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Silicon–carbon bond cleavage from a hydroboration sequence

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The reactions of internal pyridyl/trialkylsilyl alkynes with the potent hydroboration reagent bis(1-methyl-*ortho*-carboranyl)borane ($HB^{Me}oCb_2$) results in unanticipated Si–C_{alkyl} cleavage following a regioselective 1,1-hydroboration under mild conditions. The rare Si–Me bond rupture of the trimethylsilyl group occurs when using an intramolecular frustrated Lewis pair system forming a silylium heterocycle with a pendant borate bearing the methyl group. Investigating a methyl/ethyl mixed silyl substituent, $SiEtMe_2$, revealed that the reaction is completely selective in breaking the Si–Me bond over the Si–Et bond. Exposure of the silylium/borate zwitterion to methanol resulted in O–H bond cleavage and ring opening to a zwitterionic pyridinium/borate. These findings provide insight into the challenging selective functionalization of Si–C_{alkyl} bonds.

Introduction

The hydroboration of alkynes is a powerful synthetic method to access building blocks with versatile boryl functional groups.[1–4] The reaction can be mediated by a metal catalyst or proceed uncatalyzed, with the latter being possible with very Lewis acidic boranes or activated alkynes. The reaction can lead to either 1,2- or 1,1-hydroboration products.[5] Both regioisomers are desirable and highlight the versatility of alkyne hydroboration. The classical uncatalyzed 1,2-hydroboration pioneered by Brown occurs *via* a concerted 4-membered cyclic transition state **I** to furnish the vinyl borane **II** with the boryl group and hydride on adjacent carbon atoms (Fig. 1).[6,7] Contrarily, the 1,1-hydroboration gives the alternative vinyl borane isomer with the boryl and hydride on the same carbon.[8–18] The accepted reaction mechanism proceeds by isomerization to form a reactive zwitterionic vinyl borate intermediate (**III**) that undergoes a 1,2-hydride shift from the borate to the carbocation to furnish the vinyl borane (**IV**).[11,17] Wrackmeyer, Piers, Stephan, Erker, and others have investigated intermediates of type **III**, also referred to as boravinylidenes, but they were unable to characterize them.[19–21,22–29] Challenges occur due to the extremely reactive vinyl cation adjacent to the borate center.

In hydroboration reactivity, a consequence of the reactive boravinylidene is often poor regioselectivity giving mixtures of products. The highly Lewis acidic secondary borane, bis(1-methyl-*ortho*-carboranyl)borane ($HB^{Me}oCb_2$), is an effective 1,1-hydroboration reagent for phenyl ethynylsilanes ($PhC{\equiv}CSiR_3$).[30] Regioselective 1,1-hydroboration reactions are rare and in this instance is attributed to the high hydride affinity of the carborane substituted $-B^{Me}oCb_2$ boryl group that attenuates the hydride transfer as well as hyperconjugative stabilization of the vinyl cation from the silyl group.[31–33] In fact, the hydroboration attempt of a bis(trimethylsilyl)alkyne with $HB^{Me}oCb_2$ enabled the crystallographic characterization of boravinylidene **V**, as the additional silyl group sufficiently stabilized the carbocationic center (Fig. 2a).[34]

Given that silyl hyperconjugative interactions were effective for characterizing a boravinylidene, we envisioned that an internal alkyne with a trimethylsilyl and pyridyl group (**VI**) could provide mechanistic insight into 1,1-hydroboration reactions and lead to the isolation of an intramolecularly stabilized boravinylidene (**VII**, Fig. 2b). Instead, the reaction of the alkyne with $HB^{Me}oCb_2$ led to the unexpected cleavage of a Si–Me bond of the $-SiMe_3$ group (**VIII**). Generally, $-SiMe_3$ groups are considered inert, underscored by their use as protecting

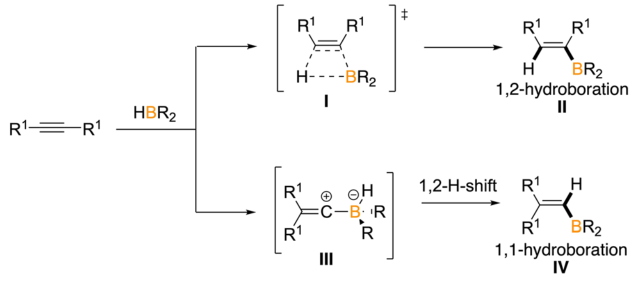

Fig. 1 1,2- and 1,1-hydroboration reactions of alkynes.

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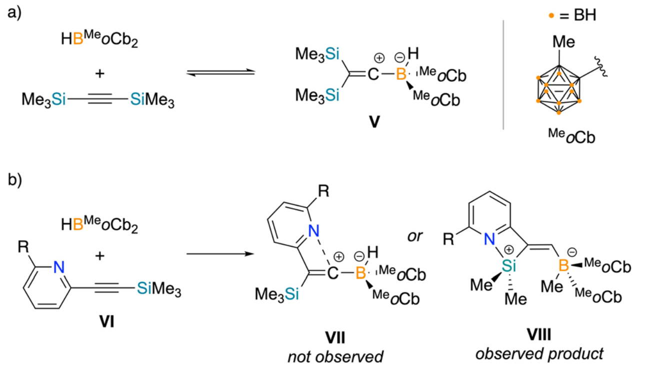


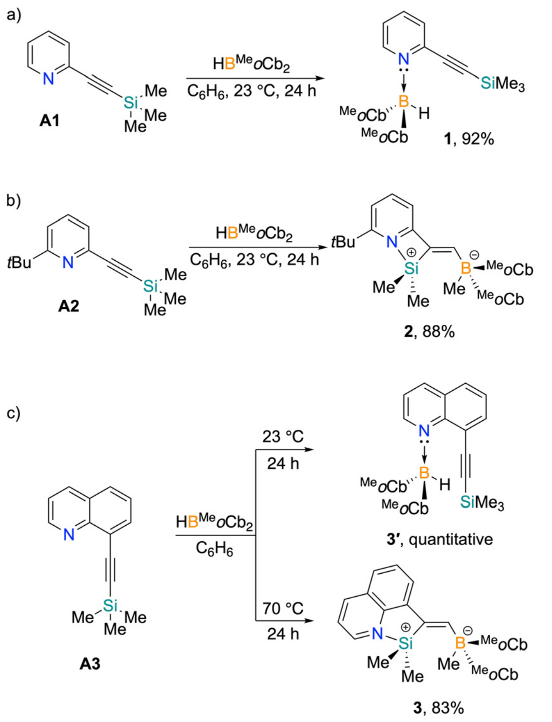
Fig. 2 (a) Characterized boravinylidene intermediate **V** and (b) reactions targeting base-stabilized boravinylidenes in this study.

groups in synthesis. The selective activation and cleavage of unactivated Si–Me bonds offer a potential means for the functionalization of alkylsilanes, moieties prominent in medicinal chemistry, as well as in polymer and materials science. Herein, we investigate the reactivity of pyridyl/silyl alkynes with $HB^{Me}oCb_2$.

Results and discussion

The equimolar reaction of commercially available 2-((trimethylsilyl)ethynyl)pyridine (**A1**) and $HB^{Me}oCb_2$ at 23 °C in benzene gave a major product after 24 hours that was isolated in 92% yield (Scheme 1a). The characteristic tricoordinate $^{11}B\{^1H\}$ NMR signal for $HB^{Me}oCb_2$ at 71.0 ppm is consumed and the identity of the product was determined by a single crystal X-ray diffraction study as the pyridine/borane adduct **1** (Fig. 3). Heating a benzene solution of **1** at 70 °C for 24 hours did not result in any conversion to a different compound.

It has been established that $HB^{Me}oCb_2$ is an effective Lewis acid and binds irreversibly with phosphines (*i.e.* PMe_3 and PPh_3), triethylphosphine oxide, 4-fluorobenzonitrile, ethylactetate, tri-*n*-butylamine, and carbene (IMes).[30,35–37] Bulky phosphines like PCy_3, $PtBu_3$, and $PMes_3$ do not make adducts due to the steric demands. Regarding pyridines, 2,6-lutidine coordinates to boron; thus, to preclude adduct formation to access hydroboration reactivity, we believed that the pyridine moiety in **A1** would require a substituent bulkier than methyl. Accordingly, we prepared an analogue of **A1** that features a *tert*-butyl group on the pyridine carbon adjacent to nitrogen, 2-(*tert*-butyl)-6-((trimethylsilyl)ethynyl)pyridine (**A2**), by a Sonagashira coupling reaction. The equimolar reaction of **A2** with $HB^{Me}oCb_2$ at 23 °C in benzene gave a major product after 24 hours that was isolated in 88% yield (Scheme 1b). The identity of the product was established as the silylium/borate zwitterion **2** by a single crystal X-ray diffraction study (Fig. 3). Studies by Piers, Gandelman, Alcarazo, Gagné, and our group have demonstrated Si–H bond splitting under mild conditions using borane/phosphine or borane/amine FLP systems.[38–54] Though the Si–C bond energies are similar to



Scheme 1 Reactions of (a) pyridine-, (b) *tert*-butyl-pyridine-, and (c) quinoline-tethered (trimethylsilyl)ethynyl species with $HB^{Me}oCb_2$.

Si–H bond energies (~90 kcal mol^{-1}), their activation is less common.[55] The compound features an intramolecular pyridine-silylium adduct in an $SiNC_2$ heterocycle consisting of the nitrogen, *ortho*-carbon of the pyridine, the *ipso*-alkyne carbon, and the silicon bearing only two methyl groups. The borate center bears the two carborane substituents as well as the migrated methyl group and is bound to the distal alkyne carbon. The hydride is introduced on the same carbon as the borate, consistent with a 1,1-hydroboration pathway.

The ^1H NMR spectrum features a singlet at 1.13 ppm integrating to 6 for the $SiMe_2$ protons and a singlet at 0.24 ppm with an integration of 3 for the migrated BMe group. The $^{29}Si\{^1H\}$ NMR signal for **2** is shifted significantly downfield from **A2** (59.9 ppm, *cf.* −17.0 ppm) and is in the range of known pyridine stabilized alkylsilylium species (45–65 ppm).[56–59] In the solid-state structure of **2**, the carbon–carbon bond is consistent with an alkene [C2–C3 1.336(3) Å] that is corroborated in the FT-IR spectrum with a C=C stretching frequency of 1600 cm^{-1}. The geometries at C2 and C3 are distorted trigonal planar due to the bulk around the double bond and the strain from the four membered ring. Compound **2** is stable under a nitrogen atmosphere at −40 °C for over 12 months with no detectable decomposition. The synthesis of **2** also works smoothly on a larger scale (236 mg, 85% yield) by reacting 0.50 mmol of **A2** and $HB^{Me}oCb_2$ in C_6H_6 (5 mL) at 23 °C for 24 hours. The reactions of **A2** with HBpin or HBcat did not result in any reaction, even after heating at 70 °C for 24 hours, indicating the importance of the electrophilic $HB^{Me}oCb_2$ reagent.

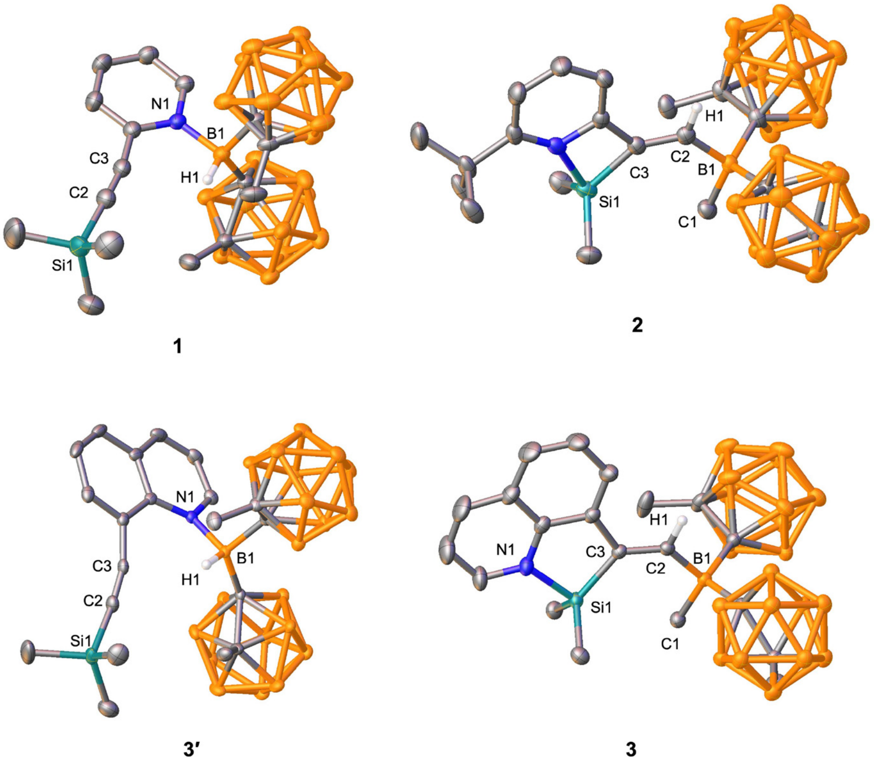


Fig. 3 Solid state structures of **1–3** and **3′**. Ellipsoids depicted at the 50% probability level. Hydrogen atoms, except on the vinylic carbon or central boron atom, and solvates are omitted for clarification.

To determine if a quinoline-tethered ethynylsilane would alter the reaction outcome, the corresponding alkyne (**A3**) was reacted with $HB^{Me}oCb_2$ at 23 °C for 24 hours. Adduct **3′** was generated as confirmed by single crystal X-ray diffraction (Fig. 3). The B1–N1 bond length in adducts **1** and **3′** are similar [1.623(3) Å, *cf.* 1.6080(19) Å] and comparable to that of the only other N-ligated $HB^{Me}oCb_2$ species, a 2,6-lutidine adduct [1.631(4) Å].[35] Heating a benzene solution of **3′** at 70 °C for 24 hours led to conversion to the Si–Me split product akin to **2** with a 5-membered sila-cycle (**3**) isolated in 83% yield (Scheme 1c). The structure of **3** was confirmed by single crystal X-ray diffraction. The $^{29}Si\{^1H\}$ NMR resonance of **3** appears downfield from the alkyne but upfield from that of **1** (**3**: 29.5 ppm *cf.* **A3**: −17.4, and **2**: 59.9 ppm).

1,1-Hydroboration reactions often suffer from poor selectivity leading to mixtures of both *E*- and *Z*-isomers.[60] The proposed mechanism for **2** involves silane to boron transmetalation between the $-SiMe_3$ group and $HB^{Me}oCb_2$ to generate the ethynylborate with a pyridine ligated silylium cation (**Int1**, Fig. 4). Hydride and silylium migration generates **Int2** that is guided by the tethered pyridine to achieve the regioselective *trans*-1,1-hydroboration. The pyridine and borane serve as an intramolecular FLP system in **Int2** to enable the Si–Me bond cleavage to form **2**. Monitoring the reaction by ^1H and ^{11}B NMR spectroscopy in C_6D_6 at 23 °C did not enable the detection of intermediates.

The controlled cleavage of Si–Me bonds is rare, often requiring harsh reaction conditions and struggles with selectivity. Thus, the selective activation of unactivated Si–Me bonds under mild reaction conditions is desirable. Transition-metals have had minimal success through oxidative addition or σ-bond metathesis pathways.[61–70] In transition-metal free approaches, potent electrophilic reagents have been effective including some boron systems.[71–82] Notably, Wang recently disclosed Si–C/B–H to Si–H/B–C bond metathesis of the carbene stabilized hydroborenium ion, $[IMe_4B(H)oCb][B$

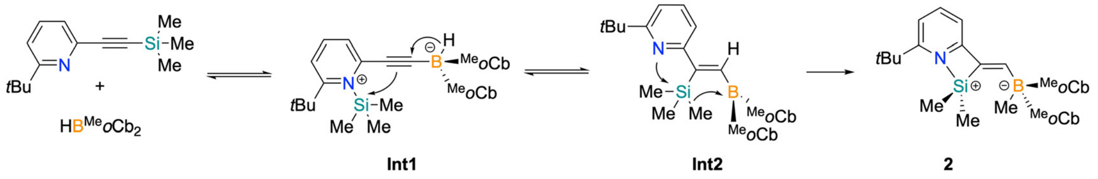


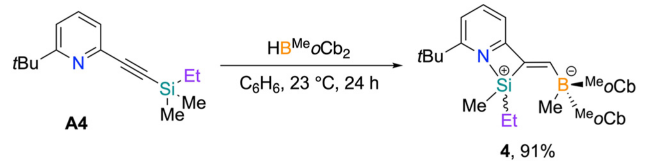
Fig. 4 Plausible reaction mechanism for the formation of **2**.

$(C_6F_5)_4]$, with alkyl and aryl silanes to furnish the hydrosilane and organoborenium species ($HSiR_3$ and $[IMe_4B(R)o\text{Cb}][B(C_6F_5)_4]$).[83] Stephan and Inoue independently reported methyl abstraction of activated N–$SiMe_3$ groups in silyl-phosphinimides $R_3P{=}N{-}SiMe_3$ (R = *t*Bu, *i*Pr, Ph) and the N-heterocyclic imine IPr=N–$SiMe_3$ by $B(C_6F_5)_3$ to generate $[MeB(C_6F_5)_3^{-}]$ anions [IPr = bis(2,6-diisopropylphenyl)imidazoline] with coordinated silylium cations.[84,85] The hydroboration sequence reported herein is a new pathway in boron mediated cleavage of unactivated Si–C bonds.

To investigate the selectivity of the Si–C bond activation, a variant of **A2** featuring a –$SiEtMe_2$ group in place of the –$SiMe_3$ group (**A4**) was reacted with $HB^{Me}o\text{Cb}_2$ at 23 °C for 24 h (Scheme 2). The reaction showed exclusive selectivity for Si–Me bond cleavage with no evidence of Si–Et activation by NMR spectroscopy. The structure was identified as silylium/borate zwitterion **4** by a single crystal X-ray diffraction study, the analogue of **2** differing in the ethyl group on silicon (Fig. 5). In the $^{29}Si\{^1H\}$ NMR spectrum, the resonance for **4** at 64.3 ppm is comparable to that for **2** (*cf.* **2**: 59.9 ppm).

Examining the X-ray diffraction structures of the silylium/borate species **2–4** reveals that the metrical parameters of the four membered products, **2** and **4**, are essentially within the error of measurement (Table 1). The N–Si bond length in **3** is slightly shorter than those of **2** and **4** attributed to the reduced ring strain [**2**: 1.8896(17) Å, **3**: 1.858(2) Å, **4**: 1.862(4) Å, Table 1].[57] The bond angles in the silacycle are more compressed in **2** and **4** compared to those in **3**, consistent with the 4- and 5-membered rings, respectively.

To probe the role of the pyridine moiety in the Si–Me bond cleavage in the generation of **2–4**, an alkyne analogue of **A1** with thiophene in place of pyridine was examined as it is a weaker Lewis base. The reaction of trimethyl(thiophen-2-ylethynyl)silane (**A5**) with $HB^{Me}o\text{Cb}_2$ in C_6D_6 at room temperature was monitored by ^1H NMR spectroscopy that revealed the 1,1-hydroboration product (**5**) within 10 minutes. The diagnostic vinyl proton in **5** appears at 6.42 ppm.[30] The vinyl carbon attached to the boron center appears broad at 152.1 ppm due to coupling with a quadrupolar ^{11}B-atom. A 2D ^1H–^{13}C HSQC correlation experiment indicates that the hydrogen and boron atoms are attached to the same carbon, confirming the 1,1-hydroboration. Stirring a solution of **5** in C_6D_6 for 8 hours did not lead to any conversion for Si–Me bond rupture, suggesting the crucial role of the pyridine moiety for the Si–C bond cleavage (Scheme 3a).



Scheme 2 Selective Si–Me bond activation of pyridine-tethered (ethyldimethylsilyl)ethynyl **A4**.

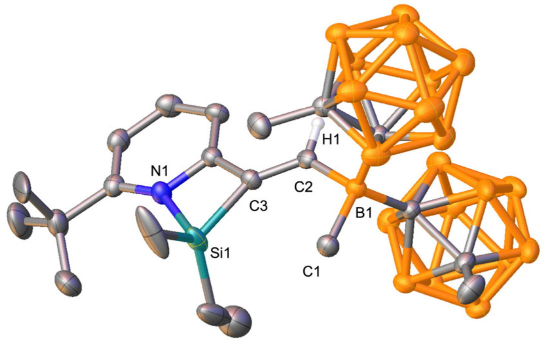
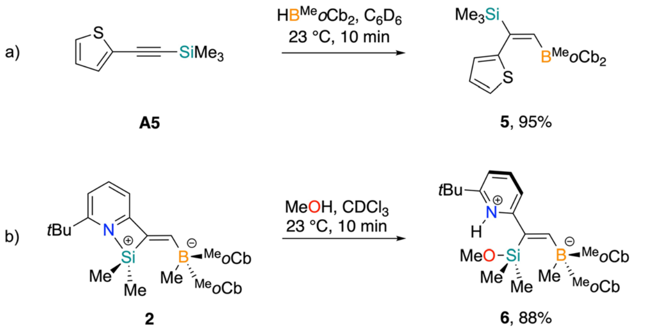


Fig. 5 Solid state structure of **4**. Ellipsoids depicted at the 50% probability level. Hydrogen atoms (except on the vinylic carbon) and solvates are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) of cyclized species **2–4**

	2	3	4
B1–C1	1.619(3)	1.618(4)	1.624(6)
B1–C2	1.616(3)	1.614(4)	1.623(5)
C2–C3	1.336(3)	1.345(3)	1.352(5)
C3–Si1	1.852(2)	1.871(3)	1.862(4)
N1–Si1	1.8896(17)	1.858(2)	1.898(3)
∠C1–B1–C2	111.61(16)	112.2(2)	110.2(3)
∠B1–C2–C3	129.51(18)	131.9(2)	128.4(3)
∠C2–C3–Si1	144.29(16)	130.86(19)	142.9(3)
∠C3–Si1–N1	73.42(8)	89.93(10)	73.48(16)



Scheme 3 Reaction of (a) **A5** with $HB^{Me}o\text{Cb}_2$ and (b) **2** with MeOH.

To examine the lability of the N–Si bond in **2**, it was reacted with acetonitrile and pyridine at 23 °C. No reaction was observed with either reagent, even after 24 h, indicating that intramolecular N–Si coordination is resilient. Attempts to abstract the –Me group from boron using MeOTf failed. At 23 °C, no reaction occurred with 10 equivalents of MeOTf and heating to 50 °C for 24 h only led to slow decomposition and a complex mixture as determined by NMR spectroscopy. Addition of MeOH to **2** resulted in O–H bond cleavage at the N/Si unit rather than B–Me bond rupture, leading to pyridinium borate zwitterionic species **6** as confirmed by NMR spectroscopy and X-ray diffraction studies (Scheme 3b and Fig. 6).

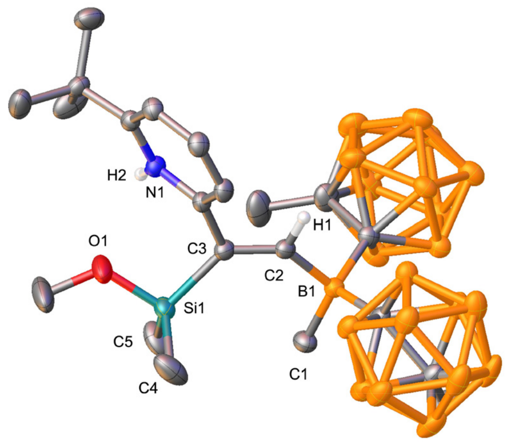


Fig. 6 Solid state structure of **6**. Ellipsoids depicted at the 50% probability level and hydrogen atoms (except on the nitrogen and vinylic carbon) are omitted for clarity. Selected bond lengths (Å) and angles (°): B1–C1 1.616(2), B1–C2 1.631(2), C2–C3 1.354(2), C3–Si1 1.903(15), Si1–C4 1.857(2), Si1–C5 1.848(19), Si1–O1 1.651(13), ∠C1–B1–C2 114.08(12), ∠B1–C2–C3 136.26(13), ∠C2–C3–Si1 132.07(11).

The resulting product was isolated in 88% yield. In the ^{1}H NMR spectrum in CDCl$_3$, the pyridinium proton appears at 12.75 ppm. The SiMe$_2$ unit shows noticeable upfield shifts in the ^{1}H (**2:** 1.13 ppm, **6:** 0.57 ppm) and ^{29}Si{^{1}H} (**2:** 59.9 ppm, **6:** 14.1 ppm) NMR spectra. The ring strain by N/Si breakage is reflected in the decrease of the ∠C2–C3–Si1 angle in the solid-state structure [**2:** 144.29(16)°, **6:** 132.07(11)°]. Additionally, the pyridinium ring is not coplanar with the alkene as it is oriented 58.2° relative to the Si1–C3–C2–B1 plane.

Conclusions

The reactions of HB$^{\text{Me}}$*o*Cb$_2$ with internal alkynes with alkyl silyl and pyridine substitution give diverse outcomes. The alkyne featuring 2-pyridyl and trimethylsilyl groups forms a Lewis acid/base adduct that is thermally stable. Installing a *tert*-butyl group on the carbon adjacent to nitrogen resulted in a 1,1-hydroboration sequence followed by –Me group migration from silicon to boron to generate a zwitterionic compound featuring a pyridine-silylium SiNC$_2$ ring with a pendant alkenylborate. Replacing an ethyl group in place of one of the methyl groups on the trimethylsilyl substituent revealed that the reaction is selective for Si–Me rupture over Si–Et. For an alkyne bearing quinoline and a trimethylsilyl group, adduct formation occurred that thermally isomerized to the zwitterionic product with a SiNC$_3$ heterocycle. The reaction outcomes are rationalized by the tremendous Lewis acidity of the –B$^{\text{Me}}$*o*Cb$_2$ unit and the opposing nitrogen donor acting as a frustrated Lewis pair to induce the Si–C bond cleavage. This study focused on silyl alkyne systems, but it may be possible to extend the element-CH$_3$ cleavage reactivity to other main group elements such as germanium. In sum, these findings reveal insight into hydroboration processes and ability of potent Lewis acidic bis(*ortho*-carboranyl)boryl groups to facilitate the cleavage of unactivated Si–C$_{\text{alkyl}}$ bonds.

Author contributions

M. O. A. carried out the synthetic experiments. A. B. performed the single crystal X-ray diffraction analyses. M. O. A. and C. D. M. conceived the project with supervision by C. D. M. M. O. A. and C. D. M. wrote the manuscript with edits from A. B.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental procedures, NMR spectra, and X-ray crystallographic data. See DOI: **https://doi.org/10.1039/d6qi00434b**.

CCDC 2523192–2523197 contain the supplementary crystallographic data for this paper.[86a–f]

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