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Articles

Lewis Donor and Acceptor Interactions of Silylenes: A Theoretical Study

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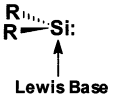
Silylenes are known to show ambiphilic character. Ab initio study on (Lewis base)→H_2Si coordination shows that the strength of the interaction depends mainly on two factors: (1) the nucleophilicity of the base and (2) the extent of π delocalization of the lone pair on silylene onto the π frame of the base. The stabilization energies due to the formation of $H_3N{\rightarrow}SiH_2$, $OC{\rightarrow}SiH_2$, and $HNC{\rightarrow}SiH_2$ complexes at the G2 level are respectively 23.22, 20.84, and 29.59 kcal/mol. The base coordination triggers the nucleophilicity of silylenes, the strength of which is again dependent on the π interaction between the lone pair on Si and the Lewis base. The energy gains due to the formation of the LB→LA complexes $(H_3N)H_2Si{:}{\rightarrow}BH_3$, $(OC)H_2Si{:}{\rightarrow}BH_3$, and $(HNC)H_2Si{:}{\rightarrow}BH_3$ are 42.08, 24.65, and 29.16 kcal/mol, respectively, at the G2 level. The electrophilic nature of base-coordinated silylenes and the nucleophilicity of double-base-coordinated silylenes have been quantitatively estimated. Natural bond orbital (NBO) analysis and charge decomposition analysis (CDA) have been carried out to quantitatively estimate electron distribution.

1. Introduction

Silylenes, $R_2Si{:}$, are divalent silicon species which prefer to exist as singlets, with the lone pair of electrons as the HOMO and an empty p orbital as the LUMO. Silylenes act as Lewis acids (**1**) or as Lewis bases (**2**),



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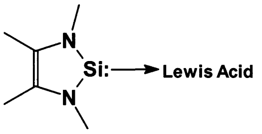

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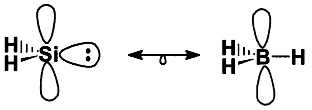
depending upon the substituents. The empty p orbital on the singlet silylenes can accept electrons from any Lewis base (LB) and form Lewis acid−Lewis base complexes. Experimental[2−8] and theoretical[9] support showing the electrophilic character of these species is available. An analogy between divalent silicon and trivalent boron (Scheme 1) was proposed by Jemmis et al.,[10] which indicates that divalent silicon possesses Lewis acidic character. Many silylene complexes with Lewis bases have been reported, and their spectroscopic data in low-temperature matrixes are available. Transient silylenes form acid−base complexes with Lewis bases such as THF and pyridine.[3] Silylenes obtained at 77 K were shown to react with carbon monoxide to give

Scheme 1



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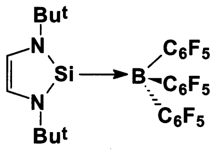
an acid−base complex rather than a silaketene.[2b,7] The first stable silylene−Lewis base complex has been reported recently.[6] Theoretical studies on the insertion reaction of silylenes into O−H, N−H, F−H, etc. bonds is also shown to proceed by the initial electrophilic attack by silylenes.[9d] Similarly, the reactions of the silylene H_2Si: with oxiranes, thiiranes, and seleniranes have been shown to proceed via an initial complexation involving electron-deficient silylene.[9a] Complexation of transient silylenes with dimethyl-d_6 ether has been shown to be due to the electron deficiency at the silylenes.[9b]

The chemistry of stable (bottleable) silylenes has been shown to be slightly different from that of their transient analogues.[11,12] They are not electrophilic, mainly because of the π electron delocalization, which pumps electron density into the pπ orbital of silicon. Ab initio calculations on the complexation between NH_3, CO, CNH and the cyclic systems (−$NHCH_2CH_2NH$−)Si: and (−NHCHCHNH−)Si: do not lead to any stable complexes. These systems show Lewis basic character, and the formation of complexes such as **3** strongly supported the nucleophilicity of cyclic silylenes.[12f] Simple transient silylenes are not known to be nucleophilic, though recent reports suggest that the transient silylenes generated from hexakis[2-((dimethylamino)methyl)phenyl]cyclotrisilanes have been shown to be nucleophilic in reactions with styrene and acetylene derivatives.[13] Mainly the cyclic, stable silylenes (for example, 1,3-di-*tert*-butyl-1,3,2-diazasilol-2-ylidene) have been shown to be nucleophilic.[12f] The formation of metal−silylene complexes such as **4** also supports the nucleophilicity of silylenes.[14] The nucleophilicity of transient silylenes can be triggered by the complexation of silylenes with Lewis bases.[15] Recently Belzner reported that the base coordinated silylenes act as nucleophiles and showed that the $H_3N \rightarrow H_2Si$: complex inserts into the H_3C−Cl bond in an S_N2 path rather than an electrophilic path.[15]



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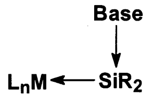

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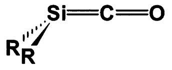
Though the LB→silylene complexes have been studied earlier, several questions have not been addressed. For example, what is the role of the lone pair of electrons on silicon in these LB→silylene complexes? Complex **5** is considered as a silaketene, but the isoelectronic complex **6** is considered as a LB−silylene complex. The delocalizations of electrons onto the pπ orbitals of silylene in stable silylene have been extensively studied,[16] but delocalization of the electrons from the silylene lone pair onto the π frame of LB has not been studied. What is the electrophilic nature of LB→Si complexes? The electronic structures of **5** and **6** indicate that the LUMO in these systems is predominantly based on the pπ orbital of silylenes,[17] indicating that **5** and **6** can further coordinate with Lewis bases, complex **7** being an example.[18] What is the strength of the nucleophilic character of base-coordinated silylenes? Is there any relation between the LB→Si: interaction to the nucleophilicity of silicon lone pair? The double-base-coordinated complex **7** has been shown to be nucleophilic.[13,15,18]



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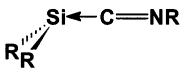

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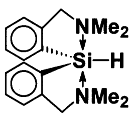

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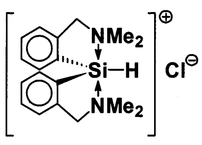

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Are the double-base-coordinated silylenes more nucleophilic than single-base-coordinated silylenes? To address these questions, we have performed ab initio MO and density functional calculations on **9**−**20** (Figure 1). Natural bond orbital (NBO) and charge decomposition analysis (CDA) using MP2(full)/6-31+G* geometries have been carried out to understand the electronic interactions present in these systems.

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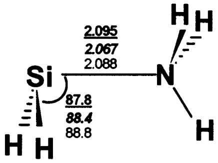

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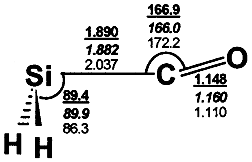

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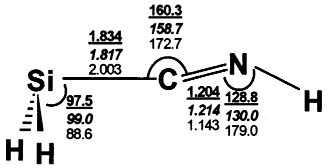

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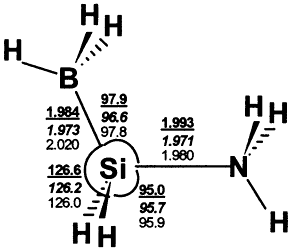

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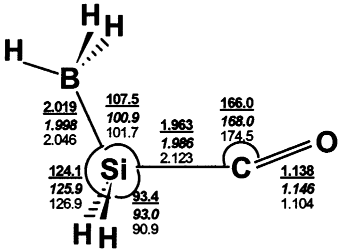

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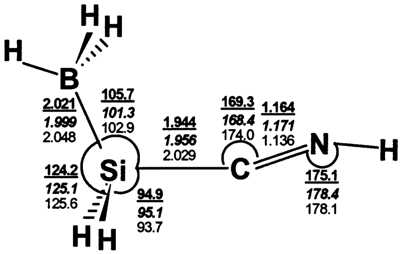

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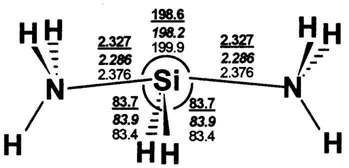

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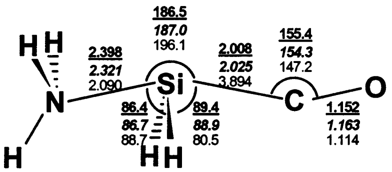

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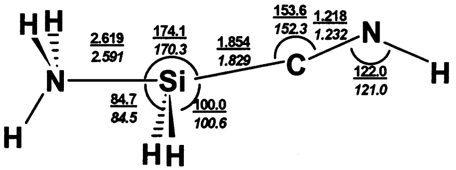

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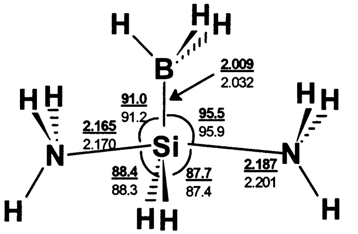

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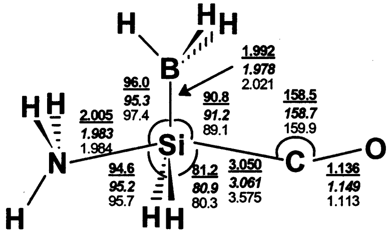

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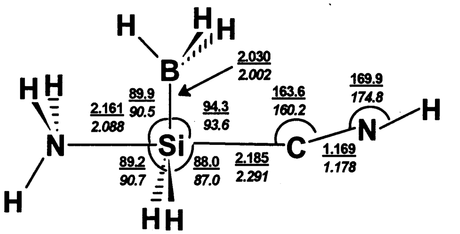

20,C_s

Figure 1. Structures of different complexes of silylenes with one Lewis base (NH_3, CO, CNH), two Lewis bases, and subsequent complexes of these with the Lewis acid BH_3, along with their important geometric parameters at three levels: viz. HF/6-31+G* (lightface type), ***MP2(full)/6-31+G**** (boldface italic type), and B3LYP/6-31+G* (boldface underlined type). Bond distances are given in angstroms, and angles are given in degrees.

Table 1. Absolute Energies (in au) of Different Complexes of Silylenes with One Lewis Base (NH_3, CO, CNH), Two Lewis Bases, and Subsequent Complexes of These with the Lewis Acid BH_3 at Various Levels

compd	sym[a]	compd no.	HF/6-31+G*	MP2(full)/6-31+G*	B3LYP/6-31+G*	G2	CBS-Q
H_2Si:	C_{2v}		−290.000 875	−290.080 120	−290.615 091	−290.167 693	−290.164 425
NH_3	C_{3v}		−56.189 499	−56.366 435	−56.556 985	−56.458 658	−56.459 103
CO	$C_{\infty v}$		−112.742 138	−113.036 546	−113.317 323	−113.177 497	−113.181 485
CNH	$C_{\infty v}$		−92.861 080	−93.142 668	−93.405 185	−93.262 105	−93.264 270
BH_3	D_{3h}		−26.390 693	−26.469 880	−26.614 935	−26.524 818	−26.522 473
SiH_2-NH_3	C_s	**9**	−346.228 973	−346.495 415	−347.216 944	−346.663 355	−346.661 902
SiH_2-CO	C_s	**10**	−402.758 673	−403.155 804	−403.976 154	−403.378 402	−403.380 878
SiH_2-CNH	C_s	**11**	−382.893 064	−383.276 359	−384.077 340	−383.476 955	−383.477 721
$SiH_2-BH_3-NH_3$	C_s	**12**	−372.665 743	−373.037 203	−373.895 874	−373.255 233	−373.253 300
SiH_2-BH_3-CO	C_s	**13**	−429.173 811	−429.668 356	−430.626 487	−429.942 501	−429.943 452
SiH_2-BH_3-CNH	C_s	**14**	−409.316 052	−409.797 583	−410.732 871	−410.048 244	−410.047 067
$SiH_2-(NH_3)_2$	C_{2v}	**15**	−402.423 092	−402.872 751	−403.783 351	−403.127 809	−403.126 888
$SiH_2-CNH-NH_3$	C_s	**16**		−439.649 914	−440.639 787	−439.939 222	−439.939 253
$SiH_2-CO-NH_3$	C_s	**17**	−458.971 646	−459.534 063	−460.543 308	−459.843 272	−459.845 002
$SiH_2-(NH_3)_2-BH_3$	C_s	**18**	−428.870 581		−430.472 293		
$SiH_2-CO-NH_3-BH_3$	C_s	**19**	−485.407 379	−486.078 096	−487.215 138		
$SiH_2-CNH-NH_3-BH_3$	C_s	**20**		−466.188 637	−467.307 746		

[a] Calculations have been carried out with C_1 symmetry. The systems **9**−**20** show overall symmetrical features as labeled after complete optimization.

Table 2. Stabilization Energies (in kcal/mol, ZPE Corrected) of Different Complexes of Silylenes with One Lewis Base (NH_3, CO, CNH), Two Lewis Bases, and Subsequent Complexes of These with the Lewis Acid BH_3 at Various Levels

compd no.	complex	HF/6-31+G*	MP2(full)/6-31+G*	B3LYP/6-31+G*	G2	CBS-Q
9	SiH_2-NH_3	24.22	30.66	28.15	23.22	24.08
10	SiH_2-CO	9.83	24.56	27.45	20.84	21.94
11	SiH_2-CNH	19.52	33.61	35.81	29.59	30.76
12	$SiH_2-BH_3-NH_3$	2.90	45.12	40.16	42.08	43.25
13	SiH_2-BH_3-CO		26.77	22.21	24.65	25.16
14	SiH_2-BH_3-CNH	14.73	32.22	25.47	29.16	29.41
15	$SiH_2-(NH_3)_2$	28.91	6.84	5.91	3.64	3.69
16	$SiH_2-CO-NH_3$	15.34	7.41	6.38	3.90	3.15
17	$SiH_2-CNH-NH_3$	20.26	4.47	3.43	2.26	1.52
18	$SiH_2-(NH_3)_2-BH_3$	35.64		46.43		
19	$SiH_2-CO-NH_3-BH_3$		46.53	35.70		
20	$SiH_2-CNH-NH_3-BH_3$	28.26	43.19	33.27		

2. Methods of Calculation

Ab initio MO[19] and density functional (DFT)[20] calculations have been carried out using the GAUSSIAN94W[21] package, the Windows version of the GAUSSIAN94 suite of programs, on an IBM-compatible PC Pentium-100 MHz with 64 MB of memory and 1 GB of disk space. Complete optimizations have been performed on different complexes of silylenes with one Lewis base (NH_3, CO, CNH) (**9**−**11**), two Lewis bases (**15**−**17**), and subsequent complexes of these with the Lewis acid BH_3 (**12**−**14, 18**−**20**) to understand Lewis donor−acceptor interactions using the HF/6-31+G* basis set. Since these molecules possess several lone pairs of electrons, the inclusion of diffuse functions in the basis set are important.[19] To study the effect of electron correlation on the geometries and energies, full optimizations have been performed at the MP2(full)/6-31+G*[22] and B3LYP/6-31+G*[23] levels. Frequencies were computed analytically for all optimized species at the HF/6-31+G* level in order to characterize each stationary point as a minimum or a transition state and to determine the zero-point vibrational energies (ZPE). The ZPE values calculated using the HF/6-31+G* level have been scaled by a factor of 0.9153.[24] To obtain accurate values of stabilization energies, calculations have been repeated at various levels of ab initio calculations, including CBS-Q[25] and G2[26] methods, as shown in Table 2. Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital approach[27] with the MP2 densities using the MP2(full)/6-31+G* wave function. MP2(full)/6-31+G* geometric parameters and G2 energies will be used in the discussion unless otherwise specifically mentioned. Charge decomposition analysis (CDA)[28] has been carried out to quantitatively estimate the donor−acceptor interactions in the above systems. The relative bond strengths have been estimated using the Wiberg bond index analysis at the MP2(full)/6-31+G* level.

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Table 3. Wiberg Bond Indexes of Different Complexes of Silylenes

	Wiberg bond index				
complex	$H_3N\rightarrow$ Si	$OC\rightarrow$ Si	$HNC\rightarrow$ Si	C=O or C=NH	$Si\rightarrow$ BH_3
$SiH_2{-}NH_3$	0.351				
$SiH_2{-}CO$		1.002		2.110 (C=O)	
$SiH_2{-}CNH$			1.242	2.228 (C=NH)	
$SiH_2{-}NH_3{-}BH_3$	0.397				1.031
$SiH_2{-}CO{-}BH_3$		0.624		2.243 (C=O)	0.977
$SiH_2{-}CNH{-}BH_3$			0.635	2.252 (C=NH)	0.985
$SiH_2{-}(NH_3)_2$	0.228				
$SiH_2{-}CO{-}NH_3$	0.196	0.842		2.072 (C=O)	
$SiH_2{-}CNH{-}NH_3$	0.108		1.340	2.131 (C=NH)	
$SiH_2{-}(NH_3)_2{-}BH_3$	0.281				1.009
$SiH_2{-}CO{-}NH_3{-}BH_3$	0.379	0.074		2.130 (C=O)	1.027
$SiH_2{-}CNH{-}NH_3{-}BH_3$	0.295		0.361	2.458 (C=NH)	0.991

3. Results and Discussion

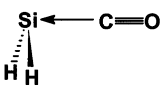
3.1. Electrophilicity of Silylenes. Complete optimization on the silylene−NH_3 complex **9** shows that it has a staggered arrangement (**9s**). The related eclipsed arrangement **9e** shows one negative frequency corresponding to the Si−N rotational transition state. The Si−N rotational barrier is 0.14 kcal/mol in **9** at the G2 level. The geometric data corresponding to **9s** at HF/6-31+G*, MP2(full)/6-31+G*, and B3LYP/6-31+G* levels is given in the Figure 1. The Si−N bond lengths at the HF/6-31+G*, MP2(full)/6-31+G*, and B3LYP/6-31+G* levels are 2.088, 2.067, and 2.095 Å, respectively. These distances are much longer than the Si−N covalent bond lengths for $H_3Si{-}NH_2$ (1.726, 1.760, and 1.740 Å at the same levels, respectively), which clearly indicate that the $LB\rightarrow H_2Si\colon$ interactions are of the coordination type. The N−Si−H angles for **9s** are 88.8, 88.4, and 87.8° at the HF/6-31+G*, MP2(full)/6-31+G*, and B3LYP/6-31+G* levels, respectively, which suggest that the $H_2Si\colon$ plane remains unperturbed during coordination. The Wiberg bond index (Table 3) for the Si−N bond in **9s** is 0.351 at the MP2(full)/6-31+G* level, indicating the weakness of the Si−N interaction. The energy stabilization due to the complexation between SiH_2 and NH_3 at the HF/6-31+G* level is 24.22 kcal/mol. After electron correlation at the MP2(full)/6-31+G* and B3LYP/6-31+G* levels is included, the stabilization energy increases to 30.66 and 28.15 kcal/mol, respectively; at the G2 and CBS-Q levels the stabilization energy due to the formation of **9** are 23.22 and 24.08 kcal/mol (Table 2). The stabilization energy due to the formation of **9** is 23.22 kcal/mol, only slightly less than that of $H_3N\rightarrow BH_3$ (26.06 kcal/mol) at the G2 level. This supports the proposed analogy between BH_3 and SiH_2 (Scheme 1)[10] and quantifies the Lewis acidic character of silylenes. The CDA analysis shows a strong electron donation (0.163e) from H_3N to SiH_2 (Table 4).

Table 4. Charge Decomposition Analysis of Different Complexes of Silylenes with Lewis Bases (NH_3, CO, CNH) and Subsequent Complexes of These with the Lewis Acid BH_3

compd	interaction	donation	back-donation	repulsive polarizn
9	$H_3N\rightarrow SiH_2$	0.163	−0.129	−0.487
10	$OC\rightarrow SiH_2$	0.300	−0.033	−0.754
11	$HNC\rightarrow SiH_2$	0.400	−0.099	−0.858
12	$(H_3N)(SiH_2)\rightarrow BH_3$	0.530	0.094	−0.551
13	$(OC)(SiH_3)\rightarrow BH_3$	0.553	0.098	−0.528
14	$(HNC)(SiH_2)\rightarrow BH_3$	0.538	0.070	−0.530
15	$H_3N\rightarrow (SiH_2)(NH_3)$	−0.006	−0.171	−0.486
16	$OC\rightarrow (SiH_2)(NH_3)$	−0.029	−0.185	−0.943
17	$HNC\rightarrow (SiH_2)(NH_3)$	0.236	−0.146	−1.151
18	$(H_3N)(SiH_2)(NH_3)\rightarrow BH_3$	0.380	0.073	−0.587
19	$(OC)(SiH_2)(NH_3)\rightarrow BH_3$	0.528	0.093	−0.574
20	$(HNC)(SiH_2)(NH_3)\rightarrow BH_3$	0.503	0.035	−0.588

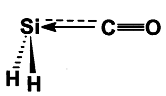
Table 5. Different Parameters Corresponding to Various Interactions from the NBO Analysis

compd	complex	donation	$E^{(2)}$	$E_{(j)} - E_{(i)}$	F_{ij}
9	Si−NH_3	$n_{Si}\rightarrow\sigma^*_{N-H}$	2.30	1.08	0.045
10	Si−CO	$n_{Si}\rightarrow\pi^*_{C-O}$	27.85	0.057	0.113
		$n_{Si}\rightarrow\sigma^*_{C-O}$	9.61	1.30	0.105
		$n_{O}\rightarrow\sigma^*_{Si-C}$	3.21	1.40	0.060
11	Si−CNH	$n_{N}\rightarrow\pi^*_{Si-C}$	37.09	0.69	0.143
		$n_{N}\rightarrow\sigma^*_{Si-C}$	12.18	0.79	0.088
16	Si−CO−NH_3	$n_{Si}\rightarrow\pi^*_{C-O}$	31.54	0.60	0.123
		$n_{Si}\rightarrow\sigma^*_{C-O}$	7.43	1.26	0.091
		$n_{O}\rightarrow\sigma^*_{Si-C}$	2.12	1.33	0.048
17	Si−CNH−NH_3	$n_{N}\rightarrow\pi^*_{Si-C}$	42.95	0.66	0.152
		$n_{N}\rightarrow\sigma^*_{Si-C}$	3.80	0.99	0.056



10a

10b



10c

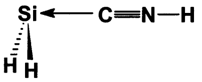
The reactions of silylenes SiH_2 and $SiMe_2$ with CO have been studied in detail using experimental and theoretical methods. The resulting complex has been considered as a silaketene by some workers and as a silylene−carbonyl complex by others.[2b,7] We have performed ab initio calculations on complex **10** to understand the electronic structure of this system. Calculation at the HF/6-31+G* level shows the structure **10** to be a (carbon monoxide)$\rightarrow SiH_2$ adduct (**10a**) with a C−Si distance of 2.037 Å. However, after electron correlation is included, the C−Si bond length was reduced by a large amount to 1.882 Å at the MP2(full) level and to 1.890 Å at the B3LYP level. The reduction in the bond length indicates that the contribution from the silaketene form (**10b**) increases. The Si−C−O bond angles for **10** are 172.2, 166.0, and 166.9°, respectively, at the HF/6-31+G*, MP2(full)/6-31+G*, and B3LYP/6-31+G* levels. The C−Si−H angles are 86.3, 89.9, and 89.4°, respectively, at the same levels. This indicates that though a strong decrease in the Si−C bond length is observed at correlated levels, the OC→silylene coordination character (**10a**) remains in **10**. The stabilization due to complexation in **10** is 9.83 kcal/mol at the HF/6-31+G* level. This gets strongly enhanced to 24.56 and 27.46 kcal/mol at the MP2(full) and B3LYP levels, respectively, supporting the observation that the Si−C interaction is stronger according to the estimates at the electron correlated levels. At the G2 and CBS-Q levels, the estimated stabilization energies are 20.84 and 21.94 kcal/mol, respectively. The Wiberg bond index calculated using the MP2(full)/6-31+G* optimized geometry is 1.002 (Table 3), supporting the strong interaction of CO and SiH_2. NBO analysis shows that the $n_{Si}\rightarrow\pi^*_{C-O}$ delocalization is very strong in **10** with a second-order energy $E^{(2)}$ of 27.85 kcal/mol (Table 5). This is also accompanied by an $n_{Si}\rightarrow\sigma^*_{C-O}$ ($E^{(2)} = 9.61$ kcal/mol)

Table 6. Occupancies of Different Molecular Orbitals Calculated Using the NBO Method

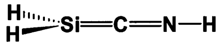
compd	complex	orbital	occ	orbital	occ	orbital	occ	orbital	occ
11	$SiH_2{-}CNH$	$\rho\ (\pi_{Si \rightarrow C})$	1.818	$\rho\ (\pi^*_{Si \rightarrow C})$	0.264	$\rho\ (\sigma_{Si \rightarrow C})$	1.857	$\rho\ (\sigma^*_{Si \rightarrow C})$	0.291
14	$SiH_2{-}CNH{-}BH_3$	$\rho\ (\sigma_{Si \rightarrow B})$	1.941	$\rho\ (\sigma^*_{Si \rightarrow B})$	0.005	$\rho\ (\sigma_{Si \rightarrow C})$	1.974	$\rho\ (\sigma^*_{Si \rightarrow C})$	0.038
17	$SiH_2{-}CNH{-}NH_3$	$\rho\ (\pi_{Si \rightarrow C})$	1.954	$\rho\ (\pi_{Si \rightarrow C})$	0.211				
20	$SiH_2{-}CNH{-}NH_3{-}BH_3$	$\rho\ (\sigma_{Si \rightarrow C})$	1.911	$\rho\ (\sigma_{Si \rightarrow C})$	0.137				
10	$SiH_2{-}CO$	$\rho\ n_{Si}$	1.775						
16	$SiH_2{-}CO{-}NH_3$	$\rho\ n_{Si}$	1.760						

negative hyperconjugative interaction. This indicates that a partial π character is developed between Si−C in **10** in addition to the coordination interaction; hence, **10c** may be a more appropriate description of **10**. NBO analysis shows that the electron density in the silicon lone pair in **10** is 1.775e, much less than the expected 2.0e, supporting the delocalization of electron density. CDA analysis shows that the LB→LA electron donation (0.300e) in **10** is very strong.

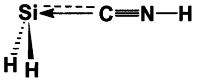
11 is the model for the experimentally known complex with the general formula **6**, with estimated Si−C distances of ~1.882 Å.[6] Complete optimizations on **11** showed that the Si−C distance is 2.003 Å, the C−Si−H angle is 88.6°, the Si−C−N angle is 172.7°, and the C−N−H angle is 179.0° at the HF/6-31+G* level. However, all these parameters show strong variation at the electron-correlated levels. The Si−C distance is reduced (to 1.817 and 1.834 Å) and the C−Si−H angle is increased (to 99.0 and 97.5° at the MP2(full) and B3LYP levels, respectively), indicating that **11** may be described as a silaketenimine in **11b**. The energy of stabilization due to the complexation between SiH_2 and CNH at the HF/6-31+G* level is 19.58 kcal/mol. After electron correlation is included, this value is strongly enhanced to 33.61, 35.81, 30.76, and 29.59 kcal/mol at the MP2(full), B3LYP, CBS-Q, and G2 levels, respectively. NBO analysis on **11** shows a π bond between silicon and carbon with an electron density of 1.818e and a π^* bond with an electron density of 0.264e (Table 6). The second-order $n_N \rightarrow \pi^*_{Si-C}$ and $n_N \rightarrow \sigma^*_{Si-C}$ delocalizations weaken the Si−C interaction. The electronic structure of **11** also shows that the contribution from **11c** is stronger in the resonance hybrid. The Wiberg bond index for the Si−C bond in **11** has been calculated to be 1.242, indicating a very strong interaction between silylenes and CNH. The CDA analysis shows strong (0.400e) electron donation from CNH to SiH_2.



11a



11b



11c

The above analysis on **9**−**11** indicates that Lewis bases such as NH_3, CO, and CNH donate electrons to the empty orbitals on silylenes to form LB−LA complexes. The interaction is mostly of the coordination type. The SiH_2 plane is almost unperturbed during the interaction. However, the lone pair on silylenes shows interaction with the LB, especially when the Lewis base has π orbitals. From the complexation energies (23.22 kcal/mol for **9**, 20.84 kcal/mol for **10**, and 29.59 kcal/mol for **11** at the G2 level), it can be concluded that CNH forms a stronger and CO forms a weaker LB−LA complex compared to NH_3. This is contradictory to the known order of Lewis basicity of these species (NH_3 > CNH > CO). The Wiberg bond indices (0.351 kcal/mol for **9**, 1.002 kcal/mol for **10**, and 1.242 kcal/mol for **11**) indicate that in an LB with a π interaction the LB→H_2Si: complexes are very strong. This is supported by the NBO analysis, which indicates that the lone pair on silylenes is delocalized in **10** and **11**. There are two important consequences of the LB→R_2Si complexes: (1) pumping electrons into the empty p orbital on Si, thereby reducing the electron deficiency of the p orbital, and (2) elevating the energy of the Si lone pair through second-order interactions. These two factors increase the Lewis basic character of silylenes. The simplest silylene, H_2Si, does not have a Lewis basic property, because the lone pair on silylenes is low-lying. Calculation on $H_2Si{-}BH_3$ does not show any stabilization; complete optimizations lead to the isomer $H_3Si{-}BH_2$. This 1,2-hydrogen shift is facilitated by the transfer of B−H bond pair electrons to the empty p orbital on silylenes. This 1,2-hydrogen shift has been observed in Me_2Si: and Cl_2Si: also. To prevent the 1,2 hydrogen shift, it is important to reduce the electron deficiency of the p orbital on silylenes. The complexation of silylenes with LB reduces the electron deficiency at Si and prevents 1,2-shifts. The activated lone pair on Si facilitates the increase in nucleophilicity, because the energy difference between the Si lone pair and the empty p orbital on BH_3 gets reduced, as shown in the schematic diagram (Figure 2). Thus, the Lewis base coordination triggers the nucleophilic character of silylenes. The CDA analysis indicates that the LB→H_2Si: electron donation increases in the order **9** (0.163e) < **10** (0.300e) < **11** (0.400e).

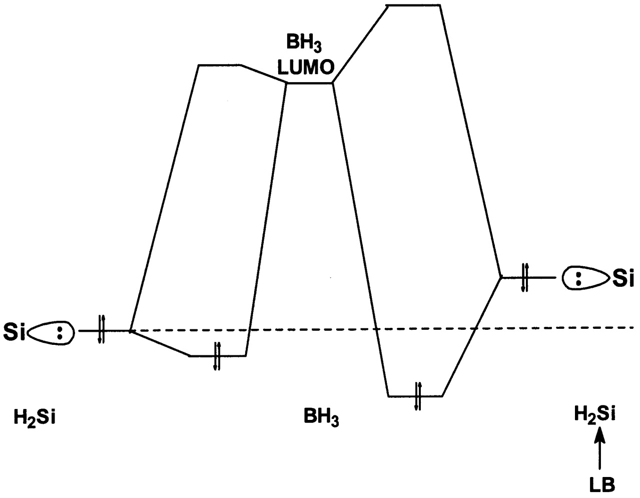


Figure 2. Schematic representation of the interactions of silylenes and base-coordinated silylenes with BH_3.

3.2. Lewis Basic Character of 9−11. The LB→SiH_2→LA complexes **12**−**14** are complexes of **9**−**11,** respectively, with BH_3. The Si−B distances in **12**−**14** at the MP2(full)/6-31+G* level are 1.973, 1.998, and 1.999 Å, respectively. These bond lengths are comparable to the Si−B covalent bond length in H_3Si-BH_2 at the MP2(full)/6-31+G* level, indicating a strong bond between Si and B. The LB−Si−H and LB−Si−B angles in **12**−**14** are in the range 93−101°, much less than the tetrahedral angle. The B−Si−H bond angles in **12**−**14** are in the range 125−126°, much larger than the tetrahedral angle. These data indicate that the spacial arrangement around Si in **12**−**14** should be considered as distorted trigonal pyramidal with LB at the apex. In **13** and **14** the Si−C distances are much larger than those in **10** and **11**. This is mainly due to the disappearance of partial Si−C π interactions in **13** and **14**. The stabilization energy due to complexation between **9** and BH_3 is 42.08 (43.25 kcal/mol) at the G2 (CBS-Q) level. This is much larger than the complexation energy between NH_3 and BH_3 (26.06 kcal/mol at G2) and between NH_3 and SiH_2 (23.22 kcal/mol). This indicates that the nucleophilicity of the H_3N→H_2Si: complex is much larger than that of NH_3. The nucleophilic character of **10** and **11** is comparable to that of NH_3 because the stabilization energies due to the formation of **13** and **14** are 24.65 (25.16) and 29.16 (29.14) kcal/mol at the G2 (CBS-Q) level. The complexation energies of **13** and **14** are smaller than that of **12** because in **10** and **11** there is a partial π character, which needs to broken before the complexation with BH_3. NBO data show the absence of the π delocalization to π^*_{C-X}, as expected in **13** and **14**. The Wiberg bond indices for the Si−B bond in **12**−**14** are 1.031, 0.977, and 0.985, respectively, at the MP2(full)/6-31+G* level. The Wiberg bond indices for Si−C bonds in **13** (0.624) and **14** (0.635) are much smaller than those in **10** (1.002) and **11** (1.242), respectively, supporting the above argument regarding the weaker Si−C interactions in **13** and **14**. The CDA analysis indicates a strong electron donation from Si to BH_3 in **12** (0.530e), **13** (0.553e), and **14** (0.538e), supporting the strong Lewis basic character of **9**−**11.**

3.3. Electrophilicity of 9−11. Complexes **9**−**11** are electron deficient. The origin of this electron deficiency can be seen in the LUMO of **9**−**11**, which is predominantly based on the pπ orbital of silicon. Experimentally known systems such as **7** support the idea that the base-coordinated silylenes can be electron deficient. To quantitatively estimate the deficiency and to note the stability of doubly coordinated silylenes, we have carried out complete optimizations on **15**−**17**. These systems have been found to be stable on their respective PE surfaces at the MP2(full)/6-31+G* and B3LYP/6-31+G* levels. However, at the HF/6-31+G* level only **15** has been found to be stable; though **16** could be located, it showed an undesirable Si−C distance. This indicates that electron-correlated levels need to be employed in studying double-base-coordinated silylenes. **15** has a C_{2v} arrangement, with an Si−N distance of 2.327 Å and an N−Si−N angle of 161.4° at the B3LYP/6-31+G* level. The Si−N distance in **15** is much longer than that in **9** but is within the limits of the Si−N coordination bond. This indicates that the 3c−4e N−Si−N interaction is equally distributed on both sides in **15**. In **16**, the CO is strongly bound to Si relative to NH_3. Similarly, CNH has been found to have a stronger interaction with Si than with NH_3 in **17**. This is surprising, because NH_3 is known to be a stronger Lewis base compared to CO and CNH. The stronger Si−C interactions can be attributed to the delocalization of the Si lone pair to CO and CNH in **16** and **17**, respectively. NBO analysis indicates that delocalization of the lone pair on Si to the π frame of CX has slightly increased, due to the complexation with NH_3 in **16** and **17**. The energy of stabilization due to the formation of **15**−**17** from **9**−**11**, respectively, are 6.84, 7.41, and 4.47 kcal/mol at the MP2(full)/6-31+G* level. These values reduce to 3.64 (3.69), 3.90 (3.15), and 2.26 (1.52) kcal/mol at G2 (CBS-Q levels). The Lewis acidities of **9** and **10** are found to be comparable, and that of **11** is much weaker. This indicates that the stronger the electron delocalization in the LB→Si complex, the weaker is the electron deficiency at Si; this weakening mainly originates from the hybridization of the orbital around Si as a function of Si−C−X delocalization. This is also reflected in the Si−N distances at MP2(full)/6-31+G* in **15** (2.286 Å), **16** (2.321 Å), and **17** (2.591 Å) and Wiberg bond indices (**15**, 0.228; **16**, 0.196; **17**, 0.108). **15**−**17** have a distorted-trigonal-bipyramidal arrangement, where the lone pair occupies the equatorial position. CDA analysis indicates that the repulsive polarization in **16** and **17** is much larger in comparison to **10** and **11**, respectively, indicating an increase in the covalent character in Si−C bonds.

3.4. Nucleophilicity of Double-Base-Coordinated Silylenes. Belzner's compound **7** is nucleophilic, it forms an acid−base complex with H^+. To quantitatively estimate the nucleophilic behavior **15**−**17**, complete optimizations have been performed on **18**−**20**. All these systems have been found to be stable on the respective PE surfaces at MP2(full)/6-31+G* and B3LYP/6-31+G* level. **18** has a C_s symmetric arrangement, with Si−N bonds in the range of 2.15−2.20 Å and Si−B distances of 1.98−2.03 Å. These geometric parameters confirm the expected H_3N-Si and $Si-BH_3$ coordination interactions. In **19**, the H_3N→Si and Si→BH_3 interactions represent strong coordination but the OC−Si interaction is very weak, almost broken (C−Si = 3.03 Å at the B3LYP level). This suggests that, upon coordination with BH_3, the weaker nucleophile (CO) dissociates from the double-base-coordinated silylenes **16**, though CO is strongly bound to Si in **16**. In **20** both H_3N and CNH are strongly electron donating to Si, NH_3 being the stronger of the two. Upon coordination with BH_3 the Si−N bond length in **18** is strongly reduced and the Si−C bond length strongly enhanced. This feature resembles a molecular-switch-like action, which is mainly due to the π interaction of the lone pair. The nucleophilicity of double-base-coordinated silylenes of **15**−**17** is slightly higher than that of singly coordinated **9**−**11**, as indicated by the complexation energies of **18**−**20** (46.43 kcal/mol for **18**, 35.70 kcal/mol for **19**, and 33.27 kcal/mol for **20** at the B3LYP/6-31+G* level). On complexation with BH_3, the Si−CO (in **19**) and Si−CNH (in **20**) interactions become weak and the Si−NH_3 interactions are strongly enhanced. This is mainly because the Si−C π delocalization disappears and hence the stronger base prevails in donation to the silylene pπ orbital, in fact the Si−CO bond almost breaks in **19** (bond length 3.061 Å at the MP2(full)/6-31+G* level). Si−B interactions are similar in **18**−**20**. In **20** the H_3N→Si and HNC→Si interactions become comparable, as the Si−C and Si−N distances are almost equal. The CDA analysis indicates there is strong donation from Si to BH_3 in **18** (0.380e), **19** (0.528e), and **20** (0.503e).

4. Conclusions

Silylenes accept electrons from Lewis bases to give stable complexes. The lone-pair electrons on silylene in LB→silylene complexes interact with the unoccupied π orbitals of the Lewis base. The chemistry of base-coordinated silylenes is mainly dictated by this electron delocalization. This second-order interaction may cause a rearrangement of the structure of the LB→Si: complex, as in the case of silaketenes. The electron-donating capacity of silylenes gets triggered upon coordination with Lewis bases, which can be quantitatively estimated. When silylenes are coordinated with two Lewis bases, the Lewis base with π orbitals shows a stronger interaction. Double-base-coordinated silylenes show stronger nucleophilicity compared to the single-base-coordinated silylenes. This suggests that there may be a correlation between the electron density in the pπ orbital of silylene and its nucleophilicity. When a double-base-coordinated silylene donates electrons to a Lewis acid, the balance of the LB→Si: interaction shifts back toward a stronger base because the lone pair on Si is not available for delocalization.

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