Bonding Studies of Compounds of Boron and the Group 3—5 Elements.[†] Part XIII.[1] He(I) Photoelectron Spectra of Phosphines R_nPX_{3-n} (R = Me or Bu^t; X = H, Cl, or F; n = 1—3), $(Me_2N)_nPCl_{3-n}$ (n = 1—3), and $(R_2N)PF_2$ (R = Me or Et)

By **Michael F. Lappert,* J. Brian Pedley,*** and **Bernard T. Wilkins,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ
Othmar Stelzer * and **Eugen Unger,** Lehrstuhl B, Institut für Anorganische Chemie Technische, Universität, Braunschweig, West Germany

The He(I) photoelectron spectra of the title compounds have been measured. An empirical assignment of most of the bands is proposed and the effects of various substituents on the phosphorus lone-pair ionisation potentials are assessed. Correlations are made with various other parameters relating to phosphine basicity, and it is concluded that the phosphorus lone-pair i.p. provides a reasonable measure of relative basicity or σ-donor ability within related series of compounds.

PHOSPHINES constitute one of the most common groups of ligands in inorganic and organometallic chemistry. There has been much discussion of chemical reactivity and i.r. or n.m.r. spectroscopic properties in terms of phosphine basicity. Additionally, there is controversy about the nature of the phosphorus–transition metal donor–acceptor bond.[2] Despite this, He(I) photoelectron (p.e.) spectroscopic investigations have so far been restricted to a small number of these molecules. Maier and Turner [3] made a detailed study of the spectra of PH_3 and PF_3 to investigate the geometry of the molecular ions, while PF_3 has been examined by Bassett and Lloyd.[4] The spectrum of PCl_3 is discussed in a paper by Potts and Price.[5] More complicated molecules such as $P(OMe)_3$ and $PhPCl_2$ have been studied by Betteridge *et al.*,[6] and molecules of the form PF_2X (X = H, halogen, or pseudohalogen) by Cradock and Rankin.[7] Cowley *et al.* have recently examined $(Me_2N)PCl_m(CF_3)_{2-m}$ (m = 0—2) [8a] and $(Me_2N)_nPF_{3-n}$ (n = 1—3).[8b] There are data on phenyl derivatives (see Table 2). Bock has recently reviewed p.e. spectroscopy of phosphorus compounds.[9]

The work here described utilises closely related series of the form R_nPX_{3-n} (R = Me or Bu^t; X = H, Cl, or F; n = 1—3). This facilitates an empirical assignment of most of the bands in the spectra, and also allows the effects of various substituents on the phosphorus lone-pair ionisation potentials to be assessed. The interaction of the phosphorus lone pair and the high-energy lone-pair orbitals of suitable symmetry on substituents has been investigated using the series $(Me_2N)_nPCl_{3-n}$ (n = 1—3) and $(R_2N)PF_2$ (R = Me or Et). In so far as there is overlap with the work of Cowley *et al.*,[8] we differ both in objectives and assignments (see ref. 10 for work on related boron compounds).

EXPERIMENTAL

The phosphines were prepared by literature methods: Me_3P by a Grignard reaction with $P(OPh)_3$;[11] $MePH_2$,[12] Bu^tPH_2,[13] and Bu$^t_2$PH [14] by reduction of the corresponding chlorophosphines with $Li[AlH_4]$; Me_2PH from $Me_2(S)PP(S)Me_2$ and $Li[AlH_4]$,[15] Bu^tPCl_2[16] and Bu$^t_2$PCl [16] from Bu^{t}MgCl and PCl_3 in diethyl ether solution; chloride–fluoride exchange with sodium fluoride in tetrahydro-1,1-dioxythiophen, $C_4H_8SO_2$, led to Bu^tPF_2 [17] and Bu$^t_2$PF;[17] PBu$^t_3$ [18] from Bu$^t_2$PCl and Bu^{t}Li in hexane; $(Me_2N)_3P$ [19] from PCl_3 and Me_2NH; $(Me_2N)_2PCl$ [20] and $(Me_2N)PCl_2$ [20] by equilibration of mixtures in appropriate stoicheiometry of $(Me_2N)_3P$ and PCl_3 at elevated temperatures; $(Et_2N)PF_2$ [21] and $(Me_2N)PF_2$ [21,22] by Cl–F exchange; and $MePF_2$ [23a] and Me_2PF [23b] from the corresponding chlorophosphines in a fluid-bed reactor filled with KF or NaF. The purity of these compounds was checked by i.r. and n.m.r. spectroscopy. All manipulations were carried out using standard high-vacuum-line techniques or under a dry-nitrogen or argon blanket.

Photoelectron (p.e.) spectra were obtained on a Perkin-Elmer PS16 spectrometer, except for the rather unstable

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[†] The series title was formerly 'Bonding studies of compounds of boron and the Group III and IV elements.'

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[8] (*a*) A. H. Cowley, M. J. S. Dewar, J. W. Gilje, D. W. Goodman, and J. R. Schweiger, *J.C.S. Chem. Comm.*, 1974, 340; (*b*) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Amer. Chem. Soc.*, 1973, **95**, 6506.

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MePF$_2$ and Me$_2$PF which were measured on the Munich PS18 instrument. Vertical ionisation energies (eV) shown in Figures 1—9 are: MePH$_2$ 9·70, 12·40, 12·70, and 14·45 (band centre); Me$_2$PH 9·10, 12·95 (band centre), 13·65, 14·15, and 15·00; Me$_3$P 8·65, 11·25, 11·50, 13·25, 13·70, 14·60, and 16·65; MePF$_2$ 10·35, 13·95, 15·20, 15·95 (sh), 17·20, and 18·05; Me$_2$PF 9·35, 11·75, 13·85, and 15·75; Me$_3$P (see above); MePCl$_2$ 9·85, 11·60 (sh), 11·90, 12·90, 13·80, 14·05 (sh), and 15·15; Me$_2$PCl 9·20, 10·95, 11·70, 12·50, 12·85, and 13·90; Me$_3$P (see above); Bu^{t}PH$_2$ 9·30, 11·00, 11·60, 12·20, and 12·70; Bu$^t_2$PH 8·35, 9·80, 11·50, 12·70, 13·15 (sh), and 14·70; Bu$^t_3$P 7·70, 9·60, 10·70, 11·60, 12·65 (band centre), 14·35, 14·95, and 16·75; Bu^{t}PF$_2$ 9·65, 11·75, 12·8, 13·3, 13·8 (band centres), 15·00, 15·75, 17·00, and 17·65; Bu$^t_2$PF 8·50, 9·90, 11·55, 11·90, 12·80, 14·7 (band centre), and 16·00; Bu$^t_3$P (see above); Bu^{t}PCl$_2$ 9·30, 11·20, 11·55, 12·60, 13·00 (sh), 14·35, and 15·40; Bu$^t_2$PCl 8·45, 9·80, 11·35, 12·5 (band centre), 14·70 and 16·90; Bu$^t_3$P (see above); (Me$_2$N)PCl$_2$ 9·50, 10·00, 11·60 (sh), 11·95, and 12·70; (Me$_2$N)$_2$PCl 8·25, 8·95, 9·50, 11·10, 12·40 (sh), 12·75, and 13·70; (Me$_2$N)$_3$P 7·30, 7·95, 8·60, 9·80, 11·45 (sh), 12·15, 12·75, and 13·31; (Me$_2$N)PF$_2$ 9·60, 10·50, 14·35 (band centre), 16·05, and 17·20 (band centre); (Et$_2$N)PF$_2$ 9·45 and 10·25; (Cl$_3$C)PF$_2$ 10·65, 11·55, 11·95, 12·45, 12·90, 15·60, 16·40, and 17·80; and (Cl$_3$C)PCl$_2$ 10·25, 11·60, 12·00, 12·70 (sh), 12·90, 13·90, 14·80, and 16·15.*

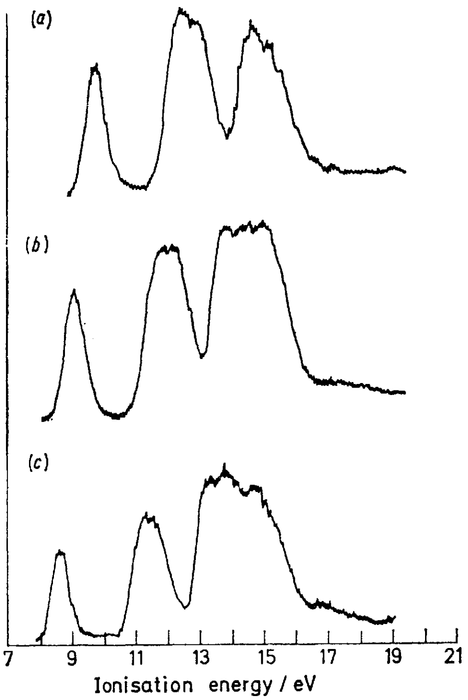

FIGURE 1 P.e. spectra of MePH$_2$ (*a*), Me$_2$PH (*b*), and Me$_3$P (*c*)

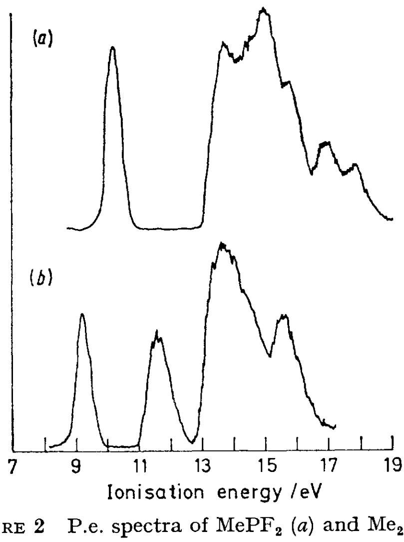

FIGURE 2 P.e. spectra of MePF$_2$ (*a*) and Me$_2$PF (*b*)

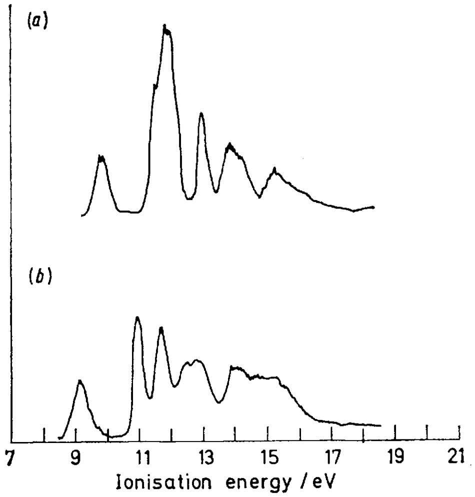

FIGURE 3 P.e. spectra of MePCl$_2$ (*a*) and Me$_2$PCl (*b*)

RESULTS AND DISCUSSION

The p.e. spectra of the phosphines studied are shown in Figures 1—9. In the series of compounds R$_n$PX$_{3-n}$

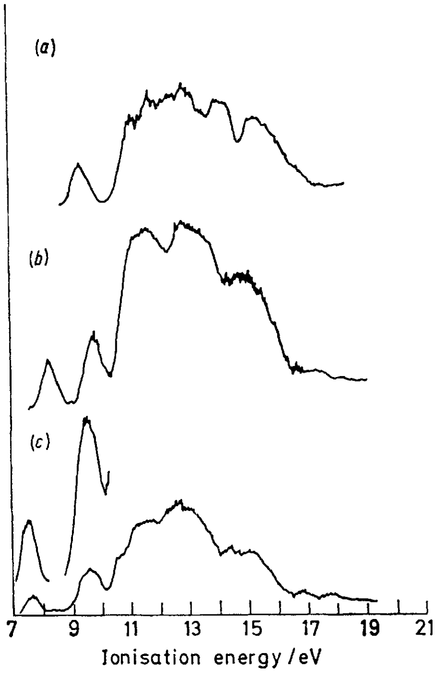

FIGURE 4 P.e. spectra of Bu^{t}PH$_2$ (*a*), Bu$^t_2$PH (*b*), and Bu$^t_3$P (*c*)

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* 1 eV ≈ 1·60 × 10^{-19} J.

($R = Me$ or Bu^t; $X = H$, Cl, or F) the first band in the spectrum in each case was assigned to the phosphorus lone pair. The first ionisation potential (i.p.) is chemically probably the most significant parameter to be derived from the spectra because of its relation to phosphine basicity. The phosphorus lone-pair energies are shown in Table 1. Replacement of a Me by a Bu^t group causes a decrease in i.p. There is very little change in i.p. on substitution of Cl for H, and (except for PCl_3 and PF_3) only a small increase in i.p. on replacing Cl by F. It therefore appears that the mesomeric and inductive effects associated with the halogen atom are almost cancelling in all cases except PF_3, where presumably the combination of F lone-pair orbitals of a_1 symmetry is too low in energy to interact significantly with the P lone-pair orbital. Compounds of the form PF_2X ($X = H$ or Cl) have been investigated by others,[7] who assigned the first i.p. values (11·0 and 11·5 eV, respectively) to a phosphorus lone pair in PF_2H and to a *chlorine* lone pair in PF_2Cl. However, these two values are consistent with the data in Table 1 only if they are both P lone-pair orbitals, since chlorine and hydrogen appear to have approximately the same effect on the energy of the P lone pair.

TABLE 1

Phosphorus lone-pair ionisation energies (eV)

Me_3P	8·63				
Me_2PH	9·08	Me_2PCl	9·19	Me_2PF	9·37
$MePH_2$	9·72	$MePCl_2$	9·83	$MePF_2$	10·34
Bu^t_3P	7·70				
Bu^t_2PH	8·35	Bu^t_2PCl	8·44	Bu^t_2PF	8·50
Bu^tPH_2	9·32	Bu^tPCl_2	9·32	Bu^tPF_2	9·63
PH_3	10·58[a]	PCl_3	10·7[b]	PF_3	12·3[c]

[a] Ref. 3. [b] Ref. 4. [c] Ref. 5.

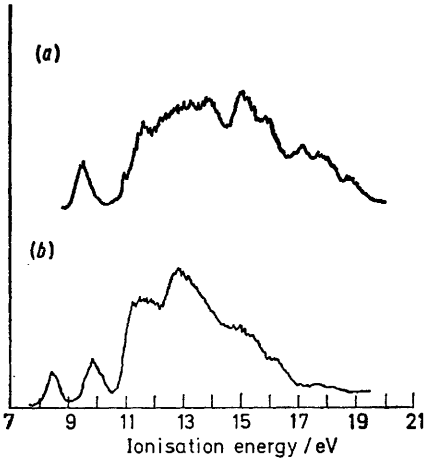

FIGURE 5 P.e. spectra of Bu^tPF_2 (*a*) and Bu^t_2PF (*b*)

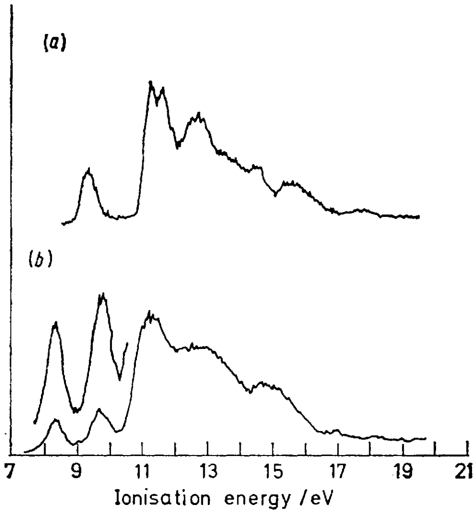

FIGURE 6 P.e. spectra of Bu^tPCl_2 (*a*) and Bu^t_2PCl (*b*)

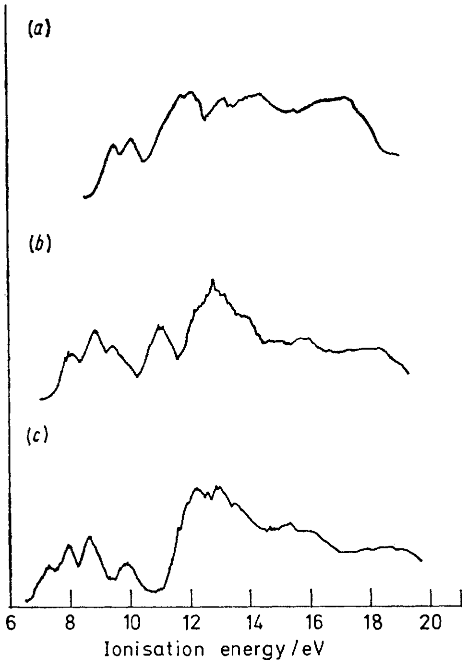

FIGURE 7 P.e. spectra of $(Me_2N)PCl_2$ (*a*), $(Me_2N)_2PCl$ (*b*), and $(Me_2N)_3P$ (*c*)

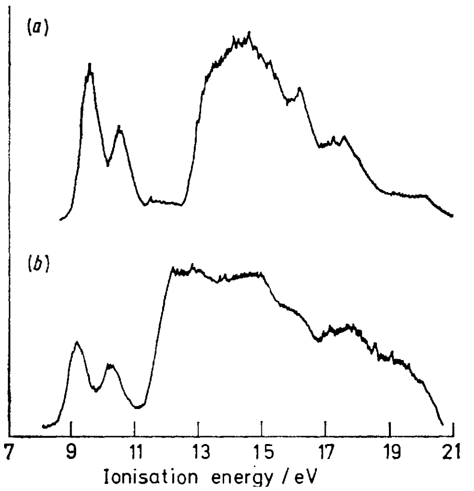

FIGURE 8 P.e. spectra of $(Me_2N)PF_2$ (*a*) and $(Et_2N)PF_2$ (*b*)

The three bonding molecular orbitals of PH_3 and PMe_3 are of symmetry types *e* and *a*. In the mixed compounds PH_2Me and $PHMe_2$, the *e* orbital becomes *a'* and *a''*. There will also be bands in the p.e. spectrum due to ionisation from predominantly C–H orbitals. The latter bands will increase monotonically in intensity relative to the P lone pair down the series PH_3 to PMe_3. Thus the third band in Figure 1 is assignable to ionisation from the ' CH_3 ' group. The second band in the spectra maintains a constant intensity relative to the lone-pair band, which suggests strongly that in the mixed compounds there is an accidental degeneracy of the *a'* and *a''* orbitals and that apart from a monotonic shift in ionisation potential from 11·35 eV for PMe_3 to 13·5 eV for PH_3 the P–H and P–C bands are very similar electronically. In the series Me_nPF_{3-n} it is noteworthy that, in this case, the second band decreased to approximately half its intensity relative to the lone pair on passing from PMe_3 to PMe_2F. This is consistent with the *e* orbital of PMe_3 becoming, in PMe_2F, the *a''* orbital involving exclusively the PMe_2 group and the *a'* orbital involving mainly the P–F bond which would ionise at a much higher potential. A similar trend is also observable in the series Me_nPCl_{3-n} where the bands due to the P–C bonds occurred after the two bands for the chlorine lone pairs.

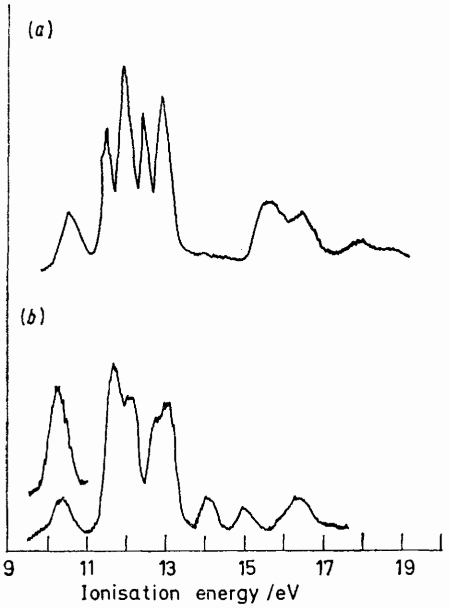

FIGURE 9 P.e. spectra of $(Cl_3C)PF_2$ (*a*) and $(Cl_3C)PCl_2$ (*b*)

In R_2PCl two separate halogen lone-pair bands are to be expected since only one lone pair (*a'*) is of the correct symmetry to interact with the phosphorus lone pair. In fact, a splitting was only observed when R = Me. In this particular case, the lower-energy component (11·70 eV) was markedly broader than that at higher energy (10·95 eV), indicating some degree of interaction. When R = NMe_2 (Figure 7) there was clearly no splitting of the band centred at 11·10 eV which we assign to the chlorine lone-pair levels. Furthermore, the band had twice the intensity of the nearby non-degenerate nitrogen lone pair. When R = Bu^t (Figure 6) the band was not so distinct and no estimate can be made. In the dichloro-compounds, $RPCl_2$, four separate bands are expected since the chlorine lone pairs transform as $2a' + 2a''$. However, as is common in polyhalogenated compounds,[24] intense overlapping bands were observed. Dichloro(methyl)phosphine had two lone-pair bands in the approximate intensity ratio 3 : 1. The possible ordering of these lone-pair bands will not be discussed. When R = NMe_2, the bands in this region were broad and featureless, but when R = Bu^t the chlorine lone-pair bands were just discernible over those due to the Bu^t group.

Fluorine lone pairs are at much lower energy and will not be discussed since they overlapped with other bands in the spectrum. Assignment of the lower-energy bands in the Bu^t compounds is also difficult because of the complex form of the band envelopes from the Bu^t groups. In Bu^t_3P (Figure 4) the shoulder on the high-energy side of the (10·70 eV) mound is assigned to the *e*(P–C) level by analogy with Me_3P. We are then left with two bands which are separated from the mound. The higher-energy band is assigned to the lone-pair level. The second band is of interest because it also appears in Bu^t_2PX (X = H, F, or Cl) (Figures 4—6) at a constant energy of 9·85 ± 0·05 eV, but does not appear in Bu^tPX_2. Also its intensity relative to the lone-pair band is 2 : 1 in Bu^t_3P, but 1 : 1 in Bu^t_2PX. We therefore suggest that this band is due to an interaction between two or more Bu^t groups, but cannot be more specific about its nature. The remaining portions of the spectra of these compounds are dominated by bands due to the alkyl groups, and will not be discussed further.

Turning now to the series $(Me_2N)_nPCl_{3-n}$ (Figure 7) we have the added complication that the nitrogen lone pairs ionise in the same region as the phosphorus lone pair. If they are of the correct symmetry and there is an appreciable physical overlap, there will be a considerable interaction. There is considerable doubt about the structure of $(Me_2N)_3P$ and its p.e. spectrum has been interpreted[8a] in terms of an asymmetric arrangement of the three NMe_2 groups to account for the presence of four bands. However, this is only one of several possible explanations. For example, if the molecule has C_{3v} symmetry, the nitrogen lone-pair atomic orbitals transform as $a_1 + e$. The a_1 combination then interacts with the phosphorus lone pair and intensity considerations indicate that the bands centred at 7·30 and 9·80 eV are due to these two a_1 combinations. The bands at 7·95 and 8·60 eV thus correspond to the nitrogen lone pairs of local *e* symmetry split by the Jahn–Teller effect. The large separation (2·5 eV) between the a_1 orbitals would then indicate large interactions between the P and N lone-pair atomic orbitals and possible near planarity. We therefore feel that the p.e. spectrum does not give a strong indication of the structure of the molecule. The lower-energy bands in the spectrum of $(Me_2N)_3P$ are also of some interest. We assign the shoulder at 11·5 eV to the P–N bonding

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[24] D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, *Mol. Photoelectron Spectroscopy*, Wiley, London, 1970.

doublet by analogy with Me_3P, while the mound as a whole bears a striking resemblance to the corresponding region in $(Me_2N)_3B$,[10] as is to be expected.

In the case of $(Me_2N)_2PCl$, the nitrogen lone pairs transform as $a' + a''$ and the phosphorus lone pair as a' under the C_s point group. Application of the above principles leads to the assignment of the first and third bands to the two a' combinations (8·25 and 9·50 eV), and the second band (8·95 eV) to the a'' nitrogen lone pair. In the third member of the series, $(Me_2N)PCl_2$ (C_s symmetry), both the nitrogen and the phosphorus lone pairs transform as a'. The peak shapes were similar, indicating some degree of interaction, but the separation was only 0·5 eV. However, the degree of interaction cannot be estimated solely on the basis of the separation of the two levels. The separation of these levels in the related compounds $(Me_2N)PF_2$ and $(Et_2N)PF_2$ was substantially greater (Figure 8), yet the two bands assert their individuality with regard to band shape. Other workers have suggested minimal interaction of the corresponding levels in $(H_2N)PF_2$ [7] because of near orthogonality of the lone pairs at equilibrium geometry.[25] A comparison of the nitrogen and phosphorus lone-pair ionisation energies in $(Me_2N)PF_2$ and $(Et_2N)PF_2$ is shown below:

	I.p./eV	
	N	P
$(Et_2N)PF_2$	9·45	10·25
$(Me_2N)PF_2$	9·60	10·50

Substitution of Et for Me causes a larger change in the phosphorus lone-pair i.p. than the nitrogen. These apparent anomalies must presumably be due to changes in both pyramidicity and angle of twist. The spectra of the series of compounds $(Me_2N)P(CF_3)_2$, $(Me_2N)P(Cl)CF_3$, and $(Me_2N)PCl_2$ have been explained[8] by lone-pair repulsions and steric effects and correlated with measured P–N torsional barriers.[26] However, we find difficulty in even qualitatively associating the separation of the N and P lone-pair levels with these parameters.

We have also studied some more complex molecules of the form X_2PCCl_3 (X = F or Cl) (Figure 9). In chloroform, which can be regarded as the 'parent' of the CCl_3 ligand, the chlorine lone-pair levels transform under the C_{3v} group as $a_1 + a_2 + 2e$. However, the p.e. spectrum showed only three bands in the expected region (11—14 eV)[11] in the intensity ratio 2 : 3 : 1, hence two of these orbitals are accidentally degenerate. In X_2PCCl_3, the local symmetry around the carbon can still be regarded as C_{3v}, and a group of bands similar to those observed in chloroform is to be expected. However, the accidental degeneracy is removed and the p.e. spectrum of F_2PCCl_3 showed four sharp bands of intensity ratio 1 : 2 : 1 : 2, although the local symmetry around the carbon appears to be retained. The spectrum of Cl_2PCCl_3 is much more complex since the four lone-pair levels from the PCl_2 moiety are expected to ionise in the same region. No definite assignments can be made for this region.

Phosphine-basicity Substituent Effects and σ-Donor Ability.—Trends in first ionisation potentials of the phosphines, which generally correspond with the phosphorus lone-pair energies, may be compared with relevant literature data (Table 2) which enable us to make correlations of first ionisation potentials with other parameters and to assess the effects of various substituents at phosphorus. Inductive, mesomeric, and steric effects may variously influence the energy of the phosphorus lone pair.

In Figure 10 the first ionisation energies are plotted against the electronegativity sum of the groups attached to phosphorus.[27] Two features emerge: (*i*) Bu^t derivatives have 0·5—1·1 eV lower i.p. values compared with the Me analogues; (*ii*) increasing the sum of electronegativities increases, for both series, the values for the first ionisation potentials. Point (*i*) illustrates the steric effect of the large t-butyl group, as the electronegativities of the methyl and t-butyl group are almost identical.[27] Similarly, the substituent constants σ^{Ph} and $\sigma_I{}^{Ph}$ derived by Kabachnik *et al.*,[28] applying the Hammett equation[29] to phosphorus acids of the type $R_2P(O)OH$, for Me and Bu^t are similar (0·96 and 1·55). With regard to point (*ii*), increasing the electronegativity sum of the substituents increases the positive charge at phosphorus and thus increases the phosphorus lone-pair energy. *Ab initio* calculations show that the charge on phosphorus increases within the series $PMe_3 < PH_3 < PCl_3 < PF_3$, and correlates linearly with the first i.p.[30] Changes of bond angle at phosphorus are also relevant in interpreting such results. In terms of a localised hybridisation model, a decrease in the bond angle at P implies greater *s* character for the lone pair and thus an

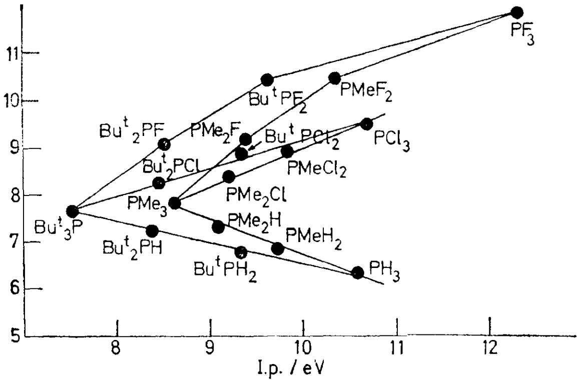

FIGURE 10 Plot of phosphine first i.p. against the sum of P-substituent electronegativities, Σ e.n.

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[25] A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, 1971, **93**, 6772.

[26] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 785.

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increase in i.p. The influence of bond angle at the central atom in compounds Me_3X (X = N, P, As, or Sb) on the first i.p. has been found to be quite pronounced and causes these values to be almost constant within this series, despite changes in valence-shell principal quantum number.[31] Unfortunately, structural data are only available (Table 2) for a limited number of trivalent phosphorus compounds.[32]

TABLE 2

Some spectroscopic and structural parameters[a] for phosphines and their complexes examined for correlation with first ionisation potentials

Ligand L	*cis*-$[Mo(CO)_4L_2]$									
	$\bar{\nu}(CO)/cm^{-1}$				Ref.	Solvent	Σ E.n.	$\Sigma\sigma_I^{Ph}$ [b]	P Cone angle (°) in the ligand L[c]	$^1J(PB)$ [d]/ Hz
$PhMe_2P$	2 011	1 912	1 895	1 878	*e*	*f*	7·90	−1·65	(8·31) [g]	59
$(Me_2N)_3P$	2 012	1 908	1 894	1 880	*h*	*f*	9·30	+0·81	N–P–N 96·5 (1·0)	95
$Bu^t{}_2PH$	2 014	1 916	1 900	1 893	*i*	*j*	7·20	−3·10		
Me_3P	2 016	1 910	1 896	1 874	*e*	*f*	7·80	−2·88	C–P–C 98·6, 99·1	59·8
	2 019	1 920	1 903	1 893	*k*	*l*	7·80			
	2 024	1 930	1 901	1 879	*m*	*n*	7·80			
$Bu^t{}_2PF$	2 025	1 927	1 912	1 907	*i*	*j*	9·03	+2·11		58
Ph_3P	2 023	1 929	1 911	1 899	*k*	*l*	8·10	+0·81	C–P–C 103·0 (7·88) [g]	
Me_2PH	2 024	1 931	1 912	1 909	*i*	*j*	7·30	−1·92	C–P–C 99·7, 99·2 C–P–H 97·0, 96·5	58
Ph_2PH	2 028	1 938	1 922	1 913	*o*	*j*	7·50	+0·54	(8·29) [g]	
Bu^tPH_2	2 028	1 936	1 920	1 913	*i*	*j*	6·75	−1·55		
$MePH_2$	2 031	1 939	1 922	1 917	*i*	*j*	6·80	−0·96	H–P–H 93·5, 93·4 C–P–H 93·4, 96·5	43·5
Me_2PCl	2 037	1 949	1 930	1 930	*i*	*j*	8·35	+2·45		
Me_2PF	2 037	1 958	1 949	1 930	*i*	*j*	9·13	+3·29		
$(MeO)_3P$	2 037	1 945	1 926	1 921	*k*	*l*	10·65	+7·44	(9·25) [m]	97
PH_3	2 040	1 947	1 925	1 897	*p*	*j*	6·30	0·0	H–P–H 93·5, 93·4	27
	2 036	1 946	1 932	1 923	*q*	*n*	6·30	0·0		
Bu^tPCl_2	2 049	1 979	1 950	1 940	*i*	*j*	8·85	+7·19		<10
Bu^tPF_2	2 053	1 980	1 957	1 951	*i*	*j*	10·41	+8·87		55
$(Et_2N)PF_2$	2 055	1 974	1 950	1 942	*r*	*j*	10·96	+10·24		
$MePCl_2$	2 056	1 991	1 959	1 959	*i*	*i*	8·90	+7·78		
$PhPCl_2$	2 054	1 985	1 963	1 963	*s*	*j*	9·00	+9·01	(9·63) [g]	
$(Me_2N)PF_2$	2 057	1 978	1 953	1 945	*t*	*j*	10·96	10·69	N–P–F 101·6, F–P–F 9·15	79
$MePF_2$	2 065	1 990	1 963	1 957	*i*	*j*	10·46	9·46	F–P–F 91·5,[u] F–P–C 97·8	
PCl_3	2 072	2 004	1 986	1 944	*k*	*l*	9·45	13·11	Cl–P–Cl 100·1	10
$(Cl_3C)PF_2$	2 079	2 015	2 010	1 990	*r*	*j*		14·62		
PF_3	2 091	2 022	2 022	2 003	*r*	Gas	11·79	+15·63	F–P–F 97·8	39
$Bu^t{}_3P$							7·65	−4·65	C–P–C 109 [v]	60
$Bu^t{}_2PCl$							8·25	+1·27		38

[a] Ref. 32 contains a collection of structural data on organophosphorus compounds. [b] Values used for the calculation of $\Sigma\sigma_I^{Ph}$ were taken from ref. 28. [c] First ionisation potentials (in eV) are given in parentheses. [d] See refs. 36 and 37. [e] J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2796. [f] $CHCl_3$. [g] T. B. Debies and J. W. Rabalais, *Inorg. Chem.*, 1974, **13**, 308; and ref. 6. [h] F. B. Ogilvie, R. L. Keiter, G. Wulfsberg, and J. G. Verkade, *Inorg. Chem.*, 1969, **8**, 2346. [i] Ref. 39. [j] n-C_6H_{14}. [k] R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301. [l] C_nH_{2n+2}. [m] J. M. Jenkins and J. G. Verkade, *Inorg. Chem.*, 1967, **6**, 2250. [n] Cyclohexane. [o] J. G. Smith and D. T. Thompson, *J. Chem. Soc.* (*A*), 1967, 1694. [p] E. O. Fischer, E. Louis, W. Bathelt, E. Moser, and J. Müller, *J. Organometallic Chem.*, 1968, **14**, P9. [q] C. G. Barlow and G. C. Holywell, *J. Organometallic Chem.*, 1969, **16**, 439. [r] C. G. Barlow, J. F. Nixon, and M. Webster, *J. Chem. Soc.* (*A*), 1968, 2216. [s] F. Zingales, F. Canziani, and F. Basolo, *J. Organometallic Chem.*, 1967, **7**, 461; O. Stelzer and E. Unger, unpublished work. [t] C G. Barlow, J. F. Nixon, and J. R. Swain, *J. Chem. Soc.* (*A*), 1969, 1082. [u] E. Codding, R. A. Creswell, and R. H. Schwendeman, *Inorg. Chem.*, 1974, **13**, 856. [v] Calculated from the ^{31}P shift value using the Van Wazer formalism; see O. Stelzer and R. Schmutzler, *J. Chem. Soc.* (*A*), 1971, 2867.

Equations have been derived which relate to the base strengths of phosphines.[33,34] Similar correlations for the ionisation potentials should be attainable assuming that the first i.p. provides a measure of relative phosphine basicity. Using either $\Sigma\sigma^{Ph}$ or $\Sigma\sigma_I^{Ph}$ (the sum of the inductive constants for the substituents attached to phosphorus) for the series $R_{3-n}PH_n$ (R = Me or Bu^t; $n = 0$—3), this is confirmed (Figure 11). However, these do not correlate directly with aryl, dialkylamino, alkoxo, fluoride, or chloride substituents, perhaps because varying degrees of mesomeric interactions become significant. It should also be stressed that corresponding correlations of pK_a against $\Sigma\sigma_I^{Ph}$ or $\Sigma\sigma^{Ph}$ have only been reported for a very limited number of structurally related phosphines $R_{3-n}PH_n$,[33,34] because the experimental procedure for determination of pK_a values[34] inevitably excludes reactive phosphines such as $P(OR)_3$, $P(NMe_2)_3$, PF_3, or PCl_3. By contrast the p.e. experiment does not have similar limitations and is therefore (apart from ion cyclotron resonance[35]) the only physical

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method available for obtaining data directly about the relative basicities of reactive ligands such as PF_3, PCl_3, or RPF_2.

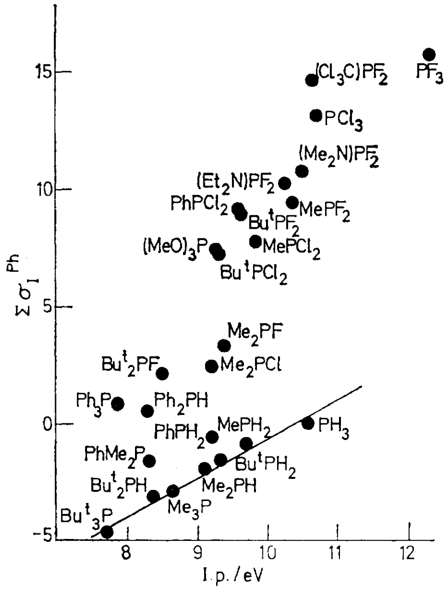

FIGURE 11 Plot of phosphine first i.p. against the sum of σ_I values of the P substituents

The magnitude of the ^{31}P–^{11}B coupling constant, $^1J(BP)$, obtained from the ^{11}B or ^{31}P n.m.r. spectra (combined with results of displacement reactions) of phosphine–borane complexes has been used to rank phosphines according to their base strengths.[36] Figure 12 shows a plot of $^1J(BP)$ against phosphine i.p. for a group of phosphine–borane complexes. We note that there is a linear correlation between these parameters, but only for the members of a series $R_{3-n}PX_n$ (R = Me, Bu^t, or Me_2N; X = H or F). This is again attributable to the existence not only of σ- but also π-electronic effects, as has been discussed in the context of $^1J(BP)$.[37]

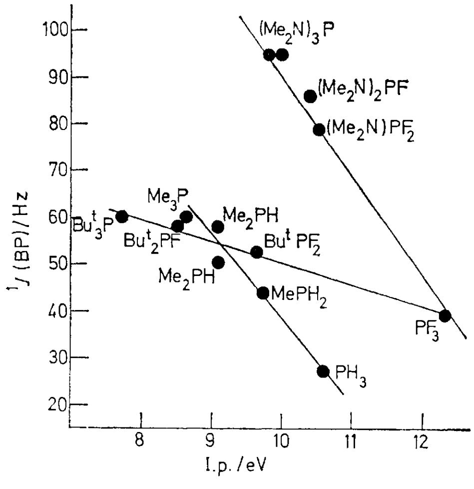

FIGURE 12 Plot of phosphine first i.p. against $^1J(BP)$ for some phosphine–borane complexes

The first ionisation potentials of phosphines may be used to rank phosphine ligands in carbonyl complexes *cis*-$[MoL_2(CO)_4]$ (L = $R_{3-n}PX_n$; R = Me, Bu^t, Ph, CCl_3, NMe_2, or NEt_2; X = H, F, or Cl; n = 0—3) according to their σ-donor ability[38] (this aspect will be discussed more extensively elsewhere[39]). A plot of $\bar{\nu}(CO)$ A_1 frequencies in the complexes *cis*-$[MoL_2(CO)_4]$ against the first ionisation potentials of the phosphine ligands L is shown in Figure 13. From this we infer that these ligands may be considered as of the three types (I), (II), and (III). Type (I) is restricted to the alkylphosphines $R_{3-n}PH_n$ (R = Me or Bu^t; n = 0—3), while type (III) includes mainly the species RPX_2 (R = Me or Bu^t; X = F or Cl), PCl_3, and PF_3. The ligands of type (II) are R_2PX (R = Me or Bu^t; X = F or Cl) and $(R_2N)PF_2$ (R = Me or Et). (This is confirmed by plots of the carbonyl-stretching force constants f_1 or f_2 against first i.p. of L.[39]) Using the hypothesis that the phosphorus lone-pair i.p. represents a relative measure of the σ-donor ability of L, the existence of these divisions may be attributed to varying π-acceptor capacities (Mo→P)[2] for the three types of ligands. Finally, CNDO/2 calculations[40] of the difference in electronic energies between phosphines $R_1R_2R_3P$ and the corresponding phosphonium salts $[R_1R_2R_3PH]^+$ are also linearly related to the first ionisation potentials of the ligands $R_1R_2R_3P$.

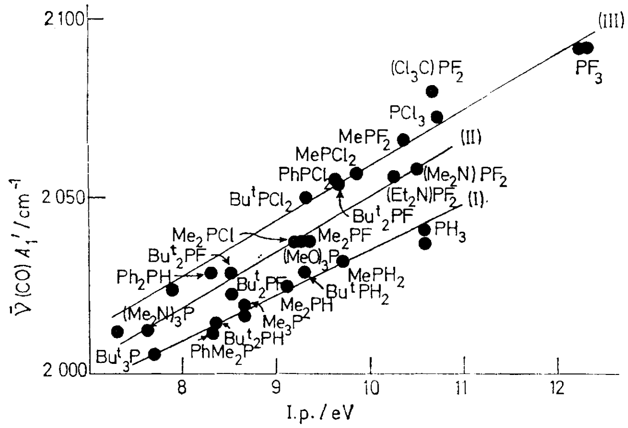

FIGURE 13 Plot of phosphine (L) first i.p. against $\bar{\nu}(CO)$ $A^1{}_1$ for *cis*-$[MoL_2(CO)_4]$ complexes

In conclusion, we believe that the phosphorus lone-pair i.p. provides a reasonable measure of *relative*

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basicity (or σ-donor ability) of phosphines within related series of compounds.

We thank the S.R.C. (B. T. W.), Deutsche Forschungsugemeinschaft, and Stiftung Volkswagenwerk (O. S.) for grants, the S.R.C. for the purchase of the spectrometer, Professor H. Nöth for measuring the p.e. spectra of $MePF_2$ and Me_2PF, Dr. A. Pinkerton [$(Me_2N)PF_2$ and $(Cl_3C)PF_2$], Bayer AG ($MePCl_2$), Farbwerke Hoechst [$Me_2P(S)Cl$], Chemische Werke Hüls AG (Bu^tCl), and Metallgesellschaft AG, Hans Heinrich Hütte, Langelsheim (Harz) (Li[AlH_4] and Bu^tLi) for gifts of chemicals (to O. S.), and Professor R. Schmutzler for his interest and Professor J. F. Labarre for discussions.

[4/2268 *Received, 4th November*, 1974]