Molecular Photoelectron Spectroscopic Studies of Some Trifluoromethyl-Substituted Phosphines and Chlorophosphines[1]

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Abstract: The He(I) photoelectron spectra (PES) of the series of compounds $(CF_3)_{3-n}PH_n$ and $(CF_3)_{3-n}PCl_n$ with $n = 0, 1,$ and 2 are described. Assignments of the observed PES bands to localized molecular orbitals are suggested and the trends in the ionization potentials are discussed.

The past 4 years have witnessed a steadily growing interest in the molecular photoelectron spectra (PES) of phosphorus compounds. The initial interest in such compounds was focused on the delineation of the bonding schemes for simple species like PH_3[2,3] and trihalophosphines.[4-6] While the concern with the bonding descriptions has been sustained[7-9] the scope of the PES studies has been broadened concomitantly, and several recent publications have addressed themselves to the applicability of this technique to such manifold questions as d orbital participation,[10-12] substituent effects,[13] stereochemistry,[14-16] and aromaticity.[17]

From a synthetic chemical standpoint the attachment of trifluoromethyl groups to phosphorus has permitted the isolation of several novel compounds,[18] some of which are alien to classical phosphorus chemistry. It therefore appeared germane to investigate the bonding in a representative selection of CF_3-substituted monophosphines by means of PES. The present article is concerned with the interpretation and ramifications of the PES data for the series of compounds $(CF_3)_{3-n}PH_n$ and $(CF_3)_{3-n}PCl_n$, $n = 0, 1,$ or 2. Inter alia comparisons are made with the published PES data for PH_3[2,3] and PCl_3.[4]

Experimental Section

The compounds $(CF_3)_3P$,[19] $(CF_3)_2PH$,[20] $(CF_3)_2PCl$,[19] and CF_3PCl_2[19] were prepared and purified according to published methods. Trifluoromethylphosphine was synthesized by the action of PH_3 on CF_3PI_2[19] and purified until its vapor pressure was in conformity with the literature value.[21] All manipulations were made in a high vacuum system of conventional design.

The PES apparatus and techniques have been described elsewhere.[22]

Results and Discussion

Of the trifluoromethyl compounds considered here only $(CF_3)_3P$[23] and CF_3PH_2[24] have known molecular structures. The skeletal geometries of these species are C_{3v} and C_s, respectively. In the ensuing discussion it will be assumed that $(CF_3)_2PH$, $(CF_3)_2PCl$, and CF_3PCl_2 possess C_s skeletal symmetry.

In common with other C_{3v} species (e.g., PH_3 (**1**) and PCl_3 (**2**)) group theoretical considerations[25] indicate that the bonding molecular orbitals for the PC_3 skeleton of $(CF_3)_3P$ (**3**) span the irreducible representations $2A_1 + E$. One of the A_1 MO's (hereafter designated $A_1(n)$) involves principally the $P(3p_z)$ atomic orbital (AO) and consequently is anticipated to occur at low binding energy. It is usually referred to as the phosphorus "lone pair". The other A_1 MO (hereafter designated $A_1(s)$) involves appreciable P(3s) character and is therefore of much higher binding energy. Like the E-type MO the $A_1(s)$ MO is essentially P-C σ bonding in character. However, there is a diminution of peak intensity near the 21.21-eV limit of He(I) PES and consequently the ionization of the $A_1(s)$ MO is expected to give rise to a very weak band with He(I) excitation. Tris(trifluoromethyl)phosphine (**3**) exhibits five PES peaks in the He(I) spectrum (Figure 1a and Table I). By analogy with PH_3 (**1**) and PCl_3 (**2**), the peak at lowest ionization potential (ip) of **3** (11.70 eV) is assigned to the ionization of the phosphorus "lone pair" of symmetry $A_1(n)$. Assignment of the second peak (13.52 eV) to the P-C σ bond of E-type symmetry is consistent with comparable assignments in trifluoromethyl-substituted polyphosphines.[12] The remaining three peaks are, therefore, assigned to nonbonding combinations of F(2p) atomic orbitals. For purposes of classification one can consider each CF_3 group as an isolated CF_3X species of C_{3v} symmetry. On this basis one expects[4] nonbonding π-type combination of symmetry E(2), A_1, and A_2. In fluoroform the energies of the MO's have been shown to be[4] in the order $2E > A_2 > A_1$ and a similar sequencing has been assumed both for **3** and the other CF_3 phosphines considered here.

As pointed out above no structural data are available for $(CF_3)_2PX$, X = H, Cl. However, assuming C_s skeletal geometry for these compounds group theoretical considerations indicate that the phosphorus "lone pair" is of symmetry A′ while the P-C and P-X (X = H, or Cl) σ bonds transform as the irreducible representations A′ and A″, respectively. As in all the phosphorus compounds studied thus far the lowest ip peak in the PES of both $(CF_3)_2PH$ (**4**) and $(CF_3)_2PCl$ (**5**) is ascribed to ionization of the phosphorus "lone pair" (Figure 1 and Table I). The assignment of the 12.42- and 13.61-eV peaks of **5** to ionization of the P-Cl and P-C σ bonds, respectively, can be made safely by analogy with ionization of the comparable bonds in PCl_3[4] and $(CF_3)_3P$ (vide supra). It will be noted that in the case of **4** the P-C and P-H σ bonds are very close in energy. The assignments which are suggested in Table I, however, seem to be the most consistent for all the compounds studied; furthermore the ip for the P-H σ bond of **1** is (very slightly) larger than that for the P-C σ bond of **3**. For both **4** and **5** the peaks in the 15-17-eV range correspond to ionizations of the fluorine nonbonding orbitals of π-type symmetry, leaving the 12.42- and 14.38-eV peaks of **5** to be assigned to the nonbonding combinations of Cl(3p) atomic orbitals. For a C_2PCl (C_s) skeleton the Cl(3p) combinations are of symmetry A′ and A″; however, it is not possible to make unequivocal assignment for these MO's. The assignments which are suggested for CF_3PH_2 (**6**) and CF_3PCl_2 (**7**) (Figure 1 and Table I) have been arrived at in a comparable manner to the foregoing. Note that although four nonbonding π-type combinations of Cl(3p) orbitals are anticipated for **7** (2A′ + 2A″) only three have been asigned. Presum-

Table I. PES Ionization Potential Data[a] and Assignments for CF_3-Substituted Phosphines and Related Compounds

C_{3v} Molecules

Compound	$A_1(n)$ P(lone pair)	E(P−X)	F nonbonding orbitals on CF_3 groups: A_2	E	E	Cl nonbonding orbitals: A_2	E	A_1	E	$A_1(s)$
PH_3 (1)	10.59[b] 10.60[c]	13.6[b] 13.4[c]								
PCl_3 (2)[d]	10.52	12.01				11.71	12.97	14.24	15.22	18.85
$(CF_3)_3P$ (3)	11.70	13.52	15.63	16.54	17.18					

C_s Molecules

Compound	A (n) P(lone pair)	A''(P−C)	A'(P−Y)[e]	F nonbonding orbitals on CF_3 groups: A_2	E	E	Cl nonbonding orbitals (A' + A'')	
$(CF_3)_2PH$ (4)	11.50	13.21	13.86	15.34	16.16	16.93		
$(CF_3)_2PCl$ (5)	11.13	13.61	12.42	15.43	16.38	17.05	12.42	14.38
	A'(n) P(lone pair)	A'(P−C)	A''(P−Y)[e]	A_2	E	E	(2A' + 2A'')	
CF_3PH_2 (6)	11.18	13.24	14.08	15.06	15.83	16.69		
CF_3PCl_2 (7)	10.70	13.88	12.21	15.13	15.91	16.96	12.21, 12.62, 14.18	

[a] Vertical ionization potentials in electron volts. [b] Data from ref 2. [c] Data from ref 3. [d] Data from ref 4. [e] Y = H or Cl.

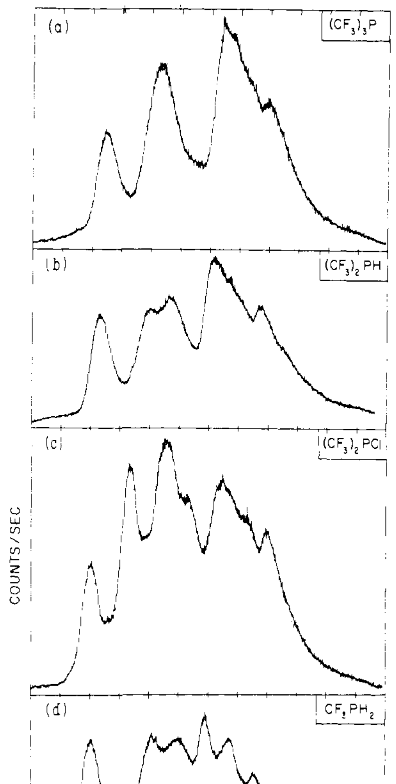

Figure 1. Molecular photoelectron spectra (PES) of (a) $(CF_3)_3P$ (3), (b) $(CF_3)_2PH$ (4), (c) $(CF_3)_2PCl$ (5), (d) CF_3PH_2 (6), (e) CF_3PCl_2 (7).

ably the fourth ionization is obscured beneath the ionization of the F(2p) nonbonding combinations.

Note that the phosphorus lone pair ip's fall in the order $(CF_3)_3P > (CF_3)_2)PX > CF_3PX_2 > PX_3$ for X = H or Cl. This is consistent with electronegativity considerations[26] in the sense that replacement of Cl or H by a more electronegative CF_3 group results in stabilization of the phosphorus "lone pair" MO. However, it is interesting to note that in contrast to considerations of simple inductive effects that (i) the phosphorus lone pair ip for PH_3 is greater than that of PCl_3 and (ii) the successive replacement of CF_3 by Cl results in progressively less change in the phosphorus lone pair ip. Both these observations could be accommodated by the postulate of a conjugative (lone pair destabilizing) interaction between the chlorine lone pairs and vacant phosphorus orbitals of the appropriate symmetry. However, these observations could also be attributed to changes in the molecular geometry. Thus, for example, the X-P-X bond angles in PH_3 (93.3°) are smaller than those of PCl_3 (100.3°). According to Walsh[25] this implies that the lone pair of PH_3 contains more P(3s) character than that of PCl_3. As is widely recognized an increase in the s character of a sp^x hybrid leads to an increase in the binding energy of the MO.

From a naive standpoint one might anticipate an inverse relationship between the magnitude of the phosphorus lone pair ip and the Lewis basicity of a phosphine. If such a correlation proved to be valid PES would, of course, offer an effective means of estimating the gas phase Lewis basicities of phosphines (and related compounds). Unfortunately, however, the limited data which are available presently do not support such a hypothesis. For example, the phosphorus lone pair ip's of PH_3,[2,3] PF_2H,[8] and PF_3[5,6] are 10.6, 11.0, and 12.3 eV, respectively, yet the order of Lewis basicity of these phosphines toward the borane unit is $PF_2H \gg PF_3 \simeq PH_3$.[27] Furthermore, despite the fact that PF_3 possesses a higher phosphorus lone pair ip (12.3 eV)[5,6] than $(CF_3)_3P$ (11.7 eV), PF_3 is capable of forming a BH_3 adduct quite readily.[28] Nevertheless in the series of compounds $(CF_3)_xPH_{3-x}$ (Table I) it is of interest to note that the phosphorus lone pair ip's do seem to correlate with the Lewis base behavior in the sense that PH_3 reacts with B_2H_6 to form the adduct PH_3BH_3,[29] $(CF_3)_2PH$ reacts with B_2H_6 only with catalysis,[30] whereas $(CF_3)_3P$ shows no tendency to interact with Lewis acids.[19] Clearly it is necessary to study systematically a representative series of phosphine Lewis bases and their Lewis acid adducts by means of PES before any useful basicity trends can be delineated.

A final noteworthy feature of the PES data (Table I) is the observation that in general the ionization potentials for the P–C, P–H, and P–Cl σ bonds follow the trends which are anticipated on the basis of the electronegativity sequence $CF_3 > Cl > H$;[26] e.g., for P–C bonds the ip's are in the order $(CF_3)_3P > (CF_3)_2PH$, CF_3PH_2, for P–H bonds the order is $(CF_3)_2PH > CF_3PH_2 > PH_3$, while for P–Cl bonds the sequence is $(CF_3)_2PCl > CF_3PCl_2 > PCl_3$. It is of interest to note that the above orderings have also been found to apply to the P–H and P–C vibrational spectroscopic force constants of trifluoromethyl-substituted phosphines and chlorophosphines.[31]

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 38027X), the Air Force Office of Scientific Research (Contract F44620-71-C-0119), and the Robert A. Welch Foundation for generous financial support. Thanks are also due to Professor Hans Bock for helpful discussion.

References and Notes

(1) It has come to our attention that the photoelectron spectra of trifluoromethyl-substituted phosphines (and arsines) have also been studied at the University of Frankfurt, and the Technische Hochschule, Darmstadt, W. Germany. We extend our thanks to Professor H. Bock, Ms. S. Elbel, and Professor J. Grobe for their courtesy in discussing these results prior to publication.

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Influence of Metal Particle Size on the Chemisorption Properties of Supported Platinum. Analogy with Cluster Compounds

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Abstract: A series of catalysts, $Pt-Al_2O_3$, with various particle size distributions has been studied by electron microscopy and infrared spectroscopy and chemisorption measurements. Well-characterized narrow distributions have been obtained in the range 15–35 Å. The stretching vibration of NO irreversibly adsorbed on these supported metals is particle size dependent: the larger the size, the lower the ν(NO) vibration. This result is interpreted by assuming that the extent of the back-donation to the π^* orbitals of NO^+ depends on the collective properties of the crystallites. This interpretation is corroborated by the spectroscopic results obtained with platinum carbonyl clusters.

In a previous publication[2] we have adopted a (σ,π) type of bonding for the Pt–CO bond in the case of carbon monoxide adsorption on platinum deposited on alumina. This concept, which is derived from the Chatt-Dewar model[3] in coordination chemistry, takes into account most of the experimental data obtained when CO is adsorbed on platinum: increase of the ν(CO) vibration with increasing platinum coverage (the number of electrons available for backbonding per CO adsorbed decreases as the coverage increases), decrease of the ν(CO) vibration upon adsorption of Lewis bases on a surface previously covered with a small amount of CO.[2,4] The shift toward low wave numbers increases as the coverage by the Lewis base increases which suggests a "long distance interaction".

However, the analogy existing between the metal-CO bonding in classical coordination complexes and in supported metals is far from being fully satisfactory. The observation of a long-distance effect, between a Lewis base and carbon monoxide adsorbed on the same particle, requires the participation of the collective properties of the crystallite. This is also corroborated by the fact that the ν(CO) vibration depends on the surface coverage. Therefore one