Flash Vacuum Thermolysis Synthesis of New Reactive Compounds Containing a Silicon−Heteroatom Double Bond

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Keywords: Flash vacuum thermolysis / Gas phase chemistry / Gas phase spectrometry / Photoelectron spectrometry / Silicon

Flash vacuum thermolysis (FVT) afforded access to various unstable heterosilenes belonging to the silanimine ($R_2Si=NR'$), phosphasilene ($R_2Si=PR'$) and silanethione ($R_2Si=S$) families. These extremely reactive monomeric compounds have been characterized in the gas phase by direct coupling of FVT with mass, millimetre wave and, particularly, photoelectron spectrometry.

Introduction

Since the first evidence, reported in 1966 by Gusel'nikov, appeared concerning the existence of dimethylsilene, the field of double-bonded silicon species has undergone considerable expansion and has been extensively reviewed.[1] The silicon π double bond is weak,[2] and so many of the known compounds of this series, starting with tetramesityldisilene (R. West, 1981), are stabilized by steric or electronic effects.[3] In the years since, several Si=N double-bonded compounds have been discovered, such as 1,1-di-*tert*-butyl-*N*-(tri-*tert*-butylsilyl)silanimine (N. Wiberg, 1985)[4] and 1,1-diisopropyl-*N*-(2,4,6-tri-*tert*-butylphenyl)silanimine (U. Klingebiel, 1986),[5] both stable at room temperature, and trimesitylsilanimine (R. West, 1986),[6] stable below −120 °C. During the same period, several phosphasilenes, strongly stabilized by bulky groups (up to 60 °C in benzene solution), have been reported by F. Bickelhaupt.[7] On the other hand, nonstabilized silenes or heterosilenes are highly reactive species, and extreme conditions are required for their synthesis and to allow their characterization as monomers. Apart from photochemical generation and IR/UV identification in a matrix, they have been obtained in many cases by thermolytic methods and analyzed directly in the gas phase by mass (MS), photoelectron (PES) and millimetre wave (MWS) spectrometry.[1,8]

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Jocelyne Levillain was born in Saint-Lô, France in 1963. She studied chemistry at the University of Caen and completed in 1994 her Ph.D. thesis on "bifunctional N-substituted 4-alkylidenequinolines by an Eschenmoser approach" under the supervision of Dr. M. Vazeux. After six months at the Royal College Surgeon in Ireland as a postdoctoral co-worker (with Prs. K. Nolan and D. Fitzgerald), she returned to Caen in J. L. Ripoll's group where she is now involved in the chemistry of reactive thioketones and silanethiones generated by flash vacuum thermolysis. She is presently Maître de Conférences at the University of Caen.

Geneviève Pfister-Guillouzo, born in 1936 in Saint-Brieuc, France, entered the french Centre National de la Recherche Scientifique (CNRS) in 1956. She received her Ph.D. at the University of Caen in 1963 for her work on thio-organic compounds in the research team of Pr. N. Lozac'h. She moved then to the University of Pau and developped her own research in physical organic and theoretical chemistry. G. Pfister-Guillouzo has been appointed as a Directeur de Recherche by the CNRS in 1972 and her activity moved towards UV photoelectron spectrometry and its applications to the study and characterization of highly reactive molecules. Her present scopes of research are heterocumulenes and low coordinated heteroatomic compounds of groups 14 and 15.

Jean-Louis Ripoll, born in Anguerny, France in 1935, prepared and submitted in 1967 at the University of Caen, under the supervision of Pr. J. M. Conia, a Ph.D. thesis on the chemistry of small ring compounds. After a one-year post-doctoral stay in the group of Pr. J. Meinwald at Cornell University, U.S.A., he joined the CNRS and in 1972 launched out into his present research field, devoted to the generation of reactive organic and organometallic species by flash vacuum thermolysis and spectrometric characterization. He is Directeur de Recherche at the CNRS since 1976.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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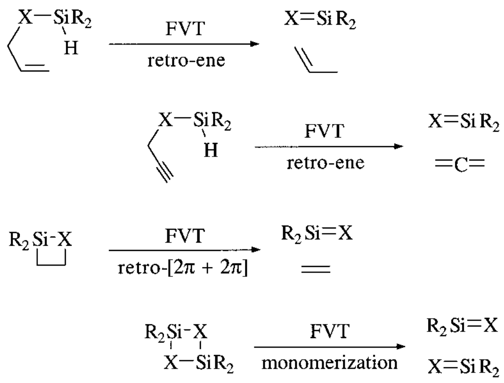
The coverage of a comprehensive review including silanones ($R_2Si=O$, not considered here), silanimines ($R_2Si=NR'$), phosphasilenes ($R_2Si=PR'$) and silanethiones ($R_2Si=S$), the main representatives of the class of heterosilenes, extends to the end of 1986.[1c] The following, nonexhaustive references refer to more recent works or reviews concerning the synthesis and reactivity of stabilized silanimines,[9] phosphasilenes[10] and silanethiones.[11] Here, we report our results, and some of other researchers, concerning the synthesis and characterization of nonstabilized heterosilenes of these three types ($R_2Si=X$ with X = NR′, PR′, S). These compounds, in addition to their fundamental importance, are of general interest as intermediates in the field of organic synthesis,[1,12] as well as in the technologies of high temperature materials (e.g., silicon nitrides or carbonitrides)[13] and chemical vapour deposition.[14] Also, the unsubstituted representatives (R, R′ = H) can be expected to exist in the interstellar medium or in circumstellar shells.[15]

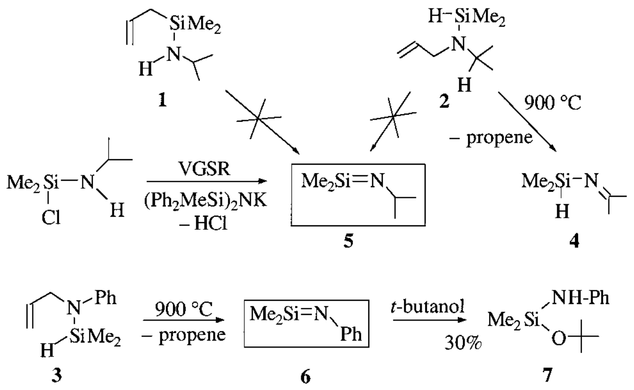
The low pressures and short transit times of flash vacuum thermolysis (FVT),[16] used in conjunction with the above-mentioned gas-phase spectrometric techniques, have the advantage that they minimize the chance of intermolecular or catalytic reactions and thus allow the direct identification of reactive, short-lived monomeric species such as the heterosilenes considered here. For the same reasons, the chosen precursors should afford these species by monomolecular thermal fragmentation. *Retro*-ene reactions,[17] [2π + 2π] cycloreversions, and cleavages of the corresponding cyclic dimers have proven particularly efficient for these purposes (Scheme 1).



Scheme 1

Silanimines ($R_2Si=NR'$)

The generation of nonstabilized silanimines was first undertaken by *retro*-ene reaction, based on the previously reported synthesis of dimethylsilanone by FVT of allyloxydimethylsilane.[18] The required precursors **1**, **2** and **3** were synthesized by reaction of the appropriate chlorosilanes and amines. Upon FVT, compounds **1** (thermally too stable) and **2** (which more easily gave the *N*-silylated imine **4**), proved to be poor precursors of *N*-isopropylsilanimine **5**. Compound **5** was, however, obtained[19] by dehydrochlorination of the corresponding chlorosilanamine under VGSR (vacuum gas-solid reaction) conditions[20] (Scheme 2). On the other hand, FVT of **3** yielded, as expected, *N*-phenylsilanimine **6**, characterized in the gas phase by FVT/HRMS, and by its adduct **7** with *tert*-butyl alcohol.[19] The relative ease of formation of a C=N double bond, compared to an Si=N one, as observed in the case of **2**, has been also exploited in the synthesis by FVT of the reactive methanimine $H_2C=N-SiMe_2H$.[21]

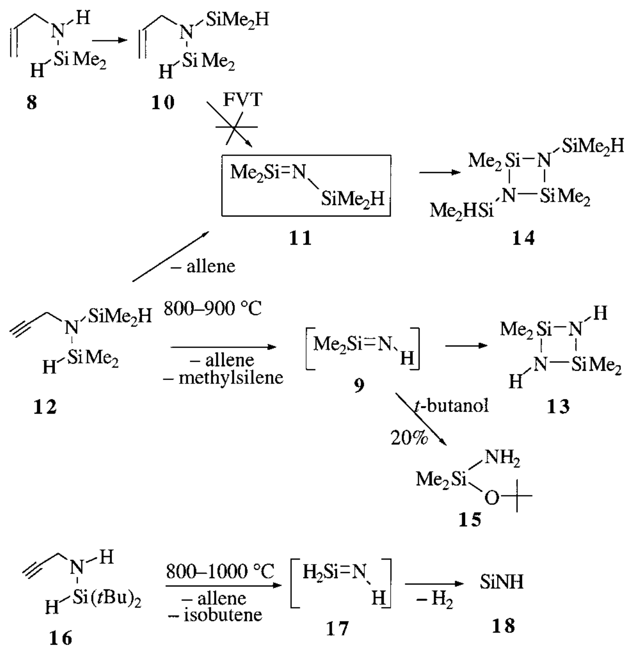


Scheme 2

Compound **8**, a priori the most direct precursor of the *N*-unsubstituted silanimine **9**, could not be used, for it disproportionated too rapidly into allylamine and disilazane **10** (Scheme 3). Furthermore, **10** required a high FVT temperature and did not yield the corresponding silanimine **11**. The allylic group in **10** was thus replaced with a propargylic one (compound **12**) in order to make the *retro*-ene reaction easier, as previously reported.[22] FVT of **12** gave the reactive silanimine **11** and cyclo-1,3-disila-2,4-diazane **13**, characterized by HRMS and PES, together with **14** (stable cyclic dimer of **11**) and azasilacyclopentenes resulting from the internal hydrosilylation of **12**. The presence of **13** is presumably the result of the cyclodimerization of silanimine **9**, obtained by β-elimination of methylsilene from the second dimethylsilyl group of **12** and too reactive to be observed in the monomeric form. The intermediacy of **9** was confirmed by the obtaining of the expected adduct **15** with *tert*-butyl alcohol.[23,24] Silanimine **9**, as well as di- and triphenylsilanimines, have been recently generated in matrix by photolysis of the corresponding silyl azides and characterized by IR and UV spectroscopy.[25]

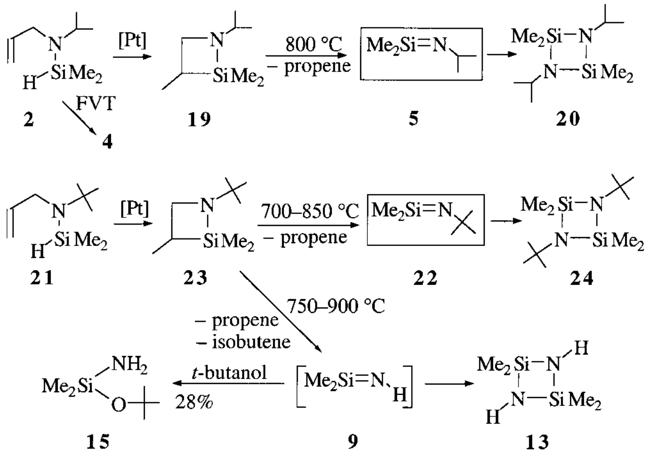
FVT of silanamine **16**, a possible precursor of the unsubstituted silanimine **17** by *retro*-ene reaction and double β-elimination of isobutene, has also been investigated in conjunction with MWS. However, **17** appeared to be dehydrogenated at the required temperatures and only silaisonitrile **18** was identified.[26] Silanimine **17** has been characterized by IR spectroscopy in the matrix photolysis of silyl azide[27] and its structural parameters and rotational constants calculated.[28]

The competing thermal processes observed when starting from allylic or propargylic silanamines led us to explore the FVT of other precursors, and particularly that of azasilacyclobutanes, accessible from *N*-allylsilanamines in the presence of a tetramethyldivinyldisiloxane/hexachloroplatinic acid complex ([Pt]), and reported to afford silanimines by



Scheme 3

thermal [2π + 2π] cycloreversion.[29] Compound **19** was thus prepared and cleanly yielded the corresponding silanimine **5** (not directly obtained from **2**), characterized by PES and as its cyclic dimer **20** (Scheme 4).[30]

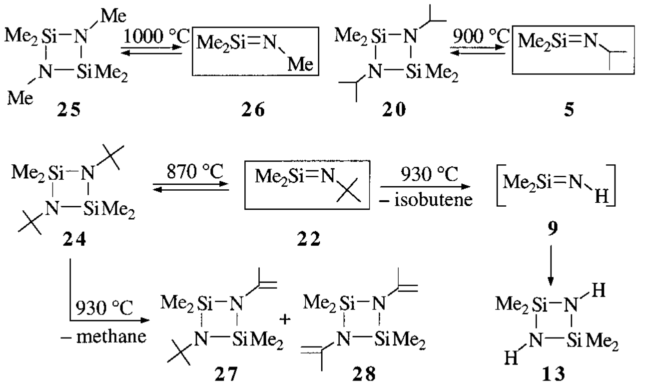


[Pt] = Pt{[(CH$_2$=CH)Me$_2$Si]$_2$O}$_2$

Scheme 4

In the same way, the temperature required for cleavage of the *retro*-ene precursor **21** (and also of its propargylic analogue) was too high to produce silanimine **22**. However, **21** could be quantitatively converted into azasilacyclobutane **23**, which gave silanimine **22** and its cyclic dimer **24** upon FVT at 700 °C. At higher temperatures, an increasing loss of isobutene and formation of cyclodisiladiazane **13** were observed, showing that silanimine **9** had been formed. Its intermediacy was also confirmed, in the presence of *tert*-butyl alcohol, by the formation of compound **15**.[23,30]

N-Alkylcyclo-1,3-disila-2,4-diazanes **25**, **20** and **24** are known, stable and easily prepared compounds.[31] Upon FVT in conjunction with PES, **25** and **20** proved to be excellent precursors for the corresponding silanimines, undergoing as their only reactions equilibria with monomeric species **26** and **5**, respectively (Scheme 5). The experimental PE spectra of **26** and **5** agree quite well with the calculated energies of the two first ionic states. These results reveal, for these silanimines, a destabilization of the π system and of the nitrogen lone pair, resulting in an enhanced nucleophilicity (see later, photoelectron spectrometry).[30]

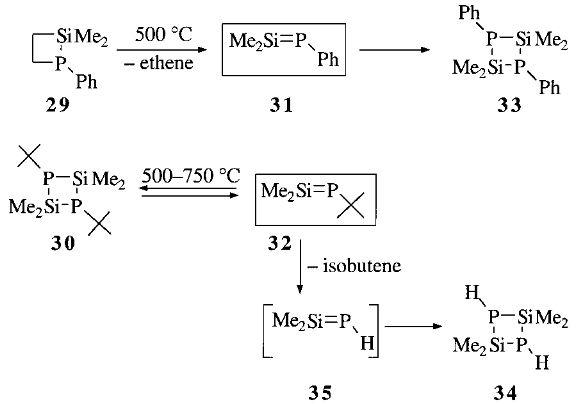


Scheme 5

After FVT of **24**, the cyclic dimer of silanimine **9** (cyclodisiladiazane **13**) was present, as well as silanimine **22**.[30] The relatively stable *N*-isopropenylcyclo-1,3-disila-2,4-diazanes **27** and **28,** resulting from the demethylation of **24**, were also characterized, by HRMS and NMR, in the thermolysis products.[32]

Phosphasilenes (R$_2$Si=PR′)

FVT of the previously described phosphasilacyclobutane **29**[33] and cyclo-1,3-diphospha-2,4-disiletane **30**[34] was investigated in a similar manner. These precursors were cleaved at moderate temperatures to give the first reported unhindered phosphasilenes, compounds **31** and **32**, characterized by HRMS and PES (Scheme 6). The stable dimer of **31**, cyclodiphosphadisiletane **33**, was also found to be present, as well as, in the FVT of **30**, the *P*-unsubstituted cyclodiphosphadisiletane **34**, obtained through the intermediacy of phosphasilene **35** by elimination of isobutene and dimerization.[35]

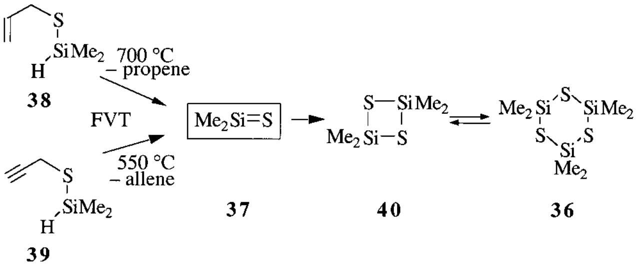


Scheme 6

Silanethiones ($R_2Si{=}S$)

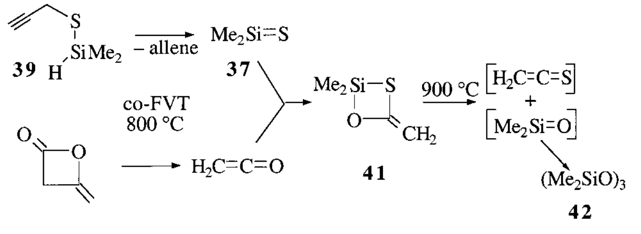
Compared to that of other compounds possessing a double bond on silicon, the direct observation of unhindered silanethiones is particularly difficult, owing to their extreme kinetic instability.[1] FVT of its cyclic trimer **36** led to dimethylsilanethione (**37**), characterized in the gas phase by PES,[36] while difluorosilanethione, $F_2Si{=}S$, was recently obtained by FVT of $(F_3Si)_2S$ and identified in matrix by IR spectroscopy.[11d] The presence of the sulfur atom makes the *retro*-ene reaction relatively rapid and specific,[37,38] and so we have investigated the possibility of obtaining simple silanethiones in this way,[39] using as precursors allylthio- and propargylthiodialkylsilanes; the latter are preferred for their lower temperatures of decomposition. These compounds have been prepared by reaction of the corresponding thiols with dialkylchlorosilanes in the presence of a base.

In the FVT of compounds **38** and **39**, silanethione **37** has been characterized by the quantitative formation of its cyclic oligomers **40** and **36**. In conjunction with PES, it has also been characterized directly in the monomeric state.[40] The ionization potentials thus obtained are in agreement with those calculated and observed previously.[36] (Scheme 7).



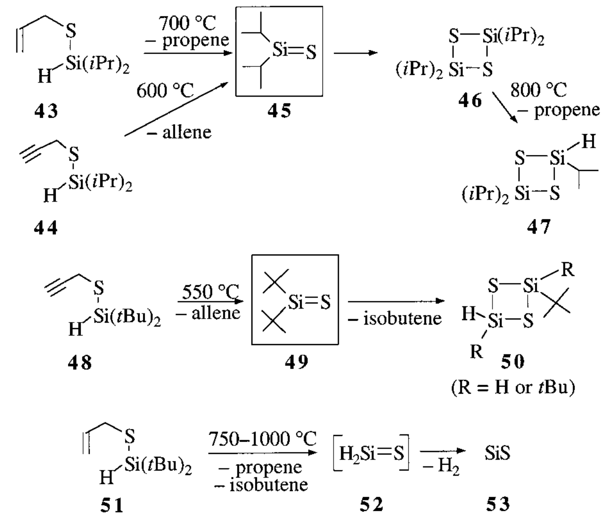
Scheme 7

Co-thermolysis of ketene dimer with thiosilane **39** resulted in cycloaddition of dimethylsilanethione (**37**) and ketene, giving oxathiasiletane **41** (Scheme 8). A tenfold excess of ketene was necessary to avoid the formation of **40**. This excess of ketene was, however, not trapped under the FVT conditions employed, and compound **41** was recovered in good purity and 60% yield. Its structure, established by HRMS and NMR, was confirmed by its FVT at higher temperature, giving thioketene and dimethylsilanone cyclic trimer **42**.[41]



Scheme 8

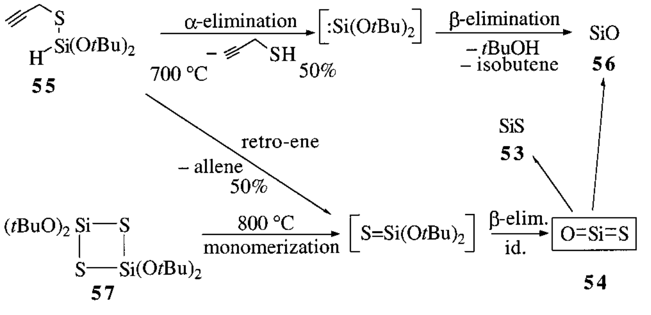
The *Si*-diisopropylated precursors **43** and **44** gave, in the same way, diisopropylsilanethione (**45**), characterized by HRMS, PES and by its cyclic dimer **46** (Scheme 9).[39] The steric crowding in **46** resulted at higher temperature in the loss of one isopropyl group to give compound **47**. FVT of the propargylic precursor **48** led similarly to a mixture of compounds probably containing, as analyzed by HRMS used in conjunction, di-*tert*-butylsilanethione (**49**) and several cyclic dimers **50**, possessing one to three *tert*-butyl groups.[42]



Scheme 9

Also, similarly to silanamine **16**, FVT of **51** gave, in place of unsubstituted silanethione (**52**), silicon monosulfide (**53**), characterized by MWS.[26]

By analogy with its interstellar counterpart carbon oxysulfide ($O{=}C{=}S$),[15] silicon oxysulfide (**54**), previously described in matrix,[43] is also a possible cosmic species. We have investigated the possibility of generating **54** in the gas phase from propargylthiosilane **55** (Scheme 10). Two competing pathways took place in the thermolysis of this compound, leading respectively, by α- and β-elimination, to silicon monoxide (**56**),[26] and probably, by *retro*-ene reaction and β-elimination, to the desired silicon oxysulfide (**54**), characterized in low quantity by IR at −196 °C, by comparison with the reported values.[43]



Scheme 10

According to FVT/IR and FVT/MS experiments, formation of **54** also occurred, in somewhat better yield, by "monomerization" of cyclo-1,3-dithia-2,4-disiletane **57**,[44] and subsequent β-elimination. The high concentrations of *tert*-butyl alcohol and isobutene generated in the thermolyses of **55** and **57**, however, precluded any characterization of silicon oxysulfide (**54**) by MWS and only compounds **53** and **56** were identified in this way as silicon derivatives.[45]

Photoelectron Spectrometry − Theoretical Results

The short-path combination of FVT with PES provided an essential gas phase, real-time method for analyzing the above-mentioned, short-lived heterosilenes. Their characterization was based on a quantum investigation effected by the ab initio method using the 6−31G(d) basis set at the HFMP2 level,[46] and/or by the density functional theory (DFT)[47] with the B3LYP functional,[48] well adapted for calculating the ionization potentials (IPs)[49] (Gaussian 94[50]).

The minimized geometries of these heterosilenes are in fair agreement with those previously determined for more encumbered homologues.[24,35,40] The calculated energies of the two first ionic states, associated with the ejection of an electron from the heteroatom lone pair and from the $\pi_{Si=X}$ bond, reflect the experimentally observed ionizations fairly well for all the heterosilenes investigated. This experimental and theoretical data set enables the differences in electronic structure between related Si=X and C=X compounds to be specified. The IPs of directly comparable molecules are collected together in Table 1.

Table 1. Experimental IPs [eV] for heteroalkenes and heterosilenes

$R^1R^2Y{=}X(R^3)$	n_X	π_{YX}
$Me_2C{=}NMe$	9.2	10.2
$H_2C{=}NMe$	9.9	11.4
$H_2C{=}NSiMe_2H$	9.1	10.7
$Me_2Si{=}NMe$ (**26**)	7.9	8.3
$Me_2Si{=}N$*t*Bu (**22**)	7.4	7.4
$Me_2Si{=}NSiMe_2H$ (**11**)	7.6	8.3
$MeHC{=}PH$	10.35	9.75
$H_2C{=}PMe$	9.97	9.69
$Me_2Si{=}P$*t*Bu (**32**)	8.2	7.0
$Me_2C{=}S$	8.6	10.46
$Me_2Si{=}S$ (**37**)	8.6	9.6

As an example, we observed − between trimethylmethanimine[51] and the corresponding silanimine **26** − a destabilization in energy of ca. 1 eV for the ionization of the nitrogen lone pair (sp^2), and of nearly 2 eV for that of the π double bond. These differences can be interpreted as a stronger p character in the silanimine nitrogen lone pair and a more diffuse 2pπ−3pπ overlapping of the π system.

Also interesting is the substitution effect contributed by an $SiHMe_2$ group on the Si=N backbone, compared to a methyl group. In the case of imines, the energetically strong $\pi_{C=N}$ bond and nitrogen lone pair are destabilized, because of the hyperconjugation effect with the σ_{SiC} groups.[24] On the other hand, in spite of the linearization of the Si=N backbone by the dimethylsilyl group, very close IPs were observed for silanimines **11** and **26**. This can be explained by a strong negative hyperconjugation effect acting on both the σ and π systems. It thus appears that *N*-substitution by an $SiHMe_2$ group can provide an interesting way to produce stabilized silanimines; not only sterically, but also electronically by negative hyperconjugation $n_N \rightarrow \sigma^*_{SiC}$ and $\pi_{Si=N} \rightarrow$ “π^*”$_{SiC}$. The same should also be true for the Si=P compounds.

When compared to propanethione,[52] dimethylsilanethione (**37**) showed the ionizations of the sulfur lone pair, which possess a pure p character, at the same energy, together with a weak destabilization (less than 1 eV) for the π double bond ionization.

The ionization order is inverted in the case of compounds with phosphorus double bonds. The s character of the phosphorus lone pair is quite strong in phosphaethene, with an angle of 95° at the phosphorus atom, and the ionization of the π electrons is energetically lower than that of the phosphorus lone pair.[53] We observed the same behaviour for phosphasilene **32**, with a stabilization of the lone pair ionization by 0.8 eV and a slight destabilization of the π double bond, relative to silanimine **22**.

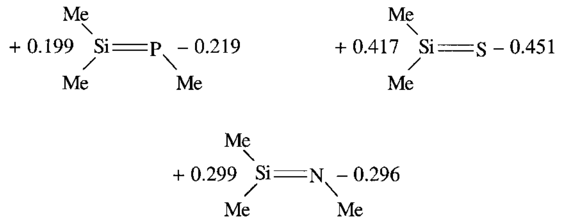
Although lacking data on identically substituted systems, a comparison of the Si=P relative to C=P moieties clearly showed, as for the Si=N/C=N counterparts, the destabilization of the π ionization.

The high reactivity of the low-coordinated silicon species originates in the π system. We observed, relative to the carbon counterparts, a similar destabilization for the $\pi_{Si=N}$ and $\pi_{Si=P}$ ionizations. The $\pi_{Si=S}$ bond ionization is less destabilized, relative to the $\pi_{C=S}$ one, and energetically the highest.

The energy of the π bond has been estimated[54] at the MP4(SDTQ) 6−31(d) level for the three parent compounds $H_2Si{=}NH$ (37.0 kcal·mol^{-1}), $H_2Si{=}PH$ (29.7 kcal·mol^{-1}) and $H_2Si{=}S$ (43.6 kcal·mol^{-1}), and we found the same order from the values observed for the ionizations associated with the ejection of a π bond electron. The authors[54] proposed a correlation between the π bond energy and the electronegativity of the X atom (P: 2.1, S: 2.5, N: 3.0).

While the π bond energies of the corresponding heteroalkenes ($H_2C{=}PH$; 49.4 kcal·mol^{-1}, $H_2C{=}S$; 55.7 kcal·mol^{-1}, $H_2C{=}NH$; 80.8 kcal·mol^{-1}) well fit the above correlation, and also that with the orbital overlapping ($3p\pi_P{-}2p\pi_C < 3p\pi_S{-}2p\pi_C << 2p\pi_N{-}2p\pi_C$), it is only by taking both these factors into account that it becomes possible, in the case of heterosilenes, to explain the higher energy of the π(Si=S) bond relative to the π(Si=N) one, the $3p\pi_{Si}{-}3p\pi_S$ overlapping being more efficient than that of $3p\pi_{Si}{-}2p\pi_N$.

This competition between electronegativity and overlapping is shown by the π charges calculated for the three corresponding, methyl-substituted compounds (Scheme 11).



Scheme 11

In fact, the above three silicon π systems are kinetically very reactive towards cyclodimerization, especially in the case of silanethiones, which have been experimentally characterized only by their cyclic dimers. The strong thermodynamic stability of the cyclodithiadisiletane ring, which, unlike its cyclodisiladiazane and cyclodiphosphadisiletane counterparts, does not form the monomer at high temperature, is presumably responsible for this enhanced reactivity.

Concluding Remarks

Flash vacuum thermolysis, mainly used in short-path conjunction with photoelectron spectrometry, allowed us to characterize a number of nonstabilized, short-lived heterosilenes, in the gas phase and in real time. However, the potential of this method approached its limits here, and several goals remained unattained. Some reasons are now put forward to explain these failures. The high temperatures required to effect the expected cleavages, especially when starting from allylic or even propargylic silanamines, often led to undesired competing reactions. In these cases, a more efficient access to silanimines was provided by using azasilacyclobutanes or, preferably, cyclo-1,3-disila-2,4-diazanes, or, in the phosphasilene series, the corresponding phosphasilacyclobutanes or cyclodiphosphadisiletanes. On the other hand, dialkyl(propargylthio)silanes cleaved at reasonable temperatures and underwent only the expected *retro*-ene reaction, leading to silanethiones and their cyclic dimers. The extremely short lifetimes of $R_2Si=NH$ and $R_2Si=PH$, as well as the specific thermal instability of $H_2Si=NH$ and $H_2Si=S$, constituted a more definitive limitation to the FVT method employed here, and precluded any characterization of these last-mentioned heterosilenes.

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Received February 7, 2000
[O00050]