Organometallics **2004,** *23,* 4723−4734 4723

Insertion of an Overcrowded Silylene into Hydro- and Haloboranes: A Novel Synthesis of Silylborane Derivatives and Their Properties

Takashi Kajiwara, Nobuhiro Takeda, Takahiro Sasamori, and Norihiro Tokitoh*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received June 16, 2004

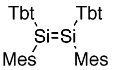
Reactions of stable silylene-isocyanide complexes Tbt(Mes)SiCNAr (**3a**, Ar = Mes*; **3b**, Ar = Tbt; **3c**, Ar = Tip; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl, Mes* = 2,4,6-tri-*tert*-butylphenyl, Tip = 2,4,6-triisopropylphenyl) with boron compounds were investigated. Reactions of **3a**,**b** with BH_3·THF afforded the first stable silylborane-isocyanide complexes, Tbt(Mes)SiHBH_2·CNAr (**4a**,**b**). Silylene complex **3a** reacted with BH_3·PPh_3 as well to give the corresponding silylborane-phosphine complex Tbt(Mes)SiHBH_2·PPh_3 (**12**). In addition, silylene **2** thermally generated from the corresponding disilene, Tbt(Mes)Si═Si(Mes)Tbt (**1**), gave **12** when reacted with BH_3·PPh_3. These results strongly suggested that the reactions of **3** with BH_3·THF and BH_3·PPh_3 proceeded via insertion of a silylene, Tbt-(Mes)Si: (**2**), into the B−H bond rather than the nucleophilic attack of the silicon atom of **3** toward the boron atom. Thermal dissociation of **4** and **12** into a base-free silylborane, Tbt(Mes)SiHBH_2 (**9**), was evidenced by the base-exchange reactions. Furthermore, silylene **2** was found to insert into boron−halogen bonds as well as boron−hydrogen bonds. The novel reactivity of silylene **2** was applied to the syntheses of a variety of silylborane derivatives such as base-free silylboranes, silylborane-isocyanide complexes, and silylborates.

Introduction

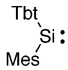
In recent years, silylboranes and their derivatives have attracted much attention from the standpoints of both fundamental and applied chemistry. Transition metal-catalyzed additions of silylboranes to unsaturated organic molecules (silaboration reactions) have been actively investigated.[1] Generation of silyl anions[2] and silyl radicals[3] from silylboranes has also been reported, showing their potential in the syntheses of organosilicon compounds. Furthermore, (triarylsilyl)dimesitylboranes have been reported to exhibit absorption in the visible region due to their Si−B moiety.[4] Despite these interesting properties and the relatively long history of silylboranes, their chemistry has not been fully disclosed yet mainly due to the limited synthetic methods for them.

Silylboranes are most commonly prepared by the reaction of silyllithium with halo-, hydro-, or alkoxyboranes.[5] However, due to the high reactivity of silylboranes and the difficulty in the preparation of precursors, only a few examples are known to date. In this context, development of a novel synthetic method of silylboranes has long been desired.

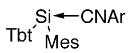
On the other hand, we have reported the synthesis of an extremely hindered disilene **1** and found the thermal dissociation of **1** into the corresponding silylene **2**,[6,7] which can be applied to the syntheses of various organosilicon compounds.[6a,8] Furthermore, we have reported the synthesis and reactions of the first stable silylene-isocyanide complexes, **3a**−**c**,[8c,9,10] which are also important as the first stable Lewis base complexes of a silylene.[11]



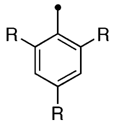
1



2



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



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

Although silylene complexes with Lewis bases have been extensively studied,[11] there has been much less

---

* Corresponding author. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

(1) For recent reviews, see: (a) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221−3256. (b) Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *680*, 43−50.

(2) Kawachi, A.; Minamimoto, T.; Tamao, K. *Chem. Lett.* **2001**, 1216−1217.

(3) Matsumoto, A.; Ito, Y. *J. Org. Chem.* **2000**, *65*, 5707−5711.

(4) Pillot, J.-P.; Birot, M.; Bonnefon, E.; Dunoguès, J.; Rayez, J.-C.; Rayez, M.-T.; Liotard, D.; Desvergne, J.-P. *Chem. Commun.* **1997**, 1535−1536.

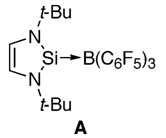
(5) For example, see: (a) Nöth, H.; Höllerer, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 551−552. (b) Nöth, H.; Höllerer, G. *Chem. Ber.* **1966**, *99*, 2197−2205. (c) Biffar, W.; Nöth, H.; Pommerening, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 56−57. (d) Biffar, W.; Nöth, H.; Schwerthöffer, R. *Liebigs Ann. Chem.* **1981**, 2067−2080. (e) Buynak, J. D.; Geng, B. *Organometallics* **1995**, *14*, 3112−3115. (f) Bonnefon, E.; Birot, M.; Dunoguès, J.; Pillot, J.-P.; Courseille, C.; Taulelle, F. *Main Group Metal Chem.* **1996**, *19*, 761−767. (g) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647−4649.

(6) (a) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428−10429. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016−1022.

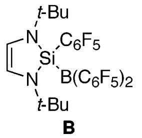
(7) For a review on silylenes, see: Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York; 1998; Vol. 2; Part 3; pp 2463−2568.

10.1021/om049558w CCC: $27.50

focus on the reactions of silylenes with Lewis acids.[12−16] Theoretical calculations by Bharatam et al. have revealed that nucleophilicity of a silylene can be shown only after its electrophilicity gets satisfied, though a silylene itself usually shows electrophilicity.[14] Indeed, a recently reported silylene-borane adduct **A**, which is slowly converted into silylborane **B**, has been obtained from the corresponding silylene having a delocalized 6 π-electron system, where the π-electrons are delocalized on the vacant p orbitals of the silicon atom.[15−17]



A



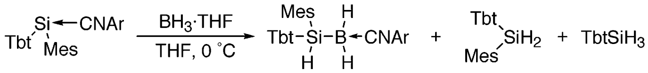
B

During the course of our studies on the properties of silylene-isocyanide complexes **3a**−**c**,[8c,9,10] we have found that they show not only reactivity as a silylene equivalent but also high reactivity toward electrophilic reagents.[9b] This finding has prompted us to investigate the reactions of silylene-isocyanide complexes **3** with boron compounds, and we have succeeded in the synthesis of the first stable silylborane-isocyanide complexes by the reaction of **3a**,**b** with BH_3·THF.[18] Here, we describe the reactions of **3** (or disilene **1**) with various kinds of hydro- and haloboranes giving base-free silylboranes or silylborane−Lewis base complexes, depending on the substituents at the boron atom. The formation mechanism of the silylboranes is discussed in detail, and the thermal reaction of resulting silylborane-isocyanide complexes is also described.

Results and Discussion

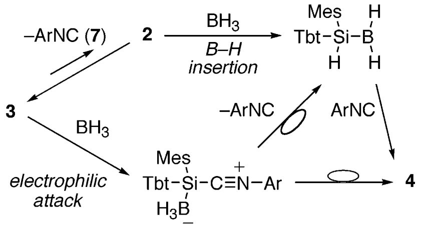
Reaction of 3 with BH_3·THF. Reaction of silylene-isocyanide complexes **3a** and **3b** with BH_3·THF afforded the corresponding silylborane-isocyanide complexes **4a** and **4b** as air-stable compounds in 33 and 35% yields, respectively, together with hydrosilanes **5** and **6** (Scheme 1). By contrast, no silylborane complex **4c** was obtained in the reaction of **3c**, although the formation of **5** and **6** was confirmed (Scheme 1). In these reactions, the yields of the products were affected by the amount of BH_3·THF used. Thus, the reaction of **3a** with an excess amount (5.5 molar equiv) of BH_3·THF gave hydrosilane **5** as a main product (59%) along with **4a** (4%) and **6** (15%) (Scheme 1).

Scheme 1. Reaction of 3 with BH_3·THF



		5	**6**
3a	**4a** : Ar = Mes* (33%)	22%	8%
3b	**4b** : Ar = Tbt (35%)	16%	3%
3c	**4c** : Ar = Tip (not obtained)	39%	8%
3a (with excess BH_3)	**4a** : Ar = Mes* (4%)	59%	15%

Scheme 2. Possible Mechanisms for the Formation of 4



The formation of **4a**,**b** can be explained by two possible mechanisms. One involves the initial dissociation of silylene-isocyanide complexes **3** into the corresponding silylene **2** and isocyanides **7**. Silylene **2** thus generated inserts into the B−H bond of BH_3. The coordination of the isocyanide to the boron atom of the resultant base-free silylborane leads to the final product **4** (Scheme 2). The other involves the initial electrophilic attack of BH_3 at the lone pair of the silicon atom of **3** to afford the Lewis acid−silylene−Lewis base adduct,[14] followed by the consecutive migration giving **4** (Scheme 2). At this stage, we can rule out neither mechanism, and the studies on the reaction mechanism will be discussed later.

Very recently, silylborane-isocyanide complexes have been postulated as reactive intermediates in the insertion reactions of isocyanides into the silicon−boron bond of silylboranes, giving the corresponding (boryl)(silyl)iminomethanes,[19] although no spectral evidence for the intermediates has been observed. Compounds **4a**,**b** are the first examples of isolation of silylborane-isocyanide complexes, and therefore, it is very attractive to investigate their structure and properties.

Spectral Properties of Silylborane-Isocyanide Complexes 4. The ^{29}Si NMR spectra of **4a**,**b** showed very broad and weak signals at −43.3 ppm for **4a** and −39.9 ppm for **4b**, respectively. This severe broadening of the signals is attributed to the fast quadrupole-induced relaxation of the boron atom and the scalar coupling with ^{10}B and ^{11}B, strongly suggesting the existence of B−Si bonds. Although the resonances for the protons assignable to the BH_2 group for **4a**,**b** and the signal of the isocyanide carbon for **4b** were not observed in the ^1H and ^{13}C NMR spectra probably due

---

(8) (a) Suzuki, H.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11572−11573. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471−2481. (c) Tokitoh, N.; Suzuki, H.; Takeda, N.; Kajiwara, T.; Sasamori, T.; Okazaki, R. *Silicon Chem.* **2002**, *1*, 313−319.

(9) (a) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1997**, *119*, 1456−1457. (b) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem. Eur. J.* **2003**, *9*, 3530−3543.

(10) (a) Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **2000**, 244−245. (b) Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **2000**, 622−623.

(11) For a review on silylene−Lewis base complexes, see: Belzner, J.; Ihmels, H. *Adv. Organomet. Chem.* **1999**, *43*, 1−42.

(12) (a) Timms, P. L.; Ehlert, T. C.; Margrave, J. L.; Brinckman, F. E.; Farrar, T. C.; Coyle, T. D. *J. Am. Chem. Soc.* **1965**, *87*, 3819−3823. (b) Kirk, R. W.; Smith, D. L.; Airey, W.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1392−1396.

(13) Bock, C. W.; Trachtman, M.; Mains, G. J. *J. Phys. Chem.* **1988**, *92*, 294−299, and references therein.

(14) (a) Prasad, B. V.; Kaur, D.; Uppal, P. *Indian J. Chem. A* **1997**, *36*, 1013−1017. (b) Bharatam, P. V.; Moudgil, R.; Kaur, D. *Organometallics* **2002**, *21*, 3683−3690. (c) Bharatam, P. V.; Moudgil, R.; Kaur, D. *Inorg. Chem.* **2003**, *42*, 4743−4749.

(15) Metzler, N.; Denk, M. *Chem. Commun.* **1996**, 2657−2658.

(16) Reactions of decamethylsilicocene Cp^*_2Si with boron halides leading to Si−B systems via intermediary silylene-borane adducts have been reported. Holtmann, U.; Jutzi, P.; Kühler, T.; Neumann, B.; Stammler, H.-G. *Organometallics* **1999**, *18*, 5531−5538.

(17) Borane adducts of intramolecularly base-stabilized germylene and stannylene have also been reported. Drost, C.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1998**, *17*, 3838−3840.

(18) Takeda, N.; Kajiwara, T.; Tokitoh, N. *Chem. Lett.* **2001**, 1076−1077.

(19) Suginome, M.; Fukuda, T.; Nakamura, H.; Ito, Y. *Organometallics* **2000**, *19*, 719−721.

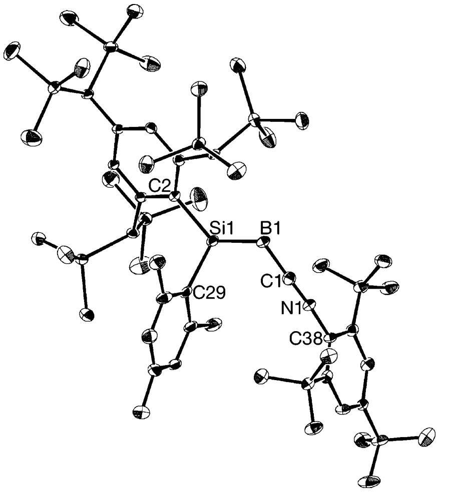


Figure 1. ORTEP drawing of **4a** with thermal ellipsoid plots (50% probability).

to the same reason (a broad signal assigned to the isocyanide carbon was observed at 151.2 ppm in the ^{13}C NMR of **4a**), the absorptions assignable to the B−H (2400 and 2369 cm^{-1} for **4a** and 2400 and 2365 cm^{-1} for **4b**) and C≡N (2213 cm^{-1} for **4a** and 2207 cm^{-1} for **4b**) stretchings were observed along with the Si−H stretchings (2139 cm^{-1} for **4a** and 2126 cm^{-1} for **4b**) in the IR spectra. The ^{11}B NMR spectra showed signals in the region of tetracoordinated borons (−42.6 ppm for **4a** and −43.0 ppm for **4b**) to support the existence of BH_2 moieties.

X-ray Structural Analysis of Silylborane-Isocyanide Complex 4a. Single crystals of **4a** suitable for X-ray crystallographic analysis were obtained by recrystallization from benzene. The ORTEP drawing of **4a** (Figure 1) shows the tetrahedral geometry of the silicon atom and the almost linear B1−C1−N1−C38 structure. The Si1−B1−C1 angle (105.9(3)°) suggests that the boron atom has a tetrahedral geometry. The Si1−B1 bond length (2.052(4) Å) of **4a** is slightly longer than those of the previously reported silylborane-phosphine complex $Me_3SiBH_2{\cdot}P(C_6H_{12})_3$ (2.007(4) Å)[20,21] and lithium silylborates $(RPh_2SiBH_3)Li$ (R = Ph, *t*-Bu) (1.984−1.993 Å)[22] and is close to those of tri- and tetrasilylborates $[(Me_3Si)_3BR]Li$ (R = Me, $SiMe_3$) (2.017−2.034 Å),[21] silylborohydride complexes of tantalum (2.02−2.030 Å),[23] and dimesityl(triphenylsilyl)borane (2.106(4) Å).[5f] The B1−C1 bond length (1.538(6) Å) of **4a** is shorter than that of *o*-$Me_3SiO{-}C_6H_4NC{\cdot}BPh_3$ (1.616(2) Å)[24] and almost equal to those of polyhedral heteroborane-isocyanide adducts (1.537−1.560 Å).[25] The C−N bond length of **4a** (1.154(4) Å)[26] is almost the same as those of the rhodium complex [RhCl(Mes*NC)$_3$] (1.142−1.175 Å),[27] the platinum complex [$Pt_2(\mu\text{-}S)$(Mes*NC)$_4$] (1.14−1.20 Å),[28] and the Tbt-substituted free isocyanide **7b** (1.156(7) Å).[9b]

Theoretical Calculations for Silylborane-Isocyanide Complex. Spectral data and structural parameters for **4a**,**b** thus obtained were compared with theoretical values[29] for $Ph_2SiHBH_2{\cdot}CNPh$, the model compound of **4a**,**b** with phenyl groups. The structure optimized at the B3LYP/6-31G(d) level was similar to that analyzed by X-ray crystallography except for the bond angles around the silicon atom (Figure 2). The observed C2−Si1−B1 bond angle (121.81(16)°) is slightly larger than the calculated ones (110.6° and 112.0°), while the C29−Si1−B1 bond angle (104.43(16)°) is smaller. These differences are probably due to the steric congestion caused by the extremely bulky Tbt group. Vibrational frequencies of B−H, C≡N, and Si−H, calculated at the B3LYP/6-31G(d) level and scaled by 0.9613,[30] were in good agreement with those experimentally observed (Table 1). Calculations of NMR chemical shifts at the GIAO-B3LYP/6-311+G(2d,p) level also gave values similar to the experimental ones, except the ^{29}Si NMR chemical shifts (Table 1). This difference is probably caused by the above-mentioned structural difference around the silicon atom, since calculations for a bulkier model compound, Mes(Ph)$SiHBH_2{\cdot}CNPh$, gave the geometry around the silicon atom (118.1° for C_{Mes}−Si−B and 110.7° for C_{Ph}−Si−B) similar to that analyzed and the ^{29}Si NMR chemical shift (−20.49 ppm) was also comparable to the observed one (Figure 2 and Table 1).[31]

---

[20] Blumenthal, A.; Bissinger, P.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, *462*, 107−110.

[21] Imamoto et al. have also reported the same compound, although structural analysis has not been reported. Imamoto, T.; Hikosaka, T. *J. Org. Chem.* **1994**, *59*, 6753−6759.

[22] Lippert, W.; Nöth, H.; Ponikwar, W.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 817−823.

[23] Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 177−183.

[24] Tamm, M.; Lügger, T.; Hahn, F. E. *Organometallics* **1996**, *15*, 1251−1256.

[25] Štíbr, B.; Holub, J.; Jelínek, T.; Fontaine, X. L. R.; Fusek, J.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1741−1751.

[26] Some of the structural parameters for **4a** reported in the preliminary communication[18] have been revised in this paper by reanalyzing with the newer version of the crystal structure analysis package.[43] The results for crystallographic analysis for **4a** described in this paper are identical with those submitted to the CCDC.

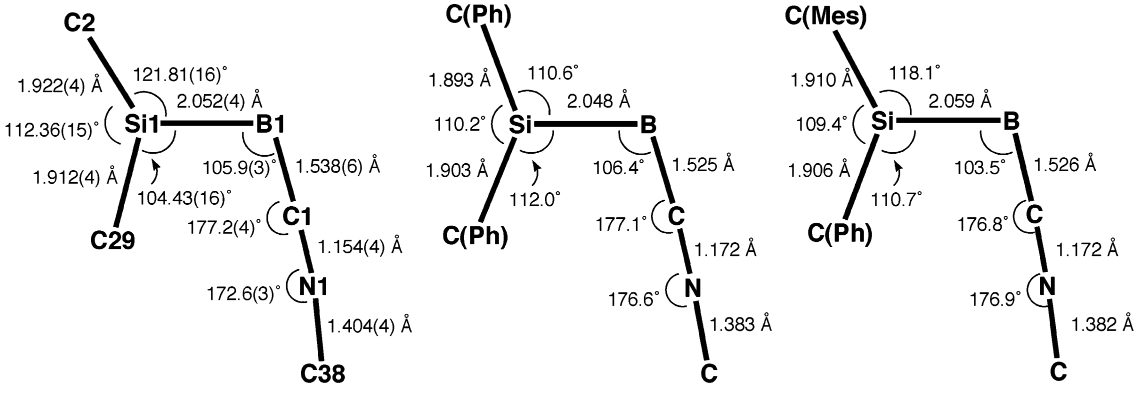
[27] Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681−1687.

[28] Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1986**, 677−680.

[29] All calculations were carried out using Gaussian 98W or Gaussian 03W programs. (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003.

[30] For the scaling factor of 0.9613, see: Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391−399.

[31] The ^{29}Si NMR chemical shift (−23.19 ppm) calculated for $Ph_2SiHBH_2{\cdot}CNPh$, the structure of which was fixed to the geometry determined by X-ray analysis, was comparable to the observed value.



4a $Ph_2SiHBH_2{\cdot}CNPh$ $Mes(Ph)SiHBH_2{\cdot}CNPh$

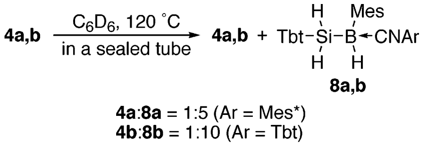
Figure 2. Structural parameters of **4a** (observed)[26] and $Ph_2SiHBH_2{\cdot}CNPh$ and $Mes(Ph)SiHBH_2{\cdot}CNPh$ (calculated).

Table 1. Spectral Data for 4a,b (observed) and $Ph_2SiHBH_2{\cdot}CNPh$ and $Mes(Ph)SiHBH_2{\cdot}CNPh$ (calculated)

	4a	4b	$Ph_2SiHBH_2{\cdot}CNPh$	$Mes(Ph)SiHBH_2{\cdot}CNPh$
δ_H(Si−*H*)	5.21	5.14	5.53[a]	5.60[a]
δ_B(Si−*B*)	−42.6	−43.0	−52.54[a]	−49.33[a]
δ_{Si}(*Si*−B)	−43.3	−39.9	−6.42[a]	−20.49[a]
δ_C(N−*C*)	151.2	not observed	160.74[a]	160.75[a]
ν(B−H)	2400, 2369	2400, 2365	2445, 2393[b]	2452, 2406[b]
ν(C≡N)	2213	2207	2201[b]	2198[b]
ν(Si−H)	2139	2126	2092[b]	2094[b]

[a] Calculated at the GIAO-B3LYP/6-311+G(2d,p) level. [b] Calculated at the B3LYP/6-31G(d) level and scaled by 0.9613.

Scheme 3. Thermolysis of 4



Thermolysis of Silylborane-Isocyanide Complexes 4. When complex **4a** was heated at 120 °C in C_6D_6, a 1:5 mixture of **4a** and the corresponding mesityl-migrated product **8a** was obtained (Scheme 3). In contrast to the case of previously reported intermediary silylborane-isocyanide complexes,[19] (boryl)(silyl)iminomethane (silyl-migrated product) was not formed in this reaction. Thermolysis of **4b** at 120 °C in C_6D_6 also gave a mixture of **4b** and **8b** with the ratio of 1:10 (Scheme 3).

The structures of **8a**,**b** were determined by ^1H, ^{13}C, and ^{11}B NMR spectra, difference NOE experiments, and IR spectra. The BH proton was not observed in the ^1H NMR spectra, as in the case of **4**, but ^{11}B NMR spectra showed signals in the region of tetracoordinated borons (−37.0 ppm for **8a** and −36.5 ppm for **8b**), suggesting the existence of a BH part. In the IR spectra were observed the absorptions assignable to the B−H stretchings (2348 cm^{-1} for **8a** and 2362 cm^{-1} for **8b**) as well as the C≡N (2199 cm^{-1} for **8a** and 2197 cm^{-1} for **8b**) and Si−H (2110 cm^{-1} for **8a** and 2084 cm^{-1} for **8b**) stretchings. The difference NOE experiments on **8a** showed the NOEs of the SiH protons only with the *o*-methine protons of the Tbt group, while both peaks for the *o*-methine protons of the Tbt group and the *o*-methyl protons of the mesityl group were enhanced by the irradiation of the SiH proton in the case of **4a** (Figure 3). These observations indicate the absence of not the Tbt group but the mesityl group on the silicon atom in **8a**. Observed spectral data were in good agreement with those calculated for $PhSiH_2BH(Ph){\cdot}CNPh$ (Table 2).[29]

Interestingly, thermolysis of the isolated **8a** at 120 °C resulted in the regeneration of the original silylborane-isocyanide complex **4a** to give a 1:5 mixture of **4a** and **8a** (Scheme 4). This product ratio was the same as that observed in the case of thermolysis of **4a**. This result strongly suggests the existence of an equilibrium between **4a** and **8a**.

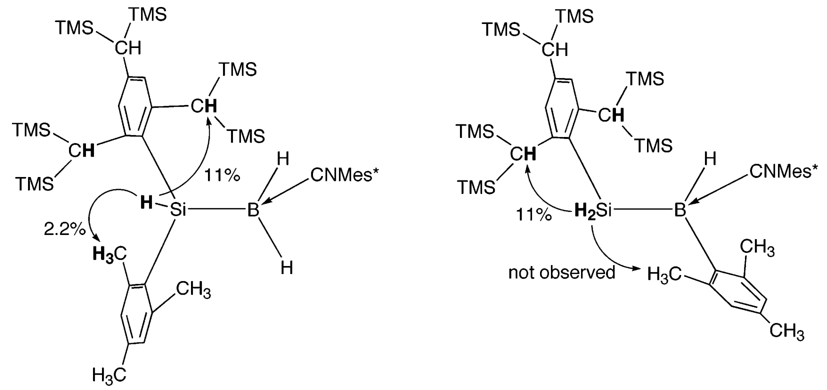
Mechanism of the Migration Reaction of 4 and 8. Thermal reaction of silylborane-isocyanide complex **4a** in the presence of isocyanide **7b** proceeded at 120 °C to give not only the migration product but also the silylborane complexes with the Tbt-substituted isocyanide **7b**. Thus, a mixture of four compounds, i.e., the original complex **4a** (trace), migration product **8a** (minor), base-exchanged product **4b** (trace), and migration and base-exchanged product **8b** (major), was obtained as judged by the ^1H NMR spectra, where **8a** and **8b** were observed with the ratio of 1:4 (Scheme 5).

The mechanism of the isocyanide-exchange reaction is reasonably interpreted in terms of the initial dissociation of silylborane complex **4a** into the corresponding base-free silylborane **9** and isocyanide **7a**, followed by the complexation of **9** with **7b** to give **4b**. Since the migration reaction and the isocyanide-exchange reaction occur at the same temperature, the migration reaction is also suggested to proceed via the initial dissociation into the free silylborane. Although the detailed mechanism of the migration reaction is not clear at present, the bridged structure **11** might be a possible intermediate (Scheme 6). There have been no reports on the doubly bridged silylborane such as **11**, but theoretical[14c] and experimental[32] evidence have been reported for several compounds having an Si−H−B bridge.[33]

---

(32) Wrackmeyer, B.; Milius, W.; Tok, O. L. *Chem. Eur. J.* **2003**, *9*, 4732−4738.

(33) A similar type of double migration ([1,2]^2-dyotropic rearrangement) has been postulated in the reactions of $Cp^*{}_2Si$ with Cp^*BCl_2; see ref 16.



4a **8a**

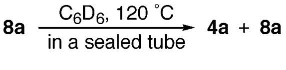
Figure 3. Observed NOEs for **4a** and **8a**.

Table 2. Spectral Data for 8a,b (observed) and $PhSiH_2BH(Ph)\cdot CNPh$ (calculated)

	8a	8b	$PhSiH_2BH(Ph)\cdot CNPh$
$\delta_H(Si-H)$	4.54−4.56	4.38, 4.69	4.91[a]
$\delta_B(Si-B)$	−37.0	−36.5	−37.75[a]
$\nu(B-H)$	2348	2362	2396[b]
$\nu(C\equiv N)$	2199	2197	2192[b]
$\nu(Si-H)$	2110	2084	2122, 2101[b]

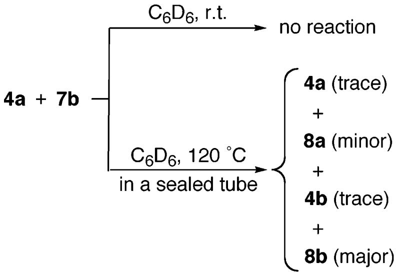
[a] Calculated at the GIAO-B3LYP/6-311+G(2d,p) level. [b] Calculated at the B3LYP/6-31G(d) level and scaled by 0.9613.

Scheme 4. Thermolysis of 8a



4a:**8a** = 1:5 (Ar = Mes*)

Scheme 5. Thermolysis of 4a in the Presence of Isocyanide 7b

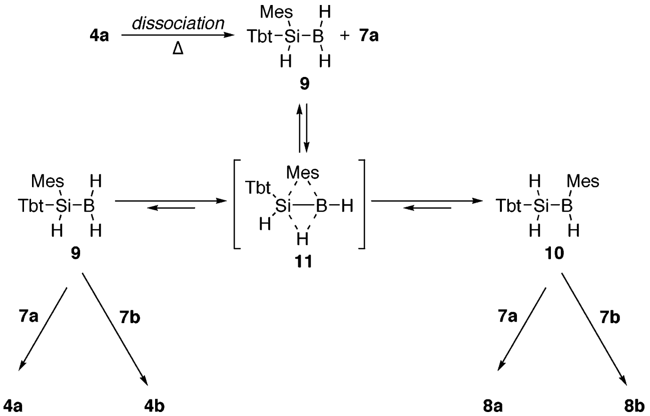


8a:**8b** = 1:4

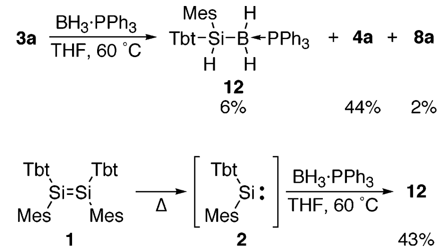
From the ratio of the two major compounds (**8a**:**8b** = 1:4), it is supposed that the less hindered isocyanide **7b** coordinates more strongly to silylborane **10** than the more hindered **7a** does. This trend is the same as that in silylene-isocyanide complexes **3**.[9b]

Reaction of 3 with $BH_3\cdot PPh_3$. To elucidate the mechanism of the reaction of silylene-isocyanide complexes **3** with BH_3, the reaction of **3** with $BH_3\cdot PPh_3$ was examined. When a THF solution of silylene-isocyanide complex **3a** and $BH_3\cdot PPh_3$ was heated at 60 °C in a sealed tube, the deep blue color of **3a** gradually disappeared. After the workup and separation with HPLC, silylborane-phosphine complex **12** was obtained as a stable compound along with the silylborane-isocyanide complexes **4a** and **8a** (Scheme 7). Since the electrophilicity at the boron atom of $BH_3\cdot PPh_3$ is suppressed by the coordination of triphenylphosphine, the formation of silylborane-phosphine complex **12** strongly suggests that this reaction proceeds via the insertion of silylene **2** rather than the electrophilic attack of the boron reagent to the silicon atom of **3**. Indeed, silylborane-phosphine complex **12** was also obtained by the reaction of $BH_3\cdot PPh_3$ with disilene **1**, which gives the corresponding base-free silylene **2** upon heating (Scheme 7).

Scheme 6. Plausible Mechanism for the Reaction of 4a with 7b



Scheme 7. Reaction of 3a or 1 with $BH_3\cdot PPh_3$



Spectral and Structural Properties of Silylborane-Phosphine Complex 12. The structure of **12** was determined by ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR and IR spectra. Although the BH_2 protons were not observed in the ^{1}H NMR spectrum, the evidence for their existence was obtained by ^{11}B NMR (−36.5 ppm) and IR (B−H stretches: 2396 and 2360 cm^{-1}) spectra, as in the case of silylborane-isocyanide complexes **4**. The observation of an absorption assignable to the B−P stretching (1437 cm^{-1}) in the IR spectrum clearly indicates the coordination of the phosphine to the boron atom. The molecular structure of **12** was determined by X-ray crystallographic analysis (Figure 4). The structural parameters for the Si−B−P moiety of **12** were similar to those of a previously reported silylborane-phosphine complex, $Me_3SiBH_2\cdot P(C_6H_{12})_3$ (**C**) (Figure 5).[20]

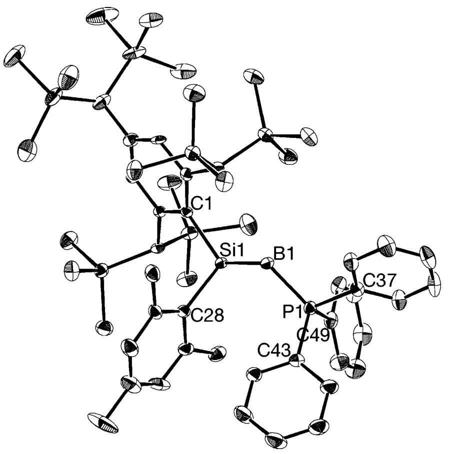


Figure 4. ORTEP drawing of **12** with thermal ellipsoid plots (50% probability).

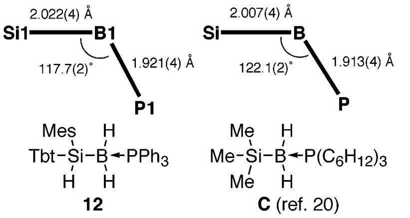
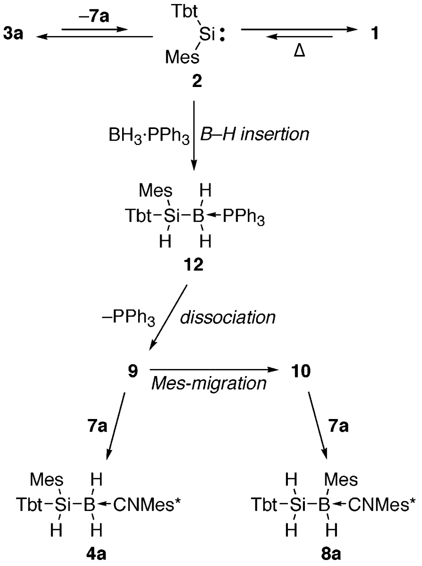


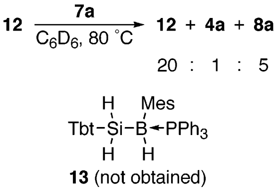
Figure 5. Structural parameters of **12** and $Me_3SiBH_2{\cdot}P(C_6H_{12})_3$.

Scheme 8. Mechanism for the Formation of 12

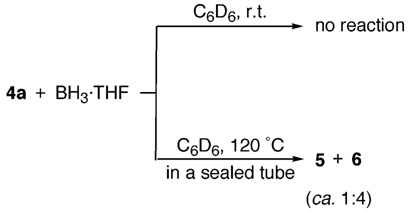


Mechanism of the Reaction of 3a with $BH_3{\cdot}PPh_3$. As described above, the formation of **12** strongly suggests the silylene-insertion mechanism for the reaction of silylene-isocyanide complexes **3** with boranes. In addition, this insertion mechanism is supported by the thermal reaction of disilene **1** with $BH_3{\cdot}PPh_3$ giving the same product **12**. A plausible mechanism for the reaction of **3a** (or **1**) with $BH_3{\cdot}PPh_3$ is shown in Scheme 8: (1) silylene **2** generated from silylene-isocyanide complex **3a** or disilene **1** inserts into the B−H bond of $BH_3{\cdot}PPh_3$, (2) the resulting silylborane-phosphine complex **12** dissociates into the corresponding base-free silylborane **9**, and then (3) the coordination of isocyanide **7a**, generated from **3a**, to **9** affords **4a**, while (4) the migration of the mesityl group in **9** followed by the coordination with isocyanide **7a** gives **8a**.

Scheme 9. Base Exchange Reaction of 12



Scheme 10. Reaction of 4a with $BH_3{\cdot}THF$



According to the mechanism shown in Scheme 8, thermal dissociation of silylborane-phosphine complex **12** may occur at 60 °C (or below), which is much lower than the dissociation temperature of silylborane-isocyanide complexes **4** and **8** (120 °C). To confirm the thermal dissociation of **12**, the base-exchange reaction of the isolated **12** was examined.

When a C_6D_6 solution of compound **12** and Mes*NC (**7a**) was heated at 60 °C for 6 h, no change was observed. The base-exchange reaction started to occur at 80 °C, although the major compound was still **12**. Heating at 80 °C for 4 h gave a mixture of **12**, **4a**, and **8a** with the ratio of 20:1:5 (Scheme 9). This difference in the ratio of products between the reaction of **3a** with $BH_3{\cdot}PPh_3$ and the reaction of **12** with **7a** may be attributed to the difference in the concentration of the reaction mixture or that in the ratio of **12** to **7a**. In both cases, mesityl-migrated silylborane-phosphine complex **13** was not obtained probably due to the severe steric repulsion.

Since silylborane-phosphine complex **C** has not been reported to liberate the base-free silylborane,[34] it is very interesting that dissociation of **12** (and also that of silylborane-isocyanide complexes **4** and **8**) proceeds upon heating. We believe that the introduction of the extremely bulky substituents to the silicon atom (and also to the isocyanides or the phosphine) facilitates the dissociation.

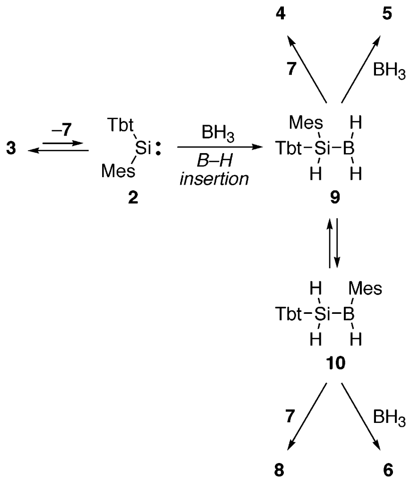
Mechanism of the Reaction of 3 with $BH_3{\cdot}THF$. The formation of silylborane complexes **4** in the reaction of silylene-isocyanide complexes **3** with hydroboranes is reasonably interpreted in terms of the insertion of a base-free silylene **2** into the B−H bond rather than the electrophilic attack of hydroboranes to the silicon atom (vide supra). To elucidate the formation mechanism of the hydrosilane byproducts **5** and **6**, the reaction of **4** with $BH_3{\cdot}THF$ was examined.

Although **4a** did not react with $BH_3{\cdot}THF$ at room temperature, the reaction at 120 °C afforded a mixture including hydrosilanes **5** and **6** (**5**:**6** = 1:4) (Scheme 10). Since **4** dissociates into the base-free silylborane **9** and isocyanides **7** at this temperature, it is strongly sug-

---

[34] See ref 5e, although details of reaction conditions have not been described.

Scheme 11. Mechanism for the Reaction of 3 with BH$_3$·THF

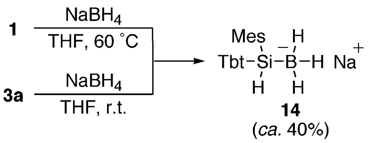


gested that hydrosilanes **5** and **6** might be derived from **9** and **10**, respectively. Thus, the following mechanism (Scheme 11) for the reaction of silylene-isocyanide complexes **3** with BH$_3$·THF is proposed: (1) B−H insertion of silylene **2** generated from **3** leads to the base-free silylborane **9**, (2) the coordination of isocyanide **7** once dissociated from **3** affords a silylborane-isocyanide complex **4**, while the reaction of **9** with an additional BH$_3$ gives dihydrosilane **5**, (3) the migration of a mesityl group of **9** before the reaction with **7** or BH$_3$ resulted in the generation of **10**, and the subsequent reaction of **10** with **7** or BH$_3$ gives silylborane-isocyanide complex **8** or trihydrosilane **6**, respectively. Although **8a** could not be isolated in the reaction of **3a** with BH$_3$·THF, the careful search on the ^{1}H NMR spectrum of the crude mixture resulted in the detection of a small amount of **8a**. It is considered that the migration reaction of silylborane **9** followed by the coordination of **7a** actually took place at 0 °C, but the resulting **8a** slowly decomposed during separation.

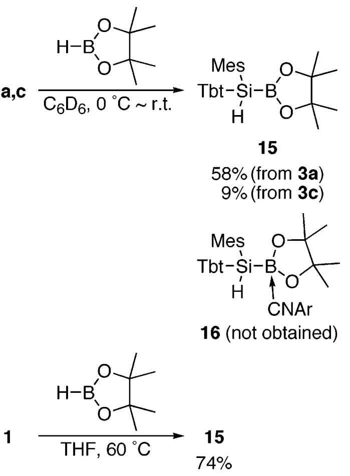
This mechanism is supported by the fact that the reaction of **3** with excess BH$_3$ resulted in the increase of the yield of hydrosilanes **5** and **6** and the decrease of that of **4**. No production of silylborane complex **4c** in the case of **3c** is also explained by this mechanism. In silylene complexes **3**, as reported previously,[9b] coordination of isocyanide **7c** is much stronger than that of **7a** and **7b**. Therefore, the concentration of silylene **2** generated in situ is much lower in this case, and there is an excess amount of BH$_3$ relative to **9** generated by the reaction of **2** with BH$_3$ in the reaction mixture. Reaction of **9** (and **10**) with an additional BH$_3$ preferentially occurred to give hydrosilanes **5** (and **6**), as in the case of the reaction of **3a** with excess BH$_3$·THF.

Reaction of Silylene 2 with NaBH$_4$. Treatment of silylene-isocyanide complex **3a** with NaBH$_4$ led to the gradual disappearance of the deep blue color of **3a**. The ^{1}H NMR spectrum of the reaction mixture showed a signal assignable to the SiH proton at 5.23 ppm, and the ^{11}B NMR spectrum showed a quartet at −38.8 ppm (J = 81 Hz). Similar chemical shifts and coupling constants of the quartets have been reported for lithium silylborates (RPh$_2$SiBH$_3$)Li (R = Ph, −42.6 ppm, 78 Hz; R = *t*-Bu, −43.8 ppm, 78 Hz),[22] strongly suggesting the formation of sodium (silyl)trihydroborate **14**. The thermal reaction of disilene **1** with NaBH$_4$ also afforded **14** via silylene **2** (Scheme 12). In both cases, unfortunately, silylborate **14** could not be isolated due to its decomposition during purification.

Scheme 12. Reaction of 2 with NaBH$_4$



Scheme 13. Reaction of 2 with Pinacolborane



Reaction of Silylene 2 with Pinacolborane. The reaction of silylene-isocyanide complex **3a** with pinacolborane proceeded in a few minutes to give the corresponding silyl(pinacol)borane **15** in 58% yield (Scheme 13). Silylborane-isocyanide complex **16** was not obtained in this case probably due to the decrease of the electrophilicity at the boron atom, which is caused by the delocalization of the lone pairs at the oxygen atoms adjacent to the vacant p orbital of the boron atom. By contrast, the reaction of **3c** with pinacolborane proceeded very slowly, and only 9% of **15** was obtained even after the reaction for several days (Scheme 13). This difference in the reactivity agrees with the previous results that isocyanide **7c** coordinates more strongly to silylene **2** than **7a** does,[9b] and these results also support the silylene-insertion mechanism. Indeed, the reaction of disilene **1** with pinacolborane also gave **15** in 74% yield (Scheme 13).

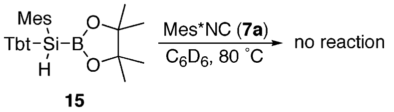
In reactions of silyllithiums with boron compounds, the formation of silylboranes is severely limited by their high propensity to react with an additional silyllithium giving silylborates.[5e,35] It is interesting that we succeeded in the synthesis of silylboranes and silylborates by the reactions of silylene **2** with hydroboranes and hydroborates, respectively.

Although insertion reactions of isocyanides into the Si−B bond of silylboranes have been reported,[19] silylborane **15** did not react with Mes*NC (**7a**) even at 80 °C (Scheme 14). This difference may be explained by the difference in the reaction conditions (solvent and/or concentration) or, probably more significantly, by the

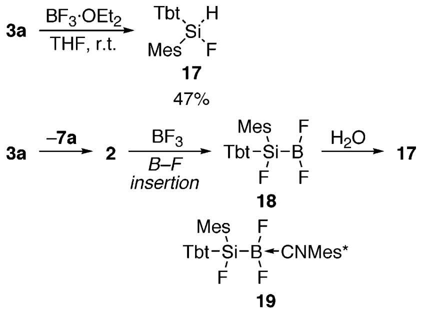
---

(35) For examples of the syntheses of silylborates, see: (a) Seyferth, D.; Raab, G.; Grim, S. O. *J. Org. Chem.* **1961**, *26*, 3034−3035. (b) Biffar, W.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 58−65. (c) Biffar, W.; Nöth, H. *Chem. Ber.* **1982**, *115*, 934−945. (d) Ref 22.

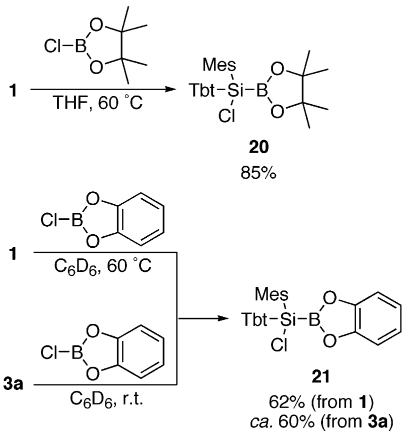
Scheme 14. Reaction of 15 with Isocyanide 7a



Scheme 15. Reaction of 3a with BF_3·OEt_2



Scheme 16. Reaction of 2 with Chloroboranes



steric congestion of the extremely hindered substituents (Tbt, Mes, and Mes* groups).

Reaction of Silylene 2 with Boron Halides. We further investigated the reactions of **1** or **3** with various kinds of boron compounds. Although reactions of **3a** with BPh_3, $B(OMe)_3$, or $B(NMe_2)_3$ did not proceed at all, the reaction of **3a** with BF_3·OEt_2 gave fluorosilane **17** after workup (Scheme 15). The formation of **17** can be explained by the hydrolysis of an intermediary silylborane, **18**, during separation. The ^{1}H NMR spectrum of the reaction mixture showed only signals corresponding to a free isocyanide **7a** in this region, strongly suggesting the formation of not silylborane-isocyanide complex **19** but base-free silylborane **18**. This result indicates that silylene **2** inserts into the B–F bond as well as B–H bonds.

Reaction of disilene **1** with *B*-chloropinacolborane proceeded smoothly to afford the corresponding B–Cl insertion product, (chlorosilyl)pinacolborane **20** (Scheme 16). X-ray crystallographic analysis of **20** showed that the anticipated structure was correct (Figure 6), although the refinement was not sufficient to provide accurate bond lengths and angles because of the poorness of the crystal. Similarly, the reaction of **1** or **3a** with *B*-chlorocatecholborane gave (chlorosilyl)catecholborane **21** (Scheme 16). Although the isolation of **21** failed due to its air-sensitivity in the case of **3a**, the recrystallization from hexane resulted in the successful isolation of pure **21** in the case of **1** (Scheme 16). Since the direct synthesis of silylcatecholboranes from silyllithiums has not been successful and only a multistep synthesis has been reported,[5e,g] our method has the great advantage of preparing a silylcatecholborane directly from a silylene.

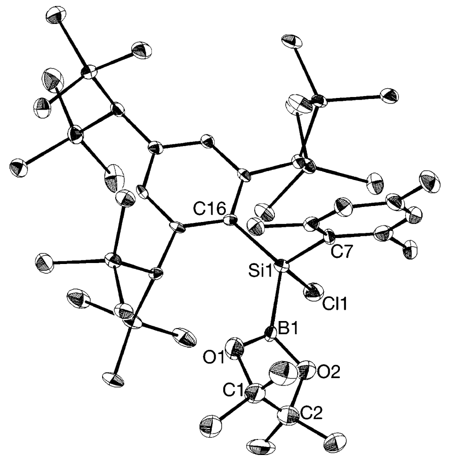


Figure 6. ORTEP drawing of **20** with thermal ellipsoid plots (30% probability).

Conclusions

Reactions of the stable silylene-isocyanide complexes **3** with hydroboranes gave the corresponding (hydrosilyl)boranes or their complexes. The reaction mechanism can be reasonably interpreted in terms of the insertion of a base-free silylene **2** into the B–H bond of hydroboranes. Although silylene **2** was inactive to B–C, B–O, and B–N bonds, **2** was found to undergo insertion into a B–halogen bond to give the corresponding (halosilyl)boranes.

Since silylboranes are generally not very stable and their synthetic method is limited, there have been only a few examples to date. Although hydrogenated or halogenated silylboranes may be versatile precursors for various kinds of functionalized silylboranes, they have been difficult to synthesize by the conventional synthetic methods. By contrast, our synthetic approach was found to give useful and versatile routes to these compounds. Further investigations on the reactivity of the (hydrosilyl)- or (halosilyl)boranes and the derivation to functionalized silylboranes are attractive.

Experimental Section

General Remarks. All experiments were performed under anhydrous conditions with an argon atmosphere unless otherwise noted. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), ^{11}B NMR (96 MHz), ^{29}Si NMR (59 MHz), and ^{31}P NMR (121 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (372 MHz) spectra were recorded on a JEOL JNM AL-400 spectrometer. The ^{1}H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the internal residual $CHCl_3$ (7.25 ppm) or C_6D_5H (7.15 ppm). The ^{13}C NMR chemical shifts were reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the carbon-13 signals of $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm). Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT techniques. The ^{11}B, ^{29}Si, ^{31}P, and ^{19}F NMR chemical shifts were referenced to the external standards BF_3·OEt_2 (0 ppm), tetramethylsilane (0 ppm), 85% phosphoric acid in water (0 ppm), and $CFCl_3$ (0 ppm), respectively. IR spectra were recorded on a JASCO FT/IR-5300 or a JASCO FT/IR-460 Plus spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. GPC-HPLC was performed on an LC-918 or an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns using chloroform or toluene as an eluent. PTLC was performed with Merck Kieselgel 60 PF_{254}.

Materials. All reaction solvents were dried and distilled from CaH_2, stored over 4 Å molecular sieves, and then freshly distilled from Na/benzophenone ketyl under argon prior to use. C_6D_6 used as a reaction solvent was dried over Na and then K mirror. Disilene **1**,[6] isocyanides **7a**,[27] **7b**,[9] and **7c**,[36] silylene-isocyanide complexes **3a**−**c**,[9] and *B*-chloropinacolborane[37] were prepared according to the procedures reported in the literature.

Synthesis of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNMes* (4a). Silylene-isocyanide complex **3a**, prepared from disilene **1** (84.1 mg, 60.1 μmol) and isocyanide **7a** (32.8 mg, 121 μmol) in THF (1.2 mL), was dissolved in THF (1.4 mL) and cooled to 0 °C. A 1.0 M solution of BH_3·THF in THF (120 μL, 120 μmol) was added, and the mixture was stirred at 0 °C for 1 h, during which time the deep blue solution turned pale yellow. After further stirring for 11 h at room temperature, the solvent was removed. The crude products were dissolved in hexane, and insoluble materials were removed by filtration through Celite. After removal of the solvent, the residue was separated with HPLC (LC-918, $CHCl_3$) to afford silylborane-isocyanide complex **4a** (38.6 mg, 39.2 μmol, 33%) together with Tbt(Mes)SiH$_2$ (**5**)[6b] (18.9 mg, 26.9 μmol, 22%) and TbtSiH$_3$ (**6**)[6b] (5.6 mg, 9.6 μmol, 8%). **4a**: colorless crystals. Mp: 173−174 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): 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 = 7.0 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 (75 MHz, $CDCl_3$): 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 ($CDCl_3$): δ −42.6. ^{29}Si NMR ($CDCl_3$): δ −43.3, 1.5, 1.8, 2.0, 2.3. IR (KBr): 2400 [ν(B−H)], 2369 [ν(B−H)], 2213 [ν(C≡N)], 2139 [ν(Si−H)] cm^{-1}. LRMS (FAB): *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.

Synthesis of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNTbt (4b). Silylene-isocyanide complex **3b**, prepared from disilene **1** (84.0 mg, 60.0 μmol) and isocyanide **7b** (69.2 mg, 120 μmol) in THF (1.4 mL), was dissolved in THF (1.4 mL) and cooled to 0 °C. To this solution was added a 1.0 M solution of BH_3·THF in THF (120 μL, 120 μmol), and the mixture was stirred at 0 °C for 1 h, during which time the greenish blue solution turned pale yellow. After further stirring for 16 h at room temperature, the solvent was removed. The crude products were dissolved in hexane, and insoluble materials were removed by filtration through Celite. After the removal of the solvent, the residue was separated with HPLC (LC-918, $CHCl_3$) and further purified with PTLC (SiO_2/hexane) to afford silylborane-isocyanide complex **4b** (54.7 mg, 42.3 μmol, 35%) together with Tbt(Mes)SiH$_2$ (**5**) (13.6 mg, 19.4 μmol, 16%) and TbtSiH$_3$ (**6**) (1.8 mg, 3.1 μmol, 3%). **4b**: colorless crystals. Mp: 153−155 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.14 (s, 9H), −0.08 (s, 9H), −0.01 (s, 36H), 0.02 (s, 36H), 0.03 (s, 18H), 1.25 (s, 1H), 1.37 (s, 1H), 1.63 (s, 2H), 2.13 (s, 3H), 2.38 (s, 6H), 2.46 (s, 1H), 2.59 (s, 1H), 5.14 (d, 1H, J = 6.9 Hz), 6.18 (s, 1H), 6.33 (s, 1+1H), 6.44 (s, 1H), 6.63 (s, 2H), the signals of BH_2 were not observed. ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.2 (q), 0.5 (q), 0.7 (q), 0.8 (q), 0.9 (q), 1.0 (q), 1.3 (q), 1.6 (q), 21.0 (q), 25.1 (d × 2), 25.6 (q), 26.9 (d), 27.1 (d), 30.0 (d), 31.4 (d), 119.8 (s), 121.5 (d), 122.3 (d), 126.1 (d), 127.4 (d), 128.7 (d), 129.6 (s), 136.6 (s), 137.1 (s), 142.1 (s), 142.2 (s × 2), 143.1 (s), 145.7 (s), 151.7 (s), 151.8 (s), the signal of NC was not observed. ^{11}B NMR ($CDCl_3$): δ −43.0. ^{29}Si NMR ($CDCl_3$): δ −39.9, 1.4, 1.9, 2.1, 2.3. IR (KBr): 2400 [ν(B−H)], 2365 [ν(B−H)], 2207 [ν(C≡N)], 2126 [ν(Si−H)] cm^{-1}. LRMS (FAB): *m/z* 1289 [(M − H)$^+$], 1275 [(M − Me)$^+$], 1217 [(M − TMS)$^+$], 1172 [(M − Mes + H)$^+$]. Anal. Calcd for $C_{64}H_{132}BNSi_{13}$: C, 59.51; H, 10.30; N, 1.08. Found: C, 59.54; H, 10.49; N, 1.08.

Reaction of Silylene-Isocyanide Complex 3c with BH$_3$·THF. Silylene-isocyanide complex **3c**, prepared from disilene **1** (74.5 mg, 53.2 μmol) and isocyanide **7c** (24.7 mg, 108 μmol) in THF (1.2 mL), was dissolved in THF (1.3 mL) and cooled to 0 °C. A 1.0 M solution of BH_3·THF in THF (90 μL, 90 μmol) was added, and the mixture was stirred for 15 h, during which time it was warmed to room temperature. The resulting yellow solution was evaporated, and hexane was added to the residue. After the filtration through Celite, the solvent was removed and the mixture was separated with HPLC (LC-918, $CHCl_3$) and PTLC (SiO_2/hexane). Tbt(Mes)SiH$_2$ (**5**) was obtained as the main product (29.0 mg, 41.3 μmol, 39%) together with TbtSiH$_3$ (**6**) (5.1 mg, 8.7 μmol, 8%).

Reaction of Silylene-Isocyanide Complex 3a with Excess BH$_3$·THF. Silylene-isocyanide complex **3a**, prepared from disilene **1** (25.2 mg, 18.0 μmol) and isocyanide **7a** (10.0 mg, 36.8 μmol) in THF (0.5 mL), was dissolved in THF (0.8 mL) and cooled to 0 °C. A 1.0 M solution of BH_3·THF in THF (200 μL, 200 μmol, 5.5 equiv) was added, and the deep blue color immediately disappeared. The mixture was warmed to room temperature, and the solvent was removed. The crude products were dissolved in hexane, and insoluble materials were removed by filtration through Celite. After removal of the solvent, the residue was separated with HPLC (LC-918, $CHCl_3$) and further purified with PTLC (SiO_2/hexane) to afford Tbt(Mes)SiH$_2$ (**5**) as the main product (14.9 mg, 21.2 μmol, 59%) together with TbtSiH$_3$ (**6**) (3.1 mg, 5.3 μmol, 15%) and silylborane-isocyanide complex **4a** (1.5 mg, 1.5 μmol, 4%).

Thermolysis of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNMes* (4a). In a 5 mm i.d. NMR tube was placed a solution of silylborane-isocyanide complex **4a** (10.3 mg, 10.5 μmol) in C_6D_6 (0.6 mL). After five freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 120 °C in the dark for 6 h and then cooled to room temperature. The ^{1}H NMR spectrum of this solution showed the formation of a migration product, TbtSiH$_2$BH(Mes)·CNMes* (**8a**). A mixture of **4a** and **8a** was obtained with the ratio of 1:5, and any other products were not observed. Further heating at 120 °C for 12 h did not change this ratio. The tube was opened, and the mixture was separated carefully with PTLC (SiO_2/hexane). The product slowly decomposed on silica gel during separation. Isolated yield: **4a**, 14% (1.5 mg, 1.5 μmol); **8a**, 69% (7.1 mg, 7.2 μmol). **8a**: colorless crystals. Mp: 94−96 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): 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 (75 MHz, C_6D_6): 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 × 2), 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), the signal of NC was not observed. ^{11}B NMR ($CDCl_3$): δ −37.0. IR (KBr): 2348 [ν(B−H)], 2199 [ν(C≡N)],

---

(36) Obrecht, R.; Herrmann, R.; Ugi, I. *Synthesis* **1985**, 400−402.
(37) Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *156*, 149−157.

2110 [ν(Si−H)] cm^{-1}. LRMS (FAB): *m/z* 983 [M$^+$], 968 [(M − Me)$^+$], 864 [(M − Mes)$^+$], 581 [(TbtSiH$_2$)$^+$]. HRMS (FAB): *m/z* 983.6493, calcd for $C_{55}H_{102}BNSi_7$, 983.6490. Anal. Calcd for $C_{55}H_{102}BNSi_7$: C, 67.08; H, 10.44; N, 1.42. Found: C, 66.45; H, 10.47; N, 1.42.

Thermolysis of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNTbt (4b). In a 5 mm i.d. NMR tube was placed a solution of silylborane-isocyanide complex **4b** (15.2 mg, 11.8 μmol) in C_6D_6 (0.6 mL). After five freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 120 °C in the dark for 9 h and then cooled to room temperature. The ^{1}H NMR spectrum of this solution showed the formation of a migration product, TbtSiH$_2$BH(Mes)·CNTbt (**8b**). A mixture of **4b** and **8b** was obtained with the ratio of 1:10, and any other products were not observed. **8b**: colorless crystals. Mp: 122−126 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$): δ −0.19 (s, 18H), −0.06 (s, 18H), 0.00 (s, 18H), 0.03 (s, 18+36H), 1.24 (s, 1H), 1.41 (s, 1H), 1.85 (br s, 2H), 1.98 (br s, 2H), 2.12 (s, 3H), 2.43 (s, 6H), 4.38 (s, 1H), 4.69 (d, 1H, *J* = 5.1 Hz), 6.18 (s, 1H), 6.29 (s, 1H), 6.36 (s, 1H), 6.47 (s, 1H), 6.65 (s, 2H), the signal of BH was not observed. ^{13}C NMR (75 MHz, C_6D_6): δ 0.4 (q), 0.5 (q), 0.6 (q), 0.9 (q), 1.0 (q), 1.37 (q), 1.44 (q), 1.6 (q), 21.0 (q), 25.9 (d × 2), 30.2 (d × 2), 30.4 (q), 30.6 (d), 31.8 (d), 120.1 (s), 121.6 (d), 121.8 (d), 126.3 (d), 128.5 (d), 128.9 (s), 129.1 (d), 129.4 (s), 134.5 (s), 142.4 (s), 143.46 (s), 143.50 (s × 2), 146.8 (s), 152.1 (s), 152.2 (s), the signal of NC was not observed. ^{11}B NMR (CDCl$_3$): δ −36.5. IR (KBr): 2362 [ν(B−H)], 2197 [ν(C≡N)], 2084 [ν(Si−H)] cm^{-1}. LRMS (FAB): *m/z* 1290 [M$^+$], 1275 [(M − Me)$^+$], 1171 [(M − Mes)$^+$]. HRMS (FAB): *m/z* 1289.7439, calcd for $C_{64}H_{132}BNSi_{13}$, 1289.7453. Anal. Calcd for $C_{64}H_{132}BNSi_{13}$: C, 59.51; H, 10.30; N, 1.08. Found: C, 59.38; H, 10.48; N, 1.21.

Thermolysis of Silylborane-Isocyanide Complex TbtSiH$_2$BH(Mes)·CNMes* (8a). In a 5 mm i.d. NMR tube was placed a solution of **8a** (5.3 mg, 5.4 μmol) in C_6D_6 (0.6 mL). After five freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 120 °C in the dark for 10 h and cooled to room temperature. The ^{1}H NMR spectrum of this solution showed the formation of **4a**. A mixture of **4a** and **8a** was obtained with the ratio of 1:5, and any other products were not observed.

Reaction of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNMes* (4a) with TbtNC (7b) at Room Temperature. Silylborane-isocyanide complex **4a** (11.0 mg, 11.2 μmol) and TbtNC (**7b**) (19.1 mg, 33.0 μmol) were dissolved in THF (1.0 mL). The solution was stirred for 107 h at room temperature. After removal of the solvent, the residue was separated by HPLC (LC-918). Starting materials were recovered quantitatively.

Reaction of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNMes* (4a) with TbtNC (7b) at High Temperature. A C_6D_6 solution (0.6 mL) of silylborane-isocyanide complex **4a** (5.4 mg, 5.5 μmol) was added to TbtNC (**7b**) (4.3 mg, 7.4 μmol) placed in a 5 mm i.d. NMR tube at room temperature. After five freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 120 °C in the dark for 6 h and then cooled to room temperature. The ^{1}H NMR spectrum of this solution showed the formation of a mixture of **4a** (trace), **8a** (minor), **4b** (trace), and **8b** (major), where **8a** and **8b** were obtained with the ratio of 1:4. Further heating at 120 °C for 6.5 h did not change this ratio.

Reaction of Silylene-Isocyanide Complex 3a with BH$_3$·PPh$_3$. A THF (0.9 mL) solution of silylene-isocyanide complex **3a**, prepared from disilene **1** (45.4 mg, 32.4 μmol) and Mes*NC (**7a**) (18.4 mg, 67.8 μmol) in C_6D_6 (0.5 mL), was added to BH$_3$·PPh$_3$ (19.5 mg, 70.6 μmol) placed in a 10 mm i.d. Pyrex glass tube at room temperature. After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 8.5 h, during which time the original deep blue color turned pale yellow. The tube was opened, and solvent was removed. Separation by HPLC (LC-918, CHCl$_3$) afforded a mixture of silylborane-isocyanide complexes **4a** and **8a** (29.4 mg, 29.9 μmol, 46%; the ratio of **4a**:**8a** was 20:1 as judged by ^{1}H NMR) together with silylborane-phosphine complex **12** (3.8 mg, 3.9 μmol, 6%). **12**: colorless crystals. Mp: 160−162 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$): δ −0.26 (s, 9H), −0.18 (s, 9H), 0.02 (s, 18H), 0.07 (s, 9H), 0.09 (s, 9H), 1.24 (s, 1H), 1.69 (s, 3H), 2.15 (s, 3H), 2.25 (s, 3H), 2.81 (s, 1H), 3.05 (s, 1H), 5.10 (d, 1H, *J* = 7.1 Hz), 6.16 (s, 1H), 6.26 (s, 1H), 6.32 (s, 1H), 6.54 (s, 1H), 7.21−7.42 (m, 15H), the signals of BH$_2$ were not observed. ^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$): δ 0.5 (*C*H$_3$), 0.8 (*C*H$_3$), 0.9 (*C*H$_3$), 1.4 (*C*H$_3$), 1.8 (*C*H$_3$), 20.9 (*C*H$_3$), 23.6 (*C*H$_3$), 25.3 (*C*H$_3$), 26.3 (*C*H), 26.6 (*C*H), 29.8 (*C*H), 122.6 (*C*H), 127.8 (*C*H), 127.9 (*C*H), 128.3 (d, $^2J_{PC}$ = 9.9 Hz, *C*H), 128.9 (*C*H), 129.8 (d, $^1J_{PC}$ = 58 Hz, *C*), 130.6 (d, $^4J_{PC}$ = 2.5 Hz, *C*H), 130.8 (d, $^3J_{PC}$ = 9.2 Hz, *C*), 133.2 (d, $^3J_{PC}$ = 9.2 Hz, *C*H), 136.2 (*C*), 137.6 (*C*), 141.6 (*C*), 141.9 (*C*), 144.9 (*C*), 151.7 (*C*), 151.9 (*C*). ^{11}B NMR (CDCl$_3$): δ −36.5. ^{31}P NMR (CDCl$_3$): δ 19.5. IR (KBr): 2396 [ν(B−H)], 2360 [ν(B−H)], 2117 [ν(Si−H)], 1437 [ν(B−P)] cm^{-1}. LRMS (FAB): *m/z* 997 [(M + Na)$^+$], 974 [M$^+$], 959 [(M − Me)$^+$], 901 [(M − TMS)$^+$], 855 [(M − Mes)$^+$], 699 [Tbt(Mes)SiH$^+$]. Anal. Calcd for $C_{54}H_{88}BPSi_7$: C, 66.48; H, 9.09. Found: C, 66.12; H, 9.18.

Reaction of Disilene 1 with BH$_3$·PPh$_3$. In a 10 mm i.d. Pyrex glass tube was placed a THF solution (0.9 mL) of a mixture of disilene **1** (46.0 mg, 32.9 μmol) and BH$_3$·PPh$_3$ (21.4 mg, 77.5 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 18 h, during which time the original orange color disappeared. The tube was opened, and the solvent was removed. Separation by HPLC (LC-918, CHCl$_3$) afforded silylborane-phosphine complex **12** (27.7 mg, 28.4 μmol, 43%).

Reaction of Silylborane-Phosphine Complex Tbt(Mes)SiHBH$_2$·PPh$_3$ (12) with Mes*NC (7a). In a 5 mm i.d. NMR tube was placed a C_6D_6 solution (0.5 mL) of silylborane-phosphine complex **12** (7.2 mg, 7.4 μmol) and Mes*NC (**7a**) (2.2 mg, 8.1 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 80 °C for 4 h and cooled to room temperature. The ^{1}H NMR spectrum of this solution showed the formation of a mixture of the original phosphine complex **12** and isocyanide complexes **4a** and **8a** with the ratio of 20:1:5.

Reaction of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNMes* (4a) with BH$_3$·THF at Room Temperature. Silylborane-isocyanide complex **4a** (9.9 mg, 10 μmol) was dissolved in THF (1.0 mL), and the solution was cooled to 0 °C. A 1.0 M solution of BH$_3$·THF in THF (20 μL, 20 μmol) was added, and the mixture was stirred at 0 °C for 1 h. After further stirring for 107 h at room temperature, the solvent was removed. Usual workup resulted in the quantitative recovery of **4a**.

Reaction of Silylborane-Isocyanide Complex Tbt(Mes)SiHBH$_2$·CNMes* (4a) with BH$_3$·THF at High Temperature. In a 5 mm i.d. NMR tube was placed a solution of silylborane-isocyanide complex **4a** (9.8 mg, 10.0 μmol) in C_6D_6 (0.6 mL). A 1.0 M solution of BH$_3$·THF in THF (20 μL, 20 μmol) was added at room temperature. After five freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 120 °C for 3.5 h and then cooled to room temperature. The ^{1}H NMR spectrum of this solution showed the disappearance of the starting material. Hydrosilanes **5** and **6** were observed with the ratio of 1:4 as judged by ^{1}H NMR.

Reaction of Silylene-Isocyanide Complex 3a with NaBH$_4$. A THF (0.8 mL) solution of silylene-isocyanide complex **3a**, prepared from disilene **1** (42.5 mg, 30.4 μmol) and isocyanide **7a** (16.5 mg, 60.8 μmol) in THF (0.8 mL), was added to NaBH$_4$ (3.6 mg, 95 μmol) at room temperature. The mixture was stirred for 10 min at room temperature, during which time the deep blue solution turned yellow. After further stirring overnight at room temperature the solvent was removed. The crude products were dissolved in hexane, and insoluble materials were removed by filtration through Celite. After removal of the solvent, the ^{1}H and ^{11}B NMR spectra were measured for the residue to observe a free isocyanide, **7a**, together with the signal assignable to silylborate [Tbt(Mes)-$SiHBH_3$]Na (**14**). Silylborate **14**, however, could not be isolated due to its decomposition during purification. The yield of **14** was ca. 40% from the ratio of the integrated intensity of the ^{1}H NMR signals. **14**: colorless crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 5.23 (br, s, 1H), other peaks could not be assigned. ^{11}B NMR (C_6D_6): δ -38.8 (q, $^1J_{HB} = 81$ Hz).

Reaction of Disilene 1 with $NaBH_4$. In a 10 mm i.d. Pyrex glass tube was placed a THF solution (0.9 mL) of a mixture of disilene **1** (49.2 mg, 35.2 μmol) and $NaBH_4$ (4.3 mg, 110 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 16 h, during which time the original orange color disappeared. The sealed tube was opened in a glovebox filled with argon, and the solvent was evaporated. The ^{1}H and ^{11}B NMR spectra were measured for the residue to confirm the formation of **14**. Silylborate **14**, however, could not be isolated due to its decomposition during purification.

Reaction of Silylene-Isocyanide Complex 3a with Pinacolborane. In a 5 mm i.d. NMR tube was placed a C_6D_6 solution (0.6 mL) of silylene-isocyanide complex **3a**, prepared from disilene **1** (52.3 mg, 37.4 μmol) and isocyanide **7a** (20.9 mg, 77.0 μmol) in THF (0.8 mL). When pinacolborane (11 μL, 76 μmol) was added to this solution at 0 °C, the original deep blue color faded in a few minutes. After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The ^{1}H NMR spectrum of this solution showed the formation of silylborane **15**. The tube was opened, and the solvent was removed. Separation by HPLC (LC-918, $CHCL_3$) gave silylborane **15** as the main product (36.2 mg, 43.7 μmol, 58%). **15**: colorless crystals. Mp: 162−164 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ -0.19 (s, 9H), -0.15 (s, 9H), 0.03 (s, 18H), 0.08 (s, 18H), 1.03 (s, 6H), 1.11 (s, 6H), 1.28 (s, 1H), 2.18 (s, 3H), 2.36 (br s, 6H), 2.38 (br, 2H), 4.96 (s, 1H, $^1J_{SiH} = 185$ Hz), 6.23 (s, 1H), 6.38 (s, 1H), 6.69 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.4 (q), 0.6 (q), 0.9 (q), 1.2 (q), 1.4 (q), 21.1 (q), 24.0 (q), 24.7 (q), 25.0 (q), 28.1 (d), 28.4 (d), 30.3 (d), 83.8 (s), 122.5 (d), 125.9 (s), 127.5 (d), 128.2 (d), 131.4 (s), 137.7 (s), 143.4 (s), 144.2 (s), 151.4 (s × 2). ^{11}B NMR ($CDCl_3$): δ 35.4. ^{29}Si NMR ($CDCl_3$): δ -62.7, 2.1, 2.3, 2.6. IR (KBr) 2151 [ν(SiH)] cm^{-1}. LRMS (FAB): *m/z* 849 [(M + Na)$^+$], 826 [M$^+$], 742 [(M − C_6H_{12})$^+$], 711 [(M − $C_6H_{12}O_2$ + H)$^+$]. Anal. Calcd for $C_{42}H_{83}BO_2Si_7$: C, 60.96; H, 10.11. Found: C, 60.49; H, 10.37.

Reaction of Silylene-Isocyanide Complex 3c with Pinacolborane. In a 5 mm i.d. NMR tube was placed a C_6D_6 solution (0.5 mL) of silylene-isocyanide complex **3c**, prepared from disilene **1** (37.0 mg, 26.4 μmol) and isocyanide **7c** (11.7 mg, 51.0 μmol) in THF (0.8 mL). To this solution was added pinacolborane (10 μL, 69 μmol) at 0 °C. After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The ^{1}H NMR spectrum of this solution showed that the reaction was very slow. After further standing for two weeks at room temperature, the tube was opened and the solvent was removed. Separation by HPLC (LC-918, $CHCl_3$) afforded silylborane **15** in 9% yield (3.9 mg, 4.7 μmol).

Reaction of Disilene 1 with Pinacolborane. In a 10 mm i.d. Pyrex glass tube was placed a THF solution (2.0 mL) of a mixture of disilene **1** (153 mg, 109 μmol) and pinacolborane (58.9 mg, 460 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 16.5 h, during which time the original orange color disappeared. The tube was opened, and solvent was removed. The crude products were dissolved in hexane, and insoluble materials were removed by filtration through Celite. After removal of the solvent, the mixture was separated by HPLC (LC-918, $CHCl_3$) to give silylborane **15** as a main product (133 mg, 161 μmol, 74%).

Reaction of Silylborane 15 with Mes*NC (7a). In a 5 mm i.d. NMR tube was placed a C_6D_6 solution (0.6 mL) of silylborane **15** (17.5 mg, 21.1 μmol) and Mes*NC **7a** (5.5 mg, 20 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 80 °C for 28 h and then cooled to room temperature. No change was observed in the ^{1}H NMR spectrum.

Reaction of Silylene-Isocyanide Complex 3a with $BF_3 \cdot OEt_2$. To a THF (0.9 mL) solution of silylene-isocyanide complex **3a**, prepared from disilene **1** (60.2 mg, 43.0 μmol) and isocyanide **7a** (23.4 mg, 86.2 μmol) in THF (0.9 mL), was added $BF_3 \cdot OEt_2$ (11 μL, 87 μmol) at room temperature. The mixture was stirred at room temperature for 1 h, during which time the deep blue solution turned pale yellow. After further stirring overnight the solvent was removed. The crude products were dissolved in hexane, and insoluble materials were removed by filtration through Celite. After removal of the solvent, the residue was separated with HPLC (LC-918, $CHCl_3$) and further purified with PTLC (hexane) to afford fluoro(hydro)-silane **17** as a main product (29.3 mg, 40.7 μmol, 47%). **17**: colorless crystals. Mp: 153.5−155.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ -0.08 (s, 9H), -0.05 (s, 9+9H), -0.01 (s, 9H), 0.04 (s, 18H), 1.32 (s, 1H), 2.08 (s, 1H), 2.25 (s, 3+1H), 2.41 (d, 6H, $^5J_{FH} = 1.9$ Hz), 5.99 (d, 1H, $^2J_{FH} = 52.4$ Hz, $^1J_{SiH} = 224$ Hz), 6.25 (s, 1H), 6.39 (s, 1H), 6.80 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 0.7 (CH_3), 0.8 (CH_3), 1.0 (CH_3), 21.1 (CH_3), 23.5 (d, $^4J_{FC} = 2.5$ Hz, CH_3), 27.3 (*C*H), 27.4 (*C*H), 30.8 (*C*H), 122.6 (*C*H), 124.3 (d, $^2J_{FC} = 13.2$ Hz, *C*), 127.4 (*C*H), 129.1 (*C*H), 129.6 (d, $^2J_{FC} = 14.8$ Hz, *C*), 140.4 (*C*), 144.0 (*C*), 145.9 (*C*), 151.9 (*C*), 152.1 (*C*). ^{29}Si NMR ($CDCl_3$): δ -11.4 (d, $^1J_{FSi} =$ 290 Hz), 1.8, 2.2, 2.5, 2.6, 2.7. ^{19}F NMR ($CDCl_3$): δ -163.9 (d, $^2J_{HF} = 52.4$ Hz, $^1J_{SiF} = 290$ Hz). IR (KBr): 2182 [ν(SiH)] cm^{-1}. LRMS (FAB): *m/z* 718 [M$^+$], 703 [(M − Me)$^+$], 645 [(M − TMS)$^+$], 626 [(M − TMS − F)$^+$]. HRMS (FAB): *m/z* 718.3955, calcd for $C_{36}H_{71}FSi_7$: 718.3925. Anal. Calcd for $C_{36}H_{71}FSi_7$: C, 60.09; H, 9.95. Found: C, 59.43; H, 9.86.

Reaction of Disilene 1 with *B*-Chloropinacolborane. In a 10 mm i.d. Pyrex glass tube was placed a THF solution (2.4 mL) of a mixture of disilene **1** (150 mg, 107 μmol) and *B*-chloropinacolborane (35.6 mg, 219 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 17 h, during which time the original orange color disappeared. The tube was opened, and the solvent was removed. Purification by silica gel chromatography (*n*-hexane/$CHCl_3$, 3:2) afforded silylborane **20** as the main product (157 mg, 182 μmol, 85%). **20**: colorless crystals. Mp: 212−215 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ -0.13 (br s, 18H), 0.04 (s, 18H), 0.07 (s, 9H), 0.09 (s, 9H), 1.09 (s, 6H), 1.13 (s, 6H), 1.30 (s, 1H), 2.19 (s, 3H), 2.45 (br, 6+2H), 6.26 (s, 1H), 6.39 (s, 1H), 6.68 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.80 (q), 0.84 (q), 1.0 (q), 1.1 (q), 1.7 (q), 1.9 (q), 20.9 (q), 24.1 (q), 24.7 (q), 25.1 (q), 27.7 (d), 28.0 (d), 30.5 (d), 84.4 (s), 122.9 (d), 127.7 (s), 128.0 (d), 129.6 (d), 130.8 (s), 138.7 (s), 143.7 (s), 144.6 (s), 151.5 (s × 2). ^{11}B NMR ($CDCl_3$): δ 33.1. ^{29}Si NMR ($CDCl_3$): δ -15.0, 1.8, 1.9, 2.7, 2.8, 3.0. LRMS (FAB): *m/z* 861 [(M + H)$^+$]. Anal. Calcd for $C_{42}H_{82}BClO_2Si_7$: C, 58.52; H, 9.59. Found: C, 58.29; H, 9.72.

Reaction of Disilene 1 with *B*-Chlorocatecholborane. In a 5 mm i.d. NMR tube was placed a C_6D_6 solution (0.6 mL) of a mixture of disilene **1** (26.4 mg, 18.9 μmol) and *B*-chlorocatecholborane (6.4 mg, 41 μmol). After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 14 h, during which time the original orange color disappeared. The ^{1}H NMR spectrum of this solution showed the formation of silylborane **21**. The tube was opened in a glovebox filled with argon, and solvent was removed. Recrystallization from *n*-hexane at −40 °C gave pure (chlorosilyl)catecholborane **21** (20.1 mg, 23.5 μmol, 62%). **21**: colorless crystals. Mp: 229−233 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ -0.19 (s, 18H), 0.02 (s, 9H), 0.05 (s, 9+18H), 1.33 (s, 1H), 2.10 (s, 1H), 2.19 (s, 1H), 2.22 (s, 3H), 2.59 (s, 6H), 6.27 (s, 1H), 6.41 (s, 1H), 6.78 (s, 2H), 7.05−7.12 (m, 2H), 7.21−7.28 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.6 (q), 0.8 (q), 1.0

(q), 1.6 (q), 1.8 (q), 20.9 (q), 25.4 (q), 29.3 (d), 29.6 (d), 30.7 (d), 113.0 (d), 122.8 (d), 123.0 (d), 127.0 (s), 127.9 (d), 128.6 (s), 130.3 (d), 139.7 (s), 144.3 (s), 145.5 (s), 148.1 (s), 151.5 (s), 151.8 (s). ^{11}B NMR ($CDCl_3$): δ 34.6. ^{29}Si NMR (C_6D_6): δ 2.1, 2.2, 3.3, 3.5, the signal of BSi was not observed. HRMS (EI): *m*/*z* 852.3820 and 854.3786, calcd for $C_{42}H_{74}B^{35}ClO_2Si_7$ 852.3855 and $C_{42}H_{74}B^{37}ClO_2Si_7$ 854.3826. Anal. Calcd for $C_{42}H_{74}BClO_2Si_7$: C, 59.08; H, 8.73. Found: C, 59.23; H, 9.06.

Reaction of Silylene-Isocyanide Complex 3a with *B*-Chlorocatecholborane. A C_6D_6 (0.5 mL) solution of silylene-isocyanide complex **3a**, prepared from disilene **1** (50.0 mg, 35.7 μmol) and isocyanide **7a** (22.5 mg, 82.9 μmol) in THF (0.8 mL), was added to *B*-chlorocatecholborane (11.5 mg, 74.5 μmol) at room temperature, and the original deep blue color faded in a few minutes. After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The ^{1}H NMR spectrum of this solution showed the formation of (chlorosilyl)catecholborane **21**. Silylborane **21**, however, could not be isolated due to its decomposition during purification. The yield of **21** was ca. 60%, as estimated from the ^{1}H NMR spectrum.

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian 98W or Gaussian 03W programs[29] with density functional theory at the B3LYP level.[38] The structural optimization was performed at the B3LYP/6-31G(d) level. The vibrational frequency was calculated at the B3LYP/6-31G(d) level and scaled by 0.9613.[30] The NMR chemical shifts were calculated at the GIAO-B3LYP/6-311+G(2d,p) level. Reference molecules for the chemical shifts were also calculated at the same level: $Si(CH_3)_4$ for H, C, and Si (0 ppm), B_2H_6 for B (16.6 ppm).[39]

X-ray Crystallographic Analysis. Single crystals of **4a**, **12**, and **20** suitable for X-ray analysis were obtained by recrystallization from benzene at room temperature (for **4a**), from hexane in a refrigerator (for **12**), and from dichloromethane/methanol at room temperature (for **20**), respectively. A colorless crystal was mounted on a glass fiber (for **4a** and **12**) or a loop (for **20**). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The structures were solved by a direct method (SIR-97)[40] and refined by full-matrix least-squares procedures on F^2 for all reflections (CRYSTALS[41] for **4a** and SHELXL-97[42] for **12** and **20**). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the silicon and boron atoms of **4a** were located in difference Fourier syntheses and included in the refinement, but all other hydrogen atoms were placed in calculated positions. Calculations for **4a** were performed using the CrystalStructure[41,43] crystallographic software package. Crystal data for **4a**: formula $C_{55}H_{102}BNSi_7$, formula weight 984.83, colorless, block, crystal dimensions (mm) 0.30 × 0.30 × 0.10, T = 93(2) K, triclinic, $P\bar{1}$ (#2), a = 9.709(5) Å, b = 16.612(7) Å, c = 20.306(10) Å, α = 83.42(1)°, β = 89.18(2)°, γ = 78.73(1)°, V = 3190.8(24) Å^3, Z = 2, D_{calc} = 1.025 g/cm^3, μ = 1.81 cm^{-1}, $2\theta_{max}$ = 55.0°, independent reflections/parameters 14 013/589, $R_1(I > 2\sigma(I))$ = 0.0670, wR_2(all data) = 0.1550, GOF = 1.064, CCDC-183015.[26] Crystal data for **12**: formula $C_{54}H_{88}BPSi_7$, formula weight 975.65, colorless, platelet, crystal dimensions (mm) 0.40 × 0.18 × 0.08, T = 93(2) K, triclinic, $P\bar{1}$ (#2), a = 12.2961(5) Å, b = 12.9373(4) Å, c = 20.9079(2) Å, α = 73.508(13)°, β = 73.145(13)°, γ = 82.555(15)°, V = 3048.12(16) Å^3, Z = 2, D_{calc} = 1.063 g/cm^3, μ = 2.14 cm^{-1}, $2\theta_{max}$ = 50.0°, independent reflections/parameters 10 523/589, $R_1(I>2\sigma(I))$ = 0.0801, wR_2(all data) = 0.1331, GOF = 1.166. Crystal data for **20**: formula $C_{42}H_{82}BClO_2Si_7$, formula weight 861.97, colorless, prism, crystal dimensions (mm) 0.35 × 0.20 × 0.10, T = 103(2) K, triclinic, $P\bar{1}$ (#2), a = 9.199(7) Å, b = 12.808(10) Å, c = 23.663(17) Å, α = 99.905(12)°, β = 92.269(11)°, γ = 108.236(13)°, V = 2595(3) Å^3, Z = 2, D_{calc} = 1.103 g/cm^3, μ = 2.66 cm^{-1}, $2\theta_{max}$ = 50.0°, independent reflections/parameters 8929/503, $R_1(I > 2\sigma(I))$ = 0.1139, wR_2(all data) = 0.2959, GOF = 1.116.

Acknowledgment. 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.

Supporting Information Available: Tables of atomic coordinates, bond distances, angles, and anisotropic displacement parameters for Tbt(Mes)$SiHBH_2$·CNMes* (**4a**), Tbt(Mes)$SiHBH_2$·PPh_3 (**12**), and Tbt(Mes)Si(Cl)B(pin) (**20**); X-ray data in CIF format are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049558W

---

(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(39) Onak, T. P.; Landesman, H.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533−1535.

(40) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(41) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, UK, 1999.

(42) Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(43) *CrystalStructure 2.00*, Crystal Structure Analysis Package; Rigaku and MSC, 2001.