Inorganica Chimica Acta, 73 (1983) 83–89

Photoelectron Spectra and Basicity of Tertiary Phosphines PMe_nPh_{3-n}

RICHARD J. PUDDEPHATT, G. MICHAEL BANCROFT and TAMMY CHAN

Department of Chemistry, University of Western Ontario, London., Ont. N6A 5B7 Canada

Received December 7, 1982

*A study of the UV photoelectron spectra of the tertiary phosphines PMe_nPh_{3-n} has been made, and an SCF-Xα-SW calculation for PMe_3 has been carried out. The calculation indicates that the HOMO for PMe_3 is the predominantly non-bonding line pair on phosphorus having 80% P 3*p *character and 10% P 3*s *character, rather than the predominant 3*s *character usually predicted. The lone pair ionization energies are PMe_3, 8.62 eV; PMe_2Ph, 8.32 eV; $PMePh_2$, 8.28 eV; PPh_3, 7.80 eV, the opposite of the trend predicted from electronegativity considerations. It is argued that the anomalous trend arises from a mixture of steric effects and Ph_π–P_π bonding effects, and that the usual assumption that PMe_3 is the strongest and PPh_3 the weakest Lewis base in this series of phosphines is probably wrong.*

Introduction

Tertiary phosphines are among the most important ligands in inorganic chemistry, and there has been great interest in the electronic and steric properties of such ligands with the aim of developing the coordination chemistry and understanding the catalytic properties of phosphine complexes in greater depth [1]. UV photoelectron spectroscopy is a particularly direct method for investigating the electronic properties of molecules, and its use in studying tertiary phosphines has been reviewed [2, 3]. In a preliminary communication it was noted that the ionization energies of the phosphorus lone pair followed the sequence $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$, the opposite of the series expected on the basis of electronegativity of the substituents of phosphorus [4]. It was therefore argued that triphenylphosphine should be a stronger Lewis base than trimethylphosphine, again the opposite of the trend which is normally assumed [1, 5]. Shaw has challenged this proposal [6], citing the well-known trend in pK_a's of the conjugate acids BH^+ in aqueous solution, which follow the series expected from electronegativity, namely pK_a for $[HPPh_3]^+$, $3.05 < [HPMePh_2]^+$, $4.65 < [HPMe_2Ph]^+$, $6.25 < [HPMe_3]^+$, 7.85 [7, 8]. Recently, proton affinity measurements have been made and show that in the gas phase triphenylphosphine is a stronger Bronsted base than trimethylphosphine [PA(kcal/mol); PPh_3, 226.7; $PMePh_2$, 226.7; PMe_2Ph, 226.0; PMe_3, 223.5], and there is a good correlation between these values and the lone pair ionization energies [9, 10]. Thus, the pK_a values are anomalous and, like the case of the similar amines $[HNR_3]^+$, are probably dominated by solvation effects, with the bulky $[HPPh_3]^+$ being most poorly solvated and hence dissociating most readily [11]. The photoelectron spectra give a good indication of the Bronsted basicity of the series of phosphines, but the Lewis basicity need not necessarily follow the same trend. There is also a need to understand why the predictions from electronegativity of substituents on the trend in ionization energies fail for the series PMe_nPh_{3-n}. In order to answer these problems, a more detailed study of the photoelectron spectra of the phosphines PMe_nPh_{3-n} using both He(I) and He(II) radiation has been carried out. There have been several previous studies including data for PMe_3, PMe_2Ph and PPh_3 [1–4, 12–18], but we felt that it was important to redetermine the ionization energies under a standard set of conditions with careful calibration. To illustrate the need for such measurements, we note that the first ionization energy for PPh_3 has been quoted in the range 7.8–8.1 eV, and the spread of values is about the same as the difference in ionization energies for neighbours in the series PMe_nPh_{3-n} [1–4, 12–18]. An SCF-Xα-SW calculation has been carried out for PMe_3 to aid assignments, and to determine the characters of the molecular orbitals of interest. Finally, a brief summary of evidence concerning the relative basicities of the phosphines PMe_nPh_{3-n} towards transition metal acceptors is presented.

Experimental

PMe_3 was prepared by the literature method [19] and purified by distillation under dry nitro-

0020-1693/83/$3.00

TABLE I. Parameters Used in Overlapping Spheres (15%) X_α-SW Calculations for Me_3P.

Region	X	Y	Z	α	Sphere Radii
P	0.0	0.0	0.0	0.7262	2.2909
C_1	3.1028	0.0	−1.6913	0.75928	1.7730
C_2	−1.5514	2.6870	−1.6913	0.75928	1.7730
C_3	−1.5514	−2.6870	−1.6913	0.75928	1.7730
H_1	4.6513	0.0	−0.3021	0.77725	1.0224
H_2	−2.3257	−4.0280	−0.3021	0.77725	1.0224
H_3	−2.3257	4.0280	−0.3021	0.77725	1.0224
H_4	3.2432	1.6985	−2.8847	0.77725	1.0224
H_5	−0.1507	−3.6579	−2.8847	0.77725	1.0224
H_6	−0.1507	3.6579	−2.8847	0.77725	1.0224
H_7	3.2432	−1.6985	−2.8847	0.77725	1.0224
H_8	−3.0925	−1.9594	−2.8847	0.77725	1.0224
H_9	−3.0925	1.9594	−2.8847	0.77725	1.0224
Extra Molecular	0.0	0.0	−1.9605	0.7591	6.4861

TABLE II. Ground State Energies and Percentage Charge Distribution for Me_3P.

Orbital	Energy (Ry)	Charge Distribution (%)[a]					
		P	3C	$3H_1$	$6H_2$	Inter	Outer
$8a_1$	−0.4959	48.13(*p*)	16.92	1.12	3.50	28.79	1.52
6e	−0.6636	28.18(*p*)	46.62(*p*)	6.53	4.64	12.22	0.81
$1a_2$	−0.7530	0.0	50.49(*p*)	0.0	34.8	14.31	0.37
5e	−0.7943	4.58	46.95(*p*)	14.28	16.13	17.43	0.62
$7a_1$	−0.8465	4.40	43.92(*p*)	21.95	7.10	21.64	0.98
4e	−0.8460	2.99	44.69(*p*)	3.65	26.82	21.37	0.47
$6a_1$	−1.0477	41.62(*s*)	30.90(*p*)	3.80	9.95	13.35	0.37
3e	−1.3274	5.25	59.55(*s*)	7.47	13.61	13.83	0.28
$5a_1$	−1.4494	25.71(*s*)	46.71(*s*)	3.60	8.58	15.28	0.13

[a] The characters of the predominant atomic orbitals are in brackets.

gen. PMe_2Ph, $PMePh_2$ and PPh_3 were commercial samples.

He(I) and He(II) photoelectron spectra were recorded in the gas phase with a McPherson ESCA 36 spectrometer. All phosphines except PPh_3 were sufficiently volatile that their P.E. spectra could be recorded at room temperature using the gas inlet system, with sample pressure maintained at 5×10^{-6} torr. PPh_3 was introduced through a heated inlet system [20] maintained at 120 °C. Spectra were calibrated using the Ar $3P_{3/2}$ line at 15.759 eV and computer fitted to Lorentzian–Gaussian lineshapes by an iterative procedure [21].

For the SCF-Xα calculation on PMe_3 Norman's non-empirical procedure was used to obtain the ratio of the sphere radii and were chosen so as to give 15% overlapping spheres [22]. Co-ordinates for PMe_3 in atomic units were derived from the following bond parameters: r(P–C) 1.87 Å, r(CH) 1.101 Å, <CPC = 99°, <HCH = 109.5° [22, 23] assuming C_{3v} symmetry. The α_{HF} exchange parameters were taken from the tabulation of Schwarz [24]. For the extramolecular region, a weighted-average α was used where the weights were the number of valence electrons (5 for P, 4 for C, 1 for H).

Outersphere coordinates were centered at the weighted-average position of all the atoms calculated using the same method as for α_{out}. The coordinates, α parameters and sphere radii used in the calculation are listed in Table I. The highest *l* values

TABLE III. Theoretical and Exxperimental Ionization Energies (eV) for PMe_3.

Orbital	SCF-X_α-SW[a]	*Ab Initio*[b]	Experiment[c]
$8a_1$	9.67	8.49	8.62
6e	11.89	12.04	11.13, 11.70
$1a_2$	12.91	13.87	13.02
5e	13.47	14.63	
$7a_1$	14.14	15.88	
4e	14.16	15.89	14.68
$6a_1$	17.21	19.05	16.74[d]
3e	20.78	25.10	
$5a_1$	22.59	27.45	

[a] Calculated using the transition potential of the $8a_1$ orbital. [b] Reference 25. [c] He(I) photoelectron spectrum is calibrated relative to the Ar $3p_{3/2}$ level at 15.759 eV. [d] Obtained from the He(II) spectrum.

used in the basis function are 3, 2, 1, 0 for the outer, phosphorus, carbon and hydrogen spheres, respectively. The initial molecular potential was constructed by superposition of the neutral atom SCF-Xα results. C_{3v} symmetry was used to factor the secular matrix for the ground state in PMe_3. No frozen core levels were used on any of the atoms during the self-consistent iterative process. The convergence criterion used was such that the difference in the constant potential between successive cycles be less than 0.001 Rydberg.

Results

The ground state eigenvalues and % charge distribution for the atomic spheres derived from the SCF-Xα-SW calculation on PMe_3 are listed in Table II. The calculated orbital ordering and orbital characters for PMe_3 are in good agreement with those from the previous *ab initio* calculations by Hillier and Saunders [17, 25]. The assignments for the He(I) and He(II) P.E. spectra of PMe_3 (Fig. 1, Table III) are then straightforward by comparison of calculated orbital energies with observed ionization energies, assuming Koopman's theorem in the usual way.

Both the *ab initio* and Xα calculations indicate that the HOMO for PMe_3 (the orbital 8a, in Table II) is mostly localised in phosphorus but, unexpectedly, this is calculated in the Xα calculation to have ~80% and in the *ab initio* calculation 67% phosphorus 3*p* character [17, 25] rather than the predominant 3*s* character usually predicted for a phosphorus lone pair orbital [26, 27]. A similar effect has been seen in both Xα and *ab initio* calculations on PH_3 (HOMO 71% 3*p* and 17% 3*s* character form the *ab initio* calculation) [17, 25, 26]. There is apparent disagreement with the usual predictions using Valence Bond theory. For example, Bent's rehybridization theory, based on the observed HPH bond angles of 93° in PH_3, predicts that the phosphorus bonding orbitals should be almost pure 3*p* orbitals and the lone pair very largely 3*s* [27]. The Xα and *ab initio* calculations on both PH_3 and PMe_3 thus cast doubt on the usual textbook explanation of the bond angles and, as deduced also from recent studies of H_2O and H_2S, the true explanation may be very complex [28]. Qualitatively, in the MO treatments, the bonding orbitals in PH_3 or PMe_3 have greater 3*s* character because there is a better energy match between the hydrogen or carbon bonding orbitals in PH_3 or PMe_3 respectively with the 3*s* orbital of phosphorus rather than the 3*p* orbitals, and hence the largely nonbonding molecular orbital $8a_1$ has mostly 3*p* character. The apparent discrepancy is considerably less once it is realized that the lone pair on phosphorus in the localized orbital concept will be a mixture of the HOMO ($8a_1$) and the much lower energy molecular orbital $6a_1$, which is P–C bonding and has predominantly phosphorus 3*s* character. This can be seen by study of the molecular orbital electron density contours shown in Fig. 2. It will be convenient to equate the HOMO with the phosphorus lone pair of Valence Bond theory, but the

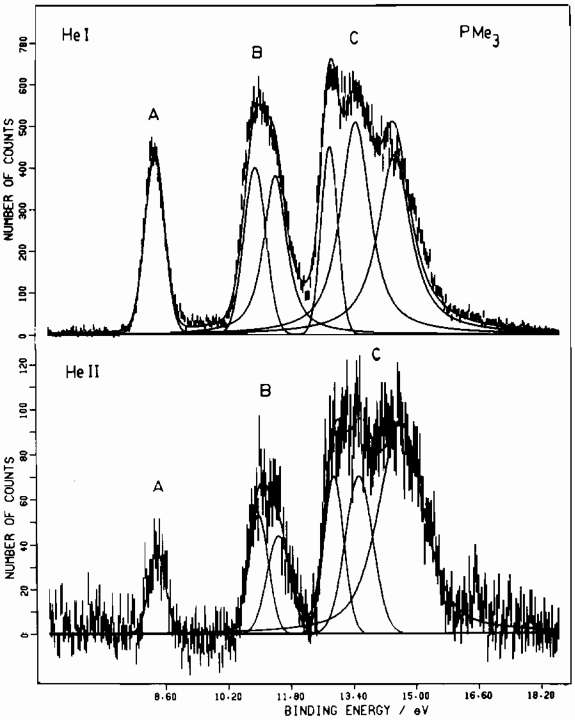

Fig. 1. He(I) and He(II) photoelectron spectra of PMe_3.

TABLE IV. Photoelectron Parameters for Tertiary Phosphine Ligands.

Ligands	Assignment	Binding Energy (eV)	FWHM (eV)	Intensity	
				He I	He II
PMe_3	P3p (8a)	8.62 (8.65)^b (8.58)^c	0.58	0.72	0.55
	P–C (6e)	11.13 (11.25)	0.7	1.0	1.0
		11.70 (11.50)	0.7	1.0	0.9
	C–H	13.02 (13.25)		7.44	8.8
	($1a_2$, 5e, $7a_1$, 4e)	13.61 (13.70)			
		14.68 (14.60)			
	P–C ($6a_1$)	16.74^a(16.65)			
PMe_2Ph	P3p	8.32 (8.45)^d (8.37)^c	0.6	0.75	
	Ph(π)	9.17 (9.2)^d	0.26	1.0	
		9.51	0.40	1.2	
	P–C	10.84	0.51	0.79	
	C–H	11.54		12.98	
		12.11			
		12.95			
		13.83			
		14.66			
$PMePh_2$	P3p	8.28 (8.07)^c	0.61	0.52	0.52^f
	Ph(π)	9.19	0.31	1.0	1.0
		9.53	0.49	1.18	1.49
	P–C	10.82	0.50	0.65	0.22
	C–H	11.54		11.64	9.22
		12.09			
		12.98			
		13.89			
		14.68			
PPh_3	P3p	7.80 (7.88)^e (8.10)^c	0.51	0.32	0.18
	Ph(π)	8.99 (9.25)^e	0.48	1.0	1.0
		9.45	0.60	0.60	1.0
	C–H	10.72		7.15	4.56
		11.68			
		12.46			
		13.21			
		13.75			
		14.49			

[a] Obtained using He(II) radiation. [b] Reference 12. [c] Reference 4. [d] Reference 18. [e] Reference 15. [f] This is almost certainly overestimated. The signal to noise was poor.

above discussion shows that this is an approximation only.

The bands due to tthe P–C σ-levels are labelled 6e and $6a_1$ (Tables II and III). The 6e level is, as expected, split into a doublet separated by 0.57 eV by Jahn–Teller splitting [29]. The 6e orbital has ~80% of the total charge localised on the phosphorus and carbon spheres, and the overlap population, obtained by a Mulliken analysis, has major contributions from phosphorus 3p and carbon 2p and 2s orbitals. The $6a_1$ orbital is at higher binding energy and is made up mostly of phosphorus 3s and carbon $2p_\sigma$ orbitals. This band was not resolved in the He(I) spectrum due to the diminution in intensity near the 21.2 eV limit for the He(I) radiation, but was resolved in the He(II) spectrum.

Of particular importance in confirming the assignments is the drop in relative intensity of the peak due to the HOMO ($8a_1$ orbital) on going from the He(I) to the He(II) spectrum. It is well known that band intensities are generally much lower in He(II) spectra for 3s and 3p orbitals compared to 2s and 2p orbitals, and so this confirms the assignment of the $8a_1$ orbital as due to the lone pair. The effect is more significant for assignment purposes for the phenylphosphines, Table IV, since cases are known where

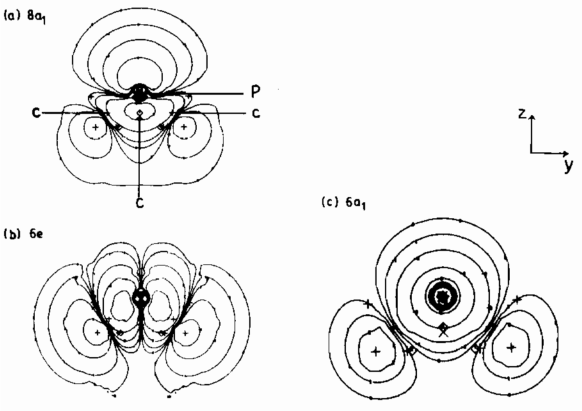

Fig. 2. Contour Maps of the Xα-SW wave functions in the yz plane (× in the plane, + below the plane, ◇ above the plane). (a) $8a_1$ MO, contour values 0, ±1, ±2, ±3, ±4 = 0.002613, 0.008264, 0.02613, 0.08264 and 0.2613 respectively. (b) 6e MO; (c) $6a_1$ MO.

inversion of π-phenyl and lone pair orbitals can occur [15, 30]. Unfortunately, the intensity change between the He(I) and He(II) spectra does not give an independent measure of the 3*s vs.* 3*p* character of the lone pair. For the phenyl-substituted phosphines the intensity criterion above allows confident assignment of the lowest energy band to the phosphorus lone pair and the next band, for which no decrease in intensity from He(I) to He(II) spectra is observed, is assigned to the π(Ph) orbitals. The degenerate $\pi(e_{1g})$ orbital of benzene is split into a_2 and b_1 components in the lower symmetry of the phenylphosphines and these peaks are partially resolved in the P.E. spectra (Fig. 3, Table IV).

Discussion

The ionization energies of the phosphorus lone pair are found to be PMe_3, 8.62 eV; PMe_2Ph, 8.32 eV; $PMePh_2$, 8.28 eV; PPh_3, 7.80 eV, and there is a need to understand why this series is the opposite of that expected from electronegativity considerations. There are two possible contributing factors. Firstly, the trend could be due to steric effects. It is well known that increasing steric effects of substituents on phosphorus leads to an increase in CPC angles and to a decrease in ionization energy [1]. Empirically, the trend of ionization energies with cone angles of the ligands and Taft σ*-values for the substituents for PMe_3 (I.P. 8.62 eV, cone angle 118°, σ* 0.00), PEt_3 (8.31 eV, 132°, −0.10), P^iPr_3 (8.05 eV, 160°, −0.19) and P^tBu_3 (7.71 eV, 182°, −0.30) illustrates how significant this effect can be, although the inductive effects will also contribute to the observed trend in ionization energies. The accepted explanation is that as the CPC angles open up due to steric effects, there is an increase in phosphorus 3*s*

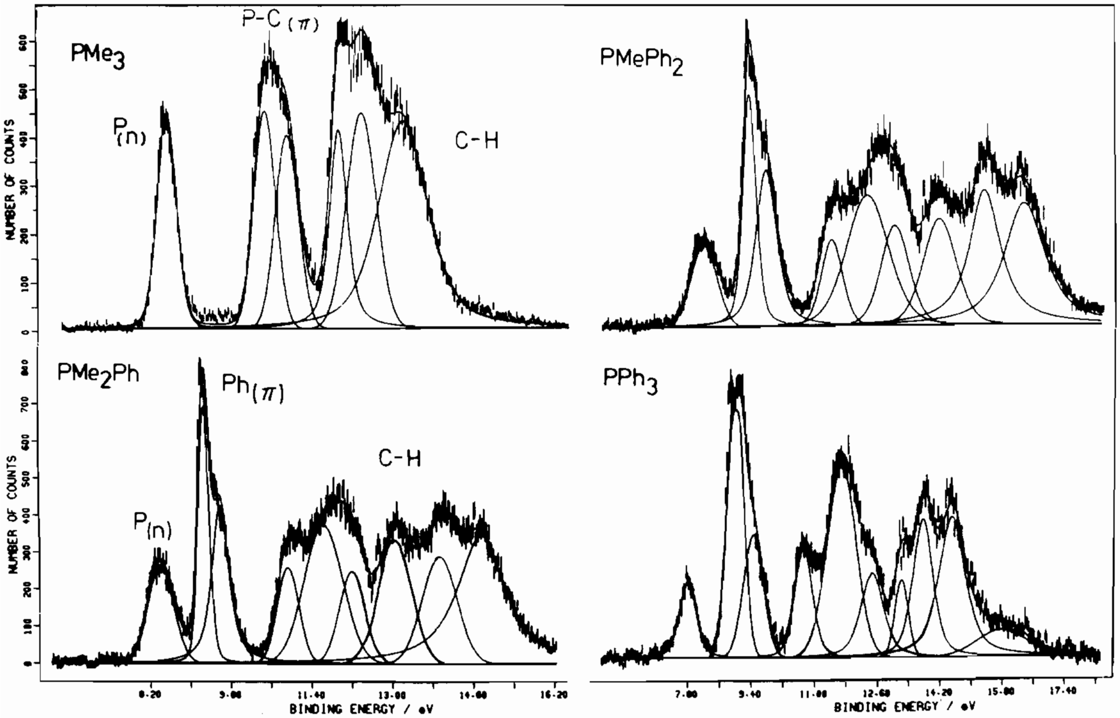

Fig. 3. He(I) photoelectron spectra for the tertiary phosphines PMe_nPh_{3-n}.

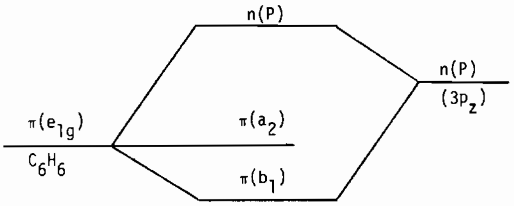

Fig. 4. A qualitative MO energy level diagram for the interaction of Ph(π) and phosphorus lone pair orbitals.

character in the PC bonds and a decrease in 3*s* character in the lone pair, thus leading to lower ionization energy [1]. Since MO calculations now suggest that the HOMO ($8a_1$ or phosphorus lone pair orbital) has largely 3*p* character even for PH_3 and PMe_3, this explanation may be questioned but the experimental facts are certainly convincing. The cone angles for the methylphenylphosphines [1] are PMe_3, 118°; PMe_2Ph, 122°; $PMePh_2$, 136°; PPh_3, 145° and, although the CPC bond angles in PMe_3 (99°) and PPh_3 (104°) are not greatly different, the steric effect is clearly expected to contribute to the observed trend in ionization energies. However, comparison with the trialkylphosphine series above suggests that the steric effect alone is not great enough to explain the observed range of ionization energies.

A second possible factor involves π-bonding effects of the phenyl groups. In phenylphosphine this effect has been predicted by CNDO calculations [15] and should lead to destabilization of the lone pair [n(P)] on phosphorus and stabilization of the $\pi(b_1)$ MO of the phenyl group (Fig. 4) [15]. A splitting of the $\pi(a_2)$ and $\pi(b_1)$ levels is expected simply because of the lower symmetry with respect to benzene, and it is difficult to interpret how significant the splittings of 0.35 eV in PMe_2Ph and $PMePh_2$ and of 0.45 eV in PPh_3 are. Clearly increasing the number of phenyl groups should progressively destabilize the phosphorus lone pair orbital. Both steric effects and π-bonding effects may contribute to the observed trend in ionization potentials, and it is apparent that the sum of these effects is great enough to overcome the expected trend from electronegativity considerations. We believe that in the phenylphosphorus derivatives the π-bonding effect is dominant.

Shaw has argued that the donor ability of phosphines may depend partly on the changes in CPC angles on complexation [6], but the effect does not appear to be significant for the present complexes. Protonation of phosphines should give similar changes in bond angles, yet the proton affinities correlate well with the lone pair ionization energies [9]. In addition the peak widths in the He(I) PE spectra are virtually identical (FWHM 0.55 ± 0.1 eV) for the series of phosphines, and the adiabatic ionization energies estimated from the onset of ionization are in each case ~0.75 eV lower than the vertical ionization energies given in Table IV. Again it seems that the changes in geometry associated with ionization cause very similar energy changes for this series of phosphines.

The basicity of tertiary phosphines towards transition metals need not parallel the Bronsted basicity and the following complicating factors should be considered.

1. If d_π–d_π backbonding can occur in phosphine complexes, it is possible that the overall ($\sigma + \pi$) donor strengths for the series of phosphines could differ from the σ-donor strengths. Thus triphenylphosphine should be a better π-acceptor than trimethylphosphine, due to conjugation of vacant phenyl π^*-orbitals with the vacant phosphorus $3d_\pi$ orbitals. Most workers now believe that such M–P π-bonding is very weak.

2. It is known tht bulky phosphines tend to give long M–P bonds [31], and this could lead to lower charge transfer from ligand to metal in complexes where steric effects are significant. The equilibrium constants for complex formation will also be greatly affected [1].

3. In phenylphosphine complexes there is often an interaction between an *ortho*-hydrogen atom of the ligand and the metal center and this could affect the overall donor power of the ligand [6]. None of these effects will be significant in protonation of the ligands.

4. In solution, it is possible that solvation effects will be significant as they are in the protonation reactions [9]. However, since most studies are carried out in non-polar solvents this will not generally be a large effect.

Let us now review briefly some experimental data on the donor power of this series of phosphines. It has been noted elsewhere [4] that the energies of the 5*d*-levels in platinum(II) and gold(III) phosphine complexes follow the same trend as the lone pair orbital of the phosphine, indicating that PPh_3 is a better donor than PMe_3 in such complexes. This could be due to the *ortho*-hydrogen interaction in the phenylphosphine square planar complexes [6]. However, a similar effect is also seen in the 18-electron complexes $[Fe(CO)_4L]$, where the Fe 3*d* ionization energies are 7.77 and 8.85 eV for L = PMe_3 and 7.55 and 8.45 eV for L = PPh_3, and for which the *ortho*-hydrogen interaction is not possible [32]. This correlation of metal *d*-orbital ionization energies with lone pair ionization energies of the ligand suggests that the lone pair ionization energy does give a good measure of the basicity of a tertiary phosphine ligand, and the observation that the Bronsted basicity series for the phosphines also correlates well with the ionization energy provides strong support.

Evidence from other sources is not in complete agreement. Carbonyl stretching frequencies are often used to estimate electronic properties of ligands. For example, in the series $[Ni(CO)_3L]$ [1] or *cis*-$[Mo(CO)_4L_2]$ [33], the ν(CO) values follow the series L = $PPh_3 > PMePh_2 > PMe_2Ph > PMe_3$ suggesting that PMe_3 is the strongest donor. At least for the $[Ni(CO)_3L]$ complexes, steric effects do not appear to be important. This evidence is in opposition to that from photoelectron spectroscopy, but there are some indications that the situation is more complex. Thus in *cis*-$[Mo(CO)_4L_2]$, the *trans*-influence of L, which is thought to reflect its σ-donor ability and which can be estimated by the difference in M–C bond lengths between the carbonyls *trans* to L and *trans* to CO, follows the series L = $PPh_3 > PMePh_2 > PMe_2Ph$ [5]. The *trans* influence in other cases, as measured for example by NMR coupling constants [34], appears to be very similar for the phosphines PMe_nPh_{3-n}.

In conclusion, we believe that the ionization energy of the HOMO of a tertiary phosphine ligand gives a good measure of the donor power of the phosphine ligand. For the acceptor H^+, this prediction is confirmed positively by the observation of a good correlation of the proton affinity with the ionization energy of the HOMO of the phosphine [9], and this proves that PPh_3 is a stronger Bronsted base than PMe_3. For the transition metal acceptors the situation is much more complex. The evidence from photoelectron spectroscopy, namely that the energies of non-bonding *d* levels on the metal correlate with the phosphine lone pair ionization energies, indicates that the lone pair ionization energy does give a good measure of the phosphine basicity. Since this is the most direct evidence available, we find it convincing but studies by other less direct methods are not in complete accord with the conclusions from photoelectron spectroscopy. We suggest that the generally accepted series of basicities of phosphines $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$ must now be seriously questioned, and it is probable that the opposite sequence is correct for both acceptors H^+ and transition metal ions.

Acknowledgements

We thank NSERC (Canada) for financial support and Dr. N. C. Baird for valuable discussions.

References

1 C. A. Tolman, *Chem. Rev., 77,* 313 (1977).
2 H. Bock, *Pure Appl. Chem., 44,* 343 (1975).
3 V. V. Zverev and Yu. T. Kitaev, *Russ. Chem. Rev., 46,* 791 (1977).
4 J. Behan, R. A. W. Johnstone and R. J. Puddephatt, *J. Chem. Soc. Chem. Comm.,* 444 (1978).
5 F. A. Cotton, D. J. Darensbourg, S. Klein and B. W. S. Kolthammer, *Inorg. Chem., 21,* 294 (1982).
6 B. L. Shaw, *J. Chem. Soc. Chem. Comm.,* 104 (1979).
7 W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc., 82,* 5791 (1960).
8 J. Clark and D. D. Perrin, *Quart. Rev., 18,* 295 (1964).
9 S. Ikuta, P. Kebarle, G. M. Bancroft, T. Chan and R. J. Puddephatt, *J. Am. Chem. Soc., 104,* 5899 (1982).
10 R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc., 99,* 6252 (1977).
11 D. H. Aue, H. M. Webb and M. T. Bowers, *J. Am. Chem. Soc., 98,* 311 and 318 (1976).
12 M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer and E. Unger, *J. Chem. Soc. Dalton Trans.,* 1207 (1975).
13 S. Cradock, E. A. V. Ebsworth, W. J. Savage and R. A. Whiteford, *J. Chem. Soc. Faraday Trans., 2,* 68, 934 (1972).
14 A. H. Cowley, R. A. Kemp. M. Lattman and M. L. McKee, *Inorg. Chem., 21,* 85 (1982).
15 T. B. Debies and J. W. Rabalais, *Inorg. Chem., 13,* 308 (1974).
16 S. Elbel, H. Bergmann and W. Ensslin, *J. Chem. Soc. Faraday Trans. 2, 70,* 555 (1974).
17 I. H. Hillier and V. R. Saunders, *Trans. Faraday Soc., 66,* 2401 (1970).
18 W. Schafer and A. Schweig, *Angew. Chem., 84,* 898 (1972).
19 W. Wolfsberger and H. Schmidbaur, *J. Organometal. Chem., 28,* 301 (1971);
Syn. React. Inorg. Metal-Org. Chem., 4, 149 (1974).
20 L. L. Coatsworth, G. M. Bancroft, D. K. Creber, R. J. D. Lazier and P. W. M. Jacobs, *J. Electron Spectr. Relat. Phenom., 13,* 395 (1978).
G. M. Bancroft, D. J. Bristow and L. L. Coatsworth, *Chem. Phys. Lett., 82,* 344 (1981).
21 G. M. Bancroft, I. Adams, L. L. Coatsworth, C. D. Bennewitz, J. D. Brown and W. D. Westwood, *Anal. Chem., 47,* 536 (1975).
22 L. S. Bartell and L. O. Brockway, *J. Chem. Phys., 32,* 512 (1960).
23 L. S. Khaikin and L. V. Vilkov, *Russ. Chem. Rev., 40,* 1014 (1971).
24 K. Schwarz, *Phys. Rev., B5,* 2466 (1972).
25 I. H. Hillier and V. R. Saunders, *J. Chem. Soc. A,* 2475 (1970);
J. Chem. Soc. Chem. Comm., 316 (1980).
26 J. G. Norman Jr., *J. Chem. Phys., 61,* 4630 (1974).
27 See for example, J. E. Huheey, 'Inorganic Chemistry', Harper and Row, (1975) p. 132. We thank Dr. N. C. Baird for valuable discussions on this problem.
28 M. B. Hall, *Inorg. Chem., 17,* 2261 (1978).
W. E. Palke and B. Kirtman, *J. Am. Chem. Soc., 100,* 5717 (1978).
F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley, New York, pp. 206–207 (1980).
29 J. P. Maier and D. W. Turner, *J. Chem. Soc. Faraday Trans., 2,* 711 (1972).
30 R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc., 95,* 3504 (1973).
31 Compare, for example, the W–P bond lengths in $[W(CO)_5(PMe_3)]$, 2.516 Å, and $[W(CO)_5(P^tBu_3)]$, 2.686 Å. F. A. Cotton, D. J. Darensbourg and B. W. S. Kolthammer, *Inorg. Chem., 20,* 4440 (1981).
32 A. Flamini, E. Semprini, F. Stetani, G. Cardaci, G. Bellachioma and M. Andreocci, *J. Chem. Soc. Dalton Trans.,* 695 (1978).
33 D. J. Darensbourg and R. L. Kump, *Inorg. Chem., 17,* 2680 (1978).
34 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev., 10,* 335 (1973).