Inorg. Chem. **2003**, *42*, 4743–4749

Inorganic Chemistry

Article

Electron Deficient Bridges Involving Silylenes: A Theoretical Study

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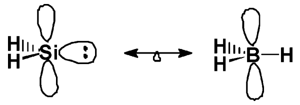
Received September 14, 2002

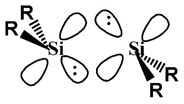
Ab initio and density functional studies show that silylenes can form complexes with BH_3 and the resultant complexes possess 3c–2e bridges. The complexation energy for the formation of the these H-bridged structures is in the range of 18–46 kcal/mol. The characteristics of the electron deficient bridges depend on the substituents attached to the silylenes. With an increase in the π-donating capacity of the substituents, the exothermicity of complex formation gets reduced but the kinetic stability of the H-bridged structures increase. The natural bond orbital analysis shows that all the H-bridged structures are associated with $\sigma_{B-H} \rightarrow p\pi_{Si}$ second-order delocalization, which is responsible for the origin of the 3c–2e bonds. The complexation energies of the silylene–BH_3 complexes have been shown to have a correlation to the singlet–triplet energy gaps of silylenes.

Introduction

Divalent silicon compounds have been shown to be analogous to trivalent boron compounds (Scheme 1), and several structural analogues based on this analogy have been suggested.[1] This analogy can be extended in correlating the Lewis acidity of silylenes and BR_3.[2] In the same vein, it may be expected that silylenes show electron-deficient bridges such as that in diborane. Such electron deficient (3c−2e) interactions have been envisaged in silicon chemistry in the past, mainly on the basis of the structural deviation observed in the disilenes (**A**)[3] and the corresponding bridged isomers (**B**).[4] Electron-deficient H-bridged silicon systems have been reported in $Si(\mu\text{-}H)_2Si$ (**C**) using ab initio MO methods and gas-phase generation.[5] The theoretical studies reported in this paper show that complexes of silylenes with BH_3 (**1**−**9**) form stable electron-deficient H-bridged isomers $R_2Si(\mu\text{-}H)BH_2$.

Scheme 1





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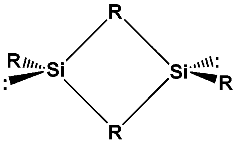

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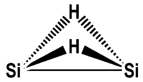

C

The influence of α substituents in R_2Si: on the chemistry of silylenes has been shown to be high; for example, electronegative substituents increase E_{ST} (the singlet−triplet energy difference), and π donor substituents stabilize the

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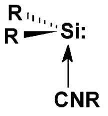
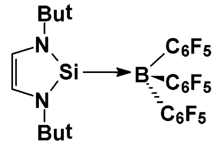
10.1021/ic026033s CCC: $25.00

singlet silylenes.[6] Similarly, the stability of the Lewis base $(LB)\rightarrow SiR_2$ complexes gets reduced with an increase in the π-donating ability of the substituent at the α position (R) on silicon; for example, the MP2(full)/6-31+G* estimated complexation energy (ΔE_c) of $H_3N\rightarrow F_2Si$: (21.4 kcal/mol) is much less than that of $H_3N\rightarrow H_2Si$: (36.7 kcal/mol).[2c] In the H-bridged systems $R_2Si(\mu\text{-}H)BH_2$ (R = H, F, Cl, CH_3, NH_2, OH, etc.) also, the electronic character of the R group exerts a significant influence on the nature of the H-bridge, as presented in this work.

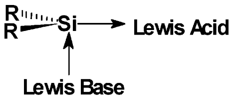
Transient silylenes have been known to be electrophilic and form complexes (**D**) with Lewis bases; the complexes of silylenes with the Lewis bases such as tetrahydrofuran (THF), pyridine, carbon monoxide, and isocyanides, etc., have been reported.[7] Stable silylenes have been shown to be nucleophilic and form complexes (**E**) with Lewis acids.[8]



D



E



F

Belzner et al. reported that transient silylenes cannot show nucleophilic character, but the nucleophilicity of transient silylenes can be triggered by the coordination with Lewis bases (**F**).[2,9,10] The H-bridged systems $R_2Si(\mu\text{-}H)BH_2$ reported in this work are examples of $R_2Si{:}\rightarrow$Lewis acid (LA) complexes, the results confirm that the nucleophilicity of transient silylenes depends on the electron density in the p_π orbital of silylenes, and the complexation energies can be correlated to the E_{ST}'s of the silylenes.

Methods of Calculations

Ab initio[11] and density functional theory (DFT)[12] calculations have been carried out using the GAUSSIAN94W[13] package. Complete optimizations have been performed on the $H_2Si{:}\rightarrow BH_3$ complex (**1**), its borane isomer (**1i**), and the transition state corresponding to a 1,2 hydrogen shift (**1t**) at HF, MP2(full),[14] B3LYP,[15] B3PW91,[16] MP4(SDQ),[17] CCD,[18] CCSD(T),[19] QCISD(T),[20] and CASSCF[4,6][21] methods using the 6-31+G* basis set to understand the nature of the 3c−2e electron-deficient bond. To obtain the accurate values of stabilization energies, calculations have been repeated at CBS-Q,[22] G1,[23] G2,[24] and G3[25] methods also. The choice of basis set does not strongly influence the kinetic stability of H-bridged system **1** or the complexation energies (Table S1 of the Supporting Information). To understand the effect of solvents on the complexation energy and kinetic stability of H-bridged system **1**, a self-consistent reaction field (SCRF)[26] study has been carried out on **1**, **1i**, and **1t** by performing complete optimizations using the Onsager method (dipole keyword in Gaussian 94W), in different solvent conditions. To study the nature of the 3c−2e electron-deficient bond as a function of different substituents on silylenes,

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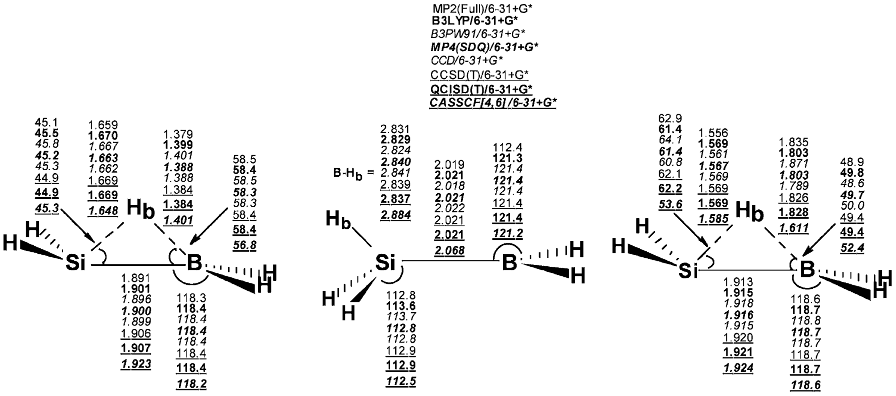

1 **1i** **1t**

Figure 1. Important geometric parameters of the bridge system SiH_2–BH_3 (**1**), isomer SiH_3–BH_2 (**1i**), and transition state SiH_2–BH_3 (**1t**) at different theoretical levels.

complete optimizations have been carried out on complexes of $H(CH_3)Si:$, $(CH_3)_2Si:$, HClSi:, HFSi:, H(OH)Si:, $H(NH_2)Si:$, $Cl_2Si:$, $F_2Si:$, $(OH)_2Si:$, $(H_2N)_2Si:$, $(CH-NH)_2Si:$, $(CH_2-NH)_2Si:$, and cyclic$(-CH_2-)_n$Si: ($n = 2-5$) with BH_3, their borane isomers, and transition states corresponding to a 1,2 hydrogen shift using HF/6-31+G*, MP2(full)/6-31+G*, and B3LYP/6-31+G* levels. To further confirm the existence of these electron-deficient bridges, complete optimizations have also been performed on H-bridged complexes (but not on their isomers) between (HC≡C)HSi:, (HC≡C-)$_2$Si:, (H_2C=CH-)HSi:, and (H_2C=CH-)$_2$Si:, with BH_3 at the same levels. Frequencies were computed analytically for all optimized species at all levels in order to characterize each stationary point as a minimum or a transition state. Natural bond orbital analysis (NBO)[27] has been performed on all H-bridged structures to understand the different electronic interactions with the MP2 densities using MP2(full)/6-31+G* wave function. MP2(full)/6-31+G* geometric parameters and energies will be used in the discussion unless otherwise specifically mentioned.

Results and Discussion

HF/6-31+G* calculations on the complexation of $H_2Si{:}\rightarrow BH_3$ and $(CH_3)_2Si{:}\rightarrow BH_3$ showed that these systems do not exist as LA→LB complexes, indicating that silylenes $H_2Si:$ and $(CH_3)_2Si:$ do not show any nucleophilic character.[2] However, complete optimizations at MP2(full)/6-31+G* and B3LYP/6-31+G* levels indicate that the $H_2Si\rightarrow BH_3$ complex has a H-bridged arrangement **1** (Figure 1). To confirm the result, complete optimizations have been performed on **1** with B3PW91, MP4(SDQ), CCD, CCSD(T), QCISD(T), and CASSCF[4,6] methods using the 6-31+G* basis set; a stable H-bridged structure has been predicted at all these levels. In **1**, the average B–H_b distance is ~1.39 Å, the Si–H_b distance is ~1.66 Å, the B–Si–H_b angle is ~45.3°, and the Si–B–H_b angle is ~58.4°; all indicate a H-bridged complex. Compound **1** is characterized by the zero imaginary frequencies at MP2(full) and B3LYP levels, confirming the local minimum character of **1**. The complex formation is highly exothermic, as indicated by the energy of stabilization (~37–50 kcal/mol, Table 1) due to the formation of **1** from $H_2Si:$ and BH_3. Complex **1** is kinetically unstable with an energy barrier (ΔE_a) for the 1,2 hydrogen shift in the range of only 1–4 kcal/mol; isomer **1i** is about 3–7 kcal/mol more stable than **1**. NBO analysis showed a strong donation of the B–H_b σ electron density to the empty p orbital on silylenes—the second-order energies $E^{(2)}$ associated with $\sigma_{B-H}\rightarrow p\pi_{Si}$ in **1** is 285.9 kcal/mol at the MP2(full)/6-31+G* level. This suggests that H-bridged complex **1** is stabilized by the 3c–2e interactions arising from the $\sigma_{B-H}\rightarrow p\pi_{Si}$ delocalization. Under polar solvent conditions (SCRF studies, B3LYP/6-31+G* optimization) the kinetic stability of the H-bridged complex shows an increase (Table 2). With an increase in the dielectric constant of the medium, ΔE_c and ΔE_a show a gradual increase and ΔE between **1** and **1i** shows a gradual decrease. These energy changes are associated with a gradual increase in the Si–B–H_b angle. The above analysis on **1** indicates that the existence of the H_2Si–BH_3 complex with the 3c–2e H-bridge may be probable.

Table 1. Stabilization Energy of **1** Due to Complexation between H_2Si and BH_3, Si–B–H_b Angles in **1**, ΔE between **1** and **1i**, and Barrier for 1,2 Hydrogen Shift in **1** To Give **1i** at Various Theoretical Levels

level	ΔE_c[a]	Si-B-H_b[b]	ΔE[a]	ΔE_a[a]
MP2(Full)/6-31+G*	46.68	58.5	4.62	3.05
B3LYP/6-31+G*	43.46	58.4	5.24	1.75
B3PW91/6-31+G*	49.36	58.5	3.38	2.47
MP4(SDQ)/6-31+G*	42.68	58.3	5.85	2.34
CCD/6-31+G*	41.05	58.3	6.47	2.21
CCSD(T)6-31+G*	43.64	58.4	4.84	2.66
QCISD(T)/6-31+G*	43.74	58.4	4.77	2.67
CASSCF[4,6]/6-31+G*	37.11	56.8	3.86	3.47
CBS-Q	44.48	58.2[c]	4.17	0.97
G1	43.67	58.4[d]	4.38	0.77
G2	43.63	58.4[d]	4.06	0.93
G3	38.00	58.4[d]	5.68	1.22

[a] Energies in kilocalories per mole. ΔE is the energy difference between the bridged and the silaborane isomers, ΔE_c is the complexation energy, and ΔE_a is the barrier for 1,2 H shift from the bridged structure to the silaborane isomer. (All relative energies are after including ZPE values.) At the CBS-Q, G1, G2, and G3 levels, the ΔE values have been listed. [b] Angles in degrees. [c] MP2/6-31G* value. [d] MP2(Full)/6-31G* value.

Substituent Effect. In an attempt to explore the generality of the silylenes with 3c–2e bridges, theoretical studies have been carried out on complexes **2**–**11** (Table 3, Figure 2) between $H(CH_3)Si:$, $(CH_3)_2Si:$, HClSi:, HFSi:, H(OH)Si:, $H(NH_2)Si:$, $Cl_2Si:$, $F_2Si:$, $(OH)_2Si:$, and $(H_2N)_2Si:$ with BH_3

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Table 2. Solvent Effect on the SiH_2–BH_3 (**1**) at the B3LYP/6-31+G* Level[a]

solvent	ϵ^b	$\Delta E_c{}^c$	Si-B-$H_b{}^d$	$\Delta E^{c,e}$ between the borane and H-bridged isomers	$\Delta E_a{}^c$
gas phase	1.00	43.42	58.4	5.24	1.75
heptane	1.92	43.74	58.7	4.97	1.96
THF	7.58	44.17	59.3	4.55	2.30
dichloromethane	8.93	44.20	59.3	4.52	2.32
dichloroethane	10.36	44.22	59.3	4.49	2.34
ethanol	24.55	44.33	59.4	4.40	2.42
acetonitile	36.64	44.35	59.5	4.37	2.45
DMSO[f]	46.70	44.36	59.5	4.36	2.45
water	78.39	44.38	59.2	4.34	2.47

[a] Self-consistent reaction field method (SCRF) using the Debye approach has been employed to carry out optimization. [b] ϵ = dielectric constant. [c] Energies in kilocalories per mole. ΔE is the energy difference between the bridged and the silaborane isomers, ΔE_c is the complexation energy, and ΔE_a is the barrier for 1,2 H shift from the bridged structure to the silaborane isomer. [d] Angles in degrees. [e] The positive values of ΔE indicate the borane isomer is more stable than the H-bridged isomer, and the barrier is for the energy required for the conversion of the H-bridged isomer to the borane isomer. [f] DMSO = dimethyl sulfoxide.

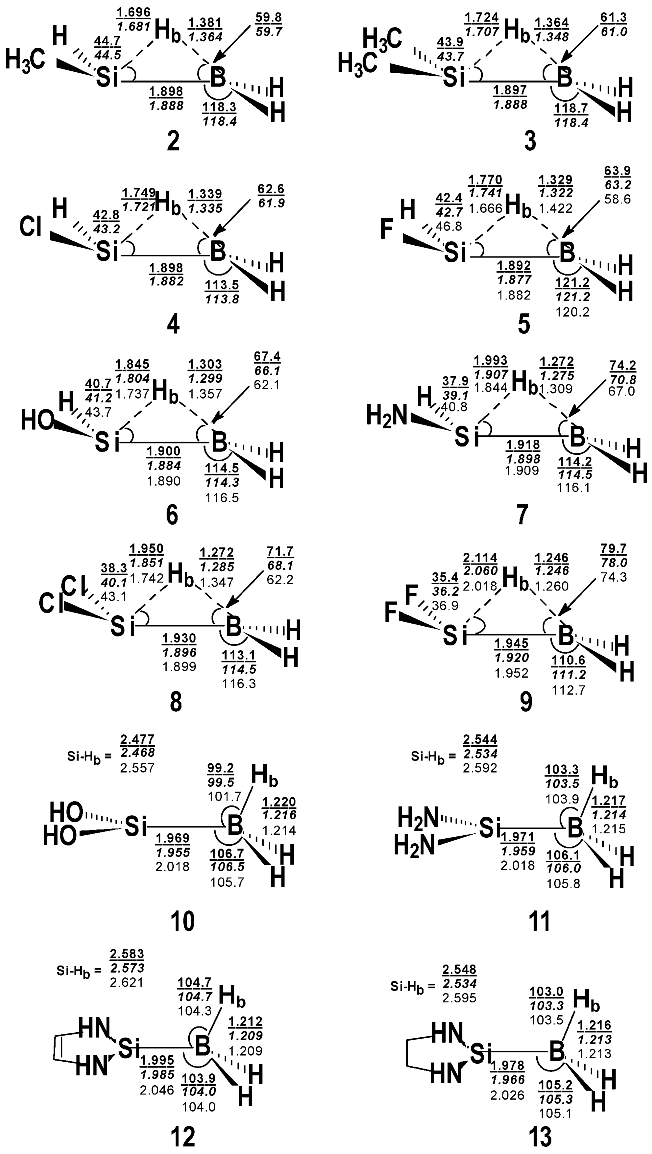

Figure 2. Important geometric parameters of **2**–**13** at three levels, viz., HF/6-31G*, MP2(Full)/6-31+G*, and B3LYP/6-31+G*.

using HF/6-31+G*, MP2(full)/6-31+G*, B3LYP/6-31+G* levels. All systems, except **10** and **11**, show H-bridged structures; the Si–B–H_b angles in these complexes increase in the order **1** (58.5°) < **2** (59.7°) < **3** (61.0°) < **4** (61.9°) < **5** (63.1°) < **6** (66.1°) < **8** (68.0°) < **7** (70.8°) < **9** (78.0°) < **10** (99.5°), **11** (103.5°, MP2 data). The B–H_b bond lengths decrease (1.379 Å in **1** to 1.214 Å in **11**) and the Si–H_b distances increase (1.659 Å in **1** to 2.534 Å in **11**) in these systems almost in the same order (Table 3, Figure 2). Calculations performed on several other systems, i.e., complexes of $(HC{\equiv}C-)HSi{:}$, $(HC{\equiv}C-)_2Si{:}$, $(H_2C{=}CH-)HSi{:}$, $(H_2C{=}CH-)_2Si{:}$, and cyclic$(-CH_{2}-)_nSi{:}$ (n = 2–5) with BH_3, also showed H-bridged hydrogen at B3LYP/6-31+G* and MP2(full)/6-31+G* levels (average Si–B–H_b angle, ~58–64°; B–H_b bond length, ~1.36 Å; Si–H_b bond length, ~1.73 Å at MP2 level; Figure 3, Table 4). All the H-bridged complexes (**1**–**9**) are associated with a $\sigma_{B-H}{\rightarrow}p\pi_{Si}$ second-order electron delocalization, which decreases with an increase in the Si–B–H_b angle (Table 3). The energy $E^{(2)}$ associated with the second-order interaction $\sigma_{B-H}{\rightarrow}p\pi_{Si}$ decreases in the order **1** (285.9) > **2** (259.8) > **3** (231.2) > **4** (224.0) > **5** (185.4) > **8** (144.4) > **6** (136.7) > **7** (106.9) > **9** (60.5) > **10** (11.1) > **11** (8.28 kcal/mol). The gradual changes in the geometric, energetic, and electronic parameters of silylene–BH_3 complexes are in the order of the increasing π-donating ability of the substituents on Si; i.e., with a decrease in the σ_R (resonance component of Hammett's substituent parameter σ; Table 3)[28] values of the substituents on silicon, the Si–B–H_b angle increases, the B–H_b distance decreases, and the $\sigma_{B-H}{\rightarrow}p\pi_{Si}$ electron donation decreases in **1**–**11**. This is also evident from the correlation between the occupancy of the $p\pi$ orbital of silylene with the Si–B–H_b and ΔE_a. For example, the Si–B–H_b angle increases (58, 61, 68, 78, and 103°), ΔE_c increases (3.1, 4.6, 10.3, 16.0, and 21.3 kcal/mol) (Figure 4), and $E^{(2)}$ for the $\sigma_{B-H}{\rightarrow}p\pi_{Si}$ interaction decreases (286, 232, 61, 11, and 8 kcal/ mol) with an increase in the electron occupation (0.00, 0.02, 0.08, 0.13, and 0.20) of the $p\pi$ orbital of $R_2Si{:}$ in the order R = H, Me, F, OH, and NH_2.[29]

The energies of stabilization due to the complexation between $R_2Si{:}$ and BH_3 are in the range of 18–37 kcal/mol, indicating the exothermic character of the $R_2Si{:}{\rightarrow}BH_3$ complexation. The complexation energies (Table 3) in **1**–**9** decrease in the order **2** (46.89) > **1** (46.67) > **3** (46.32) > **4** (36.37) > **5** (36.17) > **6** (36.15) > **7** (33.29) > **8** (24.50) > **9** (18.17 kcal/mol). This decrease is accompanied by an increase in the Si–B–H_b angle (with minor exceptions),

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(28) (a) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. (b) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 199. (c) Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 125. (d) Additivity of σ_R values assumed as defined in: Hansch, C.; Leo, A. *Exploring QSAR, Fundamentals and Applications in Chemistry and Biology*; American Chemical Society: Washington, D. C., 1995; pp 1–24.

(29) $Cl_2Si{:}$ behaves slightly differently compared to the others in the series because of the stronger 3p–3p overlap between Cl and Si, as compared to the 2p–3p overlap in other systems.

Table 3. Important Geometric, Electronic, and Energy Parameters of **1**−**13**[a]

complex	no.	ΔE_c[b]	Si-B-H_b[c]	B-H_b[d]	$E^{(2)}$ for $\sigma_{B-H_b}\rightarrow p\pi_{Si}$[b]	ΔE_a[b]	ΔE[b,e]	singlet-triplet energy[b] gap in silylenes	occupation of the pπ orbital of silylene (e)	σ_R[f]
SiH_2-BH_3	**1**	46.67	58.5	1.379	285.9	3.05	4.63	13.27	0.000	0.00
$SiH(CH_3)$-BH_3	**2**	46.89	59.7	1.364	259.8	3.82	2.90	16.72	0.019	−0.08
$Si(CH_3)_2$-BH_3	**3**	46.32	61.0	1.348	231.2	4.63	1.44	21.30	0.033	−0.16
$SiHCl$-BH_3	**4**	36.37	61.9	1.335	224.0	4.53	4.77	27.83	0.091	−0.21
$SiHF$-BH_3	**5**	36.17	63.2	1.322	185.4	5.35	4.87	32.88	0.053	−0.30
$SiH(OH)$-BH_3	**6**	36.15	66.1	1.299	136.7	8.10	−1.21	33.72	0.091	−0.41
$SiH(NH_2)$-BH_3	**7**	33.29	70.8	1.275	106.9	10.90	−5.19	36.29	*g*	−0.47
$SiCl_2$-BH_3	**8**	24.50	68.0	1.285	144.4	6.96	5.67	47.83	0.173	−0.42
SiF_2-BH_3	**9**	18.17	78.0	1.246	60.5	10.34	4.86	69.08	0.084	−0.60
$Si(OH)_2$-BH_3	**10**	27.47	99.5	1.216	11.1	16.05	−5.54	59.81	0.131	−0.82
$Si(NH_2)_2$-BH_3	**11**	31.61	103.5	1.214	8.3	21.34	−13.30	53.32	0.210	−0.94
$(CH\text{-}NH)_2Si\rightarrow BH_3$	**12**	24.12	104.7	1.209	5.9	32.06	−26.44	65.60	*g*	--
$(CH_2\text{-}NH)_2Si\rightarrow BH_3$	**13**	28.61	103.3	1.213	8.1	24.34	−18.69	72.89	0.212	--

[a] Data obtained using MP2(full)/6-31+G* basis set have been listed in this table. [b] Energies in kilocalories per mole. ΔE is the energy difference between the bridged and the silaborane isomers, ΔE_c is the complexation energy, and ΔE_a is the barrier for 1,2 H shift from the bridged structure to the silaborane isomer. [c] Angles in degrees. [d] Bond lengths in angstroms. [e] Positive values indicate that borane isomer is more stable than H-bridged systems. [f] Resonance component of Hammett's substituent parameters; the values reported are the total $\sigma = \sigma_{R1} + \sigma_{R2}$ in R1R2Si:.[26] [g] The electron occupancy is not clear from the NBO analysis because of complete delocalization of the π orbitals in these systems.

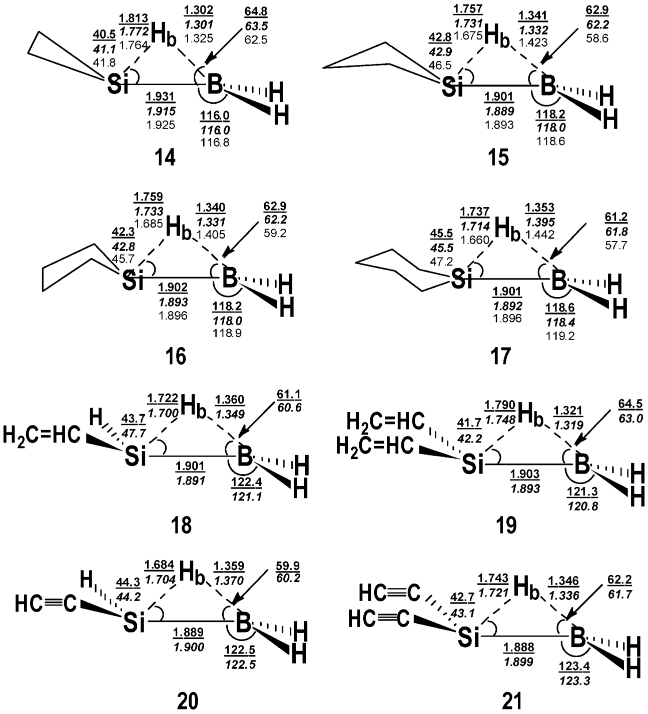

Figure 3. Important geometric parameters of **14**−**21** at three levels, viz., HF/6-31G*, MP2(Full)/6-31+G*, and B3LYP/6-31+G*.

presumably due to the decrease in the stabilization arising from the $\sigma_{B-H}\rightarrow p\pi_{Si}$ delocalization. Table 3 shows that the silylene E_{ST} values have a direct bearing on ΔE_c of the silylene−BH_3 complexes—as the singlet−triplet energy gap increases, in general, the complexation energy gets reduced in **1**−**13**. The Si−B−H_b angle increases and the $E^{(2)}$ due to the $\sigma_{B-H}\rightarrow p\pi_{Si}$ interaction decreases with an increase in the singlet−triplet energy difference in **1**−**9**. This can be rationalized in terms of orbital interactions—with an increase in the energy gap between HOMO and LUMO in silylenes, the energy difference between the electron donating B−H bond and the electron accepting the pπ orbital of silylenes also increase in the silylene−BH_3 complexes, resulting in the decrease in the $\sigma_{B-H}\rightarrow p\pi_{Si}$ second-order perturbation energy $E^{(2)}$.

The energy barriers for the 1,2-H shift in **1**−**9** increase with an increase in the Si−B−H_b angle (Table 3), suggesting that the relative kinetic stability of the H-bridged isomer increases with an increase in the p electron donating capacity of the substituents on silylenes,[29] which also can be correlated to the occupancy of the pπ orbital on silylene. Complexes **1**−**9** have energy comparable to that of their borane isomers (**1i**−**9i**), with a maximum difference of about 6 kcal/mol. In the cases of **6** and **7**, the H-bridged isomer is more stable than the borane isomer; this increases the probability of isolating H-bridged systems.[30] In complexes **10**−**13**, the H-bridged isomers could not be located, complete optimizations lead to structures with a Si−B−H_b angle of about 103−104°, and in these systems the borane isomers are relatively less stable. H-bridged systems **1**−**9** may be considered LB (silylene)→LA (BH_3) complexes, where silylene donates electrons from its lone pair and the electrons from the B−H single bond are back-donated to the empty p orbital of silylenes. With an increase in the electron density of the pπ orbital of silylenes as a function of σ_R of the R in R_2Si:, the back-donation decreases which results in an increase in the Si−B−H_b angle. The decreasing interaction between the B−H bond and pπ (Si) decreases the probability of B−H bond-breaking, and hence the kinetic stability of the H-bridged isomer increases, as reflected in the barrier for the 1,2-H shift in the H-bridged systems **6** and **7**. When there is sufficient electron density in the pπ orbital of silylenes, as in **10**−**13**, no H-bridged complex is found. Experimentally it has been observed that the silylene→BR_3 complex **E** can be obtained though it gets converted to the corresponding silylborane over a period of weeks.[8]

The H-bridged complex observed in **1** appears to be similar to the transition structure (**G**) reported in the insertion reaction of silylenes into the X−H bond (X = H, C, N, O, F, Si, P, S, Cl, etc.).[31] However, the electronic structures of **1** and **G** are completely different on various counts—(i) **1** is

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(30) Both the H-bridged isomer and the borane isomer are minima on the potential energy surface. The ΔE between the H-bridged and non-bridged isomers is much smaller in these complexes as compared to the values reported for $RSi(\mu\text{-}R)_2SiR$, R = (H, F), systems.[4a]

Table 4. Important Geometric, Electronic, and Energetic Parameters of **14-27** at the MP2(Full)/6-31+G* Level

complex	no.	ΔE_c[a]	Si-B-H[b]	singlet-triplet energy[a] gap in silylenes	B-H_b[c]	$E^{(2)}$ for $\sigma_{B-H_b} \rightarrow p\pi_{Si}$[a]
$(CH_2)_2Si \rightarrow BH_3$	**14**	21.09	63.5	26.15	1.301	175.7
$(CH_2)_3Si \rightarrow BH_3$	**15**	34.37	62.2	21.92	1.332	208.5
$(CH_2)_4Si \rightarrow BH_3$	**16**	41.83	62.2	24.94	1.331	208.5
$(CH_2)_5Si \rightarrow BH_3$	**17**	46.28	61.2	18.45	1.395	223.8
$(CH_2{=}CH\text{-})HSi \rightarrow BH_3$	**18**	42.86	60.6	19.87	1.349	239.0
$(CH_2{=}CH\text{-})_2Si \rightarrow BH_3$	**19**	38.78	63.0	34.33	1.319	195.6
$(CH{\equiv}C\text{-})HSi \rightarrow BH_3$	**20**	41.78	60.2	22.57	1.358	259.0
$(CH{\equiv}C\text{-})_2Si \rightarrow BH_3$	**21**	36.23	61.7	32.17	1.336	225.7
$F(CN)Si \rightarrow BH_3$	**22**	27.88	64.3	47.43	1.310	176.9
$FClSi \rightarrow BH_3$	**23**	22.49	71.5	58.31	1.267	104.4
$F(SH)Si \rightarrow BH_3$	**24**	23.96	74.5	49.14	1.258	83.26
$(NMe_2)HSi \rightarrow BH_3$	**25**	33.02	82.7	47.19	1.245	31.9
$Cl(OH)Si \rightarrow BH_3$	**26**	24.69	88.6	55.03	1.230	32.2
$F(OH)Si \rightarrow BH_3$	**27**	22.74	95.1	71.56	1.220	16.4

[a] Energies in kilocalories per mole. ΔE is the energy difference between the bridged and the silaborane isomers, ΔE_c is the complexation energy, and ΔE_a is the barrier for 1,2 H shift from the bridged structure to the silaborane isomer. [b] Angles in degrees. [c] Bond lengths in angstroms.

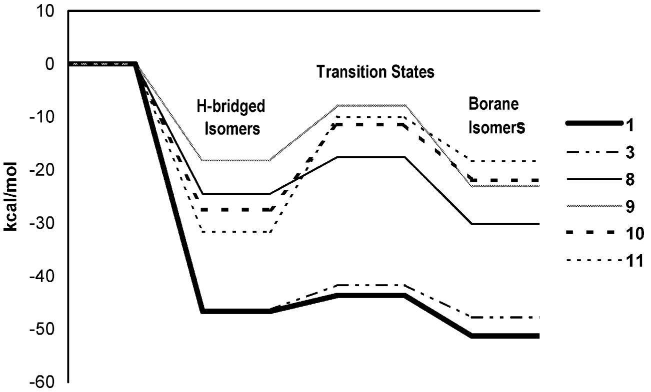
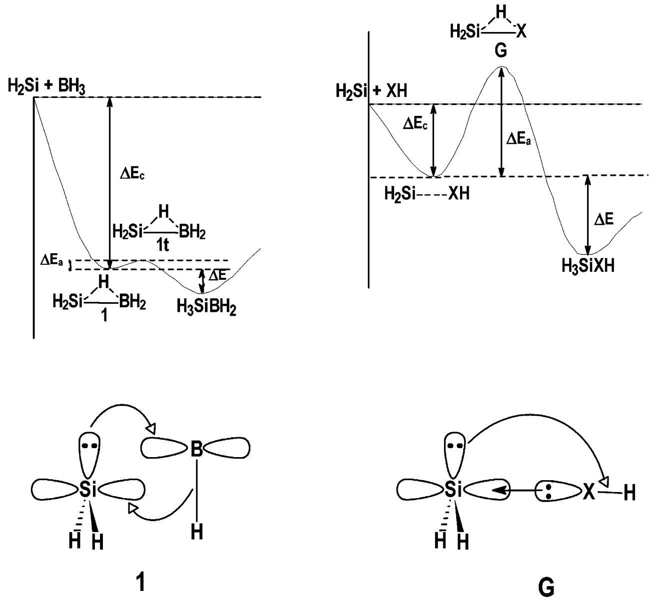


Figure 4. Comparative potential energy surfaces corresponding to the complexation of different substituted silylenes, i.e., SiH_2 (**1**), $Si(CH_3)_2$ (**3**), $SiCl_2$ (**8**), SiF_2 (**9**), $Si(OH)_2$ (**10**), $Si(NH_2)_2$ (**11**), with BH_3. The values obtained at the MP2(full)/6-31+G* level have been employed in this diagram.

a minimum, whereas **G** is a transition state on the respective potential energy (PE) surfaces (Scheme 2). (ii) In **1** the electron donation is from the σ orbital of the B−H bond to the empty pπ orbital of silylenes, whereas, in **G**, the electron donation is from the (sp^2) lone pair of Si to the σ* orbital of the X−H bond. (iii) Transition state **1t** between **1** and **1i** has a separate existence, on the PE surface, from the H-bridged structure. In fact **G** can be compared well with **1t** rather than **1**. Hence, the stable structure **1** and transition state **G** cannot be viewed as similar systems.

Silylene−BH_3 complexes **14**−**21** (Figure 3) also show strong complexation energies. The cyclic silylenes in **14**−**17** show a gradual increase in the ΔE_c, which increases with an increase in the ring size, presumably due to the decrease in the ring strain. Even in these systems, a general correlation (though not a one-to-one correlation) has been observed between the singlet−triplet energy difference and complexation energies; i.e., with a decrease in the singlet−triplet energy difference, there is an increase in the complexation energy. However, in **14**−**17**, the Si−B−H_b angle does not show much variation, supporting the observation that π-donating substituents are required to influence the $\sigma_{B-H} \rightarrow p\pi_{Si}$ back-donation. Similar trends are observed in the structural and energetic features of the complexes of vinyl and alkynyl silylenes with BH_3, **18**−**21**.

Scheme 2. Schematic Representations Depicting the Differences in the Orbital Interactions between the H-Bridged Structure **1** (Local Minimum) and **G** (a Transition-State Structure)



The gradual changes in the geometric and electronic factors observed in the H-bridged systems (Table 3) are important indicators and can be exploited in designing silylene complexes with 3c−2e bridges. To confirm this suggestion, we have carried out additional calculations on the complexes (**22**−**27**) of F(CN)Si:, FClSi:, F(SH)Si:, H(NMe_2)-

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(32) The estimated ΔE_{ST} are systematically lower than the corresponding experimental values by about 5−6 kcal/mol (see ref 6), however, in this work the trends in the values have more significance.

Si:, (OH)ClSi:, and F(OH)Si: with BH_3 whose σ_R values ($-0.21 > -0.51 > -0.55 > -0.58 > -0.62 > -0.72$)[28] show increasing π electron donation to Si in the same order. The Si−B−H_b angles in these systems at the MP2 level are 64.3, 71.5, 74.5, 82.7, 88.6, and 95.1°, respectively (Table 4), increasing with a decrease in the σ_R value, suggesting the predictability of the structural features of the H-bridged systems.

Conclusions

Ab initio and density functional studies on the complexes of silylenes with BH_3 show that they have a tendency to form electron-deficient bridges having 3c−2e bonds. The variation in the geometric, energetic, and electronic parameters clearly indicate that there is a direct correlation between partial electron density in the π orbital of silylenes and the kinetic stability and complexation energy of H-bridged structures—the minimum (threshold) electron density in the pπ orbital of silylene is required for the systems to show stable 3c−2e H-bridged structures. With an increase in the π-donating ability of the substituents, the kinetic stability of the H-bridged structures increase. The absence of electron density in the pπ orbital leads to an easier 1,2 shift as in $H_2Si{:}\rightarrow BH_3$ and excess electron density in the pπ orbital leads to nonbridged silylene-Lewis acid complex formation as in $(NH_2)_2Si{:}\rightarrow BH_3$. NBO analysis clearly shows that all the H-bridged structures are associated with $\sigma_{B-H}\rightarrow p\pi_{Si}$ second-order delocalizations, which support the possible existence of such electron-deficient H-bridged systems. The complexation energies of the silylene−BH_3 complexes decrease with an increase in the singlet−triplet energy gaps of the silylenes.

Acknowledgment. The authors thank the Department of Science and Technology, New Delhi, for financial support. We also thank the reviewers for a thorough reviewing of the paper and useful suggestions.

Supporting Information Available: Tables S1−S4 giving absolute energies of **1**, **1i**, and **1t** and H-bridged structures of many other silylene−BH_3 complexes used in this paper (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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