 3.9).^[37a] Furthermore, complex **2.20** does not react with PhSiH₃ at 60 °C in C₆D₆, which illustrates that they are not involved in the first step of catalysis. Therefore, the first step of catalysis should involve the interaction of complex **2.20** with CO₂.^[46a] In addition, H₂ can only be formed when **2.20** was reacted with *N*-methylaniline, CO₂, and PhSiH₃ together. Such a hypothesis is evidenced by the following DFT calculations.

Scheme 3. 5 DFT calculations for catalytic *N*-formylation of amines with CO_2 and PhSiH_3 .

The reaction mechanism was studied by DFT calculations (M06-2X/def2-TZVP, Scheme 3.5, Scheme S3.6). It was found that complex **2.20** is capable of mediating the catalysis, whereby the Si lone pair of electrons interact with CO_2 first to form **Int3.1** ($\Delta G_{\text{rel}} = -3.1$ kcal/mol).^[46a] The O center in **Int3.1** attacks PhSiH_3 , and subsequently, the Si–H bond reacts with the N–H bond of **3.30u** to form H_2 . The N center of **3.30u** simultaneously attacks the C=O bond via a low kinetic barrier of 13.2 kcal/mol (**TS3.7**: $\Delta G_{\text{rel}}^\ddagger = 10.1$ kcal/mol) to form **Int3.7** ($\Delta G_{\text{rel}} = -0.7$ kcal/mol). The O center in **Int3.7** then attacks the second PhSiH_3 , where the Si–H bond of PhSiH_3 inserts into the C–O bond via a low kinetic barrier (**TS3.8**, $\Delta G_{\text{rel}}^\ddagger = 20.3$ kcal/mol), resulting in the formation of **Int3.8** and regeneration of **2.20** ($\Delta G_{\text{rel}} = -15.7$ kcal/mol). Siloxane $(\text{PhH}_2\text{Si})_2\text{O}$ is then eliminated from **Int3.8** via a kinetic barrier of 15.9 kcal/mol (**TS3.9**: 0.2 kcal/mol) to form **3.31u** ($\Delta G_{\text{rel}} = -38.7$ kcal/mol). The DFT calculations are consistent with the catalytic conditions, whereby two equivalents of

PhSiH₃ are sufficient for the completion of catalysis (Table 3.1). In addition, the mechanism is different from that of the abovementioned organocatalytic *N*-formylation of amines and CO₂ using NHCs, superbases, and ionic liquids as catalysts, where they activate the amine (R₂NH) to form [catalyst–H][R₂N] in the first step of catalyses.^[35c,38]

Scheme 3. 6 Deuterium-labelling study using d₁₁-piperidine (*D*, 98%). (All catalytic trials were repeated at least in triplicate)

To further support the proposed mechanism for the dehydrogenation step occurring between **TS3.7** and **Int3.7**, a deuterium-labeling study was performed using d₁₁-piperidine **3.32g-D** (*D*, 98%, Scheme 3.6). First, the catalysis was carried out using the standard reaction conditions, where HD (triplet, δ = 4.43 ppm) and formyl –C(=O)H (δ = 7.76 ppm) signals were observed in the ¹H NMR after an hour (Figure S3.82). The formation of HD proves the mechanism in Scheme 3.5, which proceeds via a dihydrogen elimination mechanism. Second, **3.32g** and **3.32g-D** in a 1:1 ratio were subjected to catalytic *N*-formylation using the standard reaction conditions (Scheme 3.7). Full conversion was observed where H₂ and HD were formed, as well as **3.33g-D** and **3.33g** were afforded in a 1:1 ratio (Figure S3.83). Third, **3.32g** or **3.32g-D** did not react with PhSiH₃ in the absence of complex **2.20** at any temperature, refuting the possibility of H₂ formation from the coupling reaction between PhSiH₃ and amine. Fourth, no reaction was observed in the reaction of PhSiH₃ and piperidine (**3.32g-D** and/or **3.32g**) in the presence of catalyst **2.20** at any reaction temperature (Figure S3.84). This illustrates that complex **2.20** cannot attack PhSiH₃ and the subsequent amine to form H₂ and silylamide [Ph(H)₂SiNR₂]. In other words, the mechanism via **Int3.1** and **TS3.7** should be feasible.

Scheme 3. 7 Scrambling reaction with d_{11} -piperidine (D , 98%) and piperidine in 1:1 ratio.
 (All catalytic trials were repeated at least in triplicate)

Scheme 3. 8 **2.20**-catalyzed hydrosilylation of CO_2 .

It is noteworthy that complex **2.20** (10 mol %) was able to catalyze the hydrosilylation of CO_2 with PhSiH_3 in C_6D_6 to form a mixture of silylformates $[\text{PhSiH}_x\{\text{OC}(\text{O})\text{H}\}_{3-x}]$ and siloxanes (Scheme 3.8, $x = 1 - 2$; conversion: >99%; TOF = 19.4 h^{-1}), which was confirmed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Figures S3.85a,b and S3.86) and HRMS. Hydrosilylation of CO_2 mediated by a low-oxidation state silicon compound was not reported yet. These results brought up a question of whether the mechanism of **2.20**-catalyzed *N*-formylation should proceed via silylformates $[\text{PhSiH}_x\{\text{OC}(\text{O})\text{H}\}_{3-x}]$, which then react with amines to form *N*-formamides and siloxanes

Scheme 3. 9 DFT calculations for catalytic hydrosilylation of CO₂.

To answer this question, the mechanism of the **2.20**-catalyzed hydrosilylation of CO₂ was elucidated by DFT calculations (Scheme 3.9, Scheme S3.7), whereby the Si lone pair electrons interact with CO₂ to form **Int3.1** ($\Delta G_{\text{rel}} = -3.1 \text{ kcal/mol}$).^[46a] Subsequently, the Si–H bond of PhSiH₃ inserts into the C–O bond in **Int3.1** via **TS3.10** ($\Delta G_{\text{rel}}^\ddagger = 13.9 \text{ kcal/mol}$) to form the silylformate [PhH₂SiOC(O)H] ($\Delta G_{\text{rel}} = -5.7 \text{ kcal/mol}$) and regenerates complex **2.20**. The reaction occurs with higher activation barrier (17.0 kcal/mol) in comparison with the reaction of **2.20**, **3.30u**, CO₂ and PhSiH₃ via **TS3.7** (13.2 kcal/mol). This suggests that the **2.20**-catalyzed N-formylation of amines with CO₂ and PhSiH₃ should not proceed via a silylformate intermediate. Our results are in contrast to the DFT calculations of the mechanism of the 1,3,2-diazaphospholene-catalyzed N-formylation and N-methylation, which involve the formation of silylformate [PhSiH_x{OC(O)H}_{3-x}] intermediate via σ-P–H bond metathesis mechanism pathway.^[48]

In particular, the silylformates $[\text{PhSiH}_x\{\text{OC(O)H}\}_{3-x}]$ formed further reacted with PhSiH_3 to form siloxanes in the complex **2.20**-catalyzed hydrosilylation of CO_2 (Scheme 3.8). This result indicates that the complex **2.20**-catalyzed *N*-formylation (Tables 3.2 – 3.3) should not proceed via silylformates; otherwise, low yields of formamides would occur. Even if the complex **2.20**-catalyzed *N*-formylation proceeds via silylformates, which then react with amine, silanol $\text{PhSiH}_x(\text{OH})_{3-x}$ formed could hydrolyze complex **2.20** and then impede its activity. However, complex **2.20** shows high activity toward the *N*-formylation of amines with CO_2 and PhSiH_3 , signifying the implausible mechanism via a silylformate intermediate.

Table 3. 4 *N*-formylation of amines via silylformates resulting in low yields of **3.31**.^a

Entry	T (°C)	t (h)	Consumption of silane (%)	Product	Yield (%)
1	60	3	15	3.31f	11
2	40	19	24	3.31m	21
3	90	2	23	Control reaction	

^aReaction conditions: PhSiH_3 (0.20 mmol), C_6D_6 (0.5 mL), catalytic amount of complex **2.20** and CO_2 (ca. 50.0 mg). After the hydrosilylation reaction, CO_2 was removed with its crude mixture filtered into another J-young NMR tube loaded with amine (0.10 mmol) was added. Catalyst loading is relative to amine. The yield was obtained by ^1H NMR using the $-\text{CH}_2$ protons of cyclohexane as an internal standard. All the catalytic trials were repeated in triplicate.

To support our hypothesis, a stepwise mechanistic study was implemented, where **2.20**-catalyzed hydrosilylation of CO_2 was performed as the first step followed by the removal of CO_2 and addition of amine **3.30f** or **3.30m** (Table 3.4). The results showed that the conversion of the silylformates $[\text{PhSiH}_x\{\text{OC(O)H}\}_{3-x}]$ were found to be exceedingly low at 40 and 60 °C, which resulted in the poor yield of **3.31f** (11%) and **3.31m** (21%), indicative of minimal contribution of silylformates $[\text{PhSiH}_x\{\text{OC(O)H}\}_{3-x}]$ in **2.20**-catalyzed *N*-formylation. The low conversion of $[\text{PhSiH}_x\{\text{OC(O)H}\}_{3-x}]$ at 40 and 60 °C is in line with a higher kinetic barrier in DFT calculations (Scheme 3.9).

3.2.3 A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of Aldehyde, Ketone and Pyridine Derivatives

The insertion of B–H bonds into C=O of aldehydes and ketones to afford organoborane derivatives, primary and secondary alcohols are vital synthetic synthons in a wide array of organic transformations, even more so in the chemical industry. The discovery of the first stoichiometric diborane reduction of aldehydes and ketones by Brown et al. marked as the pivot from harsh metal hydride reagents with poor selectivity and steer towards catalytic transformation using milder hydride sources.^[49] They observed the direct addition of B–H bond into the C=C bond of alkenes by using the sodium borohydride aluminium chloride.

Chart 3. 10 Selected recent advances in hydroboration of carbonyl derivatives.^[25,50c,55]

Thus far, catalytic hydroboration of unsaturated substrates is saturated with transition metal- and metal-based complexes, utilizing heavier group 13 analogues gold, molybdenum, titanium or ruthenium precatalysts.^[25,50] Currently, only a handful of research groups, including Hill, Stasch, Okuda, Roesky, Wesemann, Jones, Nembenna, Kinjo and others incorporate s- and p-block elements as single-site main group catalysts for the hydroboration of aldehydes and ketones (Chart 3.10).^[25,50c]

Chart 3. 11 Recent advances in hydroboration of pyridine and quinoline derivatives.^[51-54]

On another note, dearomatization of functionalized pyridines into dihydropyridines (DHPs) is one of the essential organic syntheses to obtain a vast range of useful nitrogen-containing natural products, organic transformations and pharmaceutical drugs. These DHPs can be accessed via catalytic 1,2- and 1,4-hydroboration using secondary boranes by reducing the pyridine derivatives. Hill and Harder demonstrated that magnesium(II) hydride complexes are able to catalyze reduction of pyridines using secondary boranes (Chart 3.11). Nonetheless, such catalytic complexes are not selective, which afforded mixtures of 1,2- and 1,4-adducts.^[51]

Soon after, huge milestones were achieved by Ohmura and Suginome, and Delferro and Marks when their respective rhodium(I) and lanthanide(III) complexes are able to effectively and selectively catalyze 1,2-hydroboration of pyridines, not to mention that their catalysts can tolerate a range of functional groups (Chart 3.11).^[52] Another notable achievement was achieved by the groups of Wang and Gunanathan when they utilize their respective fluoro-organoborane Lewis acid and Ru(II) catalysts for the selective 1,4-hydroboration of pyridines in high yields under mild conditions (Chart 3.11).^[53] Lastly, Wright's selective hydroboration of pyridines. Wright discovered HBpin activates pyridine to generate the active boronium catalyst in the presence of ammonium salt, which then modulates the 1,2-hydroboration of pyridines in non-polar solvents and conversely, 1,4-products in polar solvent (Chart 3.11).^[54]

Though few metal catalysts were discovered over the past years revolving around s-block and heavier main group metal complexes (germanium, tin and lead), the chemistry involving silicon species remained unexplored until very recently, whereby Sen et al. demonstrated the first neutral silicon(IV) compound **3.40** (Chart 3.10) catalyst for hydroboration of ketone and aldehyde.^[55]

Riding on the successes of catalytic hydroboration and *N*-formylation of CO₂, the catalytic ability of complex **2.20**^[20] toward hydroboration of carbonyl compounds was further examined. First, there was no reaction between carbonyl compounds with HBpin in C₆D₆ at room temperature. Second, complex **2.20** (10 mol %) was found to be capable of catalyzing hydroboration of aromatic aldehyde ArC(O)H (Ar = Ph, **3.41a**, Table 3.5, Table S3.9) as well as its derivatives with electron-donating (Ar = MeC₆H₄ **3.41b**, MeOC₆H₄ **3.41c**) and -withdrawing substituents (MeCO₂C₆H₄ **3.41e**, FC₆H₄ **3.41n**) at different positions in 10 min, which quantitatively afforded the corresponding borate esters. In these reactions, the activity of **2.20** in terms of TOF (17 – 115.8 h⁻¹) is intermediate between the heavier group 14 element(II) compounds, namely, (amido)(hydrido)germylene **1.17** (17 – 67 h⁻¹, Chart 3.8) and -stannylene **1.18** (400 – 800 h⁻¹, Chart 3.8).^[29] Third, >99% yield was achieved for the hydroboration of nonaromatic aldehydes, namely, cyclohexanecarboxaldehyde **3.41d** and 2,2-dimethylpropanal **3.41m**. Complex **2.20** is less active in these reactions (TOF = 19.8–115.8 h⁻¹) in comparison with those catalyzed by the (amido)(hydrido)germylene **1.17** and -stannylene **1.18** (TOF = >2000 h⁻¹, Chart 3.8).^[29] Fourth, the olefinic functionality in 3-cyclohexene-1-carboxaldehyde **3.41h**, cinnamaldehyde **3.41p**, and 2-methyl-3-phenylprop-2-enal **3.41s** remains intact in the catalyses, showing that the chemoselective hydroboration of aldehydes is possible. Such selectivity is also observed in the hydroboration of thiophene-2-carbaldehyde **3.41f**, ferrocenecarboxaldehyde **3.41g**, furan-2-carbaldehyde **3.41n**, 4-formylbenzonitrile **3.41t**, and isoquinoline-5-carboxaldehyde **3.41u**, in which the functional groups such as nitrile and pyridine were not hydroborated. Such chemoselective catalyses have not been reported before for heavier group 14 element(II) compounds.^[29] In addition, excellent chemoselectivity of aldehydes over ketones was observed in the catalytic hydroboration of 4-acetylbenzaldehyde **3.41v**. Fifth, as expected, a higher reaction temperature (90 °C) and longer reaction time were required for the chemoselective hydroboration of ketones when compared to aldehydes due to their steric nature (Table 3.6, Table S3.10). Various functional groups in

aromatic and aliphatic ketones were well tolerated in these reactions, and the corresponding borate esters were afforded in high yields.

Table 3. 5 Scope of Aldehyde Substrates.^a

$ \begin{array}{c} \text{R}-\text{CHO} \\ \text{3.41} \end{array} + \begin{array}{c} \text{HBpin} \end{array} \xrightarrow[\text{C}_6\text{D}_6, 24\text{ }^\circ\text{C}]{\text{Catalyst } \mathbf{2.20} \text{ (10 mol \%)}} \begin{array}{c} \text{R}-\text{CH}_2\text{OBpin} \\ \text{3.42} \end{array} $
3.42a >99 (89) %, 115.8 h ⁻¹	3.42b >99 (91) %, 115.8 h ⁻¹	3.42c >99 (87) %, 115.8 h ⁻¹	3.42d >99 (87) %, 115.8 h ⁻¹
3.42e >99 (83) %, 115.8 h ⁻¹	3.42f >99 (82) %, 115.8 h ⁻¹	3.42g >99 (86) %, 118.8 h ⁻¹	3.42h >99 (86) %, 115.8 h ⁻¹
3.42k >99 (85) %, 115.8 h ⁻¹	3.42m >99 (83) %, 19.8 h ⁻¹	3.42n >99 (89) %, 23.8 h ⁻¹	3.42p >99 (89) %, 115.8 h ⁻¹
3.42q >99 (85) %, 115.8 h ⁻¹	3.42r >99 (89) %, 17.0 h ⁻¹	3.42s >99 (85) %, 29.7 h ⁻¹	3.42t >99 (91) %, 39.6 h ⁻¹
3.42u >99 (89) %, 39.6 h ⁻¹	3.42v^b >99 (91) %, 14.9 h ⁻¹		

^aReaction conditions: aldehyde substrates (0.10 mmol), HBpin (0.11 mmol), C₆D₆ (0.50 mL), catalyst **2.20** (10 mol %). ^bReaction performed at 40 °C. NMR yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the aldehyde and the identity of the

product was confirmed by RCH_2OBpin or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate.

Table 3. 6 Scope of Ketone Substrates.^a

$ \begin{array}{c} \text{R}-\text{C}(=\text{O})-\text{R}' \\ \text{3.43} \end{array} + \begin{array}{c} \text{HBpin} \end{array} \xrightarrow[\text{C}_6\text{D}_6, 90^\circ\text{C}]{\text{Catalyst 2.20 (10 mol \%)}} \begin{array}{c} \text{R}-\text{CH}(\text{R}')-\text{OBpin} \\ \text{3.44} \end{array} $
<p>3.44a >99 (84) %, 1.65 h⁻¹</p>	<p>3.44b >99 (90) %, 1.98 h⁻¹</p>	<p>3.44c >99 (86) %, 1.65 h⁻¹</p>	<p>3.44d >99 (85) %, 9.90 h⁻¹</p>
<p>3.44e >99 (89) %, 0.46 h⁻¹</p>	<p>3.44f 75 (66) %, 0.31 h⁻¹</p>	<p>3.44g >99 (91) %, 1.41 h⁻¹</p>	<p>3.44h 84 (75) %, 0.35 h⁻¹</p>
<p>3.44k >99 (90) %, 9.90 h⁻¹</p>			

^aReaction conditions: ketone substrates (0.10 mmol), HBpin (0.11 mmol), C_6D_6 (0.50 mL), catalyst **2.20** (10 mol %). NMR yields are determined by ^1H NMR spectroscopy on the basis of the consumption of the ketone and the identity of the product was confirmed by $\text{RC}(\text{R}')(\text{H})\text{OBpin}$ or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate.

The catalytic ability of complex **2.20** toward the hydroboration of pyridine derivatives was also studied (Table 3.7, Table S3.11). First, there was no hydroboration reaction between HBpin and pyridine derivatives in C₆D₆ at 90 °C. Second, 10 mol % of **2.20** catalyzed the reaction of pyridine **3.45a** with one equivalent of HBpin in C₆D₆ at 90 °C to quantitatively form *N*-boryl-1,4-dihydropyridine **3.46a** as the only regioisomer (TOF = 2.48 h⁻¹), whereas the 1,2-hydroborated product was not formed. Such regioselectivity is comparable with metal-free [MeB{2,4,6-(CF₃)₃C₆H₂}₂] catalyst (yield of **3.46a**: >99%)^[53a] and the 1,3,2-diazaphosphenium triflate catalyst (yield of **3.46a**: 96%).^[56] In addition, such catalysis has not been reported for heavier group 14 element(II) compounds. Third, both chemo- and regioselectivity were observed in the **2.20**-catalyzed hydroboration of functionalized pyridines **3.45b,c** and ring-fused pyridine **3.45d**. Third, the scope of substrates can further be extended to 1,2- and 1,3-pyrazines **3.45e,f**.

Table 3. 7 Scope of Pyridine Substrates.^a

 3.46a >99 (90) %, 2.48 h ⁻¹	 3.46b >99 (89) %, 39.6 h ⁻¹
 3.46c 89 (80) %, 4.45 h ⁻¹	 3.46d >99 (91) %, 1.1 h ⁻¹
 3.46e >99 (84) %, 2.48 h ⁻¹	 3.46f 67 (59) %, 1.98 h ⁻¹

^aReaction conditions: pyridine substrates (0.10 mmol), HBpin (0.11 mmol), C₆D₆ (0.50 mL), catalyst **2.20** (10 mol %). NMR yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the pyridine and the identity of the product was confirmed by C=C or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate.

Upon completing the above-mentioned catalysis (Tables 3.5 – 3.7), complex **3.28** was observed (Figures S3.88–S3.90, S3.103a, S3.113, S3.115, S3.117, S3.119, S3.123, S3.135, S3.149, S3.151, S3.153a, and S3.155a). These indicate that both complexes **2.20** and **3.28** are involved in the catalyses. Similar to the case of CO₂, it is suggested that the Si lone pair of electrons in complexes **2.20** and **3.28** activate the carbonyl compounds, which are then reacted with HBpin to form the corresponding hydroborated products, along with the regeneration of the catalysts.^[57,58] In the case of pyridine derivatives, it is proposed that the catalysis proceeds through coordination of **3.45** with HBpin first,^[53a] which induces nucleophilic attack of complexes **2.20** and **3.28** at the para-position of **3.45** due to lesser steric congestion.^[58,59] Subsequent dearomatization of **3.45** results in displacing the hydride from the borane moiety, which then attacks at the para-position to afford **3.46**, along with the regeneration of the catalysts. In supporting complex **3.28** that is involved in these catalyses, it was used to catalyze the hydroboration of benzaldehyde **3.41a** (Table S3.12), 1,4-dioxaspiro[4.5]decan-8-one **3.43d** (Table S3.13), and pyridine **3.45a** (Table S3.14), whereby complex **3.28** shows better activity in terms of TOF in comparison with complex **2.20**.

3.3 Conclusion

The NHC–parent silyliumylidene cation complex **2.20** is a versatile catalyst to catalyze the metal-free chemo- and regioselective hydroboration of carbon dioxide, carbonyl compounds, and pyridine derivatives with HBpin to form formoxyborane, borate esters, and *N*-boryl-1,4-dihydropyridine derivatives, respectively. In particular, complex **2.20** is the first non-metal catalytic system that efficiently and selectively delivers the primarily reduced formoxyborane. Its activity is better than that of currently available base-metal catalysts used for such reactions. Mechanistic studies show that complex **2.20** exhibits transition-metal-like catalysis, whereby the silicon(II) center in complex **2.20** activates the substrates and then mediates the catalytic hydroboration. In addition, complex **2.20** was slightly converted into the NHC–borylsilyliumylidene complex [(I_{Me})₂SiBpin]I (**3.28**) in the catalysis, which was also able to mediate the catalytic hydroboration.

The NHC–silyliumylidene cation complex **2.20** is a low-oxidation-state group 14 element catalytic system to promote the metal-free chemoselective *N*-formylation of amines with carbon dioxide, which efficiently and selectively delivers *N*-formamides. The byproducts of the reactions are dihydrogen gas and siloxane. The activity of **2.20** and product yields are better than that of currently available non-metal catalysts used for such catalysis. The outperformance of **2.20** is due to its transition-metal-like catalysis, whereby the silicon(II) center sequentially activates CO₂, PhSiH₃, and amines, which proceeds via a dihydrogen elimination mechanism, to form formamides, siloxanes, and dihydrogen gas. It seems reasonable that complex **2.20** will find a range of other catalytic applications (e.g., C–C bond formation, C–H bond functionalization). We are currently investigating this possibility and will report on our findings in due course. The trapping of reactive intermediates with various Lewis bases and acids will also be reported in the course of time.

3.4 Experimental

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Compound **2.20** was prepared according to the literature procedure.^[20] Toluene was dried over Na/K alloy and distilled prior to use. C₆D₆ and *d*₅-pyridine were dried over K metal and distilled prior to use. CH₂Cl₂ and CDCl₃ were dried over CaH₂ and distilled prior to use. *d*₁₁-piperidine (D, 98%) was purchased from Cambridge Isotope Laboratories, Inc. and dried with 4Å molecular sieves prior to use. Substrates were purchased and used directly without further purification. All amine substrates are commercially available and dried using CaH₂. Aldehyde and ketone substrates are commercially available and dried using molecular sieves. The ¹H, ¹¹B, ¹¹B{¹H}, ¹³C{¹H}, ²⁹Si and ²⁹Si{¹H} NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C₆D₆, CDCl₃ or *d*₅-pyridine, and the chemical shifts are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si; BF₃·Et₂O for ¹¹B, respectively. The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet and m = multiplet. Coupling constants *J* are given in Hertz (Hz). Melting points were measured in sealed glass tubes and were not corrected. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University.

3.4.1 A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of CO₂

Synthesis of compound 3.28. Compound **2.20** (4.0 mg, 0.01 mmol) and pinacolborane, HBpin (14.5 μ L, 10 equiv, 0.10 mmol) were mixed with 0.5 mL of C₆D₆ in a J-Young NMR tube at room temperature. The resulting mixture was stirred at 60 °C for 5 min. Volatiles were immediately removed at 60 °C *in vacuo*. The residue was extracted with benzene (1 mL). After filtration, the filtrate was removed *in vacuo* to afford compound **3.28** as a colorless solid (1.6 mg, Yield: 30%). When the reaction was performed for 16 hours, the yield of compound **3.28** is 63% (3.3 mg). Mp: 167 °C (dec.). HRMS (ESI): *m/z* calcd for C₂₀H₃₇BN₄O₂Si [M+H]⁺: 531.18236; found: 531.18240. Satisfactory elemental analysis data could not be obtained due to compound **3** being highly sensitive to moisture and air. ¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 3.69 (s, 12H, N-CH₃), 1.75 (s, 12H, C-CH₃), 1.08 (s, 12H, Bpin-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 0.92. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 0.95. ²⁹Si NMR (78.65 MHz, 24 °C, C₆D₆, ppm): δ = -93.0. ²⁹Si{¹H} NMR (78.65 MHz, 24 °C, C₆D₆, ppm): δ = -95.6. The Si NMR signal is relatively weak due to quadrupolar broadening with the boron nucleus (*I* = 3/2).

Decomposition of compound 3.29. Prolonged crystallization of **3.28** in C₆D₆ or toluene afforded a mixture of white precipitates [(I_{Me})₂Bpin]I and [I_{Me}-H]I. They are insoluble in C₆D₆ but are highly soluble in CDCl₃. Colorless crystals of [(I_{Me})₂Bpin]I and [I_{Me}-H]I were isolated from their concentrated CH₂Cl₂ solution. ¹H NMR of [(I_{Me})₂Bpin]I (395.9 MHz, 24 °C, CDCl₃, ppm): δ = 3.89 (s, 12H, N-CH₃), 2.22 (s, 12H, C-CH₃), 0.14 (s, 12H, Bpin-CH₃). ¹¹B NMR of [(I_{Me})₂Bpin]I (128.41 MHz, 24 °C, CDCl₃, ppm): δ = 2.37. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, CDCl₃, ppm): δ = 2.56.

Formation of Int3.1. Compound **2.20** (4.0 mg, 0.01 mmol) and 0.5 mL of *d*₅-pyridine were mixed in a J-Young NMR tube. The NMR tube was immersed in liquid nitrogen under vacuum to afford a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO₂ gas was then added. The reaction mixture was warmed to -40 °C and analyzed by NMR spectroscopy. ¹H NMR (395.9 MHz, -40 °C, *d*₅-pyridine, ppm): δ = 9.99 (s, 1H, Si-*H*), 3.71 (s, 12H, N-CH₃), 1.97 (s, 12H, C-CH₃). ²⁹Si NMR (160.5 MHz, -40 °C, *d*₅-pyridine, ppm): δ = -68.9 (¹J_{SiH} = 202 Hz). ²⁹Si{¹H} NMR (78.65 MHz, -40 °C, *d*₅-pyridine, ppm): δ = -66.2.

General procedures for the catalytic hydroboration of carbon dioxide using **2.20** as the catalyst:

Synthesis of compound **3.27a** – **3.27c**

Catalyst **2.20** (4.0 mg, 0.01 mmol), internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol, 5 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. Pinacolborane, HBpin (14.5 μL, 0.10 mmol, 10 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO₂ gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ¹H NMR signals of *pin*BOC(=O)H (**3.27a**) at 0.93 ppm and (*pin*B)₂O (**3.27c**) at 1.02 ppm with reference to the –OMe and C–H protons (3.36, 6.20 ppm) of the internal standard, 1,3,5-trimethoxybenzene. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[60] Formation of **3.27b** was not observed throughout the catalytic reaction. The catalytic studies were repeated thrice.

Characterization of compound **3.27a**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 8.15 (s, 1H, C-*H*), 0.93 (s, 12H, Bpin-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 22.0. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 22.0. ¹³C{¹H} NMR (99.5 MHz, 24 °C, C₆D₆, ppm): δ = 157.7 (s, O₂CH), 93.5 (s, CMe), 24.2 (s, CMe).

Characterization of compound **3.27c**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 1.02 (s, 24H, Bpin-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 20.9. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 20.9. ¹³C{¹H} NMR (99.5 MHz, 24 °C, C₆D₆, ppm): δ = 84.4 (s, CMe), 24.5 (s, CMe).

Synthesis of compound 3.27d – 3.27e

Catalyst **2.20** (4.0 mg, 0.01 mmol), internal standard methyltriphenylsilane (27.4 mg, 0.10 mmol, 10 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. Borane dimethylsulfide, BH₃.SMe₂ (9.5 μL, 0.10 mmol, 10 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO₂ gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ¹H NMR signals of B(OMe)₃ (**3.27d**) at 3.42 ppm and (MeOBO)₃ (**3.27e**) at 3.34 ppm with reference to the –Me protons (0.71 ppm) of the internal standard, methyltriphenylsilane. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[61] The catalytic studies were repeated thrice. Blank reaction of BH₃.SMe₂ and Ph₃SiH was conducted (90 °C, 30min, C₆D₆), no H/Ph exchange between the B and Si atoms was observed.

Characterization of compound 3.27d

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 3.42 (s, 9H, O-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 17.8. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 17.8.

Characterization of compound 3.27e

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 3.34 (s, 9H, O-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 18.2. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 18.2.

Synthesis of compound **3.27f** – **3.27g**

Catalyst **2.20** (4.0 mg, 0.01 mmol), internal standard 1,3,5-tri-*tert*-butylbenzene (2.5 mg, 0.01 mmol, 1 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. The catecholborane, HBcat (10.7 μ L, 0.10 mmol, 10 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO₂ gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ¹H NMR signals of catBOMe (**3.27f**) at 3.39 ppm and (catB)₂O (**3.27g**) at 6.72 – 6.75 ppm with reference to the –Me and C–H protons (1.35, 7.42 ppm) of the internal standard, 1,3,5-tri-*tert*-butylbenzene. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[61-62] The catalytic studies were repeated thrice. Full consumption of HBcat was observed after 24 hours.

Characterization of compound **3.27f**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 3.39 (s, 3H, O-CH₃), 6.72 – 6.75 (m, 2H, Ar-H, overlapped with **3.27g**), 6.89 – 6.91 (m, 2H, Ar-H, overlapped with **3.27g**). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.3. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.3.

Characterization of compound **3.27g**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 6.72 – 6.75 (m, 2H, Ar-H, overlapped with **3.27f**), 6.89 – 6.91 (m, 2H, Ar-H, overlapped with **3.27f**). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 22.2. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 22.2.

General procedures for the catalytic hydroboration of carbon dioxide using 3.28 as the catalyst:

Synthesis of compound 3.27a – 3.27c

Catalyst **3.28** (1.3 mg, 0.0025 mmol), internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol, 20 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. Pinacolborane, HBpin (14.5 μ L, 0.10 mmol, 40 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO₂ gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ¹H NMR signals of *pin*BOC(=O)H (**3.27a**) at 0.93 ppm and (*pin*B)₂O (**3.27c**) at 1.02 ppm with reference to the –OMe and C–H protons (3.36, 6.20 ppm) of the internal standard, 1,3,5-trimethoxybenzene. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[60] The catalytic studies were repeated thrice. Formation of **3.27b** was not observed throughout the catalytic reaction.

Table S3. 1 Catalytic table for hydroboration of CO₂ using HBpin.

Entry	Cat	X	T (°C)	t (h)	Yield				TON			TOF (h ⁻¹)			TON TOF (h ⁻¹)	
					3.27a	3.27b	3.27c	Total	3.27a	3.27b	3.27c	3.27a	3.27b	3.27c		
1	-	-	110	13.0	0.00	0.00	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	I _{Me}	0.1	90	0.25	0.12	0.02	0.05	0.19	118.1	21.80	49.60	472.4	87.20	198.4	1.90	7.58
3	2.20	5.0	24	0.08	0.22	0.00	0.03	0.25	4.38	0.00	0.59	52.57	0.00	7.06	4.97	59.63
				0.17	0.33	0.00	0.03	0.36	6.53	0.00	0.60	39.18	0.00	3.60	7.13	42.78
				1.42	0.43	0.00	0.04	0.47	8.66	0.00	0.80	6.11	0.00	0.56	9.46	6.68
4	2.20	10	24	0.08	0.41	0.00	0.02	0.43	4.12	0.00	0.17	49.46	0.00	1.99	4.29	51.45
				0.17	0.62	0.00	0.02	0.64	6.23	0.00	0.17	37.38	0.00	1.02	6.40	38.40
				1.42	0.92	0.00	0.02	0.93	9.15	0.00	0.20	6.46	0.00	0.14	9.35	6.60
5	2.20	10	60	0.08	0.57	0.00	0.01	0.57	5.68	0.00	0.06	68.11	0.00	0.74	5.74	68.85
				0.17	0.80	0.00	0.01	0.81	7.96	0.00	0.13	47.78	0.00	0.75	8.09	48.53
				0.25	0.96	0.00	0.02	0.98	9.61	0.00	0.20	38.43	0.00	0.79	9.80	39.22
				0.33	0.96	0.00	0.04	0.99	9.62	0.00	0.38	28.86	0.00	1.14	10.00	30.00
6	2.20	5	90	0.08	0.65	0.00	0.02	0.67	13.00	0.00	0.30	156.0	0.00	3.60	6.65	79.80
				0.17	0.78	0.00	0.02	0.80	15.68	0.00	0.30	94.06	0.00	1.80	7.99	47.93
				0.33	0.85	0.00	0.02	0.87	17.00	0.00	0.40	51.00	0.00	1.20	8.70	26.10
				0.50	0.88	0.00	0.02	0.90	17.52	0.00	0.40	35.04	0.00	0.80	8.96	17.92
7a	2.20	10	90	0.08	0.94	0.00	0.02	0.96	9.43	0.00	0.15	113.21	0.00	1.85	9.59	115.06
				0.17	0.98	0.00	0.02	0.99	9.79	0.00	0.21	58.73	0.00	1.27	10.00	60.00
8	3.28	2.5	90	0.08	0.85	0.00	0.06	0.91	34.17	0.00	2.20	427.08	0.00	27.54	36.37	454.62
				0.17	0.94	0.00	0.06	0.99	37.77	0.00	2.23	226.62	0.00	13.38	40.00	240.00

Reaction conditions: 0.10 mmol of HBpin in C₆D₆ (~0.5 mL), amount of catalyst is calculated and then added to obtain the desired catalytic loading, 1 bar of CO₂. The yield was obtained by ¹H NMR using the Ar-*H* and O*Me* protons of 1,3,5-trimethoxybenzene as an internal standard. TON and TOF are given to the number of hydride transferred. ^aOptimised condition.

Table S3. 2 Catalytic table for hydroboration of CO₂ using HBpin in C₆D₆ containing O₂ and/or H₂O.

Entry	Condition	Yield			TON			TOF (h ⁻¹)			TON	TOF (h ⁻¹)
		3.27a	3.27b	3.27c	3.27a	3.27b	3.27c	3.27a	3.27b	3.27c		
1	78 ppm H ₂ O ^a	0.87	0.00	0.12	0.98	8.60	0.00	1.21	25.80	0.00	3.64	9.81
2	Presence of air ^b	0.77	0.00	0.09	0.85	7.65	0.00	0.88	22.96	0.00	2.64	8.54
3	78 ppm H ₂ O and air ^c	0.87	0.01	0.12	0.98	8.60	0.00	1.23	25.80	0.00	3.69	9.83

Reaction conditions: 0.10 mmol of HBpin in C₆D₆ (~0.5 mL), amount of catalyst is calculated and then added to obtain the desired catalytic loading, 1 bar of CO₂. The yield was obtained by ¹H NMR using the Ar-*H* and C-*H* protons of 1,3,5-trimethoxybenzene as an internal standard. TON and TOF are given to the number of hydride transferred. ^aA 100 mL packaging of C₆D₆ (*D*, 99.5%, containing 78 ppm residual water) was purchased from Cambridge Isotope Laboratories, Inc and subjected to freeze-pump-thaw cycle to remove air. ^bActivated molecular sieve was added into a 100 mL packaging of C₆D₆ (*D*, 99.5%, containing 78 ppm residual water) and left to stand for 5 days, occasionally agitating the solvent. C₆D₆ was then filtered under air for catalysis. ^cA 100 mL packaging of C₆D₆ (*D*, 99.5%, containing 78 ppm residual water) was purchased and used directly without further drying and purification.

3.4.2 A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic *N*-formylation of Amines

Optimization for the reductive functionalization of CO₂ using PhSiH₃ and diisopropylamine 3.32b:

Catalyst **2.20** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 20 equiv.), phenylsilane (24.6 μ L, 0.20 mmol, 40 equiv.), diisopropylamine **3.32b** (14.0 μ L, 0.10 mmol, 20 equiv) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S3.5 (see below) and the reaction was monitored by NMR spectroscopy, which confirmed the formation of (*i*Pr)₂NC(=O)*H* **3.33b**.^[63] Formation of methylated amine was not observed throughout the catalytic reaction. The yields of product were reported according to the integration of ¹H NMR signals of (*i*Pr)₂NC(=O)*H* at 8.17 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The catalytic studies were repeated at least in triplicate.

Table S3. 5 Catalytic table for *N*-formylation of amines using CO₂.

Entry	X	H ⁺ source (eq.)	T (°C)	t (h)	Yield (%)	TON	TOF (h ⁻¹)
1	10	None	60	96	0	0.0	0.0
2	10	HBpin (3)	60	1	68	6.8	6.8
3	10	Ph ₃ SiH (3)	60	96	30	3.0	0.03
4	10	Ph ₂ SiH ₂ (3)	60	1	43	4.3	4.3
5	10	PhSiH ₃ (3)	60	1	91	9.1	9.1
6	10	PhSiH ₃ (3)	24	1	34	3.4	3.4
				3	95	9.5	3.2
7	10	PhSiH ₃ (3)	40	1	75	7.5	7.5
				2	95	9.5	4.8
8	10	PhSiH ₃ (3)	90	1	71	7.1	7.1
9	1	PhSiH ₃ (3)	60	1	84	8.4	8.4
10	5	PhSiH ₃ (3)	60	1	88	8.8	8.8
11	10	PhSiH ₃ (3)	60	1	89	8.9	8.9
12	5	PhSiH ₃ (1)	60	1	54	10.8	10.8
13 ^a	5	PhSiH ₃ (2)	60	1	90	18.0	18.0
14	5	PhSiH ₃ (3)	60	1	88	17.6	17.6

Reaction conditions: Amine **3.32b** (0.10 mmol), required amount of silane, C₆D₆ (0.5 mL), amount of catalyst was calculated, then added to obtain the desired catalytic loading and CO₂. The yield was obtained by ¹H NMR using the –CH₂ protons of cyclohexane as an internal standard. TON and TOF are assigned to the number of hydride transferred. The catalytic studies were repeated twice. ^aOptimized condition.

General procedures for the catalytic functionalization of CO₂ using PhSiH₃ and amines:

Catalyst **2.20** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 20 equiv.), phenylsilane (24.6 μ L, 0.20 mmol, 40 equiv.), required amount of amine (0.10 mmol, 20 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S3.7 – S3.8 and the reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. The yields of product were reported according to the integration of ¹H NMR signals of R¹R²NC(=O)H at *ca.* 8 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[63] Formation of methylated amine was not observed throughout the catalytic reaction. The resulting formamides were purified by silica plug or silica gel chromatography using either ethyl acetate/hexanes or tetrahydrofuran as eluent to give the corresponding *N*-formamides as oil or crystalline solid.

Procedures for the gram-scale catalytic functionalization of CO₂ using PhSiH₃ and dibenzylamine **3.32f**:

Catalyst **2.20** (0.102 g, 0.253 mmol), internal standard cyclohexane (1.00 mL, 5.07 mmol, 20 equiv.), phenylsilane (1.25 mL, 10.1 mmol, 40 equiv.), dibenzylamine **3.32f** (1.00 g, 0.97 mL, 5.07 mmol, 20 equiv.) and C₆D₆ (25 mL) were loaded into a Schlenk bottle. The Schlenk bottle was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature and heated at 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. Full conversion was observed after an hour. The yield of product was reported according to the integration of ¹H NMR signals of (PhCH₂)₂NC(=O)H of **3.33f** at 8.07 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[63] Formation of methylated amine was not observed throughout the catalytic reaction. The resulting formamides were purified by silica plug or silica gel chromatography using either ethyl acetate/hexanes or tetrahydrofuran as eluent to give the corresponding *N*-formamides as oil.

Deuterium-labelling study of catalytic *N*-formylation using *d*₁₁-piperidine **3.32g-D**:

Catalyst **2.20** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 20 equiv.), phenylsilane (24.6 μ L, 0.20 mmol, 40 equiv.), *d*₁₁-piperidine **3.32g-D** (*D*, 98%, 9.87 μ L, 0.10 mmol, 20 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature and heated at 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic trials were repeated at least in triplicate. The identity of the product was determined according to the ¹H NMR signals of R¹R²NC(=O)*H* of **3.33g-D** at 7.76 ppm. A mixture of H₂ (4.47 ppm) and HD (4.33, 4.43, 4.54 ppm, ¹*J*_{HD} = 42.7 Hz) were observed in the crude reaction after an hour due to piperidine (2%) and *d*₁₁-piperidine (98%), respectively.

Catalytic *N*-formylation using piperidine **3.32g** and *d*₁₁-piperidine **3.32g-D** in 1:1 ratio:

Catalyst **2.20** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 20 equiv.), phenylsilane (24.6 μ L, 0.20 mmol, 40 equiv.), piperidine **3.32g** (4.94 μ L, 0.05 mmol, 10 equiv.), *d*₁₁-piperidine **3.32g-D** (*D*, 98%, 4.94 μ L, 0.05 mmol, 10 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature and heated at 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. The yield was calculated based on consumption of the amine **3.32g** in addition to the integration of the formoxy –CHO and non-labelled –CH₂ functional groups of the corresponding *N*-formamide against the –CH₂ integration of the internal standard cyclohexane. The identity of the product was determined according to the ¹H NMR signals of R¹R²NC(=O)*H* of **3.33g** and **3.33g-D** at 7.76 ppm and corresponding **3.33g** signals of 3.22 – 3.25 (m, 2H, CH₂), 2.51 – 2.54 (m, 2H, CH₂), 1.04 – 1.13 (m, 4H, CH₂), 0.91 – 0.96 (m, 2H, CH₂) in C₆D₆. A mixture of H₂ (4.47 ppm) and HD (4.33, 4.43, 4.54 ppm, ¹*J*_{HD} = 42.7 Hz) were observed in the crude reaction after an hour.

Reaction of PhSiH₃ with *d*₁₁-piperidine **3.32g-D** :

Internal standard cyclohexane (10.8 μL, 0.10 mmol), phenylsilane (24.6 μL, 0.20 mmol, 2.0 equiv.), *d*₁₁-piperidine **3.32g-D** (*D*, 98%, 9.87 μL, 0.10 mmol, 1.0 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The reaction was monitored by NMR spectroscopy at 24, 60 and 90 °C over 24 h. The catalytic studies were repeated at least in triplicate. Consumption of PhSiH₃ was not observed based on the integration of the silane signal at –SiH₃ against the –CH₂ integration of the internal standard cyclohexane. H₂ and HD signals were absent. In addition, no reaction was observed when piperidine **3.32g** (9.88 μL, 0.10 mmol, 1 equiv.) was used instead of *d*₁₁-piperidine.

General Procedure for stepwise hydrosilylation and subsequent amine addition:

Catalyst **2.20** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μL, 0.10 mmol, 20 equiv.), phenylsilane (24.6 μL, 0.20 mmol, 40 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S3.6 and the reaction was monitored by NMR spectroscopy. After catalytic hydrosilylation, CO₂ was removed *in vacuo* and the resulting solution was filtered into another J-Young NMR tube. Subsequently, the required amount of amine (0.10 mmol, 20 equiv.) was added. The resultant mixture was then heated and monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate.

Table S3. 6 Catalytic table for the stepwise *N*-formylation of amines using CO₂ via silylformate intermediates.

Entry	X	T (°C)	t (h)	Consumption of silane (%)	Product	Yield of 3.31 for stepwise (%)	Yield of 3.31 for catalysis (%)
1	5	60	3	15	3.31f	11	>99
2	5	40	19	24	3.31m	21	93
3	5	90	2	23	Control reaction		

Reaction conditions: PhSiH₃ (0.20 mmol), C₆D₆ (0.5 mL), catalytic amount of complex **2.20** and CO₂ (*ca.* 50.0 mg). After the hydrosilylation reaction, CO₂ was removed with its crude mixture filtered into another J-young NMR tube loaded with amine (0.10 mmol) was added. Catalyst loading is relative to amine. The yield was obtained by ¹H NMR using the –CH₂ protons of cyclohexane as an internal standard. All the catalytic trials were repeated in triplicate. All the catalytic trials were repeated in triplicate.

Catalytic hydrosilylation of carbon dioxide using PhSiH₃:

Catalyst **2.20** (4.0 mg, 0.01 mmol), internal standard cyclohexane (10.8 μL, 0.10 mmol, 10 equiv.), phenylsilane (24.6 μL, 0.20 mmol, 20 equiv.) and of C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature and heated at 90 °C. The reaction was monitored by NMR spectroscopy, which confirmed the formation of silylformates and siloxanes as the major products after 1 h. The catalytic studies were repeated at least in triplicate. The existence of intermediate and products (silylformates and siloxanes) were confirmed by ¹H, ¹³C{¹H} and ²⁹Si NMR spectroscopy, and HRMS spectrometry. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[36a,63a,63b,64]

Characterization of Silylformates:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): $\delta = 7.51 - 8.16$ (br, CHO , overlapped with siloxanes), 4.47 (s, Si-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, C_6D_6 , ppm): $\delta = 158.8$ (CHO). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are comparable to that as reported.^[36a,63a,63b,64a-c]

HRMS of Silylformates:

HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_9\text{O}_6\text{Si}$
[$\text{M}+\text{H}$] $^+$: 241.0168; found: 241.0161.

HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_9\text{O}_4\text{Si}$
[$\text{M}+\text{H}$] $^+$: 197.0270; found: 197.0264.

HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_9\text{O}_2\text{Si}$
[$\text{M}+\text{H}$] $^+$: 153.0372; found: 153.0368.

Characterization of Siloxanes:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): $\delta = 7.51 - 8.16$ (br, Ar-H , overlapped with silylformates) 6.80 – 7.35 (br, Ar-H), 5.06 – 5.63 (m, Si-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, C_6D_6 , ppm): $\delta = 135.0$ (br, Ar-C), 131.9 (br, Ar-C); ^{29}Si NMR (78.65 MHz, 24 °C, C_6D_6 , ppm): $\delta = -72.3$ (br), -38.4 (br). The ^{29}Si NMR spectrum is comparable to that as reported.^[63a,64d]

HRMS of Primary siloxanes:

HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{15}\text{OSi}_2$
[$\text{M}+\text{H}$] $^+$: 231.0661; found: 231.0657.

HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{Si}_3$
[$\text{M}+\text{H}$] $^+$: 353.0849; found: 353.0854.

HRMS (ESI): m/z calcd for $\text{C}_6\text{H}_9\text{OSi}$
[$\text{M}+\text{H}$] $^+$: 125.0423; found: 125.0417.

HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Si}_2$
[$\text{M}+\text{H}$] $^+$: 247.0611; found: 247.0618.

HRMS of Secondary Siloxanes:

HRMS (ESI): m/z calcd for $C_{18}H_{21}O_4Si_3$
[M+H]⁺: 385.0748; found: 385.0750.

HRMS (ESI): m/z calcd for $C_6H_9O_2Si$
[M+H]⁺: 141.0372; found: 141.0378.

HRMS (ESI): m/z calcd for $C_{12}H_{15}O_3Si_2$
[M+H]⁺: 263.0560; found: 263.0564.

HRMS of Intermediate:

HRMS (ESI): m/z calcd for $C_{21}H_{32}IN_4O_2Si_2$
[M+H]⁺: 555.1108; found: 555.1100.

Characterization of compound 3.31b:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.72 (s, 1H, CHO), 3.14 – 3.18 (m, 2H, CH_2), 2.85 – 2.90 (m, 5H, CH_2 and O- CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 37.9 (CH_2), 58.9 (CH_2), 71.0 (OCH_3), 161.3 (CHO).

Characterization of compound 3.31c:

82:18 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.15 (s, 1H, CHO), 8.03 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.3 Hz), 5.72 (br, 1H, NH), 5.60 (br, 1H, NH), 3.29 (q, 2H, CH_2 , $^3J_{\text{H,H}}$ = 7.26 Hz), 3.21 (q, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.67 Hz), 1.47 – 1.54 (m, 4H, CH_2), 1.31 – 1.40 (m, 4H, CH_2), 0.91 – 0.94 (m, 6H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 13.7 (CH_3), 13.8 (CH_3), 19.7 (CH_2), 20.1 (CH_2), 31.7 (CH_2), 33.4 (CH_2), 38.0 (CH_2), 41.6 (CH_2), 161.3 (CHO), 164.7 (CHO). HRMS (ESI): m/z calcd for $\text{C}_5\text{H}_{11}\text{NONa}$ 124.0738; found 124.0735.

Characterization of compound 3.31d:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.19 (s, 1H, CHO), 5.86 (br, 1H, NH), 4.09 – 4.11 (m, 2H, CH_2), 2.25 (t, 1H, CH, $^4J_{\text{H,H}}$ = 2.92 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 28.0 (CH_2), 72.1 ($\text{C}\equiv\text{C}$), 77.4 ($\text{C}\equiv\text{C}$), 160.7 (CHO).

Characterization of compound 3e:

60:40 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.68 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.6 Hz), 8.35 (s, 1H, CHO), 8.31 (br, NH), 7.52 – 7.54 (m, 2H, Ar-H), 7.30 – 7.37 (m, 4H, Ar-H), 7.11 – 7.21 (m, 2H, Ar-H), 7.08 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 7.7 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 119.0 (Ar-C), 120.1 (Ar-C), 124.9 (Ar-C), 125.4 (Ar-C), 129.2 (Ar-C), 129.9 (Ar-C), 136.8 (Ar-C), 137.0 (Ar-C), 159.2 (CHO), 162.8 (CHO).

Characterization of compound 3.31f:

52:48 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.68 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.36 Hz), 8.40 (br, 1H, NH), 8.35 (s, 1H, CHO), 7.50 (br, 1H, NH), 7.41 (s, 1H, Ar-H), 7.29 – 7.33 (m, 1H, Ar-H), 7.19 – 7.24 (m, 2H, Ar-H), 7.00 – 7.02 (m, 1H, Ar-H), 6.95 – 6.97 (m, 1H, Ar-H), 6.91 (s, 2H, Ar-H), 2.36 (s, 3H, CH_3), 2.34 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 21.5 (CH_3), 21.6 (CH_3), 115.9 (Ar-C), 117.2 (Ar-C), 119.7 (Ar-C), 120.8 (Ar-C), 125.7 (Ar-C), 126.2 (Ar-C), 129.0 (Ar-C), 129.7 (Ar-C), 136.7 (Ar-C), 136.9 (Ar-C), 139.2 (Ar-C), 140.0 (Ar-C), 159.2 (CHO), 162.9 (CHO).

Characterization of compound 3.31g:

50:50 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.63 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.61 Hz), 8.39 (br, 1H, NH), 8.33 (s, 1H, CHO), 7.54 (br, 1H, NH), 7.41 – 7.43 (m, 2H, Ar-H), 7.11 – 7.16 (m, 4H, Ar-H), 6.98 – 7.00 (m, 2H, Ar-H), 2.33 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 20.9 (CH_3), 21.0 (CH_3), 119.3 (Ar-C), 120.2 (Ar-C), 129.7 (Ar-C), 130.3 (Ar-C), 134.2 (Ar-C), 134.5 (Ar-C), 134.6 (Ar-C), 135.3 (Ar-C), 159.2 (CHO), 163.0 (CHO).

Characterization of compound 3.31h:

57:43 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.68 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.2 Hz), 8.39 (br, 1H, NH), 8.33 (s, 1H, CHO), 7.41 (br, 1H, NH), 7.17 (s, 2H, Ar-H), 6.83 (s, 1H, Ar-H), 6.78 (s, 1H, Ar-H), 6.71 (s, 2H, Ar-H), 2.31 (s, 6H, CH_3), 2.29 (s, 6H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 21.4 (CH_3), 21.5 (CH_3), 116.6 (Ar-C), 117.8 (Ar-C), 126.7 (Ar-C), 127.1 (Ar-C), 136.7 (Ar-C), 136.8 (Ar-C), 139.0 (Ar-C), 139.7 (Ar-C), 159.1 (CHO), 162.9 (CHO).

Characterization of compound 3.31k:

51:49 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.36 (s, 1H, CHO), 8.03 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.1 Hz), 6.93 (s, 2H, Ar-H), 6.90 (s, 2H, Ar-H), 6.80 (br, NH), 2.29 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.25 (s, 6H, CH_3), 2.20 (s, 6H, CH_3); ^{13}C NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 18.5 (CH_3), 18.6 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 125.6 (Ar-C), 129.0 (Ar-C), 129.4 (Ar-C), 129.7 (Ar-C), 135.1 (Ar-C), 135.2 (Ar-C), 137.5 (Ar-C), 137.7 (Ar-C), 160.0 (CHO), 165.5 (CHO).

Characterization of compound 3.31k':

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 9.12 (br, 2H, CHO), 6.99 (s, 2H, Ar-H), 2.31 (s, 3H, CH_3), 2.20 (s, 6H, CH_3); ^{13}C NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 17.9 (CH_3), 27.0 (CH_3), 127.8 (Ar-C), 130.5 (Ar-C), 134.3 (Ar-C), 139.9 (Ar-C), 163.3 (CHO).

Characterization of compound 3.31m:

61:39 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.48 (s, 1H, CHO), 8.03 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.0 Hz), 7.30 – 7.36 (m, 2H, Ar-H), 7.19 – 7.22 (m, 4H, Ar-H), 6.96 (br, 1H, NH), 6.72 (br, 1H, NH), 3.22 (sept, 2H, CH, $^3J_{\text{H,H}}$ = 6.6 Hz), 3.12 (sept, $^3J_{\text{H,H}}$ = 5.6 Hz, 2H, CH), 1.22 (d, 12H, CH_3 , $^3J_{\text{H,H}}$ = 6.8 Hz), 1.21 (d, 12H, CH_3 , $^3J_{\text{H,H}}$ = 6.8 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 23.9 (CH_3), 23.9 (CH_3), 28.7 (CH), 29.1 (CH), 123.9 (Ar-C), 124.2 (Ar-C), 129.1 (Ar-C), 129.3 (Ar-C), 129.7 (Ar-C), 130.2 (Ar-C), 146.4 (Ar-C), 147.1 (Ar-C), 160.8 (CHO), 165.3 (CHO).

Characterization of compound 3.31n:

52:48 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.50 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.7 Hz), 8.30 (s, 1H, CHO), 8.11 (br, NH), 7.43 – 7.45 (m, 2H, Ar-H), 7.02 – 7.04 (m, 2H, Ar-H), 6.84 – 6.89 (m, 4H, Ar-H), 3.80 (s, 3H, O-CH₃), 3.78 (s, 3H, O-CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 55.7 (OCH₃), 55.8 (OCH₃), 114.4 (Ar-C), 115.1 (Ar-C), 121.9 (Ar-C), 122.0 (Ar-C), 128.7 (Ar-C), 130.2 (Ar-C), 156.9 (Ar-C), 158.0 (Ar-C), 159.2 (CHO), 163.3 (CHO). HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_9\text{NO}_2\text{Na}$ 174.0531; found 174.0531.

Characterization of compound 3.31p:

69:31 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.73 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.5 Hz), 8.45 (s, 1H, CHO), 8.36 (dd, 2H, Ar-H, $^3J_{\text{H,H}}$ = 7.9 Hz), 7.83 (br, 1H, NH), 7.71 (br, 1H, NH), 7.05 – 7.20 (m, 3H, Ar-H), 6.88 – 6.98 (m, 3H, Ar-H), 3.88 (s, 3H, O-CH₃), 3.86 (s, 3H, O-CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 55.7 (O-CH₃), 55.8 (O-CH₃), 110.2 (Ar-C), 111.4 (Ar-C), 116.7 (Ar-C), 120.6 (Ar-C), 121.2 (Ar-C), 124.4 (Ar-C), 125.3 (Ar-C), 126.2 (Ar-C), 126.3 (Ar-C), 126.9 (Ar-C), 147.9 (Ar-C), 148.8 (Ar-C), 158.9 (CHO), 161.6 (CHO).

Characterization of compound 3.31r:

60:40 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.56 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.9 Hz), 8.38 (br, 1H, NH), 8.33 (s, 1H, CHO), 7.62 (br, 1H, NH), 7.48 – 7.52 (m, 2H, Ar-H), 6.99 – 7.07 (m, 6H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 115.7 (Ar-C), 116.0 (Ar-C), 116.5 (Ar-C), 116.8 (Ar-C), 121.2 (Ar-C), 121.3 (Ar-C), 121.9 (Ar-C), 122.0 (Ar-C), 159.2 (CHO), 163.1 (CHO).

Characterization of compound 3.31s:

63:37 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.64 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.0 Hz), 8.36 (s, 1H, CHO), 8.14 (br, 1H, NH), 7.49 – 7.51 (m, 2H, Ar-H), 7.42 (br, 1H, NH), 7.28 – 7.34 (m, 4H, Ar-H), 7.02 – 7.04 (m, 2H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 115.2 (Ar-C), 120.2 (Ar-C), 121.3 (Ar-C), 129.3 (Ar-C), 130.0 (Ar-C), 130.9 (Ar-C), 135.4 (Ar-C), 135.5 (Ar-C), 159.1 (CHO), 162.6 (CHO). HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_7\text{NOCl}$ 156.0216; found 156.0217.

Characterization of compound 3.31t:

71:29 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.73 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.0 Hz), 8.50 (s, 1H, CHO), 8.42 (d, 1H, Ar-H, $^3J_{\text{H,H}}$ = 8.1 Hz), 7.68 (br, NH), 7.44 (d, 1H, Ar-H, $^3J_{\text{H,H}}$ = 8.5 Hz), 7.39 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 7.5 Hz), 7.26 – 7.31 (m, 2H, Ar-H), 7.12 – 7.17 (m, 1H, Ar-H), 7.06 – 7.10 (m, 1H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 118.6 (Ar-C), 122.1 (Ar-C), 122.6 (Ar-C), 124.2 (Ar-C), 125.3 (Ar-C), 126.0 (Ar-C), 128.0 (Ar-C), 128.2 (Ar-C), 129.3 (Ar-C), 130.5 (Ar-C), 133.8 (Ar-C), 133.9 (Ar-C), 158.9 (CHO), 161.5 (CHO).

Characterization of compound 3.31u:

84:16 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.26 (s, 1H, CHO), 8.18 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.1 Hz), 7.28 – 7.38 (m, 10H, Ar-H), 5.89 (br, NH), 4.48 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.1 Hz), 4.41 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 7.0 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 42.3 (CH_2), 45.8 (CH_2), 127.1 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 128.9 (Ar-C), 129.0 (Ar-C), 137.6 (Ar-C), 137.7 (Ar-C), 161.1 (CHO), 164.7 (CHO). HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_9\text{NONa}$ 158.0582; found 158.0582.

Characterization of compound 3.31v:

87:13 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.22 (s, 1H, CHO), 8.17 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.8 Hz), 7.21 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.8 Hz), 7.16 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 9.5 Hz), 6.85 – 6.87 (m, 2H, Ar-H), 6.71 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 9.5 Hz), 5.90 (br, NH), 4.41 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.8 Hz), 4.34 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.1 Hz), 3.80 (s, 3H, O- CH_3), 3.79 (s, 3H, O- CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 41.8 (CH_2), 55.5 (O- CH_3), 114.3 (Ar-C), 114.4 (Ar-C), 128.4 (Ar-C), 129.3 (Ar-C), 160.9 (CHO).

Characterization of compound 3.31w:

87:13 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.23 (s, 1H, CHO), 8.14 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.3 Hz), 7.27 – 7.34 (m, 4H, Ar-H), 7.19 – 7.24 (m, 4H, Ar-H), 6.12 (br, NH), 4.42 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.0 Hz), 4.36 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.8 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 41.6 (CH_2), 45.1 (CH_2), 127.9 (Ar-C), 128.4 (Ar-C), 129.0 (Ar-C), 129.2 (Ar-C), 133.6 (Ar-C), 133.9 (Ar-C), 136.1 (Ar-C), 136.3 (Ar-C), 161.2 (CHO), 164.7 (CHO).

Characterization of compound 3.31x:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.26 (s, 1H, CHO), 7.35 – 7.42 (m, 3H, Ar-H), 7.18 – 7.22 (m, 1H, Ar-H), 4.59 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.0 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 40.3 (CH_2), 127.4 (Ar-C), 129.4 (Ar-C), 129.7 (Ar-C), 130.5 (Ar-C), 133.8 (Ar-C), 135.2 (Ar-C), 161.0 (CHO).

Characterization of compound 3.33a:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.04 (s, 1H, CHO), 3.36 (q, 2H, CH_2 , $^3J_{\text{H,H}}$ = 7.1 Hz), 3.27 (q, 2H, CH_2 , $^3J_{\text{H,H}}$ = 7.1 Hz), 1.19 (t, 3H, CH_3 , $^3J_{\text{H,H}}$ = 7.2 Hz), 1.13 (t, 3H, CH_3 , $^3J_{\text{H,H}}$ = 7.2 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 12.9 (CH_3), 15.0 (CH_3), 36.7 (CH_2), 42.0 (CH_2), 162.4 (CHO). HRMS (ESI): m/z calcd for $\text{C}_5\text{H}_{12}\text{NO}$ 102.0919; found 102.0909.

Characterization of compound 3.33b:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.17 (s, 1H, CHO), 4.17 (sept, 1H, CH, $^3J_{\text{H,H}}$ = 6.8 Hz), 3.59 (sept, 1H, CH, $^3J_{\text{H,H}}$ = 6.8 Hz), 1.27 (d, 6H, CH_3 , $^3J_{\text{H,H}}$ = 6.8 Hz), 1.24 (d, 6H, CH_3 , $^3J_{\text{H,H}}$ = 6.8 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 20.3 (CH_3), 23.5 (CH_3), 44.1 (CH), 46.8 (CH), 162.0 (CHO).

Characterization of compound 3.33c:

54:46 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.07 (s, 1H, CHO), 8.00 (s, 1H, CHO), 4.16 (d, 2H, CH_2 , $^4J_{\text{H,H}}$ = 3.30 Hz), 3.99 (d, 2H, CH_2 , $^4J_{\text{H,H}}$ = 2.28 Hz), 3.01 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 2.34 (t, 1H, CH, $^4J_{\text{H,H}}$ = 2.33 Hz), 2.22 (t, 1H, CH, $^4J_{\text{H,H}}$ = 2.89 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 29.5 (CH_3), 33.2 (CH_3), 33.8 (CH_2), 39.2 (CH_2), 72.5 (CH), 73.8 (CH), 127.7 ($\text{C}\equiv\text{C}$), 134.2 ($\text{C}\equiv\text{C}$), 162.2 (CHO), 162.3 (CHO).

Characterization of compound 3.33e:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.43 (s, 1H, CHO), 7.36 – 7.41 (m, 2H, Ar-H), 7.24 – 7.28 (m, 1H, Ar-H), 7.12 – 7.14 (m, 2H, Ar-H), 3.29 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, C_6D_6 , ppm): δ = 31.1 (CH_3), 121.8 (Ar-C), 125.6 (Ar-C), 129.5 (Ar-C), 142.6 (Ar-C), 161.8 (CHO). HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_8\text{NO}$ 122.0606; found 122.0607.

Characterization of compound 3.33f:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.07 (s, 1H, CHO), 7.03 – 7.07 (m, 8H, Ar-H), 6.75 – 6.77 (m, 2H, Ar-H), 4.30 (s, 2H, CH_2), 3.60 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, C_6D_6 , ppm): δ = 44.6 (CH_2), 49.7 (CH_2), 127.7 (Ar-C), 127.9 (Ar-C), 128.8 (Ar-C), 128.9 (Ar-C), 128.9 (Ar-C), 134.6 (Ar-C), 136.7 (Ar-C), 137.1 (Ar-C), 162.4 (CHO).

Characterization of compound 3.33g:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 7.97 (s, 1H, CHO), 3.46 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.3 Hz), 3.28 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.3 Hz), 1.64 – 1.69 (m, 2H, CH_2), 1.49 – 1.59 (m, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 24.8 (CH_2), 25.2 (CH_2), 26.7 (CH_2), 40.8 (CH_2), 47.0 (CH_2), 161.0 (CHO). HRMS (ESI): m/z calcd for $\text{C}_6\text{H}_{12}\text{NO}$ 114.0919; found 114.0919.

Characterization of compound 3.33h:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.03 (s, 1H, CHO), 3.63 – 3.69 (m, 4H, CH_2), 3.54 – 3.56 (m, 2H, CH_2), 3.36 – 3.38 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 40.8 (CH_2), 45.9 (CH_2), 66.5 (CH_2), 67.3 (CH_2), 161.1 (CHO). HRMS (ESI): m/z calcd for $\text{C}_5\text{H}_9\text{NO}_2\text{Na}$ 138.0531; found 138.0531.

Characterization of compound 3.33k:

83:17 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.93 (s, 1H, CHO), 8.51 (s, 1H, CHO), 8.07 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 9.1 Hz), 7.15 – 7.25 (m, 5H, Ar-H), 7.03 – 7.07 (m, 1H, Ar-H), 4.03 – 4.31 (m, 4H, CH_2), 3.13 – 3.21 (m, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 27.3 (CH_2), 27.9 (CH_2), 44.8 (CH_2), 47.1 (CH_2), 109.5 (Ar-C), 116.8 (Ar-C), 124.4 (Ar-C), 124.8 (Ar-C), 125.0 (Ar-C), 126.2 (Ar-C), 127.7 (Ar-C), 128.0 (Ar-C), 128.1 (Ar-C), 132.1 (Ar-C), 141.2 (Ar-C), 142.9 (Ar-C), 157.7 (CHO), 159.4 (CHO).

Characterization of compound 3.33m:

93:7 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.79 (s, 1H, CHO), 8.33 (s, NH), 8.29 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 20.1 Hz), 7.08 – 7.20 (m, 8H, Ar-H), 3.81 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.0 Hz), 3.66 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 14.9 Hz), 2.90 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 14.4 Hz), 2.82 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.0 Hz), 2.02 – 2.07 (m, 2H, CH_2), 1.93 – 1.99 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 22.5 (CH_2), 27.4 (CH_2), 40.5 (CH_2), 117.3 (Ar-C), 124.8 (Ar-C), 127.4 (Ar-C), 128.1 (Ar-C), 129.2 (Ar-C), 129.9 (Ar-C), 161.4 (CHO).

Table S3. 7 Catalytic table for *N*-formylation of primary amines using phenylsilane. Isolated yields are shown in parentheses.

$$\text{CO}_2 + \text{R}-\text{N}-\text{H} \xrightarrow[\text{C}_6\text{D}_6, \text{ Temperature (T), Time (t)}]{\text{Catalyst } \mathbf{2.20} \text{ (5 mol \%)} \quad 2 \text{ equiv. PhSiH}_3} \text{R}-\text{N}-\text{C}(=\text{O})-\text{H}$$

3.30 **3.31**

Entry	Primary Amine	Product	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1	3.30a	3.31a	60	24	0	-
2	3.30b	3.31b	60	1	>99 (70)	20.0
3	3.30c	3.31c	60	1	>99 (70)	20.0
4	2d	3.31d	60	2	>99 (61)	10.0
5	3.30e	3.31e	60	2	>99 (99)	10.0
6	3.30f	3.31f	60	3	>99 (99)	6.7
7	3.30g	3.31g	60	2	>99 (99)	10.0

Entry	Primary Amine	Product	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
8	3.30h	3.31h	40	14	>99 (99)	1.4
9	3.30k	3.31k 3.31k'	40	3	75 (40) 3.31k:3.31k' in 3:2 ratio	5.0
10	3.30m	3.31m	40	19	93 (70)	1.0
11	3.30n	3.31n	60	2	>99 (99)	10.0
12	3.30p	3.31p	60	1.5	>99 (99)	13.3
13	3.30q	3.31q	60	4	>99	5.0

Entry	Primary Amine	Product	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
14	3.30r	3.31r	60	3	>99 (99)	6.7
15	3.30s	3.31s	60	3	>99 (80)	6.7
16	3.30t	3.31t	60	4	95 (42)	4.8
17	3.30u	3.31u	60	3	>99 (99)	6.7
18	3.30v	3.31v	40	3	79 (43)	5.3
19	3.30w	3.31w	40	3	>99 (99)	6.1
20	3.30x	3.31x	40	4	81 (31)	4.1

Table S3. 8 Catalytic table for *N*-formylation of secondary amines using phenylsilane. Isolated yields are shown in parentheses.

$$\text{CO}_2 + \begin{array}{c} \text{R}^1 \\ | \\ \text{N}-\text{H} \\ | \\ \text{R}^2 \\ \text{3.32} \end{array} \xrightarrow[\text{C}_6\text{D}_6, \text{ Temperature (T), Time (t)}]{\text{Catalyst } \textbf{2.20} \text{ (5 mol \%)} \\ \text{2 equiv. PhSiH}_3} \begin{array}{c} \text{R}^1 \\ | \\ \text{N}-\text{C}(=\text{O})-\text{H} \\ | \\ \text{R}^2 \\ \text{3.33} \end{array}$$

Entry	Secondary Amine	Product	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1	3.32a	3.33a	60	0.5	>99 (46)	40.0
2	3.32b	3.33b	60	1	85 (72)	17.0
3	3.32c	3.33c	60	1	>99 (70)	20.0
4	3.32d	3.33d	90	24	0	-
5	3.32e	3.33e	40	3	95 (95)	6.3
6	3.32f	3.33f	60	1	>99 (99)	20.0

Entry	Secondary Amine	Product	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
7	3.32g	3.33g	60	1	>99 (69)	20.0
8	3.32h	3.33h	60	1	>99 (70)	20.0
9	3.32k	3.33k	40	1	>99 (90)	20.0
10	3.32m	3.33m	40	1	>99 (97)	20.0
11	3.32n	3.33n	90	1	>99	20
12	3.32p	3.33p	60	2	>99	10.0

Entry	Secondary Amine	Product	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
13	3.32q	3.33q	60	3	>99	6.7
14	3.32r	3.33r	90	1	>99	20.0

3.4.3 A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of Aldehyde, Ketone and Pyridine Derivatives

General procedures for the catalytic hydroboration of aldehyde, ketone and pyridine derivatives using 2.20 as the catalyst:

Catalyst **2.20** (4.0 mg, 0.01 mmol) and 0.5 mL of C₆D₆ were added into a J-Young NMR tube. Pinacolborane, HBpin (16.0 μ L, 0.11 mmol, 10.1 equiv.) and substrates (0.10 mmol, 10 equiv.) were then added. The reaction conditions are indicated in Table S3.9 – S3.11 and the reactions were followed by NMR spectroscopy to determine their yields. The chemical shifts of the products are in good agreement with the reported values in the literatures.^[65] All the catalytic trials were repeated in triplicate.

Isolation of product **3.42a – v** and **3.44a – k**

Upon completion of the catalyses, the resulting crude solutions were filtered and the filtrates were dried under vacuum. The dried residues were then further extracted with hexane. The resultant borate esters were isolated by removing volatiles under vacuum for a few hours.

Isolation of product **3.46a – f**

Upon completion of the catalyses, the resulting crude solutions were filtered and the filtrates were dried under vacuum. The dried residues were then further extracted with either diethyl ether, pentane or hexane. The resultant *N*-boryl-1,4-dihydropyridine derivatives were isolated by removing volatiles under vacuum for a few hours.

Characterization of compound **3.42a**:

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 7.30 (d, 2H, Ar-*H*, ³*J*_{H,H} = 7.2 Hz), 7.13 (t, 2H, Ar-*H*, ³*J*_{H,H} = 7.5 Hz), 7.07 – 7.03 (m, 1H, Ar-*H*), 4.94 (s, 2H, O-CH₂), 1.04 (s, 12H, Bpin-CH₃). ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.8.

Characterization of compound **3.42b**:

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 7.25 (d, 2H, Ar-*H*, ³*J*_{H,H} = 7.7 Hz), 6.96 (d, 2H, Ar-*H*, ³*J*_{H,H} = 8.2 Hz), 4.95 (s, 2H, O-CH₂), 2.08 (s, 3H, -CH₃), 1.05 (s, 12H, Bpin-CH₃). ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.9.

Characterization of compound 3.42c:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.09 – 7.06 (m, 1H, Ar-*H*), 6.99 (s, 1H, Ar-*H*), 6.92 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.2 Hz), 6.71 (dd, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 2.3, 8.2 Hz), 4.94 (s, 2H, O-*CH*₂), 3.32 (s, 3H, O-*CH*₃), 1.05 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42d:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 3.73 (d, 2H, O-*CH*₂, $^3J_{\text{H,H}}$ = 4.5 Hz), 1.71 – 1.38 (m, 11H, Cy-*H*), 1.07 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 3.42e:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.08 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.2 Hz), 7.22 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.7 Hz), 4.85 (s, 2H, O-*CH*₂), 3.47 (s, 3H, O-*CH*₃), 1.03 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42f:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.88 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 5.0 Hz), 6.82 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 3.2 Hz), 6.69 – 6.67 (m, 1H, Ar-*H*), 4.98 (s, 2H, O-*CH*₂), 1.04 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42g:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 4.76 (s, 2H, O-*CH*₂), 4.21 (t, 2H, Cp1-*H*, $^3J_{\text{H,H}}$ = 1.8 Hz), 3.98 (s, 5H, Cp2-*H*), 3.95 (t, 2H, Cp1-*H*, $^3J_{\text{H,H}}$ = 1.8 Hz), 1.08 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42h:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 5.59 (s, 2H, $\text{C}=\text{CH}$), 3.78 (d, 2H, $\text{O}-\text{CH}_2$, $^3J_{\text{H,H}}$ = 5.9 Hz), 2.03 – 1.67 (m, 7H, Cy- H), 1.06 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 3.42k:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.90 (d, 1H, Ar- H , $^3J_{\text{H,H}}$ = 8.2), 6.75 (dd, 1H, Ar- H , $^3J_{\text{H,H}}$ = 1.8, 8.2 Hz), 6.68 (d, 1H, Ar- H , $^3J_{\text{H,H}}$ = 1.3 Hz), 6.59 (d, 1H, Ar- CH , $^3J_{\text{H,H}}$ = 15.9 Hz), 6.12 (dt, 1H, Ar- $\text{C}=\text{CH}$, $^3J_{\text{H,H}}$ = 5.2, 15.9 Hz), 4.58 (dd, 2H, $\text{O}-\text{CH}_2$, $^3J_{\text{H,H}}$ = 1.6, 5.2 Hz), 3.26 (s, 3H, CO_2-CH_3), 1.90 (s, 3H, ArO- CH_3), 1.08 (s, 12H, Bpin- CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 24 °C, C_6D_6 , ppm): δ = 168.1 ($\text{C}=\text{O}$), 151.9 (Ar- C), 140.2 (Ar- C), 136.1 ($\text{CH}=\text{CH}$), 130.3 (Ar- C), 127.7 (Ar- C), 123.3 ($\text{CH}=\text{CH}$), 119.2 (Ar- C), 110.6 (Ar- C), 82.8 ($\text{C}(\text{CH}_3)_2\text{-Bpin}$), 65.5 ($\text{O}-\text{CH}_2$), 55.3 (CO_2-CH_3), 24.7 (Bpin- CH_3), 20.3 ($\text{O}-\text{CH}_3$).

Characterization of compound 3.42m:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 3.65 (s, 2H, $\text{O}-\text{CH}_2$), 1.07 (s, 12H, Bpin- CH_3), 0.90 (s, 9H, $-\text{CH}_3$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 3.42n:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.05 (m, 1H, Ar- H), 6.13 (d, 1H, Ar- H , $^3J_{\text{H,H}}$ = 3.2 Hz), 6.02 – 6.01 (m, 1H, Ar- H), 4.85 (s, 2H, $\text{O}-\text{CH}_2$), 1.03 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42p:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.18 (d, 2H, Ar- H , $^3J_{\text{H,H}}$ = 7.2 Hz), 7.08 (t, 2H, Ar- H , $^3J_{\text{H,H}}$ = 7.2 Hz), 7.03 – 6.99 (m, 1H, Ar- H), 6.61 (d, 1H, Ar- CH , $^3J_{\text{H,H}}$ = 16.3 Hz), 6.17 (dt, 1H, Ar- $\text{C}=\text{CH}$, $^3J_{\text{H,H}}$ = 5.2, 15.9 Hz), 4.54 (dd, 2H, $\text{O}-\text{CH}_2$, $^3J_{\text{H,H}}$ = 5.2 Hz, $^4J_{\text{H,H}}$ = 1.6 Hz), 1.06 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42q:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.09 – 7.05 (m, 2H, Ar-*H*), 6.78 – 6.74 (m, 2H, Ar-*H*), 4.80 (s, 2H, O- CH_2), 1.04 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42r:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.21 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.6 Hz), 6.93 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.6 Hz), 4.73 (s, 2H, O- CH_2), 1.03 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42s:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.20 – 7.12 (m, 4H [overlap with C_6D_6], Ar-*H*), 7.06 – 7.02 (m, 1H, Ar-*H*), 6.69 (s, 1H, C= CH), 4.46 (s, 2H, O- CH_2), 1.72 (s, 3H, C- CH_3), 1.08 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 3.42t:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.99 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 4.6 Hz), 6.87 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 5.4 Hz), 4.67 (s, 2H, O- CH_2), 1.04 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 3.42u:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 9.17 (s, 1H, Ar-*H*), 8.54 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 5.9 Hz), 7.64 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.2 Hz), 7.43 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 5.9 Hz), 7.35 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.2 Hz), 7.10 (t, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.5 Hz), 5.23 (s, 2H, O- CH_2), 1.05 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 3.42v:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.75 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.2 Hz), 7.21 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.6 Hz), 4.88 (s, 2H, O- CH_2), 2.08 (s, 3H, C- CH_3), 1.05 (s 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 3.44a:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.37 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.7 Hz), 7.16 – 7.12 (m, 2H [overlap with C_6D_6], Ar-*H*), 7.07 – 7.03 (m, 1H, Ar-*H*), 5.42 (q, 1H, O- CH , $^3J_{\text{H,H}}$ = 6.5 Hz), 1.46 (d, 3H, OCH- CH_3 , $^3J_{\text{H,H}}$ = 6.3 Hz), 1.02 (s, 6H, Bpin- CH_3), 1.00 (s, 6H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 3.44b:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.85 (s, 1H, Ar-*H*), 7.62 – 7.59 (m, 3H, Ar-*H*), 7.47 (dd, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 1.8, 8.6 Hz), 7.26 – 7.20 (m, 2H, Ar-*H*), 5.58 (q, 1H, O- CH , $^3J_{\text{H,H}}$ = 6.3 Hz), 1.55 (d, 3H, OCH- CH_3 , $^3J_{\text{H,H}}$ = 6.4 Hz), 1.03 (s, 6H, Bpin- CH_3), 1.00 (s, 6H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 3.44c:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.97 – 7.95 (m, 1H, Ar-*H*), 7.88 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.2 Hz), 7.64 – 7.62 (m, 1H, Ar-*H*), 7.54 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.2 Hz), 7.30 – 7.26 (m, 1H, Ar-*H*), 7.25 – 7.20 (m, 2H, Ar-*H*), 6.19 (q, 1H, O- CH , $^3J_{\text{H,H}}$ = 6.3 Hz), 1.63 (d, 3H, OCH- CH_3 , $^3J_{\text{H,H}}$ = 6.3 Hz), 1.02 (s, 6H, Bpin- CH_3), 0.98 (s, 6H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 3.44d:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 4.35 – 4.29 (m, 1H, O-CH), 3.53 – 3.46 (m, 4H, O-CH₂), 1.92 – 1.85 (m, 6H, Cy-H), 1.58 – 1.47 (m, 2H, Cy-H), 1.06 (s, 12H, Bpin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.3.

Characterization of compound 3.44e:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 4.15 (dq, 1H, O-CH, $^3J_{\text{H,H}}$ = 6.1 Hz), 1.69 – 1.61 (m, 1H, (CH₃)₂CH), 1.16 (d, 3H, -CH₃, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.07 (s, 12H, Bpin-CH₃), 0.92 (d, 3H, -CH₃, $^3J_{\text{H,H}}$ = 6.4 Hz), 0.86 (d, 3H, -CH₃, $^3J_{\text{H,H}}$ = 6.8 Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.5.

Characterization of compound 3.44f:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.85 (dd, 1H, Ar-H, $^3J_{\text{H,H}}$ = 0.9, 3.6 Hz), 6.82 (dd, 1H, Ar-H, $^3J_{\text{H,H}}$ = 0.9, 5.0 Hz), 6.69 (dd, 1H, Ar-H, $^3J_{\text{H,H}}$ = 3.6, 5.0 Hz), 5.64 (q, 1H, O-CH, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.52 (d, 3H, OCH-CH₃, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.03 (s, 12H, Bpin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 3.44g:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.38 (d, 1H, Ar-H, $^3J_{\text{H,H}}$ = 5.0 Hz), 7.30 (d, 1H, Ar-H, $^3J_{\text{H,H}}$ = 7.7 Hz), 7.15 – 7.10 (m, 1H, Ar-H), 6.64 – 6.61 (m, 1H, Ar-H), 5.54 (q, 1H, O-CH, $^3J_{\text{H,H}}$ = 6.7 Hz), 1.60 (d, 3H, OCH-CH₃, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.13 (s, 6H, Bpin-CH₃), 1.11 (s, 6H, Bpin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 19.5.

Characterization of compound 3.44h:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ 7.23 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.6 Hz), 6.99, (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.2 Hz), 5.23 (q, 1H, O-CH, $^3J_{\text{H,H}}$ = 6.5 Hz), 1.33 (d, 3H, OCH-CH₃, $^3J_{\text{H,H}}$ = 6.4 Hz), 1.02 (s, 6H, Bpin-CH₃), 0.99 (s, 6H, Bpin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.5.

Characterization of compound 3.44k:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.02 – 6.94 (m, 4H, Ar-*H*), 5.15 (q, 1H, O-*CH*, $^3J_{\text{H,H}}$ = 6.5 Hz), 1.23 (d, 3H, OCH-*CH*₃, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.02 (s, 6H, Bpin-*CH*₃), 0.99 (s, 6H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 3.46a:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.52 – 6.50 (m, 2H, N=*CH*), 4.59 – 4.55 (m, 2H, C=*CH*), 2.83 – 2.81 (m, 2H, -*CH*₂), 0.98 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 23.1.

Characterization of compound 3.46b:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.83 (s, 1H, N=*CH*), 6.33 (d, 1H, N=*CH*, $^3J_{\text{H,H}}$ = 6.8 Hz), 4.70 – 4.68 (m, 1H, C=*CH*), 3.40 (s, 3H, O-*CH*₃), 3.20 (s, 2H, -*CH*₂), 0.93 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 23.1.

Characterization of compound 3.46c:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.82 (d, 1H, N=*CH*, $^3J_{\text{H,H}}$ = 0.9 Hz), 6.05 (dq, 1H, N=*CH*, $^3J_{\text{H,H}}$ = 1.7, 8.2 Hz), 4.30 (dt, 1H, C=*CH*, $^3J_{\text{H,H}}$ = 3.4, 8.2 Hz), 2.62 (t, 2H, -*CH*₂, $^3J_{\text{H,H}}$ = 1.4 Hz), 0.94 (s, 12H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 22.7.

Characterization of compound 3.46d:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.80 (d, 1H, $\text{N}=\text{CH}$, $^3J_{\text{H,H}} = 8.2$ Hz), 7.11 – 7.07 (m, 1H, Ar- H), 6.86 – 6.78 (m, 2H, Ar- H), 6.26 (d, 1H, Ar- H , $^3J_{\text{H,H}} = 9.1$ Hz), 5.60 – 5.56 (m, 1H, $\text{C}=\text{CH}$), 4.16 – 4.15 (m, 2H, $-\text{CH}_2$), 1.04 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 23.0.

Characterization of compound 3.46e:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.62 – 6.61 (m, 1H, $\text{N}=\text{CH}$), 6.48 (d, 1H, $\text{N}=\text{CH}$, $^3J_{\text{H,H}} = 1.8$ Hz), 4.32 – 4.30 (m, 1H, $\text{C}=\text{CH}$), 2.30 (s, 2H, $-\text{CH}_2$), 1.04 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 23.6.

Characterization of compound 3.46f:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.17 (d, 1H, $\text{N}=\text{CH}$, $^3J_{\text{H,H}} = 4.5$ Hz), 6.28 (dt, 1H, $\text{C}=\text{CH}$, $^3J_{\text{H,H}} = 1.5, 4.9$ Hz), 4.82 (s, 1H, $\text{N}=\text{CH}$), 3.83 – 3.81 (m, 2H, $-\text{CH}_2$), 1.06 (s, 12H, Bpin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 23.2.

Table S3. 9 Catalytic table for hydroboration of aldehyde derivatives using HBpin. Isolated yields are shown in parentheses.

Entry	Aldehyde	Product	Cat	X	T (°C)	t (min)	Yield (%)	TOF (h ⁻¹)
1	 3.41a	 3.42a	-	-	24	25	0	-
2	 3.41a	 3.42a	I _{Me}	0.1	24	20	23.9	717
3	 3.41a	 3.42a	2.20	1	24	25	90.1	216.2
4	 3.41a	 3.42a	2.20	5	24	20	98.0	58.8
5	 3.41a	 3.42a	2.20	10	24	10	>99 (89)	115.8
6	 3.41b	 3.42b	2.20	10	24	10	>99 (91)	115.8
7	 3.41c	 3.42c	2.20	10	24	10	>99 (87)	115.8

Entry	Aldehyde	Product	Cat	X	T (°C)	t (min)	Yield (%)	TOF (h ⁻¹)
8	3.41d	3.42d	2.20	10	24	10	>99 (87)	115.8
9	3.41e	3.42e	2.20	10	24	10	>99 (83)	115.8
10	3.41f	3.42f	2.20	10	24	10	>99 (82)	115.8
11	3.41g	3.42g	2.20	10	24	5	>99 (86)	118.8
12	3.41h	3.42h	2.20	10	24	10	>99 (86)	115.8
13	3.41k	3.42k	2.20	10	24	10	>99 (85)	115.8
14	3.41m	3.42m	2.20	10	24	30	>99 (83)	19.8
15	3.41n	3.42n	2.20	10	24	25	>99 (89)	23.8

	3.41n	3.42n						
Entry	Aldehyde	Product	Cat	X	T (°C)	t (min)	Yield (%)	TOF (h ⁻¹)
16			2.20	10	24	10	>99 (89)	115.8
	3.41p	3.42p						
17			2.20	10	24	10	>99 (85)	115.8
	3.41q	3.42q						
18			2.20	10	24	35	>99 (89)	17.0
	3.41r	3.42r						
19			2.20	10	24	20	>99 (85)	29.7
	3.41s	3.42s						
20			2.20	10	24	15	>99 (91)	39.6
	3.41t	3.42t						
21			2.20	10	24	15	>99 (89)	39.6
	3.41u	3.42u						
22			2.20	10	40	40	>99 (91)	14.9

	3.41v	3.42v			
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Table S3. 10 Catalytic table for hydroboration of ketone derivatives using HBpin. Isolated yields are shown in parentheses.

Entry	Ketone	Product	Cat	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1	3.43a	3.44a	-	-	90	24	0	-
2	3.43a	3.44a	I _{Me}	0.1	90	24	0	-
3	3.43a	3.44a	2.20	1	90	6	20.9	3.48
4	3.43a	3.44a	2.20	5	90	6	62.7	2.09
5	3.43a	3.44a	2.20	10	90	6	>99 (84)	1.65

6	3.43b	3.44b	2.20	10	90	5	>99 (90)	1.98
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Entry	Ketone	Product	Cat	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
7	3.43c	3.44c	2.20	10	90	6	>99 (86)	1.65
8	3.43d	3.44d	2.20	10	90	1	>99 (85)	9.90
9	3.43e	3.44e	2.20	10	90	14	>99 (89)	0.71
10	3.43f	3.44f	2.20	10	90	24	75 (66)	0.31
11	3.43g	3.44g	2.20	10	90	7	>99 (91)	1.41
12	3.43h	3.44h	2.20	10	90	24	84 (75)	0.35

13	3.43k	3.44k	2.20	10	90	1	>99 (90)	9.90
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Table S3. 11 Catalytic table for hydroboration of pyridine derivatives using HBpin. Isolated yields are shown in parentheses.

Entry	Pyridine	Product	Cat	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1	3.45a	3.46a	-	-	90	24	0	-
2	3.45a	3.46a	I _{Me}	0.1	90	24	0	-
3	3.45a	3.46a	I _{Me}	10	90	24	0	-
4	3.45a	3.46a	Ph ₃ SiH	10	24	24	0	0
5	3.45a	3.46a	(EtO) ₃ SiH	10	24	24	0	0

	3.45a	3.46a					
6			2.20	1	90	4	26.8 6.7
	3.45a	3.46a					

Entry	Pyridine	Product	Cat	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
7	3.45a	3.46a	2.20	5	90	4	32.5	1.63
8	3.45a	3.46a	2.20	10	90	4	>99 (90)	2.48
9	3.45b	3.46b	2.20	10	90	0.25	>99 (89)	39.6
10	3.45c	3.46c	2.20	10	90	2	89 (80)	4.45
11	3.45d	3.46d	2.20	10	90	9	>99 (91)	1.1

12	3.45e	3.46e	2.20	10	90	4	>99 (84)	2.48
13	3.45f	3.46f	2.20	10	90	24	67 (59)	1.98

General procedures for the catalytic hydroboration of aldehyde, ketone and pyridine derivatives using 3.28 as the catalyst:

Catalyst **3.28** (5.3 mg, 0.01 mmol), HBpin (16.0 μ L, 0.11 mmol, 1.1 equiv.) and substrates (0.10 mmol, 1 equiv.) were mixed with 0.5 mL of C_6D_6 in a J-Young NMR tube at ambient temperature. The reaction mixture was stirred with the reaction conditions stated in Table S3.12 – S3.14. The reactions were monitored by NMR spectroscopy to determine their yields. The chemical shifts of the products agree with the reported values in the literatures.^[65] All the catalytic trials were repeated in triplicate.

Table S3. 12 Catalytic table for hydroboration of aldehyde derivatives using HBpin.

Entry	Aldehyde	Product	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1	3.41a	3.42a	0.1	24	0.08	43	5375
2			2.5	24	0.08	86	430
			2.5	24	0.17	>99	235

Table S3. 13 Catalytic table for hydroboration of ketone derivatives using HBpin.

Entry	Ketone	Product	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1			3	90	0.08	8.9	37
			3	90	0.58	31	18
2	3.43d	3.44d	5	90	0.17	65	77
			5	90	1.00	>99	20

Table S3. 14 Catalytic table for hydroboration of pyridine derivatives using HBpin.

Entry	Pyridine	Product	X	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1			3	90	1	18	6.0
			3	90	3	72	8.0
			3	90	4	>99	8.3

3.5 Appendices

3.5.1 NMR Spectra

List of abbreviation used in NMR spectra.

Abbreviation	Definition
Cat	Catalyst
HBpin	Pinacolborane
IS	Internal standard
sm	Starting material (substrate)
pdt	Hydroboration product

A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of CO₂

Figure S3. 1 ¹H NMR spectrum of compound **3.28** (in C₆D₆).

Figure S3. 2 ^{11}B NMR spectrum of compound **3.28** (in C_6D_6).

Figure S3. 3 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3.28** (in C_6D_6).

Figure S3. 4 ^{29}Si NMR spectrum of compound **3.28** (in C_6D_6).

(a)

(b)

(c)

Figure S3. 5 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **3.28** (in C_6D_6), (a) before flattening the baseline, (b) after flattening the baseline, (c) focus view.

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 20-20 H: 37-37 B: 1-1 N: 4-4 O: 1-2 Si: 1-1 I: 1-1

C20H36BIN4O2Si

CCC-SIB 6 (0.130)

1: TOF MS ES+
1.01e+000

Figure S3. 6 ESI-MS of 3.28.

Figure S3. 7 ¹H NMR spectrum of compound [(Ime)₂Bpin]I (in CDCl₃).

Figure S3. 8 ^{11}B NMR spectrum of compound $[(\text{Ime})_2\text{Bpin}]\text{I}$ (in CDCl_3).

Figure S3. 9 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound $[(\text{Ime})_2\text{Bpin}]\text{I}$ (in CDCl_3).

Figure S3. 10 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **Int3.1** (in d_5 -pyridine).

(a)

(b)

(c)

Figure S3. 11 ^1H NMR spectra of the reaction of CO_2 with HBpin catalyzed by **2.20** (10 mol %, in C_6D_6), at (a) 24 °C, (b) 60°C and (c) 90 °C.

(a)

(b)

(c)

(d)

Figure S3. 12 NMR spectra of the resultant reaction of CO_2 with HBpin catalyzed by **2.20** (10 mol %, in C_6D_6), (a) ^1H , (b) ^{11}B , (c) $^{11}\text{B}\{^1\text{H}\}$ and (d) $^{13}\text{C}\{^1\text{H}\}$.

(a)

(b)

Figure S3. 13 NMR spectra of the reaction of CO_2 with HBpin catalyzed by **3.28** (2.5 mol %, 90 °C, in C_6D_6), (a) ^1H and (b) $^{11}\text{B}\{^1\text{H}\}$.

(a)

(b)

Figure S3. 14 ^1H NMR of the reaction of CO_2 with $\text{BH}_3\cdot\text{SMe}_2$ catalyzed by **2.20** (10 mol %, in C_6D_6), at (a) 60 °C and (b) 90 °C.

(a)

(b)

(c)

Figure S3. 15 NMR spectra of the resultant reaction of CO_2 with $\text{BH}_3 \cdot \text{SMe}_2$ catalyzed by **2.20** (10 mol %, in C_6D_6), (a) ^1H , (b) ^{11}B , (c) $^{11}\text{B}\{^1\text{H}\}$.

(a)

(b)

(c)

Figure S3. 16 NMR spectra of the resultant reaction of CO₂ with HBcat catalyzed by **2.20** (10 mol %, in C₆D₆), (a) ¹H, (b) ¹¹B, (c) ¹¹B{¹H}.

A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic *N*-formylation of Amines

Figure S3. 17 ^1H NMR spectrum of resultant compound **3.31b** (in C_6D_6).

Figure S3. 18 ^1H NMR spectrum of isolated compound **3.31b** (in C_6D_6).

Figure S3. 19 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31b** (in CDCl_3).

Figure S3. 20 ^1H NMR spectrum of isolated compound **3.31c** (in CDCl_3).

Figure S3. 21 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31c** (in CDCl_3).

Figure S3. 22 ^1H NMR spectrum of resultant compound **3.31d** (in C_6D_6).

Figure S3. 23 ¹H NMR spectrum of isolated compound **3.31d** (in CDCl₃).

Figure S3. 24 ¹³C{¹H} NMR spectrum of isolated compound **3.31d** (in CDCl₃).

Figure S3. 25 ¹H NMR spectrum of isolated compound **3.31e** (in CDCl₃).

Figure S3. 26 ¹³C{¹H} NMR spectrum of isolated compound **3.31e** (in CDCl₃).

Figure S3. 27 ¹H NMR spectrum of isolated compound **3.31f** (in CDCl₃).

Figure S3. 28 ¹³C{¹H} NMR spectrum of isolated compound **3.31f** (in CDCl₃).

Figure S3. 29 ¹H NMR spectrum of isolated compound **3.31g** (in CDCl₃).

Figure S3. 30 ¹³C{¹H} NMR spectrum of isolated compound **3.31g** (in CDCl₃).

Figure S3. 31 ¹H NMR spectrum of resultant compound **3.31h** (in C₆D₆).

Figure S3. 32 ¹H NMR spectrum of isolated compound **3.31h** (in CDCl₃).

Figure S3. 33 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31h** (in CDCl_3).

Figure S3. 34 ^1H NMR spectrum of isolated compound **3.31k** (in CDCl_3).

Figure S3. 35. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31k** (in CDCl_3).

Figure S3. 36 ¹H NMR spectrum of isolated compound **3.31m** (in CDCl₃).

Figure S3. 37 ¹³C{¹H} NMR spectrum of isolated compound **3.31m** (in CDCl₃).

Figure S3. 38 ¹H NMR spectrum of isolated compound **3.31n** (in CDCl₃).

Figure S3. 39 ¹³C{¹H} NMR spectrum of isolated compound **3.31n** (in CDCl₃).

Figure S3. 42 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31p** (in CDCl_3).

Figure S3. 43 ¹H NMR spectrum of isolated compound **3.31r** (in CDCl₃).

Figure S3. 44 ¹³C{¹H} NMR spectrum of isolated compound **3.31r** (in CDCl₃).

Figure S3. 45 ¹H NMR spectrum of isolated compound **3.31s** (in CDCl₃).

Figure S3. 46 ¹³C{¹H} NMR spectrum of isolated compound **3.31s** (in CDCl₃).

Figure S3. 49 ¹H NMR spectrum of resultant compound **3.31u** (in C₆D₆).

Figure S3. 50 ¹H NMR spectrum of isolated compound **3.31u** (in CDCl₃).

Figure S3. 51 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31u** (in CDCl_3).

Figure S3. 52 ¹H NMR spectrum of isolated compound **3.31v** (in CDCl₃).

Figure S3. 53 ¹³C{¹H} NMR spectrum of isolated compound **3.31v** (in CDCl₃).

Figure S3. 54 ¹H NMR spectrum of resultant compound **3.31w** (in C₆D₆).

Figure S3. 55 ¹H NMR spectrum of isolated compound **3.31w** (in CDCl₃).

Figure S3. 56 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.31w** (in CDCl_3).

Figure S3. 57 ¹H NMR spectrum of isolated compound **3.31x** (in CDCl₃).

Figure S3. 58 ¹³C{¹H} NMR spectrum of isolated compound **3.31x** (in CDCl₃).

Figure S3. 59 ¹H NMR spectrum of resultant compound **3.33a** (in C₆D₆).

Figure S3. 60 ¹H NMR spectrum of isolated compound **3.33a** (in CDCl₃).

Figure S3. 61 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.33a** (in CDCl_3).

Figure S3. 62 ¹H NMR spectrum of isolated compound **3.33b** (in CDCl₃).

Figure S3. 63 ¹³C{¹H} NMR spectrum of isolated compound **3.33b** (in CDCl₃).

Figure S3. 64 ¹H NMR spectrum of resultant compound **3.33c** (in C₆D₆).

Figure S3. 65 ¹H NMR spectrum of isolated compound **3.33c** (in CDCl₃).

Figure S3. 66 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.33c** (in CDCl_3).

Figure S3. 67 ¹H NMR spectrum of isolated compound **3.33e** (in CDCl₃).

Figure S3. 68 ¹³C{¹H} NMR spectrum of isolated compound **3.33e** (in C₆D₆).

Figure S3. 69 ¹H NMR spectrum of isolated compound **3.33f** (in C₆D₆).

Figure S3. 70 ¹³C{¹H} NMR spectrum of isolated compound **3.33f** (in C₆D₆).

Figure S3. 71 ¹H NMR spectrum of isolated compound **3.33g** (in CDCl₃).

Figure S3. 72 ¹³C{¹H} NMR spectrum of isolated compound **3.33g** (in CDCl₃).

Figure S3. 73 ¹H NMR spectrum of resultant compound **3.33h** (in C₆D₆).

Figure S3. 74 ¹H NMR spectrum of isolated compound **3.33h** (in CDCl₃).

Figure S3. 75 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.33h** (in CDCl_3).

Figure S3. 76 ¹H NMR spectrum of resultant compound **3.33k** (in C₆D₆).

Figure S3. 77 ¹H NMR spectrum of isolated compound **3.33k** (in CDCl₃).

Figure S3. 78 ¹³C{¹H} NMR spectrum of isolated compound **3.33k** (in CDCl₃).

Figure S3. 79 ¹H NMR spectrum of resultant compound **3.33m** (in C₆D₆).

Figure S3. 80 ¹H NMR spectrum of isolated compound **3.33m** (in CDCl₃).

Figure S3. 81 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.33m** (in CDCl_3).

(a)

(b)

Figure S3. ^1H NMR spectra of the resultant deuterium-labelling study of catalytic *N*-formylation using d_{11} -piperidine **3.32g-D**, catalyzed by **2.20** (5 mol %, 60 °C, 1 hour, in C_6D_6), (a) full spectrum, (b) enlarged spectrum.

Figure S3. 83 ¹H NMR spectra of the resultant catalytic *N*-formylation using piperidine **3.32g** and *d*₁₁-piperidine **3.32g-D** in 1:1 ratio, catalyzed by **2.20** (5 mol %, 60 °C, 1 hour, in C₆D₆), (a) full spectrum, (b) enlarged spectrum.

Figure S3. 84 ^1H NMR spectra of the resultant reaction between PhSiH_3 and d_{11} -piperidine **3.32g-D**, both in the presence and absence of **2.20** (24, 60 and 90 $^\circ\text{C}$, 24 hours, in C_6D_6), (a) full spectrum, (b) enlarged spectrum.

(a)

(c)

Figure S3. ^{85}NMR spectra of the resultant hydrosilylation of CO_2 catalyzed by **2.20** (10 mol %, 90 °C, 1 hour, in C_6D_6), (a) ^1H , (b) $^{13}\text{C}\{^1\text{H}\}$ and (c) ^{29}Si .

Figure S3. 86 Timeline study of hydrosilylation of CO₂ catalyzed by **2.20** (10 mol %, in C₆D₆), monitored by ¹H NMR spectroscopy.

A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of Aldehyde, Ketone and Pyridine Derivatives

(a)

(b)

Figure S3. 87 Stepwise hydroboration of benzaldehyde **3.41a** catalyzed by **3.28** (5 mol %, 24 °C, in C₆D₆), monitored by ¹H NMR spectroscopy, (a) first step: addition of HBpin to **2.20** to afford **3.28** and (b) second step: addition of benzaldehyde **3.41a**.

Figure S3. 88 Timeline study of hydroboration of benzaldehyde **3.41a** catalyzed by **2.20** (10 mol %, 24 °C, in C_6D_6), monitored by ^1H NMR spectroscopy.

Figure S3. 89 Timeline study of hydroboration of 3-methyl-2-butanone **3.43e** catalyzed by **2.20** (10 mol %, 90 °C, in C₆D₆), monitored by ¹H NMR spectroscopy.

Figure S3. 90 Timeline study of hydroboration of quinoline **3.45d** catalyzed by **2.20** (10 mol %, 90 °C, in C₆D₆), monitored by ¹H NMR spectroscopy.

Figure S3.91 Timeline study of hydroboration of benzaldehyde **3.41a** catalyzed by **3.28** (2.5 mol %, 24 °C, in C_6D_6), monitored by ^1H NMR spectroscopy.

Figure S3. 92 Timeline study of hydroboration of 1,4-dioxaspiro[4.5]decan-8-one **3.43d** catalyzed by **3.28** (5 mol %, 90 °C, in C₆D₆), monitored by ¹H NMR spectroscopy.

Figure S3.93 Timeline study of hydroboration of pyridine **3.45a** catalyzed by **3.28** (3 mol %, 90 °C, in C_6D_6), monitored by ^1H NMR spectroscopy.

(a)

(b)

Figure S3. 94 ^1H NMR spectrum of compound **3.42a** (in C_6D_6), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. 95 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3.42a** (in C_6D_6), (a) crude solution and (b) isolated compound.

Figure S3. 96 ¹H NMR spectrum of compound **3.42b** (in C₆D₆).

Figure S3. 97 ¹¹B{¹H} NMR spectrum of compound **3.42b** (in C₆D₆).

Figure S3. 98 ¹H NMR spectrum of compound **3.42c** (in C₆D₆).

Figure S3. 99 ¹¹B{¹H} NMR spectrum of compound **3.42c** (in C₆D₆).

Figure S3. 100 ¹H NMR spectrum of compound **3.42d** (in C₆D₆).

Figure S3. 101 ¹¹B{¹H} NMR spectrum of compound **3.42d** (in C₆D₆).

(a)

(b)

Figure S3. 102 ¹H NMR spectrum of compound 3.42e (in C₆D₆), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. $^{103}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3.42e** (in C_6D_6), (a) crude solution and (b) isolated compound.

Figure S3. 104 ¹H NMR spectrum of compound **3.42f** (in C₆D₆).

Figure S3. 105 ¹¹B{¹H} NMR spectrum of compound **3.42f** (in C₆D₆).

(a)

(b)

Figure S3. 106 ^1H NMR spectrum of isolated compound **3.42g** (in C_6D_6), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. $^{107}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.42g** (in C_6D_6), (a) crude solution and (b) isolated compound.

Figure S3. 108 ¹H NMR spectrum of compound **3.42h** (in C₆D₆).

Figure S3. 109 ¹¹B{¹H} NMR spectrum of compound **3.42h** (in C₆D₆).

Figure S3. 110 ¹H NMR spectrum of compound **3.42k** (in C₆D₆).

Figure S3. 111 ¹³C NMR spectrum of compound **3.42k** (in C₆D₆).

Figure S3. 112 ¹H NMR spectrum of compound **3.42m** (in C₆D₆).

Figure S3. 113 ¹¹B{¹H} NMR spectrum of compound **3.42m** (in C₆D₆).

Figure S3. 114 ¹H NMR spectrum of compound **3.42n** (in C₆D₆).

Figure S3. 115 ¹¹B{¹H} NMR spectrum of compound **3.42n** (in C₆D₆).

Figure S3. 118 ¹H NMR spectrum of compound **3.42q** (in C₆D₆).

Figure S3. 119 ¹¹B{¹H} NMR spectrum of compound **3.42q** (in C₆D₆).

Figure S3. 120 ¹H NMR spectrum of compound **3.42r (in C₆D₆).**

Figure S3. 121 ¹¹B{¹H} NMR spectrum of compound **3.42r (in C₆D₆).**

Figure S3. 122 ^1H NMR spectrum of compound **3.42s** (in C_6D_6).

Figure S3. 123 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3.42s** (in C_6D_6).

Figure S3. 124 ¹H NMR spectrum of compound 3.42t (in C₆D₆).

Figure S3. 125 ¹¹B{¹H} NMR spectrum of compound 3.42t (in C₆D₆).

Figure S3. 126 ¹H NMR spectrum of compound **3.42u** (in C₆D₆).

Figure S3. 127 ¹¹B{¹H} NMR spectrum of compound **3.42u** (in C₆D₆).

Figure S3. 128 ¹H NMR spectrum of compound 3.42v (in C₆D₆).

Figure S3. 129 ¹¹B{¹H} NMR spectrum of compound 3.42v (in C₆D₆).

(a)

(b)

Figure S3. ¹H NMR spectrum of isolated compound **3.44a** (in C₆D₆), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. 131 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.44a (in C_6D_6), (a) crude solution and (b) isolated compound.**

Figure S3. 132 ^1H NMR spectrum of compound **3.44b** (in C_6D_6).

Figure S3. 133 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3.44b** (in C_6D_6).

Figure S3. 134 ¹H NMR spectrum of compound **3.44c** (in C₆D₆).

Figure S3. 135 ¹¹B{¹H} NMR spectrum of compound **3.44c** (in C₆D₆).

Figure S3. 136 ¹H NMR spectrum of compound **3.44d** (in C₆D₆).

Figure S3. 137 ¹¹B{¹H} NMR spectrum of compound **3.44d** (in C₆D₆).

(a)

(b)

Figure S3. 138 ^1H NMR spectrum of compound **3.44e** (in C_6D_6), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. $^{139}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3.44e** (in C_6D_6), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. ¹H NMR spectrum of compound **3.44f** (in C₆D₆), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. 141 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3.44f** (in C_6D_6), (a) crude solution and (b) isolated compound.

Figure S3. 142 ¹H NMR spectrum of compound 3.44g (in C₆D₆).

Figure S3. 143 ¹¹B{¹H} NMR spectrum of compound 3.44g (in C₆D₆).

(a)

(b)

Figure S3. 144 ¹H NMR spectrum of isolated compound **3.44h** (in C₆D₆), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. 145 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.44h** (in C_6D_6), (a) crude solution and (b) isolated compound.

Figure S3. 146 ¹H NMR spectrum of compound **3.44k** (in C₆D₆).

Figure S3. 147 ¹¹B{¹H} NMR spectrum of compound **3.44k** (in C₆D₆).

Figure S3. 148 ¹H NMR spectrum of compound **3.46a** (in C₆D₆).

Figure S3. 149 ¹¹B{¹H} NMR spectrum of compound **3.46a** (in C₆D₆).

Figure S3. 150 ¹H NMR spectrum of compound **3.46b** (in C₆D₆).

Figure S3. 151 ¹¹B{¹H} NMR spectrum of compound **3.46b** (in C₆D₆).

(a)

(b)

Figure S3. 152 ^1H NMR spectrum of isolated compound **3.46c** (in C_6D_6), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. 153 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.46c (in C_6D_6), (a) crude solution and (b) isolated compound.**

(a)

(b)

Figure S3. 154 ¹H NMR spectrum of isolated compound **3.46d** (in C₆D₆), (a) crude solution and (b) isolated compound.

(a)

(b)

Figure S3. 155 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of isolated compound **3.46d (in C_6D_6), (a) crude solution and (b) isolated compound.**

Figure S3. 156 ¹H NMR spectrum of compound **3.46e** (in C₆D₆).

Figure S3. 157 ¹¹B{¹H} NMR spectrum of compound **3.46e** (in C₆D₆).

3.5.2 Crystallographic Data of All Structures

The X-ray diffraction intensity data were measured at 100 K with a Bruker APEX II diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073$ Å), with the SMART suite of programs.^[66] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.^[66] Structural solution and refinement were carried out with the SHELXTL suite of programs.^[67] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC-1893518 **3.29**, CCDC-2023818 **3.31m**, CDCC-2023817 **3.31p** and CCDC-2023816 **3.31w** contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Figure S3. 158 Molecular structure of $[(I_{Me})_2Bpin]I$ and $[I_{Me}-H]I$ (**3.29**, 30% ellipsoid probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1-C1 1.671(3), B2-C11 1.654(3); C1-B1-C1A 105.9(3), C11-B2-C11A 106.8(3), O1-B1-C1 111.23(10), O1-B1-C1A 110.79(11), O2-B2-C11 110.53(10), O2-B2-C11A 111.42(11).

Figure S3. 159 Molecular structure of **3.31m** (30% ellipsoid probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-C2 1.436(4), N1-C1 1.332(5), C1-O1 1.226(5); C1-N1-C2 123.9(3), N1-C1-O1 125.6(3).

Figure S3. 160 Molecular structure of **3.31p** (30% ellipsoid probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-C2 1.4097(16), N1-C1 1.3413(15), C1-O1 1.2267(14); C1-N1-C2 127.65(10), N1-C1-O1 126.64(12).

Figure S3. 161 Molecular structure of **3.31w** (50% ellipsoid probability). Selected bond lengths (Å) and angles (deg): N1-C7 1.4601(19), N1-C8 1.3239(18), C8-O1 1.2335(18); C7-N1-C8 120.84(12), N1-C8-O1 117.4.

Table S3. 15 Crystallographic data of **3.29**, **3.31m**, **3.31p** and **3.31w**.

	3.29	3.31m	3.31p	3.31w
Formula	C _{23.50} H _{42.50} BI _{1.50} N ₅ O ₂	C ₁₃ H ₁₉ NO	C ₈ H ₉ NO ₂	C ₈ H ₈ ClNO
Fw	628.28	205.29	151.16	169.60
Color	Colourless	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Hexagonal	Monoclinic	Monoclinic
Space group	<i>C12/c1</i>	<i>P 6 1</i>	<i>C 1 2/c 1</i>	<i>P 1 21/c1</i>
<i>a</i> (Å)	13.0847(6)	16.8594(11)	14.8957(7)	6.1585(4)
<i>b</i> (Å)	32.8113(16)	16.8594(11)	12.8359(6)	4.6786(2)
<i>c</i> (Å)	13.7965(7)	8.3896(7)	8.4150(3)	26.8306(16)
<i>α</i> (deg)	90	90	90	90
<i>β</i> (deg)	106.2955(18)	90	111.9279(17)	96.260(2)
<i>γ</i> (deg)	90	120	90	90
<i>V</i> (Å³)	5685.2(5)	2065.2(3)	1492.55(11)	768.46(8)
<i>Z</i>	8	6	8	4
<i>d</i>_{calcd} (g cm⁻³)	1.468	0.990	1.345	1.466
<i>μ</i> (mm⁻¹)	1.697	0.062	0.098	0.431
<i>F</i>(000)	2552	672	640	352
crystal size (mm)	0.120 x 0.140 x 0.200	0.020 x 0.040 x 0.220	0.020 x 0.040 x 0.220	0.020 x 0.120 x 0.220
<i>θ</i> range (deg)	2.47 to 35.01	2.42 to 27.87	2.95 to 30.99	3.06 to 31.02
Index range	-21 ≤ <i>h</i> ≤ 20, -52 ≤ <i>k</i> ≤ 52, -22 ≤ <i>l</i> ≤ 21	-20 ≤ <i>h</i> ≤ 22 -18 ≤ <i>k</i> ≤ 22 -10 ≤ <i>l</i> ≤ 11	-21 ≤ <i>h</i> ≤ 21 -14 ≤ <i>k</i> ≤ 18 -9 ≤ <i>l</i> ≤ 12	-8 ≤ <i>h</i> ≤ 8 -4 ≤ <i>k</i> ≤ 6 -38 ≤ <i>l</i> ≤ 38
no. of rflns collected	63404	18567	9262	11102
no. of indep rflns	12505	3278	2359	2438
<i>R</i>1, <i>wR</i>2 (<i>I</i> > 2(<i>σ</i>))	0.0451, 0.0799	0.0605, 0.1324	0.0482, 0.1199	0.0393, 0.0820
<i>R</i>1, <i>wR</i>2 (all data)	0.0868, 0.0967	0.1140, 0.1591	0.0639, 0.1393	0.0558, 0.0904
Goodness of fit, <i>F</i>²	1.022	1.022	1.071	1.040
no. of data/ restraints/params	12505 / 84 / 387	3278 / 1 / 141	2359 / 0 / 101	2438 / 0 / 100
Largest diff peaks and hole, eÅ⁻³	1.288 and -1.574	0.179 and -0.175	0.307 and -0.280	0.343 and -0.299

3.5.3 Theoretical Studies

Geometry optimizations were fully performed without any symmetry restriction by using M06-2X/def2-TZVP level of theory as implemented in the Gaussian 09 package of programs.^[68] The vibrational frequency calculations were performed to establish the nature of stationary points. The local minima were confirmed by zero imaginary frequencies, and transition states were characterized by an imaginary frequency. The thermodynamic corrections are obtained by using "temperature" keyword in Gaussian 09^[68] at M06-2X/def2-TZVP.

List of abbreviation used in theoretical studies.

Abbreviation	Definition
Cpd	Compound
HBpin	Pinacolborane
Int	Intermediate
I _{Me}	:C{N(Me)C(Me)} ₂
(PhSiH ₂) ₂ O	Siloxane
PhH ₂ SiOC(O)H	Silylformate
PhSiH ₃	Phenylsilane
TS	Transition state

List of colour coded atom used in optimised structures

Color	Definition
White	Hydrogen
Black/ Grey	Carbon
Blue	Nitrogen
Yellow	Silicon
Green	Boron
Red	Oxygen
Purple	Iodine

Parent NHC–Silyliumylidene Cation (2.20) in Catalytic Hydroboration of CO₂

Figure S3. 162 Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Figure S3. 162 (continued). Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Compound **3.28**

TS3.1

TS3.2

TS3.3

Figure S3. 162 (continued). Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Figure S3. 162 (continued). Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Table S3. 16 The theoretical calculated ^{29}Si NMR chemical shift (ppm) in solution (C_6D_6) using TMS as the reference at B3LYP/6-311 $^{++}$ G(2df,2pd)//B3LYP/6-31G** level of theory.

System(X)	^{29}Si NMR chemical shift ^a
Compound 3.28	-94.0

$$^a \delta(^{29}\text{Si}_x) = \sigma(^{29}\text{Si}_{\text{TMS}}) - \sigma(^{29}\text{Si}_x).^{[69]}$$

Figure S3. 163 Orbital interaction diagram of compound **2.20** and CO₂ at M06-2X/def2-TZVP level of theory.^[70]

Figure S3. 164 Molecular orbitals of compound **2.20**, CO₂ and **Int3.1** at M06-2X/def2-TZVP level of theory.^[70]

Table S3. 17 Natural Bond Order (NBO) of **Int3.1** at M06-2X/def2-TZVP level of theory.^[70]

Orbital	Occ.	Contribution from atoms to the orb	Atomic orbitals
1.96	45.68% Si + 54.32% C	Si: 31.75% s + 67.93% p C: 27.75% s + 72.00% p

The mechanism for the formation of **3.28** is proposed. Compound **2.20** undergoes an oxidative addition with HBpin to form **Int3.2**, along with the displacement of **I_{Me}**. Similar oxidative addition of HBpin with a silylene was reported.^[71] **I_{Me}** then reduces **Int3.2** to form **Int3.3** and **[I_{Me}-H]I**. Similar reduction was reported by Roesky et al. that NHC, $[\text{C}\{\text{N}(\text{Ar})\text{C}(\text{H})\}_2]$ (**I_{Ar}**) underwent dehydrochlorination with **HSiCl₃** to form the NHC–dichlorosilylene complex $[\text{I}_{\text{Ar}} \rightarrow \text{SiCl}_2]$.^[72] Subsequently, the dehydrogenation of **Int3.3** with **[I_{Me}-H]I** via **TS3.3** forms compound **3.28**.^[73] The Si lone pair electrons in **3.28** interact with **CO₂** to form **Int3.4**. Subsequently, the H-B bond of HBpin inserts into the C=O bond via a low kinetic barrier (**TS3.4**), which results in the formation of the formoxyborane **3.27a** and regeneration of **3.28**.

Scheme S3. 1 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, CO₂, HBpin, Int, **I_{Me}** and TS stand for compound, carbon dioxide, pinacolborane, intermediate, $[\text{C}\{\text{N}(\text{Me})\text{C}(\text{Me})\}_2]$ and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states and compounds **2.20** and **3.28** are at M06-2X/def2-TZVP level of theory. No transition state was found between compound **2.20** and **Int3.2**, which indicates that the reaction from **Cpd2.20** to **Int3.2** should have a pretty low barrier, which is not easy to find out, or a non-barrier process.

Scheme S3. 2 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, CO₂, HBpin, Int and TS stand for compound, carbon dioxide, pinacolborane, intermediate and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states and compounds **2.20** and **3.27a** are at M06-2X/def2-TZVP level of theory.

Scheme S3. 3 Mechanism for the reaction of compound **2.20** with CO_2 and HBpin to afford compound **3.27a** with the regeneration of compound **2.20**.

Scheme S3. 4 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, CO₂, Int and TS stand for compound, carbon dioxide, intermediate and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states, compounds **2.20** and **3.27a** are at M06-2X/def2-TZVP level of theory.

Scheme S3. 5 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 24 °C. The abbreviations Cpd, Int and TS stand for compound, intermediate and transition state, respectively. Geometrical coordinates of the reactants, intermediates, transition states and compounds **2.20** and **3.27a** are at M06-2X/def2-TZVP level of theory.

Table S3. 18 Optimized cartesian coordinates of compound **2.20**

M06-2X/def2-TZVP

1st frequency: 19.5 cm⁻¹

Sum of electronic and thermal Free Energies = -1354.293565 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.590631	-0.964751	1.167401
6	-2.318192	-0.426648	0.444038
6	-4.465731	-0.595928	-0.232511
6	-4.233514	0.706303	0.062913
6	-3.064275	-2.699511	-0.144590
1	-4.014680	-3.181114	-0.355313
1	-2.648374	-3.108304	0.775964
1	-2.362554	-2.892415	-0.955351
6	-5.693837	-1.274501	-0.723529
1	-6.483336	-0.542630	-0.878327
1	-6.059248	-2.012683	-0.006950
1	-5.517339	-1.783788	-1.672684
6	-5.126723	1.892572	-0.004700
1	-6.093471	1.605599	-0.412166
1	-4.709203	2.670767	-0.646389
1	-5.297369	2.325498	0.983102
6	-2.243251	1.987211	0.939911
1	-1.649035	1.744430	1.821367
1	-2.989397	2.731569	1.205534
1	-1.584288	2.387597	0.169012
6	0.401503	0.449901	0.275994
6	1.513572	1.652204	-1.253381
6	1.906240	2.080365	-0.027028
6	0.086551	-0.218944	-2.078160
1	-0.930368	-0.530870	-1.855662
1	0.747754	-1.089705	-2.100034
1	0.107762	0.298036	-3.034096
6	2.031539	1.989120	-2.603251
1	2.776964	2.777333	-2.526269
1	1.243541	2.332695	-3.275995
1	2.512565	1.112743	-3.043544
6	2.979694	3.023216	0.375083
1	3.407513	3.498113	-0.504631
1	3.776795	2.477669	0.885714
1	2.611927	3.806950	1.039706
6	1.517918	1.331916	2.307057

1	0.731332	0.820284	2.854005
1	1.624379	2.351954	2.671799
1	2.452274	0.778105	2.428317
7	-3.276674	-1.270947	0.010281
7	-2.910835	0.784197	0.480003
7	0.558560	0.677829	-1.040433
7	1.184207	1.350222	0.893972
53	3.176670	-1.382027	0.066991
1	-0.384575	-1.996627	0.104920

Table S3. 19 Optimized cartesian coordinates of HBpin

M06-2X/def2-TZVP

1st frequency: 108.6 cm⁻¹

Sum of electronic and thermal Free Energies = -411.690905 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	0.779184	-0.185850	0.054683
6	-0.779184	-0.185850	-0.054683
8	-1.060939	1.185654	-0.414203
8	1.060939	1.185654	0.414203
6	-1.465948	-0.440836	1.280943
1	-2.529825	-0.231298	1.172188
1	-1.343785	-1.476852	1.598567
1	-1.065051	0.213726	2.056004
6	-1.341506	-1.104175	-1.121494
1	-1.066036	-2.140444	-0.914452
1	-2.429198	-1.033310	-1.124086
1	-0.978871	-0.833921	-2.111084
6	1.341505	-1.104175	1.121494
1	1.066035	-2.140445	0.914452
1	2.429198	-1.033311	1.124085
1	0.978872	-0.833921	2.111083
6	1.465949	-0.440836	-1.280943
1	2.529825	-0.231297	-1.172188
1	1.343786	-1.476851	-1.598566
1	1.065050	0.213726	-2.056005
5	0.000000	1.936754	0.000000
1	0.000000	3.120304	0.000000

Table S3. 20 Optimized cartesian coordinates of **Int3.1**

M06-2X/def2-TZVP

1st frequency: 25.1 cm⁻¹

Sum of electronic and thermal Free Energies = -1542.904121 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.331917	2.129040	-0.860746
6	1.337716	1.192521	-0.649807
6	2.997037	-0.280587	-0.914938
6	3.233599	0.410402	0.232700
6	1.163035	-0.349455	-2.589233
1	0.629651	-1.239947	-2.245924
1	1.897108	-0.616970	-3.345585
1	0.473258	0.376083	-3.010779
6	3.695101	-1.444280	-1.513699
1	4.560258	-1.708145	-0.910449
1	4.037634	-1.237185	-2.529010
1	3.018380	-2.302228	-1.527017
6	4.291954	0.255095	1.261158
1	5.002321	-0.506161	0.948781
1	3.856358	-0.061806	2.210682
1	4.838993	1.184688	1.425484
6	2.104028	2.253589	1.476919
1	3.044929	2.792746	1.572372
1	1.916590	1.699122	2.396472
1	1.303988	2.974546	1.301385
6	-1.576333	0.778109	-0.356148
6	-2.716826	-0.613447	0.964029
6	-3.066237	-0.885369	-0.320545
6	-1.085427	0.905648	2.073481
1	-0.769040	1.934621	1.916739
1	-0.231515	0.240684	2.228172
1	-1.739438	0.878851	2.940793
6	-3.069458	-1.297815	2.231540
1	-3.764659	-2.109755	2.032992
1	-3.534701	-0.617042	2.946059
1	-2.166996	-1.726311	2.673781
6	-3.939179	-1.941143	-0.890614
1	-4.382813	-2.524494	-0.087865
1	-3.356435	-2.621885	-1.514539
1	-4.748461	-1.522733	-1.491544
6	-2.444592	-0.004547	-2.560385

1	-1.969190	0.889819	-2.948593
1	-3.490576	-0.000893	-2.859741
1	-1.956535	-0.893993	-2.959874
7	1.841660	0.238684	-1.449597
7	2.206036	1.317565	0.364652
7	-1.820051	0.427722	0.913277
7	-2.357628	-0.007361	-1.112724
53	0.401032	-2.272279	0.529934
1	-0.439665	2.308288	-2.316866
6	-0.871216	3.709139	0.120310
8	-0.281370	4.287296	1.022334
8	-1.974463	3.846567	-0.432313

Table S3. 21 Optimized cartesian coordinates of **Int3.2**

M06-2X/def2-TZVP

1st frequency: 5.5 cm⁻¹

Sum of electronic and thermal Free Energies = -1382.717342 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.327005	-1.218172	0.186856
6	4.528114	-0.670858	0.347273
6	4.081894	0.625248	-0.397423
6	-0.690687	0.383477	0.223176
6	-2.129304	1.963823	0.839946
6	-1.924091	2.088610	-0.498402
6	-1.414616	0.304408	2.575209
1	-0.435962	-0.055141	2.882950
1	-2.119433	-0.528390	2.500617
1	-1.765656	1.035541	3.297695
6	-3.066144	2.673147	1.747140
1	-3.595341	3.449444	1.199721
1	-2.547284	3.144154	2.583921
1	-3.806601	1.974686	2.142124
6	-2.561665	2.981098	-1.498895
1	-3.236838	3.672736	-1.000832
1	-3.145270	2.394442	-2.211210
1	-1.824128	3.567246	-2.049922
6	-0.656918	0.746508	-2.203331
1	0.383959	0.428953	-2.237736
1	-0.785013	1.603187	-2.858872
1	-1.321272	-0.067354	-2.506517

7	-1.320112	0.932265	1.269068
7	-0.998534	1.127116	-0.844567
53	-3.339345	-1.441768	-0.259618
1	-0.013828	-1.987053	1.391323
1	-0.009933	-1.923016	-1.058405
5	2.268802	-0.643393	0.130194
8	2.706025	0.318176	-0.742640
8	3.275628	-1.155158	0.895022
6	5.037909	-1.751058	-0.597554
1	6.010714	-1.486542	-1.013224
1	5.136644	-2.683995	-0.043501
1	4.337265	-1.912645	-1.417967
6	5.509326	-0.449207	1.480367
1	5.751436	-1.406311	1.941958
1	6.433411	-0.008454	1.100582
1	5.095710	0.204744	2.244951
6	4.855252	0.928486	-1.664602
1	4.479925	1.851206	-2.107217
1	5.914729	1.064784	-1.438209
1	4.752358	0.129616	-2.395800
6	4.042930	1.848219	0.509176
1	5.049000	2.177907	0.770397
1	3.535759	2.657985	-0.014923
1	3.494144	1.636109	1.427843

Table S3. 22 Optimized cartesian coordinates of I_{Me}

M06-2X/def2-TZVP

1st frequency: 108.5 cm⁻¹

Sum of electronic and thermal Free Energies = -383.254033 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-0.000000	-1.563410	0.000022
6	0.676943	0.630607	-0.000038
6	-0.676942	0.630607	0.000006
6	2.428343	-1.152289	0.000013
1	2.954135	-0.794835	-0.887318
1	2.417490	-2.238629	-0.000224
1	2.953957	-0.795218	0.887603
6	1.661043	1.745433	-0.000005
1	1.145482	2.704497	-0.000293
1	2.305969	1.711605	-0.881252

1	2.305578	1.711906	0.881538
6	-1.661042	1.745433	0.000016
1	-1.145481	2.704498	-0.000026
1	-2.305738	1.711780	0.881439
1	-2.305809	1.711731	-0.881352
6	-2.428343	-1.152289	-0.000033
1	-2.417490	-2.238628	0.000404
1	-2.953881	-0.795383	-0.887735
1	-2.954211	-0.794670	0.887187
7	1.053525	-0.707371	-0.000032
7	-1.053525	-0.707371	0.000053

Table S3. 23 Optimized cartesian coordinates of **Int3.3v**

M06-2X/def2-TZVP

1st frequency: 13.9 cm⁻¹

Sum of electronic and thermal Free Energies = -1084.428423 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.289225	1.593533	-1.389159
6	-3.455083	0.365277	0.097274
6	-2.593485	-0.828533	0.600612
6	1.689943	0.600264	-0.534787
6	3.609973	0.037665	0.520099
6	3.129387	-1.079217	-0.075390
6	2.837750	2.435507	0.655036
1	1.974212	2.716225	1.256184
1	2.881869	3.094692	-0.211152
1	3.747183	2.544079	1.239582
6	4.827752	0.242165	1.347834
1	5.360318	-0.700229	1.456609
1	4.579325	0.603119	2.347932
1	5.511307	0.960739	0.890952
6	3.650018	-2.471031	-0.104902
1	4.523117	-2.556900	0.538477
1	3.945849	-2.770281	-1.112593
1	2.898904	-3.180879	0.247127
6	1.148292	-1.601613	-1.529601
1	0.648204	-1.009180	-2.296621
1	0.389475	-2.090609	-0.922658
1	1.792481	-2.338644	-2.005283
7	2.713128	1.057128	0.224083

7	1.959960	-0.710623	-0.723323
1	0.392511	2.815340	-0.521783
5	-1.266307	0.699159	-0.475080
8	-1.367643	-0.644110	-0.132836
8	-2.453345	1.351610	-0.204520
6	-4.187111	0.055220	-1.203930
1	-5.006534	-0.647922	-1.046621
1	-4.594140	0.984089	-1.602933
1	-3.500556	-0.360371	-1.943028
6	-4.420531	0.929292	1.122195
1	-4.980188	1.752439	0.677612
1	-5.130949	0.163170	1.441557
1	-3.893291	1.307885	1.995659
6	-3.160303	-2.200269	0.288499
1	-2.495501	-2.969091	0.684575
1	-4.140607	-2.324954	0.754051
1	-3.260609	-2.352338	-0.784575
6	-2.250260	-0.722270	2.082337
1	-3.122351	-0.911655	2.710186
1	-1.484260	-1.461847	2.317287
1	-1.855159	0.267576	2.314948

Table S3. 24 Optimized cartesian coordinates of [I_{Me}-H]I

M06-2X/def2-TZVP

1st frequency: 35.4 cm⁻¹

Sum of electronic and thermal Free Energies = -681.539006 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	0.802451	-0.000017	-1.509565
6	1.835130	-0.679597	0.309473
6	1.835122	0.679640	0.309451
6	0.737796	-2.419523	-1.140113
1	0.483288	-2.491257	-2.194520
1	-0.159339	-2.586733	-0.539419
1	1.513820	-3.143725	-0.904387
6	2.276061	-1.658918	1.332668
1	2.744900	-1.141274	2.165984
1	2.995244	-2.373434	0.928818
1	1.413970	-2.208571	1.716869
6	2.276012	1.659004	1.332625
1	2.744872	1.141402	2.165955

1	1.413897	2.208631	1.716809
1	2.995162	2.373545	0.928759
6	0.737711	2.419491	-1.140141
1	0.482870	2.491101	-2.194476
1	1.513801	3.143733	-0.904753
1	-0.159240	2.586724	-0.539181
7	1.220081	-1.078611	-0.864322
7	1.220066	1.078605	-0.864356
53	-1.854399	-0.000010	0.286782
1	0.217155	-0.000034	-2.411559

Table S3. 25 Optimized cartesian coordinates of **Int3.4**

M06-2X/def2-TZVP

1st frequency: 12.6 cm⁻¹

Sum of electronic and thermal Free Energies = -1953.401962 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.153531	0.104545	-1.081748
6	1.578513	-1.163223	-0.912439
6	2.834287	-2.957318	-0.476520
6	3.655480	-1.993161	-0.973611
6	0.404243	-3.189264	-0.009904
1	0.428495	-3.273627	1.075381
1	0.438700	-4.168894	-0.484717
1	-0.510200	-2.681869	-0.294837
6	3.119254	-4.340992	-0.016762
1	4.193061	-4.510920	0.010830
1	2.676280	-5.081719	-0.685192
1	2.718833	-4.507580	0.984024
6	5.119026	-1.996697	-1.230679
1	5.558477	-2.918017	-0.855297
1	5.610607	-1.158625	-0.733992
1	5.336321	-1.928922	-2.298274
6	3.364119	0.345759	-1.805891
1	4.097745	0.109934	-2.574081
1	3.845750	0.929171	-1.020183
1	2.551022	0.904017	-2.278413
6	0.749754	1.676040	-0.139916
6	1.718342	3.268601	1.097748
6	0.758848	3.862736	0.342537
6	2.580703	0.980529	1.446452
1	2.377972	-0.024068	1.099657

1	2.369154	0.988928	2.513873
1	3.618132	1.262454	1.258804
6	2.638749	3.825962	2.121955
1	2.485898	4.898578	2.214777
1	3.684203	3.654593	1.859154
1	2.458201	3.372299	3.098140
6	0.329213	5.283213	0.265324
1	0.971934	5.898081	0.891153
1	-0.697711	5.406670	0.613817
1	0.388764	5.659958	-0.756710
6	-0.861695	3.110966	-1.406572
1	-0.402294	3.255285	-2.384000
1	-1.420066	3.992418	-1.103864
1	-1.547859	2.269558	-1.442561
7	1.562866	-2.426248	-0.462356
7	2.856863	-0.905427	-1.252606
7	1.701233	1.926081	0.777084
7	0.179113	2.863743	-0.409626
53	-0.240354	-0.713861	2.533191
6	-3.703083	-1.431227	-0.268295
6	-3.912418	0.105254	-0.451890
8	-2.311165	-1.593867	-0.650226
8	-2.580052	0.628487	-0.218098
5	-1.702168	-0.384278	-0.492963
6	-4.552993	-2.292185	-1.181711
1	-4.346329	-3.344235	-0.984217
1	-5.612934	-2.111166	-0.990608
1	-4.341411	-2.087753	-2.229438
6	-3.828311	-1.884440	1.178020
1	-4.866172	-1.836923	1.511379
1	-3.486123	-2.917309	1.252266
1	-3.203373	-1.280088	1.836179
6	-4.276146	0.490772	-1.880079
1	-5.279744	0.151833	-2.140038
1	-4.249103	1.578112	-1.964519
1	-3.554567	0.082265	-2.590475
6	-4.866057	0.731659	0.544680
1	-4.953397	1.799443	0.342241
1	-5.857922	0.284390	0.449854
1	-4.512060	0.600120	1.565078
6	0.053131	0.688988	-2.947951
8	-1.012992	0.332303	-3.461915
8	0.980909	1.393963	-3.388443

Table S3. 26 Optimized cartesian coordinates of compound **3.28**

M06-2X/def2-TZVP

1st frequency: 17.4 cm⁻¹

Sum of electronic and thermal Free Energies = -1764.803014 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	1.050232	-0.033915	1.682659
6	2.650969	-0.338326	0.634772
6	4.683723	-0.017382	-0.294074
6	4.422625	-1.344447	-0.343043
6	3.522226	1.992686	0.646983
1	4.528487	2.354369	0.846208
1	2.921672	2.119639	1.546193
1	3.064184	2.555168	-0.163336
6	5.856506	0.762766	-0.767746
1	6.523900	0.120579	-1.338248
1	6.425957	1.181205	0.064791
1	5.548113	1.588049	-1.411659
6	5.221465	-2.474139	-0.886103
1	6.089626	-2.091499	-1.418282
1	4.635169	-3.075396	-1.583477
1	5.580859	-3.134490	-0.094125
6	2.596803	-2.828681	0.510300
1	2.006645	-2.776365	1.423339
1	3.400626	-3.547451	0.650415
1	1.956518	-3.156328	-0.308869
6	-0.049869	-1.320062	0.724870
6	-0.903387	-2.729226	-0.800564
6	-1.418558	-3.070975	0.407698
6	0.499380	-0.883146	-1.670295
1	0.893602	0.052682	-1.287577
1	-0.297799	-0.656831	-2.379582
1	1.291898	-1.448351	-2.166774
6	-1.261792	-3.194594	-2.162657
1	-1.758481	-4.160977	-2.110640
1	-0.387467	-3.292431	-2.808173
1	-1.958934	-2.477365	-2.606924
6	-2.506651	-4.016460	0.756030
1	-2.779501	-4.604274	-0.117382
1	-3.387345	-3.444072	1.059615
1	-2.224181	-4.699557	1.558693
6	-1.373425	-2.077607	2.681369

1	-0.667935	-1.495476	3.269569
1	-1.495738	-3.065668	3.119916
1	-2.335085	-1.561455	2.635914
7	3.591583	0.577100	0.320769
7	3.177855	-1.523126	0.246391
7	-0.073668	-1.650279	-0.581402
7	-0.869895	-2.203130	1.325581
53	-3.454466	-0.384082	-0.422194
6	-0.274829	3.213726	-0.772910
6	-1.061082	3.458938	0.557030
8	0.729622	2.245291	-0.366424
8	-0.807006	2.251180	1.307687
5	0.271829	1.618338	0.775015
6	0.431653	4.437248	-1.327141
1	0.955795	4.167502	-2.244835
1	-0.295237	5.215277	-1.569046
1	1.154467	4.844764	-0.621639
6	-1.112429	2.551380	-1.855971
1	-1.861983	3.239389	-2.249521
1	-0.452755	2.258217	-2.675332
1	-1.627534	1.664021	-1.480262
6	-0.488131	4.602208	1.386270
1	-0.670616	5.568607	0.914452
1	-0.967888	4.594455	2.364550
1	0.586912	4.479285	1.533849
6	-2.558253	3.619205	0.380757
1	-3.016051	3.802927	1.353094
1	-2.775948	4.471132	-0.268010
1	-3.003348	2.715806	-0.035851

Table S3. 27 Optimized cartesian coordinates of compound **3.28**

B3LYP/6-311⁺⁺G(2df,2pd)//B3LYP/6-31G**

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	0.029356	1.749042	0.851462
6	1.044426	3.671426	0.191445
6	1.977924	2.923109	0.847986
6	3.425501	3.173942	1.106714
1	3.641135	3.264595	2.177681
1	4.039075	2.361872	0.700208
1	3.735280	4.104055	0.626923
6	1.151893	5.009722	-0.459523

1	2.166089	5.397021	-0.349895
1	0.930084	4.962035	-1.531618
1	0.466463	5.738178	-0.011213
6	1.987330	0.719644	2.048238
1	1.231903	0.187016	2.626920
1	2.536873	0.033329	1.397718
1	2.689451	1.189175	2.737864
6	-1.373696	3.444287	-0.390289
1	-1.207843	3.667109	-1.447820
1	-2.170694	2.711624	-0.305504
1	-1.678107	4.362810	0.119155
7	1.330736	1.761243	1.260286
7	-0.141797	2.936269	0.204509
6	-0.331301	-1.219207	0.826934
6	0.431301	-3.355385	0.883607
6	0.795693	-2.819021	-0.320881
6	1.571589	-3.399018	-1.454822
1	0.987034	-3.412924	-2.381837
1	2.485749	-2.821079	-1.633538
1	1.859587	-4.426773	-1.226714
6	0.666990	-4.713146	1.456350
1	1.189015	-5.338774	0.730677
1	1.283947	-4.672765	2.361095
1	-0.272816	-5.213421	1.715937
6	0.475564	-0.623072	-1.480265
1	-0.151379	0.253342	-1.333412
1	1.525385	-0.327777	-1.572526
1	0.161530	-1.142174	-2.388443
6	-0.824854	-2.548537	2.900228
1	-1.685484	-3.220565	2.847871
1	-0.073586	-2.974115	3.568880
1	-1.148774	-1.578062	3.278033
7	0.309416	-1.515859	-0.334173
7	-0.250498	-2.356442	1.570928
14	-1.244247	0.400469	1.435249
1	-2.434529	1.759814	4.732055
53	4.576289	-0.462369	-0.964526
6	-4.924315	0.647290	-0.710825
6	-4.537966	-0.867647	-0.896604
6	-4.051890	-1.207084	-2.311930
1	-3.615843	-2.209823	-2.305549
1	-4.873404	-1.195495	-3.034237
1	-3.283628	-0.505841	-2.649627
6	-5.604351	-1.868033	-0.455257

1	-6.514706	-1.754703	-1.052983
1	-5.232818	-2.886847	-0.597875
1	-5.861823	-1.746701	0.598293
6	-5.888664	0.896165	0.455535
1	-5.948229	1.971454	0.644702
1	-6.895008	0.531844	0.229211
1	-5.540268	0.410933	1.371325
6	-5.424288	1.353287	-1.968732
1	-6.354656	0.899055	-2.324834
1	-5.628902	2.403988	-1.743491
1	-4.689239	1.316320	-2.774635
5	-2.840414	0.246821	0.191986
1	-2.687972	2.082795	5.352961
8	-3.643709	1.242889	-0.325318
8	-3.382931	-1.005225	-0.013732

Table S3. 28 Optimized cartesian coordinates of **TS3.1**

M06-2X/def2-TZVP

1st frequency: -99.7 cm⁻¹

Sum of electronic and thermal Free Energies = -1954.578146 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.602873	-0.705015	-0.524897
6	-0.287606	0.744150	0.310075
6	-1.494668	2.594590	0.605425
6	-1.753025	1.760012	1.650187
6	-0.106769	2.473200	-1.476980
1	0.856865	2.026431	-1.715766
1	0.037014	3.545967	-1.377231
1	-0.841240	2.268611	-2.255981
6	-2.055127	3.927411	0.267259
1	-2.793155	4.217349	1.011767
1	-2.548138	3.906739	-0.706699
1	-1.280648	4.695538	0.240745
6	-2.691107	1.875213	2.794122
1	-3.238442	2.813681	2.737979
1	-2.167972	1.847217	3.751723
1	-3.405539	1.049646	2.760191
6	-1.035591	-0.526612	2.323980
1	-2.010904	-1.001062	2.235750
1	-0.864051	-0.203728	3.350381
1	-0.269022	-1.243963	2.039309

6	2.254657	-1.072989	0.337654
6	4.157159	-1.062948	1.492118
6	4.272900	-1.998317	0.510742
6	2.428004	0.631643	2.124472
1	1.419900	0.465015	2.493620
1	2.466732	1.497692	1.459131
1	3.086018	0.791047	2.972858
6	5.151142	-0.583394	2.485825
1	6.070548	-1.155808	2.391271
1	4.790659	-0.695018	3.509678
1	5.388317	0.467246	2.307984
6	5.411800	-2.870224	0.126058
1	6.261714	-2.677244	0.775796
1	5.721252	-2.668935	-0.900676
1	5.155812	-3.927712	0.210552
6	2.770552	-2.785076	-1.354448
1	1.744984	-3.149555	-1.284894
1	3.438763	-3.639919	-1.394628
1	2.915912	-2.162414	-2.238675
7	-0.587822	1.944701	-0.204449
7	-0.990840	0.634367	1.446930
7	2.888377	-0.531727	1.386847
7	3.074111	-2.002151	-0.165021
53	3.606035	1.547425	-1.274930
1	0.887620	-0.319463	-1.910887
6	-0.654333	-2.148954	-0.316893
8	-1.786736	-1.701867	-0.630667
8	-0.294765	-3.246207	0.099332
6	-5.092920	-1.048999	-1.090860
6	-4.902079	-0.017080	0.070296
8	-3.796151	-0.563304	0.806678
8	-4.588084	-2.257214	-0.509571
6	-6.092555	0.029024	1.022737
1	-5.825134	0.629202	1.894023
1	-6.969457	0.475061	0.551707
1	-6.347919	-0.974377	1.364399
6	-4.553173	1.385813	-0.395172
1	-5.338687	1.781583	-1.042643
1	-4.458482	2.048423	0.468319
1	-3.609849	1.387874	-0.940659
6	-6.538325	-1.269651	-1.501378
1	-6.984036	-0.337925	-1.857259
1	-6.572342	-1.996450	-2.312887
1	-7.133418	-1.654112	-0.675403

6	-4.249206	-0.725742	-2.320274
1	-4.286531	-1.581623	-2.994087
1	-4.637448	0.148878	-2.845894
1	-3.208225	-0.564939	-2.044831
5	-3.684401	-1.915238	0.466591
1	-3.188844	-2.710093	1.192832

Table S3. 29 Optimized cartesian coordinates of **TS3.2**

M06-2X/def2-TZVP

1st frequency: -1130.5 cm⁻¹

Sum of electronic and thermal Free Energies = -1765.951111 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-1.035795	-0.112162	-1.226415
6	-5.110565	-1.049409	-0.637824
6	-4.826436	-0.248407	0.668292
6	-0.440976	1.479153	-0.345350
6	0.481275	3.460597	0.135202
6	0.324637	2.787688	1.301483
6	0.172156	2.907730	-2.274675
1	-0.600930	2.403614	-2.845105
1	1.156981	2.537726	-2.568823
1	0.110488	3.978482	-2.450672
6	1.163818	4.745422	-0.156485
1	1.486429	5.210921	0.771700
1	0.514774	5.449453	-0.680294
1	2.051925	4.561978	-0.765788
6	0.787264	3.109885	2.673802
1	1.206623	4.112802	2.697201
1	1.572712	2.410459	2.970455
1	-0.023388	3.064709	3.403146
6	-0.356210	0.452751	1.886860
1	-1.234844	-0.140750	1.644936
1	-0.453341	0.816222	2.906525
1	0.561890	-0.133244	1.783573
7	-0.017358	2.643417	-0.861319
7	-0.265209	1.582348	0.981362
53	3.036630	0.932745	-0.122412
1	-1.075344	0.289675	-2.656872
1	-0.004919	-1.466288	-0.873581
5	-2.956152	-0.306855	-0.638531

8	-3.382346	-0.170599	0.665838
8	-3.980718	-0.693188	-1.464354
6	-5.051320	-2.558379	-0.432519
1	-5.908226	-2.916252	0.139515
1	-5.054873	-3.043447	-1.408155
1	-4.136155	-2.845079	0.087649
6	-6.390860	-0.663960	-1.352474
1	-6.505948	-1.275856	-2.246977
1	-7.253794	-0.836178	-0.705596
1	-6.378775	0.381570	-1.652878
6	-5.286354	-0.927065	1.943497
1	-5.050337	-0.294467	2.799368
1	-6.366999	-1.082649	1.921552
1	-4.796655	-1.888918	2.081173
6	-5.346944	1.182645	0.610911
1	-6.435836	1.211120	0.664781
1	-4.940759	1.737420	1.456436
1	-5.027474	1.675732	-0.308024
6	1.106784	-2.463009	-0.532822
7	2.275132	-2.396955	-1.188796
6	3.352826	-2.667772	-0.363158
6	2.832201	-2.930846	0.859493
7	1.457210	-2.794554	0.725268
6	2.399500	-1.932142	-2.554012
1	2.973667	-1.004567	-2.565307
1	2.884499	-2.687921	-3.172375
1	1.399554	-1.741848	-2.936057
6	0.502955	-3.009347	1.788449
1	0.449282	-4.065115	2.058696
1	0.780784	-2.433695	2.672065
1	-0.473418	-2.683147	1.435690
6	4.756333	-2.549701	-0.829069
1	4.939598	-3.159696	-1.715815
1	4.974105	-1.504893	-1.065971
1	5.442317	-2.870182	-0.047436
6	3.484394	-3.218997	2.162052
1	3.371442	-2.376075	2.848262
1	3.065003	-4.107348	2.639237
1	4.549639	-3.385746	2.016680

Table S3. 30 Optimized cartesian coordinates of **TS3.3**

M06-2X/def2-TZVP

1st frequency: -54.1 cm⁻¹

Sum of electronic and thermal Free Energies = -1764.773519 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.346311	-0.641173	1.270599
6	1.304546	1.490851	1.430365
6	2.710055	2.800695	0.192391
6	3.466716	1.841952	0.780791
6	0.282872	3.397522	0.240590
1	0.431465	4.418162	0.595521
1	-0.605591	2.975803	0.699733
1	0.144629	3.409542	-0.841675
6	3.071529	3.918634	-0.719014
1	4.139309	3.903684	-0.930570
1	2.830722	4.888049	-0.277603
1	2.538772	3.853069	-1.671266
6	4.918560	1.538448	0.687605
1	5.426326	2.286515	0.081389
1	5.080605	0.559156	0.226396
1	5.391270	1.524441	1.671591
6	3.017001	-0.002862	2.404442
1	2.123473	-0.514580	2.757639
1	3.573750	0.388262	3.257299
1	3.651527	-0.700580	1.855726
6	1.067361	-0.931307	-0.094971
6	2.789056	-0.712209	-1.540261
6	3.060383	-1.777397	-0.748598
6	0.858288	0.808840	-1.868901
1	-0.040677	1.085794	-1.332605
1	0.572648	0.425843	-2.849859
1	1.508286	1.674721	-1.994599
6	3.574042	-0.066511	-2.623293
1	4.497321	-0.614486	-2.799682
1	3.834105	0.960729	-2.349933
1	3.016173	-0.031368	-3.560710
6	4.222943	-2.703402	-0.723083
1	4.903618	-2.469964	-1.539125
1	3.903030	-3.740747	-0.835224
1	4.781215	-2.628194	0.213404
6	1.866596	-2.977316	1.084942

1	1.197735	-2.663035	1.884286
1	2.849034	-3.215330	1.489927
1	1.432193	-3.851102	0.599475
7	1.407389	2.566166	0.613858
7	2.592602	1.079976	1.540459
7	1.558330	-0.225580	-1.135125
7	1.993703	-1.893846	0.125353
53	-1.634022	-2.762545	-0.025350
6	-3.417238	1.433625	-0.916542
6	-3.948985	1.387843	0.549157
8	-2.004843	1.186434	-0.733536
8	-2.993932	0.533254	1.197002
5	-1.843952	0.474544	0.444554
6	-3.596605	2.766068	-1.618746
1	-3.193064	2.701994	-2.629807
1	-4.656614	3.018566	-1.691007
1	-3.082658	3.568629	-1.091667
6	-3.953488	0.298466	-1.778946
1	-5.016275	0.427233	-1.988335
1	-3.409642	0.290318	-2.723986
1	-3.795203	-0.665715	-1.293176
6	-3.890453	2.739562	1.251808
1	-4.633407	3.431540	0.852348
1	-4.086325	2.587735	2.312846
1	-2.902245	3.190243	1.151474
6	-5.332295	0.781494	0.698421
1	-5.621226	0.795821	1.749319
1	-6.067427	1.356366	0.130557
1	-5.344810	-0.251017	0.355808

Table S3. 31 Optimized cartesian coordinates of compound **3.27a**

M06-2X/def2-TZVP

1st frequency: 14.1 cm⁻¹

Sum of electronic and thermal Free Energies = -600.310083 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.293157	-0.631900	0.237345
6	-0.897692	0.818228	-0.200641
8	0.391100	0.604592	-0.823911
8	-0.001287	-1.248253	0.457698
6	-0.663970	1.750526	0.980391
1	-0.208410	2.669867	0.613916
1	-1.601474	1.996135	1.480239
1	0.018165	1.302612	1.704499
6	-1.835361	1.453210	-1.206569
1	-2.839878	1.535739	-0.786568
1	-1.482371	2.455336	-1.449186
1	-1.883817	0.874234	-2.126595
6	-2.099229	-0.707616	1.517430
1	-3.043056	-0.171067	1.401373
1	-2.323545	-1.749754	1.744735
1	-1.552683	-0.282512	2.356601
6	-1.974516	-1.419671	-0.872967
1	-2.041956	-2.464549	-0.570983
1	-2.980622	-1.044245	-1.061986
1	-1.401346	-1.365924	-1.799777
5	0.893281	-0.528187	-0.266802
8	2.198083	-0.967716	-0.473579
6	3.232106	-0.203787	-0.095025
8	3.149028	0.752213	0.611240
1	4.170109	-0.595568	-0.503617

Table S3. 32 Optimized cartesian coordinates of **TS3.4**

M06-2X/def2-TZVP

1st frequency: -102.6 cm⁻¹

Sum of electronic and thermal Free Energies = -2365.094464 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.470596	-0.357794	-0.704400
6	-0.487740	-1.474080	0.511747
6	-1.660343	-2.219667	2.258321
6	-2.011441	-2.966472	1.175712
6	-0.091034	-0.335868	2.709405
1	0.811934	0.059998	2.249628
1	0.183640	-0.836779	3.635695
1	-0.785639	0.477854	2.908614
6	-2.166245	-2.231967	3.654345
1	-2.961335	-2.967505	3.754270
1	-2.570156	-1.255130	3.927993
1	-1.380397	-2.484885	4.367922
6	-3.048688	-4.014570	1.004717
1	-3.606376	-4.141809	1.930206
1	-2.617688	-4.980651	0.736226
1	-3.742194	-3.708277	0.218362
6	-1.336957	-3.065840	-1.219749
1	-2.179289	-2.629422	-1.752935
1	-1.463628	-4.142598	-1.132948
1	-0.422413	-2.854145	-1.767364
6	2.147231	-1.193898	-1.050462
6	4.063032	-2.329557	-0.967688
6	4.195716	-1.356453	-1.908947
6	2.293027	-2.962695	0.680989
1	1.300799	-3.362635	0.486289
1	2.283837	-2.287364	1.539846
1	2.968918	-3.788383	0.880075
6	5.054710	-3.305399	-0.448004
1	5.987075	-3.208847	-0.998764
1	4.709186	-4.335157	-0.553132
1	5.264644	-3.109738	0.605367
6	5.359898	-0.961317	-2.741792
1	6.212719	-1.595304	-2.512418
1	5.643040	0.072229	-2.536273
1	5.144408	-1.056109	-3.807325
6	2.724687	0.502109	-2.749047

1	1.693754	0.471401	-3.100599
1	3.384411	0.503985	-3.611785
1	2.899116	1.384734	-2.133390
7	-0.718292	-1.312792	1.824664
7	-1.258607	-2.503717	0.123054
7	2.778264	-2.230218	-0.475601
7	2.991962	-0.692782	-1.957363
53	3.532008	0.523685	1.506109
6	0.010119	3.484126	0.965424
6	0.531414	3.781871	-0.475738
8	-0.226175	2.050299	0.912024
8	1.135668	2.519054	-0.855678
5	0.555124	1.551926	-0.089275
6	-1.293570	4.173307	1.315414
1	-1.583732	3.906179	2.332148
1	-1.170085	5.257381	1.270741
1	-2.093582	3.879747	0.638634
6	1.056822	3.720415	2.043600
1	1.251371	4.786160	2.171717
1	0.683514	3.321679	2.987843
1	1.989412	3.205504	1.809031
6	-0.591189	4.032598	-1.474095
1	-1.085787	4.985965	-1.283919
1	-0.168192	4.053800	-2.478196
1	-1.331442	3.230458	-1.437450
6	1.584476	4.868452	-0.550842
1	1.881984	5.014601	-1.589290
1	1.182471	5.811532	-0.174631
1	2.466076	4.601093	0.028422
6	-0.694794	-0.357941	-2.246054
8	-1.780256	0.114548	-1.812508
8	-0.374595	-0.767571	-3.355849
6	-4.907207	0.873647	-0.756286
6	-4.843236	-0.489285	0.009821
8	-3.912968	-1.255864	-0.771198
8	-4.579341	0.486201	-2.095412
6	-6.168943	-1.243765	-0.013288
1	-6.007326	-2.249843	0.377102
1	-6.925249	-0.751466	0.599559
1	-6.542862	-1.329645	-1.033871
6	-4.333491	-0.377898	1.435950
1	-4.962364	0.301110	2.016088
1	-4.363910	-1.360076	1.912831
1	-3.306261	-0.010745	1.451964

6	-6.278864	1.526629	-0.758783
1	-6.604291	1.744098	0.261123
1	-6.226094	2.466516	-1.308288
1	-7.021243	0.893119	-1.240027
6	-3.861348	1.876833	-0.276869
1	-3.847072	2.711643	-0.979614
1	-4.111348	2.261279	0.714303
1	-2.865406	1.434650	-0.258378
5	-3.833929	-0.666750	-2.035819
1	-3.515892	-1.278885	-2.999215

Table S3. 33 Optimized cartesian coordinates of **TS3.5**

M06-2X/def2-TZVP

1st frequency: -1306.7 cm⁻¹

Sum of electronic and thermal Free Energies = -1542.825339 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.555410	0.773145	-0.149166
6	-2.331325	0.001454	-0.088827
6	-4.577368	0.056742	-0.207275
6	-4.207703	-1.243835	-0.092182
6	-3.336191	2.250918	-0.313702
1	-4.307027	2.633522	-0.612668
1	-2.595514	2.521937	-1.064606
1	-3.036553	2.679136	0.642212
6	-5.925352	0.674744	-0.311612
1	-6.692347	-0.093006	-0.244460
1	-6.054307	1.196955	-1.261155
1	-6.095107	1.390776	0.493842
6	-5.032549	-2.479981	-0.040520
1	-6.081321	-2.227075	-0.176302
1	-4.935966	-2.991794	0.918882
1	-4.754322	-3.181259	-0.828992
6	-2.024941	-2.456776	0.164524
1	-2.684336	-3.274371	0.439744
1	-1.299461	-2.300527	0.959186
1	-1.497963	-2.718107	-0.752240
6	0.576362	-0.711248	0.215988
6	2.172353	-1.995252	1.094826
6	2.026784	-2.355415	-0.207134
6	1.246912	-0.186586	2.543381
1	0.281573	0.295686	2.659475

1	2.010964	0.584437	2.415700
1	1.470351	-0.814552	3.402288
6	3.166546	-2.418724	2.112405
1	3.810140	-3.194312	1.704308
1	2.690647	-2.810569	3.012815
1	3.794002	-1.570053	2.392427
6	2.815561	-3.288197	-1.050473
1	3.549023	-3.809995	-0.440660
1	3.352389	-2.730388	-1.820950
1	2.186205	-4.036565	-1.535552
6	0.736203	-1.424729	-2.135092
1	-0.302207	-1.134091	-2.283901
1	0.918359	-2.369021	-2.642174
1	1.393329	-0.640883	-2.524229
7	-3.410460	0.797703	-0.213911
7	-2.821716	-1.254051	-0.018560
7	1.238647	-1.009457	1.343084
7	1.008904	-1.576683	-0.717195
53	3.028821	1.224142	-0.619703
8	-0.630737	1.758491	1.155426
6	-0.361672	3.115607	0.426837
8	-0.536817	4.089656	1.045631
1	-0.301245	2.170495	-0.949651

Table S3. 34 Optimized cartesian coordinates of **Int3.5**

M06-2X/def2-TZVP

Sum of electronic and thermal Free Energies = -1542.909572 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.620871	0.826884	0.373435
6	-2.422017	0.084679	0.083864
6	-4.618885	0.256878	-0.341801
6	-4.346767	-1.055450	-0.119065
6	-3.247284	2.378043	-0.327296
1	-4.193763	2.863347	-0.105089
1	-2.929836	2.635796	-1.337018
1	-2.494775	2.701590	0.392603
6	-5.897532	0.944775	-0.659700
1	-6.687871	0.212110	-0.805677
1	-5.811800	1.537805	-1.571409
1	-6.202540	1.610988	0.149350
6	-5.236342	-2.246734	-0.121028

1	-6.232516	-1.962054	-0.451845
1	-5.329054	-2.682955	0.875566
1	-4.866770	-3.019988	-0.796532
6	-2.289285	-2.367160	0.468942
1	-1.864949	-2.815965	-0.429466
1	-2.992322	-3.062389	0.920361
1	-1.492115	-2.159087	1.176795
6	0.509556	-0.709060	0.425573
6	2.119976	-2.111716	1.047564
6	1.758819	-2.438481	-0.222051
6	1.567171	-0.250173	2.618441
1	0.750894	0.460111	2.739422
1	2.495040	0.299279	2.444917
1	1.660835	-0.899616	3.486827
6	3.218857	-2.615095	1.908083
1	3.728662	-3.441716	1.418739
1	2.852066	-2.962926	2.875137
1	3.947804	-1.820202	2.079706
6	2.354291	-3.398052	-1.184882
1	3.140371	-3.970376	-0.697936
1	2.801687	-2.853047	-2.019570
1	1.617571	-4.100946	-1.578566
6	0.253591	-1.390491	-1.922084
1	-0.757882	-0.986857	-1.897763
1	0.245889	-2.344171	-2.445150
1	0.920852	-0.680250	-2.420292
7	-3.420833	0.931731	-0.204947
7	-2.988059	-1.131568	0.148267
7	1.312934	-1.062833	1.433570
7	0.734028	-1.583078	-0.567040
53	3.052621	0.953900	-0.866077
8	-0.699354	1.648650	1.675964
6	0.196575	4.076622	0.342138
8	0.952823	4.461145	1.073666
1	-0.420814	1.398847	-0.975262

Table S3. 35 Optimized cartesian coordinates of **Int3.6**

M06-2X/def2-TZVP

1st frequency: 9.1 cm⁻¹

Sum of electronic and thermal Free Energies = -1954.587092 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.388794	-0.225724	-0.630415
6	0.281967	1.554744	0.035331
6	0.320812	3.783420	0.146192
6	-0.360492	3.322731	1.232129
6	1.426616	2.741378	-1.844195
1	2.050581	1.856451	-1.961505
1	2.082122	3.607781	-1.824874
1	0.713811	2.834942	-2.663160
6	0.638561	5.170004	-0.284372
1	0.178432	5.883344	0.395519
1	0.262317	5.366526	-1.289426
1	1.714896	5.350047	-0.285847
6	-1.023122	4.043083	2.349605
1	-0.944162	5.117450	2.200960
1	-0.564457	3.799520	3.309593
1	-2.081072	3.782198	2.407180
6	-1.027601	1.083372	2.112741
1	-2.102311	1.255767	2.071392
1	-0.646343	1.324995	3.105682
1	-0.861173	0.028458	1.869740
6	1.654966	-1.178637	0.421066
6	3.285319	-1.889799	1.757938
6	2.907208	-2.935155	0.974865
6	2.634725	0.521931	1.933877
1	1.688014	0.882765	2.329055
1	3.008884	1.161679	1.131986
1	3.363832	0.501284	2.737586
6	4.378019	-1.786460	2.758920
1	4.861630	-2.753526	2.874476
1	4.006168	-1.478982	3.737709
1	5.132040	-1.069800	2.427195
6	3.430726	-4.322765	0.889960
1	4.203996	-4.471670	1.639695
1	3.873283	-4.512312	-0.089674
1	2.645273	-5.059564	1.065060
6	1.132549	-3.252158	-0.792075

1	0.118682	-3.382537	-0.410797
1	1.620068	-4.211755	-0.932366
1	1.121666	-2.731666	-1.750571
7	0.707427	2.674009	-0.574252
7	-0.371912	1.949685	1.137249
7	2.475114	-0.825917	1.417492
7	1.891645	-2.469006	0.170839
53	4.243274	0.216839	-1.379736
1	0.937504	-0.102427	-1.992664
6	-1.277682	-1.132955	-0.303206
8	-2.264575	0.018918	-0.340492
8	-1.208543	-1.727184	0.848476
6	-5.518837	-1.356214	-0.823994
6	-5.781082	-0.133409	0.113729
8	-4.555526	0.607923	-0.002698
8	-4.098095	-1.522068	-0.716078
6	-5.921395	-0.544576	1.575302
1	-5.903465	0.353918	2.192860
1	-6.859367	-1.071272	1.755684
1	-5.091473	-1.186902	1.875463
6	-6.944088	0.744952	-0.303759
1	-7.870788	0.167296	-0.321183
1	-7.062411	1.558135	0.413050
1	-6.780230	1.177475	-1.288848
6	-6.205248	-2.639448	-0.397029
1	-7.287861	-2.499290	-0.356893
1	-5.988666	-3.425911	-1.120472
1	-5.852691	-2.968349	0.578387
6	-5.831074	-1.048790	-2.284236
1	-5.432318	-1.853171	-2.902174
1	-6.905528	-0.974693	-2.457209
1	-5.359955	-0.113764	-2.591843
5	-3.570853	-0.302627	-0.348375
1	-1.578369	-1.755245	-1.170782

Table S3. 36 Optimized cartesian coordinates of **TS3.6**

M06-2X/def2-TZVP

1st frequency: -168.3 cm⁻¹

Sum of electronic and thermal Free Energies = -1954.592477 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.174655	-1.444939	-0.376807
6	-0.287240	0.411666	0.123362
6	-0.464267	2.642478	0.174094
6	-0.382150	2.203659	1.456708
6	-0.297038	1.612552	-2.063583
1	0.705078	1.979408	-2.295851
1	-1.048317	2.295610	-2.456114
1	-0.451347	0.631758	-2.498874
6	-0.457639	4.016054	-0.386215
1	-0.498678	4.745117	0.419238
1	-1.306222	4.194379	-1.049042
1	0.468156	4.180763	-0.943186
6	-0.290169	2.950415	2.735008
1	-0.385124	4.017463	2.549635
1	0.681134	2.774493	3.202054
1	-1.073163	2.653319	3.434033
6	-0.047688	0.020030	2.577002
1	-0.770115	0.279655	3.347450
1	0.966636	0.224987	2.923473
1	-0.175580	-1.034738	2.352799
6	1.739541	-1.680117	-0.532467
6	3.857983	-2.057283	0.077297
6	3.875611	-1.580685	-1.194542
6	2.109442	-2.568156	1.770187
1	2.641424	-3.483167	2.023988
1	1.038689	-2.784472	1.783393
1	2.358057	-1.796476	2.499140
6	4.966078	-2.382463	1.009158
1	5.922156	-2.231742	0.514081
1	4.919550	-3.416966	1.353027
1	4.931725	-1.726424	1.880964
6	5.006662	-1.183141	-2.068020
1	5.950393	-1.405759	-1.576228
1	4.964664	-0.105527	-2.245792
1	4.991171	-1.705310	-3.026117
6	2.197753	-0.729860	-2.795248

1	1.148320	-0.907833	-3.001225
1	2.793179	-1.141047	-3.607356
1	2.395476	0.339128	-2.688525
7	-0.425962	1.522335	-0.624456
7	-0.293702	0.833452	1.397175
7	2.535910	-2.128714	0.449910
7	2.562667	-1.386009	-1.556164
53	3.044067	1.686308	0.090466
1	-0.577406	-1.410200	-1.807285
6	-1.461977	-2.655100	1.017849
8	-2.351774	-1.582253	1.454820
8	-0.850794	-3.219228	1.938734
6	-4.403814	-0.489249	-1.249414
6	-5.148784	0.054937	0.013353
8	-4.142998	-0.055288	1.034502
8	-3.474509	-1.428103	-0.676275
6	-6.316787	-0.832052	0.429064
1	-6.659341	-0.517101	1.414231
1	-7.147372	-0.752810	-0.273247
1	-6.009922	-1.877104	0.492632
6	-5.595924	1.500243	-0.091310
1	-6.282545	1.628356	-0.930703
1	-6.116305	1.785533	0.822877
1	-4.747124	2.168792	-0.222704
6	-5.287691	-1.208414	-2.249126
1	-6.065628	-0.538026	-2.620188
1	-4.686697	-1.538535	-3.096706
1	-5.758691	-2.081917	-1.803389
6	-3.578115	0.585306	-1.945913
1	-2.918062	0.101125	-2.667061
1	-4.212181	1.298573	-2.474212
1	-2.966571	1.126536	-1.221232
5	-3.283337	-1.055097	0.641120
1	-1.987624	-3.232931	0.244068

A Parent NHC–Silyliumylidene Cation (2.20) in Catalytic *N*-formylation of Amines

Figure S3. 165 Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Figure S3. 165 (cont.) Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Compound **3.31u**

(PhSiH₂)₂O

TS3.10

PhH₂SiOC(O)H

Figure S3. 165 (cont.) Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Scheme S3. 6 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 25 °C and 1 atm for catalytic *N*-formylation reaction. The abbreviations Cpd, der., Int and TS stand for compound, derivative, intermediate and transition state, respectively. Geometrical coordinates of the compound **2.20**, PhSiH₃, compound **3.30u**, amine derivative, intermediates, transition states, H₂, formamide **3.31u** and (PhSiH₂)₂O are at M06-2X/def2-TZVP level of theory.

Scheme S3. 7 Calculated Gibbs free energy profile (kcal/mol) in gas phase at 25 °C and 1 atm for catalytic hydrosilylation of CO₂. The abbreviations Cpd, Int and TS stand for compound, intermediate and transition state, respectively. Geometrical coordinates of the compound **2.20**, PhSiH₃, intermediates, transition states and PhH₂SiOC(O)H are at M06-2X/def2-TZVP level of theory.

Table S3. 37 Optimized cartesian coordinates of compound **2.20**

M06-2X/def2-TZVP

1st frequency: 19.5 cm⁻¹

Sum of electronic and thermal Free Energies = -1354.293565 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-0.590631	-0.964751	1.167401
6	-2.318192	-0.426648	0.444038
6	-4.465731	-0.595928	-0.232511
6	-4.233514	0.706303	0.062913
6	-3.064275	-2.699511	-0.144590
1	-4.014680	-3.181114	-0.355313
1	-2.648374	-3.108304	0.775964
1	-2.362554	-2.892415	-0.955351
6	-5.693837	-1.274501	-0.723529
1	-6.483336	-0.542630	-0.878327
1	-6.059248	-2.012683	-0.006950
1	-5.517339	-1.783788	-1.672684
6	-5.126723	1.892572	-0.004700
1	-6.093471	1.605599	-0.412166
1	-4.709203	2.670767	-0.646389
1	-5.297369	2.325498	0.983102
6	-2.243251	1.987211	0.939911
1	-1.649035	1.744430	1.821367
1	-2.989397	2.731569	1.205534
1	-1.584288	2.387597	0.169012
6	0.401503	0.449901	0.275994
6	1.513572	1.652204	-1.253381
6	1.906240	2.080365	-0.027028
6	0.086551	-0.218944	-2.078160
1	-0.930368	-0.530870	-1.855662
1	0.747754	-1.089705	-2.100034
1	0.107762	0.298036	-3.034096
6	2.031539	1.989120	-2.603251
1	2.776964	2.777333	-2.526269
1	1.243541	2.332695	-3.275995
1	2.512565	1.112743	-3.043544
6	2.979694	3.023216	0.375083
1	3.407513	3.498113	-0.504631
1	3.776795	2.477669	0.885714
1	2.611927	3.806950	1.039706
6	1.517918	1.331916	2.307057

1	0.731332	0.820284	2.854005
1	1.624379	2.351954	2.671799
1	2.452274	0.778105	2.428317
7	-3.276674	-1.270947	0.010281
7	-2.910835	0.784197	0.480003
7	0.558560	0.677829	-1.040433
7	1.184207	1.350222	0.893972
53	3.176670	-1.382027	0.066991
1	-0.384575	-1.996627	0.104920

Table S3. 38 Optimized cartesian coordinates of **Int3.1**

M06-2X/def2-TZVP

1st frequency: 25.0 cm⁻¹

Sum of electronic and thermal Free Energies = -1542.902860 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z

14	0.244638	2.074586	0.914866
6	-1.403251	1.112830	0.640150
6	-3.055573	-0.379677	0.828074
6	-3.252280	0.314943	-0.324369
6	-1.307496	-0.435953	2.584701
1	-0.811954	-1.361394	2.280328
1	-2.069392	-0.639572	3.334264
1	-0.588030	0.264699	2.997363
6	-3.758172	-1.558169	1.391073
1	-4.598771	-1.828484	0.756741
1	-4.137867	-1.366514	2.396203
1	-3.070296	-2.407065	1.421818
6	-4.270755	0.156267	-1.392280
1	-4.962558	-0.639263	-1.126739
1	-3.794992	-0.114232	-2.336850
1	-4.845337	1.071276	-1.545696
6	-2.097704	2.175599	-1.512255
1	-3.052968	2.673487	-1.669345
1	-1.828622	1.628697	-2.416008
1	-1.344104	2.932168	-1.286456
6	1.550227	0.789828	0.386602
6	2.802653	-0.485253	-0.949037
6	3.092936	-0.824384	0.333942
6	1.188324	1.041068	-2.059892
1	0.758157	2.016329	-1.844137
1	0.417065	0.321107	-2.346549

1	1.908277	1.159709	-2.865661
6	3.232159	-1.088482	-2.233691
1	3.964084	-1.871320	-2.050543
1	3.681258	-0.351580	-2.901133
1	2.368327	-1.540865	-2.727292
6	3.959794	-1.895664	0.884109
1	4.463553	-2.414068	0.072115
1	3.358024	-2.628287	1.426148
1	4.722632	-1.501192	1.557635
6	2.303334	-0.122378	2.582103
1	1.845904	0.765431	3.006020
1	3.324795	-0.195987	2.948495
1	1.747044	-1.013537	2.875829
7	-1.930430	0.150526	1.413683
7	-2.233256	1.236618	-0.406423
7	1.871628	0.524604	-0.886100
7	2.318562	-0.014813	1.136316
53	-0.297102	-2.224761	-0.539068
1	0.323890	2.201775	2.377742
6	0.750150	3.711042	0.008825
8	0.154867	4.303265	-0.881268
8	1.839100	3.866558	0.583459

Table S3. 39 Optimized cartesian coordinates of PhSiH₃

M06-2X/def2-TZVP

1st frequency: 15.7 cm⁻¹

Sum of electronic and thermal Free Energies = -522.816858 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	-2.333402	0.000006	0.006205
1	-2.835076	1.212915	-0.673911
1	-2.835458	-1.208090	-0.682133
1	-2.849710	-0.004753	1.392351
6	-0.464792	0.000044	-0.014233
6	0.253166	-1.198090	-0.010375
6	0.253213	1.198118	-0.010372
6	1.640988	-1.201256	0.003257
1	-0.276169	-2.144566	-0.023459
6	1.641062	1.201207	0.003250
1	-0.276096	2.144600	-0.023446
6	2.336574	-0.000032	0.011117

1	2.179846	-2.140149	0.004291
1	2.179972	2.140070	0.004270
1	3.419049	-0.000064	0.019313

Table S3. 40 Optimized cartesian coordinates of compound **3.30u**

M06-2X/def2-TZVP

1st frequency: 56.5 cm⁻¹

Sum of electronic and thermal Free Energies = -326.767281 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-0.496506	-1.284561	-0.021361
6	-1.853604	-1.013116	-0.126143
6	-2.304080	0.298659	-0.087170
6	-1.389215	1.332977	0.057654
6	-0.033346	1.058911	0.167058
6	0.426213	-0.254455	0.130587
1	-0.147013	-2.310335	-0.061818
1	-2.558708	-1.825876	-0.245644
1	-3.361382	0.513434	-0.174175
1	-1.734094	2.358981	0.086235
1	0.686465	1.859860	0.275926
6	1.896201	-0.565479	0.285324
1	2.135391	-0.613158	1.351819
1	2.083083	-1.566604	-0.123364
7	2.730533	0.477062	-0.301767
1	3.710006	0.294987	-0.126493
1	2.598549	0.511662	-1.305818

Table S3. 41 Optimized cartesian coordinates of **TS3.7**

M06-2X/def2-TZVP

1st frequency: -246.2 cm⁻¹

Sum of electronic and thermal Free Energies = -2392.466022 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.470114	-1.047698	0.739978
6	2.197279	-1.823625	0.361740
6	4.358435	-2.402058	0.408142
6	3.859934	-2.764915	-0.803441
6	3.480689	-1.197497	2.395668
1	3.935686	-0.218451	2.224852
1	4.122253	-1.808695	3.026630
1	2.509328	-1.092909	2.868604
6	5.741259	-2.438672	0.943822
1	6.411575	-2.882006	0.211345
1	5.806398	-3.021803	1.864195
1	6.079063	-1.417461	1.136560
6	4.525265	-3.346748	-1.995899
1	5.554271	-3.603845	-1.757193
1	4.541825	-2.625500	-2.815529
1	4.020337	-4.249852	-2.342436
6	1.635447	-2.653322	-1.925070
1	1.611374	-3.720912	-2.139907
1	2.003521	-2.120625	-2.801538
1	0.627434	-2.310490	-1.694003
6	0.964813	0.809977	0.594130
6	1.436807	2.750894	-0.415935
6	1.450610	2.971355	0.924054
6	1.146678	0.749894	-1.877592
1	0.428085	-0.069934	-1.879892
1	2.172208	0.415250	-2.054741
1	0.851103	1.454416	-2.650778
6	1.788911	3.640793	-1.548881
1	2.042309	4.630795	-1.177455
1	0.964949	3.741254	-2.257373
1	2.663860	3.238843	-2.065037
6	1.801362	4.180989	1.708652
1	1.975181	5.018059	1.037202
1	2.718066	4.014540	2.278427
1	1.006562	4.462702	2.401540
6	1.110417	1.594958	2.960425

1	0.755870	0.597055	3.192531
1	0.430355	2.324193	3.397810
1	2.109752	1.738145	3.372672
7	3.311867	-1.849688	1.110477
7	2.528556	-2.408319	-0.801913
7	1.110986	1.426304	-0.589842
7	1.150142	1.765441	1.522211
53	4.619718	1.121437	-0.313563
1	0.393139	-1.234560	2.215669
6	-1.497890	-1.336003	-0.392643
8	-1.331659	-1.289743	-1.628058
8	-2.047348	-0.212885	0.273976
14	-2.336707	1.279939	-0.385562
6	-4.168758	1.600443	-0.436730
6	-4.942496	1.425250	0.715108
6	-4.804748	2.024178	-1.603189
6	-6.305120	1.672804	0.703069
1	-4.477389	1.071705	1.629598
6	-6.172367	2.272869	-1.621385
1	-4.228666	2.156045	-2.512325
6	-6.921586	2.099562	-0.467451
1	-6.891000	1.519467	1.600350
1	-6.651478	2.599476	-2.535782
1	-7.987519	2.289741	-0.479650
1	-3.666942	-0.294189	-3.546756
1	-1.695877	2.238659	0.548118
1	-1.758560	1.452317	-1.731728
6	-5.443611	-2.186411	1.735709
6	-6.749979	-1.882416	1.385652
6	-7.054375	-1.529654	0.076222
6	-6.042901	-1.477865	-0.869485
6	-4.734547	-1.785085	-0.515446
6	-4.421467	-2.144749	0.789515
1	-5.211233	-2.468093	2.757732
1	-7.532398	-1.922952	2.133264
1	-8.071993	-1.284366	-0.199586
1	-6.264583	-1.182416	-1.887492
1	-3.952037	-1.725593	-1.262780
6	-3.009537	-2.511774	1.213465
1	-2.672793	-1.812742	1.981199
1	-3.035223	-3.498688	1.683058
7	-2.015253	-2.541821	0.165041
1	-2.232602	-3.169313	-0.598005
1	-3.060130	-0.516253	-3.176899

Table S3. 42 Optimized cartesian coordinates of **Int3.7**

M06-2X/def2-TZVP

1st frequency: 18.9 cm⁻¹

Sum of electronic and thermal Free Energies = -2391.313517 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.282394	-0.661931	0.768055
6	1.635238	-1.750990	-0.029520
6	3.565360	-2.840021	-0.307923
6	2.930246	-2.802345	-1.510171
6	3.140096	-1.912373	1.952052
1	3.801226	-1.041887	1.931254
1	3.662813	-2.772672	2.363328
1	2.259686	-1.716410	2.556172
6	4.917676	-3.322487	0.064680
1	5.408524	-3.755438	-0.803561
1	4.879598	-4.080532	0.849040
1	5.517485	-2.475040	0.406464
6	3.363442	-3.265686	-2.851787
1	4.274681	-3.852423	-2.765133
1	3.573391	-2.412374	-3.500139
1	2.603227	-3.884243	-3.330822
6	0.768643	-1.918347	-2.369763
1	0.417550	-2.883836	-2.732499
1	1.251790	-1.381369	-3.185822
1	-0.084845	-1.344075	-2.003720
6	1.126031	1.050779	0.847778
6	2.013354	2.965922	0.132089
6	2.246587	2.878750	1.470249
6	0.994700	1.475309	-1.588476
1	0.104634	0.840418	-1.605863
1	1.877289	0.984918	-2.008862
1	0.771131	2.379223	-2.149660
6	2.477772	3.955732	-0.869308
1	3.041153	4.744946	-0.377391
1	1.644503	4.412078	-1.405731
1	3.140671	3.460927	-1.582937
6	3.033612	3.750146	2.377474
1	3.363543	4.636040	1.840716
1	3.922651	3.222635	2.730567
1	2.451664	4.075451	3.241494
6	1.782252	1.217050	3.253750

1	1.111314	0.376500	3.393555
1	1.494249	2.012034	3.938697
1	2.810181	0.915880	3.459969
7	2.736674	-2.209662	0.589245
7	1.743287	-2.135316	-1.309099
7	1.306889	1.843508	-0.215326
7	1.681685	1.695777	1.888441
53	4.613802	0.611536	-0.371147
1	0.215737	-1.142184	2.160242
6	-1.475689	-0.654094	-0.043984
8	-1.610848	-0.234020	-1.267288
8	-2.160499	0.196263	0.924675
14	-2.653905	1.671988	0.348089
6	-4.174223	1.750849	-0.740617
6	-5.324900	2.357089	-0.232377
6	-4.210387	1.264511	-2.051878
6	-6.476868	2.478412	-1.000693
1	-5.327695	2.735459	0.783905
6	-5.358212	1.382373	-2.821943
1	-3.332497	0.767246	-2.447576
6	-6.493849	1.991099	-2.298625
1	-7.359556	2.946955	-0.583689
1	-5.371010	0.996872	-3.834025
1	-7.389822	2.078675	-2.900904
1	-3.022966	2.404254	1.583508
1	-1.522691	2.392508	-0.282087
6	-5.024411	-2.644807	2.180756
6	-6.386032	-2.391564	2.133494
6	-6.920449	-1.645883	1.088448
6	-6.082983	-1.168570	0.092295
6	-4.719553	-1.433753	0.140016
6	-4.174151	-2.162188	1.187692
1	-4.611507	-3.223190	3.001115
1	-7.033208	-2.772170	2.913881
1	-7.982642	-1.439787	1.055280
1	-6.476258	-0.571030	-0.722511
1	-4.077246	-1.045050	-0.640033
6	-2.685892	-2.438842	1.285464
1	-2.292068	-1.910582	2.157201
1	-2.544466	-3.506947	1.477283
7	-1.886311	-2.063715	0.133660
1	-2.329829	-2.332480	-0.738521

Table S3. 43 Optimized cartesian coordinates of **TS3.8**

M06-2X/def2-TZVP

1st frequency: -639.5 cm⁻¹

Sum of electronic and thermal Free Energies = -2914.096888 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.796497	1.586681	-1.479338
6	2.676315	2.031804	-1.130207
6	4.916006	2.194153	-1.212970
6	4.495884	2.909617	-0.140328
6	3.846864	0.687662	-2.864571
1	4.088736	-0.277301	-2.410367
1	4.618383	0.970083	-3.577376
1	2.887838	0.645045	-3.368324
6	6.283075	1.860917	-1.682629
1	7.021244	2.337912	-1.042236
1	6.453681	2.192626	-2.708650
1	6.433006	0.780752	-1.618269
6	5.260108	3.592764	0.932771
1	6.321463	3.574488	0.698019
1	5.122325	3.073606	1.883942
1	4.957655	4.634166	1.056639
6	2.303867	3.413496	0.914423
1	2.540169	4.473840	0.992044
1	2.498737	2.931245	1.872805
1	1.256231	3.296077	0.650342
6	1.067780	-0.290068	-1.038896
6	1.266507	-2.102085	0.275574
6	1.262768	-2.527167	-1.011626
6	1.200105	0.117580	1.399910
1	0.641065	1.033277	1.207592
1	2.248421	0.335656	1.619023
1	0.750384	-0.405256	2.241540
6	1.419739	-2.845612	1.549283
1	1.631457	-3.891627	1.341240
1	0.501758	-2.806079	2.143956
1	2.255942	-2.436338	2.120111
6	1.457666	-3.877689	-1.594547
1	1.497301	-4.617518	-0.797981
1	2.399113	-3.927361	-2.146544
1	0.641132	-4.143825	-2.268924
6	0.944308	-1.476234	-3.232134

1	0.853304	-0.474184	-3.636198
1	0.028158	-2.030980	-3.439461
1	1.791813	-1.985272	-3.691499
7	3.783931	1.680816	-1.808432
7	3.119680	2.803422	-0.117463
7	1.130812	-0.730424	0.228888
7	1.135336	-1.397089	-1.799529
53	4.708908	-0.853622	0.550154
1	0.974770	1.459219	-2.965107
6	-2.357793	-0.160236	-0.445748
8	-1.761414	-0.037065	0.728673
8	-1.835538	-0.970147	-1.321233
14	-2.557037	-2.558045	-0.960107
6	-2.087662	-3.609312	0.544491
6	-2.497970	-3.316704	1.845867
6	-1.288759	-4.740310	0.358771
6	-2.117686	-4.107984	2.922769
1	-3.144925	-2.462364	2.013727
6	-0.914581	-5.547172	1.424774
1	-0.958348	-4.992099	-0.642487
6	-1.321807	-5.226212	2.713075
1	-2.445114	-3.856619	3.924135
1	-0.299746	-6.422630	1.253784
1	-1.021868	-5.845458	3.548944
1	-3.836405	-2.840385	-1.670934
1	-1.587698	-3.189007	-1.940840
6	-6.037850	1.990762	-2.579125
6	-7.415049	2.087432	-2.422362
6	-8.086147	1.177001	-1.620954
6	-7.378567	0.168196	-0.977268
6	-6.005716	0.069067	-1.136628
6	-5.327462	0.982101	-1.941895
1	-5.512832	2.705191	-3.202548
1	-7.960357	2.876325	-2.923792
1	-9.158562	1.251418	-1.496335
1	-7.899958	-0.546331	-0.353710
1	-5.448461	-0.718923	-0.640261
6	-3.835283	0.860103	-2.125258
1	-3.579429	-0.063652	-2.642228
1	-3.452460	1.691034	-2.719838
7	-3.137992	0.834692	-0.846596
1	-3.346972	1.569774	-0.184218
1	-3.432781	-1.531905	0.041856
14	-2.427025	0.378047	2.212270

1	-1.587937	-0.288847	3.218682
1	-3.816588	-0.114092	2.261498
6	-2.388050	2.231687	2.342481
6	-3.052423	2.879763	3.388527
6	-1.696399	3.007184	1.407608
6	-3.020070	4.260711	3.503661
1	-3.605641	2.303582	4.123287
6	-1.670016	4.392452	1.518226
1	-1.173226	2.537051	0.577497
6	-2.327796	5.018782	2.566511
1	-3.537863	4.748081	4.319526
1	-1.136043	4.977551	0.779446
1	-2.307247	6.097539	2.653711

Table S3. 44 Optimized cartesian coordinates of **Int3.8**

M06-2X/def2-TZVP

1st frequency: 13.8 cm⁻¹

Sum of electronic and thermal Free Energies = -1559.860789 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.034590	2.849212	1.054437
6	3.413421	2.810678	1.222804
6	4.226927	2.366509	0.190915
6	3.653841	1.964206	-1.008617
6	2.278001	2.011906	-1.177183
6	1.455302	2.454984	-0.145929
1	1.401416	3.184689	1.868365
1	3.849357	3.120419	2.164461
1	5.300197	2.321669	0.323442
1	4.281629	1.604196	-1.813838
1	1.825539	1.696008	-2.108655
6	-0.039801	2.571396	-0.343528
1	-0.525118	2.610649	0.641965
1	-0.244709	3.527420	-0.831006
7	-0.604777	1.524515	-1.183473
1	-1.392931	1.856095	-1.722021
6	-1.004835	0.343853	-0.467200
8	-1.754349	-0.432209	-1.356667
8	0.103876	-0.353364	-0.005845
14	1.018070	-1.329163	-0.993174
1	1.263480	-0.686924	-2.298655

1	0.322201	-2.613892	-1.236213
6	2.592060	-1.664334	-0.064458
6	3.341664	-2.807556	-0.350771
6	3.069520	-0.780484	0.904045
6	4.537609	-3.060658	0.305171
1	2.985001	-3.516890	-1.091036
6	4.264338	-1.031312	1.564900
1	2.504475	0.114573	1.139665
6	4.999411	-2.170270	1.265908
1	5.106181	-3.952093	0.072286
1	4.622768	-0.332127	2.310514
1	5.931015	-2.366298	1.781911
1	-1.603709	0.584220	0.426892
14	-2.849055	-1.565609	-0.837910
1	-3.291925	-2.233753	-2.072295
1	-2.232744	-2.530597	0.096488
6	-4.252454	-0.712272	0.042471
6	-4.706008	-1.149933	1.287637
6	-4.882629	0.390906	-0.541666
6	-5.762115	-0.513939	1.927927
1	-4.226497	-1.996217	1.767449
6	-5.933952	1.032937	0.094833
1	-4.548012	0.752184	-1.508806
6	-6.375617	0.577824	1.331285
1	-6.102631	-0.866953	2.892946
1	-6.412203	1.884883	-0.371501
1	-7.197399	1.076619	1.829339

Table S3. 45 Optimized cartesian coordinates of **TS3.9**

M06-2X/def2-TZVP

1st frequency: -287.3 cm⁻¹

Sum of electronic and thermal Free Energies = -1559.835433 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	3.699561	0.773740	0.786769
6	4.988037	0.425188	1.173002
6	5.458625	-0.856922	0.935443
6	4.637553	-1.790398	0.313190
6	3.351852	-1.442883	-0.069537
6	2.875036	-0.155240	0.165051
1	3.328924	1.776169	0.970388
1	5.622931	1.156599	1.656055
1	6.462146	-1.130906	1.233911
1	5.000390	-2.793559	0.130279
1	2.705512	-2.170162	-0.547108
6	1.469604	0.225815	-0.227027
1	0.734893	-0.338520	0.348379
1	1.292777	1.282623	-0.028039
7	1.186973	-0.013755	-1.640923
1	1.414178	0.723494	-2.290218
6	0.435276	-1.002025	-2.088149
8	-1.454525	-0.687688	-1.853907
8	0.298419	-2.084347	-1.366929
14	-1.366288	-2.433901	-0.922892
1	-0.899774	-3.728927	-0.323393
1	-2.342246	-2.919740	-1.919836
6	-2.088005	-1.658938	0.632771
6	-3.393358	-1.161460	0.668813
6	-1.333111	-1.590676	1.805477
6	-3.922595	-0.607363	1.827802
1	-4.010434	-1.210169	-0.221632
6	-1.841889	-1.008000	2.959814
1	-0.331143	-2.010071	1.821815
6	-3.141100	-0.516772	2.972748
1	-4.940898	-0.239289	1.836420
1	-1.232406	-0.952307	3.853241
1	-3.546583	-0.074554	3.873910
1	0.323211	-1.056305	-3.166845
14	-2.115900	0.795215	-1.957046
1	-1.873732	1.333264	-3.321642

1	-3.569797	0.755139	-1.697559
6	-1.272854	2.004002	-0.795314
6	-0.444323	3.008493	-1.303370
6	-1.379964	1.884606	0.594475
6	0.267399	3.854851	-0.460630
1	-0.353803	3.135548	-2.377831
6	-0.674146	2.727766	1.442201
1	-2.013964	1.118580	1.026719
6	0.155192	3.711067	0.916334
1	0.903098	4.626966	-0.875780
1	-0.770420	2.613506	2.514731
1	0.707064	4.367682	1.577155

Table S3. 46 Optimized cartesian coordinates of compound **3.31u**

M06-2X/def2-TZVP

1st frequency: 24.1 cm⁻¹

Sum of electronic and thermal Free Energies = -440.109812 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.663456	1.233195	0.014821
6	-2.899266	0.605412	0.057537
6	-2.974849	-0.780394	0.032174
6	-1.809462	-1.530443	-0.036527
6	-0.573722	-0.899922	-0.083074
6	-0.491540	0.487611	-0.061020
1	-1.607085	2.315778	0.043370
1	-3.803335	1.197701	0.117234
1	-3.937399	-1.273470	0.071986
1	-1.860766	-2.611519	-0.051809
1	0.333134	-1.490805	-0.128355
6	0.841470	1.199262	-0.155509
1	1.083600	1.380331	-1.206463
1	0.760700	2.181046	0.316760
7	1.946556	0.466529	0.412851
1	1.942658	0.261547	1.401997
6	2.929396	-0.122903	-0.310599
8	3.807969	-0.809558	0.148525
1	2.847412	0.099248	-1.389686

Table S3. 47 Optimized cartesian coordinates of (PhSiH₂)₂O

M06-2X/def2-TZVP

1st frequency: 23.3 cm⁻¹

Sum of electronic and thermal Free Energies = -1119.787655 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
8	2.616689	0.000133	0.000004
14	2.017657	1.136280	1.022975
1	1.959053	0.594049	2.397244
1	2.927550	2.296904	0.969640
14	2.017778	-1.136072	-1.022973
1	2.927795	-2.296599	-0.969644
1	1.959118	-0.593841	-2.397240
6	0.294743	1.613564	0.497862
6	0.084633	2.281352	-0.712205
6	-0.821062	1.234780	1.246483
6	-1.198271	2.559605	-1.161948
1	0.933530	2.587293	-1.315686
6	-2.106413	1.515355	0.804479
1	-0.686853	0.698669	2.179638
6	-2.295437	2.176306	-0.401204
1	-1.343578	3.077435	-2.101562
1	-2.960392	1.206859	1.394074
1	-3.297537	2.392478	-0.749651
6	0.294914	-1.613537	-0.497863
6	0.084870	-2.281355	0.712199
6	-0.820929	-1.234856	-1.246480
6	-1.198005	-2.559739	1.161941
1	0.933799	-2.587216	1.315676
6	-2.106252	-1.515560	-0.804476
1	-0.686774	-0.698725	-2.179630
6	-2.295209	-2.176539	0.401202
1	-1.343261	-3.077591	2.101550
1	-2.960264	-1.207142	-1.394065
1	-3.297288	-2.392811	0.749649

Table S3. 48 Optimized cartesian coordinates of **TS3.10**

M06-2X/def2-TZVP

1st frequency: -744.1 cm⁻¹

Sum of electronic and thermal Free Energies = -2065.692655 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.068096	-1.675278	1.203650
6	1.926044	-1.484779	0.618461
6	4.031564	-0.744903	0.469640
6	3.843942	-1.664008	-0.516471
6	2.597278	0.201401	2.296783
1	1.590552	0.605622	2.224278
1	3.274888	1.047306	2.242097
1	2.733797	-0.353247	3.225715
6	5.196363	0.117153	0.788527
1	6.038615	-0.143705	0.152048
1	5.507541	0.003227	1.827963
1	4.931796	1.162110	0.604592
6	4.756437	-2.151656	-1.582193
1	5.696187	-1.606684	-1.539971
1	4.323298	-1.995424	-2.571526
1	4.976103	-3.215308	-1.471649
6	1.961016	-3.137208	-1.250861
1	2.670764	-3.955760	-1.351250
1	1.749646	-2.726487	-2.238126
1	1.048941	-3.524663	-0.802710
6	-0.660008	-0.033723	0.604234
6	-1.289244	1.629255	-0.739712
6	-1.605434	1.986428	0.533700
6	-0.127672	-0.290138	-1.808351
1	-0.065828	-1.353463	-1.600507
1	0.852552	0.155166	-1.996888
1	-0.778366	-0.155674	-2.670209
6	-1.406726	2.375348	-2.014481
1	-1.889203	3.334070	-1.838185
1	-2.001972	1.823786	-2.744834
1	-0.409599	2.563779	-2.419459
6	-2.168228	3.245999	1.077781
1	-2.567269	3.851056	0.266834
1	-1.392250	3.825179	1.583632
1	-2.979460	3.051631	1.780761
6	-1.443091	0.916317	2.771120

1	-2.513497	0.993913	2.961903
1	-0.925438	1.750761	3.243386
1	-1.083255	-0.023153	3.178090
7	2.841747	-0.670162	1.157867
7	2.542607	-2.111411	-0.395524
7	-0.720174	0.381933	-0.666304
7	-1.210729	0.944362	1.340565
53	2.189032	2.402204	-0.450678
1	0.282066	-1.711413	2.657787
6	-0.912899	-3.074758	0.547021
8	-1.639621	-2.757347	-0.644550
8	-0.779135	-4.257459	0.853437
14	-3.286060	-2.669675	-0.612504
1	-1.703508	-2.238471	1.522048
1	-3.817559	-3.507506	0.477309
1	-3.757912	-3.107668	-1.943233
6	-3.912976	-0.914258	-0.388031
6	-4.140434	-0.095201	-1.496988
6	-4.240150	-0.406734	0.873988
6	-4.671337	1.182045	-1.358663
1	-3.917917	-0.467993	-2.492270
6	-4.780664	0.863807	1.019481
1	-4.082600	-1.025346	1.751594
6	-4.996652	1.661163	-0.098332
1	-4.845555	1.795731	-2.233946
1	-5.052772	1.228445	2.003517
1	-5.426870	2.648787	0.013880

Table S3. 49 Optimized cartesian coordinates of PhH₂SiOC(O)H

M06-2X/def2-TZVP

Sum of electronic and thermal Free Energies = -711.430235 Hartree

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
14	0.914843	-1.237804	-0.168313
1	1.248804	-1.941577	1.089472
1	0.985109	-2.183051	-1.294565
6	-0.731347	-0.392625	-0.066096
6	-1.890433	-1.139265	0.161778
6	-0.844047	0.990699	-0.211760
6	-3.128716	-0.521738	0.244345
1	-1.831091	-2.216904	0.277934
6	-2.083689	1.611691	-0.129863
1	0.041839	1.587250	-0.395704
6	-3.224769	0.856655	0.098459
1	-4.018172	-1.112227	0.422101
1	-2.157675	2.685281	-0.245479
1	-4.190807	1.340813	0.162340
8	2.078771	-0.066603	-0.422048
6	3.062155	0.313083	0.407749
1	3.114792	-0.291602	1.327830
8	3.801790	1.210387	0.170146

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- M06-2X/def2-SVP). It is suggested that the catalysis should proceed through the activation of **3.41a** by the Si lone pair electrons in **2.20**, followed by reacting with HBpin.
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Chapter 4:

A Lewis Acid and Base-Stabilized Silicon(I) Hydride and Its Application in Catalysis

4.1 Introduction

Low-valent silicon complexes (formal oxidation state: +2, +1 and 0) constitute of a non-bonding electron pair and an unoccupied p-orbital at the Si center (described in Chapter 1).^[1] Consequently, such unique electronic attributes enabled them to exhibit Lewis ambiphilicity since they can display both electrophilic and nucleophilic behavior. As expected, they can mimic transition metal chemistry in undergoing reversible reductive elimination and oxidative addition with small molecules (described in Chapter 3).^[2] However, the examples of isolable low-valent silicon compounds for catalytic organic synthesis are rarely reported. It is because the activated small molecules hardly further undergo transformation with reagents to form new products, which can be subsequently eliminated from the silicon centres. As a consequence, catalytic organic transformations mediated by low-oxidation state silicon compounds are rare. Till date, only two low-oxidation state silicon compounds could demonstrate catalytic capability.^[3] The first example is the cyclopentadienyl–silyliumylidene cation **4.1** (Chart 4.1) catalyzing controlled degradation of oligo(ethyleneglycol) diethers.^[3a] The second example is demonstrated by our group in using *N*-heterocyclic carbene (NHC)–silyliumylidene cation complex **4.2** (Chart 4.1) to mediate various chemo- and regioselective catalytic organic syntheses, for example hydroboration of unsaturated substrates (i.e., CO₂, aldehydes, ketones and pyridines), in addition to *N*-formylation of amines with CO₂ (described in Chapter 3).^[3b,3c] Since silicon is highly abundant and relatively low toxicity, it should be a sustainable alternative to replace precious transition metal in catalysis. Henceforth, it is of utmost importance to develop more strategies that enable low-oxidation state silicon compounds catalysing organic reactions.

Chart 4.1 Low-oxidation state silicon complexes in catalysis.^[3]

Recently, dinuclear transition metal catalysts, especially palladium(I) dimers involving a palladium–palladium single bond have emerged as powerful catalysts for cross-coupling reactions (Chart 4.2).^[4] They could undergo dinuclear catalytic mechanism or act as a precursor to form active monoligated L-Pd^0 catalysts in C–C and C–heteroatom bond formations, leading to better catalytic activity in comparison with mononuclear ones.^[4–5] For example, complexes **4.3** – **4.4** (Chart 4.2) were highly efficient in catalyzing various cross coupling (C–C and C–N) transformations.^[5a,6] To elaborate, the Suzuki cross coupling reaction mediated by binuclear $\text{Pd}^{\text{I}}\text{-Pd}^{\text{I}}$ **4.4** (Chart 4.2) was akin to the reactivity catalyzed by L-Pd^0 and $\text{L-Pd}^0\text{X}^-$ species.^[5b] Theoretical studies revealed that complex **4.4** (Chart 4.2) is a pre-catalyst that converted to the active species $\text{Pd}^0/\text{Pd}^{\text{II}}$ via reduction pathway mechanism.^[5b] The unique property of the Pd^{I} center was further illustrated by Schoenobeck, whereby the pre-catalysts

4.4 (Chart 4.2) was shown to be capable of exchanging Br/I halogen between the dimeric palladium(I) compound with aryl iodides at ambient conditions, a feat that could not be accomplished by the known mono-nuclear Pd⁰ complexes subjected under the same reaction conditions, as the corresponding Pd^{II} species disfavoured the reductive elimination to afford the target products.^[5c] In addition, the dimeric palladium(I) complexes are highly versatile with its property modulated by the ligand and the bridging unit employed. For instance, complex **4.4** (Chart 4.2) is highly reactive and readily converted to Pd⁰ in the presence of a weak nucleophile, consequently the complex **4.4**-catalyzed reactions are air-sensitive.^[5c] A modification on the ligand and the bridging unit to PCy₂tBu and iodide, respectively (**4.6**, Chart 4.2) facilitated the air stable catalysis of highly selective C–C coupling (alkylation and arylation) and olefin migration reactions under ambient conditions.^[5f] Moreover, Hazari described the *in-situ* generation of an active catalyst I_{Ar}–Pd⁰ (I_{Ar} = :C{N(Ar)CH}₂, Ar = 2,6-*i*Pr₂C₆H₃) during the catalysis using monomeric pre-catalyst palladium(II) complex I_{Ar}–Pd^{II}(η³-allyl)Cl under weakly basic conditions.^[5i] However, the I_{Ar}–Pd⁰ could undergo facile comproportionation with the pre-catalyst I_{Ar}–Pd^{II}(η³-allyl)Cl to form the palladium(I) dimer **4.8** (Chart 4.2), a commonly observed phenomena in typical reactions involving Pd^{II} pre-catalyst.^[5i] Therefore, increasing the barrier for comproportionation to complex **4.8** would enhance the availability of Pd⁰ for catalytic transformations.^[5i] For example, using higher reaction temperature, bulky allene and/or solvent could reduce comproportionation to Pd^I–Pd^I. Further, bench-stable palladium(I) dimers **4.10** – **4.11** (Chart 4.2) were effective in Buchwald–Hartwig amination, resulting in high selectivity and high yields.^[5k]

Chart 4. 2 Examples of palladium(I) dimer pre-catalysts.^[5]

A close resemblance was drawn between the palladium(I) dimers with low-valent silicon compounds, in which we anticipate the dinuclear silicon(I) compounds could show palladium(I)-like reactivity as the former possess Lewis ambiphilic character, owing to the unoccupied p-orbital as well as a stereoactive electron pair on each Si(I) atom, along with a reactive Si–Si bond (described in Chapter 1). In addition, we postulate that introducing asymmetry into the silicon(I) dimers would induce greater disproportionation reaction to form the monomeric silicon(0) active species in catalytic synthesis. In this chapter, we are excited to examine the catalytic potential of silicon(I) dimer in organic transformations. Herein, we report that a NHC– and BH₃–hydridosilicon(I)–iodosilicon(I) complex **4.13** serves as a pre-catalyst to mediate CO₂ hydroboration via Si^I/Si^{II} species. The catalytic ability of complex **4.13** is further extended to *N*-formylation of amines with CO₂ and HBpin, as well as hydroboration of aldehydes and ketones.

4.2 Results and Discussion

4.2.1 Dimeric NHC-Silicon(I) Iodide (**1.13-I**) in Catalytic Hydroboration of CO₂

Our starting point was using NHC–iodosilicon(I) dimer [I_{Ar}(I)Si:]₂^[7] (**1.13-I**) as catalyst. 10 mol % of **1.13-I** was employed in the catalytic hydroboration of CO₂ with pinacolborane (HBpin) in C₆D₆ at 110 °C for 3 hours (Table 4.1, see Section 4.4.1, Table S4.1). 17% conversion was observed and diborate ether [(pinB)₂O] (**4.12a**) was afforded as the major product (entry 7). As the result is unsatisfactory, BH₃·SMe₂ was used as an additive to enhance the reactivity of HBpin, leading to better efficiency and selectivity (Table 4.1, Table S4.1, entries 11 – 12). 10 mol % of **1.13-I** and 20 mol % of BH₃·SMe₂ were used to catalyze the hydroboration of CO₂ and HBpin. 89% conversion was observed in 3 h, but the major product is **4.12a** (entry 11). When the amount of BH₃·SMe₂ was increased to 45 mol %, 93% conversion was observed (entry 12). In the catalysis, CO₂ did not undergo hydroboration with BH₃ to form B(OMe)₃ or equivalents. This indicates that BH₃·SMe₂ reacts with complex **1.13-I** to form an active catalyst. Moreover, there was no hydroboration occur when BH₃·SMe₂ (45 mol %, Table 4.1, Table S4.1, entry 2) was used as the catalyst.

Table 4. 1 Catalytic table for hydroboration of CO₂ using HBpin.^a

Entry	Cat	X	Y	T (°C)	t (h)	Yield				TON			TOF (h ⁻¹)			TON	TOF (h ⁻¹)
						4.12a	4.12b	4.12c	Total	4.12a	4.12b	4.12c	4.12a	4.12b	4.12c		
1	-	-	-	110	13	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
2	-	-	45	110	13	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
3	I _{Ar} SiI ₂	10	-	110	3	0.08	0.08	0.00	0.15	0.79	0.75	0.00	0.26	0.25	0.00	1.54	0.51
4	1.13-I	10	-	40	3	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
5	1.13-I	10	-	60	3	0.01	0.00	0.00	0.01	0.07	0.00	0.00	0.02	0.00	0.00	0.07	0.02
6	1.13-I	10	-	80	3	0.01	0.01	0.00	0.01	0.09	0.05	0.00	0.03	0.02	0.00	0.15	0.05
7	1.13-I	10	-	110	3	0.10	0.00	0.07	0.17	1.01	0.00	0.70	0.34	0.00	0.23	1.72	0.57
8	1.13-I	1	-	110	3	0.04	0.00	0.00	0.04	3.73	0.00	0.00	1.24	0.00	0.00	3.73	1.24
9	1.13-I	5	-	110	3	0.03	0.01	0.12	0.16	0.62	0.15	2.39	0.21	0.05	0.80	3.15	1.05
10	1.13-I	10	10	110	3	0.14	0.03	0.00	0.17	1.41	0.25	0.00	0.24	0.09	0.00	1.67	0.56
11	1.13-I	10	20	110	3	0.62	0.27	0.00	0.89	6.20	2.75	0.00	2.07	0.92	0.00	8.94	2.98
12 ^b	1.13-I	10	45	110	3	0.45	0.48	0.00	0.93	4.46	4.81	0.00	1.49	1.60	0.00	9.27	3.09

^aReaction conditions: 0.10 mmol of HBpin in C₆D₆ (~0.5 mL), amount of catalyst is calculated and then added to obtain the desired catalytic loading, 1 bar of CO₂. The yield was obtained by ¹H NMR using the Ar-*H* and OMe protons of 1,3,5-trimethoxybenzene as an internal standard. TON and TOF are given to the number of hydride transferred. The catalytic studies were repeated thrice. ^bOptimised condition.

4.2.2 Synthesis of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13)

To verify this, the complex **1.13-I** was reacted with three equivalents of $\text{BH}_3 \cdot \text{THF}$ in toluene at room temperature, which gave mixtures of the NHC/ BH_3 -stabilized hydridosilicon(I)–iodosilicon(I) complex $[\text{LSi}(\text{BH}_3)(\text{H})\text{--Si}(\text{BH}_3)(\text{I})\text{L}]$ (**4.13**) and unreacted $\text{BH}_3 \cdot \text{THF}$ (Scheme 4.1). The reaction mixture was then dried and extracted with THF/toluene (1:1) or fluorobenzene to afford compound **4.13** as colourless crystals (yield: 54.5%). Complex **4.13** is the first unsymmetric silicon(I) complex containing a silicon(I) hydride moiety, after a previous report of the only precedence of the cyclic alkyl(amino) carbene (cAAC)-stabilized Si_2H_2 complex comprising both ligand-stabilized disilaacetylene and 2,3-disila-1,3-butadiene electronic structures.^[8]

Scheme 4. 1 Synthesis of **4.13**.

Complex **4.13** could dissolve in THF but it is slightly insoluble in toluene and fluorobenzene. The ^1H and ^{13}C NMR spectra of **4.13** display two sets of signals assignable to the two different chemical environments of NHC backbones. The ^1H NMR spectrum displays a quartet ($\delta = 3.83$ ppm, $^3J_{\text{SiH-BH}} = 4.8$ Hz) for the Si–H proton, which is in agreement to the NHC/ BH_3 -stabilized silicon(II) dihydride $[\text{I}_{\text{Ar}}\text{SiH}_2\text{BH}_3]$ ($\delta = 3.76$ ppm).^[9] The existence of the Si–H proton is further supported by IR spectroscopy ($\nu_{\text{Si-H}}$: 2102 cm^{-1} , Figure S4.7), which is comparable with that of $[\text{I}_{\text{Ar}}\text{SiH}_2\text{BH}_3]$ ^[9] ($\nu_{\text{Si-H}}$: 2096 cm^{-1}) and the amidinate/ BH_3 -stabilized silicon(II) hydride $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{SiH}(\text{BH}_3)]$ ^[10] ($\nu_{\text{Si-H}}$: 2107 cm^{-1}). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays two signals for the Si–bonded C_{NHC} atoms ($\delta = 157.5, 167.4$ ppm), which are more upfield shifted than **1.13-I**^[7b] ($\delta = 174.2$ ppm). The ^{29}Si NMR spectrum displays two broad signals (Si-I : $\delta = 4.4$, Si-H : -37.9 ppm, Figure S4.6). The expected quartet signals (^{29}Si –

^{11}B coupling) was absent, mainly due to the quadrupolar boron nuclei. The Si–H resonance in ^{29}Si NMR ($\delta = -37.9$ ppm) is more downfield shifted than $[\text{I}_{\text{Ar}}\text{SiH}_2\text{BH}_3]$ ($\delta = -55.6$ ppm).^[9]

Figure 4. 1 Molecular structure of **4.13** (30% ellipsoids probability). Hydrogen atoms (except the H1 atom) and toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.363(4), Si1–I1 2.505(4), Si1–B1 1.981(15), Si2–B2 2.002(14), Si1–C1 1.969(10), Si2–C28 1.981(11), C1–N1 1.376(11), C1–N2 1.368(11), C28–N3 1.345(11), C28–N4 1.377(11); C1–Si1–I1 107.7(3), C1–Si1–Si2 107.2(5), C1–Si1–B1 105.1(7), B1–Si1–Si2 122.2(5), B1–Si1–I1 115.5(5), N1–C1–Si1 126.8(7), N2–C1–Si1 130.3(8), Si2–Si1–I1 98.40(16), C28–Si2–Si1 109.4(4), C28–Si2–B2 111.1(7), B2–Si2–Si1 120.7(5), N3–C28–Si2 131.9(8), N4–C28–Si2 121.5(7).

The X-ray crystal structure of **4.13** (Figure 4.1) shows a tetrahedral geometry on each silicon atoms. The Si–H bond (1.408 Å) shows a good agreement with $[\text{I}_{\text{Ar}}\text{SiH}_2\text{BH}_3]$ ^[9] (1.409(18) Å) and also falls into the range of the reported compounds containing a $\text{Si}^{\text{II}}\text{–H}$ bond (1.21 – 1.47342 Å).^[9–11] The Si1–B1 (1.981(15) Å) and Si2–B2 (2.002(14) Å) bonds are similar to that in the NHC/ BH_3 -stabilized silicon(II) dihydride $[\text{I}_{\text{Ar}}\text{SiH}_2\text{BH}_3]$ ^[9] (1.992(2) Å) and other silylene–borane adducts such as the amidinate/ BH_3 -stabilized silicon(II) hydride $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{SiH}(\text{BH}_3)]$ ^[10] (1.9624(5) Å) and the NHC-stabilized dichlorosilylene–borane adduct $[\text{I}_{\text{Ar}}\text{SiCl}_2\text{BH}_3]$ ^[12] (1.965(2) Å). The Si1–I1 bond length (2.505(4) Å) is intermediate between the singly bonded $\text{Si}^{\text{I}}\text{–I}$ in **1.13-I**^[7b] (average: 2.594 Å) and the $\text{Si}^{\text{IV}}\text{–I}$ bond lengths in $[\text{I}_{\text{Ar}}\text{SiI}_3]$ ^[13] (average 2.420 Å). The C1–Si1 (1.969(10) Å) and C28–Si2 bonds (1.981(11) Å) are comparable with those in **1.13-I** (1.949(3), 1.944(3) Å).^[7b]

4.2.3 Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (**4.13**) in Hydroboration of CO₂ and *N*-formylation

The catalytic ability of NHC/BH₃-stabilized hydridosilicon(I)–iodosilicon(I) complex **4.13** was then tested in the hydroboration of CO₂ using HBpin. First of all, without a catalyst, no observable reaction occur between CO₂ and HBpin (solvent: C₆D₆, T = 110 °C). However, catalytic amount of **4.13** (10 mol %) was capable of hydroboration of CO₂ with HBpin at 110 °C, led to the formation of the diborate ether **4.12a** and methoxyborane [pinBOMe] (**4.12b**, reaction time: 1 h, yield: 21%, TOF = 2.1 h⁻¹; reaction time: 3 h, yield: >99%, TOF = 3.3 h⁻¹; Scheme 4.2, Table S4.2). The reaction was slowly proceeded upon reduction in the catalyst loading (1, 3 and 5 mol %). The activity of the CO₂ hydroboration with HBpin mediated by complex **4.13** exceeds the TOF values of the (amido)(hydrido)germylene [Ar^I(*i*Pr₃Si)NGeH] (TOF = 0.4 h⁻¹, Ar^I = 2,6-(CHPH₂)₂-4-*i*PrC₆H₂), some non-metal-based catalysts (0.40 – 14.5 h⁻¹) and activated metal-based catalysts (0.07 – 2.5 h⁻¹).^[14] However, complex **4.13** is much less active than silicon(II) complex **4.2** (60 h⁻¹) and (amido)(hydrido)stannylene [Ar^I(*i*Pr₃Si)NSnH] (14.5 h⁻¹).^[3b,14a] In addition, no reaction observed when the borane source was changed to BH₃·SMe₂ (Table S4.3).

Scheme 4. 2 **4.13**-catalyzed reduction of CO₂.

The catalytic mechanism was studied. Complex **1.13-I** did not react with CO₂ in C₆D₆ at any temperature. Then, HBpin was reacted with complex **1.13-I** in C₆D₆ at 90 °C for 3 h to afford the NHC–diiodosilylene [I_{Ar}SiI₂]^[13] with 56% conversion. When the reaction temperature was raised to 110 °C, complex **1.13-I** was fully consumed and only NHC–diiodosilylene [I_{Ar}SiI₂]^[13] was observed, along with some unassignable septets. Notably, heating solely complex **1.13-I** at 90 °C leading to 19% of NHC–diiodosilylene [I_{Ar}SiI₂]^[13] and 23% of free I_{Ar}. NHC–diiodosilylene [I_{Ar}SiI₂]^[13] (10 mol %) was then subjected to catalytic hydroboration of CO₂ at 110 °C, in which poor selectivity and conversion were observed after three hours (yield: 15%, TOF = 0.51 h⁻¹, Table 4.1, Table S4.1, entry 3). These results show that complex **1.13-I** is capable of undergoing disproportionation reaction at 90 °C to form the NHC–diiodosilylene [I_{Ar}SiI₂]^[13] and monligated–Si⁰ [I_{Ar}–Si:] species. On the basis of catalytic results, they are not effective in mediating the hydroboration of CO₂. The addition of BH₃ in the **1.13-I**-catalyzed CO₂ hydroboration transform complex **1.13-I** into complex **4.13**. We postulate the unsymmetric silicon(I) environment facilitates disproportionation to form NHC–iodosilylene–borane complex [I_{Ar}Si(H)(I)BH₃] and NHC–silicon(0)–borane complexes [I_{Ar}SiBH₃]. In addition, BH₃ stabilizes the Si⁰ species and enhanced its catalytic reactivity.

The mechanism is proposed and computed by DFT studies (M06-2X/def2-TZVP, Scheme 4.3). Complex **4.13** undergoes disproportionation reaction to form **Int4.1** and [I_{Ar}Si(H)(I)BH₃], where the Si⁰ center of **Int4.1** is coordinated with NHC and BH₃, in addition to an agostic interaction with one of the B–H bonds. 1,2-hydride shift occurs to form **Int4.2**, where the Si electron pair donates to the unoccupied p-orbital of the boron center. Next, the H–B bond of HBpin added across the Si=B double bond in **Int4.2** to form **Int4.4**, where the silylene moiety {Si(H)(Bpin)} coordinated with NHC and BH₃. The B–H and Si–Bpin bonds then insert into CO₂ to form **Int4.5**. The formoxyborane HC(O)OBpin dissociates from the Si center to form **Int4.2** and formoxyborane **4.12c**. The second HBpin reacts with **Int4.2** to form **Int4.4**. The B–H and Si–Bpin bonds insert into the C=O double bond of formoxyborane **4.12c** to form **Int4.2** and CH₂(OBpin)₂. The –OBpin and –Bpin of CH₂(OBpin)₂ add across the Si=B double bond before the subsequent dissociation of formaldehyde H₂C(O)– to form **Int4.2**. Diborate ether **4.12a** is then eliminated to form **Int4.2**, which was reacted with the third HBpin to form **Int4.4**. The B–H and Si–Bpin bonds insert into the C=O bond of H₂C(O), subsequently deliver methoxyborane **4.12b** and regenerate **Int4.1**. The latter undergoes comproportionation with [I_{Ar}Si(H)(I)BH₃] to regenerate complex **4.13**.

Scheme 4. 3 DFT calculations for **4.13**-catalyzed hydroboration of CO₂.

Table 4. 2 Catalytic table for *N*-formylation of amines using CO₂.^a

Entry	X	H ⁺ source(eq.)	T (°C)	t (h)	Yield (%)	4.17d: 4.17d'
1	-	HBpin (2)	90	24	0	-
2	5	None	90	96	0	0.0
3	5	HBpin (2)	90	24	82	8:2
4	5	Ph ₃ SiH (2)	90	24	29	9:1
5	5	Ph ₂ SiH ₂ (2)	90	24	11	8:2
6	5	PhSiH ₃ (2)	90	24	9	8:2
7	5	Et ₃ SiH (2)	90	24	9	8:2
8	5	HBpin (1)	90	3	40	8:2
9	5	HBpin (3)	90	3	81	8:2
10	5	HBpin (2)	24	5	36	9:1
11	5	HBpin (2)	40	24	93	9:1
12	5	HBpin (2)	60	24	92	9:1
13	5	HBpin (2)	80	3	82	8:2
14	5	HBpin (2)	110	0.5	80	8:2
15	1	HBpin (2)	40	24	31	9.7:0.3
16 ^b	3	HBpin (2)	40	24	97	9.7:0.3
17	10	HBpin (2)	40	24	93	9:1

^aReaction conditions: Amine **4.16d** (0.10 mmol), required amount of silane, C₆D₆ (0.5 mL), amount of catalyst was calculated, then added to obtain the desired catalytic loading and CO₂ (ca. 50.0 mg). The yield was obtained by ¹H NMR using the –CH₂ protons of cyclohexane as an internal standard. The catalytic studies were repeated thrice. ^bOptimised condition.

Upon successful catalytic hydroboration of CO₂, we then turn our attention to the further functionalization of CO₂, namely *N*-formylation reaction of amines. Optimization was first conducted using *N*-methylaniline **4.16d** (Table 4.1, Table S4.4). First, the absence of a catalyst could not lead to any observable reaction (entry 1). Second, without a hydride source, 5 mol % of the complex **4.13** failed to modulate the reaction of **4.16d** with CO₂, even up to 90 °C (entry 2). Third, irrespective of the type of hydride sources, complex **4.13** is capable of catalyzing *N*-formylation reaction (entries 3 – 7) to deliver the corresponding *N*-formamide **4.17d** as the major product and *N*-methylaniline **4.17d'** as the minor product. HBpin demonstrated the greatest catalytic performance in all the hydride reagents screened (entry 3). The molar ratio of HBpin (entries 3, 8 – 9), reaction temperature (entries 3, 10 – 14) and catalytic loading of **4.13** (entries 11, 15 – 17) were then optimized, in which complex **4.13** exhibit the best selectivity (ratio of **4.17d**:**4.17d'** = 9.7:0.3) in *N*-formylation reaction, with catalytic loading of 3 mol % using two equivalents of HBpin over 24 hours at 40 °C (entry 16).

Following, the catalytic *N*-formylation of primary amines with CO₂ and HBpin was studied (Table 4.3, Table S4.5), subjected under the optimized conditions (Table 4.2, Table S4.4, entry 16). First, complex **4.13** (3 mol %) is efficient in catalyzing *N*-formylation of aliphatic amine *n*-butylamine (**4.14a**) to selectively afford the corresponding *N*-formamide **4.15a** (yield: >99%, TOF = 1.39 h⁻¹). Second, >99% yield was observed for aromatic aniline **4.14b** (TOF = 1.39 h⁻¹). Moreover, its derivative with electron-withdrawing and electron-donating functionalities (**4.14c** – **4.14n**) were preserved during the catalyses with high selectivity (0.28 – 1.39 h⁻¹). However, lowered yields were observed for the 2,4,6-trimethylaniline **4.15f** (46%, 0.64 h⁻¹) and 2,6-diisopropylaniline **4.14g** (26%, 0.28 h⁻¹). Third, catalytic *N*-formylation of benzylamine **4.14p** afforded **4.15p** in quantitative yield (>99 %, 1.39 h⁻¹). Its derivative with electron-withdrawing and electron-donating groups at different positions of **4.14p** were well tolerated with high yields (**4.14q** – **4.14s**, >99%, 1.39 h⁻¹). Fourth, *N*-methylation was not observed throughout the catalyses. Fifth, all of the catalyses did not afford doubly-formylated products, with the exception of amine **4.15k** that delivered mono- and di-formylated products in a 3:2 ratio.

Table 4. 3 Scope of Primary Amine Substrates^a

<div><div><div><div><div>CO_2</div><div>+</div></div><div><div><div><div><div>$\text{R}-\text{N}-\text{H}$ H</div></div><div>4.14</div></div></div><div><div><div><div><div>$\text{R}-\text{N}-\text{H}$ H $\text{C}=\text{O}$</div></div><div>4.15</div></div></div></div></div><div><div><div>Catalyst 4.13 (3 mol %) 2 equiv. HBpin</div><div>$\xrightarrow{\text{C}_6\text{D}_6, 40\text{ }^\circ\text{C}, 24\text{ h}}$</div></div></div></div></div></div>			
<div><div> </div><div>4.15a >99 (70) %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15b >99 (96) %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15c >99 %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15d >99 %, 1.39 h⁻¹</div></div>
<div><div> </div><div>4.15e >99 %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15f 46 %, 0.64 h⁻¹</div></div>	<div><div> </div><div>4.15g 20 %, 0.28 h⁻¹</div></div>	<div><div> </div><div>4.15h >99 (97) %, 1.39 h⁻¹</div></div>
<div><div> </div><div>4.15k^b 90 %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15m >99 %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15n >99 (80) %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15p >99 (93) %, 1.39 h⁻¹</div></div>
<div><div> </div><div>4.15q >99 %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15r >99 %, 1.39 h⁻¹</div></div>	<div><div> </div><div>4.15s >99 %, 1.39 h⁻¹</div></div>	

^aReaction conditions: Primary amine (0.10 mmol), 2 equiv. of PhSiH₃ (0.20 mmol), catalyst **4.13** (5 mol %), C₆D₆ (0.50 mL), CO₂ (ca. 50.0 mg). Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard, on the basis of the consumption of the amine. The identity of the product was confirmed as RHNC(=O)H. Isolated yields were reported in parenthesis. All the catalytic trials were repeated in triplicate. ^bMono- and diformylation was observed in 3:2 ratio.

Among the reported catalysts summarized in Table 4.4, the activity of **4.13** outperformed NHC catalysts such as I_{Ar} ,^[15] I_{Mes} ^[16] ($I_{Mes} = :C\{N(Mes)CH\}_2$, Mes = 2,4,6-Me₃C₆H₂) and thiazolium carbene^[17] ($:C\{N(Bn)CH=C(H)S\}$, Bn = CH₂Ph). To elaborate, the activity of complex **4.13** (TOF = 1.39 h⁻¹, Table 4.3) supersedes I_{Ar} (0.29 – 0.72 h⁻¹, Table 4.4). Moreover, I_{Mes} can only selectively deliver *N*-methylated products (Table 4.4).^[16] By modulating the reaction temperature, thiazolium carbene could selectively catalyze both *N*-formylation and *N*-methylation reactions, albeit with poorer activity and yields (0.36 – 0.57 h⁻¹, Table 4.4).^[17] Furthermore, utilizing the ionic liquids, 1-butyl-3-methylimidazolium chloride [BMIm]Cl^[18] is less effective in modulating the *N*-formylation reactions, with some instances of double-formylation and slightly lower yields (0.12 – 0.15 h⁻¹, Table 4.4). However, complex **4.13** is overshadowed by the efficacy of glycine betaine (4.5 – 4.8 h⁻¹, Table 4.4)^[19] and lecithin (1.7 – 1.8 h⁻¹, Table 4.4).^[20] Nonetheless, a mixture of mono- and diformylation were observed for amine **4.14b**, **4.14h** and **4.14p** when glycine betaine was employed. Superbases, namely 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)^[21] and *N*-butyl-*N'*,*N''*,*N'''*,*N''''*-tetramethylguanidine (BTMG)^[22] were also studied (Table 4.4). The activity of complex **4.13** in catalyzing *N*-formylation of aniline **4.14b** is intermediary between TBD^[21] (yield: 24%, TOF = 0.20 h⁻¹) and BTMG^[22] (95%, 4.3 h⁻¹), although the latter led to a mixture of *N*-formamide and urea for amine **4.14p** (Table 4.4). In general, complex **4.13** is less efficient than NHC–silyliumylidene **4.2**^[3c] (6.7 – 20.0 h⁻¹) in *N*-formylation reactions (Table 4.4). To elaborate, the activity of complex **4.2** (Table 4.4) is better than complex **4.13** when using amines **4.14a** (yield: >99%, TOF = 20 h⁻¹), **4.14b** (>99%, 10 h⁻¹), **4.14h** (>99%, 10 h⁻¹) and **4.14p** (>99%, 6.7 h⁻¹).^[3c] However, the TOF of between these two complexes are less apparent when amine **4.14e** (**4.2**: >99%, 1.4 h⁻¹ vs **4.13**: >99%, 1.39 h⁻¹) was used (Table 4.4).^[3c] Even though 1,3,2-diazaphospholene (NHP–H, TOF = 2.0 – 9.0 h⁻¹) is more active than complex **4.13**, the reaction are non-selective, affording either *N*-formylation or *N*-methylated products (Table 4.4).^[23]

Table 4. 4 Selected literature catalysts used for *N*-formylation of primary amines.^[3c,15-23]

Literature Catalysts	Selected Amines
	4.14a	4.14b	4.14h	4.14p
NHCs ^[15-17]				
I_{Ar}	-	35 %, ^a 0.29 h ⁻¹	86 %, ^a 0.72 h ⁻¹	85 %, ^a 0.71 h ⁻¹
I_{Mes}	- ^b	- ^b	- ^b	- ^b
Thiazolium	-	53 %, 0.36 h ⁻¹	83 %, 0.57 h ⁻¹	81 %, 0.55 h ⁻¹
Ionic liquids ^[18-20]				
[BMIm]Cl	62 %, ^a 0.12 h ⁻¹	76 %, 0.15 h ⁻¹	-	60 %, ^a 0.12 h ⁻¹
Glycine betaine	-	85 %, ^a 4.7 h ⁻¹	86 %, ^a 4.8 h ⁻¹	81 %, ^a 4.5 h ⁻¹
Lecitin	89 %, 1.8 h ⁻¹	91 %, 1.8 h ⁻¹	-	84 %, 1.7 h ⁻¹
Superbases ^[21-22]				
TBD	-	24 %, 0.20 h ⁻¹	-	-
BTMG	-	95 %, 4.3 h ⁻¹	-	^c
Phosphorus(II) ^[23]				
NHP-H	84 %, 9.0 h ⁻¹	-	>99 %, 2.0 h ⁻¹	97 %, 5.0 h ⁻¹
Silicon(II) ^[3c]				
4.2	>99 %, 20.0 h ⁻¹	>99 %, 10.0 h ⁻¹	>99 %, 10.0 h ⁻¹	>99 %, 6.7 h ⁻¹

^aReaction afforded a mixture of mono- and diformylated products. ^bReaction afforded solely *N*-methylated products. ^cReaction afforded a mixture of *N*-formamide and urea.

The catalytic efficacy of *N*-formylation of secondary amines was then examined (Table 4.5, Table S4.6). Firstly, complex **4.13** (3 mol %) successfully catalyzed *N*-formylation of amine with aliphatic functionality, namely diethylamine **4.16a** to afford the *N*-formamide **4.17a** (yield: >99%, TOF = 0.39 h⁻¹). Its derivatives such as piperidine **4.16b** (>99%, 1.39 h⁻¹) and morpholine **4.16c** (>99%, 1.39 h⁻¹) remained intact during the catalyses. In addition, *N*-formylation of aromatic *N*-methylaniline **4.16d** led to >97% yield of *N*-formamide **4.17d** with a minor conversion to *N,N*-dimethylaniline **4.17d'** (<3%). Lastly, >99% yield was achieved using dibenzylamine **4.16e** to give *N*-formamide **4.17e** (TOF = 1.39 h⁻¹).

Table 4. 5 Scope of Secondary Amine Substrates^a

^aReaction conditions: Secondary amine **4.16** (0.10 mmol), 2 equiv. of PhSiH₃ (0.20 mmol), catalyst **4.13** (5 mol %), C₆D₆ (0.50 mL), CO₂ (ca. 50.0 mg). Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard on the basis of the consumption of the amine. The identity of the product was confirmed as RHNC(=O)H. Isolated yields were reported in parenthesis. ^b*N*-methylated amine was obtained in <3% yield. ^cReaction was also performed in 1 g scale, leading to full conversion, under the same reaction conditions.

Table 4. 6 Selected literature catalysts used for *N*-formylation of secondary amines.^[3c,15-24]

Literature Catalysts	Selected Amines

	4.16a	4.16b	4.16d	4.16e
NHCs^[15-16]				
I_{Ar}	>99 %, 0.83 h ⁻¹	>99 %, 0.83 h ⁻¹	>99%, 0.83 h ⁻¹	-
I_{Mes}	-	-	- ^a	-
Ionic liquids^[18-20]				
[BMIm]Cl	-	98 %, 0.20 h ⁻¹	95 %, 0.19 h ⁻¹	69 %, 0.14 h ⁻¹
Glycine betaine	-	-	95 %, ^a 7.9 h ⁻¹	77%, ^a 2.1 h ⁻¹
Lecitin	97 %, 1.9 h ⁻¹	-	97 %, 1.9 h ⁻¹	-
Superbases^[21-22]				
TBD	>99 %, 0.83 h ⁻¹	>99 %, 0.83 h ⁻¹	40 %, 0.40 h ⁻¹	-
BTMG	-	84 %, ^b 10.5 h ⁻¹	95 %, ^{b,c} 11.9 h ⁻¹	-
Phosphorus(II)^[23]				
NHP-H	95 %, 38.0 h ⁻¹	94 %, 38.0 h ⁻¹	-	-
Silicon(II)^[3c]				
4.2	>99 %, 40.0 h ⁻¹	>99 %, 20.0 h ⁻¹	95 %, 6.3 h ⁻¹	>99 %, 20.0 h ⁻¹
Germanium(IV)^[24]				
Germaacylium ion	28 %, ^b 1.9 h ⁻¹	27 %, ^b 0.90 h ⁻¹	41 %, ^d 0.70 h ⁻¹	-

^aReaction afforded solely *N*-methylated products. ^bReaction afforded a mixture of *N*-formamylated and *N*-methylated products. ^cReaction afforded a mixture of mono- and diformylated products. ^dReaction afforded a mixture of *N*-formamide, *N*-aminal and *N*-methylamine products.

In comparison with complex **4.13**, the performance of NHCs such as I_{Ar} ($TOF = 0.83\text{ h}^{-1}$) is less efficient, whereas I_{Mes} selectively delivered *N*-methylamine derivatives (Table 4.6). Considering the ionic liquids, complex **4.13** is more efficient than $[BMIm]Cl$ (0.14 h^{-1})^[18] but less active than glycine betaine ($2.1 - 7.9\text{ h}^{-1}$) in *N*-formylation reactions (Table 4.6).^[19] In addition, the activity of complex **4.13** ($1.35 - 1.39\text{ h}^{-1}$, Table 4.5, Table S4.6) is intermediary between the superbases TBD^[21] ($0.40 - 0.83\text{ h}^{-1}$, Table 4.6) and BTMG^[22] ($10.5 - 11.9\text{ h}^{-1}$, Table 4.6). Although the NHP-H (38.0 h^{-1}) has higher activity than complex **4.13**, however, it non-selectively catalyzed *N*-formylation or *N*-methylation of amines (Table 4.6).^[23] Similitude to the primary amines, NHC-silyliumylidene **4.2**^[3c] ($6.3 - 40.0\text{ h}^{-1}$) outperformed complex **4.13** in *N*-formylation of secondary amines (Table 4.6). Heavier main group compound such as germa-acylium ion ($0.70 - 1.9\text{ h}^{-1}$) was also utilized in catalytic *N*-formylation but the reactions afforded mixtures of *N*-formamides, *N*-aminals and *N*-methylamines (Table 4.6).^[24] Nonetheless, complex **4.13** represents the first silicon(I) complex and among the few examples of metal-free catalyst capable of catalyzing *N*-formylation of primary and secondary amines to selectively deliver the respective *N*-formamides, under ambient conditions with relatively high yields and high selectivity.

In order to obtain the practical insight of our catalytic performance mediated by complex **4.13**, the scale of the reaction was increased to a gram. Dibenzylamine **4.16e** was subjected under the standard reaction conditions and full conversion to **4.17e** (Yield: >99%) was observed as the sole product over 24 hours, its selectivity and yield were not compromised when the reaction was scaled up.

Scheme 4. 4 Deuterium-labelling study using d_{11} -piperidine **4.16b-D** (*D*, 98%).

In all of the above-mentioned catalyses monitored by ^1H NMR spectroscopy, a weak singlet (*ca.* $\delta = 4.5$ ppm) attributable to H_2 gas was observed in all the catalyses (Figure S4.29). In order to illustrate the origin of the dihydrogen gas in the reaction, a deuterium-labelling experiment was carried out using d_{11} -piperidine **4.16b-D** (*D*, 98%, Scheme 4.3). The reaction was subjected under the optimized catalytic protocols and after 24 hours, a formyl $-\text{C}(=\text{O})\text{H}$ ($\delta = 7.76$ ppm) and HD (triplet, $\delta = 4.43$ ppm) signals were detected in the ^1H NMR spectroscopy (Figure S4.30). In addition, a blank reaction between piperidine **4.16b** with HBpin was performed, which also showed the formation of H_2 . However, subsequent addition of CO_2 did not lead to formation of products.

Scheme 4.5 Proposed mechanism for complex **4.13**-catalyzed N-formylation of amine.

The mechanism is then proposed (Scheme 4.5). Complex **4.13** undergoes disproportionation reaction to form the active silicon(0) species **Int4.1** and $[\text{I}_{\text{Ar}}\text{Si}(\text{H})(\text{I})\text{BH}_3]$. Then complex **4.13** proceeds to react with HBpin and subsequently CO_2 in a pathway illustrated in Scheme 4.3, leading to the formation of formyxyborane **4.12c** (Scheme 4.5). On the other hand, dehydrogenation of amine $\text{R}^1\text{R}^2\text{NH}$ with HBpin to give the aminoborane $\text{R}^1\text{R}^2\text{N-Bpin}$. Lastly, complex **4.12c** reacts with aminoborane delivers the *N*-formylated product.

4.2.4 Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (**4.13**) in Hydroboration of Aldehyde and Ketone Derivatives

The catalytic utility of complex **4.13** is then further extended to the reduction of carbonyl substrates using HBpin (Table 4.7, Table S4.7). First, in the absence of catalyst, no reaction was found between benzaldehyde **4.18a** and HBpin in C₆D₆ at 80 °C, over the span of 24 hours. Second, complex **4.13** (10 mol %) was able to mediate catalytic hydroboration of aromatic functionality of aldehydes ArC(=O)H (Ar = Ph, **4.18a**, TOF = 0.42 h⁻¹) and 1,3-diacetylbenzene **4.18f** (Ar = Ph, 0.45 h⁻¹) with >99% yields. The aromatic derivatives such as electron-donating (Ar = 4-MeC₆H₄ **4.18b**, 3-MeOC₆H₄ **4.18c** and 2-MeC₆H₄ **4.18m**) and electron-withdrawing substituents (Ar = 4-(MeCO₂)C₆H₄ **4.18e**, 4-FC₆H₄ **4.18q** and 4-BrC₆H₄ **4.18r**) at different positions were well tolerated over the duration of 9 – 24 h to deliver quantitative yields of the respective borate esters (TOF = 0.42 – 3.33 h⁻¹). Aliphatic functionalities such as cyclohexanecarboxaldehyde **4.18d** and pivaldehyde **4.18k** were well preserved with >99% yield (0.45 – 3.33 h⁻¹). Third, catalytic reduction of olefinic aldehydes, for example cinnamaldehyde **4.18p** and α -methylcinnamaldehyde **4.18s** using complex **4.13** was found to be chemoselective to give quantitative yield of **4.19p**. Similar chemoselectivity is also observed in other aldehyde derivatives such as arenes (thiophene-2-carbaldehyde **4.18g**, ferrocenecarboxaldehyde **4.18h** and furan-2-carbaldehyde **4.18n**), nitrile (4-formylbenzonitrile **4.18t**) and hydroxyls (3-hydroxybenzaldehyde **4.18v** and 4-hydroxybenzaldehyde **4.18w**) within similar TOF range (0.45 – 3.9 h⁻¹). Remarkably, ketone functionality in 4-acetylbenzaldehyde **4.18u** remained intact during the catalysis (>99%, 2.00 h⁻¹). In overall, complex **4.13** is less efficient than the NHC–silyliumylidene **4.2** (TOF = 14.9 – 118.8 h⁻¹) and the heavier group 14 element(II) complexes (i.e., (amido)(hydrido)germylene and –stannylene, 17 – >1000 h⁻¹).^[25] Nevertheless, complex **4.13** is the sole example of silicon(I) species and among the few heavier main group complexes capable of modulating catalytic regio- and chemoselective hydroboration reactions. Fourth, the catalytic reduction of ketone derivatives was regio- and chemoselective with excellent tolerance towards various aromatic and aliphatic substituents, albeit with extended reaction time, delivered the corresponding borate esters (0.09 – 0.42 h⁻¹, Table 4.8, Table S4.8).

Table 4. 7 Scope of Aldehyde Substrates^a

$ \begin{array}{c} \text{R}-\text{CHO} \\ \text{4.18} \end{array} + \begin{array}{c} \text{HBpin} \end{array} \xrightarrow[\text{C}_6\text{D}_6, 80^\circ\text{C}]{\text{Catalyst 4.13 (10 mol \%)}} \begin{array}{c} \text{R}-\text{CH}_2\text{OBpin} \\ \text{4.19} \end{array} $
4.19a >99 (81) %, 0.42 h ⁻¹	4.19b >99 (87) %, 0.42 h ⁻¹	4.19c >99 (95) %, 0.42 h ⁻¹	4.19d >99 (96) %, 1.11 h ⁻¹
4.19e >99 (98) %, 1.11 h ⁻¹	4.19f^b >99 (99) %, 0.45 h ⁻¹	4.19g >99 (99) %, 0.45 h ⁻¹	4.19h >99 (99) %, 3.33 h ⁻¹
4.19k 93 (80) %, 0.39 h ⁻¹	4.19m >99 (96) %, 2.00 h ⁻¹	4.19n >99 (96) %, 0.45 h ⁻¹	4.19p >99 (72) %, 0.38 h ⁻¹
4.19q >99 (84) %, 0.48 h ⁻¹	4.19r >99 (98) %, 0.45 h ⁻¹	4.19s >99 (99) %, 0.37 h ⁻¹	4.19t >99 (95) %, 2.00 h ⁻¹
4.19u >99 (97) %, 2.00 h ⁻¹	4.19v >99 (71) %, 1.43 h ⁻¹	4.19w >99 (85) %, 1.43 h ⁻¹	

^aReaction conditions: aldehyde substrates (0.10 mmol), HBpin (0.11 mmol), C₆D₆ (0.50 mL), catalyst **4.13** (10 mol %). NMR yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the aldehyde and the identity of the product was confirmed by RCH₂OBpin or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate. ^bReaction performed at 110 °C.

Table 4. 8 Scope of Ketone Substrates^a

^aReaction conditions: ketone substrates (0.10 mmol), HBpin (0.11 mmol), C₆D₆ (0.50 mL), catalyst **4.13** (10 mol %). NMR yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the ketone and the identity of the product was confirmed by RC(R')(H)OBpin or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate. ^bReaction performed at 110 °C.

4.3 Conclusion

The dimeric NHC–silicon(I) iodide **1.13-I** was capable of catalyzing hydroboration of CO₂ with its catalytic efficacy improved significantly when BH₃ additive was incorporated. The relationship between the complex **1.13-I** and BH₃ was then investigated. Stoichiometric reaction of **1.13-I** and three equivalents of BH₃·THF afforded the first asymmetrical Lewis acid- and base-stabilized hydridosilicon(I)–iodosilicon(I) complex **4.13**. Complex **4.13** exhibited similar catalytic activity and selectivity as complex **1.13-I** with BH₃ additive in the hydroboration of CO₂. In addition, complex **4.13** was found to be a diverse catalyst in catalyzing the metal-free chemo- and regioselective organic synthesis, for instance *N*-formylation of amine and reduction of carbonyl derivatives using HBpin to form *N*-formylamine and borate ester derivatives in good yields. An in-depth mechanistic studies and the trapping of reactive intermediates are ongoing progress with its findings to be documented in the course of time.

4.4 Experimental

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Compound **1.13-I** was prepared according to the literature procedure as described in Chapter 1.^[7a] THF and toluene were dried over and distilled from Na/K alloy prior to use. Fluorobenzene was dried over and distilled from CaH₂ prior to use. C₆D₆ and *d*₈-THF were dried over potassium metal and distilled prior to use. BH₃·SMe₂ and BH₃·THF were purchased from Sigma Aldrich and used without further purification. CDCl₃ was purchased and used without further purification. *d*₁₁-piperidine (**4.16b-D**, *D* 98%) was purchased directly from Sigma Aldridge and dried over 4 Å molecular sieves prior to use. All amine substrates are purchased directly and dried using CaH₂. Aldehyde and ketone substrates are purchased directly and dried using molecular sieves. C₆D₆ and *d*₈-THF were dried and distilled over K metal prior to use. The ¹H, ¹¹B, ¹¹B{¹H}, ¹³C{¹H}, ²⁹Si and ²⁹Si{¹H} NMR spectra were recorded on a JEOL ECA 400 spectrometer and Bruker 400 spectrometer. The NMR spectra were recorded in CDCl₃, C₆D₆, or *d*₈-THF, and the chemical shifts are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si; BF₃·Et₂O for ¹¹B, respectively. Elemental analyses and Electrospray ionization (ESI) mass spectra were performed were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

4.4.1 Dimeric NHC-Silicon(I) Iodide (1.13-I) in Catalytic Hydroboration of CO₂

General procedures for the catalytic hydroboration of carbon dioxide using 1.13-I as the catalyst:

Synthesis of compound 4.12a – 4.12b

Catalyst **1.13-I** (10.9 mg, 0.01 mmol), internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol, 5 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. Pinacolborane, HBpin (14.5 μ L, 0.10 mmol, 10 equiv.) and required amount of BH₃·SMe₂ were then added. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S4.1 (see below) and the reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ¹H NMR signals of [(*pinB*)₂O] (**4.12a**) at 1.02 ppm, [*pinBOMe*] (**4.12b**) at 1.04 or 3.49 ppm and *pinBOC*(=O)H (**4.12c**) at 0.93 ppm with reference to the –OMe and C–H protons (3.36, 6.20 ppm) of the internal standard, 1,3,5-trimethoxybenzene. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[26] The catalytic studies were repeated at least in triplicate.

Characterization of compound 4.12a

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 1.02 (s, 24H, Bpin-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): 21. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): 21. ¹³C{¹H} NMR (99.5 MHz, 24 °C, C₆D₆, ppm):): 24.52 (s, CMe), 84.41 (s, CMe).

Characterization of compound 4.12b

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 3.49 (s, 3H, OCH₃), 1.04 (s, 12H, Bpin-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): 22. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): 22. ¹³C{¹H} NMR (99.5 MHz, 24 °C, C₆D₆, ppm): 23.04 (s, CMe), 24.71 (s, CMe), 82.95 (s, OMe).

Characterization of compound 4.12c

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 8.16 (s, 1H, C-H), 0.94 (s, 12H, Bpin-CH₃). ¹¹B NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.9. ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆,

ppm): $\delta = 22.0$. $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 24 °C, C_6D_6 , ppm): $\delta = 157.7$ (s, O_2CH), 93.5 (s, CMe), 24.2 (s, CMe).

Table S4. 1 Catalytic table for hydroboration of CO_2 using HBpin.

Entry	Cat	X	Y	T (°C)	T (h)	Yield				TON			TOF (h ⁻¹)			TON	TOF (h ⁻¹)
						4.12a	4.12b	4.12c	Total	4.12a	4.12b	4.12c	4.12a	4.12b	4.12c		
1	-	-	-	110	13	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
2	-	-	45	110	13	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
3	I _{Ar} SiI ₂	10	-	110	3	0.08	0.08	0.00	0.15	0.79	0.75	0.00	0.26	0.25	0.00	1.54	0.51
4	1.13-I	10	-	40	3	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
5	1.13-I	10	-	60	3	0.01	0.00	0.00	0.01	0.07	0.00	0.00	0.02	0.00	0.00	0.07	0.02
6	1.13-I	10	-	80	3	0.01	0.01	0.00	0.01	0.09	0.05	0.00	0.03	0.02	0.00	0.15	0.05
7	1.13-I	10	-	110	3	0.10	0.00	0.07	0.17	1.01	0.00	0.70	0.34	0.00	0.23	1.72	0.57
8	1.13-I	1	-	110	3	0.04	0.00	0.00	0.04	3.73	0.00	0.00	1.24	0.00	0.00	3.73	1.24
9	1.13-I	5	-	110	3	0.03	0.01	0.12	0.16	0.62	0.15	2.39	0.21	0.05	0.80	3.15	1.05
10	1.13-I	10	10	110	3	0.14	0.03	0.00	0.17	1.41	0.25	0.00	0.24	0.09	0.00	1.67	0.56
11	1.13-I	10	20	110	3	0.62	0.27	0.00	0.89	6.20	2.75	0.00	2.07	0.92	0.00	8.94	2.98
12	1.13-I	10	45	110	3	0.45	0.48	0.00	0.93	4.46	4.81	0.00	1.49	1.60	0.00	9.27	3.09

Conditions: 0.10 mmol of HBpin in C_6D_6 (~0.5 mL), amount of catalyst is calculated and then added to obtain the desired catalytic loading, 1 bar of CO_2 . The yield was obtained by ^1H NMR using the Ar- H and $-\text{OMe}$ protons of 1,3,5-trimethoxybenzene as an internal standard. TON and TOF are given to the number of hydride transferred. The catalytic studies were repeated thrice. ^aOptimised condition.

4.4.2 Synthesis of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13)

A solution of $\text{BH}_3\cdot\text{THF}$ (0.57 mL, 1.0 M in THF, 0.570 mmol) was added dropwise to a solution of **1.13-I** (203 mg, 0.187 mmol) in toluene (20 mL) at 0°C . The red solution was slowly raised to room temperature and stirred for 12 hrs. After stirring for 12 hours, a pale-yellow mixture was formed. All the volatiles are removed under reduced pressure. The residue was extracted with THF (10 mL) and toluene (10 mL). After filtration and concentration of the filtrate, compound **4.13** was obtained as colorless crystals. Yield: 101 mg (54.5%). Mp: 341.8°C . ^1H NMR (395.9 MHz, 25°C , d_8 -THF, ppm): $\delta = 0.50 - 1.50$ (br, 6H, BH_3 , overlapped with $\text{CH}(\text{CH}_3)_2$), 0.86 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 0.91 – 0.97 (dd, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.04 – 1.09 (dd, 18 H, $\text{CH}(\text{CH}_3)_2$), 1.27 – 1.40 (dd, 12 H, $\text{CH}(\text{CH}_3)_2$), 2.71 – 2.77 (m, 4 H, $\text{CH}(\text{CH}_3)_2$), 2.99 – 3.06 (m, 4 H, $\text{CH}(\text{CH}_3)_2$), 3.83 (b, 1H, Si-H), 6.95 (d, 2H, Ar-H), 7.14 (s, 2H, NCH), 7.16 (s, 2H, NCH), 7.22 (d, 2H, Ar-H), 7.32 – 7.37 (m, 6H, Ar-H), 7.42 (s, 2H, Ar-H). ^1H NMR (395.9 MHz, 25°C , C_6D_6 , ppm): $\delta = 0.90$ (d, 12H, $\text{CH}(\text{CH}_3)_2$), 0.95 – 0.1.03 (t, 12H, $\text{CH}(\text{CH}_3)_2$), 1.03 – 1.10 (br, 6H, BH_3 , overlapped with $\text{CH}(\text{CH}_3)_2$), 1.31 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.37 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.66 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.71 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 2.91 – 2.95 (m, 4 H, $\text{CH}(\text{CH}_3)_2$), 3.19 – 3.26 (m, 4 H, $\text{CH}(\text{CH}_3)_2$), 4.05 (b, 1H, Si-H), 6.27 (s, 2H, NCH), 6.36 (s, 2H, NCH), 6.91 (d, 2H, Ar-H), 7.11 – 7.13 (m, 6H, Ar-H), 7.19 – 7.23 (m, 4H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 25°C , d_8 -THF, ppm): $\delta = 23.3, 23.4$ (CH_3 , $\text{CH}(\text{CH}_3)_2$), 23.6, 23.9 (CH_3 , $\text{CH}(\text{CH}_3)_2$), 25.7, 25.9 (CH_3 , $\text{CH}(\text{CH}_3)_2$), 26.1, 26.6 (CH_3 , $\text{CH}(\text{CH}_3)_2$), 28.9, 28.9 (CH , $\text{CH}(\text{CH}_3)_2$), 29.0, 29.6 (CH , $\text{CH}(\text{CH}_3)_2$), 124.1 (CH , NCH), 124.3 (CH , NCH), 124.6, 127.7, 131.0, 136.9, 146.2, 146.9, 147.2, 147.3 (Ar), 157.5, 167.4 (C, NCN). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 25°C , d_8 -THF, ppm): -37.7, -43.7. ^{11}B NMR (128.41 MHz, 25°C , d_8 -THF, ppm): -37.7 (q, $^1J_{\text{B-H}} = 96$ Hz), -43.7 (q, $^1J_{\text{B-H}} = 96$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, 25°C , d_8 -THF, ppm): $\delta = 4.1$ (br), -38.1 (br). IR (Nujol/ cm^{-1}): 2102 (w, Si-H). HRMS (ESI): m/z calcd for $\text{C}_{54}\text{H}_{80}\text{B}_2\text{IN}_4\text{Si}$ 989.5152; found 989.5153. Anal. Calcd for $\text{C}_{54}\text{H}_{79}\text{B}_2\text{IN}_4\text{Si}_2$: C, 65.58; H, 8.05; N, 5.67; Found: C, 65.04; H, 8.15; N, 5.46.

4.4.3 Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (**4.13**) in Hydroboration of CO₂ and *N*-formylation

General procedures for the catalytic hydroboration of carbon dioxide using **4.13 as the catalyst:**

Synthesis of compound **4.12a – **4.12b****

Catalyst **4.13** (9.9 mg, 0.01 mmol), internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol, 5 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. Pinacolborane, HBpin (14.5 μ L, 0.10 mmol, 10 equiv.) was then added. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S4.2 and the reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ¹H NMR signals of (pinB)₂O (**4.12a**) at 1.02 ppm, [*pinBOMe*] (**4.12b**) at 1.04 or 3.49 ppm and pinBOC(=O)*H* (**4.12c**) at 0.93 ppm with reference to the –OMe and C–H protons (3.36, 6.20 ppm) of the internal standard, 1,3,5-trimethoxybenzene. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[26] The catalytic studies were repeated at least in triplicate. Formation of **4.12c** was not observed throughout the catalytic reaction.

Attempted synthesis of compound **4.12c – **4.12d****

Catalyst **4.13** (9.9 mg, 0.01 mmol), internal standard methyltriphenylsilane (27.4 mg, 0.10 mmol, 10 equiv.) and 0.5 mL of C₆D₆ were mixed in a J-Young NMR tube. Borane dimethylsulfide, BH₃·SMe₂ (9.5 μ L, 0.10 mmol, 10 equiv.) was then added. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S4.3. The reaction was monitored by NMR spectroscopy. No conversion was observed upon heating for 24 hours. The catalytic studies were repeated at least in triplicate.

Table S4. 2 Catalytic table for hydroboration of CO₂ using HBpin.

Entry	X	T (°C)	t (h)	Yield			TON		TOF (h ⁻¹)		TON	TOF (h ⁻¹)
				4.12a	4.12b	Total	4.12a	4.12b	4.12a	4.12b		
1	10	40	3	0.02	0.02	0.03	0.17	0.18	0.06	0.06	0.35	0.12
2	10	60	1	0.03	0.03	0.06	0.28	0.33	0.28	0.33	0.61	0.61
			3	0.06	0.09	0.16	0.64	0.91	0.21	0.30	1.55	0.52
3	10	80	1	0.03	0.02	0.05	0.30	0.20	0.30	0.20	0.50	0.50
4	10	90	1	0.05	0.02	0.11	0.50	0.20	0.50	0.20	0.70	0.70
5 ^a	10	110	1	0.10	0.11	0.21	0.96	1.14	0.96	1.14	2.10	2.10
			3	0.55	0.45	1.00	5.50	4.50	1.83	1.50	10.00	3.33
6	1	110	1	0.04	0.03	0.07	3.90	3.00	3.90	3.00	6.90	6.90
7	5	110	1	0.07	0.10	0.17	1.36	2.00	1.36	2.00	3.36	3.36

Conditions: 0.10 mmol of HBpin in C₆D₆ (~0.5 mL), amount of catalyst is calculated and then added to obtain the desired catalytic loading, 1 bar of CO₂. The yield was obtained by ¹H NMR using the Ar-*H* and OMe protons of 1,3,5-trimethoxybenzene as an internal standard. TON and TOF are given to the number of hydride transferred. The catalytic studies were repeated thrice. ^aOptimised condition.

Table S4. 3 Catalytic table for hydroboration of CO₂ using BH₃·SMe₂.

Entry	X	T (°C)	t (h)	Yield			TON		TOF (h ⁻¹)		TON	TOF (h ⁻¹)
				4.12c	4.12d	Total pdt	4.12c	4.2d	4.2c	4.12d		
1	10	110	24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Conditions: 0.10 mmol of BH₃·SMe₂ in C₆D₆ (~0.5 mL), amount of catalyst is calculated and then added to obtain the desired catalytic loading, 1 bar of CO₂. The yield was obtained by ¹H NMR using the -*Me* and -*Ph* protons of methyltriphenylsilane as an internal standard. TON and TOF are given to the number of hydride transferred. The catalytic studies were repeated thrice.

Optimization for the reductive functionalization of CO₂ using HBpin and *N*-methylaniline :

Catalyst **4.13** (3.0 mg, 0.003 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 33 equiv.), HBpin (29.0 μ L, 0.20 mmol, 67 equiv.), *N*-methylaniline **4.16d** (10.8 μ L, 0.10 mmol, 33 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature. The reaction conditions are indicated in Table S4.4 and the reaction was monitored by NMR spectroscopy, which confirmed the formation of Ph(Me)NC(=O)H **4.17d** as the major product.^[23,27] The yields of product were reported according to the integration of ¹H NMR signals of Ph(Me)NC(=O)H at 2.90 ppm and PhNMe₂ at 2.55 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The catalytic studies were repeated at least in triplicate.

Table S4. 4 Catalytic table for *N*-formylation of amines using CO₂.

$$\text{CO}_2 + \text{Ph-NH} \xrightarrow[\text{C}_6\text{D}_6, \text{ Temperature (T), Time (t)}]{\text{Catalyst 4.13 (X mol \%), H}^+ \text{ source}} \text{Ph-N-C(=O)H} + \text{Ph-N-}$$

4.16d **4.17d** **4.17d'**

Entry	X	H ⁺ source(eq.)	T (°C)	t (h)	Yield (%)	4.17d : 4.17d'
1	-	HBpin (2)	90	24	0	-
2	5	None	90	96	0	-
3	5	HBpin (2)	90	2	52	8:2
				3	82	8:2
				24	82	8:2
4	5	Ph ₃ SiH (2)	90	24	29	9:1
5	5	Ph ₂ SiH ₂ (2)	90	24	11	8:2
6	5	PhSiH ₃ (2)	90	24	9	8:2
7	5	Et ₃ SiH (2)	90	24	9	8:2
8	5	HBpin (1)	90	3	40	8:2
9	5	HBpin (3)	90	3	81	8:2
10	5	HBpin (2)	24	5	36	9:1
11	5	HBpin (2)	40	5	15	10:0
				24	93	9:1
12	5	HBpin (2)	60	5	39	9:1
				24	92	9:1
13	5	HBpin (2)	80	3	82	8:2
4	5	HBpin (2)	110	0.5	80	8:2
15	1	HBpin (2)	40	24	31	9.7:0.3
16 ^a	3	HBpin (2)	40	24	97	9.7:0.3
17	10	HBpin (2)	40	24	93	9:1

Reaction conditions: Amine **4.16d** (0.10 mmol), required amount of silane, C₆D₆ (0.5 mL), amount of catalyst was calculated, then added to obtain the desired catalytic loading and CO₂ (ca. 50.0 mg). The yield was obtained by ¹H NMR using the CH₂ protons of cyclohexane as an internal standard. The catalytic studies were repeated thrice. ^aOptimised condition.

General procedures for the catalytic functionalization of CO₂ using HBpin and amines:

Catalyst **4.13** (3.0 mg, 0.003 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 33 equiv.), HBpin (29.0 μ L, 0.20 mmol, 67 equiv.), required amount of amine (0.10 mmol, 33 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen for a minute and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The mass of the J-Young NMR tube before and after the introduction of CO₂ was measured. Approximately 50 mg of CO₂ was introduced into the reaction mixture. The reaction mixture was warmed to room temperature and then heated. The reaction conditions are indicated in Table S4.5 – S4.6 and the reactions were followed by NMR spectroscopy to determine their yields. The yields of products were reported according to the integration of ¹H NMR signals of R¹R²NC(=O)H at *ca.* 8 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[23,27] Formation of methylated amine was not observed throughout the catalytic reaction except for **4.17d** (3 %). The catalytic studies were repeated at least thrice. The resulting formamides were purified by silica plug or silica gel chromatography using either ethyl acetate/hexanes or tetrahydrofuran as eluent to give the corresponding *N*-formamides as oil or crystalline solid with contamination from the boron-containing compounds.

Procedures for the gram-scale catalytic functionalization of CO₂ using HBpin and dibenzylamine **4.16e**:

Catalyst **4.13** (0.25 g, 0.25 mmol), internal standard cyclohexane (1.00 mL, 5.07 mmol, 20 equiv.), HBpin (1.5 mL, 10.1 mmol, 40 equiv.), dibenzylamine **4.16e** (1.00 g, 0.97 mL, 5.07 mmol, 20 equiv.) and C₆D₆ (25 mL) were loaded into a Schlenk bottle. . The Schlenk bottle was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature and heated at 40 °C for 24 hours. The reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. Full conversion was observed after 24 hours. The yield of product was reported according to the integration of ¹H NMR signals of (PhCH₂)₂NC(=O)H of **4.17e** at 8.05 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The chemical shifts of the products agree with the reported values in the literature and independent *in-situ* NMR-scale syntheses.^[23,27] Formation of methylated amine was not observed throughout the catalytic reaction.

Deuterium-labelling study of catalytic *N*-formylation using *d*₁₁-piperidine **4.16b-D**:

Catalyst **4.13** (3.0 mg, 0.003 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 33 equiv.), HBpin (29.0 μ L, 0.20 mmol, 67 equiv.), *d*₁₁-piperidine **4.17b-D** (*D*, 98 %, 9.87 μ L, 0.10 mmol, 33 equiv.) and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J-Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze-pump-thaw cycle and 1 bar of CO₂ gas was then added. The freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed to room temperature and heated at 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic trials were repeated at least in triplicate. The identity of the product was determined according to the ¹H NMR signals of R¹R²NC(=O)*H* of **4.17b-D** at 7.76 ppm. A mixture of H₂ (4.47 ppm) and HD (4.33, 4.43, 4.54 ppm, ¹*J*_{HD} = 42.7 Hz) were observed in the crude reaction after an hour due to piperidine (2%) and *d*₁₁-piperidine (98%), respectively.

Characterization of compound **4.15a**:

77:23 mixture of rotamers. ¹H NMR (395.9 MHz, 24 °C, CDCl₃, ppm): δ = 8.09 (s, 1H, CHO), 7.96 (d, 1H, CHO, ³*J*_{H,H} = 12.1 Hz), 6.37 (br, 1H, NH), 6.03 (br, 1H, NH), 3.25 (q, 2H, CH₂, ³*J*_{H,H} = 6.76 Hz), 3.18 (q, 2H, CH₂, ³*J*_{H,H} = 6.77 Hz), 1.44 – 1.51 (m, 4H, CH₂), 1.29 – 1.36 (m, 4H, CH₂), 0.87 – 0.93 (m, 6H, CH₃). HRMS (ESI): *m/z* calcd for C₅H₁₁NONa 124.0738; found 124.0735.

Characterization of compound **4.15b**:

55:45 mixture of rotamers. ¹H NMR (395.9 MHz, 24 °C, CDCl₃, ppm): δ = 8.66 (d, 1H, CHO, ³*J*_{H,H} = 12.06 Hz), 8.38 (s, 1H, CHO), 8.17 (br, 1H, NH), 7.54 (d, 2H, Ar-*H*, ³*J*_{H,H} = 7.9 Hz), 7.31 – 7.38 (m, 4H, Ar-*H*), 7.07 – 7.22 (m, 4H, Ar-*H*), 5.52 (br, 1H, NH).

Characterization of compound **4.15c**:

63:48 mixture of rotamers. ¹H NMR (395.9 MHz, 24 °C, CDCl₃, ppm): δ = 8.65 (d, 1H, CHO, ³*J*_{H,H} = 11.2 Hz), 8.49 (br, 1H, NH), 8.34 (s, 1H, CHO), 7.82 (br, 1H, NH), 7.41 (s, 1H, Ar-*H*), 7.32 – 7.34 (m, 1H, Ar-*H*), 7.18 – 7.26 (m, 2H, Ar-*H*), 6.89 – 7.04 (m, 4H, Ar-*H*), 2.36 (s, 3H, CH₃), 2.34 (s, 3H, CH₃).

Characterization of compound 4.15d:

50:50 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.58 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.4 Hz), 8.38 (br, 1H, NH), 8.33 (s, 1H, CHO), 7.76 (br, 1H, NH), 7.42 – 7.44 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.4 Hz), 7.12 – 7.17 (m, 4H, Ar-H), 6.99 (m, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.1 Hz), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3).

Characterization of compound 4.15e:

62:38 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.63 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.1 Hz), 8.33 (s, 1H, CHO), 8.06 (br, 1H, NH), 7.30 (br, 1H, NH), 7.17 (s, 2H, Ar-H), 6.83 (s, 1H, Ar-H), 6.77 (s, 1H, Ar-H), 6.69 (s, 2H, Ar-H), 2.31 (s, 6H, CH_3), 2.29 (s, 6H, CH_3).

Characterization of compound 4.15h:

51:49 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.49 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.3 Hz), 8.31 (s, 1H, CHO), 8.16 (br, 1H, NH), 7.55 (br, 1H, NH), 7.45 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.8 Hz), 7.04 (d, 2H, Ar-H, $^3J_{\text{H,H}}$ = 8.8 Hz), 6.85 – 6.91 (m, 4H, Ar-H), 3.81 (s, 3H, O- CH_3), 3.79 (s, 3H, O- CH_3). HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_9\text{NO}_2\text{Na}$ 174.0531; found 174.0531.

Characterization of compound 4.15k:

64:36 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.69 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.1 Hz), 8.45 (s, 1H, CHO), 7.93 (br, NH), 7.13 – 7.20 (m, 2H, Ar-H), 7.06 – 7.10 (m, 2H, Ar-H), 6.89 – 6.98 (m, 4H, Ar-H), 3.89 (s, 3H, O- CH_3), 3.84 (s, 3H, O- CH_3).

Characterization of compound 4.15k’:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.35 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 8.31 Hz), 6.73 – 6.81 (m, 4H, Ar-H), 6.05 (br, 1H, NH), 3.84 (s, 3H, O- CH_3), 3.87 (s, 3H, O- CH_3).

Characterization of compound 4.15m:

67:33 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.55 (s, 1H, CHO), 8.33 (s, 1H, CHO), 7.96 (br, 1H, NH), 7.51 – 7.55 (m, 4H, Ar-H), 6.98 – 7.09 (m, 4H, Ar-H), 6.06 (br, 1H, NH).

Characterization of compound 4.15n:

63:37 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.61 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.2 Hz), 8.34 (s, 1H, CHO), 8.27 (br, 1H, NH), 7.52 – 7.54 (m, 2H, Ar-H), 7.31 – 7.34 (m, 2H, Ar-H), 7.26 – 7.28 (m, 2H, Ar-H), 7.04 – 7.06 (m, 2H, Ar-H), 6.19 (br, 1H, NH). HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_7\text{NOCl}$ 156.0216; found 156.0217. HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_7\text{NOCl}$ 156.0216; found 156.0217.

Characterization of compound 4.15p:

83:17 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.22 (s, 1H, CHO), 8.13 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.1 Hz), 7.24 – 7.37 (m, 10H, Ar-H), 6.76 (br, 1H, NH), 6.36 (br, 1H, NH), 4.46 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.3 Hz), 4.40 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.1 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 42.3 (CH_2), 45.8 (CH_2), 127.1 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 128.9 (Ar-C), 129.0 (Ar-C), 137.6 (Ar-C), 137.7 (Ar-C), 161.1 (CHO), 164.7 (CHO). HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_9\text{NONa}$ 158.0582; found 158.0582.

Characterization of compound 4.15q:

84:16 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.21 (s, 1H, CHO), 8.15 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.4 Hz), 7.16 – 7.22 (m, 4H, Ar-H), 7.86 – 6.90 (m, 4H, Ar-H), 6.59 (br, 1H, NH), 6.13 (br, 1H, NH), 4.41 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.8 Hz), 4.35 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.1 Hz), 3.81 (s, 3H, O- CH_3), 3.80 (s, 3H, O- CH_3).

Characterization of compound 4.15r:

85:15 mixture of rotamers. ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.25 (s, 1H, CHO), 8.14 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 11.9 Hz), 7.28 – 7.6 (m, 4H, Ar-H, overlapped with CDCl_3), 7.21 – 7.24 (m, 4H, Ar-H), 6.98 (br, 1H, NH), 6.38 (br, 1H, NH), 4.44 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.1 Hz), 4.39 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.7 Hz).

Characterization of compound 4.15s:

76:24 mixture of rotamers ^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.23 (s, 1H, CHO), 8.18 (d, 1H, CHO, $^3J_{\text{H,H}}$ = 12.0 Hz), 7.35 – 7.40 (m, 2H, Ar-H) 7.22 – 7.30 (m, 2H, Ar-H, overlapped with CDCl_3), 6.27 (br, 1H, NH), 6.62 (br, 1H, NH), 4.56 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.2 Hz), 4.49 (d, 2H, CH_2 , $^3J_{\text{H,H}}$ = 6.7 Hz).

Characterization of compound 4.17a:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.04 (s, 1H, CHO), 3.36 (q, 2H, CH_2 , $^3J_{\text{H,H}}$ = 7.1 Hz), 3.27 (q, 2H, CH_2 , $^3J_{\text{H,H}}$ = 7.1 Hz), 1.19 (t, 3H, CH_3 , $^3J_{\text{H,H}}$ = 7.2 Hz), 1.13 (t, 3H, CH_3 , $^3J_{\text{H,H}}$ = 7.2 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 12.9 (CH_3), 15.0 (CH_3), 36.7 (CH_2), 42.0 (CH_2), 162.4 (CHO). HRMS (ESI): m/z calcd for $\text{C}_5\text{H}_{12}\text{NO}$ 102.0919; found 102.0909.

Characterization of compound 4.17b:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 7.97 (s, 1H, CHO), 3.46 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.3 Hz), 3.28 (t, 2H, CH_2 , $^3J_{\text{H,H}}$ = 5.3 Hz), 1.64 – 1.69 (m, 2H, CH_2), 1.49 – 1.59 (m, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 24.8 (CH_2), 25.2 (CH_2), 26.7 (CH_2), 40.8 (CH_2), 47.0 (CH_2), 161.0 (CHO). HRMS (ESI): m/z calcd for $\text{C}_6\text{H}_{12}\text{NO}$ 114.0919; found 114.0919.

Characterization of compound 4.17c:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.65 (s, 1H, CHO), 3.11 – 3.19 (m, 4H, CH_2), 3.03 – 3.06 (m, 2H, CH_2), 2.49 – 2.52 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 24 °C, CDCl_3 , ppm): δ = 40.8 (CH_2), 45.9 (CH_2), 66.5 (CH_2), 67.3 (CH_2), 161.1 (CHO). HRMS (ESI): m/z calcd for $\text{C}_5\text{H}_9\text{NO}_2\text{Na}$ 138.0531; found 138.0531.

Characterization of compound 4.17d:

^1H NMR (395.9 MHz, 24 °C, CDCl_3 , ppm): δ = 8.26 (s, 1H, *CHO*), 6.86 – 6.96 (m, 3H, *Ar-H*), 6.51 – 6.54 (m, 2H, *Ar-H*), 2.86 (s, 3H, CH_3). HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_8\text{NO}$ 122.0606; found 122.0607.

Characterization of compound 4.17e:

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.05 (s, 1H, *CHO*), 7.02- -7.08 (m, 8H, *Ar-H*), 6.75 – 6.76 (m, 2H, *Ar-H*), 4.28 (s, 2H, CH_2), 3.60 (s, 2H, CH_2).

Table S4. 5 Catalytic table for *N*-formylation of primary amines using HBpin. Isolated yields are shown in parentheses.

Entry	Primary Amine	Product	Yield (%)	TOF (h ⁻¹)
1	4.14a	4.15a	>99 (70)	1.39
2	4.14b	4.15b	>99 (96)	1.39
3	4.14c	4.15c	>99	1.39
4	4.14d	4.15d	>99	1.39
5	4.14e	4.15e	>99	1.39
6	4.14f	4.15f	46	0.64

Entry	Primary Amine	Product	Yield (%)	TOF (h ⁻¹)
13	4.14q	4.15q	>99	1.39
14	4.14r	4.15r	>99	1.39
15	4.14s	4.15s	>99	1.39

Table S4. 6 Catalytic table for *N*-formylation of secondary amines using HBpin. Isolated yields are shown in parentheses.

Entry	Secondary Amine	Product	Yield (%)	TOF (h ⁻¹)
1	4.16a	4.17a	>99 (46)	1.39
2	4.16b	4.17b	>99 (90)	1.39

Entry	Secondary Amine	Product	Yield (%)	TOF (h ⁻¹)
3	4.16c	4.17c	>99 (83)	1.39
4	4.16d	4.17d	97 (68)	1.35
5	4.16e	4.17e	>99 (71)	1.39

4.4.4 Catalytic Studies of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of Aldehyde and Ketone Derivatives

General procedures for the catalytic hydroboration of aldehyde and ketone derivatives using 4.13 as the catalyst:

Catalyst **4.13** (9.9 mg, 0.01 mmol) and 0.5 mL of C₆D₆ were added into a J-Young NMR tube. Pinacolborane, HBpin (16.0 μ L, 0.11 mmol, 10.1 equiv.) and substrates (0.10 mmol, 10 equiv.) were then added. The reaction conditions are indicated in Table S4.7 – S4.8 and the reactions were followed by NMR spectroscopy to determine their yields. The chemical shifts of the products are in good agreement with the reported values in the literatures.^[28] The catalytic studies were repeated at least thrice.

Isolation of product **4.19a – w** and **4.21a – g**

Upon completion of the catalyses, the resulting crude solutions were filtered and the filtrates were dried under vacuum. The dried residues were then further extracted with hexane. The resultant borate esters were isolated by removing volatiles under vacuum for a few hours.

Characterization of compound **4.19a**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 7.32 (d, 2H, Ar-*H*, ³*J*_{H,H} = 8.2 Hz), 7.11 – 7.18 (m, 2H, Ar-*H*), 7.03 – 7.08 (m, 1H, Ar-*H*), 4.96 (s, 2H, O-CH₂), 1.04 (s, 12H, pin-CH₃). ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.9.

Characterization of compound **4.19b**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 7.28 (d, 2H, Ar-*H*, ³*J*_{H,H} = 7.6 Hz), 6.97 (d, 2H, Ar-*H*, ³*J*_{H,H} = 7.6 Hz), 4.98 (s, 2H, O-CH₂), 2.08 (s, 3H, -CH₃), 1.04 (s, 12H, pin-CH₃). ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.9.

Characterization of compound **4.19c**

¹H NMR (395.9 MHz, 24 °C, C₆D₆, ppm): δ = 7.06 – 7.10 (m, 1H, Ar-*H*), 7.02 – 7.03 (m, 1H, Ar-*H*), 6.95 – 6.97 (m, 1H, Ar-*H*), 6.72 – 6.75 (m, 1H, Ar-*H*), 4.98 (s, 2H, O-CH₂), 3.29 (s, 3H, O-CH₃), 1.04 (s, 12H, pin-CH₃). ¹¹B{¹H} NMR (128.41 MHz, 24 °C, C₆D₆, ppm): δ = 21.9.

Characterization of compound 4.19d

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 3.80 (d, 2H, O- CH_2 , $^3J_{\text{H,H}}$ = 6.4 Hz), 1.41 – 1.75 (m, 11H, Cy- H), 1.08 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 4.19e

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.08 (d, 2H, Ar- H , $^3J_{\text{H,H}}$ = 8.2 Hz), 7.22 (d, 2H, Ar- H , $^3J_{\text{H,H}}$ = 8.2 Hz), 4.85 (s, 2H, O- CH_2), 3.47 (s, 3H, O- CH_3), 1.03 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 4.19f

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.41 (s, 1H, Ar- H), 7.22 – 7.23 (d, 2H, Ar- H , $^3J_{\text{H,H}}$ = 7.7 Hz), 7.08 – 7.12 (m, 1H, Ar- H), 4.93 (s, 4H, O- CH_2), 1.05 (s, 24H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 4.19g

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.82 – 6.84 (m, 2H, Ar- H), 6.67 (dd, 1H, Ar- H , $^3J_{\text{H,H}}$ = 5.0 Hz, $^4J_{\text{H,H}}$ = 3.6 Hz), 5.01 (s, 2H, O- CH_2), 1.03 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 4.19h

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 4.76 (s, 2H, O- CH_2), 4.22 (t, 2H, Cp1- H , $^3J_{\text{H,H}}$ = 1.8 Hz), 3.98 (s, 5H, Cp2- H), 3.95 (t, 2H, Cp1- H , $^3J_{\text{H,H}}$ = 1.8 Hz), 1.08 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 4.19k

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 3.67 (s, 2H, O- CH_2), 1.07 (s, 12H, pin- CH_3), 0.91 (s, 9H, - CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 4.19m

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.56 (d, 1H, Ar- H , $^3J_{\text{H,H}}$ = 7.3 Hz), 7.03 – 7.11 (m, 2H, Ar- H), 6.95 (d, 1H, Ar- H , $^3J_{\text{H,H}}$ = 6.9 Hz), 4.97 (s, 2H, O- CH_2), 2.07 (s, 3H, - CH_3), 1.04 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 4.19n

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.04 (m, 1H, Ar- H), 6.13 (m, 1H, Ar- H), 6.01 (dd, 1H, Ar- H , $^3J_{\text{H,H}}$ = 3.3 Hz, $^4J_{\text{H,H}}$ = 1.9 Hz), 4.85 (s, 2H, O- CH_2), 1.03 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.5.

Characterization of compound 4.19p

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.20 – 7.17 (m, 1H, Ar- H), 7.10 – 7.01 (m, 4H, Ar- H), 6.62 (dt, 1H, Ar- CH , $^3J_{\text{H,H}}$ = 15.9 Hz, $^4J_{\text{H,H}}$ = 1.8 Hz), 6.18 (dt, 1H, Ar- $\text{C}=\text{CH}$, $^3J_{\text{H,H}}$ = 15.7, 5.3 Hz), 4.55 (dd, 2H, O- CH_2 , $^3J_{\text{H,H}}$ = 5.6 Hz, $^4J_{\text{H,H}}$ = 1.7 Hz), 1.07 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 4.19q

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.07 – 7.05 (m, 2H, Ar- H), 6.78 – 6.74 (m, 2H, Ar- H), 4.80 (s, 2H, O- CH_2), 1.03 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 4.19r

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.21 (d, 1H, Ar- H , $^3J_{\text{H,H}}$ = 8.2 Hz), 6.92 (d, 2H, Ar- H , $^3J_{\text{H,H}}$ = 8.4 Hz), 4.73 (s, 2H, O- CH_2), 1.03 (s, 12H, pin- CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 4.19s

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.20 – 7.13 (m, 4H, Ar-*H*), 7.05 – 7.03 (m, 1H, Ar-*H*), 6.69 (s, 1H, C=CH), 4.46 (s, 2H, O-CH₂), 1.72 (s, 3H, -CH₃), 1.07 (s, 12H, pin-CH₃).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 4.19t

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 6.96 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.0 Hz), 6.85 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.0 Hz), 4.66 (s, 2H, O-CH₂), 1.02 (s, 12H, pin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.8.

Characterization of compound 4.19u

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.75 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.3 Hz), 7.21 (m, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.3 Hz), 4.89 (s, 2H, O-CH₂), 2.07 (s, 3H, -CH₃), 1.05 (s, 12H, pin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 22.0.

Characterization of compound 4.19v

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.01 – 6.97 (m, 1H, Ar-*H*), 6.85 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.5 Hz), 6.71 (s, 1H, Ar-*H*), 6.54–6.52 (m, 1H, Ar-*H*), 4.92 (s, 2H, O-CH₂), 1.04 (s, 12H, pin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 20.8.

Characterization of compound 4.19w

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.18 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.7 Hz), 6.59 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.6 Hz), 4.88 (s, 2H, O-CH₂), 1.03 (s, 12H, pin-CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.9.

Characterization of compound 4.21a

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.37 (d, 2H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.7 Hz), 7.16 – 7.12 (m, 2H [overlap with C_6D_6], Ar-*H*), 7.07 – 7.03 (m, 1H, Ar-*H*), 5.42 (q, 1H, O-*CH*, $^3J_{\text{H,H}}$ = 6.5 Hz), 1.46 (d, 3H, -*CH*₃, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.02 (s, 6H, pin-*CH*₃), 1.00 (s, 6H, pin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 4.21b

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.85 (s, 1H, Ar-*H*), 7.62 – 7.60 (m, 3H, Ar-*H*), 7.46 – 7.86 (m, 1H, Ar-*H*), 7.24 – 7.22 (m, 2H, Ar-*H*), 5.58 (q, 1H, O-*CH*, $^3J_{\text{H,H}}$ = 6.3 Hz), 1.55 (d, 3H, OCH-*CH*₃, $^3J_{\text{H,H}}$ = 6.4 Hz), 1.03 (s, 6H, Bpin-*CH*₃), 1.00 (s, 6H, Bpin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 20.8.

Characterization of compound 4.21c

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.06 – 7.02 (m, 7H, Ar-*H*), 6.18 (q, 1H, O-*CH*, $^3J_{\text{H,H}}$ = 6.5 Hz), 1.62 (d, 3H, -*CH*₃, $^3J_{\text{H,H}}$ = 6.4 Hz), 1.02 (s, 12H, pin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 20.0.

Characterization of compound 4.21d

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 4.37 (m, 1H, O-*CH*), 3.47 (m, 4H, O-*CH*₂), 1.98 – 1.90 (m, 8H, Cy-*H*), 1.07 (s, 12H, pin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.6.

Characterization of compound 4.21e

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 8.40 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 5.0 Hz), 7.32 (d, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 8.0 Hz), 7.03 (dt, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 7.7 Hz, $^4J_{\text{H,H}}$ = 1.7 Hz), 6.54 (dt, 1H, Ar-*H*, $^3J_{\text{H,H}}$ = 6.7 Hz, $^4J_{\text{H,H}}$ = 2.3 Hz), 5.63 (q, 1H, O-*CH*, $^3J_{\text{H,H}}$ = 6.5 Hz), 1.65 (d, 3H, -*CH*₃, $^3J_{\text{H,H}}$ = 6.4 Hz), 1.12 (s, 6H, pin-*CH*₃), 1.09 (s, 6H, pin-*CH*₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 20.3.

Characterization of compound 4.21f

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 5.66 – 5.63 (m, 1H, C=*CH*), 1.69 – 1.67 (m, 2H, Cy-*H*), 1.65 – 1.63 (m, 2H, Cy-*H*), 1.35 – 1.33 (m, 2H, Cy-*H*), 1.27 – 1.25 (m, 2H, Cy-*H*), 1.07 (s, 12H, *CH*₃-pin). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 21.7.

Characterization of compound 4.21g

^1H NMR (395.9 MHz, 24 °C, C_6D_6 , ppm): δ = 7.03-7.01 (m, 5H, H-1 – H-5), 4.74 (t, 1H, H-7, J = 7.2 Hz), 3.47 (d, 2H, H-6, J = 7.2 Hz), 1.86 (s, 3H, H-8), 1.02 (s, 12H, *CH*₃-pin). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.41 MHz, 24 °C, C_6D_6 , ppm): δ = 20.9.

Table S4. 7 Catalytic table for hydroboration of aldehyde derivatives using HBpin. Isolated yields are shown in parentheses.

Entry	Aldehyde	Product	Cat	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
1			-	80	24	< 5	-
	4.18a	4.19a					
2			Ph ₃ SiH	80	24	< 5	-
	4.18a	4.19a					
3			(EtO) ₃ SiH	80	24	< 5	-
	4.18a	4.19a					
4			4.13	80	24	>99 (81)	0.42
	4.18a	4.19a					
5			4.13	80	24	>99 (87)	0.42
	4.18b	4.19b					
6			4.13	80	24	>99 (95)	0.42
	4.18c	4.19c					

Entry	Aldehyde	Product	Cat	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
7	4.18d	4.19d	4.13	80	9	>99 (96)	1.11
8	4.18e	4.19e	4.13	80	9	>99 (98)	1.11
9	4.18f	4.19f	4.13	110	24	>99 (99)	0.42
10	4.18g	4.19g	4.13	80	22	>99 (99)	0.45
11	4.18h	4.19h	4.13	80	3	>99 (99)	3.33
12	4.18k	4.19k	4.13	80	24	93 (80)	0.39
13	4.18m	4.19m	4.13	80	5	>99 (96)	2.00

Entry	Aldehyde	Product	Cat	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
14			4.13	80	22	>99 (96)	0.45
15			4.13	80	24	92 (72)	0.38
16			4.13	80	21	>99 (84)	0.48
17			4.13	80	22	>99 (98)	0.45
18			4.13	80	24	89 (99)	0.37
19			4.13	80	5	>99 (95)	2.00
20			4.13	80	5	>99 (73)	2.00

Entry	Aldehyde	Product	Cat	T (°C)	t (h)	Yield (%)	TOF (h ⁻¹)
21	4.18v	4.19v	4.13	80	7	>99 (71)	1.43
22	4.18w	4.19w	4.13	80	7	>99 (85)	1.43

Table S4. 8 Catalytic table for hydroboration of ketone derivatives using HBpin. Isolated yields are shown in parentheses.

Entry	Ketone	Product	T (°C)	Yield (%)	TOF (h ⁻¹)
1	4.20a	4.21a	110	>99	0.42
2	4.20b	4.21b	110	>99	0.42

Entry	Ketone	Product	T (°C)	Yield (%)	TOF (h ⁻¹)
3	4.20c	4.21c	80	35	0.15
4	4.20d	4.21d	80	96	0.40
5	4.20e	4.21e	80	80 (72)	0.33
6	4.20f	4.21f	80	27	0.11
7	4.20g	4.21g	80	26	0.11

4.5 Appendices

4.5.1 NMR Spectra

List of abbreviation used in NMR spectra.

Abbreviation	Definition
Cat	Catalyst
HBpin	Pinacolborane
IS	Internal standard
sm	Starting material (substrate)
pdt	Hydroboration product

Synthesis of Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13)

Figure S4. ¹H NMR spectrum of compound 4.13 (in *d*₈-THF).

Figure S4. 2 ^1H NMR spectrum of compound 4.13 (in C_6D_6).

Figure S4. 3 ^{11}B NMR spectrum of compound 4.13 (in d_8 -THF).

Figure S4. 4 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **4.13** (in d_8 -THF).

Figure S4. 5 ^{13}C NMR spectrum of compound **4.13** (in d_8 -THF).

Figure S4. 6 ²⁹Si NMR spectrum of compound **4.13** (in *d*₈-THF).

Figure S4. 7 IR spectrum of compound **4.13**.

Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of CO₂

(a)

(b)

Figure S4. 8 ^1H NMR spectra of the reaction of CO_2 with HBpin (in C_6D_6), catalyzed by **4.13** (10 mol %), (a) 90°C and (b) 110°C .

(a)

(b)

(c)

(d)

Figure S4. 9 ¹H NMR spectra of the resultant reaction of CO₂ with HBpin (in C₆D₆), catalyzed by **4.13** (10 mol %), (a) ¹H, (b) ¹¹B, (c) ¹¹B{¹H} and (d) ¹³C{¹H}.

Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Catalytic *N*-formylation of Amines

Figure S4. 10 ^1H NMR spectrum of attempted isolation of compound **4.15a** (in CDCl_3).

Figure S4. 11 ^1H NMR spectrum of attempted isolation of compound **4.15b** (in CDCl_3).

Figure S4. 12 ^1H NMR spectrum of attempted isolation of compound **4.15c** (in CDCl_3).

Figure S4. 13 ^1H NMR spectrum of attempted isolation of compound **4.15d** (in CDCl_3).

Figure S4. 14 ^1H NMR spectrum of attempted isolation of compound **4.15e** (in CDCl_3).

Figure S4. 15 ^1H NMR spectrum of attempted isolation of compound **4.15h** (in CDCl_3).

Figure S4. 16 ^1H NMR spectrum of attempted isolation of compound **4.15k** (in CDCl_3).

Figure S4. 17 ^1H NMR spectrum of attempted isolation of compound **4.15m** (in CDCl_3).

Figure S4. 18 ^1H NMR spectrum of compound resultant **4.15n** (in C_6D_6).

Figure S4. 19 ¹H NMR spectrum of attempted isolation of compound **4.15n** (in CDCl₃).

Figure S4. 20 ¹H NMR spectrum of attempted isolation of compound **4.15p** (in CDCl₃).

Figure S4. 21 ^1H NMR spectrum of attempted isolation of compound **4.15q** (in CDCl_3).

Figure S4. 22 ^1H NMR spectrum of attempted isolation of compound **4.15r** (in CDCl_3).

Figure S4. 23 ^1H NMR spectrum of attempted isolation of compound **4.15s** (in CDCl_3).

Figure S4. 24 ^1H NMR spectrum of attempted isolation of compound **4.17a** (in CDCl_3).

Figure S4. 25 ¹H NMR spectrum of resultant compound **4.17b** (in C₆D₆).

Figure S4. 26 ¹H NMR spectrum of resultant compound **4.17c** (in C₆D₆).

Figure S4. 27 ^1H NMR spectrum of resultant compound **4.17d** (in C_6D_6).

Figure S4. 28 ^1H NMR spectrum of resultant compound **4.17e** (in C_6D_6).

Figure S4. 29 Enlarged ^1H NMR spectrum of the resultant reaction of amines, CO_2 and HBpin catalyzed by **4.13** (3 mol %, 40 °C, 24 hour, in C_6D_6). H_2 gas was found in all catalyses.

Figure S4. 30 Enlarged ^1H NMR spectrum of the resultant reaction of d_{11} -piperidine, CO_2 and HBpin catalyzed by **4.13** (3 mol %, 40 °C, 24 hour, in C_6D_6).

Lewis Acid and Base-Stabilized Silicon(I) Hydride (4.13) in Hydroboration of Aldehydes and Ketones

(a1)

(a2)

(a1)

(a2)

(b)

Figure S4. 32 Stepwise hydroboration of benzaldehyde **4.18a** catalyzed by **4.13** (in C_6D_6) at $60^\circ C$, monitored by 1H NMR spectroscopy, (a) first step: addition of HBpin and (b) second step: addition of benzaldehyde.

(a)

(b)

Figure S4. 33 Stepwise hydroboration of benzaldehyde **4.18a** catalyzed by **4.13** (in C_6D_6) at $60^\circ C$, monitored by 1H NMR spectroscopy, (a) first step: addition of 2 equiv. of HBpin, 3h and (b) second step: addition of benzaldehyde.

Figure S4. 34 ^1H NMR spectrum of isolated compound **4.19a** (in C_6D_6).

Figure S4. 35 ^{11}B NMR spectrum of isolated compound **4.19a** (in C_6D_6).

Figure S4. 36 ¹H NMR spectrum of isolated compound **4.19b** (in C₆D₆).

Figure S4. 37 ¹¹B NMR spectrum of isolated compound **4.19b** (in C₆D₆).

Figure S4. 38 ¹H NMR spectrum of isolated compound **4.19c** (in C₆D₆).

Figure S4. 39 ¹¹B NMR spectrum of isolated compound **4.19c** (in C₆D₆).

Figure S4. 40. ¹H NMR spectrum of isolated compound **4.19d** (in C₆D₆).

Figure S4. 41 ¹¹B NMR spectrum of isolated compound **4.19d** (in C₆D₆).

Figure S4. 42 ¹H NMR spectrum of isolated compound **4.19e** (in C₆D₆).

Figure S4. 43 ¹¹B NMR spectrum of isolated compound **4.19e** (in C₆D₆).

Figure S4. 44 ¹H NMR spectrum of isolated compound **4.19f** (in C₆D₆).

Figure S4. 45 ¹¹B NMR spectrum of isolated compound **4.19f** (in C₆D₆).

Figure S4. 46 ^1H NMR spectrum of isolated compound **4.19g** (in C_6D_6).

Figure S4. 47 ^{11}B NMR spectrum of isolated compound **4.19g** (in C_6D_6).

Figure S4. 48 ¹H NMR spectrum of isolated compound **4.19h** (in C₆D₆).

Figure S4. 49 ¹¹B NMR spectrum of isolated compound **4.19h** (in C₆D₆).

Figure S4. 50 ¹H NMR spectrum of isolated compound **4.19k** (in C₆D₆).

Figure S4. 51 ¹¹B NMR spectrum of isolated compound **4.19k** (in C₆D₆).

Figure S4. 52 ¹H NMR spectrum of isolated compound **4.19m** (in C₆D₆).

Figure S4. 53 ¹¹B NMR spectrum of isolated compound **4.19m** (in C₆D₆).

Figure S4. 54 ¹H NMR spectrum of isolated compound **4.19n** (in C₆D₆).

Figure S4. 55 ¹³B NMR spectrum of isolated compound **4.19n** (in C₆D₆).

Figure S4. 56 ¹H NMR spectrum of isolated compound **4.19p** (in C₆D₆).

Figure S4. 57 ¹¹B NMR spectrum of isolated compound **4.19p** (in C₆D₆).

Figure S4. 58 ¹H NMR spectrum of isolated compound **4.19q** (in C₆D₆).

Figure S4. 59 ¹¹B NMR spectrum of isolated compound **4.19q** (in C₆D₆).

Figure S4. 60 ¹H NMR spectrum of isolated compound **4.19r** (in C₆D₆).

Figure S4. 61 ¹¹B NMR spectrum of isolated compound **4.19r** (in C₆D₆).

Figure S4. 62 ¹H NMR spectrum of isolated compound **4.19s** (in C₆D₆).

Figure S4. 63 ¹¹B NMR spectrum of isolated compound **4.19s** (in C₆D₆).

Figure S4. 64 ¹H NMR spectrum of isolated compound **4.19t** (in C₆D₆).

Figure S4. 65 ¹¹B NMR spectrum of isolated compound **4.19t** (in C₆D₆).

Figure S4. 66 ¹H NMR spectrum of isolated compound **4.19u** (in C₆D₆).

Figure S4. 67 ¹¹B NMR spectrum of isolated compound **4.19u** (in C₆D₆).

Figure S4. 68 ¹H NMR spectrum of isolated compound **4.19v** (in C₆D₆).

Figure S4. 69 ¹³C NMR spectrum of isolated compound **4.19v** (in C₆D₆).

Figure S4. 70 ¹H NMR spectrum of isolated compound **4.19w** (in C₆D₆).

Figure S4. 71 ¹¹B NMR spectrum of isolated compound **4.19w** (in C₆D₆).

Figure S4. 72 ¹H NMR spectrum of isolated compound **4.21a** (in C₆D₆).

Figure S4. 73 ¹¹B NMR spectrum of isolated compound **4.21a** (in C₆D₆).

Figure S4. 74 ¹H NMR spectrum of isolated compound **4.21b** (in C₆D₆).

Figure S4. 75 ¹¹B NMR spectrum of isolated compound **4.21b** (in C₆D₆).

Figure S4.76 ^1H NMR spectrum of resultant compound **4.21c** (in C_6D_6).

Figure S4.77 ^{11}B NMR spectrum of resultant compound **4.21c** (in C_6D_6).

Figure S4. 78 ^1H NMR spectrum of resultant compound **4.21d** (in C_6D_6).

Figure S4. 79 ^{11}B NMR spectrum of resultant compound **4.21d** (in C_6D_6).

Figure S4. 80 ¹H NMR spectrum of isolated compound 4.21e (in C₆D₆).

Figure S4. 81 ¹¹B NMR spectrum of isolated compound 4.21e (in C₆D₆).

4.5.2 Crystallographic Data of All Structures

The X-ray diffraction intensity data were measured at 100 K with a Bruker APEX II diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), with the SMART suite of programs.^[29] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.^[29] Structural solution and refinement were carried out with the SHELXTL suite of programs.^[30] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table S4. 9 Crystallographic data of **4.13**.

4.13	
Formula	C ₆₁ H ₈₇ B ₂ IN ₄ Si ₂
Fw	1081.04
Color	Colourless
cryst syst	Monoclinic
space group	<i>P121/c1</i>
<i>a</i> (Å)	16.459(3)
<i>b</i> (Å)	14.980(3)
<i>c</i> (Å)	27.004(5)
<i>α</i> (deg)	90
<i>β</i> (deg)	102.390(3)
<i>γ</i> (deg)	90
<i>V</i> (Å³)	6503.(2)
<i>Z</i>	4
<i>d</i>_{calcd} (g cm⁻³)	1.104
<i>μ</i> (mm⁻¹)	0.566
<i>F</i>(000)	2288
cryst size (mm)	0.140 x 0.260 x 0.280
<i>θ</i> range (deg)	1.27 to 26.11
index range	-19 ≤ <i>h</i> ≤ 20, -18 ≤ <i>k</i> ≤ 18, -33 ≤ <i>l</i> ≤ 29
no. of rflns collected	82383
no. of indep rflns	12882
<i>R</i>1, <i>wR</i>2 (<i>I</i> > 2(<i>σ</i>))	0.1049, 0.2840
<i>R</i>1, <i>wR</i>2 (all data)	0.1685, 0.3274
goodness of fit, <i>F</i>²	1.149
no. of data/restraints/params	12882 / 4115 / 1354
largest diff peaks, eÅ⁻³	1.354 and -1.417

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Chapter 5:

Renaissance of p-block Elements: From Organoreagents to Efficient Catalysts

5.1 Main Group Elements as Transition Metals: Towards Catalysis

In general, the activation modes mediated by main group complexes [MG] could be summarized into three types (i) Lewis acid (LA) and/or Lewis base (LB) type activation of unsaturated molecules, (ii) E–H σ -bond insertion into unsaturated bond, (iii) multiply bonded heavier main group element and (iv) filled and vacant coordination site, as summarized in Chart 5.1.^[1]

(i) Lewis acid and/or Lewis Base Mechanism

(ii) σ -bond Metathesis Mechanism

(iii) Multiply Bonded Heavier Alkene Analogue

(iv) Filled and Vacant Coordination Site

Chart 5. 1 Activation modes of main group complexes in catalysis.

For Lewis acid catalysts, the electrophilic main group element weakly interacts with a nucleophilic substrates, for example O-center carbonyl substrate to generate a LA $\cdots$ substrate complex (Chart 5.1(i), **A**). For Lewis base catalysts, the lone pair of electrons at the main group element attack substrate to form a [MG]–substrate intermediate (Chart 5.1(i), **B**). In some cases, Lewis acid is commonly involved as three component system to generate the [MG]–CO₂–LA

intermediate (Chart 5.1(i), C). Another type C mechanism is the frustrated Lewis pair (FLP, Chart 5.1(ii)). For example, the FLP-mediated hydrogenation reaction involves the initial heterolytic cleavage of the dihydrogen gas to generate the protonated Lewis base and hydride addition to the Lewis acid. Then, the protonated Lewis base transfer its proton to the imine substrate and the subsequent hydride transfer eliminates the reduced product, along with the regeneration of the FLP.^[1a]

The catalytic pathway mediated by the main group hydride [MG]–H occur by the insertion [MG]–H bond into the unsaturated substrate, such as C=O of CO₂ to generate formate derivative prior to the reduction reaction. In this case, the polarization between the [MG]^{δ+}–H^{δ-} or substantial hydridic character MG–H bond is imperative for the CO₂ activation to take place (Chart 5.1(ii)). Meanwhile, the heavier main group alkene or alkyne analogues activates CO₂ to form the corresponding [2+2] cycloaddition intermediate, subsequent undergoes reduction reaction (Chart 5.1(iii)).^[1c-e] Lastly, the catalytic framework based on P^{III}/P^V with small-ring phosphacycles have been shown to be active in P^{III}/P^V=O redox cycling, reminiscent of transition metal chemistry in oxidative addition/ reductive elimination cycle (Chart 5.1(iv)).^[1f]

5.1.1 Lewis Acid Mechanism

Cationic boron complexes such as borenium cations are commonly employed in Lewis acid catalysis. It constitutes of a three-coordinate species with two σ -bonded substituents and a donor-acceptor interaction with a ligand for stabilizing a positive charge at the boron center, are useful catalysts in various reactions. Yamamoto demonstrated that chiral borenium ion **5.1** could catalyze regio- and enantioselective Diels-Alder reaction of cyclopentadienes with alkenes derivatives to deliver the corresponding norbornenes with high yields and enantioselectivity (yield: 70 – 98%, 96 – 99% ee, Chart 5.1).^[2] The same group also reported **5.1**-catalyzed regio- and enantioselective Diels-Alder reaction between cyclic and acyclic dienes with α,β -acetylenic ketones to deliver chiral hexacyclodienes (yield: 73 – 96%, 99% ee, Chart 5.1).^[3] Similarly, another chiral borenium catalyst **5.2** developed by Jiao facilitated catalytic 1,3-dipolar cycloadditions of tri-*isopropylsilyl* nitronates and 2-alkylacroleins to yield 2-isoxazolines with a chiral quaternary carbon center with excellent yields and enantiomeric excess (yield: 70 – 99%, 90 – 96% ee, Chart 5.1).^[4]

Chart 5. 2 Single site borenium ions in catalytic Diels-Alder and 1,3-dipolar cycloaddition reactions.^[2-4]

5.1.2 Frustrated Lewis Pair Mechanism

Another activation framework available to the main group elements is the dual reaction sites, prominently, the FLP. FLP is a compound or mixture consists of a Lewis acid and a Lewis base that are sterically hindered from forming classical Lewis acid–base adducts, with its Lewis acidity and basicity available for interaction with a third molecule. Essentially pioneered by Stephan and Erker in reversible activation of dihydrogen and carbon dioxide using Lewis acid–base pairs mechanisms,^[5] various FLP systems were developed for hydrogenation of unsaturated molecules.^[6] Although FLPs are capable to reduce CO₂ to deliver the methanol derivatives, they demand stoichiometric amount of FLPs.^[7]

Catalytic Hydroboration of CO₂

Catalytic N-formylation of Amines

Catalytic Hydroboration of Carbonyl Derivatives

Catalysts

Chart 5.3 FLP catalysts.^[1c,1d,8-11]

Accordingly, newer generation of FLP ion pair NHC/GaR₃ (**5.3**, NHC = *N*-heterocyclic carbene, R₃ = CH₂SiMe₃) has emerged to activate HBpin to generate structurally characterized NHC–borenium gallate–hydride [NHC-BPin][GaR₃(μ-H)GaR₃][−] intermediate, subsequently to catalyze regio- and chemoselective hydroboration of carbonyl derivatives (catalyst loading: 5 mol%, yield: 45 – 99%, TOF = 1 – 64 h^{−1}, Chart 5.3).^[8] Remarkably, Fountaine and Macron have developed the first intramolecular FLP system of phosphine/borane **5.4** that promote efficient reduction of CO₂ with a range of borane sources (catecholborane HBcat, HBpin, 9-BBN and BH₃·SMe₂) to deliver diborate ether and methoxyborane derivatives with yields up to 99% and TOF beyond >2,950 h^{−1} (time: 4 h, 1,000 equiv. BH₃·SMe₂, temperature: 70 °C, Chart 5.3).^[9] Notably, the DFT studies were revealed that FLP **5.4** activates the CO₂ before the H–B bond of the HBcat inserts into the C=O bond of CO₂ (Scheme 5.1). The subsequent addition of 2 equivalents of HBcat eliminates the diborate ether (catB)₂O and methoxyborane MeOBcat, along with the regeneration of catalyst **5.4** (Scheme 5.1). Another intramolecular FLP **5.5**, a combination of strong Lewis basic phosphorus and weak Lewis acidic boron, was also efficient in related reactions, affording a mixture of formoxyborane catBOC(=O)H, methoxyborane MeOBcat and diborate ether (catB)₂O (TOF = 400 h^{−1} for HBcat, Chart 5.3).^[10]

Scheme 5. 1 Mechanism for phosphine-borane **5.4**-catalyzed hydroboration of CO₂.^[9]

Kinjo explored a new class of aromatic diazadiborinine **5.6** in *N*-formylation of amines using CO₂ to afford good yields of *N*-formamides (yield: 76 – 98%, TOF = 2 – 12 h⁻¹) and diborate ether (pinB)₂O at 2 mol% catalytic loading (Chart 5.3).^[11a] Moreover, catalyst **5.6** is further extended to hydroboration of carbonyl derivatives, leading to almost quantitative yields of borate ethers. Using similar FLP mechanism, the formation of catalyst–CO₂ adduct is essential to simultaneously activates H–B bond of HBpin and transfers hydride to another molecule of CO₂ to deliver formoxyborane pinBOC(=O)H and regenerate catalyst–CO₂ adduct. Stoichiometric dehydrocoupling reaction between formoxyborane and amine furnishes the *N*-formamide (Scheme 5.2).

Scheme 5. 2 Mechanism for diazaborinane **5.6**-catalyzed *N*-formylation of amines.^[11a]

5.1.3 Main Group Element Hydride Mechanism

Our group illustrated that enhancing group 13 element hydrides [MG]–H facilitated their capability in catalytic hydroboration. The boronium ion **5.7** possesses highly hydridic character of the B–H bond due to the strong electron donating iminophosphoranyl substituents and hence complex **5.7** was found to be among the best catalyst for hydroboration of CO₂ using BH₃·SMe₂ to afford methanol derivatives with mere 0.1 mol% catalyst loading (yield: 84%, TOF = 2,646 h^{–1}, Chart 5.4).^[12] Catalytic versatility was observed upon changing the boron center to the heavier aluminum analogue of **5.9** (Chart 5.4). To illustrate, aluminium hydride **5.9** effectively promote hydroboration of CO₂ with pinacolborane HBpin over 2 days to deliver mixtures of methoxyborane MeOBpin and diborate ether (pinB)₂O (yield: 78%, TOF: 0.16 h^{–1}, Chart 5.4).^[13] Changing the borane source to BH₃·SMe₂ led to clean formation of trimethylborate [B(OMe)₃] (yield: >99%, TOF= 356.4 h^{–1}, Chart 5.3) and B₂O₃. Organic synthesis mediated by catalyst **5.9** is extended to hydroboration of carbonyl (yield: 70 – >99%, TOF: 2.9 – 20 h^{–1}), nitrile (yield: 23 – 99%, TOF: 1.5 – 6.6 h^{–1}) and alkyne (yield: 78 – 97%, TOF: 1.3 – 1.6 h^{–1}) derivatives (Chart 5.4).

Roesky et al. used β-diketimate aluminium(II) hydride catalyst **5.8** towards hydroboration (maximum TOF = 99 h^{–1}) and cyanosilylation of carbonyl derivatives (maximum TOF = 99 h^{–1}, Chart 5.4).^[14] Changing the OTf substituent to hydride enabled selective hydroboration of terminal alkynes (yield: 61 – 82%, TOF = 0.9 – 2.1 h^{–1}), as well as dehydrogenative coupling of hydroborane, alcohol, thiol and amine derivatives with 9-borabicyclo[3.3.1]nonane 9-BBN or HBpin (yield: 32 – 99%, TOF = 0.42 – 19.8 h^{–1}).^[15] Nikonov's β-diketimate aluminium hydride cation was also capable of catalyzing hydrosilylation of olefins via Piers–Oestreich-type and Yamamoto-type mechanisms.^[16] Lastly, a heavier analogue neutral β-diketimate gallium **5.10** was found to catalyze reduction of CO₂ using HBpin, leading to full conversion to methoxyborane MeOBpin and diborate ether (pinB)₂O (maximum TOF = 2.5 h^{–1}, Chart 5.4).^[17]

Catalytic Hydroboration of CO₂

Catalytic Hydroboration of Carbonyl Derivatives

Catalytic Cyanosilylation of Carbonyl Derivatives

Catalytic Hydroboration of Terminal Alkynes

Catalytic Hydroboration of Terminal Alkynes

Catalysts

Chart 5. 4 Single site Group 13 catalysts for hydroboration reactions.^[12-14,17]

Mechanistic studies for the hydroboration of CO₂ and carbonyl derivative mediated by compound **5.8** – **5.10** proceeded in a σ -bond metathesis manner whereby the M–H bond of catalyst activates the substrate (carbonyls, alkynes or nitriles) before the subsequent hydroboration reaction as illustrated in Scheme 5.3.^[13-14,17] On the contrary, the catalytic cyanosilylation of carbonyl derivatives mediated by complex **5.8** underwent a different mechanism, via the activation of the Si–C bond of TMSCN prior to the cycloaddition reaction with the carbonyl derivatives (Scheme 5.4).^[14]

Scheme 5.3 Mechanism for aluminum hydride **5.9**-catalyzed hydroboration of CO₂.^[13]

Scheme 5.4 Mechanism for aluminum hydride **5.8**-catalyzed cyanosilylation of carbonyl derivatives.^[14]

Catalytic Hydroboration of CO₂

Catalytic Hydroboration of Carbonyl Derivatives

Catalysts

Chart 5.5 Group 14 element hydride **5.11** in catalysis.^[18]

Moving on to Group 14, Jones elucidated the germylene- **5.11-Ge** and stannylene-hydride **5.11-Sn** (Chart 5.5), featuring powerful E–H bond and small energy separation between the frontier orbitals. They are efficient catalysts in mediating the hydroboration of unsaturated compounds.^[18b] To illustrate, germylene-hydride **5.11-Ge** could mediate hydroboration of CO₂ using HBpin to deliver a mixture of methoxyborane MeOBpin and diborate ether (pinB)₂O (time: 24 h, yield: >99%, TOF = 0.4 h^{–1}). Superior catalytic performance was observed for stannylene-hydride **5.11-Sn**, the catalysis was shortened to mere 5 minutes with the same yield and selectivity using HBcat (TOF = 1188 h^{–1}), making it one of the most active catalysts. Complex **5.11** could mimic transition metal hydride mechanism in undergoing σ-bond metathesis, oxidative addition, and reductive elimination processes in the catalyses, due to their far more reactive E^{II}–H bonds in comparison with classical E^{IV}–H bonds (Scheme 5.5). Accordingly, the germanium(II) and tin(II) hydrides **5.11** are among the most active catalysts in the hydroboration of aldehydes and ketones, driving the reaction TOF up to 13,300 h^{–1} with just 0.05 mol% catalyst loading with high selectivity and high yields.^[18a] The reaction mechanism is similar to the hydroboration of CO₂, initiated by the activation of the O-center of the substrate, induces the E–H insertion into the C=O of substrate. Lastly, σ-bond metathesis between the E–O and B–H of borane furnishes the corresponding borate ether with the regeneration of catalyst (Scheme 5.6).

Scheme 5. 5 Mechanism for germanium(II) **5.11**-catalyzed catalytic reduction of CO_2 .^[18b]

Scheme 5. 6 Mechanism for neutral tetrelene E-H **5.11**-catalyzed hydroboration of carbonyl derivatives.^[18a]

Recently, the 1,3,2-diazaphospholenes (DAPs) catalyzed an array of contemporary transformations such as reduction, hydride transfer and asymmetric synthesis of unsaturated molecules.^[19] They constitute of a lone pair of electrons, a vacant orbital and σ -bonded substituent at the phosphorus center. To illustrate, Kinjo demonstrated the first utilization of DAP hydride catalyst **5.12** in hydrosilylation of CO₂ to selectively deliver doubly-formylated silane and siloxane by-product (yield: >95%, TOF = 19 h⁻¹, Chart 5.6).^[20] In addition, the DAP hydride **5.12** is a powerful catalyst in mediating regio- and stereoselective *N*-formylation of CO₂ with primary amines selectively afforded *N*-formamides in good yields (yield: 72 – >99%, TOF = 0.7 – 10 h⁻¹, Chart 5.6). However, when the secondary amines are employed, it leads to the formation of *N*-formamides for less sterically hindered amines and *N*-methyamines for steric amines (yield: 61 – 95%, TOF = 0.6 – 38 h⁻¹, Chart 5.6). Mechanistic insight illustrated hydrophosphination of CO₂ is possible by insertion of complex DAP hydride **5.12** P–H bond into C=O bond of CO₂ to form DAP–OC(=O)H, induces formyl transfer to silane to deliver di-formoxysilane, siloxane and regenerate complex **5.12**. Subsequent reaction between di-formoxysilane and amine afforded the *N*-formamide (Scheme 5.7). Same mechanism pathway was observed for the DAP hydride **5.12**-catalyze hydroboration of carbonyl derivatives via main group element hydride σ -bond metathesis mechanism and subsequent hydroboration reaction to eliminate the corresponding borate ester (yield: 95 – 99%, TOF = 6.2 – 99 h⁻¹, Chart 5.6).^[21] Its heavier analogue of benzo-1,3,2-diazaarsole (DAAs) show similar catalytic selectivity and mechanistic pathway (yield: >95 %, TOF = 0.79 – 38 h⁻¹).^[22]

Catalytic Reduction of CO₂

Catalytic Functionalization of CO₂

Catalytic Hydroboration of Carbonyl Derivatives

Catalytic Reduction of α,β -unsaturated Esters

Transfer Hydrogenation

Catalyst

Chart 5. 6 Selected examples of DAP hydride **5.12** in catalysis.^[20-21,23]

Scheme 5. 7 Mechanism for DAP hydride **5.12**-catalyzed *N*-formylation of amines using CO₂.^[20]

Moreover, DAP hydride catalyst **5.12** mediated conjugate transfer hydrogenation as well as the 1,4-hydroboration of α,β -unsaturated esters, proceeded via initial 1,4-hydrophosphination of the α,β -unsaturated esters to afford a phosphinyl enol ether complex $\text{DAP-O(OMe)C=C(R)R'}$.^[23] In order for transfer hydrogenation of α,β -unsaturated esters to take place, aminoborane induces cleavage of P–O bond of phosphinyl enol ether complex to regenerate catalyst and simultaneously deliver the respective enol intermediate to yield ester product via tautomerization (yield: 95 – 99%, TOF = 6.3 – 99 h⁻¹, Chart 5.6). Whereas for catalytic C–C bond formation using nitrile, 1,4-hydroboration of phosphinyl enol ether complex lead to boryl enolate intermediate, subsequently undergoes coupling reaction with nitrile to yield single addition 1,3-imino ester product for methyl methacrylate substrate (yield: 71 – 78%, TOF = 0.28 – 0.42 h⁻¹, Chart 5.6) and double addition product for aryl substituted α,β -unsaturated esters (yield: 35 – 85%, TOF = 1.2 – 8.5 h⁻¹, Chart 5.6).

Catalytic Hydroboration of Pyridine Derivatives

Chart 5. 7 NHPs **5.13**- and **5.14**-catalyzed hydroboration of pyridine derivatives.^[24]

Since the Lewis ambiphilic phosphorus center and the hydridic character of the P–H bond are crucial parameters in driving catalytic reactions, an additional positive charge at the phosphorus center in the form of *N*-heterocyclic phosphonium cation NHP is anticipated to significantly improve catalytic efficacy. In short, NHP features a combination of +3 oxidation state and positive charge at the phosphorus center. To illustrate, Kinjo utilized various 1,3,2-diazaphosphenium triflate pyridine **5.13** – **5.14**, are efficient in mediating hydroboration of pyridine to afford high yields of 1,4-dihydropyridine as major product and minor 1,2-addition product in an average of >20:1 ratio (yield: 90 – 96%, TOF = 1.6 – 3 h⁻¹, Chart 5.7).^[24] The

reaction mechanism is proposed to proceed via a generation of a boronium salt $[(\text{py})_2\text{Bpin}][\text{OTf}]$ and DAP hydride as illustrated in Scheme 5.8.

Scheme 5. 8 Mechanism for NHPs **5.13**-catalyzed hydroboration of pyridine derivatives.^[24]

5.1.4 Multiply Bonded Heavier Main Group Element

Multiply bonded heavier main group elements such as the dialumene {Al=Al} **5.15** by Inoue, can catalyze hydroboration of CO₂ using HBpin (Chart 5.8).^[11b,11c] The same group studied the effect of substituents of the dialumenes resulted in vastly different catalytic activity and selectivity for **5.15-Si** (yield: 68%, TOF = 3.4 h⁻¹) versus **5.15-Ar** (yield: 66%, TOF = 0.55 h⁻¹). For example, catalyst **5.15-Si** selectively delivers mixtures of formoxyborane, methoxyborane and diborate methane. However, catalyst **5.15-Ar** afforded additional formoxyborate methane product. Based on the mechanistic studies, complex both **5.15-Si** and **5.15-Ar** reacts with CO₂ to form the corresponding carbonate species. In addition, the reaction between complex **5.15-Ar** and HBpin lead to NHC abstraction to form the inactive NHC–HBpin. Further, the absence of Al(H)–Al(Bpin) species could not explain the selectivity difference in **5.15**. Therefore, only conclusive mechanism for **5.15-Si** is drawn. To illustrate, catalyst **5.15-Si** first initiates [2+2] cycloaddition of catalyst with CO₂ to form carbonate complex, followed by concomitant coordination of exocyclic O of the carbonate and hydride transfer. Another molecule of CO₂ then inserts into the opposite end of the Al···Al plane to generate a highly reactive 8-member cyclic intermediate, further induces elimination of formoxyborane to regenerate the active carbonate catalyst (Scheme 5.9).^[11b]

As for *N*-phosphinoamidinato NHC-diborene **5.16**, features a {B=B} moiety in related *N*-formylation reaction leading to formoxyborane via an initial [2+2] cycloaddition to form catalyst–CO₂ intermediate.^[1c] Next, dehydrogenation reaction between the borane and amine delivers the corresponding amino–borane adduct, which then undergoes substitution with formoxyborane to afford *N*-formamide and diborate ether (pinB)₂O (average yield: 91.6%, TOF = 26 h⁻¹, Chart 5.8). Diborene **5.16** could also catalyze hydroboration of CO₂ using HBpin, leading to excellent yield of methoxyborane MeOBpin and diborate ether (pinB)₂O (yield: 98%, TOF = 33 h⁻¹, Chart 5.8). In addition, chemoselective hydroboration of carbonyl using catalyst **5.16** afforded the corresponding borate ethers (yield: 98%, TOF = 0.7 – 240 h⁻¹, Chart 5.8).

Catalytic Hydroboration of CO₂

Catalytic N-formylation of Amines

Catalytic Hydroboration of Carbonyl Derivatives

Catalysts

Chart 5.8 Multiply bonded Group 13 catalysts.^[1c,11b,11c]

Scheme 5.9 Mechanism for dialumene **5.15-Si**-catalyzed hydroboration of CO_2 .^[11b]

In Group 14, Sasamori and Tokito described the sole example of heavier Group 14 alkyne analogue in mediating regioselective C–C coupling reactions using a digermene pre-catalyst **5.17** (Scheme 5.10).^[1d] The digermene pre-catalyst **5.17** reacts with 2 equivalents of arylacetylene within 3 minutes to form the 3,5-diaryldigermabenzene active catalyst, further undergo redox $\text{Ge}^{\text{II}}/\text{Ge}^{\text{IV}}$ processes with the subsequent arylacetylenes to mediate cyclotrimerization of terminal alkynes to selectively deliver the corresponding 1,2,4-triarylbenzenes (Scheme 5.10).

Scheme 5. 10 Digermynes **5.17**-catalyzed cyclotrimerization of terminal arylacetylenes.^[1d]

5.1.5 Filled and Vacant Coordination Site

The Group 13 elements do not participate in the mechanism involving filled and vacant coordination site, though limited examples were reported for the Group 14 catalysts.^[1d,11d,11e,18,25] The latter could be explained by the lack of redox flexibility to switch between the +2 and +4 oxidation state in the redox active catalysis, is classical for transition metal complexes. For instance, a neutral silicon(II) species could only lead to the thermodynamically stable products such as silane(IV) derivatives, consequently, render elimination reaction implausible and impeding catalytic use. Therefore, few strategies were developed to overcome such limitation. One strategy was illustrated by Jutzi using the silicon(II) cation **5.18** in catalyzing controlled degradation of oligo(ethyleneglycol) diethers (Scheme 5.11).^[25a] The open coordination site at the silicon center enabled up to 4 contacts of oxygen atom of the dimethoxyethane to promote Si···O interaction and induce rearrangement of lone pair of electrons and σ -bond within the ether, affording dioxane and mono-ether.

Scheme 5. 11 Single site silicon(II) cation **5.18** in controlled degradation of oligoethers.^[25a]

Recently, heavier analogue of acylium cation, germa-acylium **5.19** could catalyze *N*-functionalization of CO₂ with secondary amines (Scheme 5.12).^[25e] However, selectivity could not be achieved. Nonetheless, the germa-acylium cation **5.19** provided a new mechanistic insight on the catalytic pathway (Scheme 5.12). First, reduction of the germa-acylium cation **5.19** with arylsilane generates the germanium(IV) hydride species, followed by I_{Me}•HCl elimination to form the siloxygermylene active catalyst. The lone pair of electrons at the germanium(II) center then sequentially activates the Si–H of the diphenylsilane and CO₂ to generate silylformate, which then further reacts with amine and another arylsilane to furnish the corresponding *N*-formamides, *N*-aminals and *N*-methyamines.

Catalytic C–N bond formation using CO₂

Scheme 5. 12 Mechanism for germa-acylium cation **5.19**-catalyzed C–N bond formation using CO₂ with secondary amine.^[25e]

Other examples include catalysts β -diketiminate germylene **5.20** (TOF = 4.1 h⁻¹), NHC-germylene **5.21-Ge** (TOF = 7.5 h⁻¹) and NHC-stannylene **5.21-Sn** (TOF = 10 h⁻¹) in reduction of various unsaturated substrates, such as hydroboration of carbonyl derivatives, cyanosilylation of aldehydes (Chart 5.9).^[25f-h] Contrary with the tetrelene E–H, the complexes **5.20** – **5.21** without the E–H bond offer different mechanistic insight for the related reaction as illustrated in Scheme 5.13. Furthermore, Power et al. used the methoxystannylene pre-catalyst **5.23** to catalytically dehydrocouple amine-borane adducts (Chart 5.10).^[11e]

Catalytic Hydroboration of Carbonyl Derivatives

Catalytic Cyanosilylation of Aldehydes

Catalysts

Chart 5. 9 Single site heavier Group 14 catalysts.^[25f-h]

Scheme 5. 14 Mechanism for intramolecular tetrahylenes **5.24**-catalyzed hydroboration of carbonyl derivatives.^[11d]

Lastly for Group 15, Cantat described the first metal-free proazaphosphatranes **5.25** as versatile catalyst in organic synthesis (Chart 5.11). Catalyst **5.25** efficiently mediate regio- and chemi-selective *N*-methylation of secondary amines with CO₂ using 9-BBN to afford *N*-methylamine, diborate ether and hydrogen gas (yield: 55 – 99%, TOF = 55 – 99 h⁻¹, Chart 5.11).^[26] No conversion was observed when the borane source HBpin, HBcat and BH₃·SMe₂ was used. The reaction yield was found to be dependent upon the temperature and solvent polarity parameters. For example, the reaction can perform well above 60 °C (optimal temperature: 90 °C) but led to formation of methoxyborane at 20 °C. However, catalyst **5.25** failed to mediate mono-methylation of primary amines, instead double methylated product, diborate ether and hydrogen gas were observed (yield: 33 – 85%, TOF = 33 – 85 h⁻¹, Chart 5.11). The catalytic system is tolerant towards ester and alkene functionalities, however the ketone functionalities led to a combination of reduction products, including deoxygenated products (Chart 5.11). The catalytic system **5.25** was further tested in stepwise catalytic hydroboration of nitroarenes and subsequent stoichiometric *N*-methylation of aminoborane with CO₂ to deliver dimethylamine derivatives (yield: 56 – 99%, TOF = 56 – 99 h⁻¹, Chart 5.11).

Chart 5. 11 Proazaphosphatranes catalyst **5.25** in hydroboration and functionalization of CO₂.^[26]

In order to gain mechanistic insight in which the reaction might proceed via formation of methoxyborane prior to the dehydrocoupling reaction with amine, complex **5.25** was subjected to hydroboration of CO₂ with 9-BBN to selectively delivered the expected methoxyborane MeOBBN with excellent TOF (temperature: 90 °C, TOF = 6,043 h⁻¹; temperature: 70 °C, TOF = 287 h⁻¹; room temperature, TOF = 31 h⁻¹, Scheme 5.15). However, no reaction occurred between methoxyborane and *N*-methylaniline, in the presence or absence of catalyst and 9-BBN. Notably, catalytic *N*-methylation took place between CO₂ and aminoborane (yield: 99%, TOF = 99 h⁻¹), latter was formed from stoichiometric reaction between *N*-methylaniline and 9-BBN (Chart 5.11). Therefore, Lewis base mechanism was proposed as summarized in Scheme 5.15.

Scheme 5. 15 Mechanism for proazaphosphatranes **5.25**-catalyzed *N*-methylation of CO₂.^[26]

In addition, organopnictogens are capable to accomplish catalysis resulted in a change in oxidation, which is a rare sight among the main group catalysts.^[1f] They are driven by the reducing ability at the P^{III} center and the stability of the resultant P^V complexes. Therefore, facile oxidation of the P^{III} species to afford the thermodynamically stable P^V products can be achieved even with mild oxidising agent, common phenomena among the heavier main group complexes. Similarly, the subsequent reduction reaction to revert the oxidation from P^V to P^{III} species is extremely disfavored, which is the current challenge in main group chemistry. Such barrier can be circumvented by the incorporation of the crucial T-shape geometry around the phosphorus center and the hydridic nature of the P–H bond to mediate P^{III}/P^V redox cycling for transfer hydrogenation of azobenzenes, a mechanism exclusive to the transition metal complexes (Scheme 5.16).^[1f,27] Other diazaphospholene and diazaarsolene derivatives **5.27** – **5.33** were synthesized over the years, proven to be potent pre-catalysts to the corresponding DAP hydride and DAAs active catalysts in mediating a plethora of symmetrical and asymmetrical organic transformation by the initial σ -bond metathesis reaction (Chart 5.12).^[19]

Catalytic Transfer Hydrogenation of Diphenylhydrazine

Scheme 5. 16 Phosphine **5.26** catalyst in transfer hydrogenation of diphenylhydrazine.^[1f]

Chart 5. 12 Selected examples of DAP and DAAs pre-catalysts.^[19b,22]

The final strategy involves a constrained cyclic substituent, enabled the catalyst to function in the $P^{III}/P^V=O$ cycling. Various small-ring phosphacycles or more commonly known as phosphetanes were proved to be potent catalysts in Wittig reactions, Staudinger reactions, Aza-Wittig reactions, Appel reactions, Mitsunobu reactions, as well as reductive O-atom transfer reactions as summarized in Chart 5.13 – 5.14.^[28] In addition, the heavier analogue arsolanes also efficiently catalyze related organic syntheses via $As^{III}/As^V=O$ cycling.^[1f]

Catalytic Wittig Reaction

Chart 5. 13 Phosphetanes **5.34**-catalyze Wittig reaction.^[29]

Catalytic Staudinger Reaction

Catalytic Aza-Wittig Reaction

Catalytic Appel Reaction

Catalytic Mitsunobu Reaction

Catalytic Reductive Oxygen Atom Transfer

Catalysts

5.35
Delf and Rutjes 2012
Herdewijn 2014
Rutjes 2013

5.36
O'Brien 2014

5.37
Radosevich 2015

Chart 5. 14 Selected examples of phosphetanes in catalysis.^[28]

5.2 Research Implication: Now and Then

In the previous section, we described the common strategies employed by main group catalysts in organic transformations, some are [MG]–H σ -bond metathesis, cationic mechanism, as well as Lewis ambiphilic mechanism. The latter can be simply interpreted as lone pair of electrons and vacant orbital/cation at the metal center. We postulate that a strategic design of a catalyst incorporating all of these catalysis-enabling properties would lead to strongly potent and efficient organic syntheses. As such, our group unveiled the first parent-silicon(II) cation **2.20** (Chapter 2) – the most successful result of this thesis, featuring the best combination of Lewis ambiphilic silicon(II) cation with a Si–H functionality, which its catalytic efficacy is highly anticipated.

As expected, complex **2.20** is a versatile catalyst to unlock various catalytic organic transformations. It catalyzes hydroboration of CO₂, carbonyl and pyridine derivatives, which the lone pair of electrons at the silicon(II) center activates the substrates and then mediated the catalytic hydroboration (Chart 5.15, Chapter 3).^[30] In the hydroboration of CO₂, complex **2.20** is slightly converted to another active NHC–borylsilyliumylidene catalyst [(Ime)₂SiBpin]I and undergoes similar activation mechanism. It is noteworthy that catalyst **2.20** is the sole example of non-metal catalyst in selective hydroboration of CO₂ to C₁ formoxyborane pinBOC(=O)H derivative.

In addition, catalytic *N*-functionalization of CO₂ with amines was observed, leading to selective formation of *N*-formamides (Chart 5.15, Chapter 3).^[31] New mechanistic insights were proposed, complex **2.20** sequentially activates CO₂, PhSiH₃, and amines, which proceeds via a dihydrogen elimination mechanism, to form formamides, siloxanes, and dihydrogen gas. Formation of siloxanes indicate that silicon(II) cation **2.20** could mediate catalytic siloxane coupling reaction as future work. It's catalytic activity, selectivity and yields are among the best as compared to the metal- and non-metal-based catalysts used in the related reactions, has paved a path whereby the low-valent silicon complexes could be a viable, sustainable, and competitive alternative for transition metal catalysts in the foreseeable future, rather than just an unattainable dream.

Chart 5. 15 Versatility of silicon(II) cation **2.20** (this work).^[30]

The next unlocking of catalytic potential of low-valent heavier main group complexes is supported by the NHC-stabilized iodosilicon(I) dimer **1.13-I** in hydroboration of CO₂, with its efficiency increased with an increment in BH₃ additive (Chapter 4). Stoichiometric reaction of complex **1.13-I** with borane BH₃.THF features the first unsymmetric silicon(I) complex containing a silicon(I) hydride moiety, NHC/BH₃-stabilized hydridosilicon(I)-iodosilicon(I) complex **4.13**. The asymmetrical silicon(I) dimer **4.13** exhibited similar activity as **1.13-I** in the presence of BH₃ additive (20 and 45 mol%). Referencing from the dinuclear palladium(I) dimers, a new mechanism was proposed, complex **4.13** is a pre-catalyst to mediate CO₂ hydroboration via Si⁰/Si^{II} species (Chart 5.16). An extension of work covered chemo- and regioselective catalytic *N*-formylation of primary and secondary amines to afford the respective high yields of *N*-formamides, along with its catalytic hydroboration of aldehyde and ketone derivatives to yield borate esters (Chart 5.16).

Chart 5. 16 Versatility of asymmetrical silicon(I) dimer **4.13** (this work).

The discovery of this low-valent silicon catalysts **2.20** and **4.13** have set another example in the renaissance of low-valent main group chemistry, particularly in Group 14 element complexes, a race for cheaper, greener, and sustainable metal-free catalysis. Concurrently, various research groups such as Inoue and Aldridge explored the catalytic application of metal- and non-metal complexes as well as mechanistic insights.^[1c,13,32] Additionally, our research results were also featured as one of the very rare examples of non-metal catalysts in review articles, such as “Heavier Tetrylenes as Single Site Catalysts” and “Recent Advances in Metal Catalyst Design for CO₂ Hydroboration to C₁ Derivatives”.^[33]

Khan explored the feasibility of an amidinato-hydrosilylene to mimic our silicon(II) cation **2.20** towards three-component coupling reactions for hydroboration of aldehydes to afford the structurally characterized silicon(IV) derivative of catalyst-carbonyl-borane complex,^[32a] in agreement with our mechanistic studies.^[30-31] Unfortunately, the silicon(IV) species failed to reductively eliminate to afford the borate ethers.^[32a] Moreover, DFT investigation conducted by Datta and Mandai on the *N*-formylation of primary amides using NHC–phosphinidene catalyst noted similar siloxane by-product formation when using phenylsilane as the hydride source, arising from the formation of the phosphinidene-silane intermediate to activate CO₂ to generate silylformate.^[32b]

The concept of using main group element(II) cation to mediate catalysis was also adopted by Inoue using a germanium(II) cation **5.38** for hydroboration and of aldehydes and cyanosilylation of carbonyl derivatives to afford borate ethers and cyanohydrin silylethers, respectively (Chart 5.17).^[32e] Its catalytic capability was found to be better than the neutral germanium(II) complex **5.29-Ge** developed by Khan^[25g], due to the cationic germanium center. Furthermore, the catalytic capability of the germanium(II) cation **5.38** is extended to *N*-functionalization of CO₂ with secondary amines and arylsilanes to form a mixture of *N*-formamides, *N*-aminals and *N*-methyamines (TOF = 1.25 – 19.8 h⁻¹, Chart 5.17).^[32e]

Chart 5. 17 Catalytic reactions mediated by NHC–germanium(II) cation **5.38**.^[32e]

The proposed mechanism for the catalytic reduction of mediated by germanium(II) cation **5.38**^[32e] (Scheme 5.17) proceed via substitution of one of the I_{Me} ligands (I_{Me} = :C{N(Me)C(Me)}₂) with the aldehyde substrate RC(=O)H, via the interaction between the lone pair of electrons at the O center of the aldehyde to the Ge–C_{I_{Me}} σ*-orbitals of germanium(II) cation **5.38**. The free I_{Me} then activates the B–H bond of the HBpin to form a borate complex, subsequently the B–H bond of the borate is added across the C=O of the aldehyde. Lastly, I_{Me} transfer to the Ge center of the germanium(II) cation **5.38** lead to the regeneration of catalyst along with elimination of borate ether product.

Scheme 5. 17 Mechanism for germanium(II) cation **5.38**-catalyzed hydroboration of aldehydes.^[32e]

Similitude to the mechanism for the hydroboration of aldehydes, germanium(II) cation **5.38**-catalyzed cyanosilylation of carbonyl derivatives^[32e] (Scheme 5.17) proceeded via the substitution reaction between the I_{Me} ligand with the $\text{N}\equiv\text{CSiMe}_3$ to form $[\text{Ge}(\text{II})\text{--N}\equiv\text{CSiMe}_3]$ adduct. Then, the Lewis acidic germanium center of germanium(II) cation **5.38** facilitates the cyanide transfer to the carbonyl moiety.

DFT studies elucidated the complex **5.38**-catalyzed *N*-functionalization of CO_2 with secondary amine proceeded via Lewis basic mechanism. First, the concerted interactions between the lone pair of electrons at the germanium center activates the Si--H of the phenylsilane to facilitate the hydride transfer to CO_2 as the key intermediate to generate silylformate. Lastly, the silylformate undergoes further functionalization with secondary amine to deliver *N*-formamides, *N*-aminals and *N*-methyamines (Scheme 5.18).

Scheme 5. 18 Mechanism for germanium(II) cation **5.38**-catalyzed in C–N bond formation using CO_2 .^[32e]

Similarly, industry player Wacker Chemie AG reported the high catalytic performance of silicon(II) cation **5.39** as effective catalysts for the hydrosilylation of unsaturated C–C bonds (olefins and alkynes) for organosilicon compounds and Piers–Rubinsztajn reaction for controlled silicone synthesis, both high yields under mild conditions (catalyst loading: 0.012 – 0.20 mol%, temperature: 25 – 80 °C, Scheme 5.19).^[32c] Notably, the activity of silicon(II) cation **5.39** is comparable to the platinum catalyst (catalytic loading: 0.0013 mol%, TON = 80,000), the reaction proceeded via a cationic mechanism. To illustrate, the cationic silicon center activates the Si–H bond of silane and subsequently interacts with the olefin to furnish the functionalized silane (Scheme 5.19, left). In addition, the catalytic efficacy of the silicon(II) cation **5.39** and its heavier analogue of germanium(II) cation **5.40** are further evidenced in the oxidative coupling of hydrosol(ox)anes using aldehydes for siloxane synthesis and reversible cyclotrimerization of aldehydes (Scheme 5.19).^[32d] The company proposed that the cationic silicon or germanium center activates the C=O of the aldehyde via catalyst $\cdots$ O coordination to facilitates formation of alkoxy silane intermediate and reductive eliminates siloxane and ether, along with regeneration of active catalysts (Scheme 5.19, right).^[32c,32d]

Oxidative Siloxane Coupling

Reversible Cyclotrimerization of Aldehydes

Hydrosilylation of vinylsilanes

Catalysts

Chart 5. 18 Heavier Group 14 element(II) cation **5.39** – **5.40** in organosilicon chemistry.^[32c,32d]

Scheme 5. 19 Mechanism for heavier Group 14 element(II) cation **5.39** – **5.40** in organosilicon chemistry.^[32c,32d]

5.3 Conclusion and Outlook

To conclude, this chapter has reviewed the recent advances in the catalytic organic synthesis mediated by the p-block main group complexes. Although transition metal catalysts remained as the forefront in the chemical industrial processes, few has embarked on the less taken route in main group chemistry. The recent emergence of main group chemistry is driven by its accumulated endeavor over the past three decades from organo-reagents to series of precious metal-like reactivity, to unprecedented breakthroughs in small molecule activations and spectacularly, its recent limelight in metal-free catalysis.

Incorporating various strategies by the main group complexes into a silicon center, we presented the first NHC-silicon(II) cation complex **2.20** as a powerful and efficient catalyst in various organic transformation with new mechanistic insights. Furthermore, an asymmetrical silicon(I) dimer **4.20** was found to mimic palladium(I) dimer in comproportionation to form active $\text{Si}^0/\text{Si}^{\text{II}}$ catalyst to mediate organic synthesis. Our next leap from this thesis is to curate silicon(0) catalysts to mimic transition metal(0) complexes in various cross-coupling reactions. We will also explore on the ligand designs in an array of enantioselective asymmetrical synthesis.

Referencing from the transition metal chemistry and its ligand frameworks, scientists could strategically design, develop, and uncover more novel main group-derived applications in synthetic chemistry, i.e., (i) catalyst design with improved redox efficiency, (ii) stereochemistry control in catalysis, (iii) catalytic systems to perform in non-organic medium and (iv) co-operative homo- and hetero-bimetallic main group catalytic templates to unleash robust classes of reactions. Undeniably, the p-block catalysts will have their sets of limitations, particularly the innate redox inflexibility in Group 14 species, an arduous journey that several research groups attempted to overcome such challenges. However, the potential for sustainable industrial applications will keep this voyage to be evermore exciting and fulfilling.

5.4 References

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