Photoelectron Spectra and Bonding in Metal–Trifluorophosphine Complexes

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The photoelectron spectra of $Cr(PF_3)_6$, $Fe(PF_3)_5$, and $HRh(PF_3)_4$ have been determined. The results are compared with available data on other transition metal–PF_3 complexes and analogous metal carbonyls.

THE attachment of fluorine to tervalent phosphorus affords a series of fluorophosphines, R_nPF_{3-n}, whose co-ordination properties towards transition metals are comparable with those of carbon monoxide.[1-3]

The transition metal–phosphorus bond in the fluorophosphine complexes can be considered to be formally analogous to that between the metal and carbon in metal carbonyls, *i.e.*, to involve both σ-donor and π-acceptor components. The electronegative fluorines attached to phosphorus are expected to enhance any metal–phosphorus π-bonding.

The similarity between CO and PF_3 as ligands has been established by synthetic and spectroscopic studies and it has been suggested that the π-acceptor properties of PF_3 are comparable with, or may even exceed, those of carbon monoxide.[1-5] Support for this view comes from photoelectron studies on $Ni(PF_3)_4$ and $Pt(PF_3)_4$.[6,7] We now report photoelectron spectra for three other metal trifluorophosphine complexes, namely $Cr(PF_3)_6$, $Fe(PF_3)_5$, and $HRh(PF_3)_4$.

EXPERIMENTAL

$HRh(PF_3)_4$ was synthesised either by acidification of $K[Rh(PF_3)_4]$ made from $[RhCl(PF_3)_2]_2$ as described elsewhere, or by the reaction of π-$C_3H_5Rh(PF_3)_3$ with hydrogen in the presence of excess of PF_3.[8] $Cr(PF_3)_6$ and $Fe(PF_3)_5$ were gifts from Dr. P. L. Timms, Bristol University. All compounds are appreciably volatile and were purified immediately before use by fractional condensation in the high-vacuum line. Spectra were recorded on a PE PS 16 photoelectron spectrometer. In view of the slight instability of $HRh(PF_3)_4$ at room temperature the complex was held at 0 °C immediately before recording its spectrum.

RESULTS

The data obtained from the photoelectron spectra of $Cr(PF_3)_6$, $Fe(PF_3)_5$, and $HRh(PF_3)_4$ are summarised in the Table, together with results reported previously for $Ni(PF_3)_4$, $Pt(PF_3)_4$, and PF_3 itself.[9-11] For $Cr(PF_3)_6$ which is a low-spin d^6 complex, the lowest ionisation potential

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[1] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363, and references therein.

[2] J. F. Nixon, *Endeavour*, 1973, **32**, 19, and references therein.

[3] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53, and references therein.

[4] J. Muller, K. Fenderl, and B. Mertschenk, *Chem. Ber.*, 1971, **104**, 700.

[5] Th. Kruck and R. Kobelt, *Chem. Ber.*, 1972, **105**, 3772.

[6] J. C. Green, D. I. King, and J. H. D. Eland, *Chem. Comm.*, 1970, 1121.

[7] I. H. Hillier, V. R. Saunders, M. J. Ware, P. J. Bassett, D. R. Lloyd, and N. Lynaugh, *Chem. Comm.*, 1970, 1316.

[8] J. F. Nixon and B. Wilkins, paper in preparation.

[9] P. J. Bassett, D. R. Lloyd, I. H. Hillier, and V. R. Saunders, *Chem. Phys. Letters*, 1970, 253.

[10] P. J. Bassett and D. R. Lloyd, *J.C.S. Dalton*, 1972, 248.

[11] J. P. Maier and D. W. Turner, *J.C.S. Faraday II*, 1972, 711.

(9·0 eV) corresponds to ionisation from orbitals which have mainly metal $3d$-character of t_{2g} symmetry in O_h.

Experimental ionisation potentials/eV for PF_3 and some of its complexes

PF_3	$Cr(PF_3)_6$ [a]	$Fe(PF_3)_5$ [a]	$Ni(PF_3)_4$ [b]	$HRh(PF_3)_4$ [a]	$Pt(PF_3)_4$ [b]
		8·9	9·6	9·7	9·8
	9·0				
		10·2	10·6	11·8	12·5
12·3	12·7	13·0	13·1	13·7	14·5
15·8	15·8	15·9	15·8	15·9	15·9
16·3					
17·5	17·4	17·4	17·4	17·4	17·5
18·6					
19·4	19·5	19·3	19·3	19·4	19·4

[a] This work. [b] Refs. 6 and 7.

Note: $3d$ Ionisation potentials: $Cr(CO)_6$, 8·4; $Fe(CO)_5$, 8·6; 8·9; and $Ni(CO)_4$, 8·9; 9·7.

The remaining ionisation potentials (I.P.) all have counterparts in unco-ordinated trifluorophosphine, the I.P. at 12·7 eV corresponding to ionisations largely from orbitals localised on the phosphorus atoms (lone-pair orbitals) and compare with the value of 12·3 eV reported for the free ligand. The remaining three ionisation potentials at 15·8, 17·4, and 19·5 eV represent ionisations from molecular orbitals chiefly derived from the fluorine $2p$ atomic orbitals and are little changed from the corresponding values reported for PF_3 itself. For $Fe(PF_3)_5$, which on the basis of i.r. studies is believed to have a trigonal bipyramidal structure[12] (D_{3h} symmetry), the metal $3d$-orbitals transform as A_1', E', and E'' and if we neglect initially any π-bonding interactions then the e'' (d_{xz}, d_{yz}) orbitals are non-bonding, while the e' ($d_{x^2-y^2}$, d_{xy}) orbitals and a' (d_{z^2}) orbitals are anti-bonding. For the $Fe(^0)$ d^8 configuration, therefore, the valence electrons just fill the e'' and e' orbitals.

The two bands at 8·9 and 10·2 eV in the photoelectron spectrum of $Fe(PF_3)_5$ can accordingly be assigned to ionisations from the e' and e'' orbitals respectively. The observed intensities deviate considerably from the expected 1 : 1 pattern observed for the analogous $Fe(CO)_5$ compound which is known to have a trigonal bipyramid structure. This might possibly be due to deviations from D_{3h} symmetry in the trifluorophosphine complex, but structural data are not yet available.

The ionisation potential at 13·0 eV is assigned by analogy with the results for $Cr(PF_3)_6$ and $Ni(PF_3)_4$ to ionisations from orbitals localised on the phosphorus atoms, and the remaining ionisation potentials at 15·9, 17·4, and 19·3 eV are almost identical with those found in the chromium and nickel systems.

The structure of $HRh(PF_3)_4$ is currently under study by electron diffraction; however i.r. results indicate that it probably has the same distorted trigonal bipyramid structure as $HCo(PF_3)_4$ (roughly C_{3v}) in which the four phosphorus atoms form an irregular tetrahedron round cobalt.[3] * The ^{19}F and ^1H n.m.r. spectra indicate that these compounds are fluxional in solution and it is believed that the hydrogen traverses the faces of the ML_4 tetrahedron.[13]

The photoelectron spectrum of $HRh(PF_3)_4$ shows two bands of similar intensity at 9·7 and 11·8 eV which are assigned to the two doubly degenerate orbitals of largely metal d-character having symmetry species e in the C_{3v} point group. The I.P. at 13·7 eV corresponds to ionisations from the phosphorus lone-pair orbitals while the remaining I.P.s at 15·9, 17·5, and 19·4 eV are almost identical with those described in the other metal–trifluorophosphine complexes.

DISCUSSION

It is interesting to compare the vertical ionisation potentials of the $3d$-orbitals of $Cr(PF_3)_6$, $Fe(PF_3)_5$, and $Ni(PF_3)_4$ with those reported for the analogous metal carbonyls and also for the free metal atoms.[4,14] In all cases the figures are rather similar for the PF_3 complexes and their carbonyl counterparts, the slightly larger values found for the former series being perhaps indicative of a higher positive charge on the metal resulting from the stronger electron-withdrawing properties of PF_3 than CO.

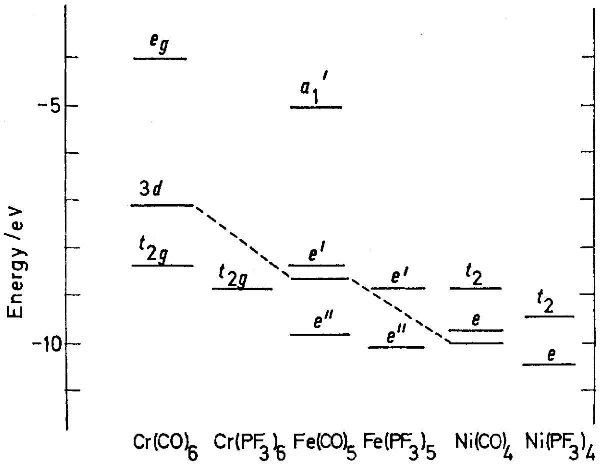

FIGURE 1 Relative energies of the d-orbitals of binary metal carbonyls and metal–trifluorophosphine complexes. The $3d$-orbital energies of the free metal atoms are joined by the broken line

The separation of the first two bands in the photoelectron spectra of $Fe(PF_3)_5$, (e'—e''), is very slightly larger than in $Fe(CO)_5$, also suggesting that the π-acceptor properties of PF_3 and CO are comparable with the former ligand slightly the stronger. Similar conclusions have been noted from a comparison of the spectra of $Ni(PF_3)_4$ and $Ni(CO)_4$ and in recent Mössbauer and mass spectroscopic studies.[4,5]

The metal d-orbital energy in $Cr(PF_3)_6$ (9·0 eV) is smaller than the mean of the first two ionisations of $Fe(PF_3)_5$ (9·55 eV) and the weighted average of the t_2—e separation in $Ni(PF_3)_4$ (9·96 eV). The relative positions of the $3d$-orbitals in binary metal carbonyls $M(CO)_x$ ($x = 6$, M = Cr; $x = 5$, M = Fe; $x = 4$, M = Ni) and those of the free atom have been discussed by Lloyd and Schlag[14] and we have summarised their results and the data for the analogous first row transition metal–PF_3 complexes in Figure 1.

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* *Note added in proof:* The structure has now been determined and is a distorted trigonal bipyramid in which the hydrogen atom occupies an axial position (D. W. H. Rankin, personal communication).

[12] Th. Kruck and A. Prasch, *Z. anorg. Chem.*, 1969, **371**, 1.

[13] P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 1797.

[14] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, 1969, **8**, 2544.

The *d*-orbital splitting in $HRh(PF_3)_4$ (2·1 eV) and $Pt(PF_3)_4$ (2·7 eV) is much larger than the values for the chromium, iron, and nickel complexes as expected for transition metals in the second and third rows.

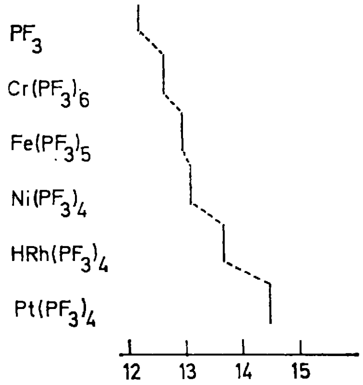

FIGURE 2 Phosphorus lone-pair energies in PF_3 and some transition-metal complexes

Figure 2 shows how the phosphorus lone-pair energies vary for PF_3 and its transition-metal complexes. There is an increase in energy in all cases compared with the free ligand value in the order of atomic number, *viz.*, Cr < Fe < Ni < Rh < Pt. Changes in the energy of the phosphorus lone-pair orbital of PF_3 on co-ordination have been related to the extent of σ-donation [7] and are particularly significant for Rh and Pt. These values should be compared with an increase in energy of **3·4** eV in going from PF_3 to POF_3. In this respect the similarity between the energies of the non-bonding fluorine orbitals in PF_3 and its transition-metal complexes contrasts with the results from POF_3 where a shift of *ca.* 1 eV has been reported.[9] Structural and photoelectron studies on other metal–trifluorophosphine complexes are continuing.

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