Ionization Potentials of Silenes (R′₂Si=CR₂). Experiment and Theory

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We have measured the photoelectron (PE) spectra of two new silenes: the kinetically stable long-lived silene *t*-BuMe₂Si(Me₃Si)Si=Ad (**3**) and a transient silene which was generated in the gas phase by pyrolysis of the corresponding precursor. Previously, PE spectra of only two transient silenes have been reported. The ionization potential (IP) of **3** is 6.9 eV, 2 eV lower than that of H₂Si=CH₂. Quantum-mechanical calculations reproduce quite well the experimental IPs. The trends in IP₁ are well-reproduced by calculations of the silene's HOMO, even at the HF/6-31G(d)//HF/6-31G(d) level of theory. However, the correct absolute IPs are reproduced quantitatively (to within 0.1−0.2 eV) only at a higher theoretical level, such as ROVGF/6-311+G(2df,p), MP4/6-311+G(2df,p), or B3LYP/6-311+G(2df,p). Lower level ab initio calculations, such as ROVGF/3-21G(d) and ROVGF/6-31G(d), reproduce the *trends* in the IPs. The theoretical and experimental data show that the effect of substituents on the HOMO energy of silenes is slightly smaller than in the corresponding alkenes. Disilyl substitution at the doubly bonded Si atom and dimethyl substitution at the doubly bonded C atom raise the HOMO energy, by 0.6 and 0.8 eV, respectively.

Since the first presentation of the evidence for the existence of compounds with a Si=C double bond (silenes) in 1967,[1] there has been growing interest in the physical and chemical properties of these compounds.[2,3] Most known silenes are transient species, and only three stable silenes have so far been characterized by X-ray spectroscopy.[4] Despite the intense activity in this field over the last three decades, very little is known experimentally about the effect of substituents on the electronic structure of silenes.[2,3] A comprehensive theoretical study on the effect of substituents on silenes was published by Apeloig and Karni in 1984,[5] but this study requires updating, in view of the new theoretical methods now available.

One of the most important properties of a molecule is the energy and the shape of its highest occupied molecular orbital (HOMO), because the HOMO is one of the major factors which controls the nucleophilic reactivity of the molecule.[6] According to Koopman's theorem, the HOMO energy is usually equated with the negative value of the first vertical ionization potential (IP₁). To date, the IP values of only two transient silenes and two transient silaaromatics have been reported.[7−9] The photoelectron (PE) spectra of the parent silene H₂-Si=CH₂ (**1**) was measured by Bock et al. in 1981, and its IP₁ value was determined to be 8.9 eV.[8] The PE spectrum of Me₂Si=CH₂ (**2**) was measured by several groups: Gusel'nikov and Nametkin in 1979,[9a] Koeng and McKenna in 1981,[9b] and Dyke et al. in 1982,[9c] producing several different IP₁ values in the range of 7.5−8.3 eV.[10] In comparison with the vast data which are available on the IPs of alkenes, the data for silenes are obviously insufficient and scarce. Also, theoretically there have been no systematic studies of the ionization energy of substituted silenes.[7]

We report here the photoelectron spectra of two silenes, *t*-BuMe₂Si(Me₃Si)Si=Ad (**3**) and (Me₃Si)₂Si=Ad

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(**4**), including the first measurement of the IP value of a stable long-lived silene. Previous measurements were always conducted on silenes generated in situ.[11] This study allows us to evaluate the effect of alkyl and silyl substituents on the IP_1 value of silenes. The experimental study is supplemented by a detailed theoretical study, allowing us to determine the level of theory required for predicting reliably the IP values of other silenes.

Experimental Section

(a) Synthesis. The synthesis of the stable silene **3** was reported previously.[4c] The transient silene **4** was produced by

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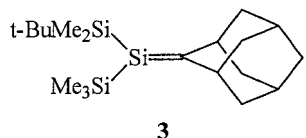
pyrolysis of disilacyclobutane (**6**; eq 1). **6** was synthesized
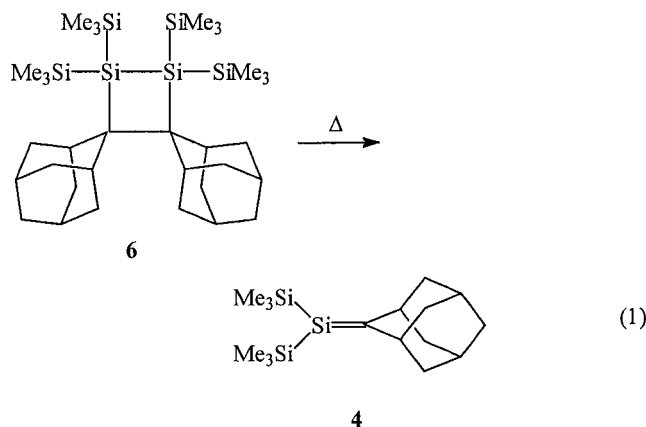
according to the literature procedure.[12] Previous trapping experiments have demonstrated that in benzene at 60 °C thermolysis of **6** results in formation of silene **4** (eq 1).[12,13]

(b) Photoelectron Spectra Measurements. The He I PE spectra were determined on a Leybold Heraeus UPG 200 photoelectron spectrometer and calibrated by using rare gas ionizations (Xe, $^2P_{3/2}$ at 12.13 eV, $^2P_{1/2}$ at 13.43 eV; Ar, $^2P_{3/2}$ at 15.76 eV, $^2P_{1/2}$ at 15.94 eV). A resolution up to 20 meV was achieved. The vapor pressure in the sample inlet system of the PE spectrometer was adjusted between 10^{-2} and 4×10^{-1} mbar. To keep the spectrometer's contamination to a minimum, the gas stream was frozen out directly after the ionization chamber at a copper block cooled with liquid nitrogen.

To record the PE spectra of disilacyclobutane **6**, of its thermolysis product **4**, and of the stable silene **3**, a heated inlet system was used. The vapor pressure in the target chamber of the PE spectrometer was adjusted through variation of the temperature of the heated inlet system. The PE spectra were digitally recorded and processed. Gas-phase thermolysis of

disilacyclobutane **6** was executed in the internal electron collision furnace[14] of the PE spectrometer. The thermolysis equipment was released from chemisorbed water in the system first by heating the system to 800 K, and then a PE spectrum of the **6** as a purity check was registered.

(c) Computational Methods. The GAUSSIAN 98[15] series of programs was used for all calculations. All molecules were fully optimized using hybrid-density functional theory[16] at the B3LYP level[17] with the 6-31G(d) basis set. HF/6-31G(d) geometry optimizations were also carried out, and the resulting HF/6-31G(d) orbital energies were used to estimate the HOMO and LUMO energies. Frequency calculations at the B3LYP/6-31G(d) level and at the HF/6-31G(d) level were performed for all molecules, to characterize the stationary points as minima or saddle points. Calculations using the B3LYP,[17] MP4,[18] and the CCSD(T)[19] method combined with the 6-31G(d) and 6-311+G(2df,p) basis sets were used for estimating the vertical ionization energies. Outer valence Green function (propagator) calculations (OVGF level)[20] with the 3-21G(d), 6-31G(d), and 6-311+G(2df,p) basis sets were also used for estimating the vertical ionization energies (the 3-21G* basis set includes polarization functions only on second-row elements). The frozen-core (fc) approximation was used in all correlated ab initio levels of theory.

Photoelectron Spectra

The PE spectra of **6** and **3** were obtained by heating the sample up to 400 K (Figure 1A and Figure 2). The temperature of the electron collision furnace[14] was increased in intervals of 50 K. At 870 K furnace temperature, only the PE spectrum of the pyrolysis product of **4** was recorded (Figure 1B).

Results and Discussion

We have measured the PE spectra of two silenes: t-BuMe$_2$Si(Me$_3$Si)Si=Ad (**3**) and (Me$_3$Si)$_2$Si=Ad (**4**), and the measured first ionization potentials (IP_1) are (see Figures 1 and 2) 6.9 eV for both **3** and **4**. Thus, the IP_1 values of the silyl-substituted **3** and **4** are ca. 2.0 eV lower than that of the parent silene **1**. The identical IP_1s of **3** and **4** are expected, as these silenes differ only by the fact that the Me$_3$Si substituent in **4** is substituted

(11) The IP_1 value of another stable silene, (Me$_3$Si)$_2$Si=C(OSiMe$_3$)-(1-Ad) (**5**), was mentioned in ref 4a, with reference to a "to be published" paper. No further details were given. The reported value of 7.7 eV[4a] is in disagreement with our calculated values for **5**. The calculations at both the OVGF/3-21G*//B3LYP/6-31G(d) (corrected by 0.5 eV, see discussion) and B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) levels (corrected by 0.2 eV, see discussion) predict the IP_1 value of **5** to be 6.6 eV.

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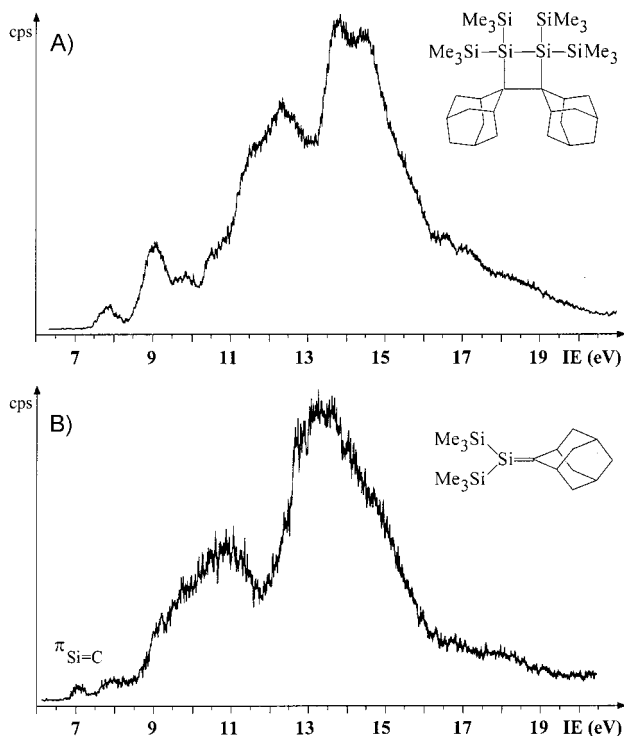
Figure 1. He I photoelectron spectra of (A) disilacyclobutane **6** and (B) its thermolysis product at 870 K.

Figure 2. He I photoelectron spectrum of the stable silene **3**. The assignment of the ionization patterns is based on an MP2/6-31G(d)//B3LYP/6-31G(d) wave function.

by a t-BuMe$_2$Si group in **3**. This supports our assumption that the spectrum measured in the gas-phase pyrolysis of **7** is that of silene **4**.

The measured first IPs of **3** and **4** are much lower than regular IPs for alkenes. Thus, IP$_1$ of ethylene is 10.51 eV[21] and IP$_1$ of (E)-(Me$_3$Si)$_3$CHC=CHC(SiMe$_3$)$_3$ is 7.78 eV,[22] the lowest measured for disubstituted ethylenes. IP$_1$ of (Me$_2$N)$_2$C=C(NMe$_2$)$_2$, a very electron rich alkene, is 5.95 eV.[23]

To understand the IP$_1$s reported above and the effect of substituents on the IP$_1$ of silenes, we have used two computational approches: (1) the calculated HOMO energies; i.e., using Koopman's theorem,[24] and (2) the calculated vertical IP$_1$s, obtained by subtracting the absolute energy of the cation radical held at the geometry of the neutral silene from the absolute energy of the neutral silene (eq 2). The first method is more

$$\text{IP(vertical)} = \text{IP}^v = E(\text{neutral}) -$$
$$E(\text{"frozen" cation radical}) \quad (2)$$

efficient because it involves the calculation of only one species, while the second method requires the calculation of two species.

(a) Energy of the HOMO of Silenes. In contrast to ethylene, the parent silene is strongly polarized, having a positively charged silicon atom and a negatively charged carbon atom (Table 1). The HOMO orbital
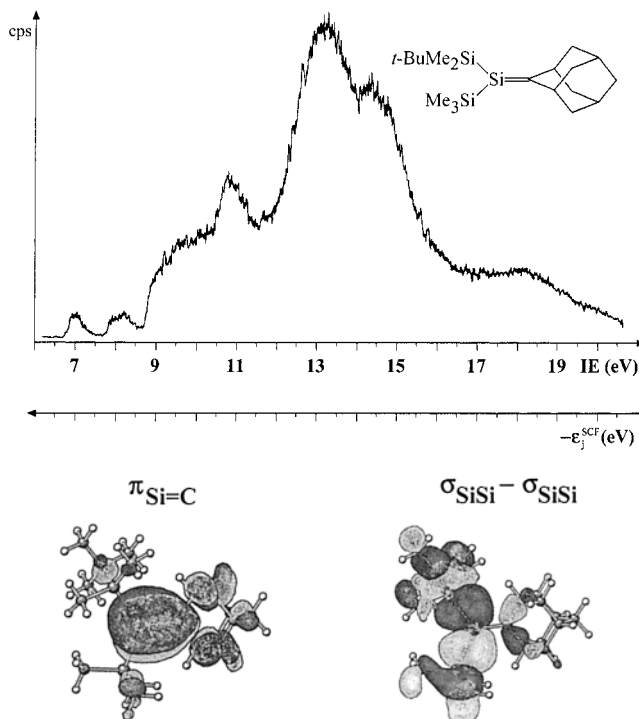
is localized mostly on the carbon atom (Table 1). The high polarity of silenes is one of the reasons for their high reactivity.[5,25] In contrast to H$_2$Si=CH$_2$, in (H$_3$-Si)$_2$Si=CMe$_2$ (**7**) the HOMO is localized mostly on the silicon atom (Table 1). **7** serves as a simple model for silenes **3** and **4**, as it has the same substitution pattern. This substitution pattern results in a reduced polarity of the silene, and it raises the energy of its HOMO.

HF/6-31G(d) energies were used to estimate the energies of the HOMO and LUMO of the silenes of interest, and the IP$_1$s of these silenes were estimated using Koopmans' theorem.[24] The calculated HOMO energies of 12 silenes are given in Table 2. Rigorous DFT orbital energies (i.e., the energies of the Kohn–Sham orbitals) have no physical meaning, and it is therefore an open question if such energies can be used in connection with Koopmans' theorem or for other FMO theory considerations.[16] However, it was recently concluded that "the Kohn–Sham orbitals are physically sound and may be expected to be more suitable for use in qualitative molecular orbital theory than either Hartree–Fock or semiempirical orbitals."[27] Hoffmann et al.[28] have recently demonstrated that, qualitatively, DFT orbitals behave similarly to HF orbitals and they proposed to use a scaling factor for the quantitative interpretation of occupied and virtual DFT orbitals. In agreement with this suggestion, we also find for the set of 12 silenes listed in Table 2 the linear correlation given

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Table 1. Normalized Squares of the Orbital Coefficients (C^2) of the HOMO[a] and Total and π Charges[a] of 1 and 7[b,c]

silene	C^2(Si)	C^2(C)	t(Si)[d]	t(C)[d]	π(Si)	π(C)
$H_2Si=CH_2$ (**1**)	0.42	0.58	0.32 (0.94)	−0.56 (−1.08)	0.13	−0.11
$(H_3Si)_2Si=CMe_2$ (**7**)	0.57	0.43	−0.01 (0.45)	−0.06 (−0.53)	0.01	−0.03

[a] Using Mülliken population analysis. [b] Coefficients and charges on heavy atoms only. [c] At the MP2/6-31G(d)//B3LYP/6-31G(d) level. [d] t = total Mülliken charge. NBO charges[26] are given in parentheses.

Table 2. Calculated HOMO Energies and Experimental IP₁ Values of Silenes and Alkenes (in eV)

		HOMO	
silene/alkene	exptl IP₁	HF[a]	B3LYP[b]
$H_2Si=CH_2$ (**1**)	8.9[8]	−8.46	−6.19
$Me_2Si=CH_2$ (**2**)	8.0[9c]	−7.89	−5.46
(t-BuMe₂Si)Me₃SiSi=Ad (**3**)	6.9	−7.14	−5.03
$(Me_3Si)_2Si=Ad$ (**4**)	6.9	−7.13	−5.02
$(H_3Si)_2Si=CMe_2$ (**7**)		−7.67	−5.62
$(H_3Si)_2Si=CH_2$		−8.39	−6.21
$(Me_3Si)_2Si=CH_2$		−7.89	−5.61
$H_2Si=CMe_2$		−7.67	−5.52
$H_2Si=Ad$		−7.52	−5.40
$Me_2Si=CMe_2$		−7.20	−4.91
$H_2C=CH_2$	10.51[21]	−10.19	−7.26
$Me_2C=CH_2$	9.23[21]	−9.39	−6.52

[a] At the HF/6-31G(d)//HF/6-31G(d) level. [b] At the B3LYP/6-31G(d)//B3LYP/6-31G(d) level.
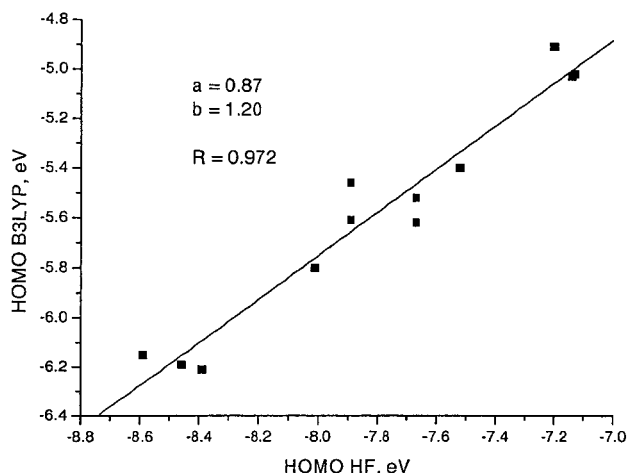
Figure 3. HF/6-31G(d)//HF/6-31G(d) vs B3LYP/6-31G(d)//B3LYP/6-31G(d) HOMO energies for the silenes in Table 2.

in eq 3 ($r = 0.972$) between the HF/6-31G(d) and B3LYP/6-31G(d) HOMO energies (Figure 3). For the HOMO, $a = 0.87$ and $b = 1.20$. Interestingly, the LUMO energies show even a better correlation ($r = 0.984$, $a = 0.84$, $b = −3.02$). The HOMO−LUMO gap gives $r = 0.997$, $a = 0.66$, and $b = −2.15$. We conclude that orbital energies calculated at the B3LYP/6-31G(d) level can be used reliably after appropriate scaling for calculating the HOMO and LUMO energies of silenes.

$$\text{orbital energy[HF/6-31G(d)//HF/6-31G(d)]} =$$
$$a(\text{orbital energy[B3LYP/6-31G(d)//B3LYP/}$$
$$6\text{-31G(d)]}) + b \quad (3)$$

(b) Direct Calculations of the Ionization Energies. First, we have tested the performance of the different theoretical methods for calculating the ionization potentials of several silenes and alkenes using eq

2. The calculated data are presented in Table 3. The calculated "vertical" ionization potentials (IP₁), obtained by eq 2, of ethylene and of the parent silene $H_2Si=CH_2$ at the MP4/6-31G(d) and CCSD(T)/6-31G(d) levels reproduce quite poorly the experimental values, the calculated values being ca. 0.4 eV too low. However, the use of the larger 6-311+G(2df,p) basis set improves the results substantially, so that the deviation from the experimental values is only about 0.1 eV (Table 3). Fortunately, the more efficient DFT B3LYP method with the 6-311+G(2df,p) basis set reproduces reasonably well the ionization potentials of $H_2Si=CH_2$ and of $Me_2Si=CH_2$.[29,30] Thus, the calculated IP₁ value of $Me_2Si=CH_2$ (**2**) is 7.93 eV relative to 8.80 eV for $H_2Si=CH_2$ (**1**), in good agreement with experiment (Table 3).[31]

DFT calculations at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level predict quite accurately IP₁ for the larger silene **3** (6.68 eV calculated vs 6.9 eV experimental). On the basis of these comparisons and the data in Table 3 we propose that the IP₁ values of silenes calculated at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level should be increased by an empirical correction of 0.1−0.2 eV to reach better agreement with experiment.

OVGF calculations[20] have been shown to reproduce accurately ionization potentials of organic molecules[32a] as well as of polysilanes,[32b] and they are also computationally inexpensive, so that relatively large molecules (up to about 20 heavy atoms) can be calculated. When a relatively large basis set is used (6-311+G(2df,p), or AUG-cc-pVQZ), the OVGF method predicts the ionization energy of ethylene and of $H_2Si=CH_2$ with an error of less than 0.2 eV (Table 4). On the basis of these results and other data in Table 4, we propose to calculate the IP₁ values of larger silenes at the OVGF/6-311+G(2df,p)//B3LYP/6-31G(d) level of theory (adding an empirical correction of 0.2 eV) and for even larger systems to use the OVGF/6-31G(d)//B3LYP/6-31G(d) (or OVGF/3-21G(d)//B3LYP/6-31G(d)) level, adding an empirical correction of 0.5 eV.

(c) Substituent Effects on the First Ionization Potential of Silenes. For the discussion of the effect of substituents on the IP of silenes, we will use the calculated vertical ionization potentials, IP₁s, calculated by the OVGF//B3LYP/6-31G(d) method with different

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(32) (a) Applications to predicting IPs of organic molecules and radicals: Danovich, D.; Apeloig, Y.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 321. (b) Applications to predicting IPs of polysilanes: Apeloig, Y.; Danovich, D. *Organometallics* **1996**, *15*, 350.

Table 3. Experimental and Calculated Vertical Ionization Energies (in eV)[a] of Silenes and of Ethylene at Several Theoretical Levels

silene	B3LYP/6-311+G(2df,p)[b]	MP4(SDTQ)/6-31G(d)[b,c]	MP4(STDQ)/6-311+G(2df,p)[b,c]	exptl
$H_2Si=CH_2$ (**1**)	8.80[f]	8.47 (8.49)[d]	8.83 (8.83)[e]	8.9
$Me_2Si=CH_2$ (**2**)	7.93[g]	7.56	7.99	8.0
t-BuMe$_2$Si(Me$_3$Si)Si=Ad (**3**)	6.69			6.9
$(Me_3Si)_2Si=Ad$ (**4**)	6.73			6.9
$(H_3Si)_2Si=CMe_2$ (**7**)	7.57	7.48	7.84	
$H_2C=CH_2$	10.58	10.20 (10.22)[d]	10.65 (10.64)[e]	10.51

[a] Calculated according to eq 2. [b] Using B3LYP/6-31G(d) optimized geometries. [c] The energy of the cation radical was calculated using the spin-projected MP4 method. [d] At the CCSD(T)/6-31G(d) level. [e] At the CCSD(T)/6-311+G(2df,p) level. [f] 8.82 eV[30] at the B3LYP/6-311G(d,p) level. [g] 7.94 eV[29] and 7.90 eV[30] at the B3LYP/6-311G(d,p) level.

Table 4. Calculated[a] and Experimental[b] First Ionization Energies (IP$_1$, eV) of Silenes and Alkenes

silene	3-21G(d)	6-31G(d)	6-311+ G(2df,p)	exptl
$H_2Si=CH_2$ (**1**)	8.38	8.37	8.72[c]	8.9
$Me_2Si=CH_2$ (**2**)	7.45		7.94	8.0
t-BuMe$_2$Si(Me$_3$Si)Si=Ad (**3**)	6.41			6.9
$(Me_3Si)_2Si=Ad$ (**4**)	6.45	6.48		6.9
$(H_3Si)_2Si=CMe_2$ (**7**)	7.40	7.39	7.71	
$(H_3Si)_2Si=CH_2$		8.12	8.46	
$H_2Si=CMe_2$		7.52	7.85	
$(Me_3Si)_2Si=CH_2$		7.48		
$H_2Si=Ad$		7.23		
$(H_3Si)_2Si=Ad$	7.03	6.99		
$Me_2Si=CMe_2$			7.18	
$(Me_3Si)_2Si=CMe_2$	6.77	6.84		
$H_2C=CH_2$		10.05	10.49	10.51
$H_2C=Ad$		8.33		8.86

[a] OVGF(fc) calculations using the B3LYP/6-31G(d) optimized geometries and the indicated basis sets. [b] Experimental values for alkenes are taken from ref 21. Additional relevant values (eV): $Me_2C=CH_2$ (9.22); Me$_3$Si(H)C=CH$_2$ (9.86); Me$_3$Si(H)C=C(H)SiMe$_3$ (9.19). [c] 8.81 eV at the OVGF/AUG-cc-pVQZ level.

basis sets (Table 4) as well as the HOMO energies calculated at the HF/6-31G(d)//HF/6-31G(d) level (Table 2; as discussed above, the HF energies correlate linearly with the DFT orbital energies).

The experimentally measured difference between silene **3** (IP$_1$ = 6.9 eV) and $H_2Si=CH_2$ (IP$_1$ = 8.9 eV) is 2.0 eV. What is the origin of this large difference? To understand this effect, we have to understand the effect of substituents on the IPs of silenes. Let us first analyze the effect of alkyl substitution. Two methyl groups attached to the silicon atom of the silene reduce the IP$_1$ value of $H_2Si=CH_2$ by 0.8 eV (the experimental decrease is 0.9 eV). The calculated difference in the HOMO energy as a result of *gem*-dimethyl substitution is smaller: only 0.6 eV.[33] *gem*-Dimethyl substitution at the carbon side of the Si=C bond reduces its IP$_1$ value by 0.9 eV. In agreement, the HOMO energy is raised by 0.8 eV. Substitution of $H_2Si=CH_2$ by four methyl groups reduces its IP$_1$ value by 1.5 eV, which is close to the additive effect of the methyl substituents when attached to the Si and the C ends of the silene (i.e., by 0.8 + 0.9 = 1.7 eV). The HOMO energy is raised by four methyl groups by 1.3 eV.

In comparison to two *gem*-dimethyl groups, an adamantyl ring attached to the carbon side of the Si=C

bond additionally reduces the ionization potential of silene by 0.4 eV (comparison of $(H_3Si)_2Si=Ad$ with $(H_3Si)_2Si=CMe_2$; Table 4), probably as a result of distortion of the C−C(sp^2)−C angle from 113.6° in $(H_3Si)_2Si=CMe_2$ to 111.3° in $(H_3Si)_2Si=Ad$.[34] The same trend is known experimentally for alkenes; $H_2C=Ad$ has an ionization potential which is 0.4 eV lower than that of $Me_2C=CH_2$ (Table 4).[21] Thus, the 2-adamantalidene substituent at the C side of the silene is responsible for a 1.3 eV decrease in the IP of silenes **3** and **4** relative to **1**. The remaining 0.7 eV is due to the *gem*-disilyl substitution at the silicon end of the silenes. In agreement, the calculations show that two *gem*-Me$_3$Si substituents reduce the IP$_1$ value relative to that of $H_2Si=CH_2$ by 0.9 eV and relative to that of $H_2Si=CMe_2$ by 0.7 eV (Table 4).[35] Thus, the theoretical results are in excellent agreement with experiment. We note that the HOMO of silene **3** is calculated to be by only 1.3 eV higher than in $H_2Si=CH_2$, the effect being significantly lower than the 2 eV found experimentally.

It is of interest to compare the effects of H$_3$Si and Me$_3$Si substituents on the IP value, as the smaller H$_3$Si group is often used in calculations as a model for the experimentally used Me$_3$Si group. The calculated ionization potential of $(H_3Si)_2Si=CMe_2$ is 1 eV smaller than that of $H_2Si=CH_2$ (in $(H_3Si)_2Si=CH_2$ it is 0.3 eV lower than in $H_2Si=CH_2$). In $(Me_3Si)_2Si=CMe_2$ the first ionization potential is 0.6 eV lower than that of $(H_3Si)_2Si=CMe_2$ (1.5 eV lower than in $H_2Si=CH_2$). The same is true for the IPs of $(H_3Si)_2Si=CH_2$ vs $(Me_3Si)_2Si=CH_2$.

In conclusion, while the calculated IPs nicely reproduce the effect of substituents on the IPs of silenes, changes in the HOMO energies (at HF/6-31G(d)//HF/6-31G(d)) as a result of substitution reproduce only partially the full substituted effect.

(d) Second Ionization Potentials of Silenes 3 and 4. The second band (IP$_2$) of the photoelectron spectrum of $H_2Si=CH_2$ is very high-lying, appearing at ca. 12.5 eV.[8] In contrast, for silenes **3** and **4** we find a relatively low lying second band around 8.0 eV (Table 5). Calculations show that this band is due to the removal of an electron from the HOMO-1 orbital, which in **3** and **4** is mostly a σ(Si−Si) orbital. This interpretation is consistent with the first IP of Me$_3$SiMe$_2$SiSiMe$_3$ at 8.19 eV.[7a] The calculations reproduce IP$_2$ very nicely; i.e., 8.0 eV for **4** (at ROVGF/6-31G(d)).

(33) Experimentally, *gem*-dimethyl groups lower the IP$_1$ value of ethylene by 1.3 eV (Table 2), while according to the calculated HOMO energies, the difference is only 0.8 eV. Thus, the calculated HOMO energies underestimate the *gem*-dimethyl effect for both ethylene and silene.

(34) Substitution of two *gem*-methyl groups at C in $H_2Si=CMe_2$ by an adamantyl ring raises the HOMO energy by 0.15 eV (Table 2).
(35) Experimentally one and two Me$_3$Si groups reduce the IP$_1$ value of ethylene by ca. 0.7 and 1.3 eV, respectively (Table 4).[21]

**Table 5. Calculated[a] and Experimental Second
Ionization Potentials (IP$_2$, eV) of Silenes**

silene	exptl	3-21G(d)	6-31G(d)
t-BuMe$_2$Si(Me$_3$Si)Si=Ad (**3**)	8.0	7.73	
(Me$_3$Si)$_2$Si=Ad (**4**)	8.0	7.86	8.00
(H$_3$Si)$_2$Si=CMe$_2$ (**7**)		9.38	9.42[b]

[a] Using the OVGF(fc) method with the indicated basis sets and
B3LYP/6-31G(d) optimized geometries. [b] 9.75 eV at the OVGF(fc)/
6-311+G(2df,p) level.

Conclusions

The PE spectra of two new silenes were measured,
including for the first time that of a stable silene. These
measurements were supplemented by the first system-
atic theoretical study of the IPs of a variety of silenes.
MP4, B3LYP, and OVGF calculations with the 6-311+
G(2df,p) basis set reproduce accurately (up to 0.2 eV)
the first ionization potential of the parent silene H$_2$Si=
CH$_2$. The B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level
of theory can be used to calculate reliably the IP$_1$ values
of larger silenes. The effect of alkyl and silyl substitu-
ents on the IP$_1$ values of silenes is slightly smaller than
for alkenes. For a set of 12 silenes, we find for the
energies of the HOMO and LUMO a linear correlation
between the calculated HF energies and B3LYP ener-
gies, suggesting that B3LYP energies can be used for

estimating the HOMO and LUMO orbital energies of
other silenes.

The ionization potential of **3** of 6.9 eV is the lowest
yet measured for a silene, and it is 2 eV lower than that
of H$_2$Si=CH$_2$. The calculations show that three factors
contribute to this very low IP (high HOMO energy): (a)
alkyl substitution at the carbon atom of the silene
contributes ca. 0.9 eV; (b) the adamantyl ring adds an
additional 0.4 eV; (c) the *gem*-Me$_3$Si substitution at the
silicon end of the silene contributes ca. 0.7 eV.

The very low IP$_1$ and the high HOMO energy of silene
3 suggest that it should exhibit a very high nucleophi-
licity and should be easily oxidized. We are currently
studying the electrochemistry of silene **3**.