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Unprecedented insertion reaction of a silylene into a B–B bond and generation of a novel borylsilyl anion by boron–metal exchange reaction of the resultant diborylsilane†

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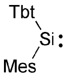
Received (in Cambridge, UK) 24th June 2004, Accepted 20th July 2004
First published as an Advance Article on the web 20th August 2004

A kinetically stabilized diarylsilylene, Tbt(Mes)Si: (1, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl), thermally generated from overcrowded disilene Tbt(Mes)Si=Si(Mes)Tbt (2) or stable silylene–isocyanide complex (3a), was found to insert into a B–B bond of bis(pinacolato)diboron, $B_2(pin)_2$ (4), and the boron–lithium exchange reaction of the resulting diborylsilane gave the first borylsilyl anion.

In recent years, silylboranes have attracted much attention from the standpoints of both fundamental and applied chemistry.[1] However, their chemistry has not been fully disclosed yet mainly due to the limited synthetic methods for them. Although silylboranes are most commonly prepared by the reactions of silyllithium with halo-, hydro- or alkoxyboranes,[2] only a few examples are known to date due to the high reactivity of silylboranes and the difficulty of the preparation of precursors.

On the other hand, we have recently reported the synthesis of stable silylborane derivatives utilizing a kinetically stabilized silylene **1**.[3] Reactions of silylene **1**, thermally generated from overcrowded disilene **2**[4] or stable silylene–isocyanide complexes **3**,[5] with hydroboranes or haloboranes proceeded smoothly to afford the corresponding (hydrosilyl)boranes or (halosilyl)boranes, respectively. The reaction mechanism was reasonably interpreted in terms of the insertion of **1** into the B–H or B–halogen bonds rather than the electrophilic attack of the boron reagents. In this paper, we present that the insertion of a silylene is feasible toward the B–B bond as well as giving the corresponding diborylsilane. In addition, the boron–metal exchange reaction of the resulting diborylsilane was examined to generate an unprecedented borylsilyl anion.



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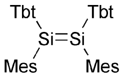

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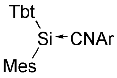
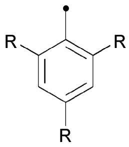
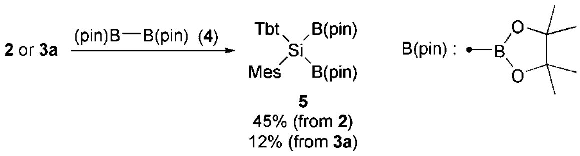


3a : Ar = Mes*
3b : Ar = Tbt
3c : Ar = Tip



Tbt : R = $CH(SiMe_3)_2$
Mes : R = Me
Mes* : R = *t*-Bu
Tip : R = *i*-Pr

When a THF or benzene suspension of disilene **2** and bis(pinacolato)diboron **4**[6] was heated at 60 °C, the original orange color faded very slowly giving a colorless solution in 5 days. Separation of the crude products by silica gel column chromatography afforded the corresponding B–B insertion compound, Tbt(Mes)Si[B(pin)]$_2$ (**5**), in 45% yield (Scheme 1). Since the reactions of **2** with pinacolborane or *B*-chloropinacolborane yielded the corresponding (hydrosilyl)- or (chlorosilyl)pinacolboranes in high yields within a much shorter reaction time (*ca.* 17 h),[3b] the B–B bond of **4** is less reactive toward silylene **1** than the B–H and B–Cl bonds. On the other hand, the reaction of silylene–isocyanide complex **3a** with **4** did not proceed at all even after heating at 60 °C for 5 days. The reaction of **3a** with **4** at 80 °C for 3 days gave the insertion product **5** in only 12% yield (Scheme 1). Since we have reported that **1** is more easily generated from **3a** than from **2**,[4,5] one may feel strange about this lower reactivity to **4** of **3a** compared with **2**. These results can be explained as follows. In this slow reaction, the insertion of **1** into the B–B bond of **4** is considered to be the rate-determining step The lower concentration of **1** in the equilibrium state in the case of **3a** than in that of **2** results in the lower yield of **5** from **3a**.

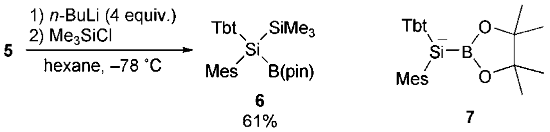


Scheme 1 Synthesis of diborylsilane **5**.

Although some examples have been reported for the insertion of a silylenoid into a B–B bond,[7,8] there have been no reports on the reaction of a silylene with diboron compounds so far. Thus, the formation of **5** by the reaction of **2** (or **3a**) with **4** should be of great interest as the first example of the insertion of a silylene into a B–B bond. Moreover, there have been only a few reports on the compounds containing a B–Si–B skeleton,[7,9] while silyl-bridged boranes and silaboranes, *i.e.*, cage compounds containing 3-center B–Si–B interactions, have been well-known.[10]

The ^{29}Si NMR spectrum of **5** showed a broad signal at −67.6 ppm. This value is similar to those of the related hydrosilanes, Tbt(Mes)SiHB(pin) (−62.7 ppm)[3b] and Tbt(Mes)-SiH$_2$ (−61.3 ppm).[4b] The molecular structure of **5** was unambiguously determined by X-ray crystallographic analysis, and the ORTEP drawing of **5** is shown in Fig. 1.‡ The Si–B bond lengths (2.038(3) Å for Si1–B1 and 2.054(3) Å for Si1–B2) are comparable to those of previously reported silylborane derivatives.[2f,3,9c,11] Interestingly, one of the two dioxaborolane rings in **5** is slightly distorted, while the other is almost planar. The ring puckering coordinates defined by Cremer and Pople[12] were $q_2 = 0.04$ Å and $\varphi_2 = 115.80°$ for the O1–B1–O2–C2–C1 ring and $q_2 = 0.31$ Å and $\varphi_2 = 128.00°$ for the O3–B2–O4–C8–C7 ring. The φ_2 value of the latter is close to the value (126°) appropriate to one of the twist forms with twist axis through B2. Similarly distorted BO_2C_2 rings have been reported for $R_2C[B(pin)]_2$ compounds, though both of the two rings are distorted.[8b]

Although boron-stabilized carbanions have been actively investigated,[13] their silicon analogues, *i.e.*, borylsilyl anions, have been completely unprecedented species. Since boron–metal exchange



Scheme 2 Reaction of **5** with *n*-BuLi.

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† Electronic supplementary information (ESI) available: spectral data for **5** and **6**. See http://www.rsc.org/suppdata/cc/b4/b409575h/

DOI: 10.1039/b409575h

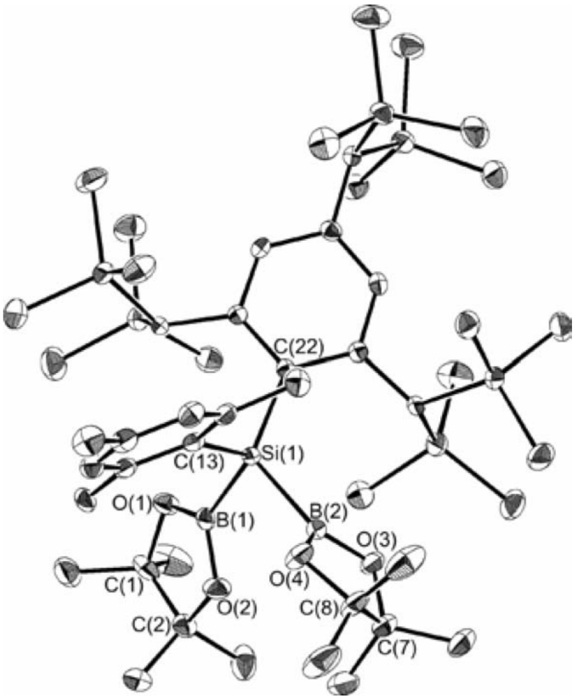

Fig. 1 ORTEP drawing of **5** (50% probability).

reactions of silylboranes have been reported by Tamao *et al.*,^{1c} diborylsilane **5** might be a good precursor for a borylsilyl anion. When diborylsilane **5** was treated with 4 molar equivalents of *n*-BuLi in hexane at −78 °C, the reaction mixture turned deep red. Addition of chlorotrimethylsilane to this solution gave the trimethylsilylated silylborane, Tbt(Mes)Si(SiMe$_3$)B(pin) **6**, in 61% yield, the structure of which was confirmed spectrographically and crystallographically.‡ The formation of TMS-substituted silylborane **6** is most likely interpreted in terms of the reaction of borylsilyl anion **7**, which is generated by a boron–lithium exchange reaction of **5**,^{1c} with chlorotrimethylsilane. It should be noted that the formation of **7** by the boron–lithium exchange reaction of **5** is the first example for the generation of a borylsilyl anion.

In summary, we have found a novel reactivity of an overcrowded diarylsilylene **1**, generated from disilene **2** or silylene–isocyanide complex **3a**, with bis(pinacolato)diboron leading to the first example of the insertion reaction of a silylene into a B–B bond. Furthermore, the reaction of diborylsilane **5** thus obtained with *n*-BuLi resulted in the generation of borylsilyl anion **7**, which was trapped by chlorotrimethylsilane to give the trimethylsilyl-substituted silylborane **6**. Further studies on the structure, stability, and reactivities of the borylsilyl anion **7**, especially on the application toward the synthesis of functionalized silylboranes, are currently in progress.

This work was partially supported by Grants-in-Aid for COE Research on Elements Science (No. 12CE2005), Scientific Research on Priority Area (No. 14078213), and the 21st Century COE Program on Kyoto University Alliance for Chemistry from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Central Glass Co., Ltd. for the generous gift of tetrafluorosilane.

Notes and references

‡ Crystallographic data for **5**: $C_{48}H_{94}B_2O_4Si_7$, MW = 953.48, triclinic, space group *P*–1 (no. 2), a = 12.189(4) Å, b = 13.204(5) Å, c = 19.744(7) Å, α = 79.858(14)°, β = 72.051(13)°, γ = 78.938(16)°, V = 2943.3(17) Å^3, Z = 2, D_{calc} = 1.076 g cm^{-1}, $R_1(I > 2\sigma(I))$ = 0.0523, wR_2(all data) = 0.1221, T = 103(2) K, GOF = 1.075. Crystallographic data for **6**: $C_{45}H_{91}BO_2Si_8$, MW = 899.71, triclinic, space group *P*–1 (no. 2), a = 13.100(7) Å, b = 20.193(10) Å, c = 24.014(11) Å, α = 65.154(12)°, β = 78.169(12)°, γ = 88.869(18)°, V = 5626(5) Å^3, Z = 4, D_{calc} = 1.062 g cm^{-1}, $R_1(I > 2\sigma(I))$ = 0.0605, wR_2(all data) = 0.1481, T = 103(2) K, GOF = 1.079. The structures were solved by a direct method (SIR-97)[14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[15] CCDC 243326 and 243327. See http://www.rsc.org/suppdata/cc/b4/b409575h/ for crystallographic data in .cif or other electronic format.

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