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Flash Vacuum Thermolysis: First Gas-Phase Generation of Unhindered Silylidenephosphanes and Characterization by Photoelectron Spectroscopy

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The flash vacuum thermolysis of cyclodisilaphosphanes, cyclotrisilaphosphanes, and a phosphasilacyclobutane, potential precursors of unhindered silylidenephosphanes ($R_2Si{=}PR'$), has been investigated by NMR as well as by coupling with HRMS and, particularly, photoelectron spectroscopy. This last technique led us to characterize for the first time, in the gas phase, two very reactive species of this series, the *P*-*tert*-butyl- and *P*-phenyl-(dimethylsilylidene)phosphanes ($Me_2Si{=}P$-*t*-Bu and $Me_2Si{=}PPh$). The first ionization potentials at weaker energy are associated with the ejection of an electron from the $\pi_{Si=P}$ bond. The ionizations of the lone pair on phosphorus are observed at higher energy.

Introduction

Silylidenephosphanes ($R_2Si{=}PR'$), compounds possessing a silicon−phosphorus double bond, remain scarcely known. Only a few members of this series, stabilized by bulky substituents, have been reported,[1−5] and some aspects of the chemistry of these compounds have recently been studied.[6] Unhindered silylidenephosphanes are expected to be extremely short-lived species and remained until now experimentally undescribed.

In the last two decades, the use of flash vacuum thermolysis (FVT) has allowed the observation of many reactive, monomeric species having a double-bonded silicon atom,[7] and we have reported the generation by FVT of several unstabilized silanimines[8,9] as well as, very recently, their unambiguous characterization by photoelectron spectroscopy (PES).[10] Our investigations have pointed out the usefulness of cyclodisilazanes and azasilacyclobutanes as precursors of these silanimines. We have thus attempted to generate and characterize simple silylidenephosphanes, starting from the corresponding precursors, cyclodisilaphosphanes and phosphasilacyclobutanes.

The presently known 2,2,4,4-tetramethylcyclodisilaphosphanes (2,2,4,4-tetramethyl-1,3-diphospha-2,4-disilacyclobutanes) are limited to 1,3-di-*tert*-butyl,[11,12] 1,3-diphenyl,[13,14] and 1,3-bis(chlorodimethylsilyl)[15] derivatives. A few cyclodisilaphosphanes substituted on silicon by groups other than methyl have been also described,[16−20] as well as 1,3,5-triphenyl-2,2,4,4,6,6-hexamethylcyclotrisilaphosphane,[13] and triphosphatrisilacyclohexanes.[21] 1-Phenyl-2,2-dimethyl-1-phospha-2-silacyclobutane also has been synthesized and shown to exist in equilibrium with its eight-membered cyclic dimer, the lowering of pressure shifting this equilibrium toward the monomeric form.[14]

The compounds investigated here are 1,3-diisopropyl- (**1a**), 1,3-di-*tert*-butyl- (**1b**),[11,12] 1,3-dicyclohexyl- (**1c**), and 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilaphos-

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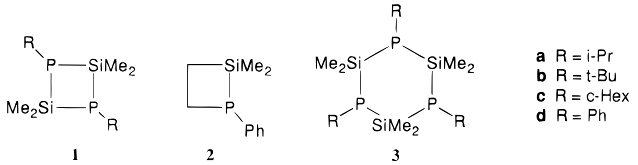
Chart 1



phane (**1d**),[13,14] as well as 1-phenyl-2,2-dimethyl-1-phospha-2-silacyclobutane (**2**).[14] Compounds **1c** and **1d** were obtained as mixtures with the corresponding cyclotrimers **3c** and **3d** (Chart 1).

Experimental Section

The mass spectra and on-line FVT/HRMS coupling have been realized using a Jeol JMS D300 spectrometer, the NMR spectra (250 MHz for ^{1}H) with a Bruker AC250. The FVT oven was an empty quartz tube (length 20 cm, i.d. 1.6 cm), and the pressure during thermolysis experiments was *ca.* 10^{-5} hPa.

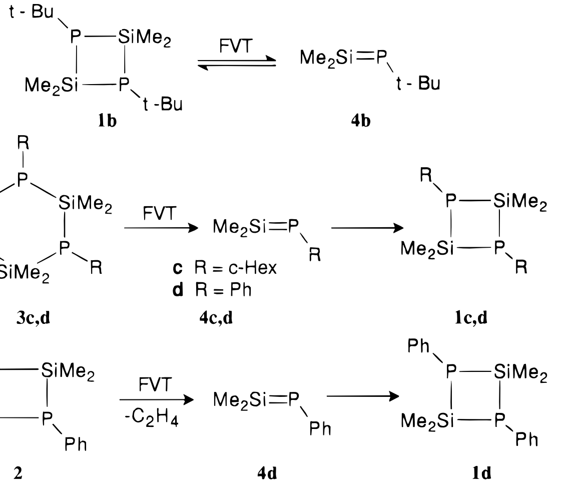
The photoelectron spectra were recorded on a Helectros 0078 spectrometer fitted with a 127° cylindrical analyzer and monitored by a microcomputer supplemented with a digital converter. The short-path FVT system has been described elsewhere.[22] The precursors were introduced under a pressure of *ca.* 10^{-2} hPa. It is estimated, under these conditions, that the detection of thermolysis products with lifetimes from 10^{-1} to 10^{-3} s can be performed.[23]

Ab initio calculations were performed with the Gaussian 92[24] package of programs. The geometry optimization and frequency calculations have been done at the MP2/6-31G(d)[25] and MP2/LANL1DZ[26] (D95V on H, C,[26a] Los Alamos ECP+DZ on Si, P[26b]) levels. The latter application is justified by the necessity to compare ionization potentials (IPs) of monomeric species with those of their large dimers. For the ionic species, the unrestricted formalism (UMP2) is employed. The value of the spin-squared operator (S^2) is 0.75 for all ionic species. Vertical IPs have been calculated either within Koopmans' approximation or, more precisely, as differences between the ionic and ground state energies, both obtained on the neutral ground state optimized geometry (ΔE_v).

We have applied the reaction of dichlorodimethylsilane with a dilithium phosphide in THF, previously reported for the synthesis of **1d**,[13] to the preparation of all the cyclodisilaphosphanes investigated here, which were thus obtained in good purity after bulb-to-bulb vacuum distillation, apart from the presence of cyclotrimers **3c** and **3d**. The cyclosilaphosphanes **1b** (yield 88%) and **1d** + **3d** (1:9, yield 46%), were identical to those already described;[11−14] **1a** and **1c** + **3c** (1:1, not separated) are new compounds.

1,3-Diisopropyl-2,2,4,4-tetramethylcyclodisilaphosphane (1a) (oil, yield 60%): NMR (C_6D_6) δ(^{1}H) 0.47 (t, J = 3.8 Hz, Si(CH$_3$)$_2$), 1.06 (dd, J = 16.4 and 6.9 Hz, *i*-Pr CH$_3$), 2.30 ppm (d hept, J = 13.8 and 6.9 Hz, *i*-Pr CH) (a possible further multiplicity, due to conformationally nonequivalent or diastereotopic isopropyl groups, was not observed); δ(^{31}P) −118.4 ppm; MS (60 eV) main fragments at *m/z* 249 (48), 207 (95), 175 (41), 133 (100), 84 (90), 73 (79), 59 (68); HRMS M$^{\bullet+}$ − CH$_3$ 249.0759 (calcd $C_9H_{23}P_2Si_2$ 249.081 25), M$^{\bullet+}$ − C_3H_7 221.0455 (calcd $C_7H_{19}P_2Si_2$ 221.050 02).

Scheme 1



1,3-Dicyclohexyl-2,2,4,4-tetramethylcyclodisilaphosphane (1c) and 1,3,5-tricyclohexyl-2,2,4,4,6,6-hexamethylcyclotrisilaphosphane (3c) (oil, yield 80%): NMR (C_6D_6) δ(^{1}H) 0.53 (t, J = 3.8 Hz, Si(CH$_3$)$_2$, assigned to **1c** for being coupled only with two equivalent P atoms), 0.69 (m, Si(CH$_3$)$_2$, **3c**), 1.10−2.60 ppm (c-hex H, **1c** and **3c**); δ(^{31}P) −123.6 and −130.6 ppm (likely assignable to **1c** and **3c**, respectively, by comparison with the values of −123.3 and −135.3 ppm previously reported for **1d** and **3d**[13]); HRMS (**1c**) M$^{\bullet+}$ − C_6H_{11} 261.0684 (calcd $C_{10}H_{23}P_2Si_2$ 261.081 33), M$^{\bullet+}$ − 2 C_6H_{11} 177.9870 (calcd $C_4H_{12}P_2Si_2$ 177.995 29).

Phosphasilacyclobutane **2** has been prepared according to the reported procedure.[14]

Results and Discussion

FVT of compounds 1−3 and MS and NMR Results. The FVT/HRMS of the P-isopropylated cyclodisilaphosphane **1a** revealed no noticeable change in the spectrum between room temperature and 1000 °C. However, owing to the distance between the FVT oven and ionization chamber (*ca.* 20 cm), a monomerization−recyclodimerization of **1a** cannot be excluded.

The NMR analysis of the FVT products of the cyclosilaphosphanes **1b** and **1c** + **3c** showed the presence of isobutene and cyclohexene, respectively, increasing with the temperature from 550 °C for **1b** and 700 °C for **1c** + **3c**. Furthermore, the FVT/HRMS investigation of the thermal behavior of **1b** pointed out, from 500 °C, the presence of a peak at *m/z* 88.9916 (calcd C_2H_6PSi 88.997 62); this peak, absent in the MS of **1b**, could be likely attributed to the presence of the monomeric *P-tert*-butyl(dimethylsilylidene)phosphane **4b** (M$^{\bullet+}$ − C_4H_9) (Scheme 1).

Upon FVT at 550 °C, the cyclotrimers **3c**,**d** were shown by NMR to be quantitatively converted into the corresponding cyclodimers **1c**,**d**. Such transformations, taking place under the conditions of FVT (it has been reported on the other hand that, in the liquid phase, **1d** was totally transformed into **3d** at 150 °C[13]) should probably involve the intermediacy of the monomeric (dimethylsilylidene)phosphanes **4c**,**d**.

Phosphasilacyclobutane **2** was known to lose ethylene by distillation under 0.1 Torr, yielding a mixture of 1,2-diphenyl-3,3-dimethyl-3-sila-1,2-phospholane and **1d**

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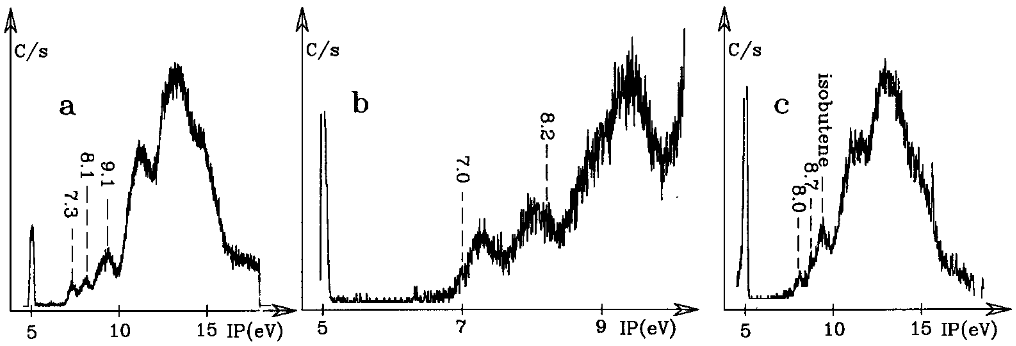


Figure 1. PE spectra: (a) precursor **1b**; (b) FVT of **1b** at 500 °C; (c) FVT of **1b** above 510 °C.

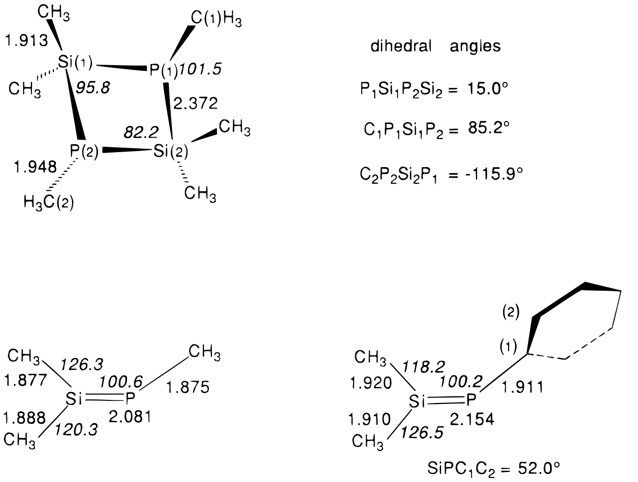


Figure 2. Geometrical parameters (bond lengths in angstroms; bond angles in degrees) of **4e** optimized at the MP2/6-31G(d) level and of **1e** and **4d** optimized at the MP2/LANL1DZ level.

(ratio 9:1).[14] On the other hand, we obtained compound **1d** as the only product in the FVT of **2**.

FVT/PES of 1b and 2: Photoelectron Spectra of Silylidenephosphanes 4b and 4d. The coupling of FVT with ultraviolet PES having been proven by us to be the most efficient method to characterize several reactive silanimines in the gas phase,[10] we have also undertaken identification of the silylidenephosphanes **4b** and **4d** by their IPs, using FVT/PES coupling.

Among the above precursors, we have retained for this investigation compounds **1b** and **2**.

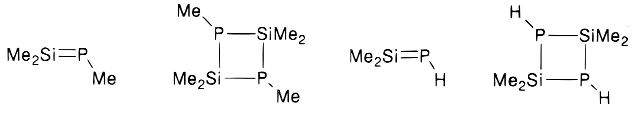
Two well-defined ionizations are observed at 7.3 and 8.1 eV in the spectrum of precursor **1b** (Figure 1a).

The geometrical parameters calculated (MP2/LANL1DZ) for its methyl counterpart **1e** correspond to a nonplanar form with a dihedral angle of 15.0° and the phosphorus substituents in a trans configuration (Figure 2). These parameters are in agreement with the crystal structure determination performed on 1,2,2,3,4,4-hexa-*tert*-butylcyclodisilaphosphane.[19]

The assignment of experimental IPs is supported by Koopmans' correlations $E^{v}_{i,n} = -\epsilon_j$. The corresponding orbital diagrams for the four radical cations states of lowest energy are shown in Table 1.

The overestimation of these values is due to the *tert*-butyl substituent effect with respect to the methyl one, and to neglecting the polarization effects, particularly in the case of the IP which corresponds to a well-localized MO on the phosphorus lone pairs and alkyl substituents (calculated 9.71 eV, observed 8.1 eV).

Chart 2



4e **1e** **4f** **1f**

We have reported in the same table the orbital energies calculated for the P-unsubstituted cyclodisilaphosphane **1f**. For this compound, the first ionization calculated at 8.29 eV is associated with the ionization of the antisymmetrical combination of the phosphorus lone pair.

The ionizations of the SiP ring bonds and the symmetrical combinations of the lone pairs are calculated to be energetically close (9.98, 10.19, 10.31 eV, respectively).

The presence of isobutene, eliminated from the *tert*-butyl substituents, was noted from 510 °C (Figure 1c). Below this temperature (500 °C) a broadening of the two first bands of **1b** was observed (Figure 1b) with two weak shoulders at 7.0 and 8.2 eV.

Above 510 °C the formation of isobutene (9.45 eV) was accompanied by a change in the spectrum, showing particularly two new ionizations at 8.0 and 8.7 eV, the persistence of which after several recordings indicated a relatively stable species under our conditions of temperature and pressure (Figure 1c). These ionizations could reasonably be attributed to **1f**, likely directly formed by loss of isobutene from **1b**. As in the case of the substituted derivatives, the polarization effects, relative to Koopmans' correlations, are more important for the fourth ionization (calculated 10.31 eV, observed 8.7eV).

In order to assign the new ionizations at 7.0 and 8.2 eV, observed below 500 °C, we have calculated the energy of the two first ionic states for trimethylsilylidenephosphane (**4e**) at the MP2 level with LANL1DZ and 6-31G(d) basis sets (Chart 2).

The geometrical parameters calculated for **4e** (6-31G-(d)), reported in Figure 2, correspond to a 2.081 Å $\mathrm{Si{=}P}$ bond and a SiPC angle of 100.6°. (We should remark that with LANL1DZ/MP2 this bond is calculated to be longer: 2.147 Å, SiPC angle of 101.3°.) These results agree with those reported for the parent compound **4g** ($\mathrm{H_2Si{=}PH}$) by Gordon ($d_{\mathrm{Si{=}P}} = 2.04$ Å, $\angle\mathrm{SiPH} = 93.7°$),[27a] Schleyer ($d_{\mathrm{Si{=}P}} = 2.06$ Å),[27b] and Driess

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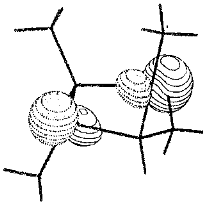
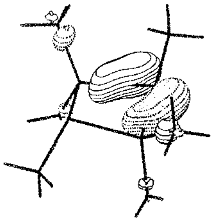
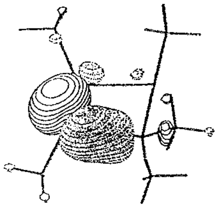
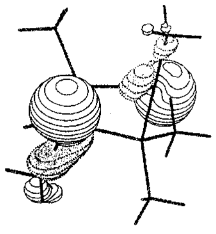
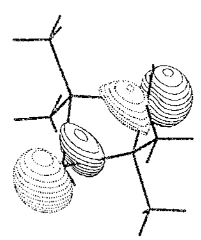
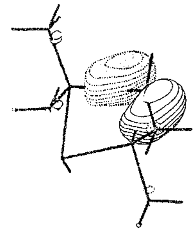
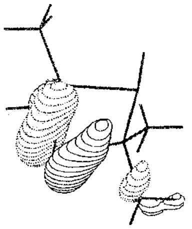
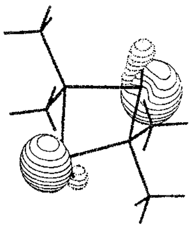
Table 1. Ionization Potentials[a]

					
		n^-_P	σ_{Si-P}	σ_{Si-P}	n^+_P
1e	a	7.79	9.61	9.69	9.71
1b	b	7.3	9.1		8.1
					
		n^-_P	σ_{Si-P}	σ_{Si-P}	n^+_P
1f	a	8.29	9.98	10.19	10.31
	b	8.0	8.7		8.7

[a] In electronvolts: (a) calculated at the MP2/LANL1DZ level, Koopmans' (**1e**, **1f**); (b) experimental values (**1b**, **1f**).

($d_{Si=P}$ = 2.06 Å, ∠SiPH = 93.7°).[27c] We observe a good agreement with the crystal structure determination performed on 1,3,4-triphospha-2-silabut-1-ene ($d_{Si=P}$ = 2.094 Å, ∠CPSi = 104.2°)[28a] and on 1-*tert*-butyl-1-isityl-3,3,3-tri-isopropyldisilaphosphene (isityl = 2,4,6-tri-isopropylphenyl) ($d_{Si=P}$ = 2.062 Å, ∠SiPSi = 112.79°: large value due to the electronic influence of the SiR_3 group).[28b]

The graphical illustration of the two highest occupied MOs of **4e** shows the diffuse character of the $\pi_{Si=P}$ orbital and the strong s character of the phosphorus lone pair (Figure 3).

The energies of the two first ionic states associated with the ionization of these orbitals previously calculated by Peyerimhoff[29] for **4g** should correspond respectively to 8.79 eV for the $^2A''$ state and 10.16 eV for the $^2A'$ state. For **4e**, we have reported in Table 2 the calculated vertical ionization energies (Koopmans and ΔE_v) at the MP2 level with different basis sets.

The first ionic state, calculated at 7.44 eV (MP2/6-31G(d)), is associated with the ejection of an electron from the Si=P bond. The second ionic state, calculated at 8.46 eV (MP2/6-31G(d)), is due to the ejection of the electron from the phosphorus lone pair. Taking into account the known destabilizing effect of the *tert*-butyl group, the new bands observed at 7.0 and 8.2 eV can be associated with the *P*-*tert*-butylsilylidenephosphane **4b**.

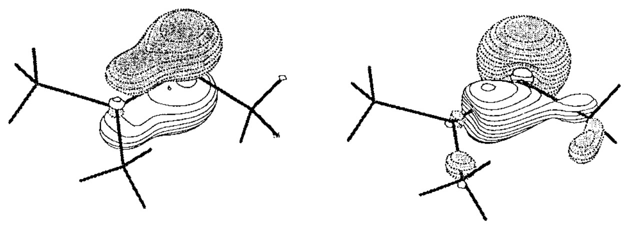


Figure 3. Graphical illustration of the two highest occupied MOs of **4e**.

This result, confirming the attribution to **4b** of the peak observed at *m*/*z* 88.9916 in the FVT/HRMS of **1b**, represents the first IP determination for a silylidenephosphane backbone, characterized by a low-energy ionization associated with the Si=P double bond. Its energy when compared with that of the nitrogen analogue is clearly weaker by *ca.* 0.5 eV.[10] The second ionization, characterizing the phosphorus lone pair, is

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Table 2. Vertical Ionization Potentials[a] of 4e Calculated at the MP2 Theory Level Using Different Basis Sets. Comparison with the Silanimine Analogue

	A″			A′		
	LANL1DZ	LANL1DZ+d	6-31G(d)	LANL1DZ	LANL1DZ+d	6-31G(d)
			$(CH_3)_2Si{=}PCH_3$			
Koopmans	7.66	7.62	7.60	9.34	9.53	9.37
ΔE_v	7.53	7.57	7.44	8.33	8.57	8.46
			$(CH_3)_2Si{=}NCH_3$			
Koopmans	8.78		8.83	9.42		9.41
ΔE_v	8.48		8.40	7.80		7.98
exptl		8.3			7.9	

[a] In electronvolts.

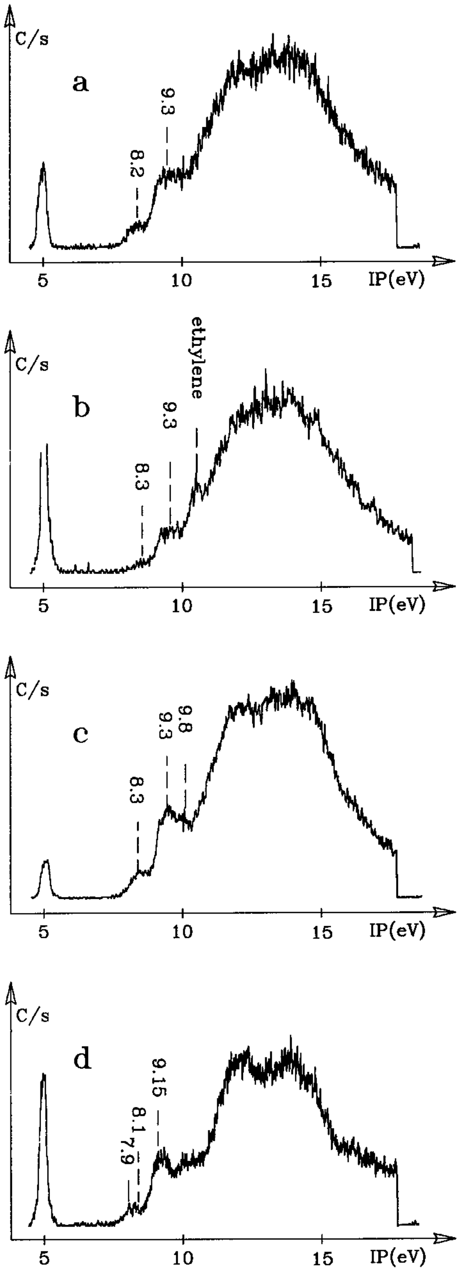


Figure 4. PE spectra: (a) precursor **2**; (b) FVT of **2** at 55 °C; (c) FVT of **2** at 70 °C; (d) cyclodimer **1d**.

stabilized by 0.8 eV when compared to the analogue silanimine,[10] pointing out the marked s character of this lone pair.

The phosphasilacyclobutane **2** having been already shown to be a precursor of cyclodisilaphosphane **1d**, likely via *P*-phenylsilylidenephosphane **4d**,[14] we also investigated the thermal behavior of this compound, using the FVT/PES coupling.

For a sample temperature of 30−35 °C, we observed a low-intensity spectrum showing a broad first band centered at 8.2 eV and another broad, more intense band at 9.3 eV (Figure 4a). This poorly resolved spectrum should correspond to a mixture of monomeric and dimeric **2**. The loss of ethylene took place upon gentle heating (Figure 4b), and a new spectrum, showing a first band at 8.3 eV and two distinct bands at 9.3 and 9.8 eV, was observed between 60 and 80 °C (Figure 4c). The formation of the cyclodimer **1d** being possible, we have also recorded its spectrum (Figure 4d), showing two weak, narrow bands at 7.9 and 8.1 eV and a more intense one at 9.15 eV. Thus, the quite different spectrum obtained from **2** between 60 and 80 °C could reasonably be attributed to the *P*-phenylsilylidenephosphane **4d**.

In order to confirm this result, we have calculated the structural parameters of **4d** (LANL1DZ basis) with the aim of specifying the orientation of the phenyl ring. The length of the Si=P bond is 2.154 Å, the SiPPh angle 100.2°, and the rotation angle of the phenyl ring of 52.0° corresponds to a weak interaction with the π system and to a more important one with the phosphorus lone pair (Figure 2).

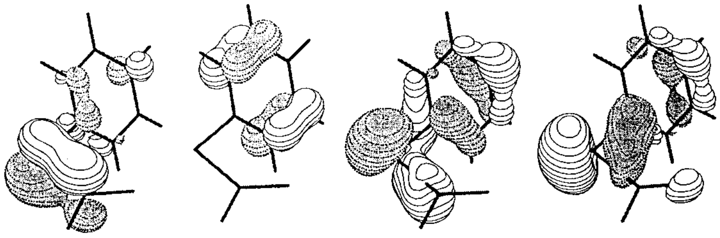
The assignments of the observed ionizations are supported by Koopmans' correlation according to the corresponding orbital diagram (Table 3).

Taking into account the correction to Koopmans, calculated to be more important for the $^2A'$ ionic state of **4e**, these values are in good agreement with the observed IPs, thus definitely attributed to silylidenephosphane **4d**. The first band at 8.3 eV is associated with the ionization of the $\pi_{Si=P}$ bond, while the band at 9.3 eV corresponds to the ionization of both practically degenerated orbitals of the phenyl ring. The ionization at 9.8 eV is due to the ejection of one electron from the phosphorus lone pair. This ionization is stabilized, owing to the spacial interaction with the $\pi^s{}_\Phi$ orbital of the phenyl group.

Conclusion

The gas-phase characterization of two unhindered silylidenephosphanes, reported herein, has been possible only in a quite restricted gap of temperature and pressure, showing a lower thermodynamic and kinetic stability, when compared with the corresponding silanimines. This kinetic instability is due to the very weak energy of the Si=P bond, originating from the diffuse character of the $3p\pi{-}3p\pi$ overlap (ionizations observed at 7.0 eV for **4b** and 7.4 eV for the corresponding

Table 3. Ionization Potentials[a] of 4d



		$\pi_{Si=P}$	π^{as}_{ϕ}	$\pi^{s}_{\phi} - n_P$	$n_P + \pi^{s}_{\phi}$
IP	a	7.90	9.24	9.32	10.55
	b	8.3	9.3		9.8

[a] In electronvolts: (a) calculated at the MP2/LANL1DZ level, Koopmans' approximation; (b) experimental values.

silanimine[10]). On the other hand, the ionization of the phosphorus lone pair is stabilized by 0.8 eV, when compared with that of the silanimine nitrogen (ionizations observed at 8.2 eV for **4b** and 7.4 eV for the corresponding silanimine). This fact points out the important s character of this lone pair. We observed previously a similar feature between methanimine ($H_2C=NH$) and phosphaethene ($H_2C=PH$).[30] Thus, compounds **4** should be considered, by their electronic structure, as silaphosphaalkenes rather than silaphosphimines.

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