# Photoelectron Spectra of the Phospha-alkynes:† 3,3-Dimethyl-1-phosphabutyne Bu$^{t}$C$\equiv$P and Phenylphosphaethyne, PhC$\equiv$P

**James C. T. R. Burckett-St. Laurent, Michael A. King, Harold W. Kroto,* John F. Nixon, and Roger J. Suffolk**
*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ*

He(I) photoelectron spectra of the phospha-alkynes Bu$^{t}$CP and PhCP have been obtained. The spectra have been assigned by comparison with spectra of related species and with the aid of *ab initio* SCF molecular orbital calculations. The first ionisation potentials are 9.61 and 8.68 eV for Bu$^{t}$CP and PhCP respectively. These correspond to electron removal from orbitals with essentially $\pi$(CP) bonding character.

The synthesis of phosphaethyne, HCP, by Gier[1] in 1961 provided the first example of a molecule in which tervalent phosphorus forms a triple bond to carbon. Since then a number of other phospha-alkynes have been synthesised and their properties investigated. These include CH$_3$CP,[2] Bu$^{t}$CP,[3] H$_2$C=CHCP,[4] HC$\equiv$CCP,[5] PhCP,[6] Si(CH$_3$)$_3$CP,[7] FCP,[8] CF$_3$CP,[9] NCCP,[10] and most recently, NCC$\equiv$CCP.[11] The existence of these compounds indicates that the chemistry of the C$\equiv$P group is considerably more extensive than was previously thought and further demonstrates the ability of second row elements to participate in $2p_\pi$–$3p_\pi$ multiple bonding.

Progress in this field has been made possible by the development of low-pressure flow-pyrolysis techniques in which unstable product species are identified and characterised by their microwave rotational and/or photoelectron (p.e.) spectra. These two techniques provide complementary information and are well suited to the study of semi-stable species for which polymerisation is the most important decomposition pathway.

Phospha-alkynes have been generated by both pyrolytic and base-induced elimination from appropriately substituted phosphines. For example, HCP is obtained in good yield by high temperature pyrolysis of PMeCl$_2$ [12,13] according to equation (1). Hydrogen chloride which is also formed can be removed by treatment with a suitable base. This method has enabled improved p.e. spectra of HCP as well as electronic emission spectra of the radical cation HCP$^+$ to be recorded.[13] Furthermore, the room temperature reaction of CF$_3$PH$_2$ vapour with KOH affords FCP in high yield [8,14] according to equation (2).

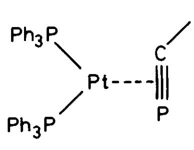
$$\mathrm{PMeCl_2 \xrightarrow{1\,000\ ^\circ C} HCP + 2HCl} \qquad (1)$$

$$\mathrm{CF_3PH_2 + 2KOH \xrightarrow{20\ ^\circ C} FCP + 2KF + 2H_2O} \qquad (2)$$

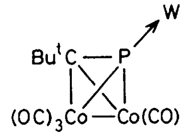
A recent development is the high temperature reaction between PCl$_3$ and CH$_3$R which gives RCP (R = C$\equiv$CH, CN, C$\equiv$CCN, and Ph).[11] The efficiency and general applicability of this type of reaction is under study.

In this paper He(I) p.e. data for 3,3-dimethyl-1-phosphabutyne, Bu$^{t}$CP, and phenylphosphaethyne, PhCP, are presented; Bu$^{t}$CP, which was first reported by Becker *et al.*,[3] is relatively stable in comparison with other phospha-alkynes. Recently, several transition metal–phospha-alkyne complexes (I),[15] (II),[16] and (III)[17] have been prepared whose structures suggest a close parallel with simple alkyne chemistry.

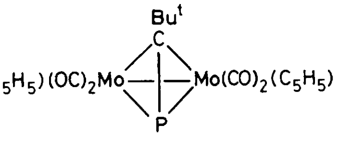
The compound PhCP, originally reported by Appel *et al.*,[6] has been the subject of a recent microwave study.[18]



(I)



(II)



(III)

Photoelectron spectroscopy provides a powerful tool for probing the electronic structure of molecules since ionisation potential (i.p.) data may be directly correlated with the results of molecular orbital (m.o.) calculations. These spectra and the associated calculations have allowed a detailed investigation of the ways in which the electronic structure of the C$\equiv$P group is modified by substituents.

## Experimental

The compound Bu$^{t}$CP was synthesised by the method described by Becker *et al.*[3] *via* base-catalysed elimination of (SiMe$_3$)$_2$O from Bu$^{t}$(Me$_3$SiO)C=PSiMe$_3$ [19] and was purified by high-vacuum fractional condensation. Its purity was checked by i.r. and $^{31}$P-{$^1$H} n.m.r. spectroscopy. The compound PhCP [6,18] was prepared by passing Ph(Me$_3$Si)C=PCl [20,21] vapour at low pressure (*ca.* 50 mTorr) through a quartz tube (i.d. 8 mm) heated to *ca.* 900 °C along *ca.* 150 mm of its length by means of a small cylindrical electric furnace. The pyrolysis products were passed through a −78 °C cold trap at which temperature PhCP condenses. No attempt was made to purify the product in order to minimise losses due to polymerisation. Samples of PhCP were stored at −196 °C.

He(I) p.e. spectra were obtained using a modified Perkin-Elmer PS16 spectrometer fitted with an ' Helectros ' high intensity He(I)–He(II) discharge lamp. Samples of Bu$^{t}$CP

---

† *Non-S.I. units employed:* eV ≈ 1.60 × 10$^{-19}$ J; Torr = (101 325)/760 Pa.

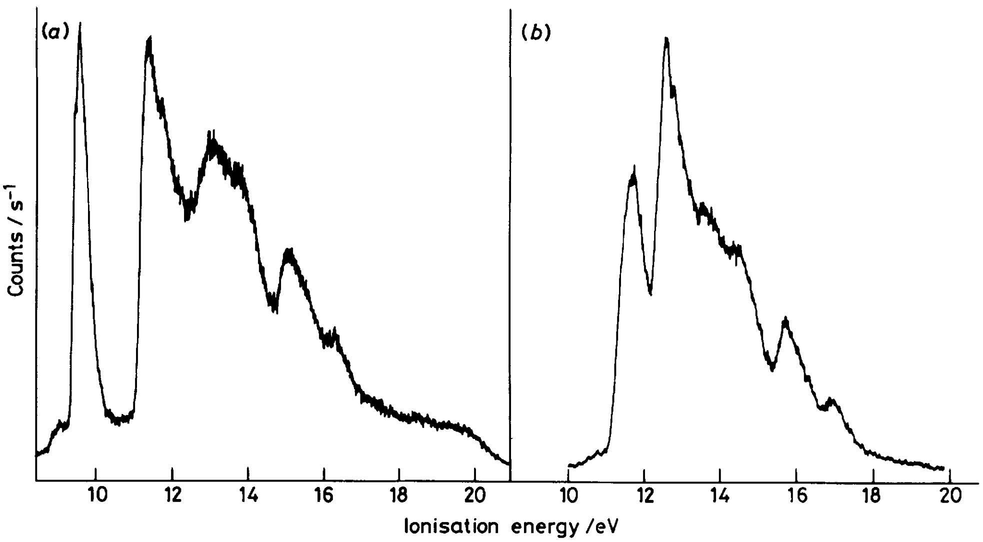


**Figure 1.** The He(I) p.e. spectra of (*a*) Bu$^t$CP and (*b*) Bu$^t$CN

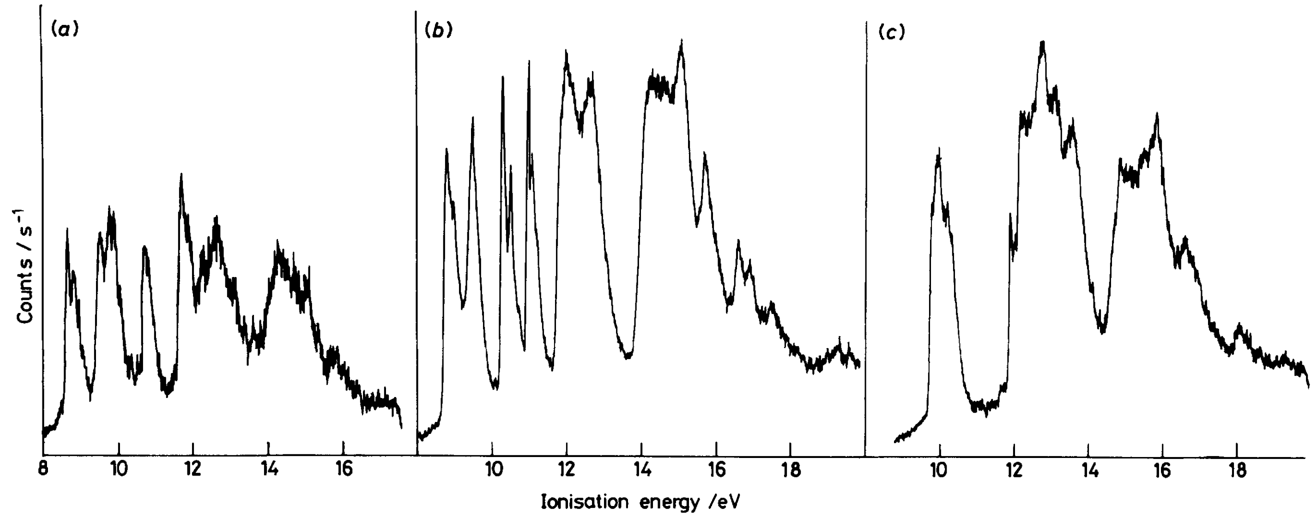


**Figure 2.** The He(I) p.e. spectra of (*a*) PhCP, (*b*) PhC≡CH, and (*c*) PhCN

and PhCP were admitted to the apparatus from glass containers held at −78 and −23 °C respectively. Spectra were calibrated against the known i.p.s of $CH_3I$ and Ar. Resolution in the experiments with Bu$^t$CP was *ca.* 30 meV full width at half-maximum (f.w.h.m.). For PhCP, the resolution was 35 meV at best but deteriorated during the course of an experiment owing to contamination of the ionisation region with polymeric material.

To assist the interpretation of the experimental data, *ab initio* SCF m.o. calculations using the GAUSSIAN 76 computer program [22] were carried out. The computed eigenvalues were obtained using a 4-31 G extended basis and the m.o. coefficients referred to are those from STO-3G calculations. Structural parameters for the calculations were taken from the microwave data of PhCP,[18] PhC≡CH,[23] PhCN,[24] Bu$^t$C≡CH,[25] Bu$^t$CN,[25] $CH_3CP$,[26] and HCP.[27]

## Results

The He(I) p.e. spectra of Bu$^t$CP and PhCP are shown in Figures 1(*a*) and 2(*a*) respectively. For comparison, the spectra of Bu$^t$CN [28] [Figure 1(*b*)], PhC≡CH [29] [Figure 2(*b*)], and PhCN [29] [Figure 2(*c*)] are also presented. Experimental i.p.s and assignments are listed in the Table together with results of the m.o. calculations.

3,3-*Dimethyl*-1-*phosphabutyne*.—The p.e. spectrum of Bu$^t$CP is characterised by relatively broad structureless bands and is qualitatively very similar to that of Bu$^t$CN [Figure 1(*b*)]. Calculation indicates that the first i.p. should be associated with removal of the $\pi$(CP) electrons and the position of this band, at 9.61 eV, is in good agreement with the predicted value of 9.46 eV (7*e*). This is in accord with the previously reported p.e. results for HCP,[30] $CH_3CP$,[2] and FCP [8] in which the highest occupied molecular orbital (h.o.m.o.) is also of $\pi$(CP) character.

The second band at 11.44 eV is assigned to the n(P) orbital (12$a_1$), which is also in agreement with calculation and the p.e. spectra of related phospha-alkynes. The $\pi$(CP)–n(P) separation of 1.83 eV may be compared with corresponding

**Table.** Ionisation potential data for Bu$^t$CP and PhCP [a]

| Bu$^t$CP I.p. | Obs. | Calc.[b] | Assignment [c] | PhCP I.p. | Obs. | Calc.[b] | Assignment |
|---|---|---|---|---|---|---|---|
| 1 | 9.61 | 9.46 | π(CP) (7*e*) | 1 | 8.68 [c] | 8.35 | π(CP) (4*b*$_1$) |
| 2 | 11.44 | 12.07 | n(P) (12*a*$_1$) | 2 | 9.60 | 9.38 | π(ring) (1*a*$_2$) |
| 3 | | 12.99 | (6*e*) | 3 | 9.87 [d] | 9.82 | π(CP) (9*b*$_2$) |
| 4 | | 14.05 | (1*a*$_2$) | 4 | 10.79 | 11.06 | π(ring) (3*b*$_1$) |
| 5 | | 14.23 | (11*a*$_1$) | 5 | 11.76 | 12.51 | n(P) (17*a*$_1$) |
| 6 | | 14.88 | (5*e*) | 6 | | 13.74 | (8*b*$_2$) |
| 7 | | 16.51 | (4*a*) | 7 | | 14.10 | (16*a*$_1$) |
| 8 | | 17.85 | (10*a*$_1$) | 8 | | 14.24 | (2*b*$_1$) |
| 9 | | 21.61 | (9*a*$_1$) | 9 | | 16.31 | (7*b*$_2$) |
| | | | | 10 | | 16.71 | (15*a*$_1$) |
| | | | | 11 | | 17.35 | (6*b*$_2$) |
| | | | | 12 | | 18.16 | (14*a*$_1$) |
| | | | | 13 | | 19.96 | (13*a*$_1$) |
| | | | | 14 | | 22.77 | (12*a*$_1$) |
| | | | | 15 | | 22.81 | (5*b*$_2$) |

[a] All i.p.s in eV. Uncertainty in observed values is ±0.03 eV. [b] Calculated i.p.s assuming Koopmans' theorem applies. [c] Vibrational frequency 1 350 ± 100 cm$^{-1}$. [d] Vibrational frequency 920 ± 100 cm$^{-1}$.

values of 2.07 eV for HCP[30] and 2.30 eV for $CH_3CP$.[2] The separations predicted from the results of 4-31 G calculations are: 2.61 (Bu$^t$CP), 2.72 (HCP), and 2.98 eV ($CH_3CP$).

Further analysis of the spectrum of Bu$^t$CP is hindered by the presence of broad and overlapping band profiles. Calculation indicates that there are *ca.* six i.p.s in the region 11.5—20.0 eV, all of which are associated with orbitals mainly localised on the alkyl group. This is confirmed by comparing with the corresponding region in the spectrum of Bu$^t$CN [Figure 1(*b*)] which contains very similar features in this region.

*Phenylphosphaethyne.*—Assignments of the first five bands in the p.e. spectrum of PhCP present few problems. This is due to their well defined nature, the presence in some cases of vibrational fine structure, and the good agreement between observed and calculated i.p.s. The results of the calculations are given in the Table and schematic representations of the four highest occupied m.o.s are shown in Figure 3.

Monosubstitution of benzene causes its $D_{6h}$ symmetry to be lowered and the highest occupied $e_{1g}$ levels to be split apart giving (in $C_{2v}$ symmetry) $a_2$ and $b_1$ orbitals. Similarly the local $C_{\infty v}$ symmetry of the two π(CP) orbitals is removed, giving rise to an in-plane $b_2$ orbital and an out-of-plane $b_1$ orbital. On a localised orbital picture the strongest interactions are expected to occur between the ring and substituent π orbitals of $b_1$ symmetry.

The region between 8.5 and 11.5 eV in the p.e. spectrum of PhCP [Figure 2(*a*)] contains four bands which are associated with ionisations involving π electrons. Calculation indicates that the first and third bands, with adiabatic i.p.s of 8.68 and 9.87 eV, are associated with the out-of-plane 4$b_1$ and in-plane 9$b_2$ orbitals respectively, both of which have predominantly π(CP) bonding character (Figure 3). The presence of vibrational structure on these bands lends further support to this assignment. The measured vibrational intervals are 1 350 ± 100 cm$^{-1}$ and 920 ± 100 cm$^{-1}$ for the 4$b_1$ and 9$b_2$ bands respectively. The first progression is identified with the C≡P stretching mode and its frequency may be compared with the corresponding values of 1 150 ± 10 cm$^{-1}$ for the $\tilde{X}^2\Pi$ state of $HCP^+$ [13] and 1 420 ± 50 cm$^{-1}$ for the $\tilde{X}^2E$ state of $CH_3CP^+$.[2] The second frequency (920 cm$^{-1}$) is probably associated with a vibration which is essentially stretching of the C–C bond between the phenyl and C≡P groups. Similarly vibrational

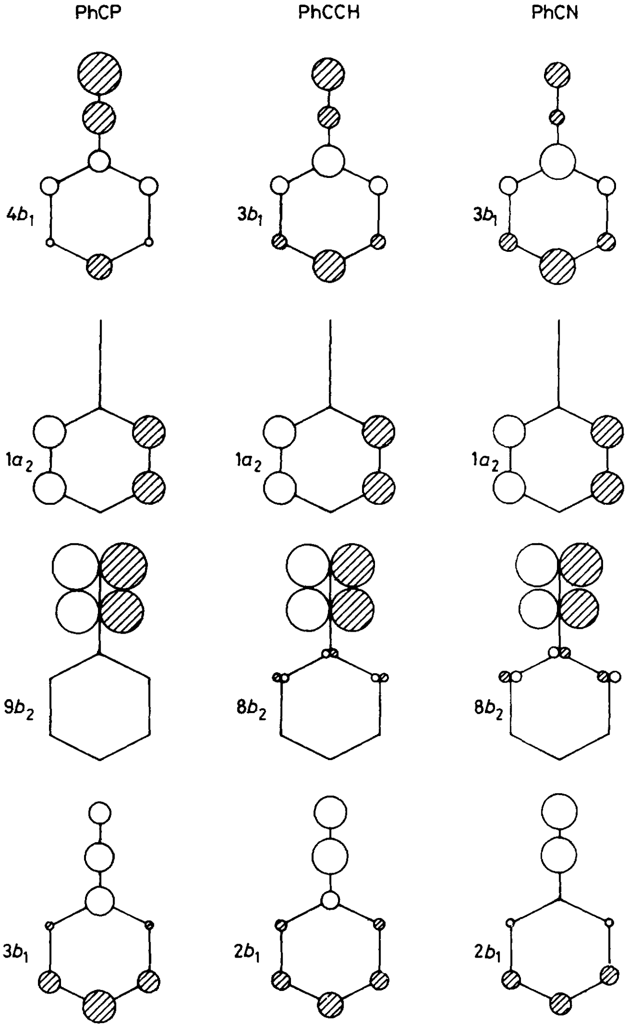


**Figure 3.** Schematic representation of the first four orbitals of PhCX (X = P, CH, and N) as obtained from STO-3G calculations. Only the valence shell *p* orbitals are represented. The diameters of the circles are proportional to the orbital coefficients. Negative lobes are shaded

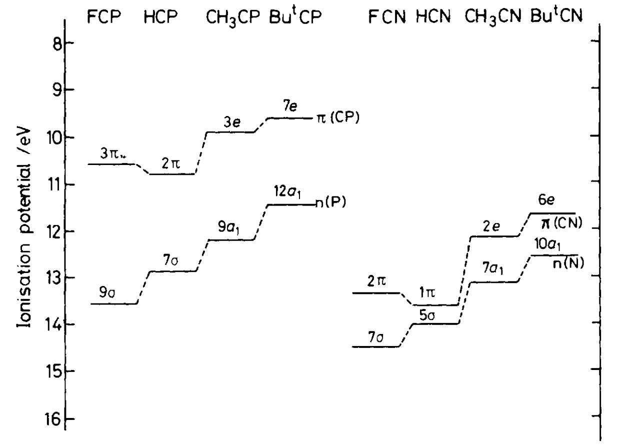


**Figure 4.** Orbital correlation diagrams for the first two i.p.s of RCP (left) and RCN (right) (R = F, H, $CH_3$, and $Bu^t$)

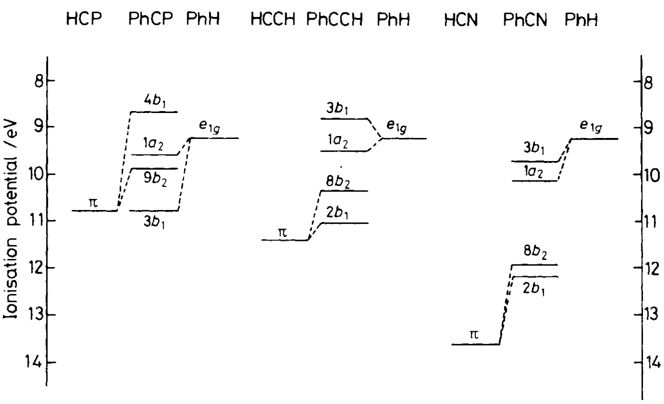


**Figure 5.** Orbital correlation diagrams for PhCX (X = P, CH, and N). The first four i.p.s are correlated with the corresponding i.p.s of benzene and HCX

structure is observed on the corresponding third and fourth bands (see Discussion section) in the p.e. spectrum of PhC≡CH [29] [Figure 2(*b*)].

The second and fourth bands at 9.60 and 10.79 eV are associated with orbitals of predominantly $\pi$(ring) character. Calculation indicates that the $1a_2$ orbital lies *ca.* 1.7 eV above the $3b_1$ orbital which can be compared with the observed separation of 1.2 eV. No vibrational structure is resolved on these bands.

The fifth band centred at 11.76 eV is relatively sharp and calculation indicates that it is associated with the $17a_1$ orbital which is of predominantly n(P) character. This assignment is also consistent with the observation of sharp bands for the analogous i.p.s of HCP [30] and $CH_3CP$.[2]

As far as the bands higher than 11.8 eV are concerned, calculation indicates there to be *ca.* eight i.p.s in the region up to 20 eV. The broadness of the features in this region precludes unambiguous assignment.

## Discussion

The calculations are in very good quantitative agreement with experiment and have allowed reliable assignments to be made, especially for ionisations associated with the C≡P group in both $Bu^tCP$ and PhCP. In Figure 4, the correlation diagram for the first and second i.p.s of FCP,[8] HCP,[30] $CH_3CP$,[2] and $Bu^tCP$ is presented together with that for the analogous nitriles FCN,[31] HCN,[30] $CH_3CN$,[32] and $Bu^tCN$.[28] For the phospha-alkynes there is an overall shift to lower i.p. as is expected when N is replaced by the less electronegative P atom. However, the most striking and perhaps the most important feature of Figure 4 is the increased $\pi$–n separation in the phospha-alkyne series as compared to that of the nitriles. This is a quantitative indicator of the reduced overlap for a $2p_\pi$–$3p_\pi$ interaction relative to that for the $2p_\pi$–$2p_\pi$ case. The main effect is the destabilisation of the $\pi$-bonding orbitals in the C≡P group. Substituent effect trends for both the P- and N-containing compounds are quantitatively remarkably similar (Figure 4). The n orbital i.p.s decrease steadily in the order F > H > $CH_3$ > $Bu^t$ for both series and this trend is readily understood in terms of increasing electron releasing ability (+*I* effect) of the substituent. For the $\pi$ orbitals, differences in substituent mesomeric effects appear to be important and are responsible for the observed ordering: H > F > $CH_3$ > $Bu^t$.

The effects of the less favourable overlap in the $2p_\pi$–$3p_\pi$ case of PhCP, as compared with the $2p_\pi$–$2p_\pi$ cases of PhC≡CH and PhCN, can be analysed with the aid of Figure 5 where the correlations between the four highest occupied $\pi$ orbitals of PhCX (X = P, CH,[29] or N [29]) and the corresponding levels in benzene [33] and HCX are shown. There appear to be roughly two dominant effects: (*i*) an overall *stabilisation* of the $\pi$(ring) components (relative to benzene) together with an associated *destabilisation* of the $\pi$(CX) components (relative to HCX); and (*ii*) splitting of the degeneracies of the $\pi$(ring) and $\pi$(CX) components. The trend in the splitting, which arises as a result of mixing of the ring and substituent components of *b* symmetry, shows a strong dependence on the energy separation of the two components, in accord with second-order perturbation theory. It is greatest for PhCP where the separation between HCP and PhH is only 1.5 eV and least for PhCN where the separation between HCN and PhH is 4.5 eV. This conjugative interaction causes the h.o.m.o. in PhCP to have predominantly $\pi$(CP) character. Thus a switch-over occurs across the series PhCN, PhCCH, PhCP from a n($b_1$) h.o.m.o. which has mainly $\pi$(ring) character to one with mainly $\pi$(CX) character (Figure 3). An opposing, parallel trend occurs for the fourth orbital. As expected, the $a_2$ and $b_2$ orbitals remain essentially localised on the ring and substituent respectively, these orbitals being subject to shifts due primarily to inductive effects.

The $\pi$–n separation in the phospha-alkynes and nitriles is of interest in connection with their co-ordination chemistry. The vast majority of nitriles are known to bond to transition metals *via* the nitrogen lone pair although there are a few (*e.g.* $CF_3CN$) which form side-bonded metal complexes. The greater separation of the $\pi$ and n levels in RC≡P suggests that side-on bonding to metals will usually be preferred, the effect being greatest for FC≡P. To date $Bu^t$C≡P has been co-ordinated in a side-on manner to $Pt^0$ in $[Pt(PPh_3)_2(PCBu^t)]$ [15] and to two cobalt or molybdenum atoms in $[Co_2(CO)_6(PCBu^t)]$ [15] and $[Mo_2(CO)_4(C_5H_5)_2(PCBu^t)]$ [16] respectively. Interestingly the effect of co-ordination of the phospha-ethyne affects the donor properties of the phosphorus lone pair which can subsequently bind to a third metal atom.[16] To date no metal complexes are known in which the phosphorus lone pair is the sole bonding site.

## Acknowledgements

We are grateful to the S.E.R.C. for grants (to J. C. T. R. B. St. L. and M. A. K.) and also to D. M. Kroto for assistance with diagrams.

## References

1 T. E. Gier, *J. Am. Chem. Soc.*, 1961, **83**, 1769.

2 N. P. C. Westwood, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Dalton Trans.*, 1979, 1405.

3 G. Becker, G. Grosser, and W. Uhl, *Z. Naturforsch., Teil B*, 1981, **36**, 16.

4 K. Ohno, H. W. Kroto, and J. F. Nixon, *J. Mol. Spectrosc.*, 1981, **90**, 507.

5 H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 512.

6 R. Appel, G. Maier, H. P. Ruseiauer, and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 197.

7 R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, 2159.

8 H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 446.

9 H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, unpublished work.

10 T. A. Cooper, H. W. Kroto, J. F. Nixon, and O. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1980, 333.

11 T. A. Cooper, M. C. Durrant, H. W. Kroto, D. McNaughton, J. F. Nixon and K. Ohno, unpublished work.

12 M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1976, 513.

13 M. A. King, D. Klapstein, H. W. Kroto, J. P. Maier, O. Marthaler, and J. F. Nixon, *Chem. Phys. Lett.*, 1981, **82**, 543.

14 K. Ohno, H. Matsuura, H. W. Kroto, and H. Murata, *Chem. Lett.*, 1982, 981.

15 J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1981, 1141.

16 J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, M. F. Meidine, and J. F. Nixon, *J. Organomet. Chem.*, 1982, **238**, C82.

17 J. C. T. R. Burckett-St. Laurent, H. W. Kroto, M. F. Meidine, and J. F. Nixon, unpublished work.

18 J. C. T. R. Burckett-St. Laurent, H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1982, **92**, 158.

19 G. Becker, *Z. Anorg. Allg. Chem.*, 1977, **430**, 66.

20 R. Appel and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 556.

21 J. C. T. R. Burckett-St. Laurent, H. W. Kroto, and J. F. Nixon, unpublished work.

22 J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, GAUSSIAN 76, Quantum Chemistry Program Exchange, 11, 1978, p. 368.

23 A. P. Cox, I. C. Ewart, and W. M. Stigliani, *J. Chem. Soc., Faraday Trans. 2*, 1975, 504.

24 J. Casado, L. Nygaard, and G. O. Sørensen, *J. Mol. Struct.*, 1971, **8**, 211: B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Chem. Phys.*, 1962, **37**, 2027.

25 L. J. Nugent, D. E. Mann, and D. R. Lide, jun., *J. Chem. Phys.*, 1962, **36**, 965.

26 H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Mol. Spectrosc.*, 1979, **77**, 270.

27 J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170.

28 R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1976, **98**, 2081.

29 J. W. Rabalais and R. J. Colton, *J. Electron Spectrosc.*, 1972/73, **1**, 83.

30 D. C. Frost, S. T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, 1973, **23**, 472.

31 G. Bieri, *Chem. Phys. Lett.*, 1977, **46**, 107.

32 D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, 1970, **4**, 533.

33 A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 1968, 22.

*Received 1st September* 1982; *Paper* 2/1508