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Electrochemistry and Computations of Stable Silylenes and Germylenes[#]

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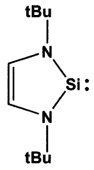
Stable silylenes, **1** and **2**, and germylenes, **3** and **4**, have been studied computationally and by cyclic voltammetry (CV). Electron affinities (E_A) and ionization potentials (I_P) were calculated; the latter agree well with available gas phase photoelectron spectroscopy data. All CV measurements in $THF-Bu_4NClO_4$ exhibit irreversible waves for all compounds, for both oxidation and reduction processes. However, in 1,2-dichlorobenzene−Bu_4NClO_4, the germylene derivative **3** shows a single reversible oxidation couple, whereas **4** exhibits a reversible couple at its second oxidation step, the first one being irreversible. In both cases, the redox couples become irreversible by replacing the electrolyte with either Bu_4NBF_4 or Bu_4NHSO_4, indicating the importance of the counteranion on the stability of the intermediates. The CV results also show that the unsaturated **1** and **3** are more easily oxidized than their saturated counterparts **2** and **4**, and oxidation is easier for the silylenes **1** and **2** than for their germanium analogues. However the measured oxidation and reduction potentials do not correlate with the calculated I_P's and E_A's, probably due to kinetic and surface effects.

Introduction

Silylenes are key intermediates in many thermal and photochemical transformations in organosilicon chemistry. These divalent carbene analogues are intensely reactive, and the study of their properties is usually restricted to matrix isolation techniques.[1] The synthesis of stable cyclic singlet silylenes, **1**[2] and **2**,[3] and the corresponding germylenes, **3** and **4**,[4] opened the way for a thorough investigation of the physical properties of these analogues of the Arduengo-type carbenes **5** and **6**.[5−7]



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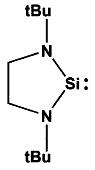

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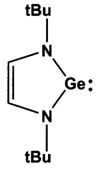

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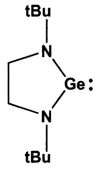

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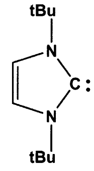

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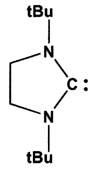

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In this paper we report the results of MO computations for the C═C unsaturated carbene **5**, silylene **1**, and germylene **3**, the saturated carbene **6**, silylene **2**, and germylene **4**, and their respective ion radicals, as well as cyclic voltammetry (CV) measurements of the neutral carbene analogues **1**−**4**.[8] Both anodic and cathodic processes are evaluated, and attempts were made to correlate the experimental results with density functional calculations of the ionization potentials (I_P) and electron affinities (E_A) of compounds **1**−**4**.

Results and Discussion

I. Computations. The structures of the carbene analogues **1**−**4** and their radical cations and anions have been optimized using the hybrid density functional B3LYP method and the 6-31G(d) basis set.[9,10] The

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[#] Dedicated to Prof. Hubert Schmidbaur on the occasion of his 75th birthday.

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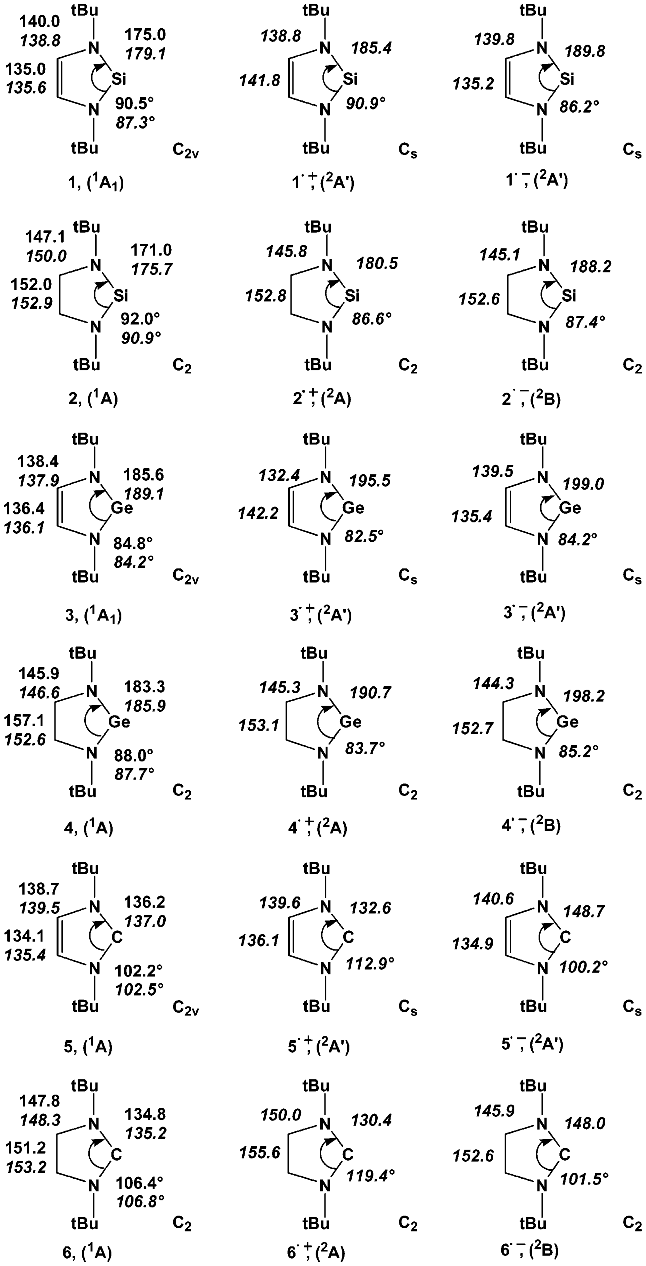

Figure 1. Structures of carbenes, silylenes, and germylenes **1**−**6** (calculated bond lengths and angles in italics, experimental values given for comparison[2−4,7a,11,12]) and their radical cations and anions (at B3LYP/6-31G(d), bond lengths in pm).

Table 1. Calculated Ionization Potentials (I_P) and Electron Affinities (E_A) for Carbenes and Carbene Analogues 1−6 (in eV, at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d))

	I_P[a]			E_A[b]	
compd	vertical	adiabatic	expt[12,13]	vertical	adiabatic
1	6.98	6.70	6.96, 7.13, 7.28	0.73	0.70
2	7.30	7.10	7.54	0.64	0.50
3	6.71	6.40	6.65, 6.85, 6.97	0.49	0.40
4	7.08	6.90		0.33	0.10
1·THF		5.91			0.52
2·THF		6.69			0.36
3·THF		5.77			0.31
4·THF		6.43			0.01
5		7.17	7.68		1.71
6		6.91			1.60

[a] I_P = E(neutral) − E(radical cation). [b] E_A = E(neutral) − E(radical anion).

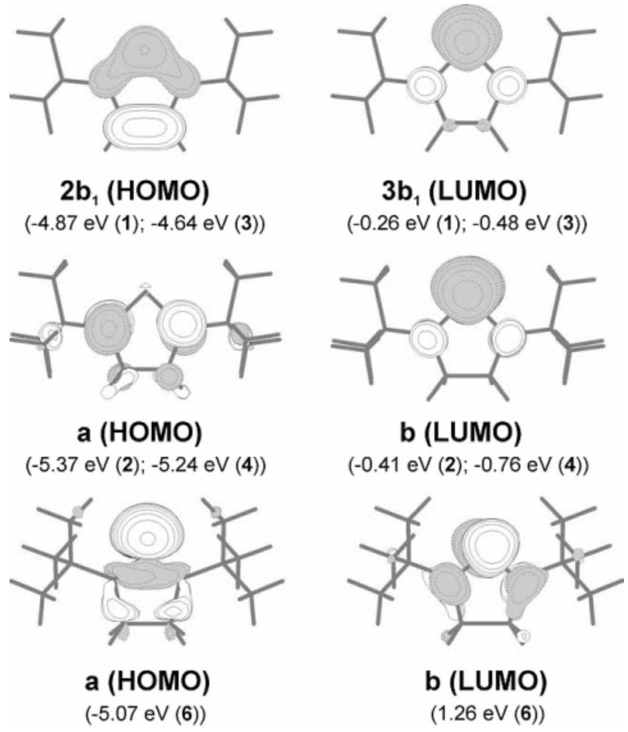

Figure 2. Plot of the frontier orbitals as calculated for **1** (molecular point group C_{2v}, first line) and **2** (molecular point group C_2, second line). Computed energies of the Kohn−Sham orbitals at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) for compounds **1**−**4** are given in parentheses. For comparison the frontier orbitals of **6** are also given (molecular point group C_2, third line).

optimized structures, along with the available experimental data, are given in Figure 1.[2−4,7a] For comparison the optimized geometries of carbenes **5** and **6** are also given.[11,12] The ionization energies and electron affinities are calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level and are summarized in Table 1 (for details see Theoretical Methods).

The predicted geometries of the neutral carbenes **5** and **6** and the carbene analogues **1**−**4** are in agreement with available experimental data (maximum deviation Δr = 4.7 pm for the bond lengths),[2−4,7a,10,11] and also the calculated vertical ionization energies are in close agreement with measured photoelectron spectroscopy (PE) data of compounds **1**−**3** and **5**.[12,13] The largest deviation between experiment and computations is found to be +0.24 eV for compound **2**.

As representative examples for the frontier orbitals of the heavy carbenes **1**−**4**, plots of HOMO and LUMO of the unsaturated silylene, **1**, and the saturated silylene, **2**, are given in Figure 2.[14] The HOMOs of **1** and **3** are essentially a combination of π-type orbitals from

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Table 2. Cyclic Voltammetry Data of Silylenes (1, 2) and Germylenes (3, 4)[a]

	oxidation (E_P)		reduction (E_P)	
compd	GC[b]	Pt	GC	Pt
1	0.67	0.45	−2.67	
2	0.95, 1.12[c]	1.30	−1.75, −2.35	
3	0.84	0.93		
4	1.20, 1.7[c]	1.23, 1.7[c],	−2.92	−2.87

[a] Peak potentials (E_P) are in V and quoted vs Ag/AgCl reference electrode. Scan rate: 100 mV/s. [substrate] = 1−2 mM in THF−0.1 M Bu_4NClO_4. [b] Glassy carbon. All measured peaks are broad, at both GC and Pt electrodes. [c] These second oxidation peaks were ill-defined and detected only when Bu_4NBF_4 was used.

all atoms of the five-membered ring with a nodal plane between the nitrogen atoms and the carbon atoms, perpendicular to the plane of the molecule. The LUMOs, both of π-symmetry, have two additional nodal planes, also perpendicular to the molecular plane. The superior π-conjugation in silylene **1** compared to germylene **3** is reflected in the lower energy of the HOMO and in the higher energy of the LUMO in **1** compared to **3**. The frontier orbitals of the saturated compounds **2** and **4** reflect their heteroallyl-type conjugation between the silicon and germanium atoms and the two nitrogen atoms. That is, the HOMOs are mainly an antisymmetric combination of nitrogen p-orbitals with no contributions from π-type orbitals of the central element. The LUMOs consist of an antisymmetric combination of the in-phase p-orbitals at the nitrogen atoms and the p-type orbital at the heavy element, with dominant contributions from the latter.[15] As noted previously,[12] the frontier orbitals of the carbenes **5** and **6** differ considerably from those of their heavier analogues. In particular, the HOMOs of both carbenes **5** and **6** consist of an essentially in-plane s,p-hybrid-type lone pair orbital.

This orbital pattern describes straightforwardly the geometric changes upon oxidation or reduction (see Figure 1). Upon oxidation, the unsaturated compounds **1** and **3** experience an increase of the length of the E−N bond and of the C=C double bond. In contrast, the inner cyclic C−N bond is shortened, in agreement with removal of an electron from the C−N antibonding HOMO. Similarly, the E−N bonds of the saturated compounds **2** and **4** are elongated, but the C−C single bond lengths are not changed upon oxidation. Due to the different nature of the HOMOs, the predicted geometric changes upon oxidation for the carbenes **5** and **6** differ significantly from its heavier analogues. Removal of an electron from the in-plane lone pair at the divalent carbon atom results in a decrease in the carbon−nitrogen bond length and a significant widening of the NCN angle, whereas in the silicon and germanium analogues the NEN angle remains nearly constant (for the unsaturated compounds **1** and **3**) or is slightly decreased (for **2** and **4**) upon oxidation. The formation of the radical anion causes for all six compounds, **1**−**6**, uniformly, a significant increase of the E−N bond due to the strongly E−N antibonding nature of all LUMOs.

II. Electrochemistry. Table 2 summarizes both oxidation and reduction potentials for all divalent derivatives of Si and Ge studied (**1**−**4**) by CV in THF−Bu_4NClO_4. No reversible waves have been observed in this medium, and therefore, none of the derivatives afford a stable anion-radical or cation-radical intermediate. This observation is not surprising due to the anticipated high reactivity of the electrogenerated species.

Changing the electrolyte to Bu_4NBF_4 usually has a negligible effect on the value of the peak potentials. However, in some cases, a second oxidation peak (at higher values), though ill-defined, could be detected. When a platinum (Pt) disk is used as the working electrode, a clearer effect on the peak potentials is observed. While the anodic peaks are shifted by ±0.05−0.3V, the effect on the reduction is much more pronounced. On a Pt anode, a reduction peak is detected only for **4**, whereas on a glassy carbon (GC) anode it is observed for **1**, **2**, and **4**. Evidently, there must be a considerable surface effect that influences both oxidation and reduction processes.

Silylene **1** exhibits an irreversible oxidation wave at about 0.45−0.67 V (depending on the working electrode used, see Table 2) upon scanning up to +2.0 V in THF. No reduction wave is observed when scanning down to −3.0 V when Pt was used, but an ill-defined one (at −2.67 V) could be detected at a GC anode. Apparently, it is relatively easy to oxidize the unsaturated silylene **1** but quite difficult to reduce it. Its unusual stability toward reduction could stem from its aromatic (6π electrons) stabilization. The cyclic conjugated nature of **1** has been supported by experimental and theoretical studies.[15−18] The unsaturated germylene **3** exhibits a higher oxidation potential (at both GC and Pt anodes) than **1**, but affords no reduction wave. This is in contrast to the theoretical results, which show that both the calculated vertical and adiabatic I_P's of **3** are lower than those of **1**, in agreement with a higher lying HOMO in **3** (see Table 1 and Figure 2). It appears that, in solution, both solvation and surface effects greatly affect the apparent measured peak potentials.

In contrast to **1**, the saturated silylene derivative **2** exhibits two distinct irreversible reduction waves (at −1.75 and −2.35 V) and one oxidation wave in the range 0.95−1.30 V upon positive scan (up to +2 V). The two reduction steps have been confirmed by chemical reduction with potassium metal.[19] In agreement with the calculated and measured I_P's, silylene **2** is more electron deficient and, therefore, more difficult to oxidize than **1**. Furthermore, the saturated **2** is easier to reduce than the unsaturated **1**, in qualitative agreement with the computations, which predict a lower electron affinity for **2** (see Table 1). Upon comparison between the saturated derivatives, namely, silylene **2** and germylene **4**, the latter shows a higher oxidation potential on GC but a lower one on Pt. In addition, **4** exhibits a significantly

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Table 3. Cyclic Voltammetry of Silylenes (1, 2) and Germylenes (3, 4) with Different Electrolytes[a]

	Bu_4NClO_4		Bu_4NBF_4		Bu_4NHSO_4	
compd	oxid. (E_P)	red. (E_P)	oxid. (E_P)	red. (E_P)	oxid. (E_P)	red. (E_P)
1	−0.15, 0.37		0.77	−2.38	0.50 (broad)	
2	1.27, 1.67		0.90 (broad)		1.15	
3	$E_{1/2}(1) = 0.41$[b,c]		1.07[d]		1.0, 2.05	
4	1.02, $E_{1/2}(2) = 1.50$[b]		1.30, 1.95	−2.25	1.07 (broad)	

[a] CV measurements were carried out in 1,2-DCB−0.1 M electrolyte, under inert atmosphere of nitrogen, using a semi-micro ($\phi = 0.01$ mm) Pt button as a working electrode. Peak potentials (E_P) are in V and quoted vs Ag/AgCl reference electrode. Scan rate: 100 mV/s. [Substrate] = 1−2 mM. (All waves are irreversible unless stated otherwise; $E_{1/2}$ stands for a reversible couple.) [b] Reversible couples were observed with ΔE_P of 150−250 mV. It is noteworthy that similar ΔE_P values were detected for ferrocene/ferrocenium couple in this solvent−electrolyte system. [c] No further oxidation wave was detected upon scanning up to +2 V. [d] A reduction peak at 0.25 V was observed on reverse scan.

more negative reduction potential than **2** (on GC), meaning it is more difficult to reduce. On the other hand, by using a Pt electrode, a reduction peak could be detected only for **4**, indicating that in this experimental setup all other species (**1**−**3**) are more difficult to reduce than **4**. Both oxidation and reduction processes indicate that kinetic and surface effects are dominating in the electrochemistry of **2** and **4**.

One cannot rule out the possibility that the discrepancy between experimental and theoretical data outlined above could stem from possible interaction of the silylene and germylene species with the donor solvent THF. If true, there is no certainty that the electrochemical measurements are of the free silylene/germylene species and not of their complexes with THF. To shed light on this issue, we have undertaken a series of CV measurements in an "innocent" solvent such as 1,2-dichlorobenzene (1,2-DCB), in the presence of different electrolytes (the results are summarized in Table 3).

At first approximation, ignoring solvation, surface, and kinetic effects, the first oxidation potential represents the energy level of the highest occupied molecular orbital (HOMO), whereas the reduction potential could be attributed to the lowest unoccupied molecular orbital (LUMO). Therefore, for many classes of compounds cyclic voltammetry (CV) has been used to study the influence of substituents or small variations in the structure and topology on the energy level of the important frontier orbitals. The electrochemical data for the heavy carbene analogues **1**−**4**, summarized in Table 2, clearly show, however, the overwhelming importance of kinetic and surface parameters. Therefore, it is not surprising that the trend observed by CV for the ease of oxidation (on GC electrode, **1** > **3** > **2** > **4**; on Pt electrode, **1** > **3** > **4** > **2**) and ease of reduction (on GC, **2** > **1** > **4** > **3**; on Pt, **4** > **1, 2, 3**) do not correlate with the trend found by calculations (oxidation, **3** > **1** > **4** > **2**; reduction, **4** > **3** > **2** > **1**).

The fact that no trend was observed for the ease of oxidation even in the presence of an innocent solvent, such as 1,2-DCB (Table 3), indicates that solvent effects play a negligible role in determining the apparent oxidation potentials. Actually the effect of electrolytes (and anode surface) is more pronounced because they are known to affect both the shape of the voltammograms and the values of redox potentials due to the formation of ion pairs. Indeed it is remarkable to observe that for the 1,2-DCB−Bu_4NClO_4 medium the unsaturated germylene **3** gives a reversible couple (at $E_{1/2}(1) = 0.41$ V, see Figure 3a) for its first oxidation process. Apparently, other studied anions (BF_4^-, HSO_4^-) do not stabilize the cation radical $\mathbf{3}^{\bullet+}$. The saturated germylene **4** affords two oxidation steps, of which only the second one (at $E_{1/2}(2) = 1.50$ V, Figure 3b) is reversible. Interestingly, the amplitude of the second wave is about half of that of the first wave (at $E_P = 1.02$ V). This may imply that the second step could be attributed to the oxidation of a dimeric product formed after the first oxidation step. Such a dimerization process is quite reasonable because a similar one was already found to occur in the case of saturated silylene **2**.[19] A reversible behavior was not found for silylenes **1** and **2** in this solvent−electrolyte system, but the trend of oxidation remained similar although with different potential values. The reduction results for compounds **1**−**4** in this system are somewhat meaningless due to the relative ease of reduction of the solvent.

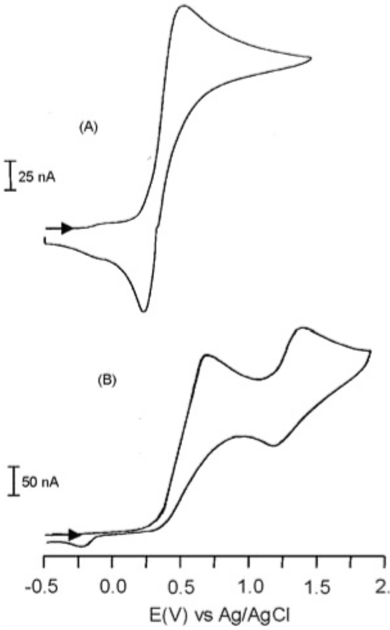

Figure 3. Cyclic voltammograms of germylenes **3** (A) and **4** (B) (1−2 mM) in 1,2-DCB−0.1 M Bu_4NClO_4 on a semi-micro Pt disk ($\phi = 0.1$ mm), under nitrogen atmosphere. Scan rate: 100 mV/s.

While the results of the density functional calculations for ionization of the carbene analogues **1**−**4** are in agreement with available gas phase photoelectron spectroscopic results (ease of oxidation: **3** > **1** > **2**; see also Table 1), there is not even a qualitative agreement with the electrochemistry data. As a first theoretical approximation to model the electrochemistry of **1**−**4** in THF solution, we computed the structures and energies of the associates between the carbene analogues **1**−**4** and THF, **1**·THF, **2**·THF, **3**·THF, **4**·THF, and their reduced and oxidized forms. In qualitative agreement with available experimental data, the neutral silylenes **1** and **2**[20] and germylenes **3** and **4** are practically not bonded to THF. This is indicated by very small calculated association energies ($E_A = -0.7$ (**1**), -0.1 (**2**), -0.6 (**3**), -0.5 kcal mol^{-1} (**4**), at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)).[21–23] While for the radical anions also only insignificant interaction energies with THF are predicted ($E_A = -4.5$ ($\mathbf{1}^{\bullet-}$), -3.4 ($\mathbf{2}^{\bullet-}$), -2.0 ($\mathbf{3}^{\bullet-}$), -2.3 kcal mol^{-1} ($\mathbf{4}^{\bullet-}$)), the associations between THF and the radical cations are relatively strong ($E_A = -18.8$ ($\mathbf{1}^{\bullet+}$), -10.9 ($\mathbf{2}^{\bullet+}$), -14.5 ($\mathbf{3}^{\bullet+}$), -9.5 kcal mol^{-1} ($\mathbf{4}^{\bullet+}$)). Therefore, this first approximation predicts an easier oxidation of the heavy carbene analogues in solution compared to the gas phase, while the changes for the reduction are insignificant. However, the relative order for oxidation and reduction in solution is the same as predicted for the gas phase (i.e., oxidation, **3** > **1** > **4** > **2**; reduction, **4** > **3** > **2** > **1**). This result implies that solvent effects are not the predominant factors that determine the relative ease of oxidation and reduction of the carbene analogues **1**−**4**, as we observed also by CV measurements carried out in different solvents.

Conclusion

We have shown that the unsaturated 6π electron compounds, **1** and **3**, are more easily oxidized than their saturated counterparts **2** and **4** and that the oxidation is easier for the silylenes **1** and **2** than for their germanium analogues. However the measured oxidation and reduction potentials correlate neither with experimental I_P's nor with calculated I_P's and E_A's, using density functional theory. This indicates that the solution electrochemistry of compounds **1**−**4** is dominated by kinetic and surface effects. All carbene analogues **1**−**4** exhibit irreversible reduction and oxidation waves in THF. However, in 1,2-DCB−Bu_4NClO_4, at a Pt anode, germylene **3** shows a sole reversible oxidation couple, whereas germylene **4** exhibits two oxidation waves, of which only the second one is reversible. No reversibility was observed for silylenes **1** and **2** in this medium.

Experimental Part

Cyclic voltammetry (CV) measurements were performed in THF−Bu_4NClO_4, using a conventional three-electrode cell. The working electrode was a platinum disk (Pt) (ca. 1 mm diameter) or glassy carbon disk (GC) (ca. 3 mm diameter), the reference electrode, Ag/AgCl, and the counter electrode, a Pt cylindrical gauze. The concentration of substrate was 1−2 mmol L^{-1}, while that of the supporting electrolyte was 0.1 mol L^{-1}. All CV experiments were carried out in a drybox ([H_2O] < 1 ppm; [O_2] < 1 ppm), under inert atmosphere of nitrogen. When 1,2-DCB−Bu_4NClO_4 was the electrolytic medium, a semi-micro (ca. 0.1 mm diameter) Pt working electrode was used. Solvents THF and 1,2-DCB were distilled (twice) over CaH_2, under argon atmosphere. All electrolytes used (Bu_4NClO_4, Bu_4NBF_4, Bu_4NHSO_4, from Aldrich or Fluka) were dried under vacuum (~30 mmHg) at 85 °C for 24 h before use. The silylenes and germylenes were prepared according to published procedures at the University of Wisconsin, kept in sealed tubes under inert atmosphere, opened in the glovebox, and used without further purification. For more specific details see footnotes underneath Tables 2 and 3.

Theoretical Methods. The geometries of the carbenes **5** and **6** and carbene analogues **1**−**4** and their radical cations and anions have been uniformly optimized using the hybrid density functional B3LYP method and the 6-31G(d) basis set using the Gaussian 98 program, revisions A3−A9.[9,10] All compounds were verified to be minima at the indicated point group by a subsequent frequency calculation. Refined energies were obtained using single-point calculations with the more extended 6-311+G(d,p) basis set. Vertical ionization energies and electron affinities were calculated from the energy of the radical ions at the neutral ground state geometry, while the adiabatic energies were computed by subtracting the energies of the optimized radical ions from the neutral carbene analogue. Orbital plots were obtained from B3LYP/6-31G(d) calculations using the Molden program. The orbitals are plotted at an isodensity surface of 0.05.

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Supporting Information Available: Table of the absolute energies of compounds **1**−**6** and of the complexes **1·THF**−**4·THF** and their radical ions and tables of their computed structures in cartesian coordinates.

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[20] The negligible interaction between the silylenes **1** and **2** and donor solvents THF, triethylamine, etc. is shown by the invariable ^{29}Si NMR chemical shift of δ^{29}Si = 78 (**1**) and δ^{29}Si = 119 (**2**) in these solvents.

[21] These values must be regarded as a lower boundary, since the dispersion energy term of the intermolecular forces is not covered by hybrid density functionals as the B3LYP functional applied here.[22] The absolute value of the dispersion energy term is, however, usually less than 2 kcal mol^{-1}; that is, for the benzene/CO complex, which is formed nearly exclusively due to dispersion forces, $E_A = -1.75$ kcal mol^{-1} was measured.[23]

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