

Photoelectron Spectrum of Chlorophosphaethyne¹

S. Lacombe,^a G. Pfister-Guillouzo,*^a J. C. Guillemin^b and J. M. Denis^b

^a *Université de Pau & des Pays de l'Adour, Laboratoire de Physico-Chimie Moléculaire, URA 474, Avenue de l'Université, 64000 PAU, France*

^b *Université de Rennes I, Groupe de Recherche de Physico-Chimie Structurale, URA 704, Campus de Beaulieu, Avenue du Général Leclerc, 85042 Rennes, France*

The photoelectron spectrum of chlorophosphaethyne, generated in the gas phase by dehydrochlorination of trichloromethylphosphine on a solid base, is reported; the spectrum is quite consistent with the spectra of the related cyanogen halides or haloacetylenes and indicates a large interaction between the degenerate P=C triple bond and the chlorine lone pair.

Phosphaalkynes are now considered as important building blocks in synthetic chemistry, and although it is a relatively new area, the chemistry of these heteroatomic triple bonds has been extensively investigated.^{2,3} A number of substituted phosphaalkynes are available and the photoelectron spectra of

alkyl- or aryl-phosphaalkynes have been reported.^{4,5} Hetero-substituted phosphaalkynes have been less studied⁶⁻⁸ and the photoelectron (PE) spectra of only the fluoro⁶ and trimethylsilyl⁵ derivatives have been obtained. Owing to our interest in the chemistry of low-coordinated phosphorus compounds,^{9,10}

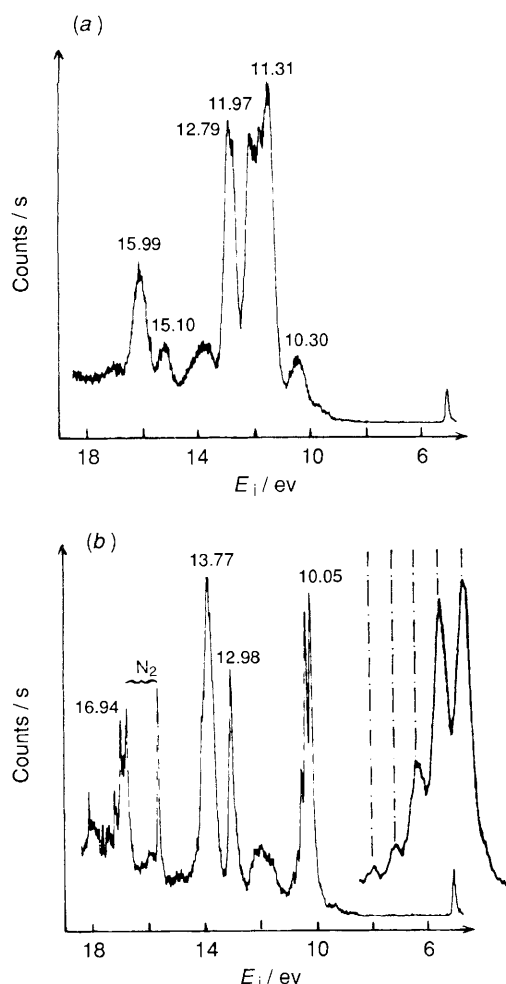


Fig. 1 Photoelectron spectra of (a) trichloromethylphosphine; (b) chlorophosphaethyne obtained by vaporising the trichloromethylphosphine on solid CaO at 500 K followed by a cryogenic trap at 188 K (insert with the broadened first band at 10.05 eV)

and the new versatile access to substituted phosphalkynes,¹¹ we intended to study the electronic structure of chlorophosphaethyne. The effect of chlorine substitution on heteroatomic double or triple bonded species could then be compared, since the photoelectron spectra of *N*-chloroimines and *P*-chlorophosphaalkenes have been previously reported.¹²

Chlorophosphaethyne was generated by vacuum dehydrohalogenation [vacuum gas-solid reaction (VGSR); for other VGSR see refs. 9–12] of trichloromethylphosphine on solid base (K_2CO_3 or CaO) and characterized by IR, ^{31}P and ^{13}C NMR, and high resolution mass spectroscopy.¹¹

The VGSR apparatus and a cold trap were consecutively attached to the PE spectrometer inlet. The trichlorophosphine was cooled to 233 K, then slowly vaporised in a 30 cm long Pyrex tube, half-filled with CaO as solid base. No remaining starting product [characterized by its bands at 10.30 eV (n_P), 11.31, 11.66, 11.97 and 12.79 eV (n_{Cl})] {Fig. 1(a)} was observed when the CaO was heated at a temperature higher than 363 K. Heating to 503 K was, however, needed to obtain the nearly pure chlorophosphaethyne, the temperature of the cold trap being 188 K [Fig. 1(b)]. The weak intensity bands observed between 11.50 and 12 eV probably arise from heavily chlorinated by-products and suggest either an incomplete separation of the less volatile components by the cryogenic trap or the decomposition of chlorophosphaethyne in the trap during its revaporisation. The spectrum obtained displays a first band at 10.05 eV with a well resolved vibrational progression (frequency $1400 \pm 50 \text{ cm}^{-1}$), a sharp second band at 12.98 eV, a broader and intense one at 13.77 eV and a fourth one at 16.95 eV partially hidden by nitrogen ionization.

Previous PE studies on substituted phosphalkynes have shown that the first ionization potential (E_i) of $R-C\equiv P$ compounds can be assigned to the ejection of an electron from the degenerate $\pi C\equiv P$ orbital (π) and the second one to the ejection of an electron from the phosphorus lone pair orbital (n_P).^{4,5} However, the extensive investigations of Heilbronner *et al.* on monohaloacetylenes¹³ and cyanogen¹⁴ halides have shown that the large interaction between the chlorine lone pairs and the π bonds of the same symmetry leads to a splitting of the π orbitals into two components, namely a $\pi - n_{Cl}$ and a

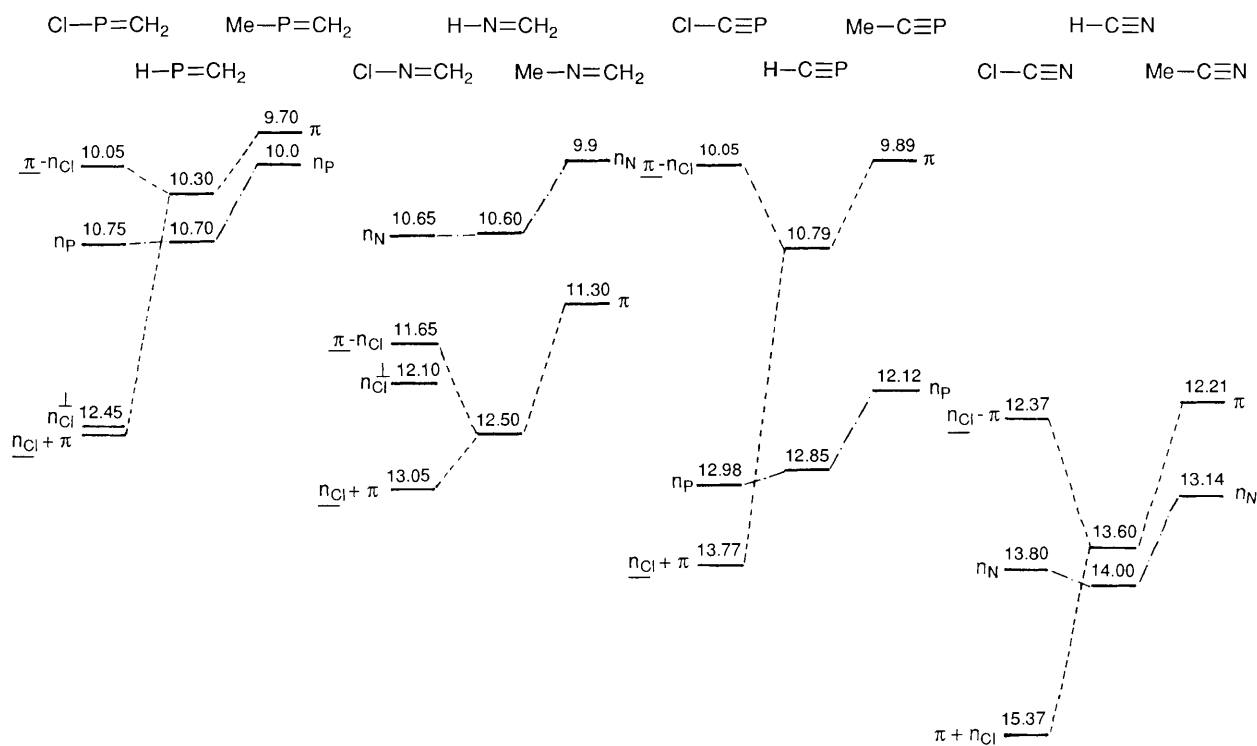


Fig. 2 Correlation diagram between substituted phosphalkenes, imines, phosphalkynes and cyanides

$\pi + n_{\text{Cl}}$ orbital (degenerate). The splitting amounts to 3.45 eV for the acetylenic compound and to 3.00 eV for the cyanide. The same type of splitting is expected for Cl-C \equiv P according to the energetic position of the π orbital of HCP (10.79 eV), inferred from its experimental PE spectrum,¹⁵ compared with the π orbital of HCN (13.60 eV) or C₂H₂ (11.40 eV). The only difference between the nitrogen and the phosphorus compounds will concern the orbital localization: the HOMO should be more heavily localized on the chlorine atom for Cl-C \equiv N and on the C \equiv P triple bond for Cl-C \equiv P (the same localization holds true for monohaloacetylenes¹³).

Accordingly the first E_i value of Cl-C \equiv P at 10.05 eV is attributed to the ejection of an electron from the $\pi - n_{\text{Cl}}$ orbital. The associated vibrational structure with a $1400 \pm 50 \text{ cm}^{-1}$ frequency is assigned to the stretching of the chlorine coupled C \equiv P triple bond of the ion. This value is consistent with the known $\nu_{\text{C}=\text{X}}$ stretching frequency in the phosphalkyne series (HCP: 1276, HCP⁺: 1110 cm^{-1} ;¹⁵ MeCP: 1558,¹⁶ MeCP⁺: 1420 cm^{-1} ¹⁷) and with the observed changes in the cyanide series (HCN: 2097, HCN⁺: 1800 cm^{-1} ;¹⁸ MeCN: 2249, MeCN⁺: 2010 cm^{-1} ;¹⁸ ClCN: 2201, ClCN⁺: 1800 cm^{-1} ¹⁴). The ionization of the $\pi + n_{\text{Cl}}$ orbital is associated with the third E_i at 13.88 eV. (This assignment follows from the broad and finely structured shape of this band, to be compared with the corresponding one of Cl-C \equiv C-H at 14.08 eV.¹⁴) The second band at 12.98 eV in the spectrum of Cl-C \equiv P is thus assigned to the ejection of an electron from the phosphorus lone pair orbital and its sharp shape is quite comparable to the corresponding band of H-C \equiv P at 12.85 eV.¹⁵ The last band at 16.95 eV is associated with the ionization of the $\sigma_{\text{C}-\text{Cl}}$ and C-P bonds. From the correlation diagram displayed in Fig. 2, the following comments arise:

(i) the substitution of both C \equiv P and C \equiv N triple bonds by chlorine gives rise to a destabilized π -HOMO as compared to the parent H-C \equiv P or H-C \equiv N. For both triple or double bonded species the observed destabilization of the π orbital induced by chlorine substitution is greater for the nitrogen compounds than for the phosphorus ones. This results from the greater diffuse character of the $\pi_{\text{C}=\text{P}}$ bond compared to $\pi_{\text{C}=\text{N}}$.

(ii) For triple-bonded compounds the phosphorus and nitrogen lone pair orbitals are poorly sensitive to chlorine substitution as the corresponding IPs are close in H-C \equiv P (12.85 eV) and Cl-C \equiv P (12.98 eV) on one hand and in H-C \equiv N (14.00 eV) and Cl-C \equiv N (13.80 eV) on the other hand (the respective positions are in agreement with phosphorus and nitrogen electronegativities). However, the inductive stabilization by fluorine (-I effect) or destabilization by alkyl groups (+I effect) is much more significant.^{4,5} In the phosphalkenes -imine series the same invariance of the lone pairs to chlorine substitution has been observed but it was accounted for by a counterbalance between the inductive chlorine effect and the spatial destabilizing interactions between halogen-hetero-

atom lone pairs.¹² This effect no longer holds true for the linear triple-bonded species.

It should be mentioned that previous *ab initio* calculations on substituted phosphalkynes predicted the ionization potentials of ClC \equiv P within Koopmans' approximation at values which were rather close to the experimental ones, namely 10.30 (π), 13.20 (n_{p}) and 14.00 eV (π).¹⁹ Extensive basis sets were used (double zeta basis set of Husinaga) which gave a quite reliable geometry for HC \equiv P.

We thank Mrs Maryse Simon for technical assistance.

Received, 21st September 1990; Com. 01042911

References

- 1 For part 43 of the series: Applications of photoelectron spectroscopy to molecular properties, see F. Chuburu, S. Lacombe, G. Pfister-Guillouzo, A. Bencheik, J. Chuche and J. C. Pommelet, *J. Am. Chem. Soc.*, in the press.
- 2 Review: M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484.
- 3 Review: M. Regitz, *Chem. Rev.*, 1990, **90**, 191.
- 4 J. C. T. R. Burckett St Laurent, M. A. King, H. W. Kroto, J. F. Nixon and R. J. Suffolk, *J. Chem. Soc., Dalton Trans.*, 1983, 755, and references cited therein.
- 5 B. Solouki, H. Bock, R. Appel, A. Westerhaus, G. Becker and G. Uhl, *Chem. Ber.*, 1982, **115**, 3747.
- 6 H. W. Kroto, J. F. Nixon, N. P. Westwood and N. P. C. Simmons, *J. Am. Chem. Soc.*, 1978, **100**, 446; H. E. Hosseini, H. W. Kroto, J. F. Nixon, S. Brownstein, J. R. Morton and K. F. Preston, *J. Chem. Soc., Chem. Commun.*, 1979, 653.
- 7 R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, **23**, 2159.
- 8 R. Appel and M. Poppe, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 53.
- 9 B. Pellerin, J. M. Denis, J. Perrocheau and R. Carrie, *Tetrahedron Lett.*, 1986, **27**, 5723.
- 10 S. Lacombe, D. Gonbeau, J. L. Cabioch, B. Pellerin, J. M. Denis and G. Pfister-Guillouzo, *J. Am. Chem. Soc.*, 1988, **110**, 6964.
- 11 J. C. Guillemin, T. Jalati, P. Guenot, P. Savigac and J. M. Denis, *Angew. Chem., Int. Ed. Engl.*, in the press. Cl-C \equiv P: ³¹P NMR: δ -116 (s); ¹³C NMR: δ 126.4 (d, J_{CP} 17 Hz); IR (film, 77 K): ν_{CP} 1460 cm^{-1} ; HRMS: m/z calc.: 77.94262, found: 77.9425.
- 12 S. Lacombe, B. Pellerin, J. C. Guillemin, J. M. Denis and G. Pfister-Guillouzo, *J. Org. Chem.*, 1989, **54**, 5958.
- 13 H. J. Haink, E. Heilbronner, V. Hornung and E. Kloster-Jensen, *Helv. Chim. Acta*, 1970, **53**, 1073.
- 14 E. Heilbronner, V. Hornung and K. A. Muszkat, *Helv. Chim. Acta*, 1970, **53**, 347.
- 15 D. C. Frost, S. T. Lee and C. A. McDowell, *Chem. Phys. Lett.*, 1973, **23**, 472.
- 16 K. Ohno and H. Matsuura, *Chem. Lett.*, 1984, 413.
- 17 N. P. C. Westwood, H. W. Kroto, J. F. Nixon and N. P. C. Simmons, *J. Chem. Soc., Dalton Trans.*, 1979, 1405.
- 18 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley Interscience, London, 1970.
- 19 M. T. Nguyen, *Z. Naturforsch., Teil A*, 1984, **39**, 169.