A Base-Stabilized Silylene-Promoted C(sp³)-H Borylation and H₂ Activation

Sabrina Khoo,^a Chi-Kit Siu^{*b} and Cheuk-Wai So^{*a}.

^aDivision of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371. ^bDepartment of Chemistry, City University of Hong Kong, Hong Kong SAR, China

ABSTRACT. Treatment of the amidinato amidosilylene [L{(Me₃Si)₂N}Si:] (**1**, L = PhC(NtBu)₂) with a slight excess of borane-tetrahydrofuran complex [BH₃•THF] in toluene at room temperature afforded the silylene-borane adduct [L{(Me₃Si)₂N}Si:→BH₃] (**2**). A triflate substituent was introduced on the boron center by reacting **2** with methyl triflate [MeOTf] (OTf = OSO₂CF₃) in toluene at room temperature to form [L{(Me₃Si)₂N}Si:→BH₂OTf] (**3**), with the elimination of CH₄ gas. The intramolecular C(sp³)-H borylation and H₂ elimination occurred by reacting complex **3** with **1** in refluxing toluene to form a C-B bond in the resulting silylene-boronium ion **5**. Complex **5** activated H₂ gas or NH₃BH₃ at room temperature to form the silylene-borane adduct **2** and [L{(Me₃Si)₂N}Si—H]OTf. Additionally, the reaction of **5** with H₂ was studied through DFT calculations.

Introduction

Silylene compounds have a lone pair of electrons and vacant p orbital on the silicon atoms. These electronic properties enable them to possess both electrophilic and nucleophilic characters, leading to Lewis ambiphilicity. In this context, silylene compounds are capable of functioning as versatile ligands in transition metal complexes for regio- and chemoselective catalysis.¹ In addition, they can display reactivity similar to transition metal complexes in the area of small molecules and enthalpically strong bonds activation, showing possible application in catalyzing organic reactions.² The catalytic application was recently demonstrated, whereby the NHC-silyliumylidene cation complex $[(\text{Ime})_2\text{SiH}]\text{I}$ ($\text{Ime} = :\text{C}\{\text{N}(\text{Me})\text{C}(\text{Me})\}_2$) catalyzed the metal-free chemo- and regioselective hydroboration of carbon dioxide, carbonyl compounds and pyridine derivatives with HBpin.³ It seems reasonable that silylene compounds will find a range of other enthalpically strong bonds activation and catalytic application.

Recently, we and research groups of Iwamoto and Roesky showed that silylene compounds can activate enthalpically strong B-H and C(sp³)-H bonds, respectively.⁴⁻⁶ These results aroused our interest to investigate whether silylene compounds could concurrently mediate both processes, resulting in C(sp³)-H borylation. Borylation of a relatively unreactive C(sp³)-H bond is of significance as the newly formed carbon-boron bond can be converted into a variety of carbon-carbon and carbon-heteroatom bonds. However, the C(sp³)-H borylation is very rare, even in the presence of transition metal complexes as catalysts.⁷ So far, only a few examples of metal-free C(sp³)-H borylation were reported.⁸⁻¹⁶ Herein, we report that an amidinato amidosilylene is capable of promoting C(sp³)-H borylation and H₂ activation.¹⁷

Results and Discussion

To begin with, the amidinato amidosilylene $[L\{(Me_3Si)_2N\}Si:]$ (**1**, $L = PhC(NtBu)_2$)¹⁸ was treated with a slight excess of borane-tetrahydrofuran complex $[BH_3 \cdot THF]$ in toluene at room temperature for 16h to afford the silylene-borane adduct $[L\{(Me_3Si)_2N\}Si \rightarrow BH_3]$ (**2**, Scheme 1) as a colourless crystalline solid (Yield: 79%). In the reaction, compound **1** donates its lone pair electrons into the empty p orbital in BH_3 . The 1H and $^{13}C\{^1H\}$ NMR spectra of **2** exhibit a set of signals attributable to the amidinate and $N(SiMe_3)_2$ ligands. The absence of B–H signal in the 1H NMR spectrum can be rationalized due to quadrupolar boron nucleus. In its ^{11}B NMR spectrum, a quartet is detected at -38.2 ppm (J_{B-H} : 91.3 Hz), corresponding to the BH_3 moiety. Two singlets (4.5 and 9.1 ppm) and one quartet (22.1 ppm, $^1J_{Si-B} = 67.1$ Hz) are attributable to the $SiMe_3$ and Si^{II} moieties in the $^{29}Si\{^1H\}$ NMR spectrum, respectively. The X-ray crystal structure (Figure 1) shows that the Si1 and B1 atoms adopt a distorted tetrahedral geometry. The Si–B bond in **2** measures 1.974(3) Å and is comparable with that in the amidinato hydridosilylene-borane complex $[L(H)Si \rightarrow BH_3]$ (1.9624(5) Å).¹⁹

Scheme 1. Synthesis of **2** - **5**

Figure 1. X-ray crystal structure of **2** with thermal ellipsoids at the 30% probability level. As 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. Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.974(3), B1-H1B 1.11(2), B1-H2B 1.11(3), B1-H3B 1.12(2), Si1-N1 1.8402(17), Si1-N2 1.8396(17), Si1-N3 1.7258(17); Si1-B1-H1B 101(1), Si1-B1-H2B 114(1), Si1-B1-H3B 107(1), N1-Si1-N2 71.12(8), N1-Si1-N3 111.81(8), N3-Si1-B1 126.1(1).

With the stable silylene-borane adduct **2** in hand, a triflate substituent was introduced on the boron center. It was anticipated that the triflate substituent could enhance Lewis acidity of the boron center or act as a leaving group to promote activation of a C(sp³)-H bond. Treatment of **2** with equimolar methyl triflate [MeOTf] (OTf = OSO₂CF₃) in toluene at room temperature for 16h furnished [L{(Me₃Si)₂N}Si:→BH₂OTf] (**3**, Scheme 1) as a colorless crystalline solid in 92% yield. The X-ray crystal structure (Figure 2) shows that the Si1-B1 bond length in **3** (2.011(6) Å) is stretched with respect to its precursor **2** (1.974(3) Å). While the ¹H and ¹³C{¹H} NMR spectra of **3** are expected and similar to those of **2**, the ¹¹B NMR signal (-9.8 ppm) is downfield-shifted and

broadened. In the ^{19}F NMR spectroscopy, a sharp singlet at -74.5 ppm verifies the non-ionized triflate in compound **3** in solution. Compound **3** did not undergo any rearrangement after refluxing the toluene solution of **3** without any additive for 16 h. In contrast, it was noted that when $[\text{L}\{\text{Ar}(\text{Me}_3\text{Si})\text{N}\}\text{SiBH}_2\text{OTf}]$ (**I**, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$; a bulky analog of **3** with a SiMe_3 group replaced by the Ar group) was refluxed in toluene, a B-H bond activation product $[\text{LB}(\text{H})\text{Si}(\text{H})(\text{OTf})\{\text{N}(\text{SiMe}_3)\text{Ar}\}]$ (**II**) was obtained through an intermediate **A** (Scheme 2).⁴ This indicates that the less bulky amido substituent $-\text{N}(\text{SiMe}_3)_2$ enhances the stability of **3**.

Figure 2. The X-ray crystal structure of **3** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 2.011(6), B1-H1A 1.01(4), B1-H1B 1.02(3), B1-O1 1.563(7), Si1-N1 1.821(3), Si1-N2 1.815(3), Si1-N3 1.711(3); Si1-B1-H1A 114(3), Si1-B1-H1B 114(2), Si1-B1-O1 104.1(3), O1-B1-H1A 112(3), B1-Si1-N1 109.7(2), B1-Si1-N2 110.1(2), B1-Si1-N3 122.0(2), N1-Si1-N3 116.4(1).

Scheme 2. B-H bond activation mediated by complex **I**⁴

When compound **3** was reacted with 4-dimethylaminopyridine (DMAP) in refluxing toluene for 16h, the OTf group was displaced by DMAP to afford the DMAP-amidinato boronium triflate [L{(Me₃Si)₂N}SiBH₂(DMAP)]OTf (**4**, Scheme 1). No B-H bond activation was observed in the reaction. Its ¹H and ¹³C{¹H} NMR spectra are unremarkable. While the free triflate unit resonates in the expected region at -77.4 ppm in the ¹⁹F NMR spectrum, the ¹¹B NMR signal at -15.7 ppm is broad with no obvious coupling patterns to the adjacent H atoms. Moreover, the ¹¹B NMR signal is only slightly upfield shifted in comparison with **3** (-9.8 ppm). The X-ray crystal structure (Figure 3) shows that DMAP coordinates to the boron center with the bond length of 1.559(9) Å. On the other hand, when compound **I** was reacted with DMAP in refluxing toluene, the reaction proceeded through the B-H bond activation (Intermediate **A**, Scheme 2) and subsequent OTf displacement with DMAP to form the amidinato DMAP-silylboronium ion [(μ-κ1:κ1-L)B(H)(DMAP)Si(H){N(Ar)SiMe₃}]OTf (**III**).⁴ The difference in the reactivity of compounds **3**

and **1** toward DMAP can be attributed to the difference in their high-temperature stability brought by the steric effect of the amido group ($-\text{N}(\text{SiMe}_3)_2$ (**3**); $-\text{N}(\text{SiMe}_3)\text{Ar}$ (**1**)) in them.

Figure 3. The X-ray crystal structure of **4** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 2.043(7), B1-H1BB 1.10(5), B1-H2BB 1.11(4), B1-N4 1.559(9), Si1-N1 1.829(4), Si1-N2 1.831(4), Si1-N3 1.710(3); Si1-B1-N4 113.3(4), Si1-B1-H1BB 102(2), Si1-B1-H2BB 104(2), N1-Si1-N2 71.7(2), N1-Si1-N3 115.4(2), N3-Si1-H1BB 121(1).

In contrast, in the presence of sterically hindered Lewis base **1**, the intramolecular $\text{C}(\text{sp}^3)\text{-H}$ borylation occurred in the reaction of **1** and **3** in refluxing toluene for 16h to form the boronium ion **5** as colorless crystals (51% yield, Scheme 1). Compound **5** was characterized by NMR spectroscopy. The ^{11}B NMR spectroscopy reveals a doublet at -33.0 ppm ($J_{\text{B-H}} = 77.7$ Hz), corresponding the central boronium atom. The ^{11}B NMR signal is comparable with other boronium complexes such as $[\{t\text{Bu}_2(\text{H})\text{P}\}_2\text{BH}_2]\text{Br}$ (-41.2 ppm) and $[\text{Cp}^*\text{B-Mes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (-41 ppm, $\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$).²⁰ The ^{19}F NMR signal of -78.8 ppm is in accordance to the ionized

triflate group. Only SiMe_n resonances could be identified in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, whereas signals for the Si^{II} centers were not observed presumably due to quadrupolar broadening of the B–Si signals. The X-ray crystal structure of **5** (Figure 4) shows that the Si–B bonds (2.028(4), 2.042(4) Å) are slightly elongated in comparison with that of **3** (2.011(6) Å). The B1–C20 bond (1.654(6) Å) is significantly stretched with respect to typical B–C single bonds (1.59 Å). The B $\cdots$ OTf interaction (8.43(1) Å) greatly exceeds the sum of covalent radii of boron and oxygen, indicating there is no interaction between these atoms. The large Si(silylene)–B–Si(silylene) angle (137.8(2)°) is evidence of a sterically-crowded environment around the distorted tetrahedral boron atom prompted by the two bulky amidosilylene moieties.

Figure 4. The X-ray crystal structure of **5** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms, disordered triflate counter anion and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): B1–H1B 1.275, B1–Si1 2.028(4), B1–Si4 2.042(4), B1–C20 1.654(6); Si1–B1–Si4 137.8(2), Si4–B1–H1B 98.9, H1B–B1–C20 114.7, C20–B1–Si1 100.9(3), B1–Si1–N3 102.5(1), Si1–N3–Si3 113.8(1), N3–Si3–C20 98.3(2), Si3–C20–B1 111.6(3).

It is proposed that in the reaction of compounds **1** and **3** at the elevated temperature, the OTf group in **3** dissociates from the boron center to form a silylene-borenium intermediate $[L\{(Me_3Si)_2N\}Si: \rightarrow BH_2]OTf$ (**B**, Scheme 3). The validity of this step is confirmed by the triflate substitution by DMAP under identical conditions (*vide supra*). Subsequently, as the steric effect of **1** precludes its direct coordination to the boron cation **B**, σ -bond metathesis occurs between $C_{SiMe_3}-H$ and $B-H$ bonds (through **C**, Scheme 3) to result in **5** and H_2 .²¹ This mechanism is supported by the reaction of **3** with a lesser bulky amidinato chlorosilylene $[LSiCl]$ ²² (than **1** and bis(amidinato)silylene) where a product **7** (Scheme 4, Figure 5) that corresponds to that of **4** was obtained. With another sterically bulky bis(amidinato)silylene, a similar product **8** (Scheme 4, Figure 6) was formed. In contrast, when **I** was reacted with **1** or $[LSiCl]$ in refluxing toluene, only **II** was formed. This result illustrates that **I** did not react with bulky Lewis bases and gave **II** through intramolecular B-H bond activation. In contrast, **3** reacted with **1** and $[LSiCl]$ to offer the $C(sp^3)-H$ bond activation and OTf group displaced products **5** and **7**, respectively (*vide supra*).

Scheme 3. Proposed mechanism for the formation of **5**

Scheme 4. Synthesis of **7** and **8**

Figure 5. The X-ray crystal structure of **7** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.972(6), Si4-B1 1.957(6), Si1-N1 1.829(4), Si1-N2 1.821(4), Si1-N3 1.715(4), Si4-N4 1.805(4), Si4-N5 1.819(4), Si4-Cl1 2.063(2); Si4-B1-Si1 130.5(3), Si1-B1-H1B1 1.715(4), Si4-N4 1.805(4), Si4-N5 1.819(4), Si4-Cl1 2.063(2); Si4-B1-Si1 130.5(3), Si1-B1-H1B1

97.4, H1B1-B1-H1B 128.6, H1B-B1-Si4 102, N2-Si1-N1 71.5(2), N1-Si1-N3 115.3(2), N3-Si1-B1 114.9(2), B1-Si1-N2 121.7(2), N5-Si4-N4 72.9(2), N4-Si4-B1 112.2(2), B1-Si4-Cl1 122.3(2), Cl1-Si4-N5 107.6(1).

Figure 6. The X-ray crystal structure of **8** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): B1-H1B 1.22(5), B1-Si1 2.018(6), B-Si4 2.023(7), B1-C21 1.650(9); Si1-B1-Si4 138.0(3), Si4-B1-H1B 103(3), H1B-B1-C21 111(3), C21-B1-Si1 100.1(4), B1-Si1-N3 104.1(2), Si1-N3-Si3 110.1(2), N3-Si3-C21 101.9(2), Si3-C21-B1 107.8(4).

As the above C(sp³)-H borylation was achieved under reflux conditions with the elimination of H₂, it is anticipated that the C(sp³)-bond in complex **5** could activate dihydrogen gas at room temperature. In this context, **5** was reacted with H₂ gas (1 atm) in THF-*d*₈ at room temperature for a week or with more potent ammonia-borane [NH₃•BH₃] in toluene at room temperature for 6 hours to afford a mixture of compound **2** and [L{(Me₃Si)₂N}Si—H]OTf (**6**, Scheme 5), which

were confirmed by both NMR spectroscopy and X-ray crystallography. The reaction proceeds through the displacement of the bulky compound **1** in compound **5** by a H₂ molecule to form **5b** (Scheme 6). Its formation was corroborated by DFT calculations (see below). Subsequent synergistic H₂ addition and C(sp³)-H bond elimination form a mixture of the silylene-borenium intermediate **5c** and compound **1**. They further reacts with another molecule of H₂ to form compounds **2** and **6**. Comparing with other examples, H₂ addition mediated by highly Lewis acidic boron compounds such as the perfluoropentaphenylborole [$\{(F_5C_6)C\}_4B(C_6F_5)\]$,²³ borane HB(C₆F₅)₂,²⁴ borinium cation [Mes₂B]⁺²⁵ and borylborenium cation [I_{Me}B(Mes)Bpin]⁺ were reported.²⁶ In addition, synergistic H₂ addition and C(sp²)-H bond elimination was reported, whereby a cationic phosphine-stabilized mesitylborenium cation underwent an addition reaction with H₂ on the boron center, followed by elimination of mesitylene from the boron center.²⁷

Scheme 5. The reaction of compound **5** with H₂ or NH₃BH₃

Scheme 6. Proposed mechanism for the reaction of **5** and H₂

The above proposed mechanism (Scheme 6) was theoretically examined with density functional theory at the B3LYP/6-311++G(2df,2pd)//B3LYP/6-31G(d,p) level performed with the Gaussian 09 quantum chemical package. The relative free energies ΔG_{298}° at room temperature (in kcal mol⁻¹) were evaluated from single-point energy calculations using the larger triplet-zeta basis set with thermal corrections computed from harmonic vibration analysis using the smaller double-zeta basis set. Effects of solvent (toluene) were included using the polarizable continuum model (PCM). The reaction profile is illustrated in Scheme 7. A H₂ molecule displaces **1** in compound **5** to form **5b** with a relative free energy of 15.7 kcal/mol. The B-C σ orbital then attacks the H-H σ^* orbital via **TS** with a kinetic barrier of 11.9 kcal/mol to form a mixture of **1** and **5c** ($\Delta G = 22.4$ kcal/mol). **5c** contains a boron empty p orbital that can readily react with an additional H₂ molecule to yield intermediate **5d** (21.6 kcal/mol), containing a H₂B⁺···H₂ moiety. A spontaneous proton transfer to the OTf group (via a transition structure with a lower relative free energy after thermal correction, 21.0 kcal/mol) results in the formation of **1**, TfOH and **2** ($\Delta G = 14.3$ kcal/mol). Then, similar proton transfer from HOTf to the Si center of compound **1** occurs and yields a mixture of **2** and **6** ($\Delta G =$

-22.0 kcal/mol). This reaction is exergonic by -32.3 kcal/mol relative to the reactants **5** + H₂. The theoretical reaction profile is in good agreement with the experimental observation.

Scheme 7. Reaction free energies (ΔG_{298}° / kcal/mol) of the proposed mechanism evaluated at the B3LYP/6-311++G(2df,2pd)//B3LYP/6-31G(d,p) level.

Conclusion

In conclusion, we demonstrated that the amidinato amidosilylene **1** promoted the amidinato silylene-borane complex **3** to undergo the intramolecular C(sp³)-H borylation and H₂ elimination to form the amidinato silylene-boronium ion **5**. The newly formed C(sp³)-H bond in complex **5** was capable of activating dihydrogen gas to form the silylene-borane adduct **2** and [L{(SiMe₃)₂N}Si—H]OTf (**6**).

Experimental Section

General consideration: All manipulations, unless otherwise stated, were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. The chemicals were purchased from commercial sources: Sigma-Aldrich, and Alfa Aesar and were used as received. Toluene and hexane were dried using a MBraun Solvent Purification System. Benzene-*d*₆, THF and THF-*d*₈ were dried and distilled over molten potassium. CD₂Cl₂ was dried and distilled over calcium hydride. All NMR spectra were recorded on Bruker Avance 400 or Jeol ECA 400 MHz spectrometers. The NMR spectra were recorded in d-solvents and the chemical shifts are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si; BF₃·Et₂O for ¹¹B. Compound **1** and [LSiCl] (L = PhC(N*t*Bu)₂) were synthesized according to literature procedures.

Synthesis of 2: [BH₃•THF] (1.0 M in THF, 9.0 mL, 1.2 equiv.) was added to a solution of **1** (3.17 g, 7.5 mmol, 1.0 equiv.) in toluene (30 mL) at ambient temperature. The mixture was allowed to stir and the solution changed from clear orange to cloudy yellow after 16 hours. Upon filtration and concentration, colourless crystals of **2** were obtained. Yield: 2.58 g (79%). M.p. 244-246 °C.

Elemental analysis (%) calcd for $C_{21}H_{44}BN_3Si_3$: C, 58.16; H, 10.23; N, 9.69. Found: C, 58.02; H, 10.13; N, 9.58. 1H NMR (395.9 MHz, C_6D_6 , 25.1 °C): δ 0.40 (s, 9H, $SiMe_3$), 0.68 (s, 9H, $SiMe_3$), 1.20 (s, 18H, tBu), 6.83-6.93 (m, 3H, Ph), 7.13-7.14 (m, 1H, Ph), 7.22-7.24 (m, 1H, Ph) ppm, H_B signals were not detected. $^{11}B\{^1H\}$ NMR (127.0 MHz, C_6D_6 , 25.4 °C): δ -38.2 (s) ppm. ^{11}B NMR (128.2 MHz, C_6D_6 , 25.3 °C): δ -38.2 (q, $^1J_{B-H} = 91.3$ Hz) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6 , 25.2 °C): δ 5.4, 5.9 ($SiMe_3$), 31.4 (CMe_3), 55.2 (CMe_3), 128.9, 130.6, 131.7 (Ph), 169.8 (NCN) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6 , 25.1 °C): δ 4.5 ($SiMe_3$), 9.1 ($SiMe_3$), 22.1 (q, $^1J_{Si-B} = 67.1$ Hz, SiB) ppm.

Synthesis of 3: A solution of MeOTf (0.755 g, 0.50 mL, 4.60 mmol, 1.0 equiv.) in toluene (10 mL) was added to a solution of **2** (2.00 g, 4.60 mmol, 1.0 equiv.) in toluene (30 mL) at ambient temperature. The mixture was allowed to stir and solution changed from clear to cloudy after 16 hours with slight bubbling. Upon filtration and concentration, colourless crystals of **3** were obtained. Washing with hexanes provided a pure sample of **3** for spectroscopic analyses. Yield: 2.45 g (92%); M.p. 162-166 °C. Elemental analysis (%) calcd for $C_{22}H_{43}BF_3N_3O_3SSi_3$: C, 45.42; H, 7.45; N, 7.22. Found: C, 45.14; H, 7.35; N, 7.16. 1H NMR (399.5 MHz, C_6D_6 , 23.7 °C): δ 0.27 (s, 9H, $SiMe_3$), 0.36 (s, 9H, $SiMe_3$), 1.12 (s, 18H, tBu), 6.86-7.07 (m, 4H, Ph), 8.04-8.06 (m, 1H, Ph) ppm, H_B signals were not detected. $^{11}B\{^1H\}$ NMR (127.0 MHz, C_6D_6 , 24.5 °C): δ -9.8 (br) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6 , 27.0 °C): δ 5.1 ($SiMe_3$), 31.2 (CMe_3), 55.7 (CMe_3), 127.3, 129.4, 130.17, 131.3 (Ph), 173.5 (NCN) ppm, C_F signal was not detected. ^{19}F NMR (375.9 MHz, C_6D_6 , 23.7 °C): δ -74.5 (s) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6 , 24.3 °C): δ 7.0, 10.8 ($SiMe_3$) ppm, Si_B signal was not detected.

Synthesis of 4: Toluene (20 mL) was added to a mixture of **3** (0.581 g, 1.00 mmol, 1.0 equiv.) and DMAP (0.122 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux for 16h. Pale yellow residue formed upon cooling of the reaction mixture to ambient temperature. The residue was confirmed to be **4** by ^1H NMR. Single crystals were grown from a saturated solution in a toluene/THF (*ca.* 1:1) mixture. Yield: 0.58 g (83%); M.p. 210 °C (dec). Elemental analysis (%) calcd for $\text{C}_{29}\text{H}_{53}\text{BF}_3\text{N}_5\text{O}_3\text{SSi}_3$: C, 49.48; H, 7.59; N, 9.95. Found: C, 49.33; H, 7.51; N, 9.90. ^1H NMR (395.9 MHz, C_6D_6 , 25.1 °C): δ 0.27 (s, 9H, SiMe_3), 0.43 (s, 9H, SiMe_3), 0.97 (s, 18H, *t*Bu), 2.42 (s, 6H, NMe_2), 6.91-6.96 (m, 4H, Ph), 7.91-8.08 (m, 5H, Ph) ppm, H_B signals were not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.5 °C): δ -15.7 (br) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $\text{THF-}d_8$, 27.8 °C): δ 5.7, 6.0 (SiMe_3), 31.5 (CMe_3), 40.1 (NMe_2), 56.3 (CMe_3), 108.7, 109.7, 128.0, 129.1, 129.8, 130.2, 131.3, 132.4, 147.0, 147.5, 156.9 (Ar), 175.6 (NCN) ppm, C_F signal was not detected. ^{19}F NMR (372.5 MHz, C_6D_6 , 24.9 °C): δ -77.4 (s) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, $\text{THF-}d_8$, 25.4 °C): δ 6.8, 9.8 (SiMe_3) ppm, Si_B signal was not detected.

Synthesis of 5: Toluene (20 mL) was added to a mixture of **3** (0.581 g, 1.00 mmol, 1.0 equiv.) and compound **1** (0.419 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux for 16h. Slow evaporation of the solvent, or gradual cooling to room temperature, afforded block-like colourless crystals of **5**. Yield: 0.509 g (51%); M.p. 229 °C (dec). Elemental analysis (%) calcd for $\text{C}_{43}\text{H}_{82}\text{BF}_3\text{N}_6\text{O}_3\text{SSi}_6$: C, 51.67; H, 8.27; N, 8.41. Found: C, 51.65; H, 8.12; N, 8.31. ^1H NMR (395.9 MHz, $\text{THF-}d_8$, -89.9 °C): δ 0.28 (s, 2H, CH_2), 0.45 (s, 9H, SiMe_3), 0.49 (s, 6H, SiMe_2), 0.55 (s, 9H, SiMe_3), 0.59 (s, 9H, SiMe_3), 1.30 (m, 36H, *t*Bu), 7.60-7.80 (m, 10H, Ph) ppm, H_B signal

was not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, THF- d_8 , 26.0 °C): δ -33.0 (s) ppm. ^{11}B NMR (127.0 MHz, THF- d_8 , 24.4 °C): δ -33.0 (d, $^1J_{\text{B-H}} = 77.7$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2 , 27.3 °C): δ 1.3, 4.7, 6.6, 7.6 (SiMe_n), 31.8, 32.1, 32.1, 32.3 (CMe_3), 55.5, 55.6, 56.4, 56.7 (CMe_3), 127.4, 128.0, 128.3, 128.7, 129.2, 129.3, 129.4, 129.8, 130.1, 132.0, 132.2 (Ph), 174.0, 176.9 (NCN) ppm, C_F signal was not detected. ^{19}F NMR (372.5 MHz, THF- d_8 , 25.8 °C): δ -78.8 (s) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, THF- d_8 , 24.5 °C): δ 4.2, 7.1, 8.2, 17.7 (SiMe_n) ppm, Si_B signals were not detected.

Regeneration of 2 and 6: Method A: Toluene (20 mL) was added to a mixture of **5** (1.00 g, 1.00 mmol, 1.0 equiv.) and $[\text{NH}_3\cdot\text{BH}_3]$ (0.031 g, 1.00 mmol, 1.0 equiv.) at ambient temperature. The reaction mixture was allowed to stir for 6 hours and the solution changed from light orange to a pale yellow suspension. Upon filtration, the residue was dried to afford **6** as a white powder. Yield: 0.054 g (11%); M.p. 189-191 °C. Elemental analysis (%) calcd for $\text{C}_{22}\text{H}_{42}\text{F}_3\text{N}_3\text{O}_3\text{SSi}_3$: C, 46.37; H, 7.43; N, 7.37. Found: C, 46.19; H, 7.15; N, 7.22. ^1H NMR of **6** (399.5 MHz, THF- d_8 , 22.5 °C): δ 0.57 (s, 9H, SiMe_3), 0.61 (s, 9H, SiMe_3), 1.32 (s, 18H, $t\text{Bu}$), 5.32 (br s, 1H, SiH), 7.63-7.71 (m, 5H, Ph) ppm. ^{19}F NMR of **6** (372.5 MHz, THF- d_8 , 25.8 °C): δ -77.7 (s) ppm. The filtrate was concentrated to afford a mixture of **2** and **6** as colorless crystals.

Method B: Compound **5** (0.05g, 0.05 mmol) and 0.5 mL of THF- d_8 were mixed in a J-Young NMR tube. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of H_2 gas was then added. The reaction mixture was warmed to room temperature. The reaction was monitored by ^1H and ^{11}B NMR spectroscopy to show a mixture of **2** and **6** with quantitative yield after 1 week.

Synthesis of 7: Toluene (20 mL) was added to a mixture of **3** (0.580 g, 1.00 mmol, 1.0 equiv.) and [LSiCl] (0.294, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux for 16h. Upon filtration and concentration, colourless crystals of **7** were obtained. Yield: 0.59 g (67%). M.p. 231 °C (dec). Elemental analysis (%) calcd for C₃₇H₆₆BClF₃N₅O₃SSi₄: C, 50.70; H, 7.59; N, 7.99. Found: C, 50.51; H, 7.48; N, 7.76. ¹H NMR (399.5 MHz, THF-*d*₈, 22.5 °C): δ 0.52 (s, 9H, SiMe₃), 0.53 (s, 9H, SiMe₃), 1.31 (s, 18H, *t*Bu), 1.34 (s, 18H, *t*Bu), 7.61-7.78 (m, 10H, Ph) ppm, H_B signals were not detected. ¹¹B{¹H} NMR (128.2 MHz, THF-*d*₈, 22.9 °C): δ -44.9 (s) ppm. ¹¹B NMR (128.2 MHz, THF-*d*₈, 22.8 °C): δ -44.9 (t, ¹J_{B-H} = 83.8 Hz) ppm. ¹³C{¹H} NMR (100.5 MHz, THF-*d*₈, 22.9 °C): δ 6.1, 6.8 (SiMe₃), 31.7, 31.8 (CMe₃), 56.6, 57.3 (CMe₃), 126.2, 128.7, 129.1, 129.2, 129.6, 129.8, 130.4, 132.7, 133.0 (Ph), 176.2, 181.2 (NCN) ppm, C_F signal not detected. ¹⁹F NMR (375.9 MHz, THF-*d*₈, 22.6 °C): δ -80.7 (s) ppm. ²⁹Si{¹H} NMR (78.7 MHz, THF-*d*₈, 24.6 °C): δ 7.3, 9.7 (SiMe₃), Si_B signals were not detected.

Synthesis of 8: Toluene (20 mL) was added to a mixture of **3** (0.581 g, 0.99 mmol, 1.0 equiv.) and [L₂Si] (0.490 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux for 16h. Colourless crystals of **8** were obtained from a saturated solution in a toluene/PhF (*ca.* 1:1) mixture. Yield: 0.71 g (66%); M.p. 201 °C (dec). Elemental analysis (%) calcd for C₅₂H₈₇BF₃N₇O₃SSi₄: C, 58.34; H, 8.19; N, 9.16. Found: C, 58.18; H, 7.97; N, 8.83. ¹H NMR (395.9 MHz, THF-*d*₈, 27.3 °C): δ 0.47 (s, 2H, CH₂), 0.52 (s, 6H, SiMe₂), 0.53 (s, 9H, SiMe₃), 1.30 (s, 18H, *t*Bu), 1.31 (s, 18H, *t*Bu), 1.34 (s, 18H, *t*Bu), 1.35 (s, 18H, *t*Bu), 7.60-7.70 (m, 15H, Ph) ppm, H_B signal was not detected. ¹¹B{¹H} NMR (127.0 MHz, THF-*d*₈, 27.2 °C): δ -38.6 (s) ppm. ¹¹B NMR (127.0 MHz, THF-*d*₈, 26.8 °C): δ -38.7 (d, ¹J_{B-H} = 81.4 Hz) ppm. ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 27.4 °C): δ 6.3, 7.7 (SiMe_n), 31.3, 31.9, 32.0, 32.3 (CMe₃), 56.8, 57.4, 57.5, 57.8 (CMe₃), 129.3, 129.6,

129.7, 130.1, 131.0, 132.3, 132.9, 133.1 (Ph), 176.5, 181.5 (NCN) ppm, C_F signal was not detected. ¹⁹F NMR (372.5 MHz, THF-*d*₈, 25.8 °C): δ -78.8 (s) ppm. ²⁹Si{¹H} NMR (78.7 MHz, THF-*d*₈, 24.5 °C): δ 8.8, 4.2 (*SiMe_n*) ppm, Si_B signals were not detected.

X-ray data collection and structural refinement: Intensity data for compounds were collected by using a Bruker APEX II diffractometer. Reflections were measured at 133(2) K for **2**, 296(2) K for **3** (in a sealed Lindemann capillary tube), 153(2) K for **4** and 103(2) K for **5**, **7**, and **8**. The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .²⁸ All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. A summary of selected crystallographic data is provided in the Supporting Information. CCDC-1965132 (**2**), -1965133 (**3**), -1965140 (**4**), -1965134 (**5**), -1965135 (**7**) and -1965136 (**8**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical computations: All density functional theory calculations were performed with the Gaussian 09 package.²⁹ Geometry optimizations and harmonic vibrational frequency analyses were done at the B3LYP/6-31G(d,p) level of theory. Effects of solvent (toluene) are included using the polarizable continuum model (PCM). All geometries located at local minima or transition states on the potential energy surface were confirmed with zero or one imaginary frequency,

respectively. The local minima, **5b** and **5c**, associated with the key transition structure, **TS**, were identified using the intrinsic reaction coordinate (IRC) method. The relative enthalpies ΔH_{298}° and free energies ΔG_{298}° at room temperature (both in kcal mol⁻¹) were evaluated from single-point energy calculations using the larger triplet-zeta 6-311++G(2df,2pd) basis set with thermal corrections computed for the geometries optimized using the smaller double-zeta 6-31G(d,p) basis set.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Selected NMR spectra and Theoretical studies (PDF)

X-ray crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*CWS@ntu.edu.sg. *chiksiu@cityu.edu.hk.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

- (1) (a) Zhou, Y.-P.; Driess, M. Isolable Silylene Ligands Can Boost Efficiencies and Selectivities in Metal-Mediated Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 3715-3728.
(b) Raoufmoghaddam, S.; Zhou, Y.-P.; Wang, Y.; Driess, M. N-heterocyclic Silylenes as Powerful Steering Ligands in Catalysis. *J. Organomet. Chem.* **2017**, *829*, 2-10. (c) Blom, B.; Gallego, D.; Driess, M. N-heterocyclic Silylene Complexes in Catalysis: New Frontiers in an Emerging Field. *Inorg. Chem. Front.* **2014**, *1*, 134-148. (d) Blom, B.; Stoelzel, M.; Driess, M. New Vistas in N-Heterocyclic Silylene (NHSi) Transition-Metal Coordination Chemistry: Syntheses, Structures and Reactivity towards Activation of Small Molecules. *Chem. –Eur. J.* **2013**, *19*, 40-62.
- (2) (a) Blom, B.; Driess, M. Recent Advances in Silylene Chemistry: Small Molecule Activation En-Route Towards Metal-Free Catalysis. *Struct. Bonding* **2014**, *156*, 85-123.
(b) Yadav, S.; Saha, S.; Sen, S. S. Compounds with Low-Valent p-Block Elements for Small Molecule Activation and Catalysis. *ChemCatChem* **2016**, *8*, 486-501. (c) Driess, M. Main Group Chemistry Breaking the Limits with Silylenes. *Nat. Chem.* **2012**, *4*, 525-526.
(d) Yao, S.; Xiong, Y.; Driess, M. Zwitterionic and Donor-Stabilized N-Heterocyclic Silylenes (NHSis) for Metal-Free Activation of Small Molecules. *Organometallics* **2011**, *30*, 1748-1767. (e) Asay, M.; Jones, C.; Driess, M. N-Heterocyclic Carbene Analogues

- with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands. *Chem. Rev.* **2011**, *111*, 354-396. (f) Cui, H.; Ma, B.; Cui, C. Metal-Free, Stereospecific Bis-Silylation of Functionalized Alkynes with NHC-Supported Silylamino-silylene. *Organometallics* **2012**, *31*, 7339-7342. (g) Li, Y.; Ma, B.; Cui, C. Reactivity of an NHC-stabilized Silylene towards Ketones. Formation of Silicon Bis-enolates vs. Bis-silylation of the C=O Bond. *Dalton Trans.* **2015**, *44*, 14085-14091. (h) Cui, H.; Zhang, J.; Tao, Y.; Cui, C. Controlled Oxidation of an NHC-Stabilized Phosphinoaminosilylene with Dioxygen. *Inorg. Chem.* **2016**, *55*, 46-50. (i) Li, J.; Ma, B.; Cui, C. Selective Silylation of Nitriles with an NHC-Stabilized Silylene to 1,2-Disilylimines and Subsequent Synthesis of Silaaziridines. *Organometallics* **2016**, *35*, 1358-1360. (j) Li, T.; Zhang, J.; Cui, C. Silole Silylene Route to NHC-Stabilized Fused 1-Silabicycles and 1,1'-Spirobisiloles. *Chem. - Asian J.* **2017**, *12*, 1218-1223. (k) Zhu, L.; Zhang, J.; Cui, C. Intramolecular Cyclopropanation of Alkali-Metal-Substituted Silylene with the Aryl Substituent of an N-Heterocyclic Framework. *Inorg. Chem.* **2019**, *58*, 12007-12010. (l) Zhu, L.; Zhang, J.; Yang, H.; Cui, C. Synthesis of Silaketenimine Anion and Its Coupling with Isocyanide. *J. Am. Chem. Soc.* **2019**, *141*, 19600-19604.
- (3) Leong, B.-X.; Lee, J.; Li, Y.; Yang, M.-C.; Siu, C.-K.; Su, M.-D.; So, C.-W. A Versatile NHC-Parent Silyliumylidene Cation for Catalytic Chemo- and Regioselective Hydroboration. *J. Am. Chem. Soc.* **2019**, *141*, 17629-17636.
- (4) Khoo, S.; Shan, Y.-L.; Yang, M.-C.; Li, Y.; Su, M.-D.; So, C.-W. B-H Bond Activation by an Amidinate-Stabilized Amidosilylene: Non-Innocent Amidinate Ligand. *Inorg. Chem.* **2018**, *57*, 5879-5887.

- (5) Swamy, V. S. V. S. N.; Raj, K. V.; Vanka, K.; Sen, S. S.; Roesky, H. W. Silylene Induced Cooperative B-H bond Activation and Unprecedented Aldehyde C-H Bond Splitting With Amidinate Ring Expansion. *Chem. Commun.* **2019**, 55, 3536-3539.
- (6) Koike, T.; Kosai, T.; Iwamoto, T. 1,4-Dehydrogenation with a Two-Coordinate Cyclic (Alkyl)(amino)silylene. *Chem. - Eur. J.* **2019**, 25, 9295-9302.
- (7) Ros, A.; Fernandez, R.; Lassaletta, J. M. Functional Group Directed C-H Borylation. *Chem. Soc. Rev.* **2014**, 43, 3229-3243.
- (8) Prokofjevs, A.; Vedejs, E. N-Directed Aliphatic C-H Borylation Using Borenium Cation Equivalents. *J. Am. Chem. Soc.* **2011**, 133, 20056-20059.
- (9) Farrell, J. M.; Posaratnanathan, R. T.; Stephan, D. W. A Family of N-heterocyclic Carbene-Stabilized Borenium Ions for Metal-Free Imine Hydrogenation Catalysis. *Chem. Sci.* **2015**, 6, 2010-2015.
- (10) Prokofjevs, A. Thermal Dehydrogenation of Base-Stabilized $B_2H_5^+$ Complexes and Its Role in C-H Borylation. *Angew. Chem., Int. Ed.* **2015**, 54, 13401-13405.
- (11) Prokofjevs, A.; Jermaks, J.; Borovika, A.; Kampf, J. W.; Vedejs, E. Electrophilic C-H Borylation and Related Reactions of B-H Boron Cations. *Organometallics* **2013**, 32, 6701-6711.
- (12) Prokofjevs, A.; Kampf, J. W.; Solovyev, A.; Curran, D. P.; Vedejs, E. Weakly Stabilized Primary Borenium Cations and Their Dicationic Dimers. *J. Am. Chem. Soc.* **2013**, 135, 15686-15689.

- (13) Bissinger, P.; Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Kupfer, T.; Radacki, K.; Wagner, K. Generation of a Carbene-Stabilized Bora-borylene and its Insertion into a C-H Bond. *J. Am. Chem. Soc.* **2011**, *133*, 19044-19047.
- (14) (a) Rochette, E.; Courtemanche, M.-A.; Fontaine, F.-G. Frustrated Lewis Pair Mediated Csp³-H Activation. *Chem. - Eur. J.* **2017**, *23*, 3567-3571. (b) Lgar, M.-A.; Courtemanche, M.-A.; Rochette, .; Fontaine, F.-G. Metal-free Catalytic C-H Bond Activation and Borylation of Heteroarenes. *Science* **2015**, *349*, 513 – 516.
- (15) Kaese, T.; Trageser, T.; Budy, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. A Redox-Active Diborane Platform Performs C(sp³)-H Activation and Nucleophilic Substitution Reactions. *Chem. Sci.* **2018**, *9*, 3881-3891.
- (16) Menard, G.; Stephan, D. W. C-H Activation of Isobutylene Using Frustrated Lewis Pairs: Aluminum and Boron σ -Allyl Complexes. *Angew. Chem., Int. Ed.* **2012**, *51*, 4409 – 4412.
- (17) Koo, Y. T. S. Amidinato Silylene Complexes for Bond Activation and Catalysis. Ph.D. Thesis, Nanyang Technological University, Singapore, 2018.
- (18) Sen, S. S.; Hey, J.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D. Striking Stability of a Substituted Silicon(II) Bis(trimethylsilyl)amide and the Facile Si-Me Bond Cleavage without a Transition Metal Catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 12311-12316.
- (19) Jana, A.; Leusser, D.; Objartel, I.; Roesky, H. W.; Stalke, D. A Stable Silicon(II) Monohydride. *Dalton Trans.* **2011**, *40*, 5458-5463.

- (20) (a) Tseng, H.-C.; Shen, C.-T.; Matsumoto, K.; Shih, D.-N.; Liu, Y.-H.; Peng, S.-M.; Yamaguchi, S.; Lin, Y.-F.; Chiu, C.-W. $[\eta^5\text{-Cp}^*\text{B-Mes}]^+$: A Masked Potent Boron Lewis Acid. *Organometallics* **2019**, *38*, 4516-4521. (b) Shuttleworth, T. A.; Huertos, M. A.; Pernik, I.; Young, R. D.; Weller, A. S. Bis(phosphine)boronium Salts. Synthesis, Structures and Coordination Chemistry. *Dalton Trans* **2013**, *42*, 12917-12925.
- (21) When the deuterium derivative $[\text{L}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Si} \rightarrow \text{BD}_2\text{OTf}]$ (**3-D**) was reacted with compound **1** in refluxing toluene for 16h, the C(sp³)-H borylation and HD elimination were occurred to form the deuterated boronium ion **5-D** (¹¹B NMR: -33.2 ppm (singlet)).
- (22) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. Synthesis and Characterization of $[\text{PhC}(\text{N}t\text{Bu})_2]\text{SiCl}$: a Stable Monomeric Chlorosilylene. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948-3950.
- (23) (a) Fan, C.; Mercier, L. G.; Piers, W. E.; Tuononen, H. M.; Parvez, M. Dihydrogen Activation by Antiaromatic Pentaarylboroles. *J. Am. Chem. Soc.* **2010**, *132*, 9604-9606. (b) Houghton, A. Y.; Karttunen, V. A.; Fan, C.; Piers, W. E.; Tuononen, H. M. Mechanistic Studies on the Metal-Free Activation of Dihydrogen by Antiaromatic Pentarylboroles. *J. Am. Chem. Soc.* **2013**, *135*, 941-947.
- (24) (a) Lu, Z.; Cheng, Z.; Chen, Z.; Weng, L.; Li, Z. H.; Wang, H. Heterolytic Cleavage of Dihydrogen by "Frustrated Lewis Pairs" Comprised of Bis(2,4,6-tris(trifluoromethyl)phenyl)borane and Amines: Stepwise versus Concerted Mechanism. *Angew. Chem., Int. Ed.* **2011**, *50*, 12227. (b) Nikonov, G. I.; Vyboishchikov, S. F.; Shirobokov, O. G. Facile Activation of H-H and Si-H Bonds by Boranes. *J. Am. Chem. Soc.* **2012**, *134*, 5488-5491.

- (25) Bamford, K. L.; Qu, Z.-W.; Stephan, D. W. Activation of H₂ and Et₃SiH by the Borinium Cation [Mes₂B]⁺: Avenues to Cations [MesB(μ-H)₂(μ-Mes)BMes]⁺ and [H₂B(μ-H)(μ-Mes)B(μ-Mes)(μ-H)BH₂]⁺. *J. Am. Chem. Soc.* **2019**, *141*, 6180-6184.
- (26) Zheng, J.; Li, Z. H.; Wang, H. Addition of Dihydrogen to a Borylborenium Center. *Chem. Sci.* **2018**, *9*, 1433-1438.
- (27) Devillard, M.; Brousses, R.; Miqueu, K.; Bouhadir, G.; Bourissou, D. A Stable but Highly Reactive Phosphine-Coordinated Borenium: Metal-free Dihydrogen Activation and Alkyne 1,2-Carboboration. *Angew. Chem., Int. Ed.* **2015**, *54*, 5722-5726.
- (28) SHELXL-2014/6 (Sheldrick, 2014); Bruker AXS Inc., Madison, WI, USA, 2014.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT. 2009.

SYNOPSIS. The amidinato amidosilylene promoted the intramolecular C(sp³)-H borylation and H₂ elimination in the amidinato silylene-borane complex. The newly formed C(sp³)-B bond formed can be activated by adding back H₂ gas.