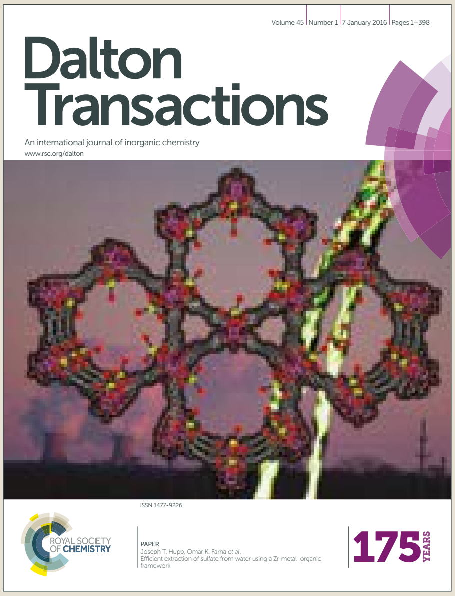
Check for updates

View Article Online
View Journal

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Dübek, F. Daniel, C. Eisenhut, P. J. Altmann and S. Inoue, *Dalton Trans.*, 2019, DOI: 10.1039/C9DT00608G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608G

ARTICLE

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript

Reactivity of an NHC-stabilized pyramidal hydrosilylene with electrophilic boron sources

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Gizem Dübek,[a] Daniel Franz,[a] Carsten Eisenhut,[b] Philipp J. Altmann,[a] Shigeyoshi Inoue*[a]

Silylenes have become an indispensable tool for molecular bond activation. Their use for the construction of silicon-boron bonds is uncommon in comparison to the numerous studies on silylene-derived silicon-element bond formations. Herein we investigate the reactivity of the pyramidal NHC-coordinated hydrosilylene $tBu_3SiSi(H)L^{Me4}$ (**1**; NHC = N-heterocyclic carbene, L^{Me4} = 1,3,4,5-tetramethylimidazolin-2-ylidene) with various boron-centered electrophiles. The reaction of **1** with $THF{\cdot}BH_3$ or $H_3N{\rightarrow}BH_3$ afforded the silylene complex **1**$\rightarrow BH_3$ or the product of insertion of the silicon(II) atom into an N–H bond with concomitant dehydrogenation along the HN–BH moiety (**2**). The respective conversion of **1** with BPh_3 yields **1**$\rightarrow BPh_3$ which readily reacts with excess L^{Me4} to form the more stable complex $L^{Me4}{\rightarrow}BPh_3$ with release of **1**. Treatment of **1** with the haloboranes $Et_2O{\rightarrow}BF_3$, BCl_3, BBr_3 and $Me_2S{\rightarrow}BBr_3$ resulted in the formation of the Lewis acid-base adducts **1**$\rightarrow BX_3$ (X = F, Cl, Br) and an equilibrium with their auto-ionization products $[\mathbf{1}_2BX_2]^+[BX_4]^-$ slowly develops. The ratio of **1**$\rightarrow BX_3$ significantly increases with rising atomic number of the halide, thus **1**$\rightarrow BF_3$ majorly transforms within hours while **1**$\rightarrow BBr_3$ is near-quantitatively retained over time. Accordingly, the complex **1**$\rightarrow BPhBr_2$ was isolated after conversion of **1** with $PhBBr_2$.

Introduction

There has always been a strong link between the chemistry of silicon and boron as implied by the diagonal relationship of these metalloids in the Periodic Table of Elements. Boron-doped silicon semiconductors are a prominent example from material science in which the combination of these elements fostered tremendous innovation.[1-3] Molecular chemistry benefits from the particular properties of the silicon-boron bond. It is sufficiently stable to craft durable compounds but also susceptible to mild methods of chemoselective cleavage to enable metallyl group transfer, thus, enriching the ever-growing library of organometallic synthesis.[4-6] The ylidenic compound class of silylenes are a subtype of molecular silicon complexes with one lone pair majorly located at the metalloid center. As a result, the formal oxidation number +II is assigned to the silicon atom. Silylenes have gained outstanding attention as key compounds to bring forward new ways for bond activation and catalysis.[4,7-15] In particular, silylenes may act as ligands to enhance the catalytic activity of transition metal complexes.[9,10,14] Moreover, the potentially ambiphilic silicon(II) atom itself may engage in bond activations via addition and insertion pathways. Taking into account their ylidenic character it does not come as a surprise that there has been made frequent use of silylenes as electron-pair donors toward boron-centered electrophiles. An early report of Metzler and Denk from 1996 described the formation of the adduct between a five-membered ring N-heterocyclic silylene (NHSi) and $B(C_6F_5)_3$ which slowly transforms to the product of Si-insertion into a B–C bond.[16] However, neither the adduct nor the insertion product were structurally characterized in the solid state (i.e. XRD study, XRD = X-ray diffraction). In fact, more than 20 years

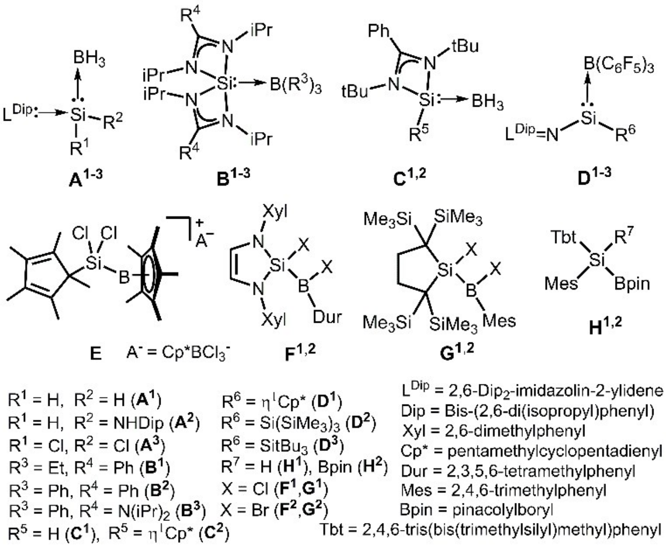


Fig. 1 Selected examples for outcomes of conversions of silylenes with various boron sources.

---

[a] Department of Chemistry, WACKER-Institute of Silicon Chemistry and Catalysis Research Centre, Technische Universität München, Lichtenbergstr. 4, 85748 Garching bei München.
[b] Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, Sekr. C2, 10623 Berlin, Germany.

† *Electronic Supplementary Information (ESI) available: Depiction of analysis spectra and crystallographic details. CCDC 1896328-1896331. See DOI: 10.1039/x0xx00000x*

View Article Online
DOI: 10.1039/C9DT00608C

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript

later, one can easily survey the stock of compounds in which conversions of a silylene with an electrophilic borane derivative resulted in the structural characterization of a species that contained a silicon-boron bond.[17-39] Often a silicon-coordinated borane moiety affords isolation of an otherwise elusive kind of silylene (i.e. “acceptor stabilization”). A prominent example for this concept is the silylene dihydride **A**[1] described by Rivard and coworkers (Fig. 1).[30] Structurally related compounds have also been reported (**A**[2], **A**[3]).[29,33] Bis(guanidato)-, as well as bis(amidinato)silylenes tend to switch between isomers with a three- or with a four-coordinate silicon atom. The high-coordinate species may be stabilized in the form of borane adducts of type **B**[1-3] (Fig. 1).[23,26] The amidinato ligand was also implemented in four-coordinate adducts between silylene and the trihydroborane group (**C**[1,2], Fig. 1).[21,31] Similar to type **B** the silylene adducts **D**[1-3] are observed in solution whereas for the respective “free” silylenes (with no borane moiety attached) the coordination number of the silicon centers rapidly changes (Fig. 1).[17]

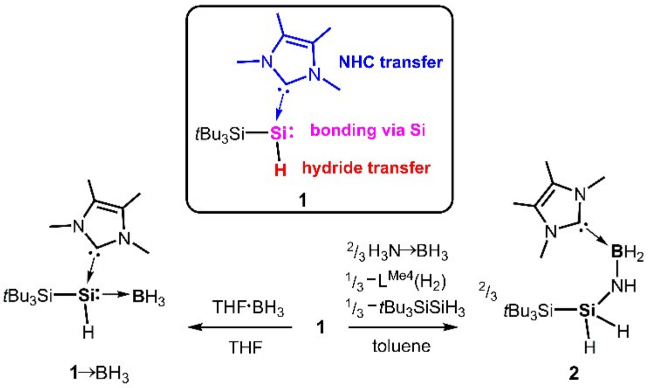
Despite these various examples for “acceptor stabilization” silylenes were often found to be prone to insertion of the silicon atom into boron-heteroatom bonds as implied by the pioneering study of Metzler and Denk (*vide supra*).[16] Jutzi and coworkers described the insertion of the high-coordinate silylene center of $Cp^*{}_2Si$ into boron-chloride bonds upon its conversion with Cp^*BCl_2 to afford **E** (Fig. 1).[38] In agreement with the high reactivity of bonds between boron and the heavier halides (e.g. Cl, Br, I) this type of insertion was also observed for low-coordinate silylenes (i.e. two-coordinate NHSi) as demonstrated by Braunschweig and coworkers with the isolation of **F**[1,2] and by the group of Iwamoto (**G**[1,2], Chart 1).[24] As verified by the synthesis of **H**[1,2] the ylidenic center in silylenes may also insert into boron-hydrogen bonds, as well as unpolarized boron-boron bonds (Fig. 1).[37] Interestingly, the group of Chiu reported the conversion of a two-coordinate bulky NHSi with borabicyclo[3.3.1]nonyl triflate (9-(OTf)BBN) to furnish the product of boron-oxygen insertion.[39] Obviously, the triflate group complies to its pseudohalide character and, thus, the reactivity of the ambiphilic NHSi with the boron-triflate functionality is reminiscent of Braunschweig’s study on treating NHSi with organoborohalides. In addition to these synthetic examples the reader is also referred to theoretical studies on the insertion of silylene into boron-element bonds.[40] In consideration of the hitherto outlined scope of compounds we were surprised that systematic investigations of one particular silylene’s reactivity towards different types of boron sources is rather uncommon with a respective report of Cui being a rare example.[25] In the context of discussing silylene-borane adducts one should note the small number of boryl-substituted silylenes, as well as the exceptional reaction of a disilicon(0) complex with $THF{\cdot}BH_3$ to outstanding silylene-borane complexes.[34,41,42] Moreover, silicon-silicon multiple bonded systems with boryl functionalities have been reported.[43-47]

Recently, we have isolated the NHC-stabilized hydrosilylene **1** and studied its reactivity towards transition metal complexes (e.g. $Ni(COD)_2$, $Fe(CO)_5$, $W(CO)_5$; COD = 1,5-cyclooctadiene) and functional organic groups (e.g. carbonyls, alkynes; Scheme 1).[48-52] As a distinct characteristic **1** marks three sites that may react with boron-centered electrophiles: (i) the ylidenic site at the silicon center, (ii) the dative bond between the NHC and the silicon atom which may be cleaved by electrophilic attack, and (iii) the Si–H functionality which may readily transfer a hydrogen atom (Scheme 1). Considering the importance of silicon-boron compounds to the community it was apparent to systematically study the reactivity of **1** towards various types of electrophilic boron-sources commonly encountered in molecular chemistry (e.g. hydro-, organo-, haloboranes). We took the marked scarceness of reports on simple Lewis acid base adducts of silylenes with haloboranes as a particular motivation for our investigation.

Results and discussion

Conversions with trihydroborane complexes.

A plethora of chemical transformations has derived from complexes of NHCs with the parent borane (i.e. $NHC{\rightarrow}BH_3$).[53-56] In sharp contrast, only few silylene adducts with the trihydroborane group are known as outlined above. In fact, two-coordinate silylenes do not commonly form simple and stable Lewis acid base adducts upon reaction with borane complexes (e.g. $THF{\cdot}BH_3$, $Me_2S{\rightarrow}BH_3$, $H_3N{\rightarrow}BH_3$; here stable means to be isolatable at room temperature in the condensed phase). This will be majorly due to the enhanced Lewis acidity of low-coordinate silylenes which causes side-reactions (i.e. hydride shift from B to Si) that follow after the initial coordination between the metalloid centers. It is apparent, that the prospect for forming stable Lewis acid-base adducts is higher for three-coordinate silylenes as the silicon center is less electrophilic because of the stabilizing effect of an additional electron-pair donor. Accordingly, the conversion of **1** with a slight excess (1.3 equiv.) of borane tetrahydrofurane complex ($THF{\cdot}BH_3$) furnished the chiral adduct **1**→BH_3 (isolated: 93%) as suggested by multinuclear NMR spectroscopy, high-resolution mass spectrometry (HRMS), as well as XRD structural study (Scheme 1). The ^{11}B NMR spectrum in C_6D_6 reveals a quartet at −40.8 ppm (J = 95 Hz) that collapses into a singlet in the proton decoupled experiment. This confirms a BH_3 group with a four-coordinate boron nucleus (cf. **A**[1]: $\delta(^{11}B) = -46.2$ ppm, J = 93 Hz,



Scheme 1 Reactive sites at the NHC-stabilized hydrosilylene **1** and its conversions with trihydroboranes.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608G

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript

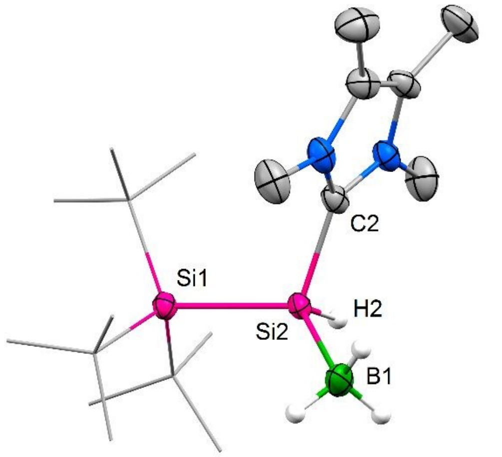


Fig. 2 Ellipsoid plot (30% level) of the molecular structure of **1**→BH_3 in the single crystal. H-atoms omitted (except on B, Si). Wireframe model for tert-butyl groups. Selected interatomic distances [Å] and angles [°]: Si2-B1 = 2.009(5), Si2-C2 = 1.942(3); Si1-Si2-B1 = 123.3(2), C2-Si2-B1 = 108.2(2), Si1-Si2-C2 = 111.3(2). Note: The Si2 and B1 atoms are disordered over two sites (occupancy levels: 0.85/0.15 each) and only the higher occupied sites are considered.

in C_6D_6). In the ^{1}H NMR spectrum the prominent Si–H functionality gives rise to a quartet at 4.31 ppm with the coupling to the boron-bonded hydrogen atoms resolved ($^{3}J_{HH}$ = 5 Hz, ^{29}Si satellites with J_{SiH} = 150 Hz). Notably, this is markedly shifted to lower field in comparison to the precursor (**1**: $\delta(^{1}H)_{SiH}$ = 3.17 ppm in C_6D_6).[48] Despite the quadrupolar momentum of the ^{11}B nucleus the NMR signal of the ^{29}Si atom is observed as a broad peak at −77 ppm in the INEPT experiment. As a prominent structural parameter the Si–B distance in the single crystal XRD study of **1**→BH_3 is found at 2.009(5) Å which resembles **A**^{1} (1.992(2) Å) and is longer than in **A**^{2,3} (1.976(2) Å (**A**^{2}), 1.965(2) Å (**A**^{3})), as well as **C**^{1,2} (1.962(1) Å (**C**^{1}), 1.972(2) Å (**C**^{2}), Fig. 2).[21,30] The bond length between the silicon center and the *ipso*-carbon atom of the NHC group seems to be unaffected by coordination of the silylene to the BH_3 fragment (Si–C_{NHC}: 1.942(3) Å for **1**→BH_3, as well as for **1**). In contrast, the band of the Si–H stretching mode in **1**→BH_3 is observed at higher wavenumber (2083 cm^{-1}) in comparison to the “free” silylene **1** (1984 cm^{-1}) which suggests strengthening of the Si–H interaction upon bonding to the Lewis acid.

As an alternate source of the trihydroborane group we converted **1** with borane trimethylamine complex (Me_3N→BH_3). However, no reaction occurred at room temperature which agrees with the pronounced stability of this adduct as compared to THF·BH_3. On the contrary, the treatment of **1** with one equivalent borane ammonia complex (H_3N→BH_3) furnishes the silylaminoborane complex **2** (46% yield isolated) (Scheme 1). Its formation can be rationalized by dehydrogenation of H_3N→BH_3 to produce H_2N–BH_2 (note: this aminoborane is prone to aggregation) and formal insertion of the silylene into the N–H bond. In the course of this reaction the NHC ligand ends up attached to the boron center which is reasonable as otherwise a five-coordinate silicon complex and a three-coordinate boron atom would coexist instead of two four-coordinate metalloid centers. In support of this reaction pathway the formation of tBu_3SiSiH_3, as well as dihydrogenated NHC (i.e. $L^{Me4}H_2$, dihydrogenated at the formerly ylidenic carbon atom) was suggested by NMR study and verified by HRMS analysis. Accordingly, half an equivalent of **1** is consumed to produce one equivalent of H_2N–BH_2 which in the following reacts with the remaining silylene to yield **2** (Scheme 1). Reminiscent of this reactivity treatment of a 1,3-diketiminosilylene with gaseous NH_3 has been described to afford the product of N–H insertion.[57] On the other hand, the conversion of a 1,3-diketiminosilylene tricarbonylnickel complex with H_3N→BH_3 resulted in dihydrogenation of the silylene with one hydrogen atom bonded to the silicon center and one additional hydrogen atom in the ligand backbone.[58] In the ^{11}B NMR analysis of **2** in C_6D_6 the compound gives rise to a signal at −18 ppm which is deshielded with respect to **1**→BH_3 in accordance with replacement of a hydride at a four-coordinate boron-center for a more σ electron-withdrawing nitrogen atom. The Si–H proton is observed at 5.2 ppm (d, J_{HH} = 4 Hz) in the ^{1}H NMR analysis. The ^{29}Si NMR spectrum of the complex exhibits a signal at −46.3 ppm for SiH_2 which is downfield shifted from the precursor (**1**: $\delta(^{29}Si)$ = −137.8 ppm). The single crystal structure of **2** was elucidated by XRD methods (Fig. 3). As expected the B–N distance of 1.542(4) Å in this bulky silylaminoborane is shorter than the length of the dative bond in typical trihydroborane complexes of bulky primary amines (e.g. $H_2(Dip)N$→BH_3, B–N = 1.620(2) Å; $H_2(Ar^*)N$→BH_3, B–N = 1.641(3) Å; Ar* = 2,6-$(Ph_2CH)_2$-4-Me-C_6H_2).[59] In agreement with the proposed dehydrogenation this distance relates to the B–N single bond length in the bulky organylaminoborane adduct L^{Dip}·$BH_2N(H)Dip$ (B–N (mean) = 1.54 Å).[29]

Conversions with triarylboranes.

If a mixture of a strong Lewis acid (typically a triarylborane) and a Lewis base does not recombine to the respective adduct

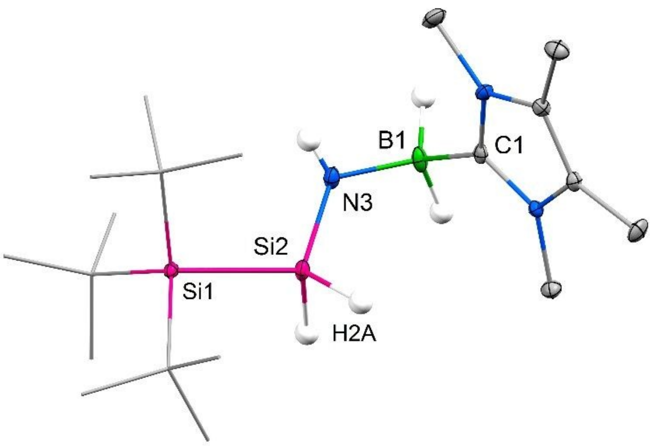


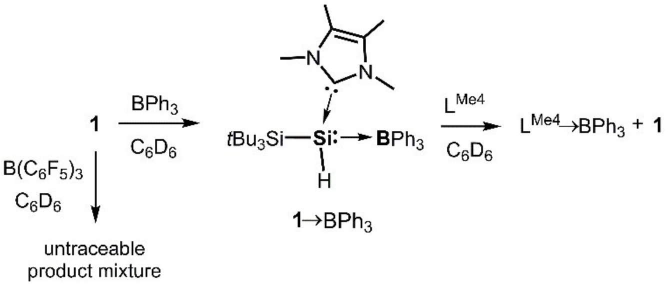
Fig. 3 Ellipsoid plot (30% level) of the molecular structure of **2** in the single crystal. H-atoms omitted (except on B, N, Si). Wireframe model for tert-butyl groups. Selected interatomic distances [Å] and angles [°]: Si2-N3 = 1.703(3), B1-N3 = 1.542(4), B1-C1 = 1.635(4); Si1-Si2-N3 = 114.4(1), Si2-N3-B1 = 123.2(2), N3-B1-C1 = 110.2 (2).

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608C

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript



Scheme 2 Conversions of the hydrosilylene **1** with triarylboranes.

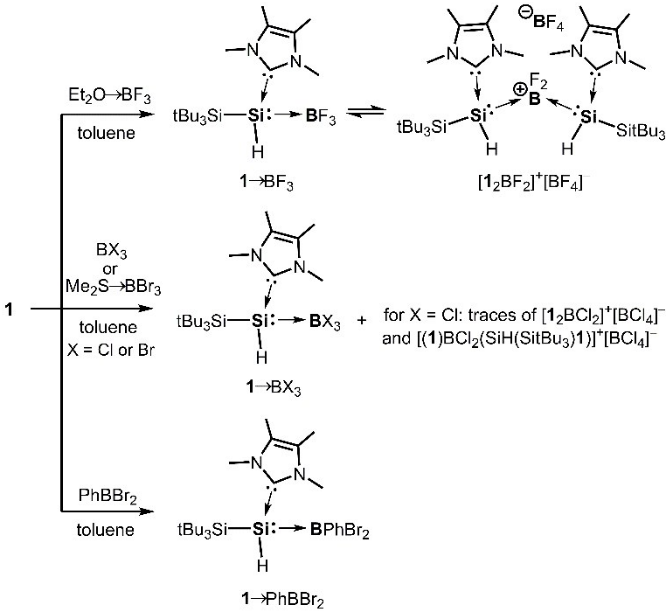
(usually due to steric hindrance) the chemical potential of the system may be exploited for the activation of bonds in unhindered *Small Molecule* substrates (i.e. Frustrated Lewis Pair (FLP) chemistry).[60-65] In order to probe the bulky silylene **1** for FLP characteristics it was converted with the archetypical boron-centered Lewis acids triphenylborane and tris(pentafluorophenyl)borane (Scheme 2). The conversion of **1** with BPh_3 was expected to afford the complex L^{Me4}→BPh_3 which may easily form via abstraction of the NHC from the silylene.[66] The cleavage of the dative type bond between silicon and NHC by virtue of triarylborane has previously been reported to afford such type of NHC-borane adducts.[25,66,67] However, when repeating the conversion in C_6D_6 in an NMR sample tube and monitoring the course of the reaction we recognized the formation of the proposed complex **1**→BPh_3. A signal at 4.38 ppm is assigned to the Si*H* hydrogen in the ^1H NMR analysis which is reminiscent of the respective chemical shift in **1**→BH_3. The ^{11}B NMR spectrum reveals a signal at −3.2 ppm. Hence, the signal of the three-coordinate borane precursor (cf. BPh_3: $\delta(^{11}B)$ = 67 ppm in Et_2O)[68] is shifted to a value for the chemical shift typical of four-coordinate boron nuclei. Another persuasive hint toward the putative **1**→BPh_3 is given by the $^1H^{13}C$ HMBC correlation experiment in which a cross-peak is given rise to by coupling between the *ipso*-carbon atoms of the BPh_3 group and the Si*H* hydrogen atom. We verified the stability of the complex in C_6D_6 solution at 50 °C for a period of two days. Nevertheless, the "free" silylene **1** is readily released upon conversion of **1**→BPh_3 with L^{Me4} and the overtly more stable L^{Me4}→BPh_3 is furnished. Interestingly, when bringing **1** into contact with the more potent Lewis acid $B(C_6F_5)_3$ we were not able to assign any silicon-containing species neither in the product mixture nor as a temporary intermediate.

Conversions with haloboranes.

In contrast to the boron sources mentioned in the previous paragraphs (e.g. trihydroboranes, triarylboranes) the conversion of silylenes with haloboranes is majorly limited to examples of the groups of Jutzi, of Braunschweig, and of Iwamoto as pointed out in the introduction. In addition, a respective study of Tokitoh and coworkers is to be highlighted in particular.[36] In these cases insertion of the silicon atom into a boron-halide bond occurs.

Considering the isolation of **1**→BH_3 after exposing **1** to the parent borane source THF·BH_3 we decided to probe boron halide reagents going from lower to higher atomic number. When the three-coordinate silylene **1** in toluene solution was brought into contact with Et_2O→BF_3 a colorless precipitate rapidly formed (Scheme 3). The solid was obtained in 87% yield after a period of 2 h and redissolved in deuterated fluorobenzene. The ^{11}B NMR analysis reveals a quartet at 4.8 ppm which is produced by a BF_3 group and deviates from the precursor (note: Et_2O→BF_3 is the external standard for the 0 ppm value of the ^{11}B nucleus). Moreover, weaker signals were observed at 10.5 ppm (triplet) and 0.4 ppm (sharp singlet), respectively. The shifts agree with four-coordinate boron centers and the resonances are diagnostic for a BF_2 group and $[BF_4]^-$. In fact, the intensity of the weaker signals significantly increased upon storage of the sample tube for a period of 20 h while the ratio of the BF_3 species decreased in the mixture. Accordingly, a signal pattern assigned to one $tBu_3SiSi(H)L^{Me4}$ moiety had been observed in the ^1H NMR spectrum after 2 h reaction time and two additional signals in a 1:1 ratio rose after storage of the sample for 20 h. From the NMR study we conclude that the initial product **1**→BF_3 slowly transforms into $[\mathbf{1}_2BF_2]^+[BF_4]^-$. Notably, the transformation equilibrates over time and full reaction to the auto-ionization product was not observed.

Moving our systematic investigation to the next heavier halide we treated a yellow colored solution of **1** in toluene with one equivalent of BCl_3 (as a 1 M solution in heptane, Scheme 3). As expected a colorless solid was isolated in 71% yield and combustion elemental analysis confirmed the stoichiometric composition of the trichloroborane compound **1**·BCl_3. The ^1H NMR analysis revealed the product to contain one major type of the $tBu_3SiSi(H)L^{Me4}$ moiety and additional species are hardly found. The ^{11}B NMR analysis (in CD_2Cl_2) showed a resonance at 5.5 ppm which is in accordance with a four-coordinate boron



Scheme 3 Reactions of the hydrosilylene **1** with different haloboranes.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608G

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript

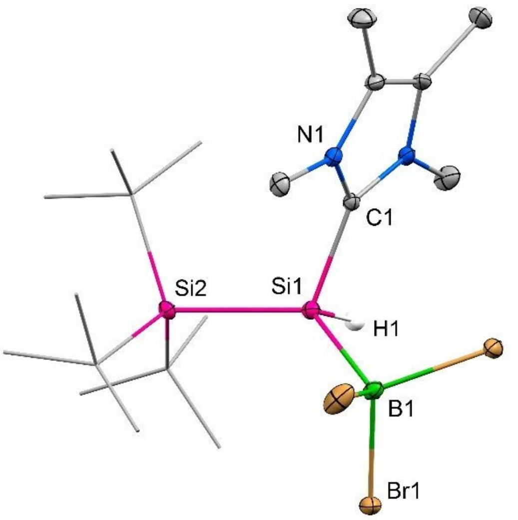


Fig. 4 Ellipsoid plot (30% level) of the molecular structure of **1**→$\mathrm{BBr_3}$ in the single crystal. H-atoms omitted (except on Si). Wireframe model for tert-butyl groups. Selected interatomic distances [Å] and angles [°]:Si1-B1 = 2.045(3), Si1-C1 = 1.922(3); Si2-Si1-B1 = 130.1(1), C1-Si1-B1 = 104.9(1), Si2-Si1-C1 = 113.6(1).

nucleus and suggests the formation of the Lewis acid base adduct **1**→$\mathrm{BCl_3}$ (note: uncomplexed $\mathrm{BCl_3}$ produces a resonance at about 40–45 ppm depending on the analytic setup). Nevertheless, a very weak signal at 6.9 ppm hints towards the presence of $[\mathrm{BCl_4}]^-$ in solution. Due to the discrepancy in the intensity ratio (a strong and a weak signal) it is precluded that the 5.5 ppm signal is produced by $[\mathbf{1}_2\mathrm{BCl_2}]^+$ the formation of which via auto-ionization of **1**→$\mathrm{BCl_3}$ should coincide with the $[\mathrm{BCl_4}]^-$ content. Most likey, the observation of the minor amounts of $[\mathbf{1}_2\mathrm{BCl_2}]^+$ is hampered by signal broadening. Thus, we surmise that **1**→$\mathrm{BCl_3}$ is prone to a similar auto-ionization process as presumed for **1**→$\mathrm{BF_3}$ but the equilibrium is shifted more to the **1**→$\mathrm{BCl_3}$ side. Notably, from the literature a few examples can be retrieved for bidentate nitrogen-based ligands to exert auto-ionization on $\mathrm{BCl_3}$ to furnish $[\mathrm{BCl_4}]^-$ salts of chelate fashioned boronium dichloride cation complexes.[69-72] For carbene or silylene ligands, however, salts of the type $[(\mathrm{ligand})_2\mathrm{BX_2}][\mathrm{BX_4}]$ (with X = halogen) are to the best of our knowledge scarcely reported in the literature. The formation of chloroborane species bearing one or two groups of **1** was corroborated by our ESI mass spectrometric analysis (positive mode) in which signals were assigned to $[\mathbf{1}\cdot\mathrm{BCl_2}]^+$, $[\mathbf{1}\cdot\mathrm{BCl_2}(\mathrm{L^{Me4}})]^+$, and the auto-ionization product $[\mathbf{1}_2\mathrm{BCl_2}]^+$. Furthermore, the spectrum includes two peaks correlated with the stoichiometries $[(\mathbf{1})\mathrm{BHCl}(\mathrm{SiH}(\mathrm{SitBu_3})\mathbf{1}]^+$ and $[(\mathbf{1})\mathrm{BCl_2}(\mathrm{SiH}(\mathrm{SitBu_3})\mathbf{1}]^+$. In fact, we obtained crystalline batches of $\mathbf{1}\cdot\mathrm{BCl_3}$ and from these single crystals of **1**→$\mathrm{BCl_3}$, as well as $[(\mathbf{1}\rightarrow\mathrm{BCl_2}\leftarrow\mathrm{SiH}(\mathrm{SitBu_3})\leftarrow\mathbf{1}]^+[\mathrm{BCl_4}]^-$ have been picked. Unfortunately, the insufficient quality of these data prohibits discussion of the respective structural parameters (see the *ESI* for details on mass spectrometry and structure depiction). It is also worth noting that incremental addition of $\mathrm{BCl_3}$ (as a 1 M solution in heptane) to an NMR sample of $\mathbf{1}\cdot\mathrm{BCl_3}$ in $\mathrm{CDCl_3}$ did not change the ^{11}B NMR spectrum except for the rising of a signal at 46 ppm produced by “free” $\mathrm{BCl_3}$. This suggests that the auto-ionization proceeds very slowly.

As expected, a colorless precipitate also formed upon treatment of a yellow solution of the pyramidal silylene **1** in toluene solution with $\mathrm{BBr_3}$ (Scheme 3). The ^{1}H NMR spectrum of the isolated solid (in $\mathrm{CD_2Cl_2}$) diagnoses one product species and the elemental combustion analysis agrees with the proposed stoichiometric composition $\mathbf{1}\cdot\mathrm{BBr_3}$. A proton resonance at 4.76 ppm is assigned to the Si*H* hydrogen atom (Si,H-satellites: ^1J(Si,H) = 168 Hz, 1 H, Si-*H*) which proves that the conceivable hydride-abstraction from the hydrosilylene by the Lewis acid is no relevant side reaction. Interestingly, while we isolated the product in moderate yield upon conversion of **1** with $\mathrm{BBr_3}$ (50%) the use of the milder boron tribromide source $\mathrm{Me_2S}$→$\mathrm{BBr_3}$ resulted in higher amounts of obtained product (74%). This also means that **1** possesses a higher affinity to $\mathrm{BBr_3}$ than dimethylsulphide. The ^{11}B NMR analysis of $\mathbf{1}\cdot\mathrm{BBr_3}$ (in $\mathrm{CDCl_3}$) shows the presence of a four-coordinate boron center as implied by a signal at −11.8 ppm (95 Hz) which is significantly shifted to higher field with respect to $\mathrm{BBr_3}$ (39 ppm in $\mathrm{CD_2Cl_2}$) and also with regard to the value of 4.5 ppm for the presumed **1**→$\mathrm{BF_3}$, as well as 5.5 ppm for **1**→$\mathrm{BCl_3}$. The upfield shift is easily explained by the "heavy atom effect" that is imposed by bromine to inflict an upfield shift on the NMR signals of attached nuclei.[73] For comparison the ^{11}B nucleus of the NHC adduct $\mathrm{L^{iPr}}$→$\mathrm{BBr_3}$ had been reported to resonate at −15 ppm (in $\mathrm{C_6D_6}$, $\mathrm{L^{iPr}}$ = 1,3-diisopropyl-4,5-dimethyl-imidazolin-2-ylidene). A signal produced by $[\mathrm{BBr_4}]^-$ (expected at about −24 ppm) is not observed. The structural formulation of $\mathbf{1}\cdot\mathrm{BBr_3}$ as the Lewis acid base complex **1**→$\mathrm{BBr_3}$ is supported by the XRD study conducted on single crystals grown from a concentrated solution of $\mathbf{1}\cdot\mathrm{BBr_3}$ in a 1:1 mixture of dichloromethane with hexane (Fig. 4). The Si–B distance amounts to 2.045(3) Å and, thus, is very similar to the respective distance in **1**→$\mathrm{BH_3}$. The Si–$\mathrm{C_{NHC}}$ bond length is determined to 1.922(3) Å which is only marginally shorter than observed in the trihydroborane complex, hence, the bonding situation within the $\mathrm{SiL^{Me4}}$ fragment seems to be affected only to a small degree by the Lewis acidity of the attached borane group. At this point it is to emphasize that we are not aware of any structural report on a simple Lewis acid base adduct between a silylene and a haloborane group as related examples commonly involve transfer of a halide from the boron- to the silicon atom.

We conclude that the susceptibility of the system consisting of **1** and a boron trihalide to auto-ionization decreases with a rise in atomic number of the halide. This agrees with the general trend reported for complexes between boron and diorganyl compounds of the heavier chalcogens (i.e. $\mathrm{R_2E}$→$\mathrm{BX_3}$ with E = S, Se, Te and X = halogen). The complex stabilities of these increase in the order F < Cl < Br for the respective chalcogen.[74-76] Moreover, the pronounced stability of the widely employed

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00628G

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

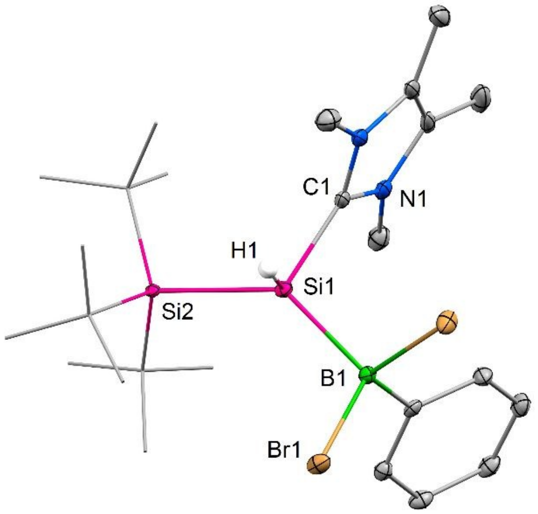


Fig. 5 Ellipsoid plot (30% level) of the molecular structure of **1**→$BPhBr_2$ in the single crystal. H-atoms omitted (except on Si). Wireframe model for tert-butyl groups. Selected interatomic distances [Å] and angles [°]: Si1-B1 = 2.074(3), Si1-C1 = 1.931(3); Si2-Si1-B1 = 131.9(1), Si2-Si1-C1 = 113.1(1), C1-Si1-B1 = 103.0(1).

$[BF_4]^-$ anion explains why the boron fluoride system is particularly prone to auto-ionization.

Because we had studied the triarylborane complex **1**→BPh_3 and the trihaloborane adducts **1**→BX_3 it was obvious that the study of a mixed system, that is an arylhaloborane, needed to be included in our systematic investigation. Further reason was given by the recent reports of Braunschweig and coworkers who have disclosed various insertions of two-coordinate NHSi into boron-halide bonds of arylhaloboranes and we sought to contrast these reactivities by employing a three-coordinate silylene in organohaloborane chemistry.[22,24] Thus, we brought $PhBBr_2$ into contact with **1** in toluene solution and, reminiscent of the related conversions described above, we observed discoloration and formation of a precipitate (Scheme 3). A sample of the isolated product (70% yield isolated) in $CDCl_3$ solution exhibited a resonance at −1 ppm in the ^{11}B NMR analysis which is deshielded in comparison to **1**→BBr_3 and corresponds to the typical chemical shift expected for four-coordinate boron nuclei. Additionally, the observation of the prominent Si*H* signal at 4.50 ppm in the ^1H NMR spectrum and the ^{13}C NMR resonance assigned to the silicon-bonded carbene center provides evidence that ligand exchange reactions between the metalloid centers are inhibited. We surmise that the silylene Lewis acid base adduct **1**→$BPhBr_2$ forms in similar fashion as found in the related reaction between **1** and BBr_3. This is confirmed by the structural characterization of single crystals of **1**→$BPhBr_2$ (Fig. 5). Geometric parameters concerning metalloid coordination differ only by increments from the tribromoborane congener **1**→BBr_3, that is the Si–B bond and the $Si–C_{NHC}$ are slightly elongated (2.074(3) Å and 1.931(3) Å) with respect to the higher brominated derivative. This can be attributed to the small increase of steric repulsion caused by the phenyl group rather than differences in the Lewis acidities of the tribromoborane and phenyldibromoborane fragments. Notably, the silicon-boron bond length of 2.024(3) Å in **F**[2] is shorter by about 0.05 Å in comparison to that in **1**→$BPhBr_2$. The respective bond length in **G**[2], however, amounts to 2.077(2) Å which is very similar to our new complex. Consequently, it can hardly be concluded on the type of silicon-boron interaction (e.g. dative bond, single bond) from this structural parameter on the scarce basis of reported examples. We envisaged that **1**→$BPhBr_2$ constitutes a promising precursor for reductive debromination, as well as bromide abstraction experiments to produce novel types of silylene-stabilized organoborylene systems and borenium cation species. In fact, Lin, Xie and coworkers have reported a borylene complexe stabilized by a bis(silylene) ligand with four-coordinate silicon centers bearing amidino groups. Unfortunately, our attempts of exposing **1**→$BPhBr_2$ to common reducing agents (e.g. KC_8, sodium naphthalenide, $NaSitBu_3$) afforded ill-defined product mixtures. Similarly, treating **1**→$BPhBr_2$ with bromide scavengers (e.g. $Ag[Al(OC(CF_3)_3)_4]$, $K[B(C_6F_5)_4]$) yielded an untraceable product.

Conclusions

The build-up of silicon-boron bonds by reaction of a three-coordinate silylene with electrophilic boron sources was systematically investigated. We treated the NHC-stabilized pyramidal hydrosilylene $tBu_3SiSi(H)L^{Me4}$ (**1**, L^{Me4} = 1,3,4,5-tetramethyl-imidazolin-2-ylidene) with trihydroboranes, organoboranes and haloboranes. The reaction of **1** with $THF{\cdot}BH_3$ or $H_3N{\rightarrow}BH_3$ afforded the silylene complex **1**→BH_3 or the product (**2**) of ammoniaborane dehydrogenation with concomittant insertion of the silicon(II) atom into an N–H bond. Conversion of **1** with BPh_3 leads to the formation of the intermediate **1**→BPh_3 complex in solution which readily converts with additional L^{Me4} to $L^{Me4}{\rightarrow}BPh_3$ and "free" silylene **1**. Treatment of **1** with the haloboranes $Et_2O{\rightarrow}BF_3$, BCl_3, BBr_3 and $Me_2S{\rightarrow}BBr_3$ resulted in formation of the Lewis acid-base adducts **1**–BX_3 (X = F, Cl, Br) which slowly equilibrated to the auto-ionization products $[\mathbf{1}_2BX_2][BX_4]$. The ratio of **1**→BX_3 significantly increased with rising atomic number of the halide. Accordingly, the complex **1**→$BPhBr_2$ was isolated after conversion of **1** with $PhBBr_2$. The relative stability of **1**→BE_3 (E = H, F, Cl, Br), as well as **1**→$BPhBr_2$ strongly correlates with the relative stability of respective borane dimethylsulphide adducts.

We envisage that the use of complexes between silylenes and boranes will complement the toolkit of organometallic synthesis similar to the ubiquitous compound class of carbene-borane complexes. The silylene-haloborane compounds in particular provide high prospect for access to hitherto unknown low-coordinate silicon-boron complexes via dehalogenation methods.

Conflicts of interest

The authors affirm that there are no conflicts to declare.

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608C

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Acknowledgements

We gratefully acknowledge financial support from WACKER Chemie AG and the European Research Council (SILION 637394). We thank Lorenz J. Schiegerl (TUM) and Dr. Maria Schlangen-Ahl (TU Berlin) for mass spectrometric analyses.

Experimental section

General Considerations. All experiments and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or an MBraun glovebox workstation. Glassware was heat dried under vacuum prior to use. Solvents were dried by standard methods. NMR spectra at ambient temperature (298 K) were recorded on a *Bruker* AV400US, DRX400, AVHD300, or AV500C device. δ(^{1}H) and δ(^{13}C) were referenced internally to the relevant residual solvent resonances. δ(^{11}B) was referenced to $Et_2O{\rightarrow}BF_3$ as an external standard. δ(^{29}Si) was referenced to tetramethylsilane (TMS) (δ = 0 ppm) as an external standard. Abbreviations: s = singlet, q = quartet, n.o. = not observed, Elemental analyses (EA) were conducted with a EURO EA (HEKA tech) instrument equipped with CHNS combustion analyzer. The silylene[48] **1**, $Me_2S{\cdot}BBr_3$[76] and $PhBBr_2$[77]were prepared according to literature procedures. $THF{\cdot}BH_3$, $H_3N{\rightarrow}BH_3$, BCl_3 (1.0 M in heptane) and BBr_3 were used as received. $Et_2O{\rightarrow}BF_3$ was distilled and stored in a fridge under argon. BPh_3 was sublimed at 80 °C prior to use.

Synthesis of 1→BH$_3$: A solution of $THF{\cdot}BH_3$ (1.0 M, 0.3 mL, 0.30 mmol) in THF was added to a solution of silylene **1** (80 mg, 0.23 mmol) in THF (5 mL) at ambient temperature dropwise. The color of the solution changed from yellow to colorless immediately. The reaction solution was stirred for additional 30 min. All volatiles were removed in vacuum to give **1**→BH_3 as colorless solid (77 mg, 93%). Colorless crystals suitable for single crystal X-ray diffraction analysis were obtained at ambient temperature from a benzene solution. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ [ppm] = 4.31 (q, ^3J(B,H) = 4.8 Hz, Si,H-satellites: ^1J(Si,H) = 150 Hz, 1H, Si-*H*), 3.71 (s, 3H, N-C*H*$_3$), 3.09 (s, 3H, N-C*H*$_3$), 1.36 (s, 27H, C(C*H*$_3$)$_3$), 1.29 (s, 3H, C-C*H*$_3$), 1.19 (s, 3H, C-C*H*$_3$), n.o. (BH). ^{11}B NMR (128.4 MHz, C_6D_6, 298 K): δ [ppm] = −40.8 (q, ^1J(B,H) = 93 Hz, *B*H$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ [ppm] = 161.8 (:*C*N$_2$), 127.0 (*C*-CH$_3$), 126.9 (*C*-CH$_3$), 35.0 (N-*C*H$_3$), 34.1 (N-*C*H$_3$), 32.1 (C(*C*H$_3$)$_3$), 24.5 (*C*(CH$_3$)$_3$), 8.5 (C-*C*H$_3$), 8.1 (C-*C*H$_3$). ^{29}Si{^{1}H} INEPT NMR (79.5 MHz, C_6D_6, 298 K): δ [ppm] = -77.0 (*Si*-H), 13.1 (*t*Bu$_3$*Si*). APCI-MS m/z = 365.2977 [M − H]$^+$, calc: 365.2974. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2974 (w), 2950 (w), 2885 (w), 2852 (s), 2311 (br, B-H), 2238 (w, B-H), 2083 (m, Si-H), 1914 (w), 1648 (w), 1468 (m), 1437 (m), 1385 (s), 1364 (m), 1131 (w), 1021 (s), 931 (w), 888 (s), 814 (s), 775 (m), 591 (s).

Synthesis of 2: To a solution of silylene **1** (250 mg, 0.71 mmol) in 10 mL toluene, NH_3BH_3 (22 mg, 0.71 mmol) in 5 mL toluene was added dropwise at ambient temperature. The yellow solution turned colorless immediately. The reaction mixture stirred additional 3 hours; toluene was removed under vacuum, hexane was added (2 x 15 mL) and it was filtered. Hexane was removed in vacuum to afford a colorless solid. Yield: 40 mg, 46%. Colorless crystals suitable for X-ray diffraction analysis were obtained from a toluene:pentane (1:1) mixture at 5 °C. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ [ppm] = 5.24 (d, ^3J(H,H) = 4 Hz, 2H, Si-*H*$_2$), 3.30 (s, 6H, N-C*H*$_3$), 1.37 (s, 27H, C(C*H*$_3$)$_3$), 1.21 (s, 6H, C-C*H*$_3$). ^{11}B NMR (128.4 MHz, C_6D_6, 298 K): δ [ppm] = −17.8 (t, *B*H$_2$, ^1J(B,H) = 94 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ [ppm] = 122.6 (*C*-CH$_3$), 31.8 (*C*(CH$_3$)$_3$), 31.1 (N-*C*H$_3$), 23.7 (C(*C*H$_3$)$_3$), 7.8 (C-*C*H$_3$), n.a (:*C*N$_2$). ^{29}Si{^{1}H} NMR (79.5 MHz, C_6D_6, 298 K): δ [ppm] = −46.3 (*Si*H$_2$), 2.4 ppm (*t*Bu$_3$*Si*). APCI-HRMS m/z = 380.3093 [M − H]$^+$, calc: 380.3083.

Synthesis of 1→BPh$_3$: Freshly sublimed triphenylborane (BPh_3) (34.4 mg, 0.14 mmol) and silylene **1** (45 mg, 0.13 mmol) were added to a NMR sample tube and dissolved in C_6D_6 (0.5 mL). After sealing the NMR-tube the spectroscopic investigation was processed. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ [ppm] =7.81 (d, 6H, C^{2,6}-*H*, C$_6$*H*$_5$), 7.22 (t, 6H, C^{3,5}-*H*, C$_6$*H*$_5$), 7.12 (m, 3H, C^4-*H*, C$_6$*H*$_5$), 4.38 (s, Si,H-Satellites: ^1J(Si,H) = 149 Hz, 1H, Si-*H*), 2.90 (s, 3H, N-C*H*$_3$), 2.62 (s, 3H, N-C*H*$_3$), 1.17 (s, 27H, C(C*H*$_3$)$_3$), 1.14 (s, 3H, C-C*H*$_3$), 1.07 (s, 3H, C-C*H*$_3$). ^{11}B NMR (160.5 MHz, C_6D_6, 298 K): δ [ppm] = −3.2 (*B*Ph$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): δ [ppm] = 161.8 (:*C*N$_2$), 156.6 (Ph*C*), 136.8 (Ph*C*H), 127.5 (*C*-CH$_3$), 126.5 (Ph*C*H), 126.3 (*C*-CH$_3$), 123.6 (Ph*C*H), 36.0 (N-*C*H$_3$), 33.8 (N-*C*H$_3$), 32.4 (C(*C*H$_3$)$_3$), 24.6 (*C*(CH$_3$)$_3$), 8.4 (C-*C*H$_3$), 7.7 (C-*C*H$_3$). ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 298 K): δ [ppm] = −76.6 (*Si*-H), 24.4 (*t*Bu$_3$*Si*).

Synthesis of 1·BF$_3$: $Et_2O{\rightarrow}BF_3$ (0.05 mL, 0.36 mmol) was added dropwise to a yellow solution of **1** (86 mg, 0.25 mmol) in 10 mL toluene. Immediate decolorization followed by formation of a colorless precipitate occured. The suspension was stirred for 2 hours at room temperature and the phases were separated. The colorless solid was washed with pentane (10 mL) and dried in vacuum to give **1**·BF$_3$ (90 mg, 87%). Mono-adduct: ^{1}H NMR (300.1 MHz, C_6D_5F, 298 K): δ [ppm] = 4.39 (s, 1H, Si-*H*), 4.01 (s, 3H, N-C*H*$_3$), 3.58 (s, 3H, N-C*H*$_3$), 1.79 (s, 6H, C-C*H*$_3$), 1.50 (s, 27H, (C(C*H*$_3$)$_3$)). ^{11}B NMR (96.3 MHz, C_6D_5F, 298 K): δ [ppm] = 4.46 (q, *J* = 85.3 Hz). ^{19}F NMR (376.5 MHz, C_6D_6, 298K)): δ [ppm] = −138.12 (q, ^1J(B,F) = 36 Hz). ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_5F, 298 K): δ [ppm] = −84.0 (*Si*-H), 19.4 (*t*Bu$_3$*Si*). Elemental analysis (%): Calcd. for $C_{19}H_{40}BF_3N_2Si_2$: C, 54.27; H, 9.59; N, 6.66. Found: C, 52.79; H, 9.61; N, 6.22 (the low value for C is reasoned by the formation of incombustible boron- and silicon carbides).

Synthesis of 1·BCl$_3$: To a solution of **1** (100 mg, 0.28 mmol) in 10 mL toluene, BCl_3 (1M in heptane, 0.3 mL, 0.3 mmol) was added dropwise at ambient temperature. The yellow solution turned colorless immediately and a colorless precipitate formed. The resulting suspension was stirred overnight. After filtration the colorless powder was dried in vacuum for 2 hours to give analytically pure **1**·BCl$_3$. Yield: 95 mg, 71%. ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 4.49 (s, Si,H-satellites: ^1J(Si,H) = 165 Hz, 1 H, Si-*H*), 3.98 (s, 3H, N-C*H*$_3$), 3.81 (s, 3H, N-C*H*$_3$), 2.23 (d, *J* = 6.5 Hz, 6H, C-C*H*$_3$), 1.21 (s, 27H, (C(C*H*$_3$)$_3$)). ^{11}B NMR (128.4 MHz CD_2Cl_2, 298 K): δ [ppm] = 5.45 ($h_{1/2}$ = 90 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ [ppm] = 155.5 (:*C*N$_2$), 129.6 (*C*-CH$_3$), 128.5

Dalton Transactions Accepted Manuscript

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608G

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript

(*C*-CH$_3$), 37.6 (N-*C*H$_3$), 35.5 (N-*C*H$_3$), 31.9 (*C*(CH$_3$)$_3$), 24.4 (C(*C*H$_3$)$_3$), 10.0 (C-*C*H$_3$), 9.4 (C-*C*H$_3$). ^{29}Si{^{1}H} NMR (79.5 MHz, CD_2Cl_2, 298 K): δ [ppm] = 19.3 (*t*Bu$_3$*Si*), n.o. (*Si*-H). Elemental analysis (%): Calcd. for $C_{19}H_{40}BCl_3N_2Si_2$: C, 48.57; H, 8.58; N, 5.96. Found: C, 48.28; H, 8.31; N, 5.61.

Synthesis of 1→BBr$_3$: To a solution of **1** (176 mg, 0.5 mmol) in 10 mL toluene, BBr_3 (0.05 mL, 0.5 mmol, d: 2.65 g/mL) was added dropwise. The yellow solution turned colorless after 15 min and a precipitate formed. The reaction mixture was stirred overnight. The suspension was filtered and the obtained off-white powder dried in vacuum for 2 hours to give analytically pure compound **1**→BBr$_3$ (152 mg, 50%). Colorless crystals were grown from dichloromethane:hexane (1:1) at room temperature. (The same product could also be obtained by using the more convenient Me$_2$S→BBr$_3$ adduct instead of BBr_3 with 74% yield). ^{1}H NMR (400.1 MHz, CD_2Cl_2, 298 K): δ [ppm] = 4.76 (s, Si,H-satellites: ^{1}*J*(Si,H) = 168 Hz, 1 H, Si-*H*)), 4.00 (s, 3H, N-C*H*$_3$), 3.80 (s, 3H, N-C*H*$_3$), 2.23 (d, *J* = 3.2 Hz, 6H, C-C*H*$_3$), 1.22 (s, 27H, (C(C*H*$_3$)$_3$)). ^{11}B NMR (128.4 MHz, CD_2Cl_2, 298 K): δ [ppm] = −11.8 ($h_{1/2}$: 95 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ [ppm] = 156.3 (:*C*N$_2$), 128.9 (*C*-CH$_3$), 127.8 (*C*-CH$_3$), 37.9 (N-*C*H$_3$), 35.3 (N-*C*H$_3$), 31.9 (*C*(CH$_3$)$_3$), 24.3 (C(*C*H$_3$)$_3$), 9.9 (C-*C*H$_3$), 9.3 (C-*C*H$_3$). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 298 K): δ [ppm] = 22.0 (*t*Bu$_3$*Si*), n.o. (*Si*-H). Elemental analysis (%): Calcd. for $C_{19}H_{40}BBr_3N_2Si_2$: C, 37.83; H, 6.68; N, 4.64. Found: C, 38.8; H, 6.66; N, 4.12.

Synthesis 1→BPhBr$_2$: $PhBBr_2$ (105 mg, 0.43 mmol) in 3 mL toluene was added dropwise to a solution of **1** (150 mg, 0.43 mmol) in 7 mL toluene. The yellow solution gradually decolorized, approximately 10 minutes later a white precipitate formed. For a complete conversion, the suspension was stirred overnight. It was filtered and the colorless solid was washed with 10 mL hexane and dried in vacuum to give analytically pure **1**→BBr$_2$Ph. Yield: 180 mg, 70%. ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.86-7.64 (m, 2H, Ph-H), 7.18-6.89 (m, 3H, Ph-H), 4.50 (s, Si,H-satellites: ^{1}*J*(Si,H) = 161 Hz, 1H, Si-*H*), 3.92 (s, 3H, N-C*H*$_3$), 3.65 (s, 3H, N-C*H*$_3$), 2.17 (s, 6H, C-C*H*$_3$), 1.06 (s, 27H, C(C*H*$_3$)$_3$). ^{11}B NMR (128.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −0.83 ($h_{1/2}$: 550 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ [ppm] = 157.5 (:*C*N$_2$), 133.8 (Ph*C*H), 128.4 (*C*-CH$_3$), 127.3 (*C*-CH$_3$), 126.6 (Ph*C*H), 125.5 (Ph*C*H), 37.7 (N-*C*H$_3$), 35.0 (N-*C*H$_3$), 31.7 (*C*(CH$_3$)$_3$), 24.0 (C(*C*H$_3$)$_3$), 9.8 (C-*C*H$_3$), 9.1 (C-*C*H$_3$). ^{29}Si{^{1}H} NMR (99.4 MHz, $CDCl_3$, 298 K): δ [ppm] = 20.2 (*t*Bu$_3$*Si*), n.o. (*Si*-H). Elemental analysis (%): Calcd. for $C_{25}H_{45}BBr_2N_2Si_2$: C, 50.01; H, 7.55; N, 4.67. Found: C, 49.05; H, 7.27; N, 4.47 (the low value for C is reasoned by the formation of incombustible boron- and silicon carbides).

References

1. Y. Cui, X. Duan, J. Hu and C. M. Lieber, *J. Phys. Chem. B*, 2000, **104**, 5213-5216.
2. Y. Cui and C. M. Lieber, *Science*, 2001, **291**, 851-853.
3. N. Fukata, *Adv. Mater.*, 2009, **21**, 2829-2832.
4. M. Oestreich, E. Hartmann and M. Mewald, *Chem. Rev.*, 2013, **113**, 402-441.
5. C. Kleeberg and C. Borner, *Eur. J. Inorg. Chem.*, 2013, **2013**, 2799-2806.
6. E. Yamamoto, R. Shishido, T. Seki and H. Ito, *Organometallics*, 2017, **36**, 3019-3022.
7. Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479-3511.
8. M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354-396.
9. B. Blom, M. Stoelzel and M. Driess, *Chem.–Eur. J.*, 2013, **19**, 40-62.
10. Z. Benedek and T. Szilvási, *RSC Advances*, 2015, **5**, 5077-5086.
11. C. Marschner, *Eur. J. Inorg. Chem.*, 2015, **2015**, 3805-3820.
12. T. Troadec, A. Prades, R. Rodriguez, R. Mirgalet, A. Baceiredo, N. Saffon-Merceron, V. Branchadell and T. Kato, *Inorg. Chem.*, 2016, **55**, 8234-8240.
13. J. A. Cabeza, P. García-Álvarez and D. Polo, *Eur. J. Inorg. Chem.*, 2016, **2016**, 10-22.
14. S. Raoufmoghaddam, Y.-P. Zhou, Y. Wang and M. Driess, *J. Organomet. Chem.*, 2017, **829**, 2-10.
15. C. Weetman and S. Inoue, *ChemCatChem*, 2018, **10**, 4213-4228.
16. N. Metzler and M. Denk, *Chem. Commun.*, 1996, **1996**, 2657-2658.
17. D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue and B. Rieger, *J. Am. Chem. Soc.*, 2017, **139**, 8134-8137.
18. H. Wang, L. Wu, Z. Lin and Z. Xie, *J. Am. Chem. Soc.*, 2017, **139**, 13680-13683.
19. Y. Suzuki, S. Ishida, S. Sato, H. Isobe and T. Iwamoto, *Angew. Chem. Int. Ed.*, 2017, **56**, 4593-4597.
20. Y. Li, R. K. Siwatch, T. Mondal, Y. Li, R. Ganguly, D. Koley and C.-W. So, *Inorg. Chem.*, 2017, **56**, 4112-4120.
21. S. Kaufmann, S. Schäfer, M. T. Gamer and P. W. Roesky, *Dalton Trans.*, 2017, **46**, 8861-8867.
22. H. Braunschweig, T. Brückner, A. Deißenberger, R. D. Dewhurst, A. Gackstatter, A. Gärtner, A. Hofmann, T. Kupfer, D. Prieschl, T. Thiess and S. R. Wang, *Chem.–Eur. J.*, 2017, **23**, 9491-9494.
23. F. M. Mück, J. A. Baus, R. Bertermann, C. Burschka and R. Tacke, *Organometallics*, 2016, **35**, 2583-2588.
24. A. Gackstatter, H. Braunschweig, T. Kupfer, C. Voigt and N. Arnold, *Chem.–Eur. J.*, 2016, **22**, 16415-16419.
25. H. Cui, M. Wu and P. Teng, *Eur. J. Inorg. Chem.*, 2016, **2016**, 4123-4127.
26. K. Junold, J. A. Baus, C. Burschka, C. Fonseca Guerra, F. M. Bickelhaupt and R. Tacke, *Chem.–Eur. J.*, 2014, **20**, 12411-12415.
27. R. Rodriguez, T. Troadec, T. Kato, N. Saffon-Merceron, J.-M. Sotiropoulos and A. Baceiredo, *Angew. Chem. Int. Ed.*, 2012, **51**, 7158-7161.
28. S. Inoue and K. Leszczyńska, *Angew. Chem. Int. Ed.*, 2012, **51**, 8589-8593.
29. S. M. I. Al-Rafia, R. McDonald, M. J. Ferguson and E. Rivard, *Chem.–Eur. J.*, 2012, **18**, 13810-13820.
30. S. M. I. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson and E. Rivard, *Chem. Commun.*, 2012, **48**, 1308-1310.
31. A. Jana, D. Leusser, I. Objartel, H. W. Roesky and D. Stalke, *Dalton Trans.*, 2011, **40**, 5458.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608G

Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

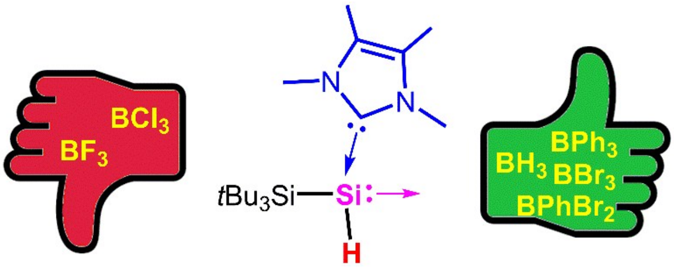
Dalton Transactions Accepted Manuscript

32. A. Jana, R. Azhakar, S. P. Sarish, P. P. Samuel, H. W. Roesky, C. Schulzke and D. Koley, *Eur. J. Inorg. Chem.*, 2011, **2011**, 5006-5013.
33. R. Azhakar, G. Tavčar, H. W. Roesky, J. Hey and D. Stalke, *Eur. J. Inorg. Chem.*, 2011, **2011**, 475-477.
34. M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2011, **133**, 8874-8876.
35. R. S. Ghadwal, H. W. Roesky, S. Merkel and D. Stalke, *Chem.–Eur. J.*, 2010, **16**, 85-88.
36. T. Kajiwara, N. Takeda, T. Sasamori and N. Tokitoh, *Organometallics*, 2004, **23**, 4723-4734.
37. T. Kajiwara, N. Takeda, T. Sasamori and N. Tokitoh, *Chem. Commun.*, 2004, **2004**, 2218-2219.
38. U. Holtmann, P. Jutzi, T. Kühler, B. Neumann and H.-G. Stammler, *Organometallics*, 1999, **18**, 5531-5538.
39. H.-C. Tsai, Y.-F. Lin, W.-C. Liu, G.-H. Lee, S.-M. Peng and C.-W. Chiu, *Organometallics*, 2017, **36**, 3879-3882.
40. B. Geng, C. Xu and Z. Chen, *J. Mol. Model.*, 2016, **22**, 134.
41. A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500-6503.
42. R. S. Alfredo, A. B. Isabel, B. Antoine, S. M. Nathalie, M. Stéphane, B. Vicenç and K. Tsuyoshi, *Angew. Chem. Int. Ed.*, 2017, **56**, 10549-10554.
43. S. Inoue, M. Ichinohe and A. Sekiguchi, *Chem. Lett.*, 2008, **37**, 1044-1045.
44. K. Takeuchi, M. Ichinohe and A. Sekiguchi, *Organometallics*, 2011, **30**, 2044-2050.
45. T. Kosai and T. Iwamoto, *J. Am. Chem. Soc.*, 2017, **139**, 18146-18149.
46. T. Kosai and T. Iwamoto, *Chem.–Eur. J.*, 2018, **24**, 7774-7780.
47. K. Takeuchi, M. Ikoshi, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2010, **132**, 930-931.
48. S. Inoue and C. Eisenhut, *J. Am. Chem. Soc.*, 2013, **135**, 18315-18318.
49. C. Eisenhut, T. Szilvási, N. C. Breit and S. Inoue, *Chem.–Eur. J.*, 2015, **21**, 1949-1954.
50. C. Eisenhut, N. C. Breit, T. Szilvási, E. Irran and S. Inoue, *Eur. J. Inorg. Chem.*, 2016, **2016**, 2696-2703.
51. C. Eisenhut and S. Inoue, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 2016, **191**, 605-608.
52. C. Eisenhut, T. Szilvási, G. Dübek, N. C. Breit and S. Inoue, *Inorg. Chem.*, 2017, **56**, 10061-10069.
53. T. Kawamoto, S. J. Geib and D. P. Curran, *J. Am. Chem. Soc.*, 2015, **137**, 8617-8622.
54. T. R. McFadden, C. Fang, S. J. Geib, E. Merling, P. Liu and D. P. Curran, *J. Am. Chem. Soc.*, 2017, **139**, 1726-1729.
55. D. P. Curran, A. Solovyev, M. M. Brahmi, L. Fensterbank, M. Malacria and E. Lacôte, *Angew. Chem. Int. Ed.*, 2011, **50**, 10294-10317.
56. A. Prokofjevs, J. W. Kampf, A. Solovyev, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2013, **135**, 15686-15689.
57. A. Jana, C. Schulzke and H. W. Roesky, *J. Am. Chem. Soc.*, 2009, **131**, 4600-4601.
58. M. Stoelzel, C. Präsang, S. Inoue, S. Enthaler and M. Driess, *Angew. Chem. Int. Ed.*, 2012, **51**, 399-403.
59. K. J. Sabourin, A. C. Malcolm, R. McDonald, M. J. Ferguson and E. Rivard, *Dalton Trans.*, 2013, **42**, 4625-4632.
60. D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, **50**, 12338-12348.
61. D. W. Stephan, *Science*, 2016, **354**, aaf7229-aaf7229.
62. S. A. Weicker and D. W. Stephan, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1003-1016.
63. D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018-10032.
64. D. W. Stephan, *Acc. Chem. Res.*, 2014, **48**, 306-316.
65. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400-6441.
66. A. C. Filippou, O. Chernov, K. W. Stumpf. and G. Schnakenburg, *Angew. Chem. Int. Ed.*, 2010, **49**, 3296-3300.
67. H. Cui, J. Zhang and C. Cui, *Organometallics*, 2013, **32**, 1-4.
68. H. C. Brown and U. S. Racherla, *J. Org. Chem.*, 1986, **51**, 427-432.
69. K. V. Vasudevan, M. Findlater and A. H. Cowley, *Chem. Commun.*, 2008, **2008**, 1918-1919.
70. H. A. Jenkins, C. L. Dumaresque, D. Vidovic and J. A. C. Clyburne, *Can. J. Chem.*, 2002, **80**, 1398-1403.
71. W. Lothar, F. Jan, S. Hans-Georg and N. Beate, *Eur. J. Inorg. Chem.*, 2006, **2006**, 5048-5056.
72. M. M., H. K., D. K., M. J., G. H. and F. D., *Z. Anorg. Allg. Chem.*, 1996, **622**, 1692-1700.
73. A. C. Neto, L. C. Ducati, R. Rittner, C. F. Tormena, R. H. Contreras and G. Frenking, *J. Chem. Theory Comput.*, 2009, **5**, 2222-2228.
74. C. K. Y. A. Okio, W. Levason, F. M. Monzittu and G. Reid, *J. Organomet. Chem.*, 2017, **848**, 232-238.
75. H. C. Brown and N. Ravindran, *Inorg. Chem.*, 1977, **16**, 2938-2940.
76. M. Schmidt and H. D. Block, *Chem. Ber.*, 1970, **103**, 3705-3710.
77. D. Kaufmann, *Chem. Ber.*, 1987, **120**, 853-854.

Please do not adjust margins

View Article Online
DOI: 10.1039/C9DT00608G

An NHC-stabilized three-coordinate hydrosilylene dehydrogenates ammonia borane and forms more stable complexes with BH_3, BPh_3, BBr_3 and $BPhBr_2$ but less stable ones with BF_3, and BCl_3 for which ligand scrambling occurs.



Published on 03 April 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 4/3/2019 1:55:31 PM.

Dalton Transactions Accepted Manuscript