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B-H Bond Activation by an Amidinate-Stabilized Amidosilylene: Non-Innocent Amidinate Ligand

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ABSTRACT

The activation of B-H and B-Cl bonds in boranes by base-stabilized low valent silicon compounds is described. The reaction of the amidinato amidosilylene-borane adduct $[L\{Ar(Me_3Si)N\}SiBH_3]$ (**1**, $L = PhC(NtBu)_2$, $Ar = 2,6-iPr_2C_6H_3$) with MeOTf in toluene at room temperature formed $[L\{Ar(Me_3Si)N\}SiBH_2OTf]$ (**2**). $[LSiN(SiMe_3)Ar]$ in compound **2** then underwent a B-H bond activation with BH_2OTf in refluxing toluene to afford the B-H bond activation product $[LB(H)Si(H)(OTf)\{N(SiMe_3)Ar\}]$ (**3**). On the other hand, when compound **2** was reacted with 4-

dimethylaminopyridine (DMAP) in refluxing toluene, another B-H bond activation product $[(\mu-\kappa 1:\kappa 1-L)B(H)(DMAP)Si(H)\{N(Ar)SiMe_3\}]OTf$ (**4**) was afforded. Mechanistic studies show that “ $(\mu-\kappa 1:\kappa 1-L)B(H)(OTf)Si(H)\{N(Ar)SiMe_3\}$ ” (**2A**) is the key intermediate in the above-mentioned reactions. The formation of **2A** is further evidenced by the activation of the B-Cl bond in $PhBCl_2$ by the amidinato silicon(I) dimer $[LSi:]_2$ to form the B-Cl bond activation product $[(\mu-\kappa 1:\kappa 1-L)B(Cl)(Ph)Si(Cl)]_2$ (**6**). Compounds **2** – **4** and **6** were characterized by NMR spectroscopy and X-ray crystallography.

INTRODUCTION

Applications of N-heterocyclic carbenes (NHCs) have grown rapidly since their isolation and characterization.¹ Their use in main-group element and transition-metal chemistry, especially, as ligands in homogeneous catalysis² and in stabilizing main-group elements in the oxidation state of 0,³ are now well established. Although NHCs are usually regarded as stable spectator ligands, they are capable of activating main-group element-hydride bonds in beryllium,⁴ boron,⁵ aluminum⁶ and silicon hydrides⁷ by sequential oxidative addition, ring expansion and hydride migration.⁸ In each case, two hydrides originally bound to the main-group atom migrate to the C_{carbene} atom of an NHC giving an endocyclic CH_2 group, along with insertion of the resulting main-group element fragment into a C-N bond of the NHC to form a six-membered heterocycle (Chart 1a).

Similarly, N-heterocyclic silylenes (NHSis) are powerful spectator ligands in homogeneous transition metal-mediated catalysis⁹ and in stabilizing group 14 elements in the oxidation state of 0.¹⁰ However, the activation of main-group element hydrides by NHSis is scarcely known. Very recently, Baceiredo and Kato et al. reported the only example that the

phosphine-stabilized NHSi can activate the Si-H and P-H bonds of phenyl-silanes and phosphane (Chart 1b).¹¹

Chart 1. (a) NHC-ring expansion products **I** – **IV** by the reaction of :C{N(Ar)CH}₂ (Ar = 2,6-*i*Pr₂C₆H₃) with beryllium, boron and silicon hydrides. (b) P-H and Si-H bond activation by the phosphine-stabilized *N*-heterocyclic silylene **V**.

In comparison with Si-H and P-H bonds, the activation of a B-H bond is difficult because B-H bond dissociation energy is significantly high (for example, three-coordinate boron, BH₃: 105.5 kcal/mol; catecholborane: 111.3 kcal/mol; four-coordinate boron, NH₃BH₃: 102.6 kcal/mol).¹² In addition, B-H bond dissociation energies of boranes with different substituents are almost identical.¹² Moreover, borane prefers to use vacant p orbital, instead of B-H σ* orbital, to accept electrons, while B-H σ orbital is a poor donor.¹³ In this context, B-H bond activation by a singlet carbene and its heavier analogue is a synthetic challenge. No examples of B-H bond activation by NHSis were reported due to their weak nucleophilicity, while B-H bond activation

of non-amino-substituted boranes such as BH_3 and pinacolborane can only be achieved by using a singlet carbene and carbenoid, with pronounced nucleophilicity and/or electrophilicity.¹³

Since amidinate-stabilized low-valent silicon compounds possess fruitful results in coordination chemistry and small molecules activation,¹⁴ we were interested in investigating the feasibility of these compounds toward B-H bond activation. Herein, the B-H and B-Cl bond activation of boranes by an amidinato amidosilylene and silicon(I) dimer is reported.

RESULTS AND DISCUSSION

The amidinato amidosilylene $[\text{LSiN}(\text{SiMe}_3)\text{Ar}]$ ($\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, Scheme 1) was selected to activate B-H bond. It was prepared easily by the reaction of the amidinato chlorosilylene $[\text{LSiCl}]$ ¹⁵ with one equivalent of $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ ¹⁶ in toluene (Scheme 1). Colourless crystals of $[\text{LSiN}(\text{SiMe}_3)\text{Ar}]$ were harvested from a saturated toluene solution stored at 0 °C for 3 days. As shown in Figure 1, the Si1 atom is tricoordinated by two amidinate N donors and one amido ligand. The sum of bond angles around Si1 (281.82°) resembles that of other amidinato amidosilylenes $[\text{L}(\text{R}_2\text{N})\text{Si}:]$ ($\text{R} = \text{Me}$, 274.5°; $\text{R} = \text{SiMe}_3$, 289.59°).¹⁷ Its distorted trigonal pyramidal geometry corroborates the existence of a stereoactive lone pair. The Si–N(amidinate) bond lengths in this case are typical at 1.932(2) and 1.926(2) Å,^{15,17} while the Si–N(amido) bond length of 1.785(2) Å indicates it is a single bond.

Figure 1. Molecular structure of [LSiN(SiMe₃)Ar] with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-N1 1.932(2), Si1-N2 1.926(2), Si1-N3 1.785(2), C5-N1 1.341(3), C5-N2 1.342(3); N1-Si1-N2 67.80(9), N2-Si1-N3 106.88(9), N3-Si1-N1 107.14(9), N1-C5-N2 106.7(2).

[LSiN(SiMe₃)Ar] was then reacted with BH₃·THF in toluene to form the amidinato amidosilylene-borane adduct [L{Ar(Me₃Si)N}SiBH₃] (**1**, Scheme 1). The ¹H and ¹³C{¹H} NMR spectra elucidate one set of signals due to the amidinate and amido ligands. The ¹¹B{¹H} NMR signal occurs at δ -44.30 ppm, common for four-coordinate boron species. Additionally, a 1:3:3:1 quartet is observed when the spectroscopy is allowed to couple with ¹H, affirming the coordination of a BH₃ unit. Only a signal at δ 6.66 ppm, attributed to the SiMe₃ group, is observed in the ²⁹Si{¹H} NMR spectrum. Due to quadrupolar coupling with the neighbouring B atom, the boron-coordinated H and Si resonances could not be observed. Compound **1** was also characterized by X-ray crystallography (Figure 2), which shows that the Si-B bond length is 1.623(11) Å.

Scheme 1. Synthesis of [LSiN(SiMe₃)Ar] and **1**.

Figure 2. Molecular structure of **1** with thermal ellipsoids at 50% probability level. Selected hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.623(11), B1-H 0.98, Si1-N1 1.926(3), Si1-N2 1.898(2), Si1-N3 1.773(3); Si1-B1-H 109, H1BB-B1-H2BB 110, N1-Si1-N2 68.1(1), N1-C5-N2 106.9(3), N2-Si1-N3 107.7(1), B1-Si1-N3 126.4(5), B1-Si1-N1 113.8(5).

Compound **1** was then reacted with MeOTf in toluene at room temperature to form the amidinato amidosilylene-borane adduct [L{Ar(Me₃Si)N}SiBH₂OTf] (**2**, Scheme 2). Compound **2**

was characterized by multinuclear NMR spectroscopy. Similar to **1**, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra correspond well to the ligands and are unremarkable; the boron-coordinated H and Si resonances likewise could not be detected. The ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, however, both exhibit a broad signal at δ -11.37 ppm which precludes an investigation of the coupling constant with adjacent H atoms. The ^{19}F NMR spectrum displays a sharp singlet at δ -74.89 ppm, indicating that the triflate group is covalently attached onto the boron center. This is affirmed by the molecular structure of **2** determined by X-ray crystallography (Figure 3). The B-Si bond length observed in this case is 1.998(5) Å.

Scheme 2. Synthesis of **3** and **4** via B-H bond activation of BH_2OTf in **2**. The proposed mechanism for the formation of **3** through the intermediate **2A** is also shown.

Figure 3. Molecular structure of **2** with thermal ellipsoids at 50% probability level. Selected hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.998(5), B1-H1BB 1.15(4), B1-H2BB 1.09(4), B1-O1 1.601(5), Si1-N1 1.857(3), Si1-N2 1.835(3), Si1-N3 1.724(3); Si1-B1-H1BB 109(2), Si1-B1-H2BB 112(2), Si1-B1-O1 105.2(3), O1-B1-H2BB 110(2), N1-Si1-N2 71.4(1), N1-C5-N2 106.4(3), N1-Si1-N3 116.8(1), N3-Si1-B1 117.6(2), B1-Si1-N2 113.9(2).

While compound **1** was inert even upon heating at 120 °C in solution overnight, compound **2** underwent a B-H bond activation in refluxing toluene to form the B-H bond activation product [LB(H)Si(H)(OTf){N(SiMe₃)Ar}] (**3**, Scheme 2). It is a constitutional isomer of **2** and was isolated as colorless crystals from the reaction mixture. Its ¹H NMR spectrum shows one set of signals due to the amidinate and N(SiMe₃)Ar ligands. It also shows a broad singlet at δ 5.91 ppm for the Si-*H* proton, which falls in the expected region in comparison with that of silyl triflates [RR'SiH(OTf)] (¹H NMR, R, R' = Ph: δ 4.64; R = Ph, R' = Cl: 5.86; R = Me, R' = Ph: 4.83 ppm).¹⁸ The ¹¹B NMR signal (δ -5.45 ppm, d, ¹J_{B-H} = 109.3 Hz) is upfield shifted in comparison with that of the amidinato

boranes such as $[\text{PhC}(\text{N}i\text{Pr})_2\text{B}(\text{C}_6\text{F}_5)_2]$ ¹⁹ (δ 1.1 ppm) and $[\text{PhC}(\text{NCy})_2\text{BCl}_2]$ (δ 6.25 ppm).²⁰ The ^1H NMR signal of the B-*H* proton cannot be observed but the ^{29}Si INEPT spectrum reveals a broad signal at δ 4.91 ppm corresponding to the boron-coordinated Si atom. The X-ray crystal structure of **3** (Figure 4) shows that the amidinato ligand is bidentate coordinated to the B atom, which adopts a tetrahedral geometry. The $\text{N}_{\text{amidinato}}\text{-B}$ bond lengths (1.569(9), 1.572(8) Å) are comparable with those of the amidinato borane $[\text{PhC}(\text{N}i\text{Pr})_2\text{B}(\text{C}_6\text{F}_5)_2]$ (1.596(2), 1.597(2) Å).¹⁹ The B1-Si1 bond length (2.033(7) Å) is comparable with that of Lewis base-silylborane complexes such as $[\text{C}_5\text{H}_5\text{NB}(\text{Br})_2\text{Si}i\text{tBu}_3]$ (2.116(6) Å)²¹ and $[\text{I}_{i\text{PrMe}}\text{B}(\text{pin})\text{SiPh}_3]$ (2.123(1) Å, $\text{I}_{i\text{PrMe}} = \text{:C}\{\text{N}(i\text{Pr})\text{CMe}\}_2$).²²

Figure 4. Molecular structure of **3** with thermal ellipsoids at 50% probability level. Selected hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): B1-Si1 2.033(7), B1-H1B 1.2(1), B1-N1 1.569(9), B1-N2 1.572(8), Si1-H1SI 1.4(2), Si1-O1 1.781(5), Si1-N3 1.722(5); Si1-B1-H1B 117(8), N1-B1-Si1 115.7(5), N2-B1-H1B 111(8),

N1-B1-N2 82.2(5), N1-C5-N2 100.9(6), B1-Si1-O1 108.5(3), O1-Si1-N3 105.3(3), N3-Si1-H1SI 106(6), H1SI-Si1-B1 116(6).

The isomerization from **2** to **3** proceeds through the donation of lone pair electrons on the imino nitrogen atom to the σ^* orbital of the B-H bond in **2**, while the B-H σ electrons synergistically donate back to the empty p orbital on the Si centre (Scheme 3). In other words, the B-H bond of BH₂OTf undergoes an 1,1-oxidative addition on the Si^{II} centre of the amidinato amidosilylene, along with the N₂CSi four-membered ring opening to form **2A**. The Si-N σ bond in **2A** then attacks the boron center, along with a 1,2-migration of the OTf group to the Si atom, to form **3**. This mechanism is supported by theoretical studies (see below).

Scheme 3. Proposed mechanism for the isomerization of **2** to **3**.

In support of the feasibility of the bridging coordination mode of the amidinate ligand in **2A**, compound **3** was reacted with 4-dimethylaminopyridine (DMAP) in refluxing toluene in order to alter the coordination mode of the amidinate ligand in compound **3** by coordinating the boron centre with the Lewis base. This reaction resulted in the formation of the silylboronium cation in $[(\mu-\kappa 1:\kappa 1-L)B(H)(DMAP)Si(H)\{N(Ar)SiMe_3\}]OTf$ (**4**, Scheme 2). Compound **4** was isolated as a colorless crystalline solid. Its ¹H NMR spectrum shows two singlets at δ 0.97 and 1.06 ppm for two different *t*Bu chemical environments of the amidinate ligand. It also shows one set of signals

due to the N(SiMe₃)Ar substituent and a broad singlet at δ 5.02 ppm corresponding to the Si-*H* proton. The ¹¹B NMR signal (δ -44.33 ppm, d, $J_{\text{B-H}} = 89.2$ Hz) is significantly upfield shifted in comparison with that of **2** (δ -11.37 ppm). Similar upfield shift was observed in comparing the ¹¹B NMR signal of the 9-bromo-9-borafluorene (δ 65.8 ppm) with the corresponding bis(DMAP)-boronium bromide [(DMAP)₂B(Fl)]Br (δ 4.6 ppm, Fl = fluorene).²³ While the ¹H NMR signal of the *H*-B proton remains elusive for compound **4**, the presence of a proton on Si allows for an effective ²⁹Si INEPT experiment, which reveals a broad resonance at δ -0.52 ppm corresponding to the boron-coordinated Si atom.

Figure 5. Molecular structure of compound **4** with thermal ellipsoids at 50% probability level. Selected hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): B1-Si1 1.998(3), B1-H1B 1.09(3), B1-N3 1.580(4), B1-N2 1.570(5), Si1-H1S 1.38(4), Si1-N1 1.818(3), Si1-N4 1.748(2), C5-N1 1.365(4), C5-N2 1.345(4); Si1-B1-N2 100.8(2), N2-B1-N3 109.0(2), N3-B1-H1B 108(2), H1B-B1-Si1 115(2), B1-Si1-N1 89.6(1), N1-Si1-N4 113.5(1), N4-Si1-H1S 107(1), H1S-Si1-B1 113(1), N1-C5-N2 119.1(3).

Interestingly, only one of the four possible diastereomers (S_B , R_{Si}) is formed in this reaction. The X-ray crystal structure of **4** (Figure 5) shows a separated ion pair with the B...O distance (7.186 Å) being longer than the sum of their van der Waal's radii (ca. 3.48 Å). The amidinate ligand is $\mu-\kappa 1:\kappa 1$ -bridged between the boron and silicon centres, which adopt tetrahedral geometries. The C-N bond lengths are unequal (C5-N1: 1.365(4); C5-N2: 1.345(4) Å), but they are comparable with those of **2** (1.347(4), 1.342(4) Å). The N1-Si1 bond length (1.818(3) Å) is comparable with those of **2** (1.835(3), 1.857(3) Å) in which the amidinate ligand is bidentate coordinated to the Si^{II} centre. The N_{amidinate}-B bond length (N2-B1: 1.570(5) Å) is comparable with **3**. In addition, the DMAP-boron bond length (B1-N3: 1.580(4) Å) is comparable with that of [(DMAP)₂B(Fl)]Br (1.582(5) Å).²³ Moreover, the B1-Si1 bond (1.998(3) Å) is shorter than that **3**. On the basis of these X-ray crystallographic data and ¹¹B NMR signal, it is concluded that the positive charge in the cation of **4** is delocalized between the boron and silicon centres (Scheme 4).

Scheme 4. Resonance structures of the cation in compound **4**.

The mechanism for the reaction of **3** with DMAP in refluxing toluene is proposed. The reaction proceeds through the donation of lone pair electrons from the N donor of DMAP to the

boron centre in **3** (Scheme 5). As a result, one of the N donors on the amidinate ligand is displaced, forming intermediate **3A**. The structure of **3A** is suggested in accordance to the NMR data collected for the species that forms immediately upon addition of DMAP to **3** (see below). Upon its fast generation, the imino nitrogen atom of the amidinate ligand on **3A** follows to donate its lone pair electrons to the silicon centre, along with the displacement of the OTf group, to form **4**. Similar amidinate ring opening for small molecules activation was found in the reaction of $[\{HC(NR)_2\}B(C_6F_5)_2]$ ($R = iPr, tBu$) toward CO, $tBuNC$, $PhC(O)H$, etc..¹⁹

In support of the mechanism, the reaction was monitored by 1H NMR spectroscopy. Upon addition of DMAP to a solution of **3** in C_6D_6 , the latter disappeared quickly even at room temperature, with an immediate shift in the signals, most prominently of Si-*H* and NMe_2 signals. New singlets was observed at δ 5.78 and 2.86 ppm with an integral ratio of 1:6, suggesting the formation of an intermediate **3A** with similar Si-*H* environment as **3** but with DMAP already coordinated. This intermediate is short-lived in solution at ambient temperature (ca. 30 min) and ultimately transforms into compound **4** over a period of 5 hours (Figure S 23, see supporting information).

Scheme 5. Proposed mechanism for the formation of **4** from **3** via **3A**.

On the basis of the X-ray crystal structure of **4**, it seems that compound **4** could be directly formed by the displacement of OTf in **2A** with DMAP in refluxing toluene. In this context, compound **2** was reacted with DMAP in refluxing toluene and the reaction was monitored by ^1H NMR spectroscopy. Upon addition of equimolar DMAP, **2** converted cleanly to **4** over a period of ca. 24 hours at 60 °C in C_6D_6 without observation of **3** (Figure S 24). These illustrate that $[\text{LSiN}(\text{SiMe}_3)\text{Ar}]$ undergoes a B-H bond activation with BH_2OTf to form the intermediate **2A** first. In the presence of DMAP, compound **4** was formed by the displacement of the OTf substituent in **2A** (Scheme 6). Otherwise, **2A** isomerizes to form compound **3**.

Scheme 6. Proposed mechanism for the formation of **4** from **2** via **2A**.

In support of the feasibility of **2A** in the mechanism, we investigated the activation of B-X bonds ($\text{X} = \text{H}, \text{Cl}, \text{Br}$) by other amidinato low-valent silicon compounds, so that an analogue of **2A** can be isolated. After numerous attempts, it was found that the amidinato silicon(I) dimer $[\text{LSi:}]_2$ (**5**)²⁴ reacted with PhBCl_2 in toluene to form the B-Cl bond activation product $[(\mu-\kappa 1:\kappa 1-\text{L})\text{B}(\text{Cl})(\text{Ph})\text{Si}(\text{Cl})]_2$ (**6**, Scheme 7), which can be viewed as a dimer analogue of intermediate **2A**. The mechanism for the formation of **6** is similar to that of **3**. It is proposed that the reaction proceeds through a dimeric silicon(I)-borane adduct intermediate “ $\{\text{LSiBCl}_2(\text{Ph})\}_2$ ” (**5A**, Scheme 7). Subsequently, the imino nitrogen atom of the amidinate ligand donates its lone pair electrons to the σ^* orbital of the B-Cl bond, while the B-Cl σ electrons synergistically donate back to the

empty p orbital on the Si centre. Compound **6** did not further undergo isomerization in contrast to the intermediate **2A**, which suggests that the Cl substituent at the boron centre cannot proceed 1,2-migration.

Scheme 7. Synthesis of **6**. The proposed mechanism for the formation of **6** through the silylene-borane intermediate **5A** is also shown.

Compound **6** was isolated as an air- and moisture-sensitive colorless crystalline solid. The ^1H NMR spectrum shows two signals for the *t*Bu substituents (δ 1.24, 1.26 ppm), which indicate two different N environments. The ^{11}B NMR signal (δ 7.11 ppm) is downfield shifted in comparison with that of **3**. All attempts to obtain a ^{29}Si NMR spectrum were unsuccessful due to the adjacent quadrupolar boron atom. As in compound **4**, only one diastereomer of **6** is formed selectively, with both chiral Si centers adopting *R*-configurations. The X-ray crystal structure (Figure 6) shows that compound **6** has a gauche-bent geometry. The amidinate ligand is μ - $\kappa 1:\kappa 1$ -bridging between the Si and B atoms leading to a puckered boron-silicon five-membered ring, while the Si and B atoms adopt tetrahedral geometries. The N-Si [N1-Si1: 1.805(4), N3-Si2:

1.800(4) Å], N-B [B1-N2: 1.582(7), B2-N4: 1.579(6) Å], B-Si [B1-Si1: 1.998(6), B2-Si2: 1.999(6) Å] and C-N [N1-C5: 1.365(6), N2-C5: 1.337(6) Å] bond lengths are comparable with those of **3**. The Si-Si bond length (2.3725(19) Å) is shorter than that of compound **5** (2.413(2) Å).²⁴

Figure 6. Molecular structure of compound **6** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-B1 1.998(6), Si1-N1 1.805(4), B1-N2 1.582(7), Si1-Cl2 2.0939(18), Si1-Si2 2.3725(19), Cl1-B1 1.915(6), N1-C5 1.365(6), N2-C5 1.337(6); Cl2-B1-Cl2 108.48(12), Si1-B1-N2 99.7(3), Si1-B1-Cl1 106.9(3), N2-B1-Cl1 111.0(4), N1-Si1-B1 91.9(2), N1-Si1-Cl2 107.44(14), B1-Si1-Cl2 112.66(18), N1-Si-Si2 113.39(14), B1-Si1-Si2 118.54(18), Cl2-Si-Si2 110.10(17).

In support of the experimental observations, DFT calculations for the reaction mechanism were carried out at M06-2X/Def2-TZVP//M06-2X/Def2-SVP level of theory (Figures 7 and 8).²⁵ The reference point of reaction profile is the sum of the energy of **1**, MeOTf and DMAP at infinite separation. As seen in Figure 7, compound **1** reacts with MeOTf to form thermodynamically stable

compound **2** ($\Delta G_{1+MeOTf \rightarrow 2} = -43.9 \text{ kcal mol}^{-1}$). Subsequently, $[LSiN(SiMe_3)Ar]$ in **2** undergoes a B-H bond activation with BH_2OTf through the transition state **TS1** (activation energy: $32.5 \text{ kcal mol}^{-1}$, Figure S 25), in which there is a synergic electronic transfer between the imine nitrogen lone pair orbital and the B-H bond, to form **2A** ($\Delta G_{1+MeOTf \rightarrow 2A+CH_4} = -40.1 \text{ kcal mol}^{-1}$, Figure S 26). This relatively high activation barrier corroborates the hypothesis that formation of **2A** is a slow process.

In the presence of DMAP (Scheme 6), the displacement of the OTf substituent in **2A** proceeds through the transition state **TS4** (activation energy: $35.7 \text{ kcal mol}^{-1}$, Figure S 27), in which the B atom interacts weakly with an incoming DMAP molecule and a leaving OTf moiety, eventually leading to the production of **4** ($\Delta G_{1+MeOTf+DMAP \rightarrow 3+CH_4} = -49.1 \text{ kcal mol}^{-1}$).

On the other hand, in the absence of DMAP, the isomerization of **2A** to **3** easily occurs (Scheme 3). It proceeds through the transition state **TS2** (Figure S 28) with a significantly small activation energy of 5 kcal mol^{-1} , in which the OTf group undergoes 1,2-migration from the boron to silicon centre, along with the formation of the $N_{amidinate}$ -B bond.

Subsequent reaction of **3** with DMAP (Scheme 5) proceeds to **TS3** ($-12.9 \text{ kcal mol}^{-1}$, Figure S 29) which exhibits a weak interaction between the B atom and the N donor of DMAP, as well as an elongated Si-N interaction. The structure presented in **TS3** is akin to our proposed intermediate **3A**, substantiating its formation. Finally, compound **4** is afforded due to the attack of DMAP to the boron centre in **3**, followed by the displacement of the OTf group by the chelation of the amidinate ligand (Scheme 5).

Figure 7. Free energy profile (kcal/mol) for the formation of **3** and **4**. The abbreviations TS stands for transition state; optimized geometries of the transition states for the formation of **3** and **4** at M06-2X/Def2-SVP are given in the supporting information.

Topological analysis was also performed to understand the nature of the B-Si bond in the cation of **4** using QTAIM (Quantum Theory of Atoms in Molecules) calculations.²⁵ The electron density, $\rho(r)$, at the (3,-1) bond critical points (BCPs) of N-B (0.14) and N-Si (0.10) bonds, along with the correspondingly positive Laplacian [$\nabla^2\rho(r)$; +0.24 and +0.30], indicate closed-shell interaction i.e., donor-acceptor bond. This is further supported by contour plot of Laplacian distribution (Figure 8), showing charge concentration at the nitrogen end of the amidinate ligand

(solid lines) and charge depletion at the boron and silicon end (dotted line), respectively. In contrast, the $\rho(r)$ at the BCPs of the B–Si (0.12) bond, along with the negative Laplacian (-0.19), indicate open-shell interaction i.e., covalent bond. This is supported by the calculated Laplacian distribution, exhibiting charge concentration in the middle of B-Si bond.

Figure 8. Contour plot of Laplacian distribution [$\nabla^2\rho(r)$] in the N-B-Si plane and QTAIM of the cation in **4**. Solid lines indicate the areas of the charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$). Brown, blue, orange dots denote (3,-3), (3,-1), (3,+1) critical points respectively. Solid lines connecting atomic nuclei (black) are the bond paths, and those lines (purple) separating the atomic basins indicate the zero-flux surface crossing the molecular plane.

CONCLUSION

B-H and B-Cl bonds in BH_2OTf and PhBCl_2 can be activated by the amidinato amidosilylene and silicon(I) dimer, respectively. The mechanism proceeds through the synergic effort of the amidinate ligand and low-valent silicon centre to promote double electron transfer with the B-X (X = H, Cl) bonds, that is, donation of electrons to the B-X σ^* orbitals and simultaneous back donation of the B-X σ electrons to the empty p orbital on the low-valent silicon centre.

EXPERIMENTAL

General considerations: All manipulations, unless otherwise stated, were carried out by using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Pentane, diethyl ether, hexane and toluene were dried using a MBraun Solvent purification system, degassed, and stored under an atmosphere of argon prior to use. Tetrahydrofuran (THF) was dried and distilled over molten potassium. All NMR spectra were recorded on a JEOL ECA 400 or Bruker 400 spectrometer. ^1H NMR spectra were referenced to residual solvent peaks. All chemicals, unless otherwise stated, were used as purchased without further purification. $[\text{LSiCl}]$,¹⁵ $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ ¹⁶ and **5**²⁴ were synthesized according to literature procedures.

Synthesis of $[\text{LSiN}(\text{SiMe}_3)\text{Ar}]$: Toluene (ca. 40 mL) was added to a mixture of $[\text{LSiCl}]$ (L = $\text{PhC}(\text{N}t\text{Bu})_2$; 1.47 g, 5.00 mmol, 1.0 equiv) and $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ (Ar = 2,6-*i*PrC₆H₃; 1.28 g, 5.00 mmol, 1.0 equiv). The reaction mixture was allowed to stir for 16 hours. Volatiles were removed under vacuum and the resulting residue was washed with hexane to afford the product as a yellowish powder. Yield: 4.66 g (92 %); Mp: 60-65 °C; ^1H NMR (400.1 MHz, C₆D₆, 25.9 °C): δ = 0.33 (s, 9H, SiMe₃), 1.29 (s, 18H, *t*Bu), 1.37 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 6H, CHMe₂), 1.42 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 6H, CHMe₂), 4.02 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 2H, CHMe₂), 6.87–7.10 (m, 5H, ArH), 7.19–7.26

(m, 2H, ArH), 7.32–7.35 (m, 1H, ArH) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 27.0 °C): δ = 4.37 (SiMe₃), 24.73 (CHMe₂), 28.13 (CHMe₂), 33.33 (CMe₃), 54.61 (CMe₃), 124.77, 125.33, 127.64, 129.72, 131.89, 135.94, 145.37, 148.49 (Ph), 164.56 (NCN) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 26.9 °C): δ = 1.16 (LSiN), 3.48 (SiMe₃) ppm; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{50}\text{N}_3\text{Si}_2$: 508.3543 [(M+H)]⁺; found: 508.3538.

Synthesis of (1): Borane tetrahydrofuran complex (1.0 M in THF, 13.3 mL, 2.0 equiv.) was added to a solution of [LSiN(SiMe₃)Ar] (3.40 g, 6.69 mmol, 1.0 equiv.) in toluene (20 mL) at ambient temperature. The mixture was allowed to stir and solution changed from clear orange to cloudy yellow after 16 hours. After filtration, the filtrate was concentrated to afford the product as colorless crystals. Yield: 2.37 g (69 %); Mp: 200–203 °C; ^1H NMR (399.5 MHz, C_6D_6 , 25.6 °C): δ = 0.27 (s, 9H, SiMe₃), 1.27 (s, 18H, *t*Bu), 1.29 (d, $^3J_{\text{H-H}}$ = 6.9 Hz, 6H, CHMe₂), 1.54 (d, $^3J_{\text{H-H}}$ = 6.9 Hz, 6H, CHMe₂), 3.84 (sept, $^3J_{\text{H-H}}$ = 6.9 Hz, 2H, CHMe₂), 6.83–6.99 (m, 3H, ArH), 7.11–7.15 (m, 2H, ArH), 7.18–7.25 (m, 3H, ArH) ppm, H_B signal was not detected; $^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, C_6D_6 , 25.9 °C): δ = -44.30 (s) ppm; ^{11}B NMR (128.2 MHz, C_6D_6 , 25.9 °C): δ = -44.05 (q, $^1J_{\text{B-H}}$ = 92.9 Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 26.9 °C): δ = 3.72 (SiMe₃), 25.34 (CHMe₂), 26.86 (CHMe₂), 28.31 (CHMe₂), 32.46 (CMe₃), 56.16 (CMe₃), 125.01, 126.27, 130.13, 130.65, 132.66, 142.58, 147.45 (Ph), 176.03 (NCN) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 26.6 °C): δ = 6.66 (SiMe₃) ppm, Si_B signal was not detected; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{53}\text{BN}_3\text{Si}_2$: 522.3871 [(M+H)]⁺; found: 522.3854.

Synthesis of (2): Methyl trifluoromethanesulfonate (0.192 g, 0.13 mL, 1.17 mmol, 1.0 equiv.) was added to a solution of **1** (0.608 g, 1.17 mmol, 1.0 equiv.) in toluene (20 mL) at ambient temperature. The mixture was allowed to stir and solution changed from pale yellow to colourless after 16 hours with slight bubbling. After filtration, the filtrate was concentrated to afford the

product as colorless crystals. Yield: 0.570 g (73 %); Mp: 125-130 °C; ^1H NMR (395.9 MHz, C_6D_6 , 26.4 °C): δ = 0.17 (s, 9H, SiMe_3), 1.17 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CHMe_2), 1.21 (s, 18H, $t\text{Bu}$), 1.39 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CHMe_2), 3.60 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, CHMe_2), 6.87–7.13 (m, 7H, ArH), 7.67–7.69 (m, 1H, ArH) ppm, H_B signal was not detected; $^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, C_6D_6 , 26.0 °C): δ = -11.37 (br) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 26.4 °C): δ = 3.44 (SiMe_3), 25.58 (CHMe_2), 26.63 (CHMe_2), 28.39 (CHMe_2), 32.25 (CMe_3), 56.54 (CMe_3), 125.46, 127.11, 127.91, 129.45, 130.26, 130.99, 131.32, 139.84, 146.47, 147.01 (Ph), 178.40 (NCN) ppm, C_F signal was not detected; ^{19}F NMR (372.5 MHz, C_6D_6 , 26.6 °C): δ = -74.89 (s) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 26.4 °C): δ = 9.60 ppm, Si_B signal was not detected; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{52}\text{BF}_3\text{N}_3\text{O}_3\text{SSi}_2$: 670.3313 [$(M+H)^+$]; found: 670.3323.

Synthesis of (3): **2** (0.669 g, 1.00 mmol) was stirred overnight in refluxing toluene (20 mL). After filtration, the filtrate was concentrated to afford the product as colorless crystals. Yield: 0.601 g (90 %); Mp: 146-151 °C; ^1H NMR (395.9 MHz, C_6D_6 , 24.9 °C): δ = 0.37 (s, 9H, SiMe_3), 0.94 (s, 9H, CMe_3), 1.20 (s, 9H, CMe_3), 1.24 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.27 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.48 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.58 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 3.68–3.77 (m, 2H, CHMe_2), 5.91 (br s, 1H, SiH), 6.79–7.15 (m, 7H, ArH), 7.95 (br, 1H, ArH) ppm, H_B signal was not detected; $^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.3 °C): δ = -5.51 (s) ppm; ^{11}B NMR (127.0 MHz, C_6D_6 , 25.2 °C): δ = -5.45 (d, $^1J_{\text{B-H}} = 109.3$ Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 23.8 °C): δ = 2.76 (SiMe_3), 25.05 (CHMe_2), 25.53 (CHMe_2), 25.99 (CHMe_2), 26.73 (CHMe_2), 28.46 (CHMe_2), 26.64 (CHMe_2), 30.52 (CMe_3), 31.37 (CMe_3), 53.20 (CMe_3), 53.37 (CMe_3), 115.74, 115.95, 124.73, 125.22, 126.44, 130.45, 133.24, 140.73, 147.28, 147.44 (Ph), 167.63 (NCN) ppm, C_F signal was not detected; ^{19}F NMR (372.5 MHz, C_6D_6 , 25.0 °C): δ = -76.55

(s) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 23.8 °C): δ = 4.91 (br, *SiB*), 9.72 (*SiMe*₃) ppm; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{52}\text{BF}_3\text{N}_3\text{O}_3\text{SSi}_2$: 670.3313 [$(M+H)$]⁺; found: 670.3304.

Synthesis of (4): *Method A:* Toluene (20 mL) was added to a mixture of **2** (0.669 g, 1.00 mmol, 1.0 equiv.) and 4-dimethylaminopyridine (0.122 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. After filtration, the filtrate was concentrated to afford the product as colorless crystals. *Method B:* Toluene (20 mL) was added to a mixture of **3** (0.669 g, 1.00 mmol, 1.0 equiv.) and 4-dimethylaminopyridine (0.122 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. After filtration, the filtrate was concentrated to afford the product as colorless crystals. Yield: 0.670 g (85 %); Mp: 131-135 °C; ^1H NMR (399.5 MHz, C_6D_6 , 23.5 °C): δ = 0.34 (s, 9H, *SiMe*₃), 0.97 (s, 9H, *CMe*₃), 1.06 (s, 9H, *CMe*₃), 1.16 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 3H, *CHMe*₂), 1.21–1.27 (m, 9H, *CHMe*₂), 2.39 (s, 6H, *NMe*₂), 3.52 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 1H, *CHMe*₂), 3.61 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 1H, *CHMe*₂), 5.02 (br s, 1H, *SiH*), 6.92–7.10 (m, 7H, *ArH*), 7.18–7.21 (m, 1H, *ArH*), 7.57–7.61 (m, 1H, *ArH*), 8.01–8.03 (m, 2H, *ArH*), 8.98–9.00 (m, 1H, *ArH*) ppm, *H_B* signal was not detected; $^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, C_6D_6 , 23.7 °C): δ = -44.30 (s) ppm; ^{11}B NMR (128.2 MHz, C_6D_6 , 23.7 °C): δ = -44.33 (d, $^1J_{\text{B-H}}$ = 89.2 Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 23.8 °C): δ = 4.30 (*SiMe*₃), 25.91 (*CHMe*₂), 25.97 (*CHMe*₂), 26.01 (*CHMe*₂), 26.35 (*CHMe*₂), 28.38 (*CHMe*₂), 29.06 (*CHMe*₂), 33.40 (*CMe*₃), 33.63 (*CMe*₃), 39.25 (*NMe*₂), 60.23 (*CMe*₃), 63.25 (*CMe*₃), 109.59, 125.00, 125.30, 126.12, 126.66, 129.25, 130.36, 131.54, 133.97, 134.14, 143.46, 144.00, 146.47, 146.85, 156.23 (*Ar*), 182.34 (*NCN*) ppm, *C_F* signal was not detected; ^{19}F NMR (375.9 MHz, C_6D_6 , 23.6 °C): δ = -77.54 (s) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 23.8 °C): δ = -0.52 (br, *SiB*), 8.45 (*SiMe*₃) ppm; HRMS (ESI): m/z calcd for $\text{C}_{37}\text{H}_{61}\text{BN}_5\text{Si}_2$: 642.4559 [$(M-OTf)$]⁺; found: 642.4572.

Synthesis of (6): Dichlorophenylborane (0.32 g, 2.00 mmol, 2.0 equiv.) was added dropwise to the solution of **5** (0.52 g, 1.00 mmol, 1.00 equiv.) in toluene (30 mL) at ambient temperature. The resulting yellow mixture was stirred for 16 hours. After filtration, the filtrate was concentrated to afford the product as colorless crystals. Yield: 0.420 g (51 %); Mp: 214 °C (decomposed); ^1H NMR (399.5 MHz, C_6D_6 , 24.3°C): δ = 1.24 (s, 18H, *t*Bu), 1.25 (s, 18H, *t*Bu), 6.79–6.84 (m, 2H, Ph), 6.88–6.97 (m, 4H, Ph), 7.06 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 2H, Ph), 7.23–7.28 (m, 2H, Ph), 7.48–7.54 (m, 4H, Ph), 7.62 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 2H, Ph), 7.90 (d, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, Ph), 8.21 (d, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, Ph) ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 24.3°C): δ = 7.11 (s) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 24.3°C): δ = 33.10 (*CMe*₃), 35.08 (*CMe*₃), 60.80 (*CMe*₃), 65.56 (*CMe*₃), 125.73, 126.83, 127.07, 127.28, 130.73, 131.29, 131.99, 132.32, 132.98, 134.26 (Ph), 178.46 (NCN) ppm; Si_B signal was not detected; HRMS (ESI), *m/z* calcd for $\text{C}_{42}\text{H}_{56}\text{B}_2\text{Cl}_4\text{N}_4\text{Si}_2$: 835.3062 [*(M+H)*]⁺; found: 835.3076.

X-ray data collection and structural refinement: Intensity data for all compounds were collected by using a Bruker APEX II diffractometer. Experimental data is summarized below. The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .²⁶ All non-hydrogen 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.

ASSOCIATED CONTENT

Supporting Information.

Crystallographic data and details of DFT calculations (PDF)

X-ray data for compounds [**LSiN(SiMe₃)Ar**], **1–4** and **6** (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡S.K. and Y.-L.S. contributed equally.

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SYNOPSIS.

Through the synergic effort of the amidinate ligand and low-valent silicon centre, the amidinato amidosilylene-borane adduct **2** underwent a B-H bond activation to afford **3** and **4**.