

Reaction of Dihalodiboranes(4) with *N*-Heterocyclic Silylenes: Facile Construction of 1-Aryl-2-Silyl-1,2-Diboraindanes

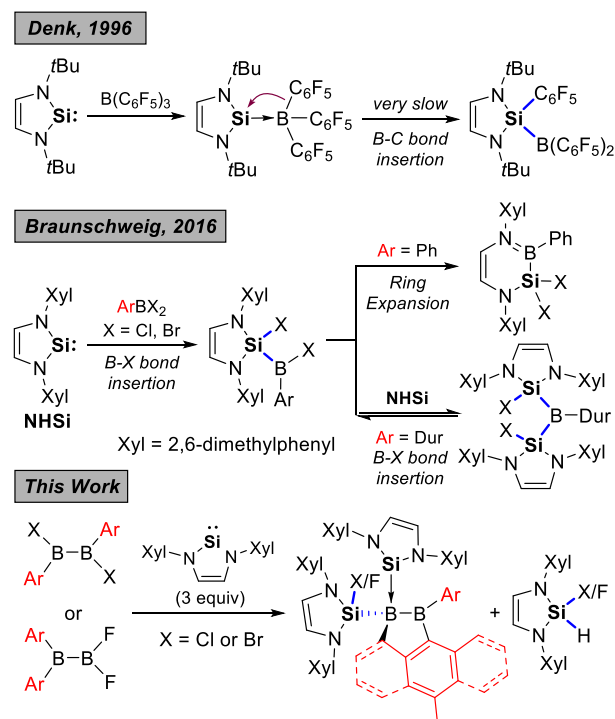
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Abstract: Dihalodiboranes(4) react with an *N*-heterocyclic silylene (NHSi) to generate NHSi-adducts of 1-aryl-2-silyl-1,2-diboraindanes as confirmed by X-ray crystallography, featuring the functionalization of both B–X (X = halogen) bonds and a C–H bond under mild conditions. Coordination of a third NHSi to the proposed 1,1-diaryl-2,2-disilyldiborane(4) intermediates, generated by a two-fold B–X insertion, may be crucial for the C–H borylation that leads to the final products. Notably, our results demonstrate the first C–H borylation with a strong B–F bond activated by silylene insertion.

Trigonal planar boranes constitute an important class of Lewis acids and react with a wide range of bases, leading in most cases to Lewis acid-base adducts that have found extensive applications.^{1,2} Electron-precise diboranes(4) can be regarded as boryl-substituted trigonal boranes, as demonstrated by the fact that quaternization of one boron atom of diboranes(4) with either a neutral or anionic base can provide practical “boryl anion” surrogates in organic synthesis.^{3,4} Either halide-bridged 1:1 adducts or inorganic-Wagner-Meerwein rearrangements were observed in the reactions of dihalodiboranes(4) with various bases, depending on the steric bulk of the latter.⁵ Transformations following the Lewis pair formation were also discovered in the case of bases such as CO, isonitriles, and *N*-heterocyclic carbenes (NHC), leading to the formation of cyclic boron compounds including boraindane regioisomers and NHC-ring-expansion products.⁶ Thus, both the monoborane-like reactivity and the cooperative reactivity of the two bound borane units could be anticipated for diboranes(4).

N-heterocyclic silylenes (NHSi) were first described in 1994 by the group of West.^{7,8} In comparison to NHCs, NHSis are poorer σ -donors, but stronger π -acceptors.⁸ This electronic nature may account for the prevalence of σ -bond insertion of boranes into silylenes,^{9,10} via the shift of a *B*-substituent to the π -

accepting Si-center in the Lewis acid-base adducts (Scheme 1). To integrate this unique insertion ability of NHSi with the cooperative reactivity of the two bound borane units in diboranes(4), we became interested in their reaction with NHSis.¹¹ Dihalodiboranes(4) were found to react readily with 3 equiv of NHSi to give the NHSi-adducts of 1-aryl-2-silyl-1,2-diboraindanes and the formal HX (X = halogen) silylene insertion products (Scheme 1).¹² Apparently, beyond the simple Lewis acid-base reaction, transformations including inorganic-Wagner-Meerwein rearrangement,^{5b} B–X insertion,^{9b,10b} and C–H borylation¹³ are involved in this process. Notably, the reaction of Mes₂B–BF₂ with NHSi represents the first B–F bond activation by silylene insertion.^{2k,14} These findings are reported in this contribution.



Scheme 1. *N*-Heterocyclic silylenes in boron chemistry.

According to our previous study of the reaction of NHSi **1** with monoboranes,^{9b} B₂Mes₂Cl₂ (**2a**) was initially treated with 1 equiv of **1** in benzene at room temperature (Figure 1). The reaction solution immediately turned dark red upon mixing and then decolorized to light red after stirring for ca. 30 mins. A new, weak high-field resonance at –23.1 ppm, along with the intense resonance of **2a** (δ = 86.2 ppm), was observed in the ¹¹B NMR

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spectrum. Reactions of **2a** with 2 or 3 equiv of **1** were subsequently attempted and only the latter reaction showed full conversion of **2a**, as revealed by ^{11}B NMR spectroscopy (Figure 1).¹⁵ A sharp high-field resonance at -23.1 ppm and a broad low-field resonance at 96.4 ppm in the ^{11}B NMR spectrum of the reaction mixture clearly indicated the highly selective formation of the $\text{sp}^2\text{-sp}^3$ diborane product **3a**.^{4a} To demonstrate the generality of the reaction, $\text{B}_2\text{An}_2\text{Br}_2$ (An = 9-anthryl) (**2b**)¹⁶ and $\text{Mes}_2\text{B-BF}_2$ (**2c**) were also investigated, which selectively afforded the corresponding products **3b,c** as indicated by ^{11}B NMR spectroscopy (Figure 2).

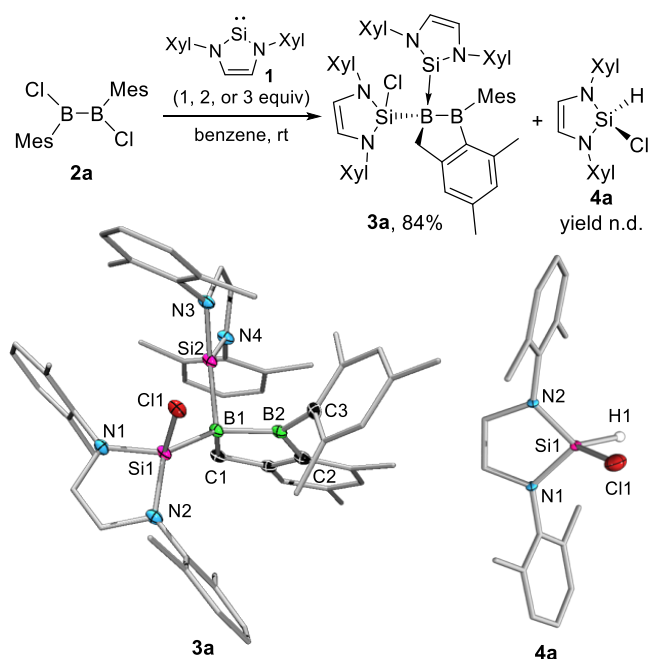


Figure 1. Reaction of **2a** with different amounts of **1** and molecular structures of **3a** and **4a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms (except for that on Si1 atom of **4a**) and solvent molecules (benzene in **3a**) are omitted for clarity. Selected bond lengths [Å] and angles [°] for compound **3a**: B1-B2 1.766(4), B1-Si1 1.998(3), B1-Si2 1.969(2), B1-C1 1.657(3), B2-C2 1.561(4), B2-C3 1.583(3), Si1-Cl1 2.131(1); Si1-B1-Si2 110.8(1), B2-B1-C1 101.4(2), B1-B2-C2 103.6(2), B1-Si1-Cl1 104.75(8), $\Sigma \angle_{\text{Si2}}$ 357.4(3).

By fractional recrystallization, red and colourless crystals were successively obtained from the crude product mixture of the reaction of **2a** with **1**, and their molecular structures were determined by X-ray crystallography as the NHSi-coordinated 2-silyl-1,2-diboraindane **3a** and the formal HCl insertion product **4a**, respectively (Figure 1).¹⁵ These results were consistent with the reaction stoichiometry. Similarly, red crystals of **3b,c** suitable for single-crystal X-ray analyses were obtained. The molecular structures are shown in Figure 2.¹⁷ Although the first and only NHSi-borane adduct was isolated by Denk et al. in 1996, no X-ray crystallographic data was obtained.^{9a} Thus, X-ray crystallographic data of **3a-c** provide, for the first time, structural details of NHSi-borane adducts. The dative B-Si bonds are slightly shorter than the covalent B-Si bond in the same molecule [1.982(3) vs 2.003(3) Å (**3b**), 1.969(2) vs 1.998(3) Å (**3a**), and 1.947(3) vs 1.991(3) Å (**3c**)] and this difference increases as the halogen substituent becomes smaller: Br (**3b**) < Cl (**3a**) < F (**3c**). While this finding appears counterintuitive, the

shorter dative bonds are most likely due to the lower coordination number of the associated Si center. The geometry around the tricoordinate Si in **3** becomes more pyramidalized as the steric demand of the substituents increases, as indicated by the sum of the bond angles [$\Sigma \angle_{\text{Si2}}$: 359.8° (**3b**), 358.1° (**3c**), and 357.4° (**3a**)]. Such pyramidalization around Si atoms has not been observed in NHSi-based transition metal complexes.¹⁸

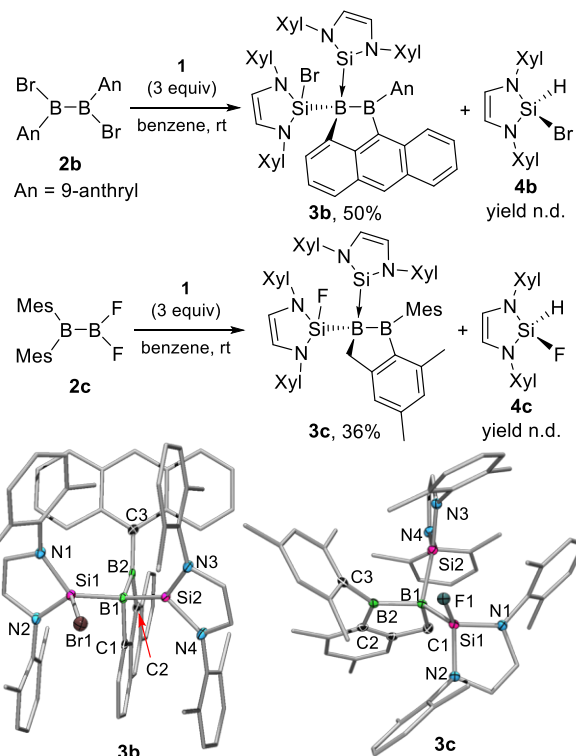
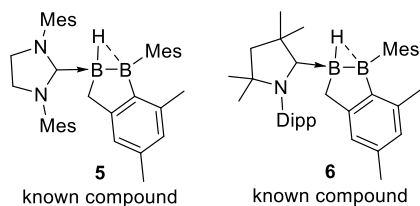


Figure 2. Synthesis and molecular structures of **3b** and **3c**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]. Compound **3b**: B1-B2 1.749(4), B1-Si1 2.003(3), B1-Si2 1.982(3), B1-C1 1.644(4), B2-C2 1.560(4), B2-C3 1.570(4), Si1-Br1 2.3626(9); Si1-B1-Si2 113.1(1), B2-B1-C1 99.3(2), B1-B2-C2 104.7(2), B1-Si1-Br1 101.64(8), $\Sigma \angle_{\text{Si2}}$ 359.8(3). Compound **3c**: B1-B2 1.756(4), B1-Si1 1.991(3), B1-Si2 1.947(3), B1-C1 1.653(4), B2-C2 1.555(4), B2-C3 1.583(3), Si1-F1 1.609(2); Si1-B1-Si2 112.2(1), B2-B1-C1 101.7(2), B1-B2-C2 103.7(2), B1-Si1-F1 107.5(1), $\Sigma \angle_{\text{Si2}}$ 358.1(3).

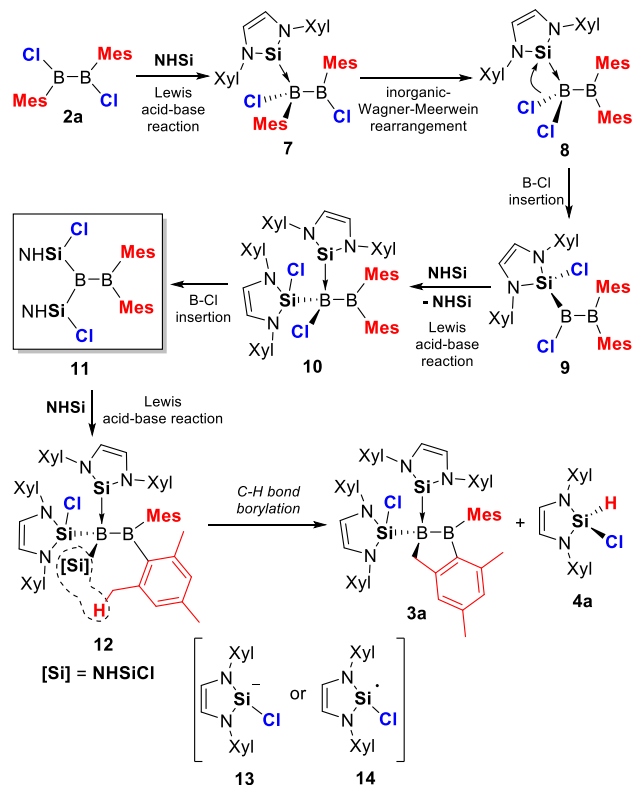
Organosilylboranes display absorptions in the visible light region, which has previously been attributed to a significant charge transfer from the silicon atom to the boron atom of the Si-B bond.¹⁹ While the known non-silylated 1,2-diboraindanes **5** and **6** are both pale yellow (Scheme 2),^{2e,5c} the silylated 1,2-diboraindanes **3** are intense red in color. Thus, solution UV-vis absorption spectra of **3a-c** were measured to understand the origin of their coloration.¹⁵ The local maximum of the long-wavelength absorption band of **3a** and **3c** are located at $\lambda = 387$ nm and 367 nm in pentane, respectively. Due to the strong anthryl-related absorptions ($\lambda_{\text{max}} = 370$ and 389 nm), only a weak shoulder at $\lambda = 408$ nm of the long-wavelength absorption band was observed in the UV-vis absorption spectrum of **3b** in THF. The long-wavelength absorption band is red-shifted upon decreasing the electronegativity of the halide substituent on Si, which suggests that the coloration of silylboranes **3** stems from a charge transfer from silicon to boron.¹⁹



Scheme 2. Structures of 1,2-diboraindanes **5** and **6**.

The mechanism for the formation of **3** is thus far inconclusive, and no simple silylene–borane adduct or any other intermediate was observed spectroscopically. However, based on previous investigations and our experimental results, a plausible mechanism for the reaction of **2a** with **1** is proposed in Scheme 3. Like the reaction of **2a** with *N*-heterocyclic carbenes (NHC),^{2e,5b} an inorganic-Wagner-Meerwein rearrangement of the simple Lewis acid-base adduct **7** produces intermediate **8**, which then undergoes a B-to-Si halide-shift to give the B–Cl insertion product **9**. It should be noted that F₂BBMes₂ has been shown to bind Lewis bases PMe₃ and P(OMe)₃ exclusively through the -BMes₂ boron atom.^{5d} However, in the reaction that forms **3c**, the silylene Lewis base is considerably more bulky, which could force the base to bind at the -BF₂ unit and facilitate the insertion.

A reversible second B–Cl insertion reaction, as observed in the reaction of hindered dihalomonoboranes with **1** (Scheme 1),^{9b} would be expected in the present reaction as well, which then generates the intermediate 1,1-dimesityl-2,2-disilyldiborane(4) **11**. The Lewis acid-base reaction between **11** and a third NHSi might not be energetically favored due to the steric hindrance. However, the transient formation of **12** might immediately collapse to **3a** by extrusion of one molecule of **4a** to release the steric tension, as shown in Scheme 3. Either ionic (**13**) or free radical (**14**) intermediates could be possible for the C–H borylation. For example, silyl anions such as **13** could be formed by deprotonation of cyclic diaminochlorosilanes similar to **4a** with NHCs.²⁰ On the other hand, reactions of NHSis with organohalides were reported to give halosilyl free radicals similar to **14**, which were able to cleave inert C–H bonds.⁸ It is easy to understand that in the reaction of difluorodiborane(4) **2c** with NHSi **1**, no inorganic-Wagner-Meerwein rearrangement is required, which generates the intermediate similar to **8** direct via a conventional Lewis acid-base reaction. The formation of an equally strong Si–F bond may compensate for the breaking of a strong B–F bond, which makes the B–F silylene insertion feasible. Also, a two-fold B–F insertion product of **2c** would be expected to display a close reactivity to **11**, leading to the formation of **3c**. The formation of **3c** represents the first example of two-fold B–F activation by silylene insertion, one of which further borylates an intramolecular C–H bond. This is notable in the context of our mild B–F activation of BF₃ by zerovalent platinum,^[14b] and the recent C–F bond activation by a cyclic (alkyl)(amino)carbene by Radius.^[21]



Scheme 3. Proposed reaction pathways between **2a** and **1**.

In conclusion, the reaction of dihalodiboranes(4) with an NHSi was investigated for the first time, leading to the functionalization of both B–X bonds and a C–H bond under mild conditions. NHSi-adducts of 1-aryl-2-silyl-1,2-diboraindanes were formed, along with the generation of HX insertion products, both structures of which were confirmed by X-ray crystallography, thus explaining the consumption of 3 equiv of NHSi in the reaction. Coordination of a third NHSi to the proposed 1,1-diaryl-2,2-disilyldiborane(4) intermediates, generated by a two-fold B–X insertion, may be crucial for the C–H borylation that leads to the final products. Furthermore, the first C–H borylation with a strong B–F bond activated by silylene insertion was demonstrated.

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Keywords: diborane(4) • *N*-heterocyclic silylenes • diboraindanes • C–H borylation • B–F activation

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