Reaction of Stable Silylene–Isocyanide Complexes with Boranes: Synthesis and Properties of the First Stable Silylborane–Isocyanide Complexes

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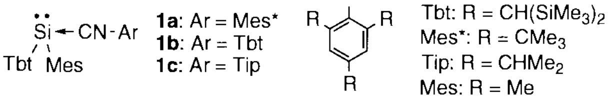
Stable silylene–isocyanide complexes [Tbt(Mes)SiCNAr (Ar = Tbt, Mes*; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = mesityl; Mes* = 2,4,6-tri-*t*-butylphenyl)] reacted with BH_3·THF to give the first stable silylborane–isocyanide complexes [Tbt(Mes)$SiHBH_2CNAr$]. The thermal equilibrium between Tbt(Mes)$SiHBH_2CNAr$ and $TbtSiH_2BH$(Mes)CNAr was observed.

In recent decades, much attention has been paid to the chemistry of silylenes (silicon analogues of carbenes) from the standpoints of not only fundamental chemistry but also applied chemistry such as material science and organic syntheses.[1] Also, silylene complexes with Lewis bases have been extensively studied and some complexes have been synthesized in low temperature matrices so far.[2] However, their properties have not been fully disclosed yet due to their instability at ambient temperature.

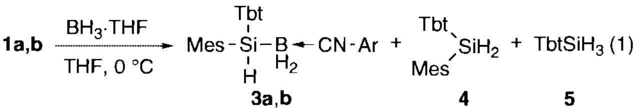
Recently, we have succeeded in the synthesis of the first stable silylene–Lewis base complexes **1a–c**[3] by the reaction of a disilene bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter),[4] with hindered isocyanides. In the reaction with Et_3SiH, nitrile oxides,[5] and 1,3-dienes,[6] complexes **1a–c** showed the reactivity as a silylene equivalent, and these results suggest the facile dissociation of **1a–c** into the silylene, Tbt(Mes)Si**:** (**2**), and the corresponding isocyanides at room temperature. Furthermore, we have revealed that **1c** reacted with methanol as a sila-ylide to undergo the 1,2-addition to the Si–C bond.[3] In this paper, we present the reaction of silylene complexes **1a,b** with BH_3·THF giving the first stable silylborane–isocyanide complexes.



1a: Ar = Mes*
1b: Ar = Tbt
1c: Ar = Tip

Tbt: R = $CH(SiMe_3)_2$
Mes*: R = CMe_3
Tip: R = $CHMe_2$
Mes: R = Me

Treatment of silylene complex **1a** with BH_3·THF in THF at 0 °C led to the gradual disappearance of the blue color of **1a**, and the corresponding silylborane–isocyanide complex **3a** was obtained as a stable compound in 34% yield along with Tbt(Mes)SiH_2 (**4**) (20%) and $TbtSiH_3$ (**5**) (5%) (eq 1). Reaction of complex **1b** with BH_3·THF also gave the corresponding silylborane–isocyanide complex **3b** (44%), **4** (12%), and **5** (8%). By contrast, the reaction of **1c** afforded a complex mixture and no silylborane complex **3c** was obtained, although the formation of **4** and **5** were confirmed. Since silylboranes and silylborates have attracted much attention especially from a synthetic point of view,[7] it should be very interesting to elucidate the properties of these novel compounds containing a Si–B bond. Furthermore, similar type of silylborane–isocyanide complexes have recently been postulated as reactive intermediates in the insertion reactions of isocyanides [RNC] into the silicon–boron bond of silylboranes [$PhMe_2SiBX_2$] giving the corresponding (boryl)(silyl)iminomethanes [($PhMe_2Si$)(X_2B)C=NR].[8]



$$\mathbf{1a,b}\xrightarrow[\text{THF, 0 °C}]{BH_3\cdot THF}\underset{\mathbf{3a,b}}{\text{Mes-}\overset{\text{Tbt}}{\underset{\text{H}}{\text{Si}}}\text{-}\underset{H_2}{\text{B}}\leftarrow\text{CN-Ar}}+\underset{\mathbf{4}}{\text{Tbt(Mes)SiH}_2}+\underset{\mathbf{5}}{\text{TbtSiH}_3}\quad(1)$$

The formation of **3a**,**b** was confirmed by ^1H, ^{13}C, and ^{11}B NMR and IR spectra.[9] Although the BH_2 protons were not observed on the ^1H NMR spectra probably due to the extreme broadening and the complicated coupling of the signals, the existence of the BH_2 part was evidenced by the observation of absorptions assigned to B–H stretch on the IR spectra (2400 and 2369 cm^{-1} for **3a** and 2400 and 2365 cm^{-1} for **3b**) and signals in the region of tetracoordinated borons on the ^{11}B NMR spectra (–42.6 ppm for **3a** and –43.0 ppm for **3b**). The molecular structure of **3a** was finally determined by X-ray structural analysis (Figure 1).[10] The ORTEP drawing of **3a** shows the tetrahedral geometry of the silicon atom and the linear B1–C1–N1–C4 structure. The Si1–B1–C1 angle (105.9(3)°) suggests that the boron atom has tetrahedral geometry. The Si1–B1 bond length (2.052(4) Å) is slightly longer than that of a silylborane–phosphine complex [$Me_3Si–BH_2P(C_6H_{12})_3$] (2.007(4) Å)[11] and lithium silylborates [Li($Ph_2RSi–BH_3$); R = Ph, *t*-Bu] (1.984–1.993 Å).[12] This value is close to those of tri- and tetra-silylborates [$LiRB(SiMe_3)_3$; R = $SiMe_3$, Me] (2.017–2.034 Å).[12] The B1–C1 bond length (1.538(6) Å) is shorter than that of *o*-$Me_3SiO–C_6H_4NC–BPh_3$ (1.616(2) Å)[13] and almost equal to those of polyhedral heteroborane–isocyanides adducts (1.537–1.560 Å).[14] The C–N bond length (1.155(5) Å) is almost the same as that of TbtNC (1.156(7) Å).[15]

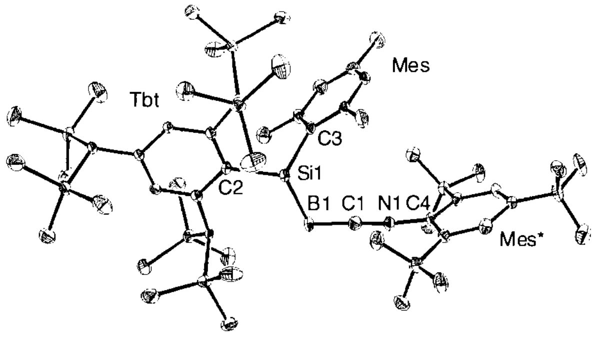
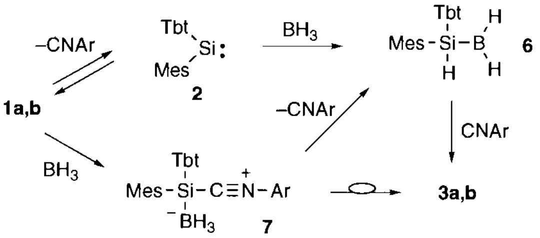


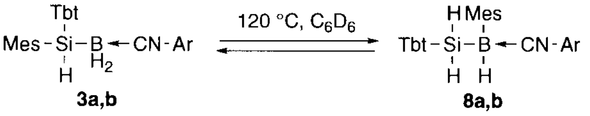
Figure 1. ORTEP drawing of **3a** with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and bond angles (deg): Si1-B1, 2.052(4); Si1-C2, 1.922(4); Si1-C3, 1.912(4); B1-C1, 1.538(6); C1-N1, 1.155(5); N1-C4, 1.404(4); C2-Si1-C3, 112.4(2); C2-Si1-B1, 121.8(2); C3-Si1-B1, 104.4(2); Si1-B1-C1, 105.9(3); B1-C1-N1, 177.2(4); C1-N1-C4, 172.6(3).

The formation of **3a,b** may be reasonably interpreted in terms of the initial insertion of silylene **2** to the B–H bond of BH_3·THF followed by the coordination of the isocyanide to the boron atom of the resulting silylborane **6** (Scheme 1). However, the mechanism via the initial coordination of BH_3 on the silicon atom of the silylene complex **1a,b** cannot be ruled out at present. In order to elucidate the mechanism for the formation of **4** and **5**, the reaction of **1a** with an excess (5.5 molar equivalents) of BH_3·THF was examined. This reaction gave **4** (59%) as a main product along with **3a** (4%) and **5** (15%). Since **3a** did not react with BH_3·THF, it was considered that these hydrosilanes **4** and **5** were generated by the reaction of the intermediary **6** and/or **7** with BH_3·THF.



Scheme 1.

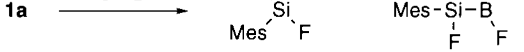
Although silylborane–isocyanide complex **3a** are stable towards moisture and air, thermolysis of **3a** at 120 °C gave a 1 : 5 mixture of **3a** and the corresponding migration product **8a**[16] (eq 2) in contrast to the previously reported intermediary silylborane–isocyanide complexes which give the corresponding (boryl)(silyl)iminomethanes as final products.[8] The structure of **8a** was determined by ^1H, ^{13}C, and ^{11}B NMR spectra, difference NOE experiments, and IR spectrum. The difference NOE experiments on **8a** showed the NOEs of the SiH proton only with the *o*-methine protons of the Tbt group. On the other hand, in the case of **3a**, the irradiation of the SiH protons resulted in the enhancement of both peaks for the *o*-methine protons of the Tbt group and the *o*-methyl protons of the mesityl group. These NOE experiments indicate the absence of the mesityl group on the silicon atom in **8a**. Since the 1:5 mixture of **3a** and **8a** was also obtained from the isolated compound **8a** on heating at 120 °C, the existence of the equilibrium between **3a** and **8a** is strongly suggested. Also, thermolysis of **3b** at 120 °C resulted in the formation of the mixture of **3b** and **8b** with the ratio of 1:10.



$$\text{Mes-}\underset{\text{H}}{\overset{\text{Tbt}}{\text{Si}}}\text{-}\underset{\text{H}_2}{\text{B}}\leftarrow\text{CN-Ar}\ \underset{}{\overset{120\ °\text{C},\ C_6D_6}{\rightleftharpoons}}\ \text{Tbt-}\underset{\text{H}}{\overset{\text{H}}{\text{Si}}}\text{-}\underset{\text{H}}{\overset{\text{Mes}}{\text{B}}}\leftarrow\text{CN-Ar} \quad (2)$$

3a,b **8a,b**

Reaction of **1a** with $BF_3·Et_2O$ gave the fluorosilane **9** in 47% yield (eq 3). The formation of **9** can be explained by the hydrolysis of intermediary silylborane **10** during separation. The lack of the stable silylborane–isocyanide complex in this reaction might be due to the low Lewis acidity of fluoroboranes compared to hydroboranes. Reactions of **1a** with BPh_3, $B(NMe_2)_3$, and $B(OMe)_3$ did not proceed.[17]



$$\textbf{1a}\ \xrightarrow{BF_3·Et_2O}\ \text{Tbt(Mes)SiHF}\quad \text{Mes-}\underset{\text{F}}{\overset{\text{Tbt}}{\text{Si}}}\text{-BF}_2 \quad (3)$$

9 (47%) **10**

Further investigations on the properties of silylborane–isocyanide complexes **3a**,**b**, the equilibrium between **3a,b** and **8a,b**, and reactions of silylene–isocyanide complexes **1a**,**b** with other boranes are currently in progress.

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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9 Spectral data for **3a**: colorless crystals, mp 173–174 °C (decomp); ^1H NMR ($CDCl_3$, 300 MHz) δ –0.14 (s, 9H), –0.08 (s, 9H), 0.02 (s, 18H), 0.04 (s, 18H), 1.26 (s, 1H), 1.29 (s, 18H), 1.30 (s, 9H), 2.14 (s, 3H), 2.37 (s, 6H), 2.49 (s, 1H), 2.61 (s, 1H), 5.21 (d, 1H, J = 7 Hz), 6.19 (s, 1H), 6.33 (s, 1H), 6.61 (s, 2H), 7.31 (s, 2H), the signals of BH_2 were not observed; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.6 (q), 0.8 (q), 0.90 (q), 0.94 (q), 1.2 (q), 1.5 (q), 20.9 (q), 25.3 (q), 26.8 (d), 27.0 (d), 29.7 (q), 30.0 (d), 31.2 (q), 35.4 (s), 35.5 (s), 120.3 (s), 122.1 (d), 122.4 (d), 127.5 (d), 128.5 (d), 129.3 (s), 136.8 (s), 137.2 (s), 142.2 (s), 143.4 (s), 147.5 (s), 151.2 (s), 151.7 (s), 151.8 (s), 152.3 (s); ^{11}B NMR ($CDCl_3$, 96 MHz) δ –42.6; IR (KBr) 2400 [ν(BH)], 2369 [ν(BH)], 2213 [ν(CN)], 2139 [ν(SiH)] cm^{-1}; FABMS *m/z* 1006 [$(M+Na)^+$], 983 [M^+], 968 [$(M - Me)^+$], 864 [$(M - Mes)^+$], 699 [$Tbt(Mes)SiH^+$]. Anal. Calcd for $C_{55}H_{102}BNSi_7$: C, 67.08; H, 10.44; N, 1.42%. Found: C, 66.94; H, 10.69; N, 1.50%.
10 Crystal data for **3a**: Formula $C_{55}H_{102}BNSi_7$, fw = 984.83, triclinic, space group $P\bar{1}$(#2) $Z = 2$, $a = 9.709(5)$ Å, $b = 16.612(7)$ Å, $c = 20.306(10)$ Å, $\alpha = 83.42(1)°$, $\beta = 89.18(2)°$, $\gamma = 78.73(1)°$, $V = 3190.8(24)$ Å^3, $D_{calcd} = 1.025$ g/cm^3, $\mu = 1.81$ cm^{-1}, $2\theta_{max} = 55.0°$, $T = 93$ K, $R1$ (I > 2σ(I)) = 0.068, $wR2$ (all data) = 0.155, GOF = 1.07 for 14013 reflections and 688 parameters.
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16 Spectral data for **8a**: colorless crystals, ^1H NMR ($CDCl_3$, 300 MHz) δ –0.18 (s, 18H), 0.01 (s, 18H), 0.02 (s, 18H), 1.25 (s, 1H), 1.31 (s, 9H), 1.41 (s, 18H), 1.92 (br s, 2H), 2.17 (s, 3H), 2.42 (s, 6H), 4.54–4.56 (br m, 2H), 6.18 (s, 1H), 6.30 (s, 1H), 6.68 (s, 2H), 7.36 (s, 2H), the signal of BH was not observed; ^{13}C NMR (C_6D_6, 75 MHz) δ 0.9 (q), 1.0 (q), 1.1 (q), 1.3 (q), 1.5 (q), 1.7 (q), 21.1 (q), 26.0 (d), 30.0 (q), 30.6 (d), 31.0 (q), 31.8 (q), 35.4 (s), 35.8 (s), 120.9 (s), 121.7 (d), 122.5 (d), 126.4 (d), 128.7 (s), 128.9 (d), 129.1 (s), 134.7 (s), 142.9 (s), 143.2 (s), 149.0 (s), 152.0 (s), 152.1 (s), 153.2 (s); ^{11}B NMR ($CDCl_3$, 96 MHz) δ –37.0; IR (KBr) 2348 [ν(BH)], 2199 [ν(CN)], 2110 [ν(SiH)] cm^{-1}; FABMS *m/z* 983 [M^+].
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