Catalytic competence of silicon, aluminium and phosphorous

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SINGAPORE

**CATALYTIC COMPETENCE OF SILICON, ALUMINIUM
AND PHOSPHOROUS**

[CHIA CHER CHIEK]

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

[2020]

CATALYTIC COMPETENCE OF SILICON, ALUMINIUM AND PHOSPHOROUS

CHIA CHER CHIEK

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2020

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Abstract

This thesis describes the usage of a silicon compound, an aluminium compound and a phosphorous compound in catalysing C-C bond formation and reduction of small molecules.

In **Chapter I**, amidinato silicon(I) compound **1.1** was paired with $\text{B}(\text{C}_6\text{F}_5)_3$ to form a Lewis acid-base pair and their ability to catalyse C-C bond formation with a variety of α,β -unsaturated carbonyl compounds was demonstrated. Mechanistic studies were

carried out and the catalytic mechanism was proposed. In the initiation step, two silicon(I) atoms in compound **1.1** and $\text{B}(\text{C}_6\text{F}_5)_3$ undergo a concerted addition with two molecules of an α,β -unsaturated carbonyl compound to form an zwitterionic active complex. Next, propagation occurs when **1.A** reacts with α,β -unsaturated carbonyl molecules to form C-C bonds yielding polymeric chains. In the termination step, the methyl group of the enolate chain at the end of a poly(MMA) chain reacts with the Si-C bonds at the opposite end of the polymeric chains to form polymers along with regeneration of compound **1.1**.

Next, in **Chapter II**, bis(phosphoranyl)methanido aluminium hydride **2.2** was synthesised. Compound **2.2** demonstrated the ability to perform catalytic hydroboration of CO_2 with pinacolborane (HBPin), catecholborane (HBCat) and borane ($\text{BH}_3\cdot\text{SMe}_2$). On top of that, compound **2.2** can also perform catalytic reduction of various unsaturated bonds such as carbonyl groups, nitriles and acetylenes. Stepwise reaction of **2.2** with CO_2 suggested that the first step of catalysis involves two highly hydridic H atoms to reduce C=O double bonds in CO_2

molecules to form a formate complex **2.4**. Theoretical calculations had been carried out to further understand the overall mechanism. The catalytic cycle initiated by the coordination of borane to **2.4** followed by σ -bond metathesis to regenerate **2.2**.

Lastly, in **Chapter III**, N-heterocyclic carbene phosphinidene adducts $[(\text{NHC})\text{PH}]$ **3.1** also demonstrated the ability to undergo catalytic hydroboration of aldehydes, ketones and CO_2 . Stepwise reaction of **3.1** with CO_2 resulted in a red precipitate. ^{31}P NMR of the red precipitate suggested the intermediate **3.7** and **3.8** is likely to be the reduced product. The catalytic cycle was proposed below, **3.1** reacted with CO_2 to form intermediate **3.6**, subsequently, HBPIn reacts with **3.6** via σ -bond metathesis to regenerate **3.1**.

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Chapter I. A Base-Stabilized Silicon(I) and B(C₆F₅)₃ Catalyst toward Catalytic C-C Bond Formation of Methacrylate Compounds

I.I. Introduction

L = ligands

Chart 1.1. Ambiphilic character of Silylenes.

Power et al. pointed out that heavier main-group elements can exhibit transition-metal-like reactivity. Much studies have been carried out to develop the replacement of precious transition metal using main-group elements.^[1] Among main-group elements, silicon has attracted much attention due to its non-toxicity and high abundance in the Earth crust. Silicon compounds do not have any available d-orbitals, but their low-valent derivatives with the oxidation state of II, I or 0 on the silicon atom possess a lone pair of electrons and vacant orbital (Chart 1.1). These provide them Lewis ambiphilic properties which can react as either nucleophilic or electrophilic or even both at the same time. In other words, low-valent silicon compounds could exhibit transition-metal-like reactivity.

Chart 1.2. Examples of stable silylenes.

On the basis of the interesting structure of these silylenes, several groups developed strategies to isolate stable and persistent silylenes (Chart 1.2). West et al. showed that low-valent silylene could be stabilized by using sterically hindered ligands.^[2] The resulting N-heterocyclic silylene (NHSi), which is the heavier congener of N-heterocyclic carbene (NHC), was stabilised thermodynamically by the electron donating N atoms and kinetically by the bulky *tert*-butyl group and the cyclic backbone. After that, Roesky et al. further developed the chemistry of a 4-membered ring functionalized silylene.^[3] Despite N-donor is essential in providing the σ -acceptor/ π -donor stabilisation, research groups of Kira and Iwamoto independently proved that stable silylenes with lesser or even no N donors are possible.^[4] Kira's dialkylsilylene was stable at 0°C while Iwamoto's cyclic(alkyl)(amino)silylene (cAASi) can be stored and handled at normal temperature. Moreover, Power et al. successfully isolated an acyclic silylene stabilised by two S atoms with sterically hindered substituent.^[5]

Chart 1.3. Reversible oxidative addition and/or reductive elimination of silylenes.

The above mentioned low-valent silicon compounds can show transition-metal-like chemistry,^[6] whereby they underwent reversible oxidative addition and reductive elimination toward small molecules. For example, Power's acyclic two-coordinate disulfidosilylene $[\text{:Si}(\text{SAr}^{\text{Mes}})_2]$ ($\text{Ar}^{\text{Mes}} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$) showed a reversible complexation of ethylene.^[6a] When the Si center underwent addition reaction to ethylene, it was oxidised from the oxidation state of II to IV. This resembles oxidative addition of transition metal. Subsequent reductive elimination regenerated the low-valent silicon centre. Similarly, Kato's silylene phosphine complex (Chart 1.3, second) was also capable of undergoing reversible binding to ethylene at ambient

temperature.^[6b] In addition, they illustrated that the phosphine-stabilized (amido)(hydrido)silylene underwent a reversible oxidative addition with Si^{IV}-H and P^{III}-H single bonds at room temperature (Chart 1.3, third).^[6c, 6d] Furthermore, Inoue et al. demonstrated that their acyclic iminosilylene (Chart 1.3, fourth) can undergo reversible C-C bond activation.^[6e] Unfortunately, catalytic transformation of organic molecules using stable low-valent silicon compounds are seldom reported. It is possible due to the kinetic and thermodynamic stabilization of the supporting ligands in the low-valent silicon compound suppress the Lewis ambiphilic character and catalytic potential of the Si centre.

Chart 1.4. Catalytic reactions of silylenes.

To the best of our knowledge, only two examples of silicon(II) compounds show catalytic capability, whereby the cyclopentadienyl silyliumylidene cation [Cp^{*}Si]⁺ (Cp^{*}

= C₅Me₅) catalysed the controlled degradation of oligo(ethyleneglycol) diethers (Chart 1.4,top),^[7] as well as the NHC-silyliumylidene cation complex [(I_{Me})₂SiH]⁺ (I_{Me} = :C{N(Me)C(Me)}₂) usefully catalysed the metal-free chemo- and regioselective hydroboration of carbon dioxide, carbonyl compounds and pyridine derivatives with HBpin (Chart 1.4,bottom).^[8] In this context, it is indispensable to develop a strategy to unlock the catalytic ability of low-valent silicon compounds, which would greatly advance sustainable catalysis.

Chart 1.5. Metal free catalytic hydrogenation of polarized bonds.

Since the pioneering work of Stephan's frustrated Lewis pair (FLP),^[9] it has been a promising strategy to catalyse organic transformation without the use of transition metal.^[10] For example, phosphonium borohydride [R₂PH(C₆F₄)BH(C₆F₅)₂] is capable to catalyse several examples of metal-free catalytic hydrogenation of polarized multiple bonds or single bonds (chart 1.5).^[10b, 11]

FLP =

Chart 1.6. Polymerizations initiated by FLP type catalysts.

On top of that, FLPs were used in activating polymerization of various monomers.^[12] Chen et al. used strong Lewis acidic tris(pentafluorophenyl)alane $Al(C_6F_5)_3$ together with phosphines or NHCs to form FLPs to activate polymerization of methacrylates.^[12a] Moreover, they found that silanes R_3SiH can interplay with different Lewis acidic counterparts such as alane,^[12b] borane^[12c] or silylium cation^[12d] to form FLP-type catalysts that could activate polymerization of methacrylates (Chart 1.6).

Chart 1.7. Living polymerization initiated by FLP type catalysts.

All these polymerization reactions were found to be living polymerization.^[12g, 13] For example, Chen et al. reported that the N-heterocyclic olefin and methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide) form a FLP that can initiate living polymerization of MMA (Chart 1.7).^[12g] The FLP initiated the polymerization and remained attached on the polymer throughout the polymerization to form high molecular weight polymer. The FLP were not regenerated after the entire polymerization and hence this is not a catalytic transformation.

Chart 1.8. FLP-catalysed polymerization.

Thus far, only one example of catalytic polymerization mediated by FLP system was reported. In a recent paper, Chen et al. used methylaluminum bis(2,6-di-tert-butyl-4-

methylphenoxide) (MAD) together with NHC to form a FLP to polymerize methyl crotonate.^[14] They found that the obtained polymer does not involve the fragments of the FLP as the end groups. This suggested that the fragments of FLP were dissociated and regenerated after the catalytic cycle. In their proposed mechanism (Chart 1.8), NHC was used to deprotonate the monomer and initiate the polymerization. At the termination step of the polymerization, NHC was regenerated by losing a proton along with formation of the targeted polymer. The regeneration of the catalyst is the crucial step for this “true” catalytic polymerization.

FLP Catalytic system

Lewis base :

Lewis acid :

α,β -Unsaturated carbonyl substrates

Chart 1.9. Choice of FLP and Michael-type substrates.

Recent theoretical studies show that the amidinato silicon(I) compound $[PhC(NtBu)_2Si:]_2$ (**1.1**) possesses strong σ -donating and π -accepting properties similar to *N*-heterocyclic carbenes (NHCs).^[15] In this context, it could act like NHCs in

catalysing chemical bond synthesis such as C-C bond formation in benzoin condensation,^[16] the Stetter reaction,^[17] and polymerization.^[18] Herein, we report that the amidinato silicon(I) compound $[\text{PhC}(\text{NtBu})_2\text{Si}]_2$ ^[15] cooperates with $\text{B}(\text{C}_6\text{F}_5)_3$ to catalyse polymerization toward α,β -unsaturated carbonyl compounds [methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), phenyl methacrylate (PhMA), benzyl methacrylate (BnMA), allyl methacrylate (AMA), 2-hydroxyethyl methacrylate (HEMA), isopropenyl methyl ketone (MIK) and α -methylene- γ -valerolactone (MMBL), Chart 1.9]. In addition, mechanistic studies regarding the cooperation of the silicon(I) atoms and $\text{B}(\text{C}_6\text{F}_5)_3$ in the catalysis are described.

Section I.2. Results and discussion

Table 1.1. Results of MMA polymerization catalysed by **1.1**/ $\text{B}(\text{C}_6\text{F}_5)_3$.^[a]

Run	[MMA]:[1.1]:[$\text{B}(\text{C}_6\text{F}_5)_3$]	Reaction Time (hr)	Conv. (%)	M_n ($\times 10^3$ g/mol)	$\bar{D}$ (M_w/M_n)
1	200:1:0	24	3	1.1	1.11
2	200:0:2	24	0	-	-
3	200:1:0.2	24	20	28.3	2.11
4	200:1:2	1	100	3.1	1.55
5 ^[b]	200:1:2	1	100	3.2	1.55
	50:1:2	1.5	100	0.85	1.21

[a] All polymerizations were performed at room temperature in toluene (6 ml). MMA conversion (%) is measured by ^1H NMR spectroscopy. M_n and $\bar{D}$ were determined by gel permeation chromatography (GPC) relative to poly(MMA) standards. [b] The reaction was conducted in a [MMA]:[**1**]:[$\text{B}(\text{C}_6\text{F}_5)_3$] ratio of 200:1:2 first. After consuming all MMA, second portion of 50 equivalents of MMA was added to the reaction mixture.

Compound **1.1** was used to mediate the C-C bond formation of MMA (Table 1.1). 0.5 mol% of **1.1** was added into a toluene solution of MMA with stirring at room temperature. The conversion of MMA into PMMA was determined by drawing 0.01 ml of solution from the reaction mixture into 0.50 ml of d-chloroform, which was then analyzed by ^1H NMR spectroscopy. After 24 hrs of stirring, only a conversion of 3 % was observed. This indicated that compound **1.1** could mediate the C-C bond formation, but the reaction rate was extremely slow. It is anticipated that enhancing the reactivity of MMA by coordinating with a Lewis acid could facilitate the **1**-mediated MMA polymerization

In this context, 0.1 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ was added into the solution of MMA and 0.5 mol% of **1.1**, a conversion of 20% was achieved in 24hrs under room temperature stirring. The obtained product was quenched with hexane and the resulting white precipitate was characterised as high molecular weight PMMA ($M_n = 28.3 \times 10^3 \text{ g mol}^{-1}$, $n = 283$, Đ : 2.11). The presence of $\text{B}(\text{C}_6\text{F}_5)_3$ as the Lewis acid had greatly accelerated the reaction rate. A control reaction (Run 2, Table 1.1) was also carried out to show that $\text{B}(\text{C}_6\text{F}_5)_3$ alone could not mediate the C-C bond forming reaction. The toluene solution of MMA and 1 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ did not show any reaction. This confirmed that both compound **1.1** and $\text{B}(\text{C}_6\text{F}_5)_3$ took part in the catalytic formation of PMMA.

Next, the ratio of compound **1.1** : $\text{B}(\text{C}_6\text{F}_5)_3$ was increased into 1:2. This ensured each Si center in compound **1.1** was paired with one $\text{B}(\text{C}_6\text{F}_5)_3$ moiety. 0.5 mol% of **1.1** and 1 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ reacted with MMA in toluene (6 ml) very swiftly. Within 1hr of stirring, a conversion of 100% was achieved. A low molecular weight PMMA (**P1**, M_n : $3.1 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 31$; polydispersity index, Đ : 1.55) was obtained after working up (Scheme 1.1). MALDI-TOF mass spectrum was used to determine

the structure of the obtained PMMA. The MALDI-TOF mass spectrum of **P1** shows a set of fragments at an interval of m/z 100 (1 MMA unit) (Figure 1.1), which illustrates that **P1** does not comprise fragments of **1.1** and $B(C_6F_5)_3$ in the skeleton. Moreover, the 1H NMR spectrum of **P1** shows signals at δ 6.15, 5.23 and 3.41 ppm in a ratio of 1:1:35 corresponding to the alkenyl protons $C=C(H_a)(H_b)$ and methoxide protons OMe , respectively. ^[19] On the basis of these experimental data, the end groups of **P1** are H and $CH_2C(=CH_2)CO_2Me$ (Scheme 1.1).^[19] In comparison with other MMA polymerization, the initiator AIBN and catalytic chain transfer agent $[(iPr)(H_2O)Co(dmgbF_2)_2]$ ($dmgbF_2$ = difluoroboryldimethylglyoxime) can lead to poly(MMA) with the same end groups of H and $CH_2C(=CH_2)CO_2Me$.^[19] The molecular structure of **P1** evidenced that the low-valent silicon centres and $B(C_6F_5)_3$ were regenerated after the catalysis. The silicon centres and $B(C_6F_5)_3$ do not simply activate and initiate the polymerization. This is a rare example where a Lewis pair of **1.1** and $B(C_6F_5)_3$ truly catalyse the production of polymer. Prior to this study, only one example of FLP-catalysed polymerisation was reported by McGraw and Chen et al. where they used NHC/MAD FLP to polymerise methyl crotonate (Chart 1.8) and the catalytic mechanism was initiated by abstracting a proton source from the methyl group by the NHC.^[14] In contrast, their catalyst system failed to catalyse MMA as there is no acidic proton in MMA for the NHC to initiate catalysis. This hints that our **1.1**/ $B(C_6F_5)_3$ system has a totally different mechanism.

To evidence that the low-valent silicon centres and $\text{B}(\text{C}_6\text{F}_5)_3$ were regenerated after the catalysis, in Run 4 (Table 1.1), a mixture of MMA, 0.5 mol % of **1.1** and 1 mol % of $\text{B}(\text{C}_6\text{F}_5)_3$ (i.e. $[\text{MMA}]:[\textbf{1.1}]:[\text{B}(\text{C}_6\text{F}_5)_3]: 200:1:2$) were added to toluene. After 60 mins, another 50 equivalents of MMA were further added in the reaction mixture and the resulting mixture was stirred for another 90 mins (Table 1.1). Gel permeation chromatography (GPC) analysis showed two poly(MMA)s of $M_n = 3.2 \times 10^3 \text{ g mol}^{-1}$, $n = 32$ and $M_n = 0.85 \times 10^3 \text{ g mol}^{-1}$, $n = 9$ (Figure 1.2b). The former polymer was formed by the $[\text{MMA}]:[\textbf{1.1}]$ ratio of 200:1, being consistent with **P1** (Run 4, Table 1.1, $M_n = 3.1$

$\times 10^3 \text{ g mol}^{-1}$, Figure 2a), while the latter polymer was formed by the [MMA]:[**1.1**] ratio of 50:1. This study shows that low-valent silicon centre and $\text{B}(\text{C}_6\text{F}_5)_3$ are regenerated after the first catalytic process. It also shows that the first poly(MMA) ($M_n = 3.2 \times 10^3 \text{ g mol}^{-1}$), which was formed by the first portion of MMA, did not further undergo propagation in the reaction mixture after second addition of MMA. Instead, a new second poly(MMA) ($M_n = 0.85 \times 10^3 \text{ g mol}^{-1}$) was formed. The catalyst can be regenerated more than four times until the solution became too viscous and required too much time for the reaction to be completed (Table 1.2).

Figure 1.2. GPC profiles of **P1** from (a) Run 4, Table 1.1 and (b) poly(MMA)s from Run 5, Table 1.1.

Table 1.2. Studies on the recoverability of **1.1**/ $\text{B}(\text{C}_6\text{F}_5)_3$

Run	Total MMA (mmol)	Conv. (%)	Reaction Time (hr)	$n^{[a]}$
1	0.08	100	1	10
2	0.16	100	1.5	10
3	0.24	100	3	10
4	0.36	100	10	10

[a] n: Calculated number of repeating unit, based on ^1H NMR studies

As a comparison, mononuclear silylene namely amidinato amidosilylene $[\text{LSiN}(\text{SiMe}_3)_2]$ (**1.3**)^[1d] was used to perform the polymerisation reaction (Scheme 1.2). 1 mol% of **1.3** and 1 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ were used to mediate MMA polymerization in toluene at room temperature for 1h, whereby medium molecular weight poly(MMA) **P2** [$M_n = 1.04 \times 10^4 \text{ gmol}^{-1}$; $\bar{D}$: 1.97] was afforded. The ^1H NMR spectrum of **P2** does not have any signals for H and $\text{CH}_2\text{C}(\text{=CH}_2)\text{CO}_2\text{Me}$ of **P1**. This suggested **P2** was polymerised using a different mechanism.

Scheme 1.2. Synthesis of **P2** by the **1.3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ FLP.

To further support this assumption, 1 mol% of **1.3** and 1 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ were reacted with MMA in toluene (i.e. $[\text{MMA}]:[\mathbf{1.3}]:[\text{B}(\text{C}_6\text{F}_5)_3]$: 100:1:1, Figure 1.3a). After 60 mins, another 25 equivalents of MMA were further added to the reaction mixture and the resulting mixture was stirred for another 1.5 hr. GPC analysis showed that only one poly(MMA) was afforded [Figure 1.3b, $M_n = 1.29 \times 10^4 \text{ gmol}^{-1}$; $\bar{D}$: 2.02]. No chain transfer was occurred. In addition, the increment of M_n is in accordance with the amount of MMA added ($[\text{MMA}]:[\mathbf{1.3}]:[\text{B}(\text{C}_6\text{F}_5)_3]$ = 100:1:1, $M_n = 1.04 \times 10^4 \text{ gmol}^{-1}$; (100+25):1:1, $M_n = 1.29 \times 10^4 \text{ gmol}^{-1}$). The results show that the **1.3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ -mediated MMA polymerization is living polymerization. It seems that alternating steric and electronic property of low-oxidation state silicon compounds could lead to different

results in MMA polymerization because compound **1.1** and **1.3** possess different nucleophilic and electrophilic characters based on theoretical studies.^[1d]

Figure 1.3. GPC profiles of **P2** from (a) [MMA]:[**1.3**]:[B(C₆F₅)₃] = 100:1:1 and (b) [MMA]:[**1.3**]:[B(C₆F₅)₃] = (100+25):1:1.

To understand how **1.1** and B(C₆F₅)₃ catalysed the polymerisation, a series of experiments were carried out. In the first experiment, **1.1** was reacted with two equivalents of B(C₆F₅)₃ in C₆D₆ (Scheme 1.3). The reaction mixture was monitored by ¹H and ¹¹B NMR spectroscopy. The ¹H NMR spectrum indicates that compound **1.1** was fully consumed, while the upfield ¹¹B NMR signal (δ -22.4 ppm) is attributable to a four-coordinate boron compound, which indicates that compound **1.1** could coordinate with B(C₆F₅)₃. Subsequently, MMA was added to the reaction mixture. However, no MMA polymerization was observed. This result illustrates that **1.1** does not react with B(C₆F₅)₃ in the first step of catalysis.

Scheme 1.3. Synthesis of intermediate **1.1**-B(C₆F₅)₃ and attempt to polymerize MMA.

In the second experiment, **1.1** was reacted with two equivalents of MMA in toluene to form the [1+4] cycloaddition product [PhC(N*t*Bu)₂Si{OC(OMe)C(Me)CH₂}]₂ (**1.2**, Scheme 1.4, Figure 1.4 for X-ray crystal structure). Formation of **1.2** suggested both silicon centres were involved in the activation of MMA. Stirring of **1.2** with 20 equivalents of MMA at room temperature for 2hr does not show any conversion of MMA into PMMA. This suggest that **1.2** is unlikely to be the intermediate for the polymerization. Next, **1.2** was reacted with two equivalents of B(C₆F₅)₃ to *in situ* generate a colorless oil (Scheme 1.4). The ¹H NMR and ¹¹B NMR spectra indicate that compound **1.1** and B(C₆F₅)₃ are fully consumed to form a four-coordinate boron compound (¹¹B NMR: δ -20.1 ppm). The experimental data suggest that a zwitterionic intermediate [LSi{CH₂C(Me)=C(OMe)O}B(C₆F₅)₃]₂ (**1.A**, L = PhC(N*t*Bu)₂, Scheme 1.7) was formed in the reaction. After which, 20 equivalents of MMA were added to the solution and stirred for 1hr to yield 100% conversion into PMMA. This result shows that the second step of catalysis involve the formation of a zwitterionic species. This zwitterionic species then undergoes ionic chain propagation to form the polymeric chain.

Figure 1.4. Molecular structure of **1.2** (50% ellipsoids probability). There are two independent molecules in the asymmetric unit. Herein only one molecule is presented. Selected bond lengths (Å) and angles (°): Si1-Si2 2.3812(13), O1-Si1 1.776(3), C18-O1 1.357(4), C18-O2 1.375(4), C20-O2 1.430(4), C17-C18 1.325(5), C17-C19 1.500(5), C16-C17 1.507(5), C16-Si1 1.911(4); N2-Si1-N1 67.70(12), O1-Si1-C16 90.09(14), C17-C16-Si1 105.1(2), C18-C17-C16 112.6(3), C17-C18-O1 120.9(3), C18-O1-Si1 111.0(2).

Scheme 1.4. Zwitterionic active species **1.A**

To understand the chain propagation mechanism, a model reaction of **1.1**, two molecules of MMA and one molecule of $\text{B}(\text{C}_6\text{F}_5)_3$ was investigated by DFT calculations (M06-2X/def2-SVP, Scheme 1.5). MMA reacts with a $\text{B}(\text{C}_6\text{F}_5)_3$ molecule to form a Lewis acid-base adduct, which is endergonic ($\Delta G_{\text{MMA}+\text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{MMA-B}(\text{C}_6\text{F}_5)_3} = 7.3$ kcal/mol). The Si(I) centre in compound **1.1** attacks the C=C double bond of the adduct to form a zwitterionic intermediate **Int1.1** ($\Delta G_{1.1 \rightarrow \text{Int1.1}} = -15.6$ kcal/mol) via a kinetic barrier of 17.2 kcal/mol. **Int1.1** then undergoes nucleophilic attack with another molecule of MMA, which proceeds via **TS1.2** (activation energy: 17.9 kcal/mol), to produce zwitterionic **Int1.2** ($\Delta G_{\text{Int1.1} \rightarrow \text{Int1.2}} = -22.2$ kcal/mol). The overall exergonic gain in energy ($\Delta G = 22.2$ kcal/mol) suggests that the MMA chain propagation via zwitterionic active species $[\text{LSi}\{\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{OMe})\text{O}\}\text{B}(\text{C}_6\text{F}_5)_3]_2$ (**1.A**, Scheme 1.7) is feasible. The postulation of zwitterionic active species can also be found in other Lewis Pair-mediated polymerization of α,β -unsaturated carbonyl compounds.^[12a, 12e-g, 13, 19-20]

Scheme 1.5. DFT calculations of MMA chain propagation (M06-2X/def2-SVP)

Based on the end groups, H and $\text{CH}_2\text{C}(\text{=CH}_2)\text{CO}_2\text{Me}$, in **P1**, a mechanism for termination is proposed (Scheme 1.6), where methyl group of the enolate at the end of a poly(MMA) chain on the Si-Si skeleton reacts with the Si-C bond of the adjacent poly(MMA) chain to form the polymer **P-B(C₆F₅)₃**. The chain termination mechanism is different from that of NHC/ $\text{Al}(\text{C}_6\text{F}_5)_3$ Lewis pair, whereby intramolecular backbiting cyclization involving nucleophilic attack of the growing polymer chain by enolate active chain end was observed.^[20c]

Scheme 1.6. Proposed mechanism for the termination step.

Table 1.3. Studies on the $\text{B}(\text{C}_6\text{F}_5)_3$ -mediated hydride abstraction^[a]

Run	[MMA]:[1.1]:[$\text{B}(\text{C}_6\text{F}_5)_3$]	Conv. (%)	Time (min)	$M_n (\times 10^3 \text{ g mol}^{-1})$	GPC Yield (%)	$\bar{D}$
1	200:1:10	100	60	5.8	58.5	1.48
				1.0	41.5	1.05
2	200:1:30	100	60	4.9	40.1	1.38
				0.7	59.9	1.05
3	200:1:70	100	60	3.8	30.8	1.79
				0.6	69.2	1.07
4	200:5:70	100	60	2.6	28.1	1.46
				0.5	67.8	1.07
				0.2	4.1	1.05

[a] All polymerizations were performed at room temperature in toluene (6 ml).

In support of this mechanism, excess $\text{B}(\text{C}_6\text{F}_5)_3$ was employed in catalysis in the fourth experiment. In Table 1.3, Run 1, when 0.5 mol% of **1.1** and 5 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ were used to catalyse MMA in toluene, a short oligo(MMA) was observed in the reaction mixture ($M_n = 1.0 \times 10^3 \text{ g mol}^{-1}$, $n = 10$, $\bar{D} = 1.05$, GPC yield, 41.5%). When the catalytic amount of $\text{B}(\text{C}_6\text{F}_5)_3$ increased (Run 2: 15 mol%; Run 3: 35 mol%, Table 1.3), significant shorter oligo(MMA)s, but with a higher yield, were observed in the reaction mixture (Run 2: $M_n = 0.7 \times 10^3 \text{ g mol}^{-1}$, $n = 7$, $\bar{D} = 1.05$, GPC yield = 59.9%; Run 3: $M_n = 0.6 \times 10^3 \text{ g mol}^{-1}$, $n = 6$, $\bar{D} = 1.07$, GPC yield = 69.2%). On the other hand, when the amount of $\text{B}(\text{C}_6\text{F}_5)_3$ was reduced to 0.1 mol% (Run 3, Table 1.1), significantly higher molecular weight poly(MMA) was afforded ($M_n = 28.3 \times 10^3 \text{ g mol}^{-1}$, $n = 283$, $\bar{D} = 2.11$). The results show that the increment of $\text{B}(\text{C}_6\text{F}_5)_3$ concentration facilitates H^- -abstraction and -transfer, which leads to the formation of a short poly(MMA) chain. Moreover, by increasing the catalytic amount of **1.1** [Run 4, Table 1.3, 2.5 mol% of **1.1**, 35 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$], shorter oligo(MMA), namely pentakis(MMA) (Yield: 67.8 %) was achieved.

On the basis of experimental and theoretical studies, a catalytic cycle is proposed (Scheme 1.7). Initiation takes place by reacting Si(I) atoms in **1** with two molecules of MMA and $\text{B}(\text{C}_6\text{F}_5)_3$ to form a zwitterionic species **1.A**. Subsequent C-C bond formation with MMA molecules results in the formation of two poly(MMA) chains in **1.B**. Then, the methyl group of the enolate chain at the end of a poly(MMA) chain reacts with the Si-C bond of the adjacent poly(MMA) chain on the Si-Si skeleton to form the polymer **P1-B(C₆F₅)₃** and compound **1**. The latter then reacts with MMA molecules and **P-B(C₆F₅)₃** for successive catalytic cycle, as well as the formation of the polymer **P**.

Scheme 1.7. Proposed catalytic mechanism.

Table 1.4. Catalytic C-C bond formation toward α,β -unsaturated carbonyl compounds.

Mn=5.0; n=44; yield= 12.0%; Đ=1.17 Mn=1.1; n=10; yield= 74.4%; Đ=1.09 Mn=0.4; n=4; yield= 9.9%; Đ=1.02 Mn=0.2; n=2; yield= 3.7%; Đ=1.02	Mn=4.3; n=37; yield= 23.4%; Đ=1.34 Mn=0.7; n=6; yield= 67.9%; Đ=1.09 Mn=0.4; n=3; yield= 8.6%; Đ=1.01	Mn=8.3; n=66; yield= 48.8%; Đ=1.24 Mn=0.99; n=8; yield= 51.2%; Đ=1.11
Mn=1.7; n=9; yield= 50.0%; Đ=1.34	Mn=3.1; n=25; yield= 45.0%; Đ=1.62 Mn=0.56; n=4; yield= 55.0%; Đ=1.10	Mn=0.98; n=7; yield= 10.0%; Đ=1.08 Mn=0.43; n=3; yield= 40.0%; Đ=1.03
Mn=1.3; n=15; yield= 100%; Đ=1.05	Mn=9.8; n=87; yield= 100%; Đ=1.21	

To investigate the scope and limitation of this novel **1.1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ catalytic system, a variety of Michael-type substrates was tested. The purity of the resulting polymers were confirmed by NMR spectroscopy and GPC analysis. Firstly, **1.1** and $\text{B}(\text{C}_6\text{F}_5)_3$ were capable of catalysing C-C bond toward a series of steric hindered methacrylates, such as EMA, BMA and PhMA (Table 1.4) with 100% conversion. Similar to **P1**, the poly(EMA), poly(BMA) and poly(PhMA) have low molecular weight ($n \leq 10$) and their end groups are H and $\text{CH}_2\text{C}(\text{=CH}_2)\text{CO}_2\text{R}$ ($\text{R} = \text{Et, Bu and Ph, respectively}$). These illustrate that their catalytic mechanisms are same as that for the formation of **P1**. Moving on to the bulkiest methacrylate BnMA, 50% conversion was achieved using 2.5 mol% of **1.1** and 35 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$. Secondly, the allyl substituent in AMA and hydroxide substituent in HEMA, which readily react with the silicon(I) centres in **1.1**, did not inhibit **1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ catalytic activity at all (Table 1.4). The end groups of the corresponding polymers are H and $\text{CH}_2\text{C}(\text{=CH}_2)\text{CO}_2\text{R}$ ($\text{R} = \text{allyl and 2-hydroxyethyl}$).

In addition, MMBL, which is the cyclic analogue of MMA, was found to be compatible with the catalytic system. The high number of repeating units ($n=87$) suggested the polymerisation might occur in a different mechanism. Further mechanistic studies need to be carried out to understand the difference with MMA polymerisation. Moving on to other Michael-type substrate, isopropenyl methyl ketone can also undergo catalytic C-C bond formation with **1.1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ to form the poly(MIK) with narrow dispersity as well as the end groups of H and $\text{CH}_2\text{C}(\text{=CH}_2)\text{COMe}$ (Table 1.4).

Section I.3. Conclusion

In conclusion, a Lewis pair of the amidinato silicon(I) compound **1.1** and $\text{B}(\text{C}_6\text{F}_5)_3$ is the first non-metal catalytic system being capable of chemoselectively catalyse C-C bond formation toward a variety of α,β -unsaturated carbonyl compounds to form the corresponding polymers. Mechanistic studies show that two silicon(I) atoms in compound **1.1** and $\text{B}(\text{C}_6\text{F}_5)_3$ undergo a concerted addition with two molecules of an α,β -unsaturated carbonyl compound to form a zwitterionic active species. Subsequently, it reacts with α,β -unsaturated carbonyl molecules, which result in the formation of C-C bonds to form two polymeric chains. The number of C-C bonds depends on the catalytic amount of **1.1** and $\text{B}(\text{C}_6\text{F}_5)_3$. In the last step of catalysis, the methyl group of the enolate chain at the end of a poly(MMA) chain reacts with the Si-C bond of the adjacent poly(MMA) chain on the Si-Si skeleton to form the polymer. It seems reasonable that complex **1.1** will find a range of other catalytic applications (e.g. benzoin condensation and the Stetter reaction) with non-metal Lewis acid. We are currently investigating this possibility and will report on our findings in due course.

Section I.4. Experimental

General procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Toluene was dried over and distilled over Na/K alloy prior to use. $B(C_6F_5)_3$, methyl methacrylate (MMA, >99%), ethyl methacrylate (EMA, >95%), butyl methacrylate (BMA, >95%), phenyl methacrylate (PhMA, >97%), benzyl methacrylate (BnMA, >96%), allyl methacrylate (AMA, >99%), 2-hydroxyethyl methacrylate (HEMA), isopropenyl methyl ketone (MIK, >95%), α -methylene- γ -valerolactone (MMBL, >97%) were purchased from TCI and MMA was dried with CaH_2 before use. $[PhC(NtBu)_2Si:]_2$ (**1**) was prepared according to the literature procedures.^[18] D_6 -benzene was dried and distilled over K metal prior to use. $CDCl_3$ was used directly without purification. 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.

(a) MMA polymerization

General procedures. Polymerizations were performed in 10 ml dried vials or 100 ml Schlenk flasks under Ar gas at room temperature (25 °C). A low-valent silicon compound was added to a solution of MMA in 6 ml of toluene in the glovebox. After mixing completely, Lewis acid $B(C_6F_5)_3$ was rapidly added under stirring. The conversion percentage of monomer was obtained by analysing 1H NMR spectroscopy ($CDCl_3$) of the 0.01 ml aliquot, which was taken from the reaction mixture via syringe, after the measured time interval. The poly(MMA) was precipitated by the addition of

the crude product solution into 40 ml of 5% HCl-acidified *n*-hexane. The crude polymers were filtered, washed with hexane and methanol, and dried under vacuum.

Polymerization using compound 1.1 (Run 1, Table 1.1): In a glovebox, compound **1.1** (0.0026 g, 0.005 mmol) was added to 6 ml of toluene and MMA (0.10 g, 1.0 mmol) mixture in a 10 ml dried vial. After mixing completely, the mixture was stirred for 24 hours. Only 3% conversion of MMA was observed by ^1H NMR spectroscopy. GPC of the crude solution was measured. M_n (g mol^{-1}): 1100; $\bar{D}$: 1.11.

$\text{B}(\text{C}_6\text{F}_5)_3$ with MMA (Run 2, Table 1.1): In a J-Young NMR tube, $\text{B}(\text{C}_6\text{F}_5)_3$ (0.0051 g, 0.010 mmol) was added to the C_6D_6 solution (0.50 ml) of MMA (0.10 g, 1.0 mmol) and the reaction mixture was stirred for 24 hours. NMR spectroscopy was used to track the conversion. Only unreacted MMA signals were observed in the reaction.

200:1:0.2 ratio of [MMA]:[1.1]:[$\text{B}(\text{C}_6\text{F}_5)_3$] (Run 3, Table 1.1): A 10 ml reaction vial was charged with **1.1** (0.0052 g, 0.010 mmol) and toluene (3.0 ml). MMA (0.20 g, 2.0 mmol) was then added. The color of the reaction mixture changed from red to colorless. $\text{B}(\text{C}_6\text{F}_5)_3$ (0.0010g, 0.0020 mmol) was subsequently added to the solution, which was stirred with a stirrer. After 24 hours, the reaction was stopped by removing the stirrer. The reaction mixture showed a 20 % conversion of MMA, confirmed by ^1H NMR spectroscopy. The crude solution was analysed by GPC. M_n (g mol^{-1}): 28300; $\bar{D}$: 2.11.

200:1:2 ratio of [MMA]:[1.1]:[$\text{B}(\text{C}_6\text{F}_5)_3$] (Run 4, Table 1.1): In a glovebox, compound **1.1** (0.0026 g, 0.005 mmol) was added to 6 ml of toluene and MMA (0.10 g, 1.0 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, $\text{B}(\text{C}_6\text{F}_5)_3$ (0.0051 g, 0.010 mmol) was rapidly added under stirring. Subsequent procedures follow method A or B:

Method A: The reaction mixture was stirred for 60 min and dried under vacuum to obtain **P1** as white solid. Isolated yield: 0.095 g, 95 %.

Method B: The reaction was stirred for 60 min. **P1(quenched)** was precipitated by the addition of the reaction solution into 40 ml of 5% HCl-acidified *n*-hexane. **P1(quenched)** was filtered. It was then washed with hexane and dried under vacuum. Yield: 0.091 g, 91 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 6.15 (m, =CH₂ of the CH₂C(=CH₂)CO₂Me end-group), 5.23 (m, =CH₂ of the CH₂C(=CH₂)CO₂Me end-group), 3.41-3.33 (m, OMe), 2.21-2.00 (br m, CH₂), 1.34-1.09 (m, Me). M_n (g mol⁻¹): 3100; Đ: 1.55. (Figure 1.2, Solid line)

Synthesis of the poly(MMA) in Run 5 (Table 1.1): On the basis of the procedure of Run 4 (Table 1.1), a mixture of MMA (0.10 g, 1.0 mmol) and **1.1** (0.0026 g, 0.0050 mmol) was reacted with B(C₆F₅)₃ (0.0051 g, 0.010 mmol) in 6 ml of toluene. After 60 mins, MMA (0.025 g, 0.25 mmol) in a [MMA]:[**1.1**] ratio of 50:1 was added in the reaction mixture and the resulting mixture was stirred for another 90 mins until all MMA was converted. The reaction solution was dried under vacuum to afford the poly(MMA) as white solid. The ¹H NMR spectrum of the obtained poly(MMA) shows identical chemical shifts as **P1** (Figure 1.S11). M_n (g mol⁻¹): 3200/850; Đ: 1.55/1.21. (Figure 1.2, Dashed line)

100:1:1 ratio of [MMA]:[1.3**]:[B(C₆F₅)₃]** (Scheme 1.2): In a glovebox, compound **1.3** (0.0042 g, 0.01 mmol) was added to 6 ml of toluene and MMA (0.10 g, 1.0 mmol) mixture in a 10 ml dried vial. Then, B(C₆F₅)₃ (0.0051 g, 0.010 mmol) was rapidly added under stirring. The reaction mixture was stirred for 60 min to afford the poly(MMA) **P2**.

^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 3.71 (s, OMe), 1.96 (br m, CH_2), 1.34-1.09 (m, Me). GPC: $M_n = 1.04 \times 10^4 \text{ g mol}^{-1}$; $\bar{D} = 1.55$. (Figure 1.3, solid line).

To prove that P2 is living polymer (Figure 1.3b): The above procedure was repeated. After that, MMA (0.025 g, 0.25 mmol) in a [MMA]:[**1.3**] ratio of 25:1 was added in the reaction mixture and the resulting mixture was stirred for another 90 mins. GPC: $M_n = 1.29 \times 10^4 \text{ g mol}^{-1}$; $\bar{D} = 2.02$. (Figure 1.3, dash line).

(b) Synthesis of **1.2**, the reaction of **1.2** with $\text{B}(\text{C}_6\text{F}_5)_3$, and the reaction of **1.1** with $\text{B}(\text{C}_6\text{F}_5)_3$

Synthesis of 1.2: MMA (0.20 g, 2.0 mmol) was added rapidly to a toluene solution of **1.1** (0.52 g, 1.0 mmol) at room temperature. The red solution turned to pale-yellow immediately. The reaction mixture was stirred for 1 hour and dried under vacuum to remove all volatiles. The residue was extracted with 5 ml of toluene/*n*-hexane (1:1) mixture. After filtration and concentration of the filtrate, colorless crystals of **1.2** were grown. Yield: 0.40 g (56 % based on **1.1**). Mp: 157 °C (dec.). Elemental analysis calcd for $\text{C}_{40}\text{H}_{62}\text{N}_4\text{O}_4\text{Si}_2$ (719.13): C, 66.81; H, 8.69; N, 7.79. Anal. Found: C, 66.64; H, 8.18; N, 7.33. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.69 (d, 2H, Ph-*H*), 7.9-7.67 (m, 8H, Ph-*H*), 3.74 (s, 6H, OMe), 2.21 (d, 2H, SiCH_2), 2.04 (s, 6H, =CMe), 1.85 (d, 2H, SiCH_2), 1.30 (s, 18H, *t*Bu-*H*), 1.14 ppm (s, 18H, *t*Bu-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, C_6D_6 , ppm): δ 169.0 (NCN), 158.4 (OC(OMe)=), 130.2 - 127.7 (Ph-C), 78.8 (=C(Me) CH_2), 55.6 (OMe), 55.1, 52.9 (CMe_3), 34.3, 32.8 (CMe_3), 31.3 (SiCH_2), 15.3 ppm (=CMe). $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, C_6D_6 , ppm): δ -59.3 ppm.

The reaction of 1.2 with $\text{B}(\text{C}_6\text{F}_5)_3$: $\text{B}(\text{C}_6\text{F}_5)_3$ (0.51 g, 1.0 mmol) was added to a 10 ml toluene solution of **1.2** (0.36 g, 0.50 mmol). The reaction mixture was stirred for 1 hour.

A colorless oil was formed at the bottom of the flask, which was then collected by syringe after removing the solution. Yield: 0.76 g (87 % based on **1.1**). ^1H NMR (395.9 MHz, CDCl_3 , ppm): δ 7.90-7.20 (br, Ph-*H*), 4.10-3.50 (br, OMe), 1.90-0.80 ppm (br, Me). ^{11}B NMR (128 MHz, CDCl_3 , ppm): δ -20.1 ppm.

The reaction of 1 with $\text{B}(\text{C}_6\text{F}_5)_3$: A sealed J-young NMR tube was charged with **1.1** (0.0026 g, 0.0050 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (0.0052 g, 0.010 mmol). Then, C_6D_6 (0.50 ml) was added. The color of the reaction mixture changed from red to colorless rapidly. The reaction mixture was well mixed and checked with NMR spectroscopy without further purification. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.04 – 6.95 (br, 10H, Ph), 1.33 – 0.43 ppm (br, 36H, *t*Bu). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ -22.4 ppm.

(i) Studies on the MMA chain initiation

MMA with *In situ* product in the reaction of 1.1 with $\text{B}(\text{C}_6\text{F}_5)_3$: A sealed J-young NMR tube was charged with **1.1** (0.0026 g, 0.0050 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.0052 g, 0.010 mmol). Then, C_6D_6 (0.50 ml) was added. The color of the reaction mixture changed from red to colorless rapidly. The reaction mixture was well mixed. MMA (0.010 g, 0.10 mmol) was added to the reaction mixture, which was stirred for 24 hours. NMR spectroscopy was used to track the conversion. Only unreacted MMA signals were observed in the reaction.

2 with MMA at room temperature: A 10 ml vial was charged with **1.2** (0.0036 g, 0.0050 mmol). Toluene (6 ml) and then MMA (0.010 g, 0.1 mmol) was added. The reaction mixture was stirred with a stirrer at room temperature. After 2 hours, the reaction was stopped by removing the stirrer and the conversion was recorded by NMR spectroscopy. Only unreacted MMA and **1.2** were observed.

The colorless oil from the reaction of compound 1.2 and $B(C_6F_5)_3$: $B(C_6F_5)_3$ (0.0026 g, 0.0050 mmol) was added to the C_6D_6 solution (0.50 ml) of **1.2** (0.0018 g, 0.0025 mmol) to yield a colorless oil. MMA (0.005 g, 0.05 mmol) was then added to the reaction mixture. The reaction was stirred for 1hr at room temperature. NMR spectroscopy was used to track the conversion. The reaction mixture showed a 100 % conversion of MMA into poly(MMA) by 1H NMR spectroscopy. The 1H NMR spectrum of the obtained poly(MMA) shows identical chemical shifts as **P1** (Figure 1.S11).

(ii) Studies on the regeneration of catalytic system

A sealed J-young NMR tube was charged with **1.1** (0.0010 g, 0.0020 mmol) and C_6D_6 (0.50 ml). MMA (0.0080 g, 0.080 mmol) was then added (Run 1, Table 1.2). The color of the reaction mixture changed from red to colorless. $B(C_6F_5)_3$ (0.0021 g, 0.0040 mmol) was subsequently added to the solution, which was stirred with a stirrer. The reaction was tracked by using NMR spectroscopy. When 100% conversion was observed, the reaction time was recorded and fresh MMA (0.0080 g, 0.080 mmol) was added for further reaction (run 2–4). This was repeated until the 4th time (Run 4) where the reaction mixture was too viscous and took 10 hrs for completion.

(iii) Studies on the $B(C_6F_5)_3$ -mediated hydride-transfer chain termination

Herein, the detailed MMA polymerization with 200:1:10 (Table 1.3, Run 1) and 200:1:30 (Table 1.3, Run 2) ratio of [MMA]:[**1.1**]:[$B(C_6F_5)_3$] were described for examples.

200:1:10 ratio of [MMA]:[1.1]:[$B(C_6F_5)_3$] (Table 1.3, Run 1): A 10 ml reaction vial was charged with **1.1** (0.0026 g, 0.0050 mmol) and toluene (1.5 ml). MMA (0.10 g, 1.0 mmol) was then added. The colour of the reaction mixture changed from red to

colorless. $\text{B}(\text{C}_6\text{F}_5)_3$ (0.026g, 0.050mmol) was subsequently added to the solution, which was stirred with a stirrer. After 1 hour, the reaction was stopped by removing the stirrer. The reaction mixture showed a 100 % conversion of MMA, confirmed by ^1H NMR spectroscopy. The solution was dried and the poly(MMA) was analysed by ^1H NMR spectroscopy (Figure 1.S13) and GPC (Figure 1.S1). M_n (g mol^{-1}): 5800/1000; GPC yield (%): 58.5/41.5; $\bar{D}$: 1.48/1.05.

200:1:30 ratio of [MMA]:[1.1]:[$\text{B}(\text{C}_6\text{F}_5)_3$] (Table 2, Run 2): A 10 ml reaction vial was charged with **1.1** (0.0026 g, 0.0050 mmol) and toluene (1.5 ml). MMA (0.10 g, 1.0 mmol) was then added. The colour of the reaction mixture changed from red to colorless. $\text{B}(\text{C}_6\text{F}_5)_3$ (0.078 g, 0.15 mmol) was subsequently added to the solution, which was stirred with a stirrer. After 1 hour, the reaction was stopped by removing the stirrer, which showed a 100 % conversion of MMA, confirmed by ^1H NMR spectroscopy. The solution was dried and the poly(MMA) was analysed by ^1H NMR spectroscopy (Figure 1.S14) and GPC (Figure 1.S1). M_n (g mol^{-1}): 4900/700; GPC yield (%): 40.1/59.9; $\bar{D}$: 1.38/1.05.

Figure 1.S1. GPC profiles and characteristic data of the poly(MMA)s obtained from 200:1:10 and 200:1:30 ratios of [MMA]:[**1.1**]:[$\text{B}(\text{C}_6\text{F}_5)_3$] reactions.

In addition, the experiments showed that when the 200:5:70 (Table 1.3, Run 5) ratio of [MMA]:[**1.1**]:[B(C₆F₅)₃] was employed, the lowest M_n (500 gmol⁻¹) of polymer with high GPC yield (67.8%) and low Đ (1.07) can be obtained. Accordingly, the study of other monomers polymerization (Table 1.4) were based on this ratio.

(iv) Polymerizations of other monomers.

Synthesis of poly(EMA) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and EMA (0.057 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, B(C₆F₅)₃ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(EMA)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(EMA)** was filtered. It was then washed with methanol, dichloromethane, and dried under vacuum. Yield: 0.053 g, 93 %. ¹H NMR (395.9 MHz, CDCl₃, ppm): δ 6.19 (m, =CH₂ of the CH₂C(=CH₂)CO₂Et end-group), 5.45 (m, =CH₂ of the CH₂C(=CH₂)CO₂Et end-group), 4.11-4.00 (br s, OCH₂Me), 1.92-1.80 (br m, CH₂), 1.25-0.86 (br m, OCH₂Me + Me). M_n (gmol⁻¹): 5000/1100/400/200; GPC yield (%): 12/74.4/9.9/3.7; Đ: 1.17/1.09/1.02/1.01.

Synthesis of poly(BMA) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and BMA (0.071 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, B(C₆F₅)₃ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(BMA)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(BMA)** was filtered. It was then washed with methanol, dichloromethane, and dried under vacuum. Yield:

0.064 g, 90 %. ^1H NMR (395.9 MHz, CDCl_3 , ppm): δ 6.17 (m, $=\text{CH}_2$ of the $\text{CH}_2\text{C}(=\text{CH}_2)\text{CO}_2\text{Bu}$ end-group), 5.44 (m, CH_2 , $=\text{CH}_2$ of the $\text{CH}_2\text{C}(=\text{CH}_2)\text{CO}_2\text{Bu}$ end-group), 3.93 (br m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.00-1.30 (br m, CH_2 + $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.10-0.80 (m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ + Me). M_n (g mol^{-1}): 4300/700/400; GPC yield (%): 23.4/67.9/8.6; Đ : 1.34/1.09/1.01.

Synthesis of poly(PhMA) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and PhMA (0.081 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, $\text{B}(\text{C}_6\text{F}_5)_3$ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(PhMA)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(PhMA)** was filtered. It was then washed with methanol, dichloromethane, and dried under vacuum. Yield: 0.069 g, 85 %. ^1H NMR (395.9 MHz, CDCl_3 , ppm): δ 7.30-6.90 (m, PhH), 6.55 (br, $=\text{CH}_2$ of the $\text{CH}_2\text{C}(=\text{CH}_2)\text{CO}_2\text{Ph}$ end-group), 5.81 (br, $=\text{CH}_2$ of the $\text{CH}_2\text{C}(=\text{CH}_2)\text{CO}_2\text{Ph}$ end-group), 2.39-2.20 (br, CH_2), 1.70-1.30 (br, Me). M_n (g mol^{-1}): 8300/990; GPC yield (%): 48.8/51.2; Đ : 1.24/1.11

Synthesis of poly(BnMA) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and BnMA (0.088 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, $\text{B}(\text{C}_6\text{F}_5)_3$ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(BnMA)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(BnMA)** was filtered. It was then washed with methanol, dichloromethane, and dried under vacuum. Yield: 0.039 g, 44 %. ^1H NMR (395.9 MHz, CDCl_3 , ppm): δ 7.40-7.20 (m,

PhH), 6.16 (br, =CH₂ of the CH₂C(=CH₂)CO₂Bn end-group), 5.59 (br, =CH₂ of the CH₂C(=CH₂)CO₂Bn end-group), 4.87 (br, OCH₂), 2.00-1.70 (m, CH₂), 1.00-0.60 (br, Me). M_n (g mol⁻¹): 8300/990; GPC yield (%): 48.8/51.2; Đ: 1.24/1.10.

Synthesis of poly(AMA) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and AMA (0.063 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, B(C₆F₅)₃ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(AMA)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(AMA)** was filtered. It was then washed with methanol and dried under vacuum. Yield: 0.054 g, 89 %. ¹H NMR (395.9 MHz, CDCl₃, ppm): δ 5.86 (br, CH=CH₂ + =CH₂ of the CH₂C(=CH₂)CO₂CH₂CH=CH₂ end-group), 5.50-5.20 (m, CH=CH₂ + =CH₂ of the CH₂C(=CH₂)CO₂CH₂CH=CH₂ end-group), 4.44 (br, OCH₂), 2.00-1.70 (br m, CH₂), 1.30 - 1.25 (br m, CH₂), 0.85 (br, Me). M_n (g mol⁻¹): 3100/560; GPC yield (%): 45/55; Đ: 1.65/1.11.

Synthesis of poly(HEMA) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and HEMA (0.065 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, B(C₆F₅)₃ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. Reaction mixture was quenched by the addition of 10 ml of 5% HCl-acidified *n*-hexane to yield a colourless oil. Yield: 0.030 g, 46.2 %. ¹H NMR (395.9 MHz, CD₃OD, ppm): δ 6.12 (d, =CH₂ of the CH₂C(=CH₂)CO₂CH₂CH₂OH end-group), 5.63 (m, =CH₂ of the CH₂C(=CH₂)CO₂CH₂CH₂OH end-group), 4.30-4.10 (m, OCH₂CH₂O), 3.80-3.60 (m,

OCH₂CH₂O), 1.95 (d, CH₂), 1.25-1.10 (m, Me). M_n (g mol⁻¹): 980/430; GPC yield (%): 10/40; Đ: 1.08/1.03.

Synthesis of poly(MIK) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and MIK (0.042 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, B(C₆F₅)₃ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(MIK)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(MIK)** was filtered. It was then washed with methanol, dichloromethane, and dried under vacuum. Yield: 0.037 g, 88 %. ¹H NMR (395.9 MHz, CDCl₃, ppm): δ 2.12 (br, CH₂), 2.00-1.40 (br, OMe), 1.40-0.80 (br, Me). (Chemical shifts of terminal alkene protons cannot be observable due to low integration ratio; Structure of terminal groups were supported by LC-MS.) M_n (g mol⁻¹): 1300; GPC yield (%): 100; Đ: 1.05.

Synthesis of poly(MMBL) (Table 1.4): In a glovebox, compound **1.1** (0.0065 g, 0.0125 mmol) was added to 1 ml of toluene and MMBL (0.056 g, 0.50 mmol) mixture in a 10 ml dried vial. After mixing completely, the colour of the solution changed from red to pale yellow. Then, B(C₆F₅)₃ (0.091 g, 0.18 mmol) was rapidly added under stirring. The reaction was stirred for 90 min. **Poly(MMBL)** was precipitated by the addition of the reaction solution into 10 ml of 5% HCl-acidified *n*-hexane. **Poly(MMBL)** was filtered. It was then washed with methanol, dichloromethane, and dried under vacuum. Yield: 0.049 g, 88 %. ¹H NMR (395.9 MHz, CDCl₃, ppm): δ 5.08 (br, C=CH of the end-group), 4.80-4.40 (br, OCH), 2.50-1.60 (br, CH₂), 1.60-1.20 (br, Me). M_n (g mol⁻¹): 9800; GPC yield (%): 100; Đ: 1.21.

Polymer characterization

Analytical GPC. The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300×8.0 mm; bead size = $7 \mu\text{m}$; pore size = 20–200 Å). The eluent was THF at a flow rate of 1.0 ml/min (40°C). Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent.

LC-MS. The LC-MS spectra were recorded on a ThermoFinnigan LCQ Fleet MS. (Poly(EMA), Poly(BMA), Poly(BnMA), Poly(AMA), Poly(HEMA) and Poly(MIK) were analyzed using LC-MS.)

MALDI-TOF-MS. The matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL Ltd., Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared the polymer solution (polymer: 10 mg/ml in THF), matrix solution (DCTB: 10 mg/ml in THF), and cationization agent solution (NaTFA: 10 g/L in THF). The MALDI-TOF-MS samples were prepared by the dried droplet method.^[21] Polymer sample, matrix, and cationization agent solution (all in THF) were mixed together in a ratio of 1/5/1 (v/v/v) for polymer/DCTB/NaTFA. Then, 5 μL of the mixed solution was deposited on the target plate and dried in the air at room temperature. Poly(MMA), Poly(PhMA) and Poly(MMBL) were analyzed using MALDI-TOF-MS due to high M_n .

Section I.5. Appendixes

Selected spectra

Figure 1.S2. ^1H NMR spectrum of compound **1.2** (C_6D_6)

Figure 1.S3. ^{13}C NMR spectrum of compound **1.2** (C_6D_6)

Figure 1.S4. ^{29}Si NMR spectrum of compound **1.2** (C_6D_6)

Figure 1.S5. HMBC NMR spectrum of compound **1.2** (C_6D_6)

Figure 1.S6. HMQC NMR spectrum of compound **1.2** (C_6D_6)

Figure 1.S7. 1H NMR spectrum for the reaction of **1.1** with $B(C_6F_5)_3$ (C_6D_6)

Figure 1.S8. ^{11}B NMR spectrum the reaction of **1.1** with $\text{B}(\text{C}_6\text{F}_5)_3$ (C_6D_6)

Figure 1.S9. ^1H NMR spectrum of the colorless oil from the reaction of compound **1.2** and $\text{B}(\text{C}_6\text{F}_5)_3$

Figure 1.S10. ^{11}B NMR spectrum of the colorless oil from the reaction of compound **1.2** and $\text{B}(\text{C}_6\text{F}_5)_3$

Figure 1.S11. ^1H NMR spectrum of **P1** (C_6D_6)

Figure 1.S12. ^1H NMR spectra (range= 3.3ppm – 6.8ppm) of four consecutive MMA polymerization, showing the regeneration of catalysts.(Table 1.2)

Figure 1.S13. ¹H NMR spectrum (range = 3.3ppm – 6.8ppm) (in CDCl₃) of the poly(MMA) obtained from the reaction of the 200:1:10 ratio of [MMA]:[**1.1**]:[B(C₆F₅)₃] after the 100 % conversion of MMA.

Figure 1.S14. ¹H NMR spectrum (range = 3.3ppm – 6.8ppm) (in CDCl₃) of the poly(MMA) obtained from the reaction of the 200:1:30 ratio of [MMA]:[**1.1**]:[B(C₆F₅)₃] after the 100 % conversion of MMA.

Figure 1.S15. ¹H NMR spectrum of poly(EMA) (CDCl₃)

Figure 1.S16. ¹H NMR spectrum of poly(BMA) (CDCl₃)

Figure 1.S19. ¹H NMR spectrum of poly(AMA) (CDCl₃)

Figure 1.S20. ¹H NMR spectrum of poly(HEMA) (CD₃OD)

Figure 1.S21. ^1H NMR spectrum of poly(MIK) (CDCl_3)

Figure 1.S22. ^1H NMR spectrum of poly(MMBL) (CDCl_3).

Figure 1.S23. LC-MS spectrum of poly(EMA)

Figure 1.S24. LC-MS spectrum of poly(BMA)

Figure 1.S25. MOLDI-TOF mass spectrum of poly(PhMA)

Figure 1.S26. LC-MS spectrum of poly(BnMA)

Figure 1.S27. LC-MS spectrum of poly(AMA)

Figure 1.S28. LC-MS spectrum of poly(HEMA)

Figure 1.S29. LC-MS spectrum of poly(MIK)

Figure 1.S30. MALDI-TOF mass spectrum of poly(MMBL)

X-ray data collection and structural refinement

A crystal of compound **1.2** was mounted onto a quartz fiber. The X-ray diffraction intensity data were measured at 296 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.^[22] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.^[23] Structural solution and refinement were carried out with the SHELXTL suite of programs.^[24] The structure was 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-1575243 (**1.2**) contains 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 1.S1 Crystal data for compound **1.2**

	1.2
Formula	C ₄₀ H ₆₂ N ₄ O ₄ Si ₂
<i>M</i>	719.11
Crystal System	Orthorhombic
Space group	<i>P</i> 21 21 21
<i>a</i> /Å	18.5839(3)
<i>b</i> /Å	19.8116(5)
<i>c</i> /Å	22.0906(5)
α /deg	90
β /deg	90
γ /deg	90
<i>V</i> /Å ³	8133.2(3)
<i>Z</i>	8
<i>d</i> _{calcd} /g cm ⁻³	1.175
μ /mm ⁻¹	0.131
<i>F</i> (000)	3120
Crystal size/ mm	0.253 x 0.295 x 0.368
Index range	-24 ≤ <i>h</i> ≤ 22
	-26 ≤ <i>k</i> ≤ 25

	-29≤ <i>l</i> ≤29
No. of reflections collected	82667
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0462, 0.1210
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0718, 0.1557
GOF, <i>F</i> ²	0.719
no. of data/ restraints/ param	20197 / 0 / 933
largest diff peak, hole/ eÅ ⁻³	0.310, -0.410

Discussion of the molecular structure of compound **1.2**

Compound **1.2** was characterized by X-ray crystallography (Figure 1.3). There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. Compound **1.2** comprises two five-membered SiC₃O rings linked by the Si1-Si2 bond. The Si-Si bond length (ca. 2.38 Å) is slightly shorter than that of [PhC(N^{*t*}Bu)₂Si:]₂ (ca. 2.41 Å).^[18] The two planar SiC₃O rings (the sums of bond angles: 539.69°) are arranged in a *trans* conformation to reduce the steric congestion. Both silicon atoms are five-coordinate and adopt a distorted trigonal bipyramidal geometry. The Si-C bond lengths (avg. 1.90 Å) in **1.2** fall in the range of typical Si-C single bonds (1.87-1.91 Å). In addition, the Si-O bond lengths (avg. 1.78 Å) in **1.2** are longer than typical Si-O single bond lengths (ca. 1.66 Å).^[25]

Theoretical studies

Methods

All structure-optimizations were carried out without any symmetry restriction using M06-2X functional as implemented in the Gaussian 16 package of programs.^[26] Harmonic vibrational frequency calculations were performed on all structures to verify the nature of the stationary points. The relative Gibbs free energies (ΔG) at 298.15 K and 1 atm were therefore computed at the same level of theory.

Table 1.S2
M06-2X/def2-SVP
MMA

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-0.245460	-0.398537	-0.000049
8	-0.631549	-1.536550	-0.000131
8	-1.079721	0.650913	0.000054
6	1.189899	0.037120	-0.000010
6	2.111170	-0.929884	0.000120
1	1.801028	-1.976407	0.000162
1	3.177478	-0.695903	0.000183
6	1.488180	1.508097	-0.000071
1	1.046414	1.994500	-0.881471
1	1.046233	1.994607	0.881178
1	2.571075	1.683666	0.000021
6	-2.461957	0.334011	0.000067
1	-2.998019	1.288075	0.000273
1	-2.722563	-0.253975	-0.890501
1	-2.722475	-0.254311	0.890436

Table 1.S3
M06-2X/def2-SVP
Cpd1.1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.234103	-1.289769	-1.973331
6	-1.981607	-1.052677	-3.291766
1	-3.069026	-1.101929	-3.135861
1	-1.708608	-1.818770	-4.033297
1	-1.726097	-0.061436	-3.693751
6	-1.620465	-2.654997	-1.392742
1	-1.166666	-2.801115	-0.400875
1	-1.254534	-3.450021	-2.059361
1	-2.708790	-2.770030	-1.299457
6	0.276692	-1.259942	-2.226450
1	0.570713	-0.295749	-2.671003
1	0.574466	-2.064473	-2.914721
1	0.811032	-1.372675	-1.271197
6	-2.581960	0.134360	-0.339147
6	-3.823899	-0.676975	-0.189949
6	-4.855169	-0.522569	-1.123608
1	-4.734891	0.194917	-1.937977
6	-6.028645	-1.262542	-1.002076
1	-6.828682	-1.135596	-1.732891
6	-6.181090	-2.159562	0.055517
1	-7.100995	-2.738313	0.151580
6	-5.157441	-2.314716	0.990090
1	-5.274873	-3.016175	1.817256
6	-3.980621	-1.576215	0.868946
1	-3.173187	-1.700128	1.593658
6	-3.132090	2.201922	1.046826
6	-4.637643	2.228075	0.754770
1	-4.820141	2.482137	-0.300029
1	-5.114988	2.994479	1.383124
1	-5.119472	1.265725	0.973485
6	-2.881649	1.685620	2.469181
1	-3.232645	0.647323	2.570884
1	-3.420075	2.304026	3.203035
1	-1.806043	1.725146	2.700081
6	-2.572555	3.621295	0.917528
1	-1.489773	3.626209	1.118300
1	-3.059230	4.288404	1.643194
1	-2.742574	4.012349	-0.096230
6	3.132091	2.201923	-1.046823
6	2.881653	1.685624	-2.469179
1	3.232651	0.647328	-2.570884
1	3.420080	2.304033	-3.203031
1	1.806048	1.725150	-2.700081
6	4.637643	2.228076	-0.754763
1	4.820138	2.482136	0.300037

1	5.114989	2.994482	-1.383115
1	5.119473	1.265726	-0.973480
6	2.572556	3.621296	-0.917523
1	1.489773	3.626210	-1.118297
1	3.059231	4.288407	-1.643187
1	2.742572	4.012348	0.096236
6	2.581959	0.134358	0.339145
6	3.823898	-0.676976	0.189948
6	3.980623	-1.576212	-0.868948
1	3.173192	-1.700125	-1.593663
6	5.157444	-2.314713	-0.990091
1	5.274879	-3.016170	-1.817258
6	6.181091	-2.159561	-0.055514
1	7.100996	-2.738312	-0.151576
6	6.028642	-1.262544	1.002080
1	6.828677	-1.135600	1.732898
6	4.855166	-0.522572	1.123611
1	4.734885	0.194912	1.937982
6	1.234102	-1.289773	1.973327
6	1.981610	-1.052684	3.291761
1	3.069028	-1.101936	3.135852
1	1.708613	-1.818780	4.033290
1	1.726100	-0.061445	3.693749
6	1.620461	-2.654999	1.392733
1	1.166659	-2.801115	0.400868
1	1.254530	-3.450025	2.059352
1	2.708786	-2.770034	1.299446
6	-0.276692	-1.259944	2.226449
1	-0.570710	-0.295753	2.671008
1	-0.574467	-2.064478	2.914717
1	-0.811034	-1.372671	1.271196
7	-1.487978	-0.196968	-1.034660
7	-2.389487	1.379050	0.090731
7	2.389486	1.379049	-0.090731
7	1.487976	-0.196970	1.034658
14	-0.792079	1.564524	-0.919331
14	0.792079	1.564522	0.919332

Table 1.S4
M06-2X/def2-SVP
 B(C₆F₅)₃

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	0.004713	0.000338	0.008089
6	-0.556538	1.467791	0.003161
6	-1.746214	1.805294	-0.653873
6	0.101689	2.518145	0.654330
6	-2.251907	3.099758	-0.680622
6	-0.382090	3.821106	0.664570
6	-1.564962	4.110294	-0.012165
6	-0.989362	-1.216622	0.009309
6	-0.702374	-2.411959	-0.660766
6	-2.219635	-1.167571	0.675635
6	-1.578260	-3.491111	-0.685119
6	-3.112602	-2.232720	0.689529
6	-2.787744	-3.398159	-0.000615
6	1.555444	-0.251403	0.007100
6	2.449418	0.612799	-0.637544
6	2.128496	-1.357298	0.647556
6	3.822672	0.399108	-0.659210
6	3.497929	-1.595079	0.661499
6	4.346521	-0.711111	-0.000851
9	2.002337	1.681750	-1.282287
9	4.628859	1.232971	-1.289826
9	5.643950	-0.924996	-0.004445
9	3.997679	-2.644408	1.287698
9	1.366724	-2.228408	1.295077
9	-2.438488	0.882174	-1.307808
9	-3.370021	3.376847	-1.325679
9	-2.033715	5.338911	-0.020405
9	0.264610	4.779734	1.301586
9	1.229327	2.294990	1.315522
9	0.434865	-2.550093	-1.329007
9	-1.277439	-4.595480	-1.342964
9	-3.624811	-4.412797	-0.006047
9	-4.257630	-2.151079	1.341410
9	-2.575852	-0.081146	1.348065

Table 1.S5
M06-2X/def2-SVP
 TS

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	0.925489	0.684829	2.396206
8	0.061423	0.084586	1.771687
8	0.745509	1.910657	2.847886
6	2.264618	0.138928	2.750771
6	2.387869	-1.191947	2.799435
1	1.534244	-1.839667	2.595948
1	3.337748	-1.655807	3.073545
6	3.351745	1.122670	3.071852
1	3.485656	1.828913	2.240282
1	3.086798	1.712753	3.960360
1	4.298462	0.601677	3.257965
6	-0.542416	2.508270	2.689730
1	-0.507459	3.442233	3.257385
1	-0.749752	2.706032	1.630920
1	-1.318648	1.838107	3.077580
5	-0.236809	-0.153696	-0.304602
6	-0.099646	1.397596	-0.659438
6	-1.122450	2.150863	-1.239320
6	1.062473	2.109459	-0.348888
6	-1.019216	3.524489	-1.458500
6	1.205144	3.477298	-0.539682
6	0.149087	4.190804	-1.102567
6	-1.686101	-0.794394	-0.176810
6	-2.026402	-2.029737	-0.730324
6	-2.707778	-0.145575	0.520391
6	-3.289469	-2.601390	-0.588992
6	-3.975486	-0.685267	0.694916
6	-4.267483	-1.924776	0.130474
6	1.001393	-1.109778	-0.578533
6	2.022701	-0.822753	-1.485145
6	1.134831	-2.311699	0.119462
6	3.129842	-1.649497	-1.664271
6	2.232875	-3.151768	-0.012101
6	3.235744	-2.818911	-0.919026
9	1.981243	0.274125	-2.234166
9	4.073756	-1.334034	-2.534685
9	4.282537	-3.606816	-1.066693
9	2.332996	-4.251768	0.716176
9	0.199724	-2.686505	0.986915
9	-2.259483	1.583095	-1.618307
9	-2.015110	4.193865	-2.010417
9	0.260116	5.488068	-1.304805
9	2.322316	4.097362	-0.200849
9	2.106077	1.477150	0.191145
9	-1.144608	-2.727723	-1.437522

9	-3.562995	-3.774345	-1.134198
9	-5.467705	-2.450820	0.275180
9	-4.904710	-0.031904	1.373041
9	-2.497782	1.057584	1.049695

Table 1.S6
M06-2X/def2-SVP
MMA-B(C₆F₅)₃

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-0.730862	-0.907965	2.433361
8	-0.040045	-0.169318	1.708273
8	-0.204935	-1.934150	3.030892
6	-2.156772	-0.701590	2.770911
6	-2.602238	0.559702	2.806654
1	-1.943358	1.399549	2.587876
1	-3.633197	0.773704	3.096892
6	-2.956218	-1.916193	3.146410
1	-2.917750	-2.665025	2.343704
1	-2.545358	-2.380640	4.053763
1	-4.000969	-1.639759	3.330392
6	1.194339	-2.217552	2.867740
1	1.374861	-3.123492	3.451539
1	1.427654	-2.373232	1.808474
1	1.784170	-1.374423	3.243932
5	0.107700	0.131601	0.071528
6	0.462662	-1.352312	-0.507381
6	1.624647	-1.690668	-1.199801
6	-0.401604	-2.418676	-0.257990
6	1.918912	-2.999351	-1.591569
6	-0.154787	-3.733761	-0.624532
6	1.027603	-4.025191	-1.301451
6	1.347385	1.177329	0.024707
6	1.354837	2.381483	-0.677562
6	2.530763	0.885712	0.702074
6	2.438932	3.259489	-0.673575
6	3.634297	1.728212	0.736259
6	3.585034	2.931745	0.039251
6	-1.319450	0.742135	-0.398739
6	-2.183585	0.176618	-1.334326
6	-1.762974	1.941078	0.160099
6	-3.419610	0.736081	-1.664890
6	-2.985657	2.530107	-0.129446
6	-3.823441	1.918346	-1.058810
9	-1.874195	-0.945978	-1.978267
9	-4.203065	0.149284	-2.554609
9	-4.990086	2.458186	-1.357494
9	-3.354490	3.656180	0.460331
9	-0.994897	2.578486	1.049112
9	2.527159	-0.775298	-1.531567
9	3.039386	-3.267579	-2.239329
9	1.293838	-5.263673	-1.669813
9	-1.020322	-4.695018	-0.347622
9	-1.558558	-2.185500	0.382311
9	0.308636	2.764534	-1.405756

9	2.383907	4.396503	-1.347810
9	4.621516	3.749878	0.051642
9	4.729395	1.390956	1.400454
9	2.663110	-0.286027	1.333760

Table 1.S7
M06-2X/def2-SVP
 TS1.1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.410190	0.600273	1.844581
6	1.655905	1.374798	2.933229
1	2.208955	2.269004	3.248766
1	1.525745	0.732014	3.816883
1	0.664236	1.671008	2.567185
6	3.867354	0.380144	2.256488
1	4.369441	-0.215031	1.480564
1	3.915778	-0.161474	3.213691
1	4.400068	1.336062	2.375378
6	1.740248	-0.760151	1.639777
1	0.692170	-0.632124	1.332931
1	1.759370	-1.352531	2.566572
1	2.261511	-1.320099	0.847357
6	2.872863	2.411561	0.093607
6	3.508458	3.491628	0.900984
6	2.741787	4.284822	1.762768
1	1.672912	4.096691	1.854405
6	3.336216	5.328352	2.469234
1	2.727104	5.948624	3.128362
6	4.699478	5.586194	2.327776
1	5.162895	6.404385	2.881146
6	5.468821	4.796618	1.473984
1	6.536087	4.991385	1.359979
6	4.876117	3.756882	0.760358
1	5.478078	3.142465	0.090522
6	2.843547	3.488276	-2.224793
6	2.505601	4.873515	-1.657863
1	1.545048	4.844913	-1.121933
1	2.420686	5.589856	-2.488125
1	3.277491	5.246104	-0.972012
6	4.262866	3.474205	-2.803541
1	5.008206	3.672997	-2.021031
1	4.367260	4.247127	-3.579380
1	4.475946	2.493820	-3.256802
6	1.853062	3.170536	-3.349305
1	2.023765	2.151622	-3.734494
1	1.980031	3.880627	-4.178641
1	0.820251	3.241889	-2.976952
6	-0.912579	0.785632	-2.791602
1	-1.154183	1.304516	-1.869237
1	-0.350864	1.330867	-3.551080
6	-1.461734	-0.425443	-3.080256
6	-2.214124	-1.062420	-2.031778
6	-1.333129	-1.119256	-4.407637
1	-0.575530	-0.617321	-5.022831

1	-2.289730	-1.100581	-4.951296
1	-1.047282	-2.173762	-4.291560
6	-3.353390	-3.087952	-1.411774
1	-4.449036	-3.064938	-1.451228
1	-2.998639	-2.844589	-0.404046
1	-2.991867	-4.079137	-1.710488
6	1.783517	-3.349548	-1.488171
6	1.498887	-4.085018	-0.173226
1	2.310543	-4.770501	0.103581
1	0.582282	-4.681399	-0.294642
1	1.326229	-3.378270	0.650724
6	2.131527	-4.358553	-2.589880
1	2.350241	-3.832091	-3.530503
1	1.292454	-5.050592	-2.756556
1	3.011284	-4.953500	-2.305284
6	0.542682	-2.555666	-1.897527
1	0.242475	-1.856779	-1.101245
1	-0.294990	-3.238396	-2.110592
1	0.752629	-1.971054	-2.807627
6	4.045146	-2.414728	-0.771392
6	4.611878	-3.567279	-0.018243
6	4.523926	-3.588971	1.377634
1	4.027697	-2.765292	1.895843
6	5.057001	-4.657886	2.092699
1	4.982654	-4.673812	3.180822
6	5.683579	-5.707163	1.418367
1	6.102566	-6.543470	1.979929
6	5.774300	-5.687216	0.027131
1	6.266294	-6.505613	-0.500540
6	5.238121	-4.619610	-0.692557
1	5.310259	-4.596378	-1.781931
6	6.057415	-0.853329	-0.914343
6	6.793851	-1.325193	-2.175354
1	6.766555	-2.423652	-2.241217
1	7.847512	-1.008586	-2.149349
1	6.317188	-0.910975	-3.075278
6	6.776503	-1.403940	0.323263
1	6.218570	-1.189952	1.245506
1	7.760171	-0.917758	0.399943
1	6.941805	-2.487406	0.261869
6	6.051383	0.675712	-0.849882
1	5.493041	1.096906	-1.701200
1	7.076281	1.074743	-0.872456
1	5.559461	1.002138	0.077482
7	2.350288	1.268322	0.540582
7	2.697439	2.416436	-1.232205
7	2.861821	-2.362980	-1.374604
7	4.645107	-1.240943	-1.001238
8	-2.213673	-0.622159	-0.850603
8	-2.837393	-2.165751	-2.372273
14	1.740477	0.780596	-1.173024
14	3.294786	-0.725102	-2.243265
5	-3.242032	-0.151147	0.225061

6	-4.736963	-0.601602	-0.243974
6	-5.178449	-0.255275	-1.520990
6	-5.630622	-1.362305	0.506579
6	-6.406066	-0.633771	-2.049186
6	-6.878766	-1.758951	0.023299
6	-7.265940	-1.396037	-1.261663
6	-2.990962	1.473287	0.219194
6	-1.688861	1.911017	0.461401
6	-3.900836	2.474346	-0.108739
6	-1.277254	3.227016	0.299780
6	-3.533715	3.813050	-0.263906
6	-2.211330	4.191738	-0.062486
6	-2.744163	-0.754926	1.655240
6	-1.714116	-1.666192	1.857580
6	-3.296732	-0.211740	2.814099
6	-1.227886	-1.995867	3.122145
6	-2.852158	-0.516977	4.094975
6	-1.795095	-1.412453	4.247458
9	-5.328849	-1.781075	1.732437
9	-7.695540	-2.479285	0.775431
9	-8.443661	-1.765709	-1.730841
9	-6.767348	-0.275683	-3.270476
9	-4.387487	0.481807	-2.307156
9	-5.184951	2.198108	-0.313863
9	-4.434249	4.723928	-0.595821
9	-1.840191	5.451424	-0.217904
9	-0.006556	3.573043	0.496319
9	-0.752130	1.037299	0.829295
9	-1.108174	-2.279631	0.832211
9	-0.218335	-2.849267	3.252160
9	-1.345316	-1.712922	5.454366
9	-3.409815	0.031967	5.162634
9	-4.308601	0.648041	2.704180

Table 1.S8
M06-2X/def2-SVP
 Int1.1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.175275	0.851443	1.689188
6	1.556337	1.816733	2.705308
1	2.249165	2.628768	2.964647
1	1.329964	1.259176	3.625650
1	0.622698	2.247712	2.325004
6	3.595820	0.477883	2.119012
1	4.033432	-0.211621	1.382720
1	3.580391	-0.010090	3.105426
1	4.235641	1.371628	2.191792
6	1.326307	-0.413303	1.551514
1	0.324312	-0.174922	1.167346
1	1.215633	-0.925158	2.519311
1	1.808588	-1.116470	0.850164
6	2.768176	2.536755	-0.154733
6	3.155994	3.726776	0.648779
6	2.142379	4.592731	1.071806
1	1.102579	4.382243	0.814725
6	2.465556	5.710399	1.837703
1	1.673280	6.383764	2.166653
6	3.792629	5.957019	2.189753
1	4.043215	6.829730	2.794487
6	4.801145	5.088872	1.771782
1	5.838818	5.281171	2.047132
6	4.486964	3.974002	0.996263
1	5.274855	3.299789	0.655297
6	3.071359	3.393014	-2.549249
6	1.964490	4.453489	-2.565693
1	0.973851	3.995650	-2.692877
1	2.129244	5.152218	-3.398513
1	1.965123	5.033855	-1.632125
6	4.433485	4.076006	-2.381807
1	4.442452	4.757703	-1.521364
1	4.652911	4.668674	-3.281505
1	5.233428	3.332748	-2.255050
6	3.060533	2.597492	-3.857764
1	3.864838	1.845206	-3.866433
1	3.208367	3.271198	-4.712647
1	2.099582	2.077868	-4.001589
6	0.193322	1.090955	-1.901764
1	-0.310132	1.367008	-0.966723
1	0.251984	2.005790	-2.518520
6	-0.579037	0.033655	-2.630815
6	-1.587995	-0.614636	-2.008162
6	-0.203197	-0.231661	-4.058228
1	0.865868	-0.508774	-4.150000

1	-0.347670	0.665882	-4.685887
1	-0.806676	-1.040719	-4.486245
6	-2.585771	-2.775455	-2.202186
1	-3.648912	-3.023751	-2.329346
1	-2.326413	-2.840635	-1.135056
1	-1.984891	-3.498110	-2.776405
6	1.993615	-3.550586	-1.088995
6	1.719671	-4.120206	0.306211
1	2.584472	-4.660851	0.711883
1	0.885071	-4.832061	0.230763
1	1.410794	-3.334261	1.009946
6	2.518631	-4.652602	-2.016626
1	2.717312	-4.247469	-3.020159
1	1.774103	-5.456710	-2.106612
1	3.445669	-5.090384	-1.618247
6	0.701816	-2.966798	-1.651195
1	0.276374	-2.211283	-0.973826
1	-0.041054	-3.765208	-1.774625
1	0.869044	-2.504819	-2.639557
6	4.152311	-2.319354	-0.501147
6	4.801047	-3.297011	0.414759
6	4.584123	-3.212150	1.792946
1	3.915146	-2.445174	2.187693
6	5.208586	-4.115207	2.649434
1	5.035855	-4.050571	3.724311
6	6.046376	-5.104504	2.133127
1	6.532487	-5.811921	2.806363
6	6.256883	-5.194709	0.757521
1	6.907112	-5.971231	0.352663
6	5.634576	-4.292277	-0.103820
1	5.794239	-4.359868	-1.182167
6	6.053287	-0.645371	-0.886906
6	6.901643	-1.229723	-2.023251
1	7.005219	-2.318011	-1.901124
1	7.908746	-0.787437	-2.017636
1	6.433070	-1.031911	-2.998247
6	6.744823	-0.910651	0.455181
1	6.116576	-0.604910	1.303138
1	7.672714	-0.321551	0.487478
1	7.014014	-1.966540	0.583550
6	5.889901	0.862965	-1.079727
1	5.367697	1.074445	-2.027178
1	6.866109	1.368888	-1.102053
1	5.285646	1.276227	-0.257252
7	2.226759	1.418453	0.328778
7	2.828576	2.404699	-1.483147
7	2.955620	-2.434749	-1.070238
7	4.690744	-1.187120	-0.965531
8	-1.818564	-0.487241	-0.708172
8	-2.371470	-1.474640	-2.712375
14	1.985525	0.748414	-1.374558
14	3.338386	-1.044035	-2.287175
5	-3.076598	-0.248649	0.070035

6	-4.392846	-0.945902	-0.616739
6	-4.834511	-0.488104	-1.858518
6	-5.097174	-2.025662	-0.097194
6	-5.895979	-1.049304	-2.554889
6	-6.176440	-2.619889	-0.756557
6	-6.572743	-2.131485	-1.993643
6	-3.266626	1.403092	0.235801
6	-2.184570	2.144481	0.696960
6	-4.418416	2.160236	0.017200
6	-2.189091	3.522826	0.878484
6	-4.472920	3.545515	0.178609
6	-3.348381	4.237819	0.612284
6	-2.761326	-0.828915	1.583123
6	-1.723227	-1.696445	1.910125
6	-3.526163	-0.400605	2.668198
6	-1.401186	-2.042949	3.221995
6	-3.257909	-0.740224	3.990818
6	-2.170368	-1.562398	4.272161
9	-4.764269	-2.584401	1.068250
9	-6.811930	-3.653657	-0.218806
9	-7.594967	-2.680119	-2.632166
9	-6.276004	-0.574009	-3.733155
9	-4.226215	0.553799	-2.422595
9	-5.564307	1.593392	-0.344363
9	-5.595760	4.207617	-0.059583
9	-3.384148	5.551426	0.777837
9	-1.096640	4.153129	1.323095
9	-1.033656	1.531649	1.022544
9	-0.947528	-2.270061	0.979603
9	-0.349104	-2.822694	3.470066
9	-1.879504	-1.889632	5.523160
9	-4.018391	-0.292010	4.979664
9	-4.593400	0.370758	2.458853

Table 1.S9
M06-2X/def2-SVP
 TS1.2

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.721425	0.854624	-2.097014
6	-1.571888	-0.013196	-2.617100
1	-0.621517	0.507883	-2.436502
1	-1.675627	-0.190392	-3.698563
1	-1.550383	-0.976800	-2.091727
6	-2.723857	2.181216	-2.867232
1	-3.495670	2.867994	-2.490271
1	-2.958233	1.956824	-3.917485
1	-1.756079	2.696228	-2.842137
6	-4.081061	0.185457	-2.358808
1	-4.139924	-0.804431	-1.890358
1	-4.238344	0.078477	-3.442612
1	-4.885849	0.809451	-1.943551
6	-2.199829	2.074231	0.119457
6	-1.540444	3.303908	-0.407900
6	-0.165119	3.261423	-0.649646
1	0.396840	2.347413	-0.443666
6	0.493963	4.390731	-1.137106
1	1.568956	4.353685	-1.309335
6	-0.225253	5.557612	-1.391385
1	0.289310	6.439520	-1.775362
6	-1.599121	5.600850	-1.147369
1	-2.160768	6.515745	-1.340743
6	-2.256279	4.479217	-0.650652
1	-3.327947	4.513339	-0.450177
6	-1.993603	2.509360	2.589283
6	-0.516819	2.197388	2.873973
1	-0.363712	1.124275	3.048379
1	-0.186290	2.740263	3.771650
1	0.123437	2.509818	2.036029
6	-2.175122	4.032518	2.507713
1	-1.424103	4.512631	1.868863
1	-2.070073	4.451212	3.519133
1	-3.177177	4.291546	2.134386
6	-2.860772	1.995235	3.741956
1	-3.914896	2.274433	3.595093
1	-2.512475	2.424459	4.692232
1	-2.820561	0.900084	3.818492
6	-1.634634	-0.925868	1.803479
1	-0.660535	-0.495460	1.483247
1	-1.736679	-0.712382	2.878828
6	-1.710133	-2.391768	1.497526
6	-2.418559	-2.622127	0.342067
6	-2.735245	-3.997330	-1.540504
1	-3.000099	-5.042643	-1.731786

1	-1.778595	-3.767493	-2.036613
1	-3.510528	-3.334517	-1.946651
6	-6.343958	-2.779085	1.072769
6	-6.021708	-3.480187	-0.248427
1	-6.760475	-3.223468	-1.021245
1	-6.024576	-4.572305	-0.115952
1	-5.025878	-3.163018	-0.580618
6	-7.765467	-3.120802	1.535687
1	-8.025080	-2.535829	2.430685
1	-7.821994	-4.188987	1.791740
1	-8.507771	-2.923580	0.751306
6	-5.354663	-3.225340	2.151900
1	-4.325050	-2.956623	1.872436
1	-5.397548	-4.315779	2.280039
1	-5.592844	-2.748314	3.114374
6	-6.807617	-0.437674	0.182616
6	-7.990706	-0.673951	-0.693418
6	-7.800381	-0.915736	-2.057312
1	-6.784350	-0.966673	-2.454781
6	-8.900560	-1.076433	-2.897581
1	-8.748441	-1.262554	-3.961521
6	-10.193033	-0.993990	-2.379819
1	-11.053620	-1.115718	-3.039066
6	-10.385843	-0.759665	-1.017941
1	-11.395979	-0.700217	-0.610594
6	-9.287631	-0.601205	-0.174787
1	-9.432799	-0.423921	0.892854
6	-6.716653	2.108632	0.169370
6	-7.730746	2.496313	1.253775
1	-8.619311	1.850622	1.195069
1	-8.056716	3.538914	1.122548
1	-7.283388	2.385752	2.252169
6	-7.348967	2.297128	-1.215773
1	-6.694601	1.912417	-2.011265
1	-7.499514	3.372924	-1.387963
1	-8.326209	1.805129	-1.301732
6	-5.480364	3.003143	0.273619
1	-4.967036	2.845017	1.235883
1	-5.758176	4.064542	0.193263
1	-4.773269	2.751761	-0.531738
7	-2.559641	1.010989	-0.635615
7	-2.436216	1.798670	1.376403
7	-6.157954	-1.332487	0.920018
7	-6.230343	0.745717	0.412028
8	-2.971837	-1.630204	-0.302513
8	-2.612831	-3.862966	-0.136399
14	-3.007467	-0.082914	0.777337
14	-5.182437	0.011043	1.826453
6	-1.435512	-3.464385	2.510664
1	-1.601520	-4.461062	2.078449
1	-0.409716	-3.421998	2.906200
1	-2.115574	-3.356425	3.373030
6	0.377019	-2.883761	0.193277

1	0.063012	-2.860196	-0.851285
1	0.172035	-3.792984	0.754484
6	1.286506	-1.969545	0.655958
6	1.755104	-1.953747	2.087744
1	1.926965	-2.979335	2.443598
1	2.690708	-1.395504	2.197834
1	0.997463	-1.488980	2.737121
6	1.855234	-1.032147	-0.269099
8	2.766142	-0.216276	0.068025
8	1.426073	-1.051859	-1.510028
6	1.926856	-0.093545	-2.444468
1	1.692605	0.921464	-2.100726
1	3.010058	-0.190781	-2.574898
1	1.415693	-0.309776	-3.386531
6	4.813693	1.144292	-0.815291
6	4.068352	2.302801	-0.995488
6	6.168045	1.253946	-1.133922
6	4.616516	3.486304	-1.492618
6	6.756456	2.410000	-1.630590
6	5.965993	3.542931	-1.812218
6	4.965411	-0.247941	1.372097
6	6.018687	-1.041760	1.819821
6	4.490567	0.692453	2.288249
6	6.542132	-0.948683	3.109356
6	4.978233	0.813085	3.585999
6	6.018320	-0.015408	3.996512
6	4.627778	-1.608115	-1.006142
6	4.441675	-2.863663	-0.424724
6	5.032130	-1.642515	-2.339735
6	4.637684	-4.067905	-1.092144
6	5.245981	-2.822405	-3.051121
6	5.047413	-4.044895	-2.421416
5	4.317572	-0.253227	-0.131193
9	2.762532	2.350963	-0.702609
9	3.854716	4.564288	-1.658026
9	6.495016	4.659334	-2.283102
9	8.045324	2.449671	-1.926729
9	6.956491	0.193343	-0.965644
9	3.519643	1.535511	1.933865
9	4.480639	1.714405	4.420550
9	6.505413	0.085917	5.221859
9	7.537034	-1.734286	3.492554
9	6.583688	-1.947623	1.025679
9	4.070043	-2.953236	0.852154
9	4.444260	-5.224687	-0.478614
9	5.238653	-5.173885	-3.080506
9	5.621123	-2.786101	-4.320398
9	5.207566	-0.516195	-3.036395

Table 1.S10
M06-2X/def2-SVP
 Int1.2

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.931865	0.708319	2.278514
6	2.058873	-0.310484	3.020043
1	0.998269	-0.044678	2.907261
1	2.316981	-0.328937	4.089130
1	2.195528	-1.321802	2.616470
6	2.825253	2.052043	3.008537
1	3.397097	2.839539	2.498102
1	3.251276	1.920875	4.013254
1	1.789368	2.393767	3.121593
6	4.413753	0.300756	2.303196
1	4.583217	-0.665608	1.811519
1	4.760825	0.234736	3.345466
1	5.016760	1.057258	1.779618
6	1.874884	1.748218	0.167975
6	1.237213	2.982579	0.711276
6	-0.088807	2.917723	1.140463
1	-0.629214	1.972426	1.074790
6	-0.721752	4.070616	1.609266
1	-1.770156	4.025821	1.902914
6	-0.029205	5.277294	1.660889
1	-0.528386	6.175903	2.026157
6	1.295201	5.341488	1.222977
1	1.835653	6.288717	1.245883
6	1.925886	4.200441	0.738755
1	2.951022	4.259003	0.374485
6	1.156256	1.957756	-2.259764
6	-0.336259	1.616789	-2.144116
1	-0.522514	0.535245	-2.081766
1	-0.868518	1.988951	-3.031125
1	-0.802600	2.082757	-1.264999
6	1.319139	3.477513	-2.393494
1	0.754902	4.023324	-1.627833
1	0.932474	3.786317	-3.375186
1	2.378366	3.771034	-2.335382
6	1.749558	1.299020	-3.507626
1	2.810430	1.565100	-3.631622
1	1.198530	1.630662	-4.398187
1	1.673931	0.203324	-3.456833
6	1.626298	-1.472824	-1.375579
1	0.688274	-0.960676	-1.611519
1	2.074798	-1.781298	-2.337185
6	1.343326	-2.708430	-0.517636
6	2.482054	-2.820288	0.458189
6	3.470193	-4.055995	2.216154
1	4.388262	-4.456423	1.768511

1	3.058188	-4.773282	2.931853
1	3.681298	-3.096617	2.704912
6	6.416554	-2.609590	-1.135968
6	6.602901	-3.222767	0.255318
1	7.516887	-2.848499	0.736266
1	6.683937	-4.317837	0.180573
1	5.740842	-2.963554	0.886023
6	7.683320	-2.793580	-1.980167
1	7.564986	-2.298412	-2.955500
1	7.864771	-3.864313	-2.154697
1	8.565954	-2.380729	-1.474191
6	5.247150	-3.288401	-1.853906
1	4.318682	-3.156503	-1.282816
1	5.438633	-4.364196	-1.968920
1	5.105110	-2.854015	-2.855867
6	6.733646	-0.167059	-0.497949
6	8.057919	-0.203846	0.184627
6	8.125337	-0.366850	1.571357
1	7.203710	-0.510331	2.139538
6	9.359783	-0.330754	2.216687
1	9.409911	-0.453471	3.299336
6	10.527919	-0.131573	1.480742
1	11.492888	-0.098986	1.988495
6	10.463499	0.024761	0.096085
1	11.376846	0.177230	-0.480364
6	9.230677	-0.010768	-0.552600
1	9.174769	0.110590	-1.636519
6	6.362713	2.358196	-0.674020
6	7.120479	2.800226	-1.931819
1	8.086593	2.279129	-2.000272
1	7.316345	3.882104	-1.901696
1	6.535148	2.571209	-2.834008
6	7.182107	2.711171	0.573173
1	6.730412	2.293475	1.484397
1	7.205294	3.805720	0.675110
1	8.219529	2.359251	0.507319
6	5.012606	3.070854	-0.599914
1	4.377335	2.795781	-1.458412
1	5.143226	4.162873	-0.602171
1	4.487772	2.772010	0.320608
7	2.495421	0.770136	0.865953
7	1.914712	1.413941	-1.108150
7	6.057568	-1.192179	-1.017259
7	6.032559	0.932267	-0.775320
8	3.332875	-1.938796	0.581798
8	2.477930	-3.895036	1.203230
14	2.849492	-0.195251	-0.669206
14	4.891656	-0.028754	-1.941605
6	1.264259	-4.001754	-1.344843
1	1.101120	-4.868776	-0.691221
1	0.430973	-3.938513	-2.054000
1	2.190268	-4.163087	-1.917809
6	0.065475	-2.536979	0.383136

1	0.335151	-1.976770	1.289220
1	-0.222767	-3.552662	0.705895
6	-1.091730	-1.836487	-0.271195
6	-1.613562	-2.351627	-1.584080
1	-1.841201	-3.427535	-1.526697
1	-2.535156	-1.834522	-1.871126
1	-0.881904	-2.210215	-2.399441
6	-1.638007	-0.743671	0.312773
8	-2.644762	-0.042221	-0.157353
8	-1.025923	-0.207300	1.423504
6	-1.859309	0.238693	2.475263
1	-1.235757	0.858861	3.133674
1	-2.697776	0.844248	2.102323
1	-2.252547	-0.615442	3.049728
6	-4.783178	1.276439	0.313531
6	-4.095395	2.480460	0.391575
6	-6.164921	1.378450	0.473646
6	-4.719872	3.703760	0.640020
6	-6.832283	2.573295	0.715555
6	-6.096786	3.753385	0.802504
6	-4.755401	-0.586183	-1.496980
6	-5.772165	-1.499185	-1.765151
6	-4.288259	0.121679	-2.606078
6	-6.256165	-1.746725	-3.049956
6	-4.737129	-0.097525	-3.905210
6	-5.734926	-1.040960	-4.127163
6	-4.456510	-1.303281	1.166874
6	-4.282284	-2.669622	0.948944
6	-4.835579	-0.971910	2.466846
6	-4.471913	-3.644783	1.923804
6	-5.045854	-1.911582	3.475866
6	-4.857864	-3.260288	3.202776
5	-4.128082	-0.200539	-0.016991
9	-2.764864	2.545311	0.262199
9	-3.994955	4.816112	0.741519
9	-6.705810	4.905631	1.042713
9	-8.148121	2.605186	0.872677
9	-6.908345	0.271884	0.422586
9	-3.361608	1.072665	-2.458733
9	-4.241455	0.594490	-4.924545
9	-6.180874	-1.263910	-5.354883
9	-7.213350	-2.642948	-3.251745
9	-6.340549	-2.204734	-0.789801
9	-3.931203	-3.119205	-0.254579
9	-4.291791	-4.929492	1.644950
9	-5.040537	-4.168458	4.149680
9	-5.397835	-1.526347	4.696251
9	-4.981853	0.301591	2.844436

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Chapter II. Aluminum Hydride-Catalysed Hydroboration of Unsaturated Compounds

II.I. Introduction

Chart 2.1. Electronic structure of non-ambiphilic Al(III).

In this chapter, we discuss the use of aluminum as an alternative to precious transition-metal species in chemical catalysis due to its high abundance and non-toxicity.^[1] Aluminum is one of the greatest abundant main-group elements and its Lewis acidic compounds have been using in catalysing a wide range of classical organic reactions, for example, Meerwein-Ponndorf-Verley reduction of carbonyls,^[2] Friedel-Crafts acylation of aromatics,^[3] ring-opening polymerization of cyclic esters.^[4] However, aluminum lacks available d-orbitals (Chart 2.1), which cause it challenging to perform like a transition metal in catalysis.

Chart 2.2. Examples of aluminium catalysts that poses transition metal like reactivity.

In the past few years, this limitation has been overcoming by designing novel aluminum hydride compounds with highly polarized Al-H bonds and very hydridic H atoms, which show reactivity similar to transition metal hydride complexes.^[5] For example (Chart 2.2, top left), Berben et al. showed that the bis(imino)pyridine complex of aluminium catalysed the dehydrogenative coupling of benzylamine,^[6] dehydrogenation of formic acid,^[7] and electrocatalytic production of hydrogen via a metal-ligand cooperative mechanism.^[8] Thomas and Cowley et al. reported that commercially available aluminium hydride DIBAL-H, $\text{Et}_3\text{Al} \cdot \text{DABCO}$ or LiAlH_4 catalysed (Chart 2.2, top middle, top right and bottom left) hydroboration of alkynes, alkenes and nitriles via a σ -bond metathesis mechanism, respectively.^[9] Research groups of Harder and Mulvey reported that lithium aluminates underwent catalytic hydrophosphination of alkynes and hydrogenation of imine through a Li-Al cooperation mechanism (Chart 2.2, bottom left).^[10] Rueping et al. reported the first asymmetric hydroboration of ketones using aluminium complexes bearing chiral biphenol-type ligands (Chart 2.2, bottom right).^[11]

Chart 2.3. Catalytic cycle for β -diketiminato aluminium hydride catalysed hydroboration of aldehyde.

The β -diketiminato aluminium hydride catalysed a wide range of organic small molecules activation and their mechanism has been studied extensively. Roesky et al. illustrated that the β -diketiminato aluminium hydride complexes mediated catalytic hydroboration of carbonyl compounds and alkynes.^[12] The catalytic cycle was initiated by hydride attack of the highly polarized Al-H bond to the small molecules, followed by σ -bond metathesis to obtain the hydroborated product and regeneration of the aluminium hydride catalyst (Chart 2.3). Nikonov et al. demonstrated that the β -diketiminato aluminium hydride complex catalysed hydrosilylation of alkenes via the activation of silane by the Lewis acidic aluminium centre in the first step of the catalysis.^[13] These results evidenced that tailor-made aluminium hydride complexes exhibit transition-metal like reactivity in mediating catalytic reduction of unsaturated polar bonds (C=O, C=N) and C-C multiple bonds.

Chart 2.4. Nickel hydride catalysed hydroboration of CO₂.

Given the successive catalytic reduction of the unsaturated bonds, the next target is to reduce the more challenging CO₂. Reduction of CO₂ has been achieved by wide range of transition metal catalyst.^[14] One of the common mechanistic routes for the catalytic reduction of CO₂ involves transition metal hydride complex. For example, catalytic hydroboration of CO₂ using a nickel hydride complex were reported by Guan et.al (Chart 2.4).^[15] Stepwise mechanistic study shown that the highly hydridic H atom can undergo insertion to CO₂ to form the resulting nickel formate species. Addition of HBCat to this formate species resulted in regeneration of the nickel hydride along with formation of methoxy derivatives. Next, several studies also demonstrated that non-transition metal catalyst such as FLPs^[16] and strong bases^[17] could catalyse reduction of CO₂.

Chart 2.5. Stoichiometric reduction of FLP-activated CO₂ with ammonia borane.

Stephan et al. also showed that catalytic reduction of CO₂ could be achieved by aluminum catalyst.^[18] They used a Al-Based FLP to perform a stoichiometric reduction of CO₂ with the H₂ source, ammonia borane, into methanol (Chart 2.5). This result showed that reduction of CO₂ with aluminium compound is possible.

Chart 2.6. Insertion product of β -diketiminato aluminium hydride into CO_2 and its reactivity towards BH_3SMe_2 .

Since aluminium hydride complexes showed great potential in catalysing the reduction of polar multiple bonds, it is of great interest to test whether aluminium hydride complexes could perform catalytic reduction of CO_2 . Unfortunately, the implementation of aluminium hydride complexes for catalytic hydroboration of CO_2 is unknown as yet. Aldridge et al. showed that the β -diketiminato aluminium hydride complexes were not feasible to catalyse the hydroboration of CO_2 with boranes due to unfavourable thermodynamic σ -bond metathesis mechanism.^[19] They showed that the β -diketiminato aluminium hydride complexes underwent stoichiometric insertion into CO_2 to form an aluminium formate product (Chart 2.6). This formate product was reduced by excess BH_3SMe_2 to form a borate product. An attempt to regenerate the aluminium hydride via σ -bond metathesis failed, which ruled out the possibility of the β -diketiminato aluminium hydride to mediate catalytic hydroboration of CO_2 .

Chart 2.7. Stepwise reaction of N-heterocyclic imido aluminium hydride complex with CO_2 and BH_3SMe_2 .

Inoue et al. reported that the N-heterocyclic imido aluminium hydride complexes could promote CO₂ reduction (Chart 2.7). Based on their mechanistic studies, they revealed that the aluminium hydride reacted with CO₂ to form a formate species. Further reacting the formate species resulted decomposition into a mixture of ill-defined products. These ill-defined mixtures suggested that the catalysis proceeded through a non-aluminium-containing intermediate.^[20] In this context, it is imperative to develop a strategy in activating the ability of aluminium hydride complexes to catalytically convert the C1 feedstock, CO₂, into value-added chemicals and fuels.

Chart 2.8. Ylidic structure in bis(phosphoranyl)methanediide and methanide complexes of main-group elements (E).

Recently, a series of bis(phosphoranyl)methanediide and methanide complexes of main-group elements were synthesized, whereby the ylidic PN bonds ($P=N \leftrightarrow P^+—N^-$; Chart 2.8) of the ligands promote strong electron transfer from the N atoms to main-group elements.^[21]

Chart 2.9. Catalytic hydroboration of CO₂ using bis(iminophosphoranyl)methanido boron hydride [ClC(PPh₂=NMes)₂BH₂].

Our group utilized this ligand to synthesize a highly active borohydride complex (Chart 2.9). This borohydride complex achieved an excellent reactivity (TOF = 661 h⁻¹) in catalysing hydroboration of CO₂ with BH₃.^[22] Based on DFT calculations, the borohydride complex has a large negative charge at the N atoms, positive charge at the B center and a large negative charge at the H atoms, whereby the very strong hydridic character of the B-H centre plays a key role in the catalytic cycle and leads to the excellent catalytic property. Based on this structure, we anticipate that an aluminum hydride with the same ligand will possess an enhanced hydridic character. Herein, we report the synthesis of a bis(phosphoranyl)methanido aluminium hydride and its catalytic hydroboration of CO₂. DFT calculations of catalytic mechanism are also described.

Section II.2. Results and discussion

Scheme 2.1. Synthesis of the bis(phosphoranyl)methanido aluminium hydride **2.2**.

The lithium carbenoid $[\text{Li}(\text{Cl})\text{C}(\text{PPh}_2\text{NMe}_3)_2]$ (**2.1**, Mes = $\text{C}_6\text{H}_2\text{Me}_3$) was treated with two equivalents of $\text{AlH}_3\cdot\text{NEtMe}_2$ (2.0 mmol) in toluene at -78°C . The reaction was then warmed to room temperature and stirred for 1 hour, whereby white suspension was observed. Volatiles and NEtMe_2 were removed in vacuo and the residue was extracted by toluene. After filtration, the filtrate was concentrated to afford $[\text{ClC}(\text{PPh}_2\text{NMe}_3)_2\text{AlH}_2]$ (**2.2**) as a colorless crystalline solid (Scheme 2.1). The white precipitate residue was analysed by ^{27}Al NMR spectroscopy ($\delta=106.20\text{ppm}$), which corresponds to LiAlH_4 . The results show that $\text{AlH}_3\cdot\text{NEtMe}_2$ undergoes a disproportionation to form AlH_4^- and AlH_2^+ species in the presence of compound **2.1**.

Figure 2.1. X-ray crystal structure of **2.2** with thermal ellipsoids at 50% probability. All H atoms except on the Al1 atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl1-C1 1.786(4), C1-P2 1.725(4), P2-N2 1.623(3), N2-Al1 1.887(3), Al1-N1 1.900(3), N1-P1 1.625(3), P1-C1 1.719(4), P2-C1-P1 133.3(2), N2-B1-N1 103.6(1).

Compound **2.2** was analysed by NMR spectroscopy and X-ray crystallography (Figure 2.1). The ^1H NMR spectrum shows a set of signals for the ligand backbone. It also features a broad signal at 5.0 ppm with an integration of 2 for the AlH_2^+ moiety. The ^{31}P NMR spectroscopy shows a new singlet at 38.98 ppm. X-ray crystal structure of **2.2** features a six-membered CPNAINP ring in a half chair conformation due to the presence of a AlH_2^+ moiety (Al-N: 1.877(3), 1.900(3) Å). The C1 atom is planar, which suggests that it does not comprise any hydrogen atom. The P-N bond lengths in **2.2** are elongated (1.623(3), 1.625(3) Å) in comparison with those in **2.1** (1.596(3) and 1.593(2) Å), which indicate that the negative charge on the C1 atom in **2.2** is more delocalized into the P-N π^* orbitals by negative hyperconjugation. Compound **2.2** is air- and moisture-sensitive, as well as soluble and stable in non-polar solvents like benzene and toluene up to 120°C. The formation of free ligand was not observed in the toluene solution of compound **2.2** at 110°C.

Scheme 2.2. **2.2**-catalysed hydroboration of CO₂ with HBPin. Yields were calculated based on conversion of H.

The catalytic ability of the bis(phosphoranyl)methanido aluminium hydride complex **2.2** toward hydroboration of CO₂ with boranes was examined. To begin with, there was no reaction between CO₂ and borane (HBpin, BH₃.SMe₂, HBcat) in C₆D₆ at any temperature. However, in the presence of **2.2** (10 mol%), the reduction of CO₂ with HBpin in C₆D₆ at 110 °C afforded a mixture of methoxyborane [MeOBpin] (Scheme 2.2, **2.3a**; reaction time: 48h, H-conversion yield: 78 %, TOF: 0.16 h⁻¹) and diborate ether [pinBOBpin] (**2.3b**). The catalytic activity in terms of TOF is comparable with those of the activated non-transition metal catalysts (TOF = 0.07 - 2.5 h⁻¹) and the non-metal catalysts (TOF = 0.40 - 14.5 h⁻¹).^[23]

Scheme 2.3. **2.2**-catalysed hydroboration of CO₂ with BH₃SMe₂. Yields were calculated based on conversion of H.

When more potent $[\text{BH}_3\cdot\text{SMe}_2]$ was used instead of HBpin, the catalytic reaction was extremely clean, resulting in the formation of trimethyl borate $[\text{B}(\text{OMe})_3]$ and white precipitate (catalytic loading: 1 mol%, reaction time: 60 min, TOF: 292.8 h^{-1} , Scheme 2.3). The white precipitate was dissolved in D_2O and the solution contains boric acid only, being confirmed by ^{11}B NMR spectroscopy. This indicates that the white precipitate formed in the catalysis corresponds to B_2O_3 . No other identifiable boron-containing products were found in the reaction mixture. When the amount of complex **2.2** increased (10 mol%), the catalytic activity is considerably increased (reaction time: 5 min, TOF: 356.4 h^{-1}). Compound **2.2** is one of the very few main-group element examples that catalyse the reduction of CO_2 with BH_3 , including the ambiphilic phosphine-borane compound $[\text{1-B}(\text{OR})_2\text{-2-PR}'_2\text{-C}_6\text{H}_4]$ (TOF: $257 - 853\text{ h}^{-1}$; R and R' = supporting substituent),^[17, 24] bis(thiophosphinoyl)methanide-supported lithium borohydride $[\text{H}_5\text{B}_2\text{-C}(\text{PPh}_2=\text{S})_2\text{Li}(\text{OEt}_2)]$ (TOF: 150 h^{-1}),^[25] bis(iminophosphoranyl)methanido boron hydride $[\text{ClC}(\text{PPh}_2=\text{NMe})_2\text{BH}_2]$ (TOF: 157 h^{-1}),^[22] ring expansion product arising from phosphine-derived carbenes with 9-borabicyclo[3.3.1]nonane (9-BBN)^[26] and NHC-silyliumylidene complex $[(\text{Ime})_2\text{SiH}]\text{I}$ (TOF: 19.8 h^{-1} , $\text{Ime} = \text{:C}\{\text{N}(\text{Me})\text{C}(\text{Me})_2\}$).^[27] Moreover, the activity of complex **2.2** exceeds most of these examples in terms of both reaction time and TOF. It should be the most active non-transition metal catalyst reported for reduction of CO_2 . In comparison with other main-group element catalysts, the amino hydridostannylene compound has high TOF in the reduction of CO_2 with HBcat (TOF: 1188 h^{-1}).^[28]

Scheme 2.4. **2.2**-catalysed hydroboration of CO₂ with HBCat. Yield were calculated based on conversion of H.

On the other hand, the **2.2**-catalysed reduction of CO₂ with catecholborane HBCat slowly proceeded (Scheme 2.4, 24 h, 28.8% conversion) to afford a mixture of diborate ether [(catB)₂O] and methoxyborane [catBOMe].

Scheme 2.5. Insertion of the Al-H bond into CO₂.

The catalytic mechanism was studied by performing stoichiometric step-wise reduction with the aim to isolate reactive intermediates. Complex **2.2** was reacted with CO₂ in toluene at room temperature for 15 mins, whereby complex **2.2** was fully consumed (Scheme 2.5). The ³¹P NMR spectrum of the reaction mixture showed a new signal at δ 40.5 ppm, while the ¹H NMR spectrum showed a new singlet at δ 8.5 ppm with an integration of 1 suggesting the formation of a formate moiety. The spectroscopic data illustrate that one Al-H bond in complex **2.2** inserts into CO₂ to form [ClC(PPh₂=NMe)₂Al(H){OC(O)H}] (**2.4**). However, an attempt in isolating X-ray quality crystals of **2.4** failed. It is because **2.4** was unstable in solution such as toluene and

CH₂Cl₂, which slowly converted into a new complex with a ³¹P NMR signal at δ 42.5 ppm. The ¹H NMR spectrum showed a singlet at δ 8.24 ppm with an integration of 4 indicating the formation of OCH₂O.

Figure 2.2. X-ray crystal structure of **2.4-D** with thermal ellipsoids at the 50% probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and angles (deg): Cl1-C1 1.797(5), C1-P1 1.747(6), C1-P2 1.704(6), P2-N2 1.632(4), P1-N1 1.624(4), N1-Al1 1.881(5), N2-Al1 1.891(4), Al1-O2 1.731(4), Al1-O1 1.710(8), O1-C32 1.392(11), O2-C32 1.476(8), N1-Al1-N2 104.64(19), O1A-Al1-O2 109.2(5), N1-Al1-O1A 119.5(4), N2-Al1-O2 108.80(19), Al1-O2-C32 116.6(4) , O2-C32-O1 111.2(8).

The observation was in line with the X-ray crystal structure of colorless crystals obtained from the CH₂Cl₂ solution of **2.4** at 0°C for one week, whereby [LAl(OCH₂O)₂AlL] (**2.4-D**, L = ClC(PPh₂=NMe)₂) was isolated (Figure 2.2). In other words, the Al-H bond in complex **2.4** undergoes an intermolecular insertion of the OC(O)H moiety to form **2.4-D**. In the X-ray crystal structure, complex **2.4-D** comprises a Al(OCH₂O)₂Al eight membered ring. The ring structure (Al-O: 1.731(4), 1.710(8) Å)

is comparable with the one supported by β -diketiminate ligand $[\text{RAl}(\text{OCH}_2\text{O})_2\text{AlR}]$ (Al-O: 1.7123(11), 1.7239(11) Å; R = $\text{HC}\{\text{C}(\text{Me})\text{NDipp}_2\}$), which was isolated from the reaction of the germanium(II) formate $[\text{RGeOC}(\text{O})\text{H}]$ and aluminium hydride $[\text{RAlH}_2]$.^[29]

In the presence of CO_2 , complex **2.4** was further reacted with HBpin or $\text{BH}_3\cdot\text{SMe}_2$ in toluene at 110°C to form the hydroborated products (Scheme 2.2 and Scheme 2.3), along with the regeneration of complex **2.4** after the reactions. In the absence of CO_2 , compound **2.4** can react with $\text{BH}_3\cdot\text{SMe}_2$ at room temperature to form a mixture of compounds, but no free ligand was observed, being confirmed by ^{31}P NMR spectroscopy. In contrast, complex **2.4-D** did not react with HBpin or $\text{BH}_3\cdot\text{SMe}_2$ in toluene at 110°C in the presence/absence of CO_2 . The results show that complex **2.4** is an intermediate in the catalytic reduction of CO_2 .

Scheme 2.6. Catalytic cycle for the hydroboration of CO_2 with HBpin.

On the basis of these experimental studies, catalytic cycle for the hydroboration of CO_2 with HBpin is proposed (Scheme 2.6). First, complex **2.2** undergoes the insertion

of Al-H bond with CO₂ to form complex **2.4**. Then, the HBpin adds across the C=O bond in **2.4** to form intermediate **2.A**. It undergoes a σ -bond metathesis between the Al-O and C-OBpin bonds to form intermediate **2.B** and paraformaldehyde. After that, HBpin undergoes a σ -bond metathesis with the Al-O bond in **2.B** to form complex **2.2** and pinBOBpin. Subsequently, the Al-H bond of complex **2.2** reacts with the C=O bond of paraformaldehyde to afford intermediate **2.C**. Finally, MeOBpin and complex **2.2** are formed via a σ -bond metathesis between complex **2.C** and HBpin.

Scheme 2.7. DFT calculation for the hydroboration of CO₂ with HBpin.

DFT calculations (Scheme 2.7) also suggest that complex **2.2** is capable of catalysing hydroboration of CO₂ with BH₃, whereby CO₂ inserts into the Al-H bond in complex **2.2** via a low kinetic barrier to form complex **2.4**. BH₃ then coordinates with the formate

without any barrier to form intermediate **Int2.1**, whereby the B-H bond inserts into the C=O bond via **TS2.1** to form intermediate **Int2.2-AIH** and its isomer **Int2.2-AIH-BH₃**. The O atoms in **Int2.2-AIH-BH₃** stepwise coordinates with two molecules of BH₃ to form intermediate **Int2.3** and **Int2.4**. The hydride of BH₃ (highlighted in red) attacks on the OCH₂O moiety, leading to the displacement of MeOBH₂ and formation of intermediate **Int2.5**. The substitution reaction among three molecules of MeOBH₂ into B(OMe)₃ is favorable, while σ -bond metathesis between the Al-O and B-H bonds in intermediate **Int2.5** results in the regeneration of complex **2.2** and formation of O(BH₂)₂. The substitution reaction among O(BH₂)₂ molecules affords B₂O₃ and BH₃.

Table 2.1. Catalytic hydroboration of aldehydes and ketones^[a]

<p style="text-align: center;">2.5 2.6</p>
<p>2.6a; x = 5; T = 60; t = 1; conversion = 93%; TOF=18.6h⁻¹ t = 1.5; conversion = >99% (96%)</p>	<p>2.6b; x = 5; T = 60; t = 2; conversion = 97% (94%); TOF=9.7h⁻¹</p>	<p>2.6c; x = 5; T = 60; t = 2; conversion = >99%; TOF=9.9h⁻¹</p>
<p>2.6d; x = 5; T = 60; t = 2; conversion = >99%; TOF=9.9h⁻¹</p>	<p>2.6e; x = 5; T = 60; t = 3; conversion = >99% (95%); TOF=6.6h⁻¹</p>	<p>2.6f; x = 5; T = 60; t = 1; conversion = 93%; TOF=18.6h⁻¹</p>

2.6g ; x = 5; T = 60; t = 1; conversion = 92%; TOF=18.4h ⁻¹	2.6h ; x = 5; T = 60; t = 1; conversion = 93% (88%); TOF=18.6h ⁻¹	2.6i ; x = 5; T = 60; t = 1; conversion = >99% (92%); TOF=19.8h ⁻¹
2.6j ; x = 10; T = 110; t = 6; conversion = 88% (68%); TOF=1.5h ⁻¹	2.6k ; x = 10; T = 110; t = 6; conversion = 70% (54%); TOF=1.2h ⁻¹	2.6l ; x = 10; T = 110; t = 6; conversion = 89%(73%); TOF=1.5h ⁻¹

[a] Conversion obtained from integration of ¹H NMR spectroscopy. Isolated yield written in brackets.

Complex **2.2** also shows good catalytic activity towards hydroboration of carbonyl, alkyne and nitrile derivatives. First, there were no reaction between substrates with HBpin in C₆D₆ at room temperature or 110 °C. Second, complex **2.2** (5 mol %) was found to be capable of catalysing hydroboration of aldehydes RC(O)H (Table 2.1) with electron donating and withdrawing substituents at different positions, which afforded the corresponding borate esters in high yield. In these reactions, take benzaldehyde as an example, complex **2.2** is less active (TOF = 18.6 h⁻¹) in comparison with the diamido aluminium hydride [MesN{C(Me)₂C(H)(MeNMes)AlH.NMe₂Et} (TOF = 99.0h⁻¹).^{5c} As expected, a higher reaction temperature (110 °C) and longer reaction time were required for the hydroboration of ketones due to their steric nature.

Table 2.2. Catalytic hydroboration of nitriles^[a]

$ \text{R}\text{C}\equiv\text{N} + 2 \text{H}-\text{B}(\text{OC}(\text{CH}_3)_3)_2 \xrightarrow[1.5 \text{ h, } 110^\circ\text{C, C}_6\text{D}_6]{\text{Catalyst } \mathbf{2.2} \text{ (10 mol\%)}} \text{R}-\text{CH}_2-\text{CH}_2-\text{B}(\text{OC}(\text{CH}_3)_3)_2 $ <p style="text-align: center;">2.7 2.8</p>
<p>2.8a; conversion = 99% (73%); TOF=6.6h⁻¹</p>	<p>2.8b; conversion = 88%; TOF=5.9h⁻¹</p>	<p>2.8c; conversion = 38%; TOF=2.5h⁻¹</p>
<p>2.8d; conversion = 92% (87%); TOF=6.1h⁻¹</p>	<p>2.8e; conversion = 91% (89%); TOF=6.0h⁻¹</p>	<p>2.8f; conversion = 58%; TOF=3.9h⁻¹</p>
<p>2.8g; conversion = 38%; TOF=2.5h⁻¹</p>	<p>2.8h; conversion = 23%; TOF=1.5h⁻¹</p>	

[a] Conversion obtained from integration of ¹H NMR spectroscopy. Isolated yield is written in brackets.

Table 2.3. Catalytic hydroboration of alkynes^[a]

2.10a ; conversion = 97% TOF=1.6h ⁻¹	2.10b ; conversion = 78% TOF=1.3h ⁻¹	2.10c ; conversion= 88% TOF=1.5h ⁻¹
2.10d ; conversion= 88% TOF=1.5h ⁻¹	2.10e ; conversion= 0%	

[a] Conversion obtained from integration of ¹H NMR spectroscopy.

Third, in the presence of complex **2.2** (10 mol%), aryl-substituted nitrile compounds with either electron donating or withdrawing functional groups smoothly reacted with HBpin at 110°C to form the corresponding diboryl amine products [RCH₂N(Bpin)₂] with high yields (Table 2.2, **2.8a**, **2.8b**, **2.8d**, and **2.8e**) demonstrating a negligible electronic effect. Similar substituent effect was reported by Cowley and Thomas when they performed hydroboration of alkenes using aluminium catalyst. ^[31] Increasing the bulkiness of aryl group resulted in slower reaction rate (**2.8c**). Changing the substituting group at nitrile to alkyl group also resulted in slower reaction and lower yields (**2.8f-h**). Similarly, complex **2.2** (10 mol%) can also catalyse hydroboration of

alkyne into trans-boryl alkene *trans*-[Ph(H)C=CH(Bpin)]. Aryl substituted alkynes was catalytically hydroborated in moderate yields (Table 2.3, **2.10a-d**). The activity of **2.2** in terms of TOF (for **2.10a**: 1.6h⁻¹) in these reactions is lower compared with those of the β -diketiminato aluminium hydride complex (TOF for **2.10a**: 2.03 h⁻¹)¹⁰ and *i*Bu₂AlH (TOF for **2.10a**: 4.25 h⁻¹).¹¹ Attempt to hydroborate 1-hexyne did not resulted in any conversion after heated at 110°C for 6hrs. This suggested hydroboration of alkyl-substituted alkynes is harder to be achieved.

Section II.3. Conclusion

In conclusion, a novel aluminium hydride complex **2.2** was synthesised. Detail NMR and x-ray crystallographic analysis were carried out for complex **2.2**. **2.2** is capable to carry out hydroboration of CO₂ at elevated temperature using boranes as hydride source. Stepwise reduction reveal that the first step of the catalysis involves hydride attack of **2.2** onto CO₂ to form formate product **2.4** as intermediate. Calculations suggested that the next step of the mechanism is coordination of the borane. We proposed the last step is regeneration of the **2.2** by σ -bond metathesis between B-H and Al-O. Besides CO₂, **2.2** also show capability to catalyse reduction of different unsaturated bonds, ranging from carbonyl, nitriles and acetylenes.

Section II.4. Experimental

General procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Toluene was dried over and distilled over Na/K alloy prior to use. Dichloromethane were dried with CaH_2 before use. **2.1** were prepared according to the literature procedures. D_6 -benzene was dried and distilled over K metal prior to use. Nitriles and aldehydes were used directly without purification. The NMR spectra were recorded on a JEOL ECA 400 spectrometer and Bruker 400 spectrometer.

(c) Synthesis of **2.2**, **2.4** and **2.4D**

Synthesis of 2.2: $\text{AlH}_3\cdot\text{EtNMe}_2$ (2.0 mmol) was added dropwise to a toluene solution of **2.1** (1.0 mmol) under -78°C . The reaction mixture was raised to room temperature and white suspension was observed in the solution. The mixture was stirred for 1 hour and then dried under vacuum to remove amine. The residue was extracted with 10 ml of toluene to yield a white precipitate. Yield: 0.65 g, 0.92 mmol (91.7% based on **2.1**). Colorless crystals of **2.2** were grown from concentrated toluene solution of **2.2**. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 8.02 (m, 8H, *m*-Ph-*H*), 7.04 (m, 12H, *o,p*-Ph-*H*), 6.55 (s, 4H, *m*-Mes-*H*), 5.00 (br, 2H, AlH_2), 2.23 (s, 12H, *o*- CH_3), 2.01 (s, 6H, *p*- CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, C_6D_6 , ppm): δ 138.30 (t, Ph *m*-C), 137.81 (s, Mes *m*-C), 134.26 (t, Ph *o*-C), 133.96 (s, Mes *o*-C), 131.14 (s, Ph *p*-C), 130.75 (d, $J_{\text{P-C}} = 102.95$ Hz, Ph *ipso*-C), 130.60 (t, P_2C), 129.71 (s, Mes *p*-C), 127.29 (t, $J_{\text{P-C}} = 5.72$ Hz, Mes *ipso*-C), 20.83 (s, Mes *o*- CH_3), 20.42 (s, Mes *p*- CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6) δ 38.98 (s). **HRMS** (ESI): *m/z* calcd for $\text{C}_{43}\text{H}_{45}\text{N}_2\text{AlP}_2\text{Cl}$: 713.2562 $[(\text{M} + \text{H})]^+$; found: 713.2573.

Synthesis of 2.4: **2.2** (1.43 g, 2.0 mmol) was dissolved in 40 ml of toluene in a reaction flask. The reaction mixture was frozen and thawed under vacuum. CO₂ gas (1 bar) was streamed into the flask along with vigorous stirring. After 15 minutes, the reaction mixture was dried under vacuum to yield a white precipitate. Yield: 1.51 g (100%). ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 8.52 (s, 1H, OC=OH), 8.12 (m, 4H, *m*-Ph-*H*), 7.88 (m, 4H, *m*-Ph-*H*), 7.10 (m, 4H, *p*-Ph-*H*), 7.02 (m, 8H, *o*-Ph-*H*), 6.57 (s, 2H, *m*-Mes-*H*), 6.50 (s, 2H, *m*-Mes-*H*), 2.26 (s, 6H, *o*-CH₃), 2.12 (s, 6H, *o*-CH₃), 1.99 (s, 6H, *p*-CH₃). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, ppm): δ 161.6 (s, C(O)H), 138.1 (d, *J*_{P-C} = 53.2 Hz, Mes, ipso-C), 136.4 (s, Mes *o*-C), 134.8 (s, Ph *m*-C), 134.3 (s, Ph *o*-C), 131.5 (s, Mes *p*-C), 131.3 (s, Ph *m*-C), 129.8 (d, *J*_{P-C} = 53.2 Hz, Ph ipso-C), 124.4 (s, Ph *p*-C), 20.8 (s, Mes *p*-CH₃), 20.4 (s, Mes *o*-CH₃), not observable (PCP). ³¹P{¹H} NMR (121.5 MHz, C₆D₆, ppm): δ 40.55 (s). **HRMS** (ESI): *m/z* calcd for C₄₄H₄₅N₂O₂AlP₂Cl: 757.2460 [(M + H)⁺ ; found: 757.2467.

Synthesis of 2.4D: **2.2** (1.43 g, 2.0 mmol) was dissolved in 40 ml of toluene in a reaction flask. The reaction mixture was frozen and thawed under vacuum. CO₂ gas (1 bar) was streamed into the flask along with vigorous stirring. After 16 hrs, white precipitate were observed in the flask. The reaction mixture was dried under vacuum and extracted with DCM (10 ml) hexane (1 ml) mixture. Resulting filtrate was placed under 0°C to yield a colourless crystal of **3**. Yield: 0.08g (5.3%). ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 8.24 (s, 4H, OC=OH), 8.02 (m, 16H, *m*-Ph-*H*), 7.08 (m, 24H, *o,p*-Ph-*H*), 6.52 (s, 8H, *m*-Mes-*H*), 2.13 (s, 24H, *o*-CH₃), 1.98 (s, 12H, *p*-CH₃). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, ppm): δ 161.3 (s, O-CH₂-O), 138.1 (s, Mes *o*-C), 135.5 (s, Ph *m*-C), 135.1 (s, Ph *o*-C), 134.4 (t, Mes, ipso-C), 131.7 (s, Mes *p*-C), 129.8 (s, Ph *m*-C), overlapped with solvent (Ph ipso-C), 124.4 (s, Ph *p*-C), 20.5 (s, Mes *p*-CH₃), 20.3 (s, Mes *o*-CH₃),

not observable (PCP). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6 , ppm): δ 40.55 (s). **HRMS** (ESI): m/z calcd for $\text{C}_{88}\text{H}_{89}\text{N}_4\text{O}_4\text{Al}_2\text{P}_4\text{Cl}_2$: 1513.4842 $[(\text{M} + \text{H})]^+$; found: 1513.4854.

(d) Catalytic hydroboration of CO_2

Hydroboration with HBPIn: In a reaction J-Young type NMR tube, solid of **2.2** (0.035 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0245 g, 0.10 mmol, internal standard) was dissolved in toluene (0.5 ml). HBPIn (0.064g, 0.5 mmol) were then added into the tube. The reaction mixture was frozen and thawed under vacuum. CO_2 gas (>1 bar) was streamed into the tube. The tube was heated under 110°C for 48 hrs. Yield was calculated based on total number of protons converted into methoxy products based on integral of internal standard. Yield = 78.4%.

Hydroboration with BH3: In a reaction J-Young type NMR tube, solid of **2.2** (0.0035 g, 0.005 mmol) was dissolved in toluene (0.5 ml). $\text{BH}_3\cdot\text{SMe}_2$ (0.038g, 0.5 mmol) were then added into the tube. The reaction mixture was frozen and thawed under vacuum. CO_2 gas (>1 bar) was streamed into the tube. The tube was heated under 80°C for 16 hrs or 110°C for 1 hr. CH_3 protons of SMe_2 were used as the internal standard for calculating yield. Yield was calculated based on total number of protons converted into methoxy products. Yield = 97.6% at 110°C and <1% at 80°C .

Hydroboration with HBCat: In a reaction J-Young type NMR tube, solid of **2.2** (0.035 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0182 g, 0.074 mmol, internal standard) was dissolved in toluene (0.5 ml). HBCat (0.064g, 0.5 mmol) were then added into the tube. The reaction mixture was frozen and thawed under vacuum. CO_2 gas (>1 bar)

was streamed into the tube. The tube was heated under 110 °C for 24 hrs. Yield was calculated based on total number of protons converted into methoxy products based on integral of internal standard. Yield = 28.8%.

(e) Catalytic hydroboration of other substrates

General procedures for hydroboration of carbonyl, nitriles and acetylenes.

Hydroboration (table 2.2, table 2.3 and table 2.4) were performed in J-Young NMR tube under Ar gas. Compound **2.2** was dissolved into 0.5 ml of C₆D₆ in glovebox filled with Ar gas. HBPin was then added into the solution and followed by addition of substrate. The solution was stirred with a stirrer and heated with a beaker of oil bath. The conversion percentage of substrate was obtained by analysing ¹H NMR spectroscopy (C₆D₆) of the reaction solution after the measured time interval. Isolated yield of selected products were measured. The products were isolated by drying with vacuum pump followed by extraction with n-hexane. The isolated yield was measured by weight of the obtained products.

1. Catalytic hydroboration of aldehyde

2.6a: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. PhCHO(**2.5a**) (0.050 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 60 minutes. Conversion percentage of 93% into **2.6a** was observed from ¹H NMR. The reaction solution was further heated under 60 °C for 30 minutes. A conversion of >99% were observed. Product **2.6a** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.109 g, 96 %. ¹H NMR (395.9

MHz, C₆D₆, ppm): δ 7.30-7.28 (m, 2H), 7.14-7.11 (m, 2H), 7.09-7.04 (m, 1H) 4.94 (s,2H), 1.04 (s,12H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.83.

2.6b: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. o-MePhCHO(**2.5b**) (0.060 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 120 minutes. A conversion of 97% were observed. Product **2.6b** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.116 g, 94 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.55 (d, J = 7.3 Hz, 1H), 7.07 (m, 2H), 6.95 (d, J = 7.3Hz, 1H), 4.97 (s, 2H), 2.07 (s, 3H), 1.05 (s, 12H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.65

2.6c: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. p-MePhCHO(**2.5c**) (0.060 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 120 minutes. A conversion of >99% were observed. Product **2.6c** was not isolated. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.23 (d, J = 7.8Hz, 2H), 6.96 (d, J = 7.8Hz, 2H), 4.93 (s,2H), 2.09 (s,3H), 1.05 (s,12H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.86.

2.6d: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. p-(CO₂Me)PhCHO(**2.5d**) (0.082 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 60 minutes. A conversion of 89% were observed. Product **2.6d** was not isolated. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 8.02 (d, J = 8.2Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 4.84 (s,2H), 3.51 (s,3H), 1.04 (s,12H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.56.

2.6e: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. p-CF₃PhCHO(**2.5e**) (0.087 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 180 minutes. A conversion of >99% were observed. Product **2.6e** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.143 g, 95 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.29 (d, J = 8.2Hz, 2H), 7.08 (d, J = 7.7 Hz, 2H), 4.78 (s,2H), 1.04 (s,12H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.62. ¹⁹F NMR (128 MHz, C₆D₆, ppm): δ -62.10.

2.6f: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. p-MeOPhCHO(**2.5f**) (0.068 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 60 minutes. A conversion of 93% were observed. Product **2.6f** was not isolated. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.24 (m, 2H), 6.74 (m, 2H), 4.90 (s,2H), 3.32 (s,3H), 1.06 (s,12H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.83.

2.6g: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. PrCHO(**2.5g**) (0.036 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 60 minutes. A conversion of 92% were observed. Product **2.6g** was not isolated. ¹H NMR (395.9 MHz, C₆D₆, ppm): 3.68 (d, J = 6.44Hz, 2H), 1.77 (sept, 1H), 1.06 (s, 12H), 0.83 (d, J = 6.40Hz, 6H). ¹¹B NMR (128 MHz, C₆D₆): 21.53.

2.6h: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. *t*BuCHO(**2.5h**) (0.043 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 60 minutes. A

conversion of 93% were observed. Product **2.6h** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.094 g, 88 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): 3.67 (s, 2H), 1.07 (s, 12H), 0.91 (s, 9H). ¹¹B NMR (128 MHz, C₆D₆): 21.64.

2.6i: In a glovebox, compound **2.2** (0.0175 g, 0.025 mmol) was dissolved in 0.5 ml C₆D₆. cyHexCHO(**2.5i**) (0.056 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 60 °C for 60 minutes. A conversion of >99% were observed. Product **2.6i** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.110 g, 92 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): 3.79 (d, J = 6.40Hz, 2H), 1.75-1.70 (m, 2H), 1.63-1.59 (m, 2H), 1.56-1.45 (m, 2H), 1.18-1.04 (m, 3H), 1.08 (s, 12H), 0.97-0.84 (m, 2H). ¹¹B NMR (128 MHz, C₆D₆): 21.58.

2.6j: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. PhC=OMe(**2.5j**) (0.060 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 6 hours. A conversion of 88% were observed. Product **2.6j** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.084 g, 68 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.35-7.00 (m, 5H), 5.39 (m, 1H), 1.43 (d, J = 6.80Hz, 3H), 1.00 (s, 6H), 0.97 (s, 6H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.68.

2.6k: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. C₁₀H₇C=OMe(**2.5k**) (0.085 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 6 hours. A conversion of 70% were observed. Product **2.6k** was isolated by drying the reaction

solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.080 g, 54 %. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.97 – 7.95 (m, 1H), 7.86 (d, 1H), 7.64 – 7.61 (m, 1H), 7.54 (d, 1H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 6.17 (q, 1H), 1.62 (d, , J = 6.40Hz, 3H), 1.02 (s, 6H), 0.98 (s, 6H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 22.25.

2.6I: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . $i\text{PrC=OMe}$ (**2.5I**) (0.043 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 6 hours. A conversion of 89% were observed. Product **2.6I** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.078 g, 73 %. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 4.18 – 4.12 (m, 1H), 1.68-1.63 (m, 1H), 1.16 (d, J = 6.40Hz, 3H), 1.07 (s, 12H), 0.92 (d, J = 6.88Hz, 3H), 0.86 (d, J = 6.84Hz, 3H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 21.47.

2. Catalytic hydroboration of nitriles

2.8a: In a glovebox, compound **2.2** (0.0143 g, 0.02 mmol) was dissolved in 0.5 ml C_6D_6 . PhCN (**2.7a**) (0.021 g, 0.20 mmol) and HBPin (0.051 g, 0.40 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of >99% were observed. Product **2.8a** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.052 g, 72 %. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.60 (d, J = 7.2 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 4.62 (s, 2H), 1.05 (s, 24H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 26.73.

2.8b: In a glovebox, compound **2.2** (0.0143 g, 0.02 mmol) was dissolved in 0.5 ml C₆D₆. p-MeOPhCN(**2.7b**) (0.027 g, 0.20 mmol) and HBPIn (0.051 g, 0.40 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 88% were observed. Product **2.8b** was not isolated. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.54 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.56 (s, 2H), 3.36 (s, 3H), 1.05 (s, 24H).

2.8c: In a glovebox, compound **2.2** (0.0143 g, 0.02 mmol) was dissolved in 0.5 ml C₆D₆. MesCN(**2.7c**) (0.029 g, 0.20 mmol) and HBPIn (0.051 g, 0.40 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 38% were observed. Product **2.8c** was not isolated. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 6.79 (s, 2H), 4.55 (s, 2H), 2.51 (s, 6H), 2.17 (s, 3H), 1.00 (s, 24H).

2.8d: In a glovebox, compound **2.2** (0.0143 g, 0.02 mmol) was dissolved in 0.5 ml C₆D₆. p-CF₃PhCN(**2.7d**) (0.034 g, 0.20 mmol) and HBPIn (0.051 g, 0.40 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 92% were observed. Product **2.8d** was isolated by drying the reaction solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.074 g, 87 %. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.42 – 7.39 (m, 2H), 6.91 – 6.86 (m, 2H), 4.46 (s, 2H), 1.02 (s, 24H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 26.44. ¹⁹F NMR (128 MHz, C₆D₆, ppm): δ -61.86.

2.8e: In a glovebox, compound **2.2** (0.0143 g, 0.02 mmol) was dissolved in 0.5 ml C₆D₆. m-F₂PhCN(**2.7e**) (0.028 g, 0.20 mmol) and HBPIn (0.051 g, 0.40 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 91% were observed. Product **2.8e** was isolated by drying the reaction

solution under vacuum followed by extraction with n-hexane. Isolated Yield: 0.070 g, 89 %. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.35 (s, 3H), 4.41 (s, 2H), 0.95 (s, 24H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 25.59. ^{19}F NMR (128 MHz, C_6D_6 , ppm): δ -62.59.

2.8f: In a glovebox, compound **2.2** (0.0357 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . MeCN(**2.7f**) (0.020 g, 0.5 mmol) and HBPin (0.128 g, 1.0 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 58% were observed. Product **2.8f** was not isolated. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 3.40 (q, J = 6.7 Hz, 2H), 1.27 (t, J = 6.9 Hz, 3H), 1.06 (s, 24H).

2.8g: In a glovebox, compound **2.2** (0.0357 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . PrCN(**2.7g**) (0.035 g, 0.5 mmol) and HBPin (0.128 g, 1.0 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 38% were observed. Product **2.8g** was not isolated. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 3.42 (7.), 1.75-1.66 (m, 2H), 1.41-1.34 (m, 2H), 1.03 (s, 24H), 0.83-0.78 (m, 3H).

2.8h: In a glovebox, compound **2.2** (0.0143 g, 0.02 mmol) was dissolved in 0.5 ml C_6D_6 . BnCN(**2.7h**) (0.023 g, 0.20 mmol) and HBPin (0.051 g, 0.40 mmol) were then added into the solution. The solution was heated under 110 °C for 90 minutes. A conversion of 23% were observed. Product **2.8h** was not isolated. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.26-7.10 (m, 5 H), 3.64 (t, J = 7.80 Hz, 2H), 2.97 (t, J = 7.32 Hz, 2H), 0.99 (s, 24 H).

3. Catalytic hydroboration of acetylenes

2.10a: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. PhCCH(**2.9a**) (0.051 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 60 minutes. A conversion of 97% were observed. The reaction solution is further heated for 12hrs to achieve complete conversion of >99%. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.76 (d, J = 18.32 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.03 – 7.00 (m, 3H), 6.46 (d, J = 18.32 Hz, 1H), 1.13 (s, 12H).

2.10b: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. p-FPhCCH(**2.9b**) (0.060 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 60 minutes. A conversion of 78% were observed. The reaction solution is further heated for 12hrs to achieve complete conversion of >99%. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.60 (d, J = 18.32 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.67 – 6.62 (m, 2H), 6.26 (d, J = 18.32 Hz, 1H), 1.13 (s, 12H).

2.10c: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. p-CF₃PhCCH(**2.9c**) (0.085 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 60 minutes. A conversion of 88% were observed. The reaction solution is further heated for 12hrs to achieve complete conversion of >99%. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.55 (d, J = 18.32 Hz, 1H), 7.19 (d, J = 8.24 Hz, 2H), 7.05 (d, J = 8.24 Hz, 2H), 6.35 (d, J = 18.32 Hz, 1H), 1.13 (s, 12H).

2.10d: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. p-MeOPhCCH(**2.9d**) (0.066 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were

then added into the solution. The solution was heated under 110 °C for 60 minutes. A conversion of 88% were observed. The reaction solution is further heated for 12hrs to achieve complete conversion of >99%. ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 7.78 (d, J = 18.32 Hz, 1H), 7.29 (d, J = 8.24 Hz, 2H), 6.61 (d, J = 8.24 Hz, 2H), 6.36 (d, J = 18.32 Hz, 1H), 3.22 (s, 3H), 1.15 (s, 12H).

2.10e: In a glovebox, compound **2.2** (0.035 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. CH₃(CH₂)₃CCH(**2.9e**) (0.041 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated under 110 °C for 60 minutes. No conversion were observed.

Section II.5. Appendixes

Selected spectra

Figure 2.S1. ^1H NMR spectrum of compound 2.2 (C_6D_6)

Figure 2.S2. ^{13}C NMR spectrum of compound 2.2 (C_6D_6)

Figure 2.S3. ^{31}P NMR spectrum of compound **2.2** (C_6D_6)

Figure 2.S4. ^1H NMR spectrum of compound **2.4** (C_6D_6)

Figure 2.S5. ^{13}C NMR spectrum of compound 2.4 (C_6D_6)

Figure 2.S6. ^{31}P NMR spectrum of compound 2.4 (C_6D_6)

Figure 2.S7. ¹H NMR spectrum of compound **2.4D** (C₆D₆)

Figure 2.S8. ¹³C NMR spectrum of compound **2.4D** (C₆D₆)

Figure 2.S9. ^{31}P NMR spectrum of compound 2.4D (C_6D_6)

Figure 2.S10. ^1H NMR spectrum of hydroboration of CO_2 using HBPIn

Figure 2.S11. ¹H NMR spectrum of hydroboration of CO₂ using BH₃SMe₂ at 80°C

Figure 2.S12. ¹H NMR spectrum of hydroboration of CO₂ using BH₃SMe₂ at 110°C

Figure 2.S13. ^{13}B NMR spectrum of hydroboration of CO_2 using BH_3SMe_2 at 110°C

Figure 2.S14. ^1H NMR spectrum of hydroboration of CO_2 using HBCat

Figure 2.S15. ¹H NMR spectrum of 2.6a

Figure 2.S16. ¹³B NMR spectrum of 2.6a

Figure 2.S17. ^1H NMR spectrum of 2.6b

Figure 2.S18. ^{13}B NMR spectrum of 2.6b

Figure 2.S19. ¹H NMR spectrum of 2.6c

Figure 2.S20. ¹³C NMR spectrum of 2.6c

Figure 2.S21. ¹H NMR spectrum of 2.6d

Figure 2.S22. ¹³B NMR spectrum of 2.6d

Figure 2.S23. ^1H NMR spectrum of 2.6e

Figure 2.S24. ^{13}B NMR spectrum of 2.6e

Figure 2.S25. ^{19}F NMR spectrum of 2.6e

Figure 2.S26. ^1H NMR spectrum of 2.6f

Figure 2.S27. ^{13}B NMR spectrum of **2.6f**

Figure 2.S28. ^1H NMR spectrum of **2.6g**

Figure 2.S29. ^{13}B NMR spectrum of 2.6g

Figure 2.S30. ^1H NMR spectrum of 2.6h

Figure 2.S31. ^{13}B NMR spectrum of **2.6h**

Figure 2.S32. ^1H NMR spectrum of **2.6i**

Figure 2.S32. ^{13}B NMR spectrum of 2.6i

Figure 2.S33. ^1H NMR spectrum of 2.6j

Figure 2.S34. ^{13}B NMR spectrum of **2.6j**

Figure 2.S35. ^1H NMR spectrum of **2.6k**

Figure 2.S36. ^{13}B NMR spectrum of 2.6k

Figure 2.S37. ^1H NMR spectrum of 2.6l

Figure 2.S38. ^{13}B NMR spectrum of **2.6I**

Figure 2.S39. ^1H NMR spectrum of **2.8a**

Figure 2.S40. ^{13}B NMR spectrum of **2.8a**

Figure 2.S41. ^1H NMR spectrum of **2.8b**

Figure 2.S42. ¹H NMR spectrum of **2.8c**

Figure 2.S43. ¹H NMR spectrum of **2.8d**

Figure 2.S44. ^{13}B NMR spectrum of 2.8d

Figure 2.S45. ^{19}F NMR spectrum of 2.8d

Figure 2.S46. ¹H NMR spectrum of 2.8e

Figure 2.S47. ¹³B NMR spectrum of 2.8e

Figure 2.S48. ¹⁹F NMR spectrum of 2.8e

Figure 2.S49. ¹H NMR spectrum of 2.8f

Figure 2.S50. ¹H NMR spectrum of 2.8g

Figure 2.S51. ¹H NMR spectrum of 2.8h

Figure 2.S52. ^1H NMR spectrum of 2.10a

Figure 2.S53. ^1H NMR spectrum of 2.10b

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Chapter III. Exploring the catalytic reactivity of P-H bond on a N-heterocyclic carbene phosphinidene adduct.

III.1. Introduction

Chart 3.1. Electronic structure of Phosphines.

In this chapter, we discuss capability of low-valent phosphorous compounds, that is, phosphinidene toward catalytic reduction of unsaturated compounds. The chemistry of phosphines has been well established. Typical phosphines (R_3P) consist of a lone pair orbital and available σ^* orbitals of P-R bonds (Chart 3.1), which serve as ligands in transition metal catalysts or play a vital role in FLP^[1] and organocatalysis^[2].

Chart 3.2. Formation of the phosphine $\rightarrow$ CPh₃⁺ adduct.

In contrast, the use of phosphines, which comprise a P-H bond, as an alternative to transition metal hydride complexes in catalysis is less studied. It is because the small difference in electronegativity between P and H atoms leads to almost non-polar P-H bond. The H atom in a P-H bond usually show non-hydridic character. For example,

Lambert et al. showed that the secondary phosphine did not undergo a hydride abstraction with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, instead the phosphine $\rightarrow \text{CPh}_3^+$ adduct was afforded (Chart 3.2).^[3]

Chart 3.3. Hydride abstraction from phosphine.

To increase the hydridic character in a P-H bond, the research group of Corriu showed that the coordination of a Lewis base in a chelating ligand to the P atom can enhance the hydridic character of a P-H bond (Chart 3.3),^[4] which resulted in undergoing a hydride abstraction with $[\text{Ph}_3\text{C}][\text{PF}_6]$ to form a phosphonium salt.

Chart 3.4. Stoichiometric reduction of benzaldehyde by 1,3,2-diazophosphalene.

A more hydridic P-H bond was synthesized by the research group of Gudat,^[5] whereby a 1,3,2-diazophosphalene exhibited π -delocalization in the back-bone leading to hydridic character in a P-H bond. Calculations showed that the six π -electrons in the C_2N_2 unit hyperconjugated into the P-H σ^* -orbital and hence resulted in weakening the P-H bond.^[6] The enhanced hydridic character allowed the 1,3,2-diazophosphalene

to perform a stoichiometric reduction of benzaldehyde to form the corresponding benzyloxy derivative (Chart 3.4).

3.A

Chart 3.5. σ -bond metathesis and catalytic hydroboration of benzaldehyde.

The research group of Kinjo further used a stoichiometric amount of HBPIn to perform a σ -bond metathesis with the benzyloxy derivative to regenerate the P-H bond.^[7] This σ -bond metathesis completed the catalytic cycle and allowed the 1,3,2-diazaphospholes **3.A** to perform catalytic hydroboration of carbonyl products (Chart 3.5). These indicate the hydridic character of P-H bond is crucial in catalytic transformation.

Chart 3.6. Examples of catalytic reduction catalysed by 1,3,2-diazaphospholene **3.A**.

After that, the 1,3,2-diazaphospholene emerged as a versatile catalyst in catalysing various organic reactions, such as the reduction of diazenes, unsaturated esters and carbon dioxide(Chart 3.6, top).^[8] Speed et al. also showed that the 1,3,2-diazaphospholene catalysed the reduction of imines and conjugate acceptors(Chart 3.6, bottom).^[9]

Chart 3.7. NHC=PH and its reactivity towards borane and transition metal complexes.

Recently, N-heterocyclic carbene phosphinidene adducts $[(\text{NHC})\text{PH}]$ has attracted much attention.^[10] Its reactivity is governed by the inversely polarized C-P bond as well as the lone pair orbital of the P atom. Research groups of von Hähnisch^[11] and Bertrand independently showed that $[(\text{NHC})\text{PH}]$ ($\text{NHC} = [\text{:C}(\text{N}(\text{Ar}^*)\text{CH})]$, $\text{Ar}^* = 2,6$ -dibenzhydryl-4-methylphenyl; Chart 3.7 top) coordinated with Lewis acids such as $\text{BH}_3 \cdot \text{SMe}_2$ to form the corresponding borane adducts.^[12] Tamm et al. also showed that $[(\text{NHC})\text{PH}]$ ($\text{NHC} = [\text{:C}(\text{N}(\text{Dipp})\text{CH})]$; Chart 3.7 bottom) is a very strong electron donating ligand to coordinate with transition metals.^[13]

3.A

$\delta = 6.07$ ppm

$^1J(\text{P,H}) = 181$ Hz

3.1

$\delta = 2.63$ ppm

$^1J(\text{P,H}) = 166$ Hz

Chart 3.8. Comparison of chemical shift and coupling constants.

On the basis of the fact that the decrement of *p*-character in a P centre results in weakening the P-H bond, the P-H bond in (NHC)PH **3.1** (NHC =[:C(N(*i*Pr)CH)]; Chart 3.8) should be more reactive than 1,3,2-diazaphospholene (**3.A**) as the P centre possess a sp^2 hybridization. In comparison the ^{31}P NMR signals of the **3.A** and **3.1**, **3.1** has a weaker P-H bond ($J_{\text{P-H}} = 164$ Hz)^[15] than that in **3.A** ($J_{\text{P-H}} = 181$ Hz).^[5c] In addition, the P-H chemical shift in **3.1** is more upfield than **3.A**, indicating more hydridic character of P-H bond. In this context, **3.1** should be a promising candidate for metal-free catalytic hydroboration.

In this chapter, we discuss the catalytic activity of (NHC)PH **3.1** toward hydroboration of benzaldehyde and carbon dioxide. Preliminary mechanistic studies suggested that the first step of catalysis does not involve the coordination of **3.1** to HBPin. Exposure of **3.1** under atmosphere of carbon dioxide suggested the P-H insertion into carbon dioxide occurred. A mechanism is proposed based on the available preliminary results.

Section II.2. Results and discussion

Scheme 3.1. Testing stability of compound **3.1**.

First, the stability of **3.1** was tested in various deuterated solvents (Scheme 3.1). Compound **3.1** rapidly decomposed in CDCl_3 to form red precipitate, which is silent in both ^1H and ^{31}P NMR. In addition, **3.1** reacted with d-acetonitrile, whereby the P-H bond inserted into the $\text{C}\equiv\text{N}$ bond confirmed by ^1H and ^{31}P NMR spectroscopy. However, **3.1** is stable in d-benzene for more than 48hrs. Hence, d-benzene was chosen as the reaction solvent for hydroboration of aldehydes.

Then, **3.1** was used to catalyse hydroboration of benzaldehyde **3.2a**. In a J-Young NMR tube, 1 mol% of **3.1** was mixed with **3.2a**, followed by addition of 1.2eq of HBPIn. The reaction mixture was stirred for 20 mins, whereby **3.3a** (conversion: 45.0%) was achieved confirmed by ^1H NMR analysis. The solution was further stirred for 1hr, but did not show any further conversion. The hydroboration did not further proceed even heating the reaction solution at 60°C for 16hrs. This indicated that compound **3.1** is not stable in catalysis. This prompted us to increase the loading of the catalyst to 10 mol% whereby complete conversion was achieved in 20 mins (Table 3.1, **3.2a**).

Table 3.1. Catalytic hydroboration of aldehydes.

[a] Conversions was obtained from integration of ¹H NMR

Using the optimized reaction conditions, the scope of this catalytic reaction was tested with other aldehydes (**3.2b-f**). Hydroboration of aromatic aldehyde with electron withdrawing group such as CF₃ group at the para position of phenyl ring was catalysed in a faster rate (10 min). In contrast, the electron donation group at the ortho position of phenyl ring resulted in a slower reaction rate (**3.2c**, 20 mins, 35% conversion). The conversion can increase to 92 % when the reaction was reacted for 24 hrs. Importantly, aliphatic aldehydes (**3.2d-f**) were catalysed in a faster rate (TOF = 30-40 h⁻¹) than 1,3,2-diazaphospholene **3.A** (TOF = 19-21 h⁻¹). Even the sterically hindered aliphatic aldehydes (**3.2f**) could achieve complete conversion in 15 mins stirring at room temperature. For comparison, the turnover frequency (TOF=36 h⁻¹) of catalysing

hydroboration of aldehyde **3.2f** is higher compared to that using diazophospholenes as catalysts ($\text{TOF} = 20.4 \text{ h}^{-1}$).^[7] This suggested catalyst **3.1** has comparable catalytic ability as the diazophospholenes catalyst reported by Kinjo et. al.

Scheme 3.2. Testing **3.1** as catalyst of hydroboration of different substrates.

To test the catalytic capability of **3.1** toward other functional groups, hydroboration of ketones, acetylene, nitriles and CO_2 were tested (Scheme 3.2). Nitriles and acetylene did not show any sign of catalytic transformation even at 110°C for 24hrs. Hydroboration of ketone **3.4a** was achieved by using **3.1** as the catalyst. Stirring **3.4a** together with HBPin in the presence of 10 mol% **3.1** at room temperature for 1hr resulted in 78% conversion into **3.5a** ($\text{TOF}=7.8\text{h}^{-1}$). Further stirring the reaction solution for 2hrs can lead to full conversion. Compound **3.1** can also selectively mediate catalytic hydroboration of CO_2 (1 bar) at room temperature for 16h to form **3.5d** in 26%. Heating up the reaction solution resulted in no catalytic transformation

along with formation of red precipitate. This suggested high temperature might denature the catalyst. The reason for these poor catalytic properties might be due to the non-polar reaction solvent. Considered the good catalytic properties of diazophospholenes catalyst in polar solvents,^[8,9] we proposed that changing to a more polar solvent might facilitate the catalytic reactions.

Scheme 3.3. catalytic hydrosilylation using compound **3.1**.

10 mol% of **3.1** was also used to catalyse hydrosilylation of CO_2 with Ph_2SiH_2 in d-benzene, but no conversion was observed even at 60°C for 2hrs. When the solvent was changed to d-acetonitrile, at 15min of reaction time, some formatosilane product **3.5e** was generated along with some resonances at methoxy region. After 1 hr of stirring, all the diphenylsilane and formatosilane **3.5e** were consumed (Scheme 3.3.). Multiple products, which show ^1H NMR signals at methoxy region. This suggested that the formatosilane **3.5e** was further reduced into methoxy derivatives. Note that compound **3.1** could not be the actual catalyst for this reaction as it is not stable in d-acetonitrile.

Scheme 3.4. Reaction of **3.1** with HBPIn.

To gain an insight into the mechanism of the catalytic hydroboration of CO₂, stepwise mechanistic study was performed. First, HBPIn and **3.1** were mixed in a 1:1 ratio, whereby only unreacted starting materials were observed in ¹H, ³¹P and ¹¹B NMR spectroscopy (Scheme 3.4). This indicated that the first step of the catalysis does not involve the coordination of **3.1** with HBPIn.

Scheme 3.5. Stepwise reaction of **3.1** with carbon dioxide.

3.1 was exposed to CO₂ atmosphere to immediately form a red precipitate at room temperature (Scheme 3.5), which was insoluble in most organic solvents. An attempt to crystallize the precipitate was not successful. The ³¹P{¹H} NMR of the reaction mixture showed one signal at -241.4ppm. The ³¹P NMR showed a quartet at -241.4ppm (³J_{PH}=184.86Hz). This indicates that there are three neighboring H atoms to the P atom. When the reaction was repeated at -40°C, on top of the signal at -241.4ppm, a triplet at -212.1ppm (³J_{PH} = 198.56 Hz) was observed. This indicates that there are two neighboring H atoms to the P atom. The ¹H NMR has multiple signals, but two doublets at 1.53 ppm (³J_{PH}=188.12Hz) and 2.08 ppm (³J_{PH}=199.16Hz) were observed with same coupling constant as found in the ³¹P NMR. With these NMR data, it is proposed that compounds **3.7** and **3.8** could be formed in the reaction, which were further conformed by HR-MS with m/z: [M + H]⁺ value of 413 and 215 respectively.

Scheme 3.6. Proposed intermediates.

The formation of intermediates **3.7** and **3.8** suggested that **3.1** could undergo hydride attack to CO₂ at -40°C to form intermediate **3.6**, which then undergoes further hydride insertion with **3.1** to form **3.7**, **3.8** (Scheme 3.6). Note that intermediate **3.6** and **3.9** were not observed in ³¹P NMR.

On the basis of the proposed intermediate **3.6**, it is suggested that the catalytic hydroboration should involve σ -bond metathesis between P-O bond with HBPin. To support this, **3.1** was exposed to atmosphere of CO₂ at -78°C and was left to warm to room temperature. Once the red precipitate was formed in the reaction mixture, one equivalent of HBPin was added, which results in a new signal at 8.62 ppm in the ¹H NMR spectroscopy, suggesting the formation of **3.5d**. This proves that the intermediate **3.6** exists and undergoes σ -bond metathesis with HBPin to form **3.5d**. In addition, the ³¹P NMR of the reaction mixture showed the presence of **3.1**, **3.7** and **3.8**. The presence of **3.7** and **3.8** suggest that **3.1** reacts with CO₂ to form **3.6**, **3.7** and **3.8**, but only **3.6** can react with HBPin to form **3.5d** and regenerate **3.1**. These explain the low yield (26%) of **3.5d** in the **3.1**-catalysed hydroboration of CO₂. This suggested the metathesis of P-O bond in **3.6** is favourable than that in **3.7** and **3.8**. This also explain the selective formation of **3.5d** in the catalytic hydroboration of CO₂.

Scheme 3.7. Proposed catalytic cycle.

A mechanism cycle was proposed based on the above experiments (Scheme 3.7). First, **3.1** undergoes hydride attack to form intermediate **3.6**. Next, HBPIn undergoes a σ -bond metathesis with **3.6** via a 4-membered intermediate. This resulted in formation of **3.5d** along with regeneration of the catalyst **3.1**.

Section III.3. Conclusion and future work

In conclusion, NHC=PH **3.1** was found to be able to catalyse reduction of aldehyde, ketones and CO₂. The hydroboration of aldehyde catalysed by **3.1** has a moderate rate of reaction (TOF=10-60 h⁻¹) which is comparable to the 1,3,2-diazaphospholene **3.A** catalyst. Particularly, **3.1** catalyse hydroboration of aliphatic aldehydes (TOF=30-40 h⁻¹) faster than **3.A**(TOF=19-21 h⁻¹). **3.1** can also perform catalytic hydroboration of CO₂ with a low yield (26%). Stepwise reaction suggested that the first step of the catalytic reduction of CO₂ started by hydride attack of the P-H to form the formate product **3.6**. **3.6** then rapidly undergoes further reduction to form **3.7** and **3.8** which explains the low yield of the catalyst. A mechanism was proposed based on the available information.

This work opens the possibility of utilising the P-H bond reactivity of NHC=PH in doing catalysis. It is interesting to explore further the chemistry of these P-H bonds as the electronic property of the coordinating carbene can be easily altered. A choice of different carbene could lead to a better catalytic property.

For example, the poor stability of **3.1** in polar solvents had hindered our choice of solvent. Based on the experiment to perform hydrosilylation of CO₂ in d-ACN, it seems like the reactivity of **3.1** is faster in polar solvents. Hence, our future work will be focused on changing the coordinating carbene into a bulkier carbene to obtain a more stable NHC=PH.

Section III.4. Experimental

General procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Toluene was dried over and distilled over Na/K alloy prior to use. Dichloromethane were dried with CaH_2 before use. **3.1** were prepared according to the literature procedures. D_6 -benzene was dried and distilled over K metal prior to use. Nitriles and aldehydes were used directly without purification. The NMR spectra were recorded on a JEOL ECA 400 spectrometer and Bruker 400 spectrometer.

Catalytic hydroboration of aldehyde

3.3a: (1mol% catalyst) In a glovebox, compound **3.1** (0.0046 g, 0.025 mmol) was dissolved in 0.5 ml C_6D_6 . PhCHO(**3.2a**) (0.250 g, 2.50 mmol) and HBPin (0.320 g, 0.50 mmol) were then added into the solution. The solution was stirred with a stirrer. After stirring for 20minutes, the stir bead was removed and the conversion percentage was recorded by ^1H NMR. Conversion: 45.0%. Stirrer was added back to the reaction solution and stirred for another hour. ^1H NMR was checked after 1hr of stirring. Conversion: 45.0%. Then, the reaction solution was heated in a 60°C oil bath for 16hrs. ^1H NMR show no further conversion.

3.3a: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . PhCHO(**3.2a**) (0.050 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was stirred with a stirrer. After stirring for 20minutes, the stir bead was removed and the conversion percentage was recorded by ^1H NMR. Conversion: >99%. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.28-7.25 (m, 2H), 7.15-7.12

(m, 2H), 7.10-7.08 (m, 1H), 4.90 (s, 2H), 1.04 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 21.86.

3.3b: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . *p*- CF_3PhCHO (**3.2b**) (0.087 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was shaken vigorously. After 10 minutes, the conversion percentage was recorded by ^1H NMR. Conversion: >99%. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.29 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 4.78 (s, 2H), 1.04 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 21.8. ^{19}F NMR (128 MHz, C_6D_6 , ppm): δ -62.06.

3.3c: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . *p*-MeOPhCHO (**3.2c**) (0.068 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was stirred with a stirrer. After stirring for 20 minutes, the stir bead was removed and the conversion percentage was recorded by ^1H NMR. Conversion: 35%. Next, the stirrer was added back to the reaction solution and further stirred for 24 hrs. At the end of 24 hrs, ^1H NMR were recorded. Conversion: 92% ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.28-7.25 (m, 2H), 6.77-6.73 (m, 2H), 4.94 (s, 2H), 3.28 (s, 3H), 1.05 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 21.63.

3.3d: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . *i*PrCHO (**3.2d**) (0.036 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was shaken vigorously. After 15 minutes, the conversion percentage was recorded by ^1H NMR. Conversion: >99%. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 3.72 (d, J = 6.40 Hz, 2H), 1.79 (sept, J = 6.40 Hz, 1H), 1.06 (s, 12H), 0.85 (d, J = 6.88 Hz, 6H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 21.62.

3.3e: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. *t*BuCHO (**3.2e**) (0.043 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was stirred with a stirrer. After stirring for 15 minutes, the stir bead was removed and the conversion percentage was recorded by ¹H NMR. Conversion: 77%. Next, the stirrer was added back to the reaction solution and further stirred for 1 hr. At the end of 1 hr, ¹H NMR were recorded. Conversion: >99% ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 3.66 (s, 2H), 1.07 (s, 12H), 0.90 (s, 9H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 21.65.

3.3f: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. cycHexCHO (**3.2f**) (0.056 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was stirred with a stirrer. After stirring for 15 minutes, the stir bead was removed and the conversion percentage was recorded by ¹H NMR. Conversion: 90%. Next, the stirrer was added back to the reaction solution and further stirred for 1 hr. At the end of 1 hr, ¹H NMR were recorded. Conversion: >99% ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 3.79 (d, J = 6.40 Hz, 2H), 1.75-1.70 (m, 2H), 1.63-1.58 (m, 2H), 1.56-1.45 (m, 2H), 1.18-1.04 (m, 3H), 1.08 (s, 12H), 0.97-0.91 (m, 2H). ¹¹B NMR (128 MHz, C₆D₆, ppm): δ 22.54.

Catalytic hydroboration of other substrates

3.5a: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C₆D₆. *p*-CF₃PhCOMe (**3.4a**) (0.094 g, 0.50 mmol) and HBPin (0.064 g, 0.50 mmol) were then added into the solution. The solution was stirred with a stirrer. After stirring for 1 hr, the stir bead was removed and the conversion percentage was recorded by ¹H NMR. Conversion: 78%. Next, the stirrer was added back to the reaction solution and further

stirred for 2 hrs. At the end of 3rd hr, ^1H NMR were recorded. Conversion: >99%. ^1H NMR (395.9 MHz, C_6D_6 , ppm): δ 7.28-7.25 (m, 2H), 7.12-7.09 (m, 2H), 5.22-5.18 (m, 1H), 1.27 (d, $J = 6.40$ Hz, 3H), 0.97 (s, 6H), 0.94 (s, 6H). ^{11}B NMR (128 MHz, C_6D_6 , ppm): δ 21.40. ^{19}F NMR (128 MHz, C_6D_6 , ppm): δ -62.07.

Attempt to reduce **3.4b**: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . PhCN (**3.4b**) (0.050 g, 0.50 mmol) and HBPIn (0.128 g, 1.0 mmol) were then added into the solution. The solution was heated at 110°C . 24 hrs, the conversion percentage was recorded by ^1H NMR. Only starting material was observed in the reaction solution. Conversion: 0%.

Attempt to reduce **3.4c**: In a glovebox, compound **3.1** (0.0092 g, 0.05 mmol) was dissolved in 0.5 ml C_6D_6 . PhCCH (**3.4c**) (0.050 g, 0.50 mmol) and HBPIn (0.064 g, 0.50 mmol) were then added into the solution. The solution was heated at 110°C . 24 hrs, the conversion percentage was recorded by ^1H NMR. Only starting material was observed in the reaction solution. Conversion: 0%.

3.5d: In a reaction J-Young type NMR tube, solid of **3.1** (0.0092 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0245 g, 0.10 mmol, internal standard) was dissolved in C_6D_6 (0.5 ml). HBPIn (0.064 g, 0.5 mmol) were then added into the tube. The reaction mixture was frozen and thawed under vacuum. CO_2 gas (>1 bar) was streamed into the tube. The tube was stirred with a stirrer. After 16 hrs, stirrer was removed and yield was calculated based on total number of protons converted into **3.5d** based on integral of internal standard. Yield = 26.0%. Heating the reaction solution resulted in formation of a red precipitate. No further conversion could be observed after formation of red precipitate.

Attemp to form 3.5e: In a reaction J-Young type NMR tube, solid of **3.1** (0.0092 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0245 g, 0.10 mmol, internal standard) was dissolved in C₆D₆ (0.5 ml). H₂SiPh₂ (0.054g, 0.5 mmol) were then added into the tube. The reaction mixture was frozen and thawed under vacuum. CO₂ gas (>1 bar) was streamed into the tube. The tube was stirred and heated at 60°C. After 2 hrs, stirrer was removed and ¹H NMR was recorded. Only starting material was observed in the NMR.

3.5e: In a reaction J-Young type NMR tube, solid of **3.1** (0.0092 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0245 g, 0.10 mmol, internal standard) was dissolved in C₆D₆ (0.5 ml). H₂SiPh₂ (0.054g, 0.5 mmol) were then added into the tube. The reaction mixture was frozen and thawed under vacuum. CO₂ gas (>1 bar) was streamed into the tube. The tube was shaken vigorously. After 15 mins, ¹H NMR was recorded. Multiple methoxy products along with formate product **3.5e** was observable. Further. After that, stirrer was placed into the reaction solution and stirred. After 1hr, stirrer was removed and ¹H NMR was recorded. H₂SiPh₂ and **3.5e** were all consumed to form multiple products at methoxy region.

Stepwise reaction of **3.1** with CO₂

3.8: In a reaction J-Young type NMR tube, solid of **3.1** (0.0092 g, 0.05 mmol) was dissolved in C₆D₆ (0.5 ml). The reaction mixture was frozen and thawed under vacuum. CO₂ gas (>1 bar) was streamed into the tube. The tube was allowed to warm to room temperature. When the tube approaches room temperature, a red precipitate formed inside the NMR tube. ³¹P NMR, ³¹P{¹H} NMR and ¹H NMR of the tube were recorded.

3.7: In a reaction J-Young type NMR tube, solid of **3.1** (0.0092 g, 0.05 mmol) was dissolved in C₆D₆ (0.5 ml). The reaction mixture was frozen and thawed under vacuum. CO₂ gas (>1 bar) was streamed into the tube. The tube was dipped into a -78°C bath. Low temperature ³¹P NMR, ¹H NMR and ¹H{³¹P} NMR of the tube were recorded at -40°C. HRMS of the solution were recorded.

3.6 In a reaction J-Young type NMR tube, solid of **3.1** (0.0092 g, 0.05 mmol) was dissolved in C₆D₆ (0.5 ml). The reaction mixture was frozen and thawed under vacuum. CO₂ gas (>1 bar) was streamed into the tube and the tube was dipped into a -78°C bath. The tube was allowed to warm to room temperature slowly and brought into the glovebox while warming it. Once the temperature approaches room temperature and the red precipitate was starting to be formed, HBPIn were added into the NMR tube. ¹H NMR of the tube were recorded.

Section III.5. Appendixes

Selected spectra

Figure 3.S1. ¹H NMR spectrum of compound 3.3a

Figure 3.S2. ^{11}B NMR spectrum of compound **3.3a**

Figure 3.S3. ^1H NMR spectrum of compound **3.3b**

Figure 3.S4. ^{11}B NMR spectrum of compound **3.3b**

Figure 3.S5. ^{19}F NMR spectrum of compound **3.3b**

Figure 3.S6. ^1H NMR spectrum of compound **3.3c**

Figure 3.S7. ^{11}B NMR spectrum of compound **3.3c**

Figure 3.S8. ^1H NMR spectrum of compound **3.3d**

Figure 3.S9. ^{11}B NMR spectrum of compound **3.3d**

Figure 3.S10. ^1H NMR spectrum of compound **3.3e**

Figure 3.S11. ^{11}B NMR spectrum of compound **3.3e**

Figure 3.S12. ^1H NMR spectrum of compound **3.3f**

Figure 3.S13. ^{11}B NMR spectrum of compound 3.3f

Figure 3.S14. ^1H NMR spectrum of compound 3.5a

Figure 3.S15. ^{11}B NMR spectrum of compound **3.5a**

Figure 3.S16. ^{19}F NMR spectrum of compound **3.5a**

Figure 3.S17. ^1H NMR spectrum of compound **3.5d** obtained from hydroboration of CO_2 using HBPIn and **3.1** as catalyst.

Figure 3.S18. ^1H NMR spectrum of hydrosilylation of CO_2 using H_2SiPh_2 and **3.1** as catalyst.

Figure 3.S19. ^{31}P NMR spectrum of red precipitate obtained from **3.1** reacted with CO_2

Figure 3.S20. ^{31}P NMR spectrum of red precipitate obtained from **3.1** reacted with CO_2 at -40°C (tol-D3)

Figure 3.S21. ^1H NMR spectrum of red precipitate obtained from **3.1** reacted with CO_2 at -40°C (tol-D3)

Figure 3.S22. $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of red precipitate obtained from **3.1** reacted with CO_2 at -40°C (tol-D3)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 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

24 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 9-11 H: 15-23 N: 0-3 O: 0-2 P: 0-2

C₁₀H₂₂N₂PO

CCC-1A 34 (0.721)

1: TOF MS ES+
3.89e+000

Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
215.1314	215.1313	0.1	0.5	2.5	10.4	0.0	C10 H20 N2 O P	

Figure 3.S23. HRMS showing existence of 3.8

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 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

10 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 18-20 H: 33-35 N: 4-5 O: 0-3 P: 0-3

C₁₀H₂₂N₂PO

CCC-1A 16 (0.333)

1: TOF MS ES+
4.52e+000

Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
413.2234	413.2235	-0.1	-0.2	5.5	10.8	0.0	C19 H35 N4 O2 P2	

Figure 3.S24. HRMS showing existence of 3.7

Figure 3.S21. ^1H NMR spectrum showing formation of **3.6**. Reaction of newly formed red precipitate with HBPIn.

Figure 3.S21. ^{31}P NMR spectrum of reaction of newly formed red precipitate with HBPIn.

Section III.6. Citations

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