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Hard−Soft Acid−Base Interactions of Silylenes and Germylenes

Julianna Oláh,[†,‡] Frank De Proft,[†] Tamás Veszprémi,[‡] and Paul Geerlings*[,†]

Vrije Universiteit Brussel (VUB), General Chemistry Department (ALGC), Pleinlaan 2, B-1050, Brussels, Belgium, and Budapest University of Technology and Economics (BUTE), Inorganic Chemistry Department, Szent Gellért tér 4, H-1521, Budapest, Hungary

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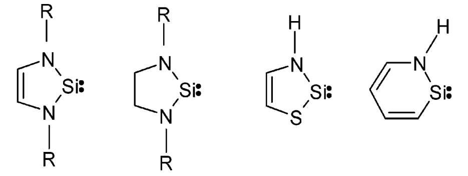
A detailed investigation of the electrophilic and nucleophilic character of singlet silylenes and germylenes, divalent compounds of silicon and germanium, respectively, substituted by first- and second-row elements is presented. In a first part, the Lewis acid properties of these compounds were studied through their complexation reaction with the Lewis bases NH_3, PH_3, and AsH_3. The results indicate that this complexation is most favorable with the hardest base NH_3, classifying these compounds as hard Lewis acids. This is confirmed by the linear correlation between the interaction energies and the value of the electrostatic potential, used as an approximation to the local hardness, near the empty p orbital of these compounds, indicating a charge-controlled interaction in the complex. Also the electrophilicity index, proposed by Parr et al., computed both at the global and the local level, correlates linearly with the complexation energies of the compounds with NH_3. The Lewis base character of these silylenes has been investigated, through their interaction with the acids BH_3 and AlH_3. Also in this case, the electrostatic potential can be used to probe the reactivity of the compounds. It will finally be demonstrated that an increasing stability of the silylenes and germylenes is accompanied by an increase in their nucleophilicity and a decrease of the electrophilicity.

1. Introduction

Divalent compounds of the Group 14 elements, such as carbenes, silylenes, and germylenes, are usually known as short-lived, reactive intermediates. Their ground state influences their electronic properties and reactivity; while singlet species react stereoselectively, following a concerted mechanism, compounds with a triplet ground state are involved in stepwise radical reactions. Their most important reactions include the insertion into O−Si, Si−Si, etc. bonds, addition to carbon−carbon double and triple bonds, and 1,3-dienes.[1] The singlet−triplet gap separating the lowest lying singlet and triplet states is the subject of intense interest, e.g., in the case of iodocarbenes,[2] several experimental and theoretical studies contradict each other. The singlet−triplet gap of these divalent compounds has been shown to correlate linearly[3] with their spin-philicity[4] and spin-donicity index. The singlet−triplet gap of silylenes has been related to their dimerization energy[5] and to their stability; the larger the singlet−triplet gap, the more stable silylenes are against dimerization. Therefore, it is not surprising that all stable silylenes synthesized until today possess a *singlet* ground state. Several experiments demonstrate that silylenes form complexes with Lewis bases;[6] the formation of the silylene−Lewis base complex is characterized by a strong blue shift of the $n-\pi$ absorption band.[6,7] The base, by donating electrons into the empty 3p orbital on the silicon, greatly increases the energy of the S_1 excited state. The frequency shift upon complexation depends on the nature of both the base and silylene. For Me_2Si, the frequency shifts increase in the order phosphines < CO < sulfides < ethers < amines, which is in satisfactory agreement with the stability order of the base−silylene complexes predicted from theoretical calculations: $HCl < H_2S < H_2O < PH_3 < NH_3$.[8] Although there is much spectroscopic evidence for the existence of silylene−Lewis base complexes, stable complexes have been only recently prepared.[9]

SCHEME 1: Cyclic Silylenes Investigated in This Study



1 **2** **3** **4**

1a, R=t-But
1b, R=H
2a, R=t-But
2b, R=H

Unlike the transient silylenes, thermally stable silylenes are not electrophilic. The first stable silylene **1a** (Scheme 1) was synthesized by Denk et al. in 1994,[10] and later its saturated form **2a** was prepared as well.[11] Among the several factors,[12] which stabilize these compounds, one of the most important is the π-electron donation to the 3p orbital of the silicon, which results in the decrease of the electrophilicity of the silylene. The most efficient substituents to stabilize the divalent silicon center is NH_2[13] followed by SH[14] and OH groups. Disubstitution by these groups increases the stability of the silylene, but the effect of the second substituents is smaller than that of the first one.[15] This has been attributed to the saturation of the empty 3p orbital of the silicon with electrons. The knowledge of stabilizing factors helps in the design of new possible targets for silylene synthesis; e.g., the systematic analysis of ring stress led to the design of **4**.[16] The stable silylenes possess a nucleophilic character, which is strongly supported by the formation of complexes such as **5**[17] and by the formation of metal−silylene complexes such as **6** (Scheme 2).[18] Bharatam et al. investigated

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* To whom correspondence should be addressed. E-mail: pgeerlin@vub.ac.be. Telephone: +32-2-629-33-14. Fax: +32-2-629-33-17.

[†] Vrije Universiteit Brussel (VUB).

[‡] Budapest University of Technology and Economics (BUTE).

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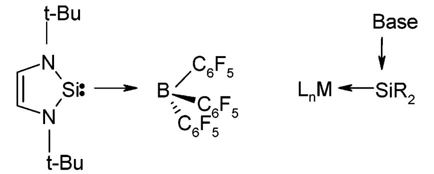
SCHEME 2



5 **6**

the electrophilic and nucleophilic character of silylenes by natural bond orbital analysis (NPA) and charge decomposition analysis (CDA).[19] The examination of the complexes of H_2Si with NH_3, CO, and CNH led to the conclusion that the interaction is mainly composed of the coordination type and, during the coordination the H_2Si plane, remains unperturbed. They also showed that the nucleophilicity of silylenes can be triggered by the addition of Lewis bases to the silylene, because it decreases the electron deficiency of the silicon empty 3p orbital and increases the energy of the silicon lone pair. This increased nucleophilicity of silylenes is supported experimentally, because the $H_3N \rightarrow :SiH_2$ complex inserts into the H_3C-Cl bond in an S_{N2} mechanism rather than in an electrophilic path.[20]

Although there has been much work done on the electrophilic and nucleophilic character of silylenes, it would be useful if one could quantify electrophilicity and nucleophilicity. On the basis of the original idea of Maynard et al.,[21] Parr et al. have introduced a formula to calculate the electrophilicity of molecules[22] within the context of the conceptual density functional theory (DFT)[23]

$$\omega = \frac{\mu^2}{2\eta} \qquad (1)$$

where $\mu = (\partial E/\partial N)_v$ is the electronic chemical potential[24] and $\eta = (\partial^2 E/\partial N^2)_v$ is the hardness[25] of the molecule, with E being the energy of the system and N being the number of electrons. Chattaraj et al. generalized the concept of philicity.[26] They claim that the local philicity is the most powerful concept of reactivity and selectivity when compared to the global electrophilicity index, Fukui function, or global/local softness. The local electrophilicity index[27] was already earlier applied by Pérez,[28] who found good qualitative agreement between the theoretical and experimental philicity of carbenes. She compared the local and global electrophilicity of singlet carbenes to the experimental Moss scale,[29] which is based on a kinetic model of the carbene addition to simple alkenes. Mendez and Garcia-Garibay[30] applied the electronegativity equalization principle for the reaction of 16 carbenes with 4 alkenes and found that the trends in electron donation between the various carbenes and alkenes correlate well with the Moss scale. Furthermore, the interaction energies were the most favorable with parameters, which reflect mutual electron donation, reflecting the simultaneous acidity and basicity of carbenes. The disadvantage of the Moss scale is that it can only be applied to singlet carbenes, and therefore, Sander et al. have set up a two-dimensional scale for the electrophilicity of carbenes,[31] which can be used for singlet as well as triplet carbenes. So far, no similar scale has been proposed for the nucleophilicity and electrophilicity of silylenes. In our work, we study the Lewis acid and base character of singlet silylenes, using DFT-based indices such as the Fukui function, softness, hardness, etc.[23] to determine their properties and analyze their interactions. We try to set up a theoretical scale to predict the electrophilicity and nucleophilicity of silylenes, which implies the probing of the electrophilic and nucleophilic properties of the silicon atom in different regions in space. To the best of our knowledge, this is the first example of the use of DFT-based descriptors in such a context. We investigated the properties of singlet germylenes in a manner similar to that of silylenes, to be able to discuss the similarities and differences of these two groups of molecules and to get a better overall understanding of the divalent compounds of the Group 14 elements.

2. Theory and Computational Details

Conceptual DFT descriptors have been used to investigate the Lewis base and Lewis acid character of singlet silylenes and germylenes. On the basis of Pearson's hard−soft acid−base principle,[32] which has been shown theoretically to be of great value, hard acids prefer interacting with hard bases and soft acids with soft bases. Several works in the literature demonstrate that in many cases the softness matching principle works very well for soft−soft interactions.[33] The global softness (S) and the local softness (s) of all reacting partners have been calculated as

$$S = \frac{1}{2\eta} \approx \frac{1}{I - A} \qquad (2)$$

and

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right)_v = Sf(\mathbf{r}) \qquad (3)$$

where I and A are the vertical ionization energy and electron affinity of the system, respectively. In eq 3, $f(\mathbf{r})$ is the Fukui function, either for nucleophilic [$f^+(\mathbf{r})$] or electrophilic [$f^-(\mathbf{r})$] attack

$$f^+(\mathbf{r}) = \left(\frac{\partial \rho}{\partial N}\right)_v \approx \rho_{N_0+1}(\mathbf{r}) - \rho_{N_0}(\mathbf{r}) \qquad (4)$$

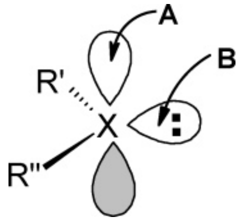
$$f^-(\mathbf{r}) = \left(\frac{\partial \rho}{\partial N}\right)_v \approx \rho_{N_0}(\mathbf{r}) - \rho_{N_0-1}(\mathbf{r}) \qquad (5)$$

where $\rho_{N_0}(\mathbf{r})$, $\rho_{N_0+1}(\mathbf{r})$, and $\rho_{N_0-1}(\mathbf{r})$ are the densities of the N_0, $N_0 + 1$, and $N_0 - 1$ electron system, computed at the equilibrium geometry of the N_0 electron system (constant external potential v). The local electrophilicity index has been calculated as

$$\omega^+ = f^+(\mathbf{r})S \qquad (6)$$

The definition of the counterpart of the local softness, the local hardness, is ambiguous,[34] and so far, no consensus has been reached, but the local hardness has, among others, been shown to be proportional to both the electronic part of the electrostatic potential and the total potential in each point in the valence region of the molecule (e.g., at a distance of 4 Bohr from the atom, very good results have been obtained[34]). Because the Si atom may react with Lewis bases through its empty orbital and with Lewis acids with its lone pair, we determined the electrostatic potential in two points around the silylene molecule. When a nucleophile attacks a silylene, it approaches perpendicular to the plane of the silylene from the direction of the empty p orbital localized on the Si; therefore, the electrostatic potential has been calculated 2 Å above the Si atom perpendicular to the plane of the silylenes (point A in Scheme 3). Although the use of the electrostatic potential for a nucleophilic attack is not straightforward and must be treated with caution, it can in most cases be assumed that regions with a small

SCHEME 3: Regions in Space A and B, where the Electrostatic Potential of the Silylenes and Germylenes was Computed



probability for an electrophilic attack have a high probability for a nucleophilic attack.[35] To investigate the Lewis base character of silylenes, the minimum of the electrostatic potential has been determined in the lone-pair region of the Si atom. (point B in Scheme 3).

To get a general idea about the Lewis acid and base characters of silylenes and germylenes, we calculated all of the silylenes and germylenes substituted by first- and second-row elements. The ground state of these molecules is a singlet (with the exception of the Li, Na, and MgH substituted species); therefore, we examined them only in their singlet state. Divalent silicon and germanium compounds can be stabilized by π-electron-donating substituents, and the effect of disubstitution by NH_2, OH, F, SH, and Cl groups is expected to decrease the electrophilicity and increase the nucleophilicity of silylenes. These disubstituted species are of special interest because previous works have shown that these substituents are the most efficient ones in stabilizing the divalent silicon center;[13,14] these disubstituted species have been considered in the set as well. As it was already mentioned, the stable species possess different electrophilic and nucleophilic properties than the transient silylenes; therefore, we included **1**−**4** in the set (see Scheme 1). NH_3, PH_3, and AsH_3 were used as Lewis bases, and BH_3 and AlH_3 were used as Lewis acids.

Because the ground state of most silylenes and germylenes is a singlet, therefore, all structures treated in this work were fully optimized in their singlet states at the B3LYP[36] level of theory with the 6-311+G(d,p) basis set[37] using Gaussian 03.[38] Analytical second-derivative calculations were performed to ensure that all of the stationary points were real minima on the potential energy surface. Although several works have shown that DFT methods, e.g., using the B3LYP exchange-correlation functional, reliably describe the properties of carbenes, we nevertheless compared the B3LYP reaction energies of the complexation of the silylenes with NH_3 and PH_3 with CBS-Q[39] reaction energies. In the CBS-Q (complete basis set) reaction energies, no correction for basis set superposition error is necessary. It turned out that the correlation between the reaction energies calculated at the CBS-Q and B3LYP levels is excellent both in the case of NH_3 and PH_3 ($R^2 = 0.99$ and 0.98, respectively); therefore, the further calculations were performed only at the B3LYP level.

Atomic charges were computed using the natural population analysis (NPA)[40] at the B3LYP/ 6-311+G(d,p) level.

3. Results and Discussion

(a) Electrophilicity of Silylenes and Germylenes. In Table 1, the calculated interaction energies of the different silylenes with the Lewis bases NH_3, PH_3, and AsH_3 are listed, together with some selected DFT reactivity indices of these silylenes. Table 2 contains the same quantities for the germylenes wih the same Lewis bases. Thorough investigation of the reaction energies reveals that the silylenes and germylenes react with the Lewis bases in a similar way; the correlation coefficient of the fit between the complexation energies of the silylenes and germylenes with NH_3, $\Delta E_{Si}^{NH_3}$ and $\Delta E_{Ge}^{NH_3}$, amounts to 0.949. The correlation coefficient of the fit between the complexation energies of the silylenes and germylenes with PH_3, $\Delta E_{Si}^{PH_3}$ and $\Delta E_{Ge}^{PH_3}$, is 0.974. This very good linear correlation between the reaction energies of the silylenes and germylenes with the same Lewis base indicates that these are similarly controlled.

The interaction of silylenes (and germylenes) with NH_3 and PH_3 is however different. If one plots $\Delta E_{Si}^{NH_3}$ against $\Delta E_{Si}^{PH_3}$, a

TABLE 1: Calculated Interaction Energies (in kcal/mol) of Differently Substituted Silylenes with NH_3, PH_3, and AsH_3[a]

molecule	$\Delta E_{Si}^{NH_3}$	$\Delta E_{Si}^{PH_3}$	$\Delta E_{Si}^{PH_3,fixed}$	$\Delta E_{Si}^{AsH_3}$	f_{Si}^{+}	S	s_{Si}^{+}	ω	ω_{Si}^{+}	V_A	$-V_{A,el}/2N$
HSiH	−26.75 (−24.07)	−21.86 (−22.4)	−20.34	−18.14	1.032[b]	3.27	3.37	0.12	0.13	0.069	0.253
HSiBeH	−25.36 (−23.79)	−26.44 (−29.2)	−24.70	−22.30	0.926	4.01	3.72	0.14	0.13	0.069	0.234
$HSiCH_3$	−21.89 (−20.91)	−15.25 (−16.66)	−12.42	−11.71	0.912	3.40	3.10	0.10	0.09	0.060	0.230
$HSiNH_2$	−9.55 (−9.00)	−2.22 (−2.88)	*c*	−1.29	0.857	3.01	2.58	0.08	0.07	0.033	0.234
HSiOH	−16.70 (−15.05)	−6.301 (*c*)	−5.20	−4.30	0.915	3.10	2.83	0.09	0.09	0.052	0.236
HSiF	−22.52 (−19.67)	−11.37 (−10.56)	−9.54	−8.73	0.954	3.03	2.89	0.12	0.11	0.069	0.237
HSiMgH	−23.19 (−21.96)	−25.33 (−29.10)	−23.94	−21.43	0.856	4.56	3.90	0.13	0.11	0.067	0.209
$HSiAlH_2$	−26.57 (−26.12)	−24.67 (−29.07)	−22.12	−20.46	0.869	4.02	3.49	0.13	0.11	0.067	0.209
$HSiSiH_3$[d]	−26.99 (−26.56)	−22.77 (−26.70)	−20.36	−18.81	0.863	3.76	3.25	0.14	0.12	0.071	0.207
$HSiPH_2$	−21.44 (−21.04)	−13.46 (−17.21)	−8.74	−9.98	0.773	3.48	2.69	0.11	0.09	0.052	0.214
HSiSH	−20.05 (−18.99)	−10.28 (−12.62)	−6.33	−7.65	0.787	3.16	2.49	0.11	0.09	0.051	0.215
HSiCl	−23.95 (−22.31)	−13.21 (−14.47)	−10.91	−10.03	0.858	3.25	2.79	0.13	0.11	0.068	0.217
$Si(NH_2)_2$	−0.56 (−1.67)	*c*	*c*	*c*	0.807	2.75	2.22	0.06	0.05	0.013	0.224
$Si(OH)_2$	−7.94 (−7.05)	*d* (−1.52)	*c*	*c*	0.867	2.66	2.31	0.08	0.07	0.039	0.227
$Si(SH)_2$	−11.96 (−12.34)	*d* (−3.37)	−0.74	*c*	0.655	3.20	2.10	0.10	0.07	0.043	0.202
SiF_2	−17.45 (−14.25)	−3.85 (−3.21)	−3.18	−2.62	0.918	2.48	2.28	0.12	0.11	0.068	0.229
$SiCl_2$	−20.48 (−19.97)	−5.93 (−8.25)	−3.83	−3.72	0.751	3.03	2.27	0.13	0.10	0.068	0.205
H_2NSiOH	−4.35 (−4.17)	c	c	*c*	0.830	2.76	2.29	0.07	0.06	0.025	0.225
H_2NSiSH	−6.04 (−6.57)	−0.15 (*c*)	*c*	*c*	0.703	2.95	2.07	0.08	0.05	0.030	0.211
HOSiSH	−10.67 (−10.45)	*c*	−0.76	*c*	0.752	2.94	2.21	0.09	0.07	0.043	0.212
1b	*c*	*c*	*c*	*c*	0.747	3.17	2.37	0.05	0.04	0.004	0.203
2b	*c*	*c*	*c*	*c*	0.792	3.00	2.38	0.06	0.05	0.013	0.195
3	−2.29	*c*	*c*	*c*	0.649	3.17	2.06	0.07	0.05	0.019	0.191
4	−1.98	*c*	*c*	*c*	0.523	3.22	1.68	0.07	0.04	0.013	0.201

[a] Fukui function on silicon for nucleophilic attack (f_{Si}^{+}, in au), global (S, in au), and local (s_{Si}^{+}, in au) softness, electrophilicity (ω, in au), local electrophilicity on silicon (ω_{Si}^{+}, in au), global electrostatic potential (V_A, in au), and its electronic part ($V_{A,el}$, in au) calculated in point A (Scheme 3) at the B3LYP/6-311+G(d,p) level (interaction energies at the CBS-Q level are in parentheses). [b] f_{Si}^{+} is larger than one, and f_{H}^{+} is negative ($f_{H}^{+} = -0.016$ au). [c] No stable complex has been found. [d] No stable complex has been found at the B3LYP level.

TABLE 2: Calculated Interaction Energies (in kcal/mol) of Substituted Germylenes with NH_3 and PH_3[a]

molecule	$\Delta E^{NH_3}_{Ge}$	$\Delta E^{PH_3}_{Ge}$	f^+_{Ge}	S	s^+_{Ge}	ω	ω^+_{Ge}	V_A
HGeH	−22.78	−18.70	1.293[b]	3.238	4.185	0.250	0.323	0.071
HGeBeH	−21.26	−22.26	0.923	3.997	3.688	0.271	0.250	0.070
$HGeCH_3$	−18.83	−13.30	0.919	3.391	3.119	0.212	0.195	0.063
$HGeNH_2$	−9.31	*c*	0.866	2.989	2.590	0.170	0.147	0.038
HGeOH	−16.16	*c*	0.915	3.077	2.817	0.205	0.188	0.058
HGeF	−21.65	−11.57	0.953	3.004	2.862	0.250	0.238	0.080
HGeMgH	−19.81	−21.55	0.859	4.561	3.920	0.255	0.219	0.069
$HGeAlH_2$	−22.69	−20.57	0.879	4.010	3.524	0.259	0.227	0.069
$HGeSiH_3$[d]								
$HGePH_2$	−17.92	−12.18	0.797	3.565	2.843	0.231	0.185	0.052
HGeSH	−15.43	−7.79	0.795	3.134	2.492	0.230	0.183	0.054
HGeCl	−21.51	−12.58	0.864	3.234	2.794	0.262	0.227	0.072
$Ge(NH_2)_2$	−3.23	*c*	0.827	2.813	2.326	0.133	0.110	0.020
$Ge(OH)_2$	−10.58	−1.63	0.861	2.653	2.285	0.192	0.165	0.050
$Ge(SH)_2$	−10.92	−1.96	0.653	3.184	2.079	0.217	0.142	0.047
GeF_2	−19.99	−6.82	0.914	2.446	2.236	0.274	0.250	0.076
$GeCl_2$	−19.64	−7.76	0.750	2.992	2.246	0.287	0.215	−0.004
H_2NGeOH	−6.69	*c*	0.829	2.737	2.272	0.160	0.133	0.033
H_2NGeSH	−6.99	−0.63	0.714	2.943	2.101	0.170	0.121	0.035
HOGeSH	−11.60	*c*	0.754	2.917	2.202	0.204	0.154	0.050

[a] Fukui function on germanium for nucleophilic attack (f^+_{Ge}, in au), global (S, in au), and local (s^+_{Ge}, in au) softness, electrophilicity (ω, in au), local electrophilicity (ω^+_{Ge}, in au) on germanium, and global electrostatic potential (V_A, in au) calculated in point A (Scheme 3) at the B3LYP/6-311+G(d,p) level. [b] f^+_{Ge} is larger than one, and f^+_H is negative ($f^+_H = -0.1465$ au). [c] No stable complex has been found. [d] The germylene is not stable at the B3LYP level.

correlation coefficient of 0.72 is obtained, while for the germylenes, the plot of $\Delta E^{NH_3}_{Ge}$ against $\Delta E^{PH_3}_{Ge}$ results in a R^2 value of 0.66. This suggests that the interaction of the harder Lewis base NH_3 with the silylenes is unrelated to the interaction of the softer Lewis base PH_3 with the same compounds. However, the difference between the interaction of PH_3 and AsH_3 is negligible, with the correlation coefficient between the reaction energies of PH_3 and AsH_3 with the silylenes amounting to 0.99. From the data, it is evident that silylenes and germylenes react very similarly, and therefore, one can assume that germylenes would show the same reactivity toward AsH_3 as toward PH_3. This different behavior of NH_3 in comparison with PH_3 (and AsH_3) combined with the similar properties of PH_3 and AsH_3 is in accordance with a typical observation in the elements of the p block, often exhibiting quite different behavior of the first-row elements as compared with their heavier congeners that are more similar. The difference in our particular case is most probably due to the well-known fact that the donor atom in NH_3 is sp^3-hybridized and thus contains the lone pair in a sp^3 orbital, whereas the donor atoms in PH_3 and AsH_3 possess an s-type lone pair. Further analysis of the reaction energies shows that the interaction is the most favorable with NH_3 in nearly all cases and becomes less favorable (i.e., less negative reaction energies) when the Lewis bases become softer.

The computed trends in the complexation energies will now be investigated using the reactivity indices emerging from DFT. In the first step, we will investigate the application of the local hard and soft acids and bases principle. When the reaction is orbital-controlled, the smallest differences in local softness between the donor and acceptor atoms should be observed ("softness-matching"). However, it turns out that this procedure is unsuccessful in explaining the trends of the complexation energies. Moreover, the correlation does not improve when the interaction of the softest acid and the softest base is considered. Finally, it was found that the approximation of the interaction energy between species A and B in an orbital-controlled reaction,

$$\Delta E_{AB} \approx -\frac{1}{2}\frac{(\mu_A - \mu_B)^2}{S_A + S_B} S_A S_B - \frac{1}{2}\frac{\lambda}{S_A + S_B} \qquad (7)$$

put forward by Gazquez et al.[41] and elaborated and successfully applied in softness dominated reactions by some of the present authors,[42] does not yield any correlation between the estimated reaction energy and the calculated reaction energy using the global or the local softness of the reacting partners. Although Chandrakumar and Pal[43] have shown the usefulness of the above equation for a small set of substituted NH_3 and BH_3 derivatives both in hard−hard and soft−soft interactions, their method did not yield a good correlation for our compounds. They defined the λ value as the difference of electron densities of the interacting system A (or alternately B) before and after the interaction

$$\lambda_A = \sum_{j=1}^{M} \rho^{eq}_{Aj} - \sum_{j=1}^{M} \rho^{0}_{Aj} \qquad (8)$$

In our case, λ turned out to be around 0.9 in every case, and substituting half of it into eq 7 (see ref 43) did not improve our results. The failure of eq 7 probably follows from the fact that in the silylenes there is a lone pair and an empty orbital localized on the silicon (germanium) in the silylenes (germylenes). Therefore, the reactivity of these species should be investigated at the local level, avoiding the condensation of properties to atoms. This statement is supported by the fact that during the $H_2Si + NH_3$ reaction, the H_2Si moiety of the reacting molecules remains unperturbed, indicating that local effects dominate the observed reactivity trends.[19]

All of these findings suggest that these Lewis acid−base complexation reactions are mainly charge-controlled. As it was mentioned earlier, the local hardness of the molecule in the valence region will be approximated by the (total) electrostatic potential. This quantity is computed at a distance of 2 Å from the Si or Ge atom, respectively, perpendicular to the plane formed by this atom and the first atoms of the two substituents (the numerical value of the electrostatic potential at this point is denoted as V_A). Figure 1a shows the correlation of the electrostatic potential with the interaction energy of the silylenes with NH_3; in Figure 1b, the same plot is shown for the germylenes interacting with NH_3. As can be seen, in both cases, the electrostatic potential in the region of the empty p orbital

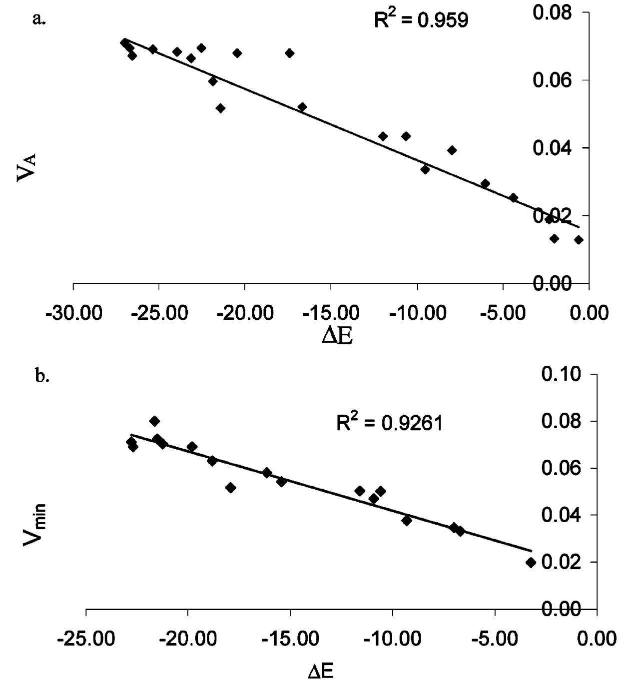


Figure 1. Electrostatic potential calculated at point A (V_A) versus the reaction energy ΔE (in kcal/mol) of the silylenes (**2a**) and germylenes (**2b**) with NH_3 (SiF_2 and $SiCl_2$ are excluded from the fit).

of the divalent species correlates linearly with their interaction energy with the hard base NH_3. The quality of this correlation diminishes progressively as one goes from NH_3 to the softer bases PH_3 and AsH_3. Quite surprisingly, the electrostatic potential values of the halogen and dihalogen substituted species (HSiF, SiF_2, HSiCl, and $SiCl_2$) are almost equal, whereas the interaction energies of these molecules somewhat differ. For these compounds, the stabilization energy trend HSiCl > HSiF > $SiCl_2$ > SiF_2 probably results from the interplay of two opposite effects, which are hard to quantify; although the overlap of the empty 3p on Si and the fluorine 2p is somewhat less effective than the Si 3p Cl 3p overlap, the Si−F distance is shorter than the Si−Cl bond distance. The same trend is observed for the complexation energies of the silylenes with PH_3 and AsH_3. If these molecules are excluded from the set, R^2 improves to 0.90 for the correlation between the electrostatic potential and $\Delta E_{Si}^{PH_3}$ and to 0.72 for the correlation between the electrostatic potential and $\Delta E_{Si}^{AsH_3}$. As can be seen, the correlation between the local hardness descriptor for the silylenes and germylenes and the interaction energies decreases when the hardness of the Lewis base decreases. It can thus be invoked that this reaction is essentially a charge-controlled interaction.

The energetics of this complexation reaction between these Lewis acids and bases can however be separated into two main parts: a perturbation of the species in their number of electrons, corresponding to an electronic reorganization, and a perturbation in their external potential because of the geometry relaxation. During the silylene + NH_3 reaction, the energy gain is mainly due to the overlap of the silicon empty orbital and the NH_3 lone pair because the change of the geometrical parameters of the interacting species is negligible. For the reactions of PH_3 and AsH_3, however, the geometry of the base changes considerably; during the coordination, the P and As atoms become much more like sp^3 hybrids. This is reflected by the changes of the pyramidalization degree of the P and As atoms; for P, it decreases from 52.1° to 47.9° and for As from 53.1° to 48.6° during coordination. To estimate the effect of this geometry relaxation on the complexation energies, we computed the reaction energies by fixing the geometry of the silylenes and PH_3. In the case of As, similar results are to be expected. After fixing the geometry of the reagents, we optimized the distance between the interacting atoms in the acid and base. The calculated interaction energies are tabulated in Table 1. In all cases, the interaction energies are only 2−3 kcal/mol less favorable than upon geometry relaxation. This uniform trend proves that effects of geometry relaxation are not responsible for the decrease of the correlation between the local hardness descriptor and complexation energies in the case of the silylene + PH_3 and AsH_3 complexation reactions.

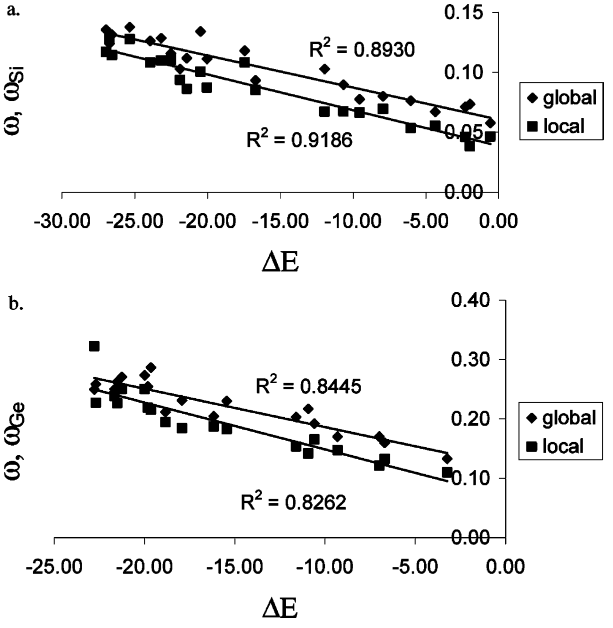


Figure 2. Global (ω) and local (ω_{Si} and ω_{Ge}) electrophilicity of the silylenes (**2a**) and germylenes (**2b**) versus the reaction energies (ΔE, in kcal/mol) of their complexation reaction with NH_3.

In the literature, the electronic part of the electrostatic potential, divided by twice the number of electrons of the system $(-1/2N)V^{el}(\mathbf{r})$ has been used as another approximation of the local hardness.[44] The calculated values for the silylenes are collected in Table 1. The correlation of these values with the interaction energies is poor, suggesting that, in this case, the total electrostatic potential is a more suited approximation for the local hardness. As indicated earlier in this work, it was demonstrated that germylenes are very similar to silylenes, the $(-1/2N)V^{el}(\mathbf{r})$ approximation of the local hardness was not used in their case.

In these complexation reactions, the silylenes and germylenes, readily interacting with Lewis bases, can be considered to be electrophilic. We therefore computed the electrophilicity index ω (eq 1) for these compounds[22] and correlated these values with the interaction energies with the different bases. As can be seen from Figure 2, a very good correlation emerges between ω for the silylenes and germylenes and their interaction energies with the hardest base NH_3. Also, the local electrophilicity, introduced by Domingo et al.,[27] computed on the acceptor atom of the Lewis acid (i.e., on Si or Ge), turns out to be a good indicator of the reactivity of the silylenes or germylenes with hard Lewis bases, as shown in Figure 2. In the case of the reactions with PH_3 and AsH_3, a poorer correlation between the electrophilicity index and the interaction energies is observed, which can, as was already discussed in this contribution, probably be attributed to the important geometry relaxation when the Lewis acid−base complexes are formed.

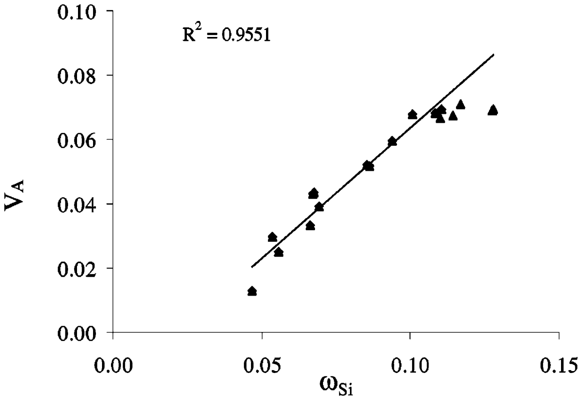


Figure 3. Electrostatic potential calculated in point A (V_A) against the local electrophilicity on the silicon atom (ω_{Si}) in the silylenes.

Finally, as shown in Figure 3, a good agreement is observed between the local electrophilicity index and the electrostatic potential, indicating that they are related in the case of silylenes. If the electrostatic potential is larger (i.e., more positive) in the silicon empty orbital, it suggests that it is less filled with electrons. It is known about silylenes that they can be stabilized by electron flow to the 3p orbital of the silicon. Silylenes (similarly to carbenes[45]) are electron-deficient intermediates, with the central silicon atom having only six electrons in its outer shell. Therefore, they are highly electrophilic in their reactions, and the more electron withdrawing the substituents, the more strongly electrophilic the silylene. If the 3p orbital is less filled with electrons (larger, i.e., more positive electrostatic potential), it will be much more electrophilic than those species in which the 3p orbital is filled to a larger extent (obviously, these species are more stable as well). In those silylenes that are highly stable, the 3p orbital of the silicon is filled with electrons, which is reflected by a small positive or slightly negative electrostatic potential and small electrophilicity. In turn, in those silylenes in which there are no π-electron-donating groups, the 3p orbital will not be filled with electrons; they will be unstable, have a large positive electrostatic potential, and large electrophilicity.

(b) Nucleophilicity of Silylenes. The nucleophilic character of silylenes was examined, studying their complexes with two representative Lewis acids BH_3 and AlH_3. Because the electrophilic character of the germylenes turned out to be largely parallel the behavior of the silylenes, only the latter was considered in this part. As it was mentioned in the Introduction, the nucleophilicity of silylenes can be triggered by the addition of Lewis bases; therefore, we examined the reactions of the ($H_2Si + NH_3$) and ($H_2Si + 2NH_3$) complexes with BH_3 and AlH_3.

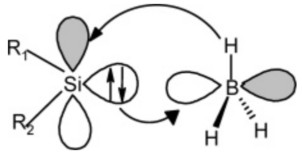
As Table 3 demonstrates, most of the silylenes do not form stable complexes with BH_3 and AlH_3. In the case of the reaction with BH_3, the formal silylene−BH_3 complex is a saddle point on the PES and the IRC calculations lead to a stable product in which one of the H is in a bridging position between the Si and B atoms. Scheme 4 depicts a possible explanation of the reaction. It is well-known that boron hydrides (e.g., B_2H_6) as well as silicon hydrides (e.g., Si_2H_2[46] and Si_2H_4[47]) prefer forming bridged compounds, which contain three-centered two-electron bonds. The silylene + BH_3 reaction allows the formation of similar compounds; the silicon lone pair overlaps with the empty orbital of the boron, and as a result, the electronic population of boron increases. The electrons flow toward the hydrogens, which in turn prefer to interact with the empty orbital localized on the silicon. If R_1 and/or R_2 substituents donate electrons to this empty orbital (e.g., **1**−**4** or the disubstituted silylenes), the interaction with the hydrogen becomes unfavorable; thus, no bridged species but a classical Lewis base−Lewis acid complex will be formed. These silylenes have been previously shown to be more stable by isodesmic reactions than the monosubstituted silylenes;[5] therefore, this result confirms the presumptions that only the stable silylenes are nucleophilic. From these results, it can be concluded that the lone pair of the silylene will only show nucleophilic character if the 3p orbital of the silicon is filled with electrons. The strength of the interaction between BH_3 and the nucleophilic silylenes is well-predicted by the minimum of the electrostatic potential (V_{min}) calculated in the lone pair (Figure 4). Both the interaction energies and the Gibbs free energies correlate linearly with V_{min} ($R^2 = 0.97$ for $\Delta G_{Si}^{BH_3}$ V_{min}, and $R^2 = 0.99$ for $\Delta E_{Si}^{BH_3}$ V_{min}, $\Delta G_{Si}^{AlH_3}$ V_{min}, and $\Delta E_{Si}^{AlH_3}$ V_{min} fits). The ΔG values are larger by 11−13 kcal/mol than the ΔE values, which is in accordance with the decrease of the entropy of the system during complexation compared to the free molecules. The interaction energy of the disubstituted species depends much less on the electrostatic potential. Previously, it was shown by isodesmic reaction energies that the effect of the second NH_2, SH group is much smaller on the stability of the silylenes,[15] and it was explained by the saturation of the silicon empty orbital with electrons. This implies that the “electrophilicity of the empty orbital” influences the nucleophilicity of the silylene. This relationship between the nucleophilicity and electrophilicity is clearly demonstrated in Figure 5, showing that V_A linearly correlates with V_{min} in the case of the ambiphilic (disubstituted) silylenes.

TABLE 3: Calculated Interaction Energies (in kcal/mol) of the Differently Substituted Silylenes with BH_3 and AlH_3 and the Minimum in the Electrostatic Potential (V_{min}, in au) in the Lone-Pair Region of the Silylenes[a]

substituent	$\Delta E_{Si}^{BH_3}$	$\Delta E_{Si}^{AlH_3}$	V_{min}
HSiH	*b*	*b*	−0.033
HSiBeH	*b*	*b*	−0.039
$HSiCH_3$	*b*	*b*	−0.042
$HSiNH_2$	*b*	−17.62	−0.043
HSiOH	*b*	*b*	−0.029
HSiF	*b*	*b*	−0.016
HSiMgH	*b*	*b*	−0.040
$HSiAlH_2$	*b*	*b*	−0.030
$HSiSiH_3$[c]	*b*	*b*	−0.028
$HSiPH_2$	*b*	*b*	−0.028
HSiSH	*b*	*b*	−0.027
HSiCl	*b*	*b*	−0.014
$Si(NH_2)_2$	−30.33	−17.73	−0.047
$Si(OH)_2$	−24.26	−12.20	−0.020
$Si(SH)_2$	−24.13	−12.07	−0.010
H_2NSiOH	−25.43	−12.93	−0.033
H_2NSiSH	−26.57	−14.30	−0.025
HOSiSH	−24.75	−11.69	−0.015
1b	−23.86	−14.14	−0.037
2b	−27.95	−16.21	−0.043
3	−21.77	−12.09	−0.024
4	*b*	−18.96	−0.048
$HSiH + NH_3$	−40.77	−30.03	−0.081
$HSiH + 2NH_3$	−46.24	−36.31	−0.098

[a] All values have been obtained at the B3LYP/6-311+G(d,p) level. [b] No stable complex has been found. [c] No stable complex has been found at the B3LYP level.

SCHEME 4: Interaction of BH_3 with Unstable Silylenes



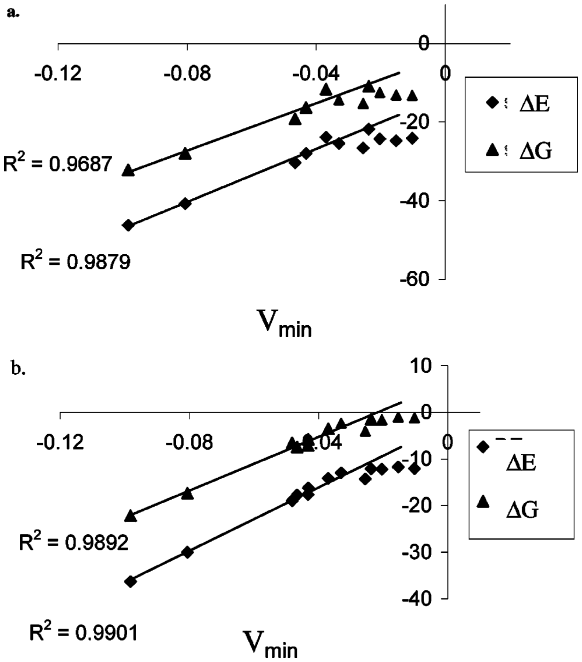


Figure 4. (a) Reaction energies (ΔE) and Gibbs free energies (ΔG) (in kcal/mol) of the complexation of the silylenes with BH_3 plotted against the minimum of the electrostatic potential (V_{min}, in au) (b) Reaction energies (ΔE) and Gibbs free energies (ΔG) (in kcal/mol)of the complexation of the silylenes with AlH_3 reaction plotted against the minimum of the electrostatic potential (V_{min}, in au). The doubly substituted species are not included in the fit.

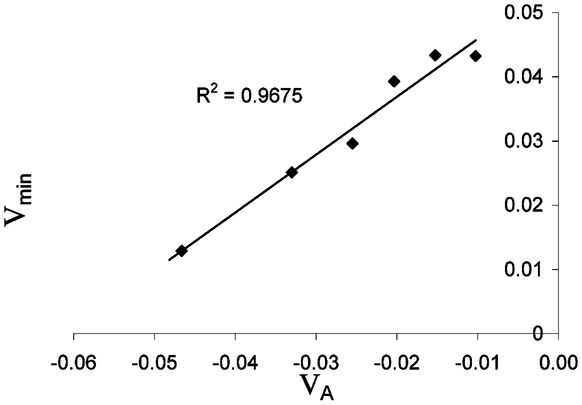


Figure 5. Minimum in the electrostatic potential (V_{min}) versus the electrostatic potential calculated in the region of the empty 3p orbital (point A, V_A) for the disubstituted silylenes (values are in au).

The reaction of silylenes with the softer acid AlH_3 shows similar trends as in the case of BH_3 (Figure 4b). However, the compounds, which preferred to form bridged species with BH_3, rearrange during the optimization to the classical tetravalent silicon compound, in which the aluminum is trivalent. This also means that these compounds do not act as Lewis bases against AlH_3 and do not show nucleophilic character. Those compounds, which formed a Lewis base−Lewis acid complex with BH_3, form a complex with AlH_3 as well, and the interaction energy is generally 11 kcal/mol lower.

4. Conclusions

A systematic study of the electrophilic and nucleophilic character of silylenes and germylenes was presented. Our results show that the interaction of these compounds with Lewis bases are essentially charge-controlled. As the Lewis base becomes softer, the interaction becomes less favorable, which is reflected by the decrease of the interaction energies in the $NH_3 > PH_3 > AsH_3$ series. The electrostatic potential computed in the region of the empty 3p (Si) or 4p (Ge) orbital and used as a measure of the local hardness is linearly correlated with these complexation energies, with the correlation coefficient decreasing when the softness of the base is increasing.

However, a small group of disubstituted silylenes behave both as Lewis acids and Lewis bases, indicating their ambiphilic character. The substituents of the divalent silicon determine whether the silylene will possess a Lewis acid or base character. If the substituents do not donate electrons to the silicon empty 3p orbital, the silylenes are electrophilic, but electron-donating substituents decrease their electrophilicity and increase their nucleophilicity. Both reactions are thus essentially influenced by the silicon empty orbital.

As a result, the nucleophilicity of silylenes and germylenes is strongly related to their stability; π-electron-donating substituents yield higher stabilization and increase their nucleophilicity and decrease their electrophilicity at the same time.

This study demonstrates the very similar behavior of silylenes and germylenes, which are different from the other members of the divalent compounds of Group 14 elements. They are highly unstable like carbenes, but because their ground state is different, they display a different reactivity pattern. On the other hand, they differ markedly from the stable divalent tin compounds.

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Supporting Information Available: Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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