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Gas-Phase Thermolysis of Phosphine−Borane Complexes Studied by Helium I Photoelectron Spectroscopy†

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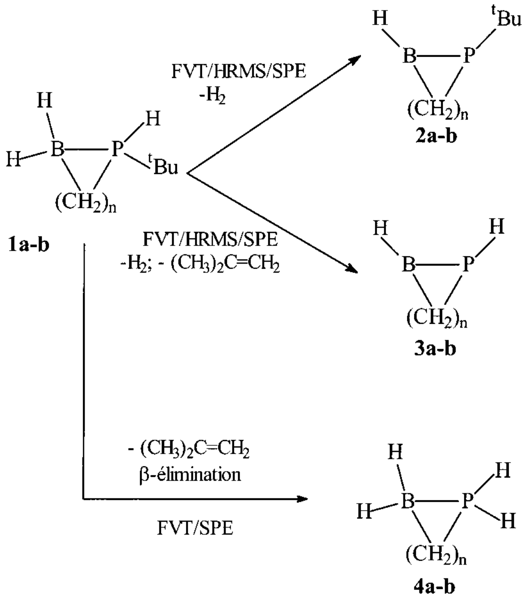
Flash vacuum thermolysis (FVT) of cyclic phosphine−borane complexes and direct analysis of the gaseous flow by ultraviolet photoelectron spectroscopy allowed us to characterize transient phosphinoboranes and to provide information about their electronic properties. This study was also supported by HRMS results. Ab initio calculations with the hybrid functional B3LYP and the basis set 6-311G (d, p) allowed us to assign the different ionizations of the PE spectra and provided more information about the character of the BP bond.

Introduction

Analogies between organic and inorganic chemistry have captured the imagination of chemists. Many studies have been carried out not only from a theoretical point of view but also from a synthetic one. Development of main group low coordination chemistry attests to this fact.[2] Among corresponding structures, ethylene analogues containing a boron atom occupy a fundamental position. Thus, the aminoborane intermediate H_2NBH_2,[3] one of the simplest species with a BN bond, has been characterized by photoelectron spectroscopy. This highly reactive intermediate is of interest notably as a precursor of the ring trimer $B_3N_3H_6$ isolobal to benzene and as a potential single-source precursor of boron nitrides.[4] In contrast, the phosphinoborane analogue H_2PBH_2 has never been identified. Calculations predict that the nonplanar form of H_2PBH_2 with C_s symmetry should be more stable than the corresponding plane form with C_{2v} symmetry.[5] The main explanation for this behavior is the well-known tendency of phosphorus to stay pyramidal where the inversion barrier is relatively high. The first fully characterized phosphinoboranes were stabilized by bulky groups positioned at heteroatoms.[6] More recently, another strategy has been adopted for the preparation of unstabilized derivatives; this consists of introducing a *tert*-butyl substituent on the phosphorus atom, which acts both as a bulky group and a "masked hydrogen atom" (loss of isobutene by thermally induced β-elimination). This process allowed the Rennes group to characterize for the first time the quasi-naked cyclic phosphinoborane **3a,3b** (Scheme 1)[7] by use of a tandem FVT/MS device.

Scheme 1. Thermolysis of 1a (n = 3) and 1b (n = 4): Different Decomposition Processes



Determination of ionization potentials by photoelectron spectroscopy is one of the most convenient methods

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(7) (a) Gaumont, A. C.; Bourumeau, K.; Denis, J. M.; Guenot, P. *J. Organomet. Chem.* **1994**, *484*, 9. (b) Bourumeau, K. Ph.D. Thesis no. 1720, Université de Rennes, France, 1996. [Spectroscopic data for **1b**: ^{31}P NMR ($CDCl_3$) δ 15.6 ppm (dq, $^1J_{PH}$ = 355 Hz, $^1J_{PB}$ = 40 Hz); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, $^3J_{PH}$ = 14 Hz, 9H, CH_3), 1.30 [m, 4H, (-CH_2-)$_2$], 2 (m, 2H, -CH_2-), 4.11 (d, m $^1J_{PH}$ = 355 Hz); ^{13}C NMR ($CDCl_3$) δ 15.0 (tdm $^1J_{CH}$ = 128 Hz, $^1J_{CP}$ = 28 Hz, P-CH_2), 26.4 (dm, $^1J_{CP}$ = 31 Hz, CH_3-C-P), 26.6 (qdm, $^1J_{CH}$ = 127 Hz, $^2J_{CP}$ = 2.5 Hz, -CH_3), 26.9 (tdm, $^1J_{CH}$ = 130 Hz, $^2J_{CP}$ = 3.9 Hz, P-CH_2-CH_2), 28.3 (tdm, $^1J_{CH}$ = 123 Hz, $^3J_{CP}$ = 6.3 Hz, P-CH_2-CH_2-CH_2); ^{11}B NMR ($CDCl_3$) δ 31.8 (td, $^1J_{BH}$ = 94 Hz, $^1J_{BP}$ = 14 Hz). HRMS: $[M+1]^+$ calcd 100.016, found 100.061.

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for real-time gas-phase detection of unstable low-coordinated compounds.[8,9] In this work a special FVT/He I photoelectron spectrometer was used to obtain ionization potentials and therefore information on the electronic properties of the cyclic phosphinoboranes **2a**,**2b** and **3a,3b**. The thermolyzed gas flow was introduced directly in the ionization chamber close to the UV source (internal thermolysis). This technique reduces the rearrangement and oligomerization of the transient species to a minimum and consequently gives important structural information complementary to that previously obtained by FVT/MS.[7a]

Experimental Section

Preparation. All experiments were performed under a dry nitrogen atmosphere. ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded on Bruker AM 300 and AC 300 spectrometers. ^1H and ^{13}C chemical shifts are in parts per million (ppm) relative to tetramethylsilane as an external standard. ^{11}B and ^{31}P NMR are reported in ppm with a positive sign relative to external $BF_3{\cdot}Et_2O$ and 85% H_3PO_4, respectively. Mass spectra were recorded on a Varian MAT 311. **1a** and **1b** were prepared according to the previously described method.[7a,b]

Photoelectron Spectra. All PES spectra were measured on a Helectros 078 spectrometer specially designed to study reactive species. A resistively heated furnace was used to achieve FVT reaction near the photoionization zone.[10] The furnace can also be placed outside the ionization chamber (external thermolysis)[11] in order to identify and separate the stable compounds. The vapor pressure of the starting material was sufficient enough to allow He I spectra to be recorded with an acceptable signal-to-noise ratio. Spectral calibration was achieved by comparison with the known ionizations of N_2 and He autoionization.

Computational Details. Ab initio calculations were performed with Gaussian 94/DFT.[12,13] The density functional theory method[14] was used with the functional hybrid Becke 3LYP[15] in conjunction with the basis set 6-311G(d, p). The structures were optimized and the second derivatives were calculated in order to determine if a minimum or a saddle point existed for the resulting geometry. To determine vertical ionization energies, the energy difference between the neutral molecule and that of the ion (both at the optimum geometry of the neutral molecule) was calculated (ΔSCF).

We have computed the first two ionic states for the C_{2v} H_2BNH_2 ($^2B_1$, 11.36 eV; $^2B_2$, 11.85 eV) with the hybrid functional B3LYP and the basis set 6-311G(d, p). A good agreement is found with the experimental ionization potentials of 11.36 and 12.08 eV. The use of DFT afforded a reasonable electronic structure description of unusually coordinated boron compounds.

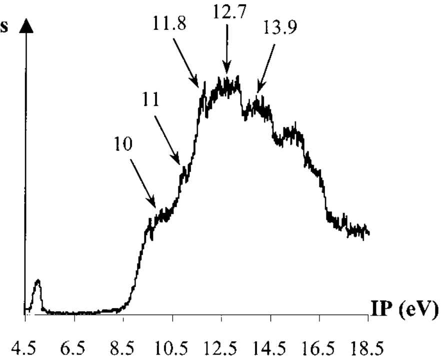
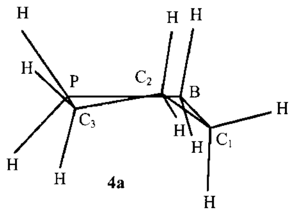
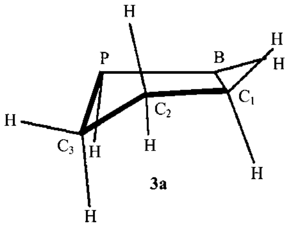


Figure 1. Photoelectron spectrum of **1a**.

Table 1. Geometrical Parameters of 4a and 3a



4a



3a

Bond Lengths (Å)		Bond Lengths (Å)	
PB	2.004	PB	1.898
BC_1	1.638	BC_1	1.569
C_1C_2	1.542	C_1C_2	1.546
C_2C_3	1.547	C_2C_3	1.542
C_3P	1.856	C_3P	1.890
Bond Angles (deg)		**Bond Angles (deg)**	
PBC_1	96.60	PBC_1	108.16
BC_1C_2	110.28	BC_1C_2	109.66
$C_1C_2C_3$	108.85	$C_1C_2C_3$	108.67
C_2C_3P	104.12	C_2C_3P	103.78
C_3PB	98.69	C_3PB	91.22

Photoelectron Studies: Results and Discussions

The He I PES of **1a** (Figure 1) shows broad bands. One of them is centered at 10.0 eV with a shoulder at 11.0 eV. A broader band is observed at 12.7 eV.

Assignment was made with reference to the results of the DFT calculations. Computed structural parameters of the parent compound **4a** (Table 1) correspond to an envelope form, which is a minimum on the potential hypersurface. Table 2 summarizes the experimental vertical ionization potentials (IP) and the Kohn–Sham values (KS). The first ionic state's energy, calculated at 9.80 eV, corresponds to the ionization of the orbital localized on the BC σ framework. KS energies suggest the presence of three ionizations in the first broad experimental band corresponding to the σ_{BC}, σ_{BH}, and σ_{BP} orbital ionizations. These ionizations are slightly destabilized by the *t*Bu group on phosphorus. Finally, the feature at 11–14 eV is a composite band due to the σ_{CC} and σ_{CH} electron ionizations.

No change were observed below 400 °C. At 440 °C, the bands corresponding to the starting material **1a** are still present, but new features now appear (Figure 2a).

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Table 2. Experimental Ionization Potentials,[a] Kohn−Sham Energies, and First Ionization Energies[b]

1a	exp		10		11−11.8
4a	E_{KS}	−7.63 (σ_{BC})	−7.69 (σ_{BH})	−8.05 ($\sigma_{BP} + \sigma_{BH}$)	−9.26 ($\sigma_{CC} + \sigma_{CH}$)
	IE	9.80			
	exp	9.0	10.6	11.4	12
3a	E_{KS}	−6.65 ($\pi_{B=P}$)[c]	−8.25 (σ_{BP})	−8.93 (σ_{BC})	−9.26 ($\sigma_{CC} + \sigma_{CH}$)
	IE	8.91			
1b	exp		9.5		11.1
4b	E_{KS}	−7.41 (σ_{BC})	−7.60 (σ_{BH})	−7.67 ($\sigma_{BP} + \sigma_{BH}$)	−8.98 ($\sigma_{CC} + \sigma_{CH}$)
	IE	9.52			
	exp	9.0	10.6	11.3	11.9
3b	E_{KS}	−6.15 ($\pi_{B=P}$)	−8.03 (σ_{BP})	−8.37 (σ_{BC})	−9.18 ($\sigma_{CC} + \sigma_{CH}$)
	IE	8.68			

[a] Experimental ionization potentials (exp) are given in electron volts for compounds **1a**, **3a**, **1b**, and **3b**. [b] Kohn−Sham energies (E_{KS}) and first ionization energies (IE) are given in electron volts for compounds **4a**, **3a**, **4b**, and **3b**. [c] $\pi_{B=P}$ means pseudo $\pi_{B=P}$.

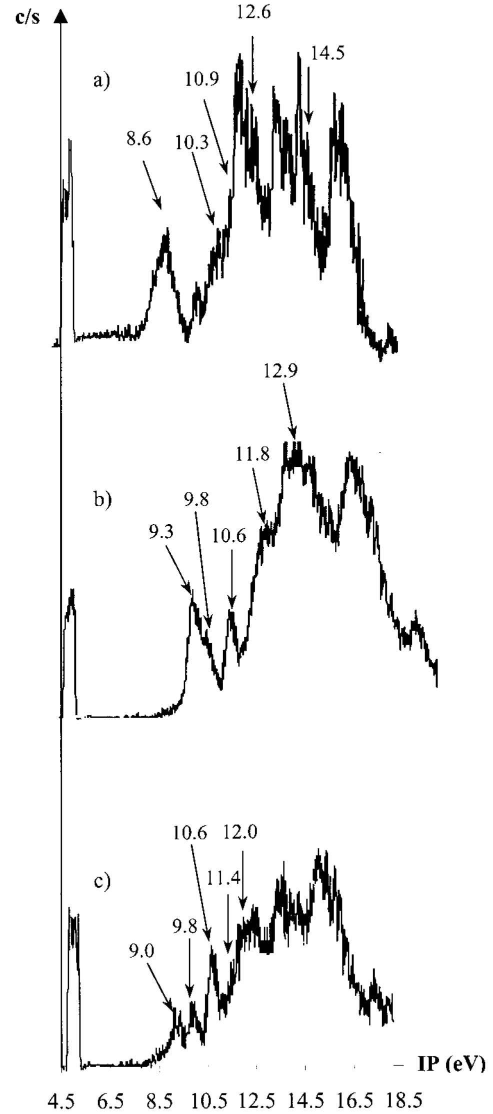

Figure 2. (a) Thermolysis spectrum of **1a** at 440 °C. (b) Thermolysis spectra of **1a** at 700 °C (black spectrum) and of isobutene (gray spectrum). (c) Difference spectrum between the thermolysis spectrum of **1a** at 700 °C and that of isobutene.

Digital subtraction gives a clearer spectrum with the bands at 8.6 and 10.3 eV.[16]

Increasing the thermolysis temperature to 700 °C leads to a new spectrum (Figure 2b) in which the band at 8.6 eV has disappeared. Signals arising from isobutene were observed and then confirmed by an external thermolysis reaction.[11] Two distinct bands appear in the "fingerprint" range at 9.8 and 10.6 eV. Another band is observed at 9.0 eV after digital subtraction of isobutene (Figure 2c).

Comparison of the MS results and the evolution of the PE spectra allow us to propose the formation of **2a** at 440 °C (dehydrogenation) and that of **3a** at 700 °C (dehydrogenation and loss of isobutene). Calculations carried out on **3a** (Table 1) indicate that the boron atom is planar whereas the phosphorus atom is pyramidal ($\Sigma P = 298.97°$). The calculated first ionic state IE at 8.91 eV corresponds to the ejection of an electron located on an orbital with a high phosphorus lone pair character and weak $p\pi{-}p\pi$ character, which can be called "pseudo-π" (Table 2).

The experimental value of this "pseudo-π" IP is observed for **3a** at 9 eV (Figure 2c). As expected, a pseudo-π band is also observed for the tBu derivative **2a** (8.6 eV, Figure 2a), the difference being attributed to the destabilization induced by the bulky substituent. According to the calculations, the second ionization arises from the ejection of an electron localized on the σ_{BP} orbital. In agreement with the energetic Kohn−Sham gap (1.6 eV), the band at 10.6 eV, observed at 700 °C, is associated with the ionization of the σ_{BP} orbital of **3a**. Comparatively, the second ionization at 10.3 eV observed from the spectrum at 440 °C is assigned to the ionization of the σ_{BP} orbital of the compound **2a,** the difference with the parent compound assuming the *t*Bu effect. We note a stabilization of the σ_{BP} orbital of **2a** with regard to that of the starting derivative **1a**. This is indicative of stronger σ_{BP} character in **2a** than in **1a**. Finally, the broad feature at 12 eV is assigned to the ionization of the σ_{BC}, σ_{CC}, and σ_{CH} orbitals.

The ionization at 9.8 eV (Figure 2c) cannot be assigned to **3a**. Taking into account the presence of the precursor **1a** at 440 °C, it seems reasonable to propose the formation under these conditions of **4a** (Scheme 1) by direct isobutene β-elimination from **1a**, the energy

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[16] We did not observe the loss of H_2 even if it occurred. An explanation could be found in the weak photoionization cross section of the hydrogen and probably the overlap of characteristic ionization with other bands. Such observation has already been reported: (a) Dyke, J. M.; Groves, A. P.; Morris, A.; Ogden, J. S.; Dias, A. A.; Oliveira, A. M. S.; Costa, M. L.; Barros, M. T.; Cabral, M. H.; Moutinho, A. M. C. *J. Am. Chem. Soc.* **1997**, *119*, 6883. (b) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485.

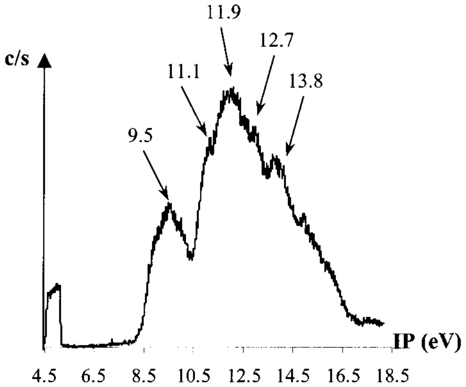
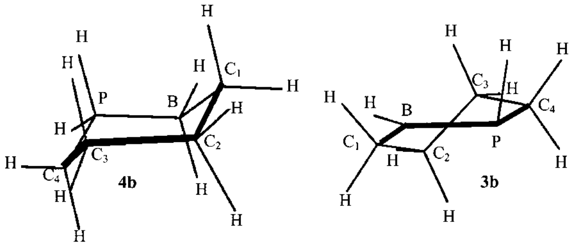


Figure 3. Photoelectron spectrum of **1b**.

Table 3. Geometrical Parameters of 4b and 3b



Bond Lengths (Å)		Bond Lengths (Å)	
PB	1.964	PB	1.880
BC_1	1.632	BC_1	1.570
C_1C_2	1.542	C_1C_2	1.542
C_2C_3	1.540	C_2C_3	1.540
C_3C_4	1.543	C_3C_4	1.537
C_4P	1.842	C_4P	1.885
Bond Angles (deg)		**Bond Angles (deg)**	
PBC_1	103.92	PBC_1	120.05
BC_1C_2	116.14	BC_1C_2	116.97
$C_1C_2C_3$	114.32	$C_1C_2C_3$	112.86
$C_2C_3C_4$	114.32	$C_2C_3C_4$	113.58
C_3C_4P	110.20	C_3C_4P	114.81
C_3PB	108.02	C_3PB	104.05

of the first ionic state calculated for the later at 9.80 eV being consistent with such a hypothesis (Table 2).

The six-membered ring derivative **1b** spectrum (Figure 3) shows a first band centered at 9.5 eV followed by a broader band centered at 11.9 eV. In this case, theoretical results on **4b** show two minima corresponding to the twisted and chair forms, the latter being slightly more stable (5.3 kcal/mol). Geometrical parameters for the chair form are listed in Table 3. In comparison with the five-membered ring previously studied, only the BP distance is found to be smaller because of the steric hindrance reduction.

Table 2 shows the KS and the first ionization energies of the six-membered ring derivatives. We observe for the starting material a decrease in the ionization energy associated with a σ_{BC} orbital from a six- to a five-membered ring. These results are in good agreement with the experimental ones (9.5 eV for **1b** and 10 eV for **1a**). The other experimental ionization potentials follow in the same way where the energy order of the orbital sequence being σ_{BC}, σ_{BH}, σ_{BP}/σ_{BH}, and σ_{CC}/σ_{CH}.

The six-membered ring derivatives show a similar behavior upon thermolysis to the five-membered ring. The spectrum for thermolysis of **1b** at 500 °C (Figure 4a) presents a vertical ionization potential at 8.3 eV corresponding to the *pseudo*-π_{BP} orbital of **2b** with the band centered at 9.8 eV being tentatively associated to the σ_{BP} orbital ionization.

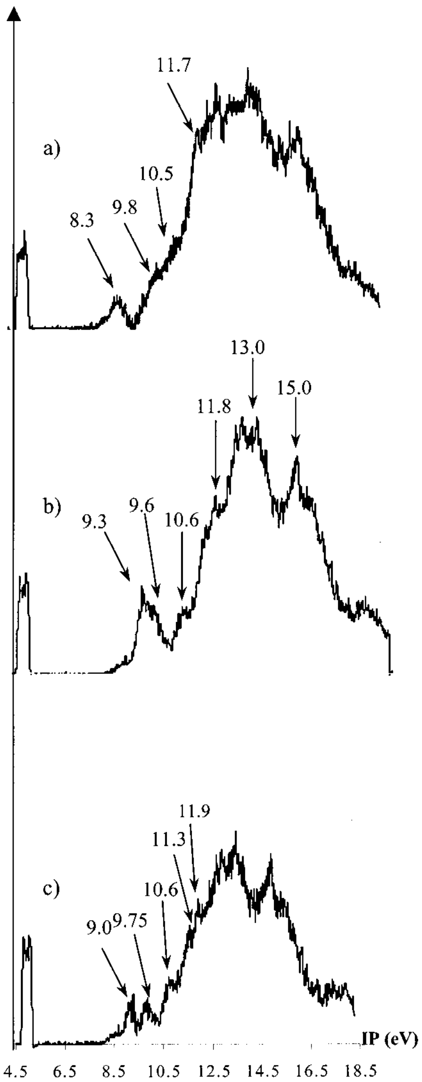
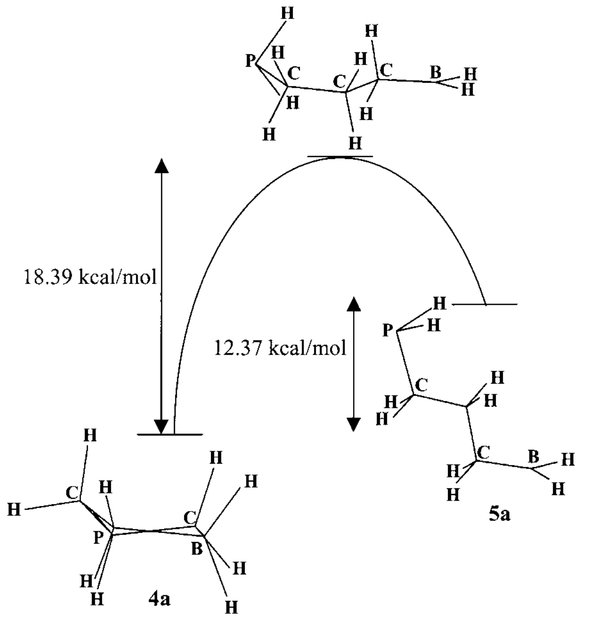


Figure 4. (a) Thermolysis spectrum of **1b** at 500 °C. (b) Thermolysis spectrum of **1b** at 660 °C (black spectrum) and of isobutene (grey spectrum). (c) Difference spectrum between the thermolysis spectrum of **1b** at 660 °C and that of isobutene.

After thermolysis at 660 °C (Figure 4b,4c) the resulting spectrum is consistent with the formation of the phosphinoborane **3b** and isobutene. The two bands at 9 and 10.6 eV can be assigned respectively to the pseudo-π_{BP} and σ_{BP} orbitals (Table 2). It is interesting to note the similarity between the two spectra presented in Figures 2c and 4c. However, formation of the compound **4b** must be envisaged to explain the band at 9.75 eV (Scheme 1), thus following the same hypothesis previously presented for the formation of **4a** (IE calculated at 9.52 eV; Table 2).

As previously reported, the free phosphines were the sole compounds to be characterized in the thermolysis of acyclic phosphine–borane complexes (decomplexation process).[7] The difference in behavior between acyclic and cyclic phosphine–borane could be explained by a ring strain that is imposed for the latter, where there are close geometric parameters between the starting material and the final compound, thus giving a less energetic

Scheme 2. Decomplexation Process of 4a [B3LYP/6-311G(d,p)]



dehydrogenation process and a weak geometric deformation. Here the structural strain does not favor the BP bond breaking. The calculated decomplexation energy barrier for the cyclic compound 1a is near 18.4 kcal (Scheme 2).

The decomplexation process of **1a** cannot be excluded since the first two calculated ionization bands of the free phosphine **5a** (Scheme 2) are close (8.6 and 11 eV) to those observed for the phosphinoborane **2a** (8.6 and the shoulder at 10.9 eV). Nevertheless, since the ionization observed at 10.3 eV can only be assigned to the phosphinoborane **2a** formed by loss of H_2,[16] the decomplexation process, if it exists, should be a minor process as compared to the dehydrogenation one. These results are in good agreement with those obtained in the HRMS study.

Conclusion

We have characterized unstabilized phosphinoboranes by photoelectron spectroscopy. This approach was only possible by starting from cyclic phosphine−boranes as precursors. The ionization of the $\pi_{B=P}$ bond appears at low energy (9 eV), pointing out a weak interaction of the lone pair with the vacant orbital of the boron atom and the pyramidal character of the phosphorus atom. The observed high instability is a consequence of the nonplanarity. This observation makes clear the difficulty of obtaining such species without the help of substituents able to increase the planarity the $\pi_{B=P}$ bond and to enhance the $\pi_{B=P}$ bond overlap. In the experiments described here, this difficulty has been overcome.

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