Organometallics **1999,** *18,* 4795−4799

Gas-Phase Generation and Photoelectron Spectra of Dimethyl- and Diisopropylsilanethiones[1]

Anna Chrostowska, Sylvie Joantéguy, and Geneviève Pfister-Guillouzo*

Laboratoire de Physico-Chimie Moléculaire, UMR CNRS 5624, Université de Pau et des Pays de l'Adour, 64000 Pau, France

Valérie Lefèvre and Jean-Louis Ripoll

Laboratoire de Chimie Moléculaire et Thioorganique, URA CNRS 480, ISMRA, Université de Caen, 14050 Caen, France

Received March 9, 1999

The flash vacuum thermolysis of propargylthio- and allylthiodialkylsilanes, potential precursors of unhindered silanethiones ($R_2Si{=}S$), has been investigated by photoelectron spectroscopy. This technique allowed us to characterize in the gas phase two very reactive species of this series, dimethyl- and diisopropylsilanethione. According to the values observed for the ionization potentials associated with the ejection of a π electron, the $\pi_{Si=S}$ double bond is energetically more stable than the earlier studied Si=N double bond.

As unstabilized heterosilenes[2] are highly reactive species, extreme conditions are required for their characterization in the monomeric state. Our solution is a combination of flash vacuum thermolysis (FVT) and ultraviolet photoelectron spectroscopy (PES).[3] We have shown that this is the most effective method to characterize several reactive silanimines[4a,b] and silylidenephosphanes[5] in the gas phase. We have now undertaken the identification of simple silanethiones, analogues of thiformaldehyde molecule,[6] which are rare species owing to their kinetic instability. Only two silanethiones, stabilized either by intramolecular coordination or by bulky substituents, have ever been described.[7]

We have investigated the possibility of synthesizing and characterizing dimethylsilanethione (**1**) and diisopropylsilanethione (**2**) by a retro-ene reaction. The precursors are propargylthio- and allylthiodialkylsilanes (compounds **1b**, **1c**, **2b**, **2c** in Scheme 1), the propargylthio derivatives being preferred because of their lower temperatures of decomposition. One of us[8] has already reported the characterization by PES of silanethione **1**, generated from the corresponding cyclotrimer, but these results have not been confirmed by complementary studies.

Since thermolysis can lead to monomeric and dimeric species, these experimental data have been compared with the results of a complete quantum study of the ionic states of these two species. Ab initio calculations[9] were undertaken at the HF/6-31G(d) MP2[10] level as well as with density functional theory (DFT)[11] using the B3LYP[12] method in conjunction with the 6-31G(d) basis set.

Experimental Results

Preparation of Compounds 1b−2c. Precursors **1b**−**2c** were prepared by reaction of chlorodimethyl- or chlorodiisopropylsilane with 2-propyne- or 2-propene-1-thiol using either *n*-butyllithium (for **1b**, **1c**) or triethylamine (for **2b**, **2c**) to deprotonate the thiols.

Propargylthiodimethylsilane 1b has been already described; see ref 13.

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* Corresponding author. E-mail: genevieve.pfister@univ-pau.fr.

(1) Application of photoelectron spectroscopy to molecular properties. Part 54. Part 53: Arsenic Low Coordination Chemistry: Studies of Aminoiminoarsanes Using UV Photoelectron Spectroscopy and Density Functional Theory. Miqueu, K.; Sotiropoulos, J. M.; Pfister-Guillouzo, G.; Romanenko, V. D. *J. Am. Chem. Soc.*, submitted.

(2) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627−1650.

(3) .Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427−444.

(4) (a) Métail, V.; Joantéguy, S.; Chrostowska-Senio, A.; Pfister-Guillouzo, G.; Systermans, A.; Ripoll, J. L. *Inorg. Chem.* **1997**, *36*, 1482−1487. (b) Métail, V.; Joantéguy, S.; Chrostowska-Senio, A.; Pfister-Guillouzo, G.; Systermans, A.; Ripoll, J. L. *Main Group Chem.* **1997**, *2*, 97−106.

(5) Lefèvre, V.; Ripoll, J. L.; Dat, Y.; Joantéguy, S.; Métail, V.; Chrostowska-Senio, A.; Pfister-Guillouzo, G. *Organometallics* **1997**, *16*, 1635−1640.

(6) Solouki, B.; Rosmus, P.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 6054−6055.

(7) (a) Arya, P.; Boyer. J.; Carré, F.; Corriu. R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016−1018. (b) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki. R. *J. Am. Chem. Soc.* **1994**, *116*, 11578−11579.

(8) Guimon, C.; Pfister-Guillouzo, G.; Lavayssiere, H.; Dousse, G.; Barrau, J.; Satgé, J. *J. Organomet. Chem.* **1983**, *249*, 17−20.

(9) Ab initio calculations were performed with the Gaussian 94 package of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Ragavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chem, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Drefrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(10) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *62*, 2257. (b) Hariharam, P. C.; Pople, J. A. *Theor. Chim. Acta* **1979**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

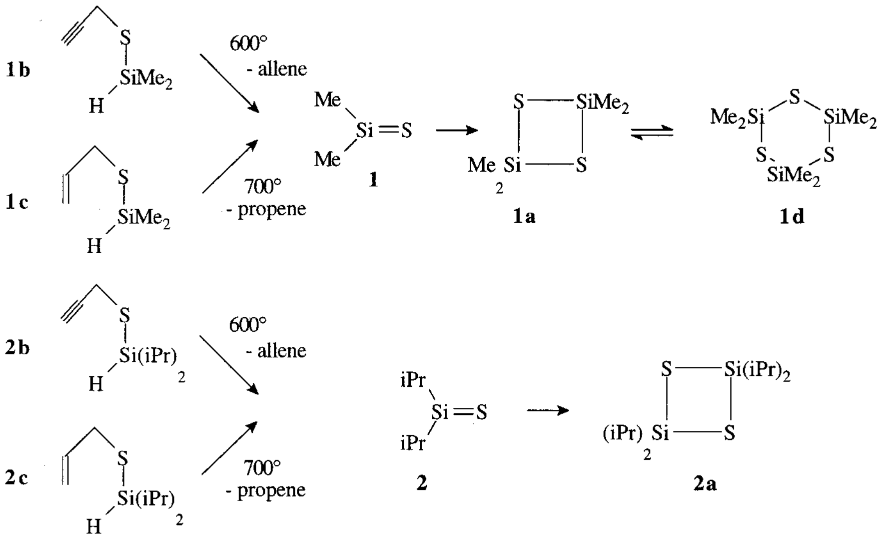
(11) (a) March, N. H. *Electron Density Theory of Atoms and Molecules*; Academic Press: San Diego, CA, 1992. (b) Labanowski, J. K., Andzelm, J. W. *Density Functional Methods in Chemistry*; Springer-Verlag: New York, 1991. (c) Parr, R. G.; Yang, W. *Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(12) (a) Becke, A. D. *Phys. Rev.* **1986**, *A33*, 2786. (b) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(13) Lefèvre, V.; Dat, Y.; Ripoll, J. L. *Tetrahedron Lett.* **1996**, *37*, 7017−7018.

10.1021/om9901729 CCC: $18.00
Publication on Web 10/15/1999

Scheme 1



Allylthiodimethylsilane 1c. *n*-Butyllithium (1.6 M in hexane, 43.1 mL, 68.9 mmol) was added slowly, at − 30 °C under nitrogen, to a stirred solution of commercial 80% 2-propene-1-thiol (5.79 g, 62.6 mmol) in anhydrous ether (40 mL). After warming to room temperature followed by cooling to −50 °C, chlorodimethylsilane (6.51 g, 68.9 mmol) was added dropwise. The mixture was allowed to warm to room temperature. After 1 h, the solids were removed by filtration under nitrogen, the solvents were evaporated under vacuum, and the residue was purified by distillation to give compound **1c**, bp 60 °C/40 Torr (5.78 g, 70%). ^{1}H NMR (CDCl$_3$): δ 0.35 (6 H, d, 3.4 Hz), 3.16 (2 H, dm, 6.9 Hz), 4.68 (1 H, hept, 3.4 Hz), 4.99 (1 H, dt, 9.9 and 1.5 Hz), 5.12 (1 H, dt, 16.9 and 1.5 Hz), 5.84 ppm (1 H, ddt, 16.9, 9.9 and 6.9 Hz). ^{13}C NMR (CDCl$_3$): δ_C −1.7 (2 C), 30.5, 116.0, 137.4 ppm. Anal. Calcd for $C_5H_{12}SSi$: S, 24.25. Found: S, 23.96.

Propargylthiodiisopropylsilane 2b. A solution of 2-propyne-1-thiol (1.97 g, 27.4 mmol, prepared according to ref 14) in anhydrous ether (50 mL) was stirred at 0 °C under nitrogen. Triethylamine (3.05 g, 30.2 mmol) and then chlorodiisopropylsilane (4.55 g, 30.2 mmol) were added slowly. After heating at reflux (6 h), evaporation of solvents, and removal of salts by cryogenic transfer under vacuum, compound **2b** was purified by distillation, bp 120 °C/30 Torr (3.62 g, 71%). ^{1}H NMR (CDCl$_3$): δ 1.05 (12 H, d, 3.7 Hz), 1.14 (2 H, m), 2.25 (1 H, t, 2.7 Hz), 3.29 (2 H, d, 2.7 Hz), 4.29 ppm (1 H, t, 2.0 Hz). ^{13}C NMR (CDCl$_3$): δ_C 17.3, 27.0 (2 C), 28.2 (4 C), 70.9, 82.0 ppm. High-resolution mass spectrum, *m*/*z*: calcd for $C_9H_{17}SSi$ (M$^+$ − H), 185.0977; found, 185.0978.

Allylthiodiisopropylsilane 2c. **2c** was prepared as for **2b**, with commercial 2-propene-1-thiol (2.53 g, 27.4 mmol) in place of 2-propyne-1-thiol, bp 82 °C/12 Torr (3.30 g, 64%). ^{1}H NMR (CDCl$_3$): δ 1.01 (2 H, d, 3.0 Hz), 1.04 (12 H, d, 3.0 Hz), 3.15 (2 H, dt, 6.8 and 1.5 Hz), 4.14 (1 H, t, 1.8 Hz), 4.97 (1 H, dt, 9.9 and 1.5 Hz), 5.09 (1 H, dt, 16.9 and 1.5 Hz), 5.82 ppm (1 H, ddt, 16.9, 9.9 and 6.8 Hz). ^{13}C NMR (CDCl$_3$): δ_C 12.8 (2 C), 18.3 (4 C), 31.2, 115.9, 136.6 ppm. Anal. Calcd for $C_9H_{20}SSi$: S, 17.02. Found: S, 16.54.

FVT−High-Resolution Mass Spectrometry (HRMS) Coupling. The FVT of precursors **1b**−**2c** has been investigated in conjunction with HRMS. The results are summarized in Scheme 1.

Upon FVT at 600 °C, **1b** gave, in addition to allene, cyclodimer **1a** (M$^+$ 179.9908, calcd 179.9918); monomeric dimethylsilanethione **1** was not observed by this method. Compound **1c**, when thermolyzed at 700 °C, gave the same results, with propene instead of allene. On the other hand, the FVT of precursors **2b** and **2c** at 600 and 700 °C, respectively, yielded besides cyclodimer **2a** (M$^+$ − i-Pr 249.0612, calcd 249.0623) the monomeric diisopropylsilanethione **2**, characterized by its molecular peak at *m*/*z* 146.0512 (calcd 146.0585). The structure of cyclodimers **1a** and **2a** was confirmed by their NMR spectra recorded in CDCl$_3$ [**1a**: ^{1}H NMR δ 0.77 ppm; ^{13}C NMR δ_C 10.1 ppm (**1a** gave slowly in solution, as previously described,[15] cyclotrimer **1d**). **2a**: ^{1}H NMR δ 1.14 (24 H, d, 6.7 Hz), 1.27 ppm (4 H, hept, 6.7 Hz); ^{13}C NMR δ_C 13.3 (4 C), 17.2 ppm (8 C)].

FVT−PES Coupling, Photoelectron Spectra. The photoelectron spectra were recorded on a Helectros 0078 spectrometer using a short-path coupling with the FVT oven, as previously described.[4,5]

FVT of 1b. The photoelectron spectrum of precursor **1b** (Figure 1a) shows a first band at 9.0 eV, followed by a broad band at 10.4 eV, and a large signal between 13 and 15.5 eV. The first band corresponds to the ionization of the sulfur lone pair and that at 10.4 eV to the ionization of the electrons of the $\pi_{C\equiv C}$ degenerate orbitals.

A broadening of the first band and the allene ionizations at 10.0 and 10.6 eV are observed from 600 °C in the FVT of **1b** (Figure 1b). The FVT was, however, incomplete, and the new spectrum (Figure 1c) was obtained by subtraction from the measured PE of the spectrum of **1b**. It shows a weak first band at 8.7 eV and a stronger one at 9.2 eV.

FVT of 1c. The spectrum of **1c** (Figure 2a) shows a first band at 8.7 eV followed by two broad bands at 9.8 and 11.3 eV, attributed to the ionizations of the sulfur lone pair and of the electrons of the $\pi_{C=C}$ orbitals. A new band at 9.2 eV and the ionization of propene at 10.0 eV are observed from 600 °C (Figure 2b). However, the new bands cannot be definitely assigned, due to the close ionizations of the unconverted precursor **1c** still present.

FVT of 2b. The spectrum of **2b**, shown in Figure 3a (8.7, 10.4, and 11.8 eV, interpreted as for **1b**), appears to be strongly modified from 600 °C (Figure 3b). The first band of **2b** at 8.7 eV is no longer present, indicating a complete cleavage of the precursor. Three new ionizations at 8.5, 8.9, and 9.3 eV are observed, accompanied by those of allene at 10.0 and 10.6 eV.

FVT of 2c. The spectrum of **2c** (8.5 and 9.9 eV, Figure 4a) is modified from 600 °C (Figure 4b). A first band at 8.5 eV is still present, with a new ionization at 8.9 eV and one at 10.0 eV (propene). The spectrum obtained (Figure 4c) by subtraction of that of the propene product, as well as the ionizations of **2c**

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(14) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988.

(15) Moedritzer, K. *J. Organomet. Chem.* **1970**, *21*, 315−320.

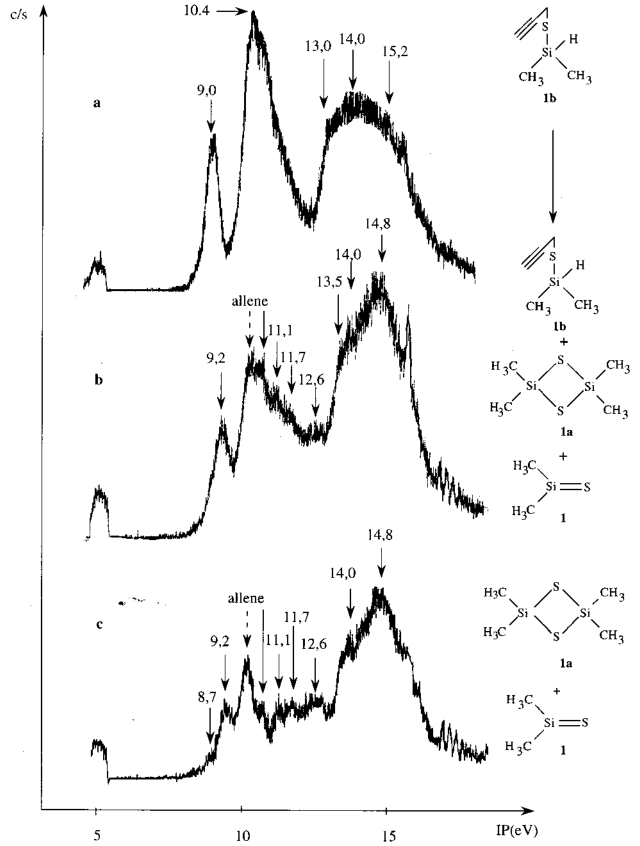


Figure 1. Photoelectron spectra of (a) **1b** and (b) **1b** at 600 °C and (c) spectrum **b** − spectrum **a**.

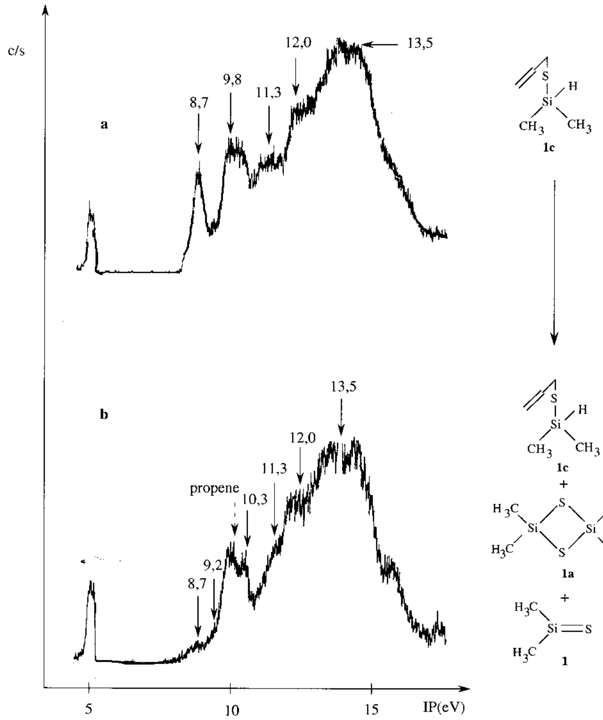


Figure 2. Photoelectron spectra of (a) **1c** and (b) **1c** at 600 °C.

at 8.5 and 9.9 eV, consists of two bands at 8.4 and 8.9 eV and a shoulder at 9.3 eV.

It appears from the three new ionizations observed in the spectra at 600 °C that the involved retro-ene reaction, confirmed by the presence of allene or propene, should lead to two products, most likely the expected silanethione **2** and its

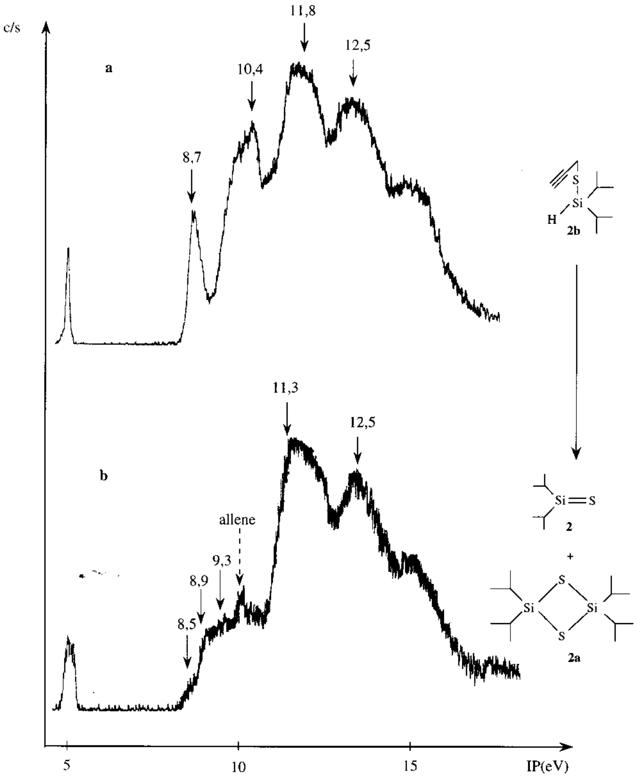


Figure 3. Photoelectron spectra of (a) **2b** and (b) **2b** at 600 °C.

cyclodimer **2a**. A calculation of the energies for the ionic states of these species was thus necessary for the interpretation of the above experimental data.

Theoretical Results

The energies of the ionic states of **1** and **2** have been calculated at the MP2 level and/or using the DFT B3LYP with the 6-31G(d) basis set. The reliability of the B3LYP method has been checked by calculating the energies of the thioformaldehyde (**3**) ionic states. Also, we broadened the experiment−theory comparison with the calculation of the energies of the ionic states of dimethylgermanethione (**4**), previously generated by FVT of its cyclotrimer **4d** and characterized by two ionizations at 8.6 and 9.55 eV (8.6 and 10 eV for its cyclodimer).[8]

Silanethiones 1 and 2. The geometries of silanethione **1**, optimized by the MP2 and B3LYP methodologies [6-31G(d) basis set, lengths in angströms, angles in degrees] are given in Scheme 2.

The Si═S double bond length was calculated to be 1.958 and 1.966 Å, respectively, using the MP2 and B3LYP methods. These values are in agreement with the length of the Si═S double bond (1.95 Å) determined by X-ray analysis of a stable silathione[7b] Tbt(Tip)Si═S with the two sterically bulky protecting groups, namely, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-tris(isopropyl)phenyl (Tip).

The ionic states energies calculated for **1**, **2**, **3**, and **4** are reported in Table 1. The gap between the experimental and theoretical values remains fairly low (0.2 eV) for **3** and **4**.

The spectra obtained by FVT of compounds **2b** and **2c** show common ionizations at 8.4−8.5, 8.9, and 9.3

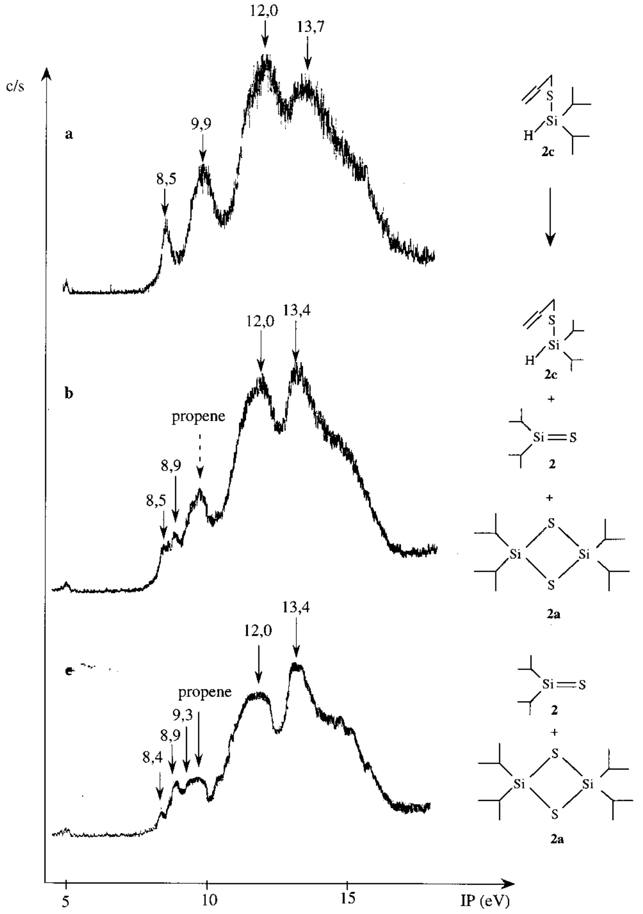
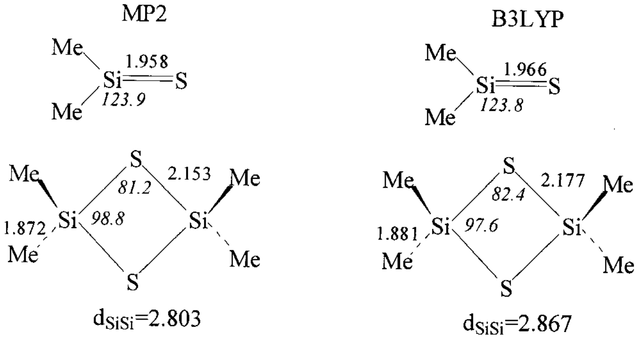


Figure 4. Photoelectron spectra of (a) **2c** and (b) **2c** at 600 °C and (c) spectrum **b** − spectrum **a**.

Scheme 2



eV, whereas **1b** and **1c** present an ionization at 9.2 eV with a shoulder at 8.7 eV.

The formation of diisopropylsilanethione **2** is confirmed by comparison of the experimental data with the theoretical values. The n_S orbital ionization, calculated at 8.20 eV, is observed at 8.4−8.5 eV, and that of the $\pi_{Si=S}$ orbital, calculated at 9.10 eV, is observed at 9.3 eV. These results are in agreement with those obtained by mass spectrometry, indicating the formation only of the monomeric silanethione in the FVT of diisopropyl precursors.

In the FVT of **1b**, the weak band at 8.7 eV could be associated with the presence of small amounts of monomeric dimethylsilanethione **1**. The second ionization of **1**, expected at 9.6−9.7 eV, should be hidden by that of allene.

Table 1. Vertical Ionization Potentials Calculated at the MP2 Theory Level and B3LYP Method with the 6-31G(d) Basis Set and Experimental Values of 3, 1, 2, and 4

	A′(n_S)	A″ ($\pi_{X=S}$)
	H_2C=S, **3**	
MP2	9.31	11.40
B3LYP	9.27	11.73
experimental	9.4	11.8
	Me_2Si=S, **1**	
MP2	8.41	9.17
B3LYP	8.64	9.41
experimental	8.7	9.6−9.7 (estimated)
	$^iPr_2Si$=S, **2**	
B3LYP	8.20	9.10
experimental	8.4−8.5	9.3
	Me_2Ge=S, **4**	
B3LYP	8.41	9.33
experimental	8.6	9.55

Table 2. Vertical Ionization Potentials of the Dimer 1a Calculated at the MP2 Theory Level and B3LYP Method with 6-31G(d) Basis Set

	MP2	B3LYP
$b_{3g}(n^-_S)$	8.59	8.54
$b_{2u}(n^+_S)$	8.79	8.71

To confirm the assignment of the ionizations observed at 9.2 (FVT of **1b**, **1c**) or 8.9 eV (FVT of **2b**, **2c**) to the corresponding cyclodimers **1a** and **2a**, we have also theoretically investigated cyclodisilthiane **1a**.

Tetramethylcyclodisilthiane 1a. The structure of **1a** has been determined by X-ray analysis.[16] This structure has been shown to be planar (D_{2h} symmetry), with a Si−S bond length of 2.15 Å and SiSSi and SSiS angles of 82.5° and 97.5°, respectively. The distance between both silicon atoms is of 2.837 Å.

The geometrical parameters of **1a**, optimized using the 6-31G(d)/MP2 and B3LYP methods, are reported in Scheme 2. The SiSSi and SSiS angles obtained by both methods are in good agreement with the experimental angles. The Si−S bond length is overestimated by 0.025 Å using the B3LYP formalism. On the other hand, that obtained by the MP2 method is in quite good agreement with the experimental value. The Si−Si distance, when calculated by the MP2 and B3LYP methods, is found to be shorter or longer than the experimental one by ca. 0.03 Å, respectively.

On the whole, the theoretically obtained geometrical parameters of **1a** are in fairly good agreement with the results of the X-ray structure determination.

The calculated energies of the two first ionic states of **1a** are respectively related to the ejection of one electron from the antisymmetrical b_{3g} (n^-_S) and symmetrical b_{2u} (n^+_S) combinations of the sulfur lone pairs (Table 2). The small gap of 0.2 eV (MP2) or 0.17 eV (B3LYP) calculated for these ionizations leads one to expect a single band.

In the case of hexamethyldisilazane, the calculated values of ionization energies obtained by the MP2 and B3LYP methods are lower by ca. 1 eV than the reported experimental ones.[4a] The ionizations of cyclodimer **1a** are thus expected beyond 9 eV, and the band observed

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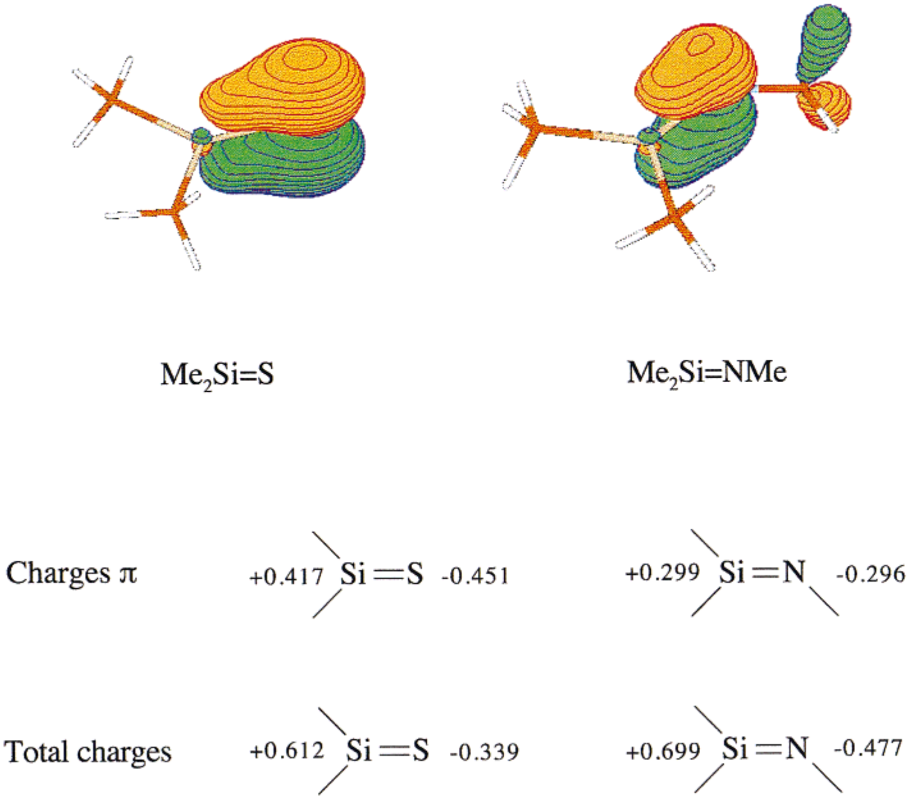
(16) Schklower, W. E.; Strutschkow, Y. T.; Gusel'nikov, L. E.; Wolkowa, W. W.; Awakyan, W. G. *Z. Anorg. Allg. Chem.* **1983**, *501*, 153−156.

Scheme 3. Graphic Visualization of the Molecular Orbitals $\pi_{Si=X}$



at 9.2 eV in the FVT of **1b** and **1c**, and at 8.9 eV for **2b** and **2c**, should be due to the dimeric species **1a** and **2a**.

The FVT of **1b** and **1c** appears thus to give mainly cyclodisilthiane **1a**, the band observed at 10.3 eV in the FVT of **1c** being associated with the ionizations of the σ_{Si-S} orbitals of **1a**. The FVT of **2b** and **2c** leads to a mixture of monomeric silanethione **2** and its cyclodimer **2a**.

Conclusion

This investigation points out the difficulty of characterizing the Si=S group in the $R_2Si=S$ monomer. This very likely is due in part to its facile dimerization, but mainly to the thermodynamic stability of the cyclodisilthiane ring (unlike the cyclodisilazane and cyclodisilaphosphane). Thus, according to the values observed for the ionization associated with the ejection of a π electron, the $\pi_{Si=S}$ double bond is energetically more stable than the Si=N double bond (8.3 eV for $Me_2Si=NMe$). This observation agrees with the estimation of Schleyer,[17] who proposed a correlation between the π bond energy and electronegativity ($S = 2.5$, $N = 3.0$). It seems essential to add to this a more efficient overlap for sulfur ($3p\pi-3p\pi$) than for nitrogen ($3p\pi-2p\pi$), as shown in Scheme 3 by the graphical representation of the $\pi_{Si=X}$ orbitals and the π charges calculated in both cases.

Acknowledgment. We thank IDRIS (CNRS, Orsay) for calculation facilities and Dr Gijs Schaftenaar for allowing us to use his graphical program Molden.[18]

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[17] Schleyer, P. von R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105−2109.

[18] See: http://www-srs.caos.kun.nl/schaft/molden.