Photoelectron Spectroscopic Study of Metal Trifluorophosphine and Hydridotrifluorophosphine Complexes

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Photoelectron spectra of the complexes $[M(PF_3)_6]$ (M = Cr, Mo, and W), $[M(PF_3)_5]$ (M = Fe and Ru), $[HM(PF_3)_4]$ (M = Co, Rh, and Ir), and $[HMn(PF_3)_5]$ are presented. Spectra are assigned by analogy with those of PF_3 and the corresponding metal carbonyl complexes. It is concluded that: (*i*) PF_3 has a greater overall electron-withdrawing effect than CO; (*ii*) *d*-orbital ionisation potentials generally increase across a series and down a vertical group; (*iii*) metal–phosphorus σ bonding increases across a series and down a vertical group; and (*iv*) the degree of π bonding is not readily ascertained from the p.e. spectra.

HELIUM(I) photoelectron spectroscopy is proving to be an invaluable asset in the study of bonding in transition-metal complexes. Obvious candidates for an early study were the transition-metal carbonyls, due to their ready availability, volatility, high symmetry, and the relative simplicity of the ligand. Several binary carbonyls have been studied,[1-3] together with some derivatives.[3-6] Phosphorus trifluoride is believed to act as a very similar ligand to CO; the series $[M(PF_3)_4]$ (M = Ni, Pd, and Pt) has been widely studied by photoelectron (p.e.) spectroscopy [7-9] and the spectra probably conclusively assigned. We have previously published preliminary results on several PF_3 complexes,[10] and in this paper we present a much more extensive study of binary transition-metal trifluorophosphine and hydrido-derivatives. This allows a comprehensive study to be made of trends both across and down the transition series. The bonding in metal trifluorophosphine complexes is believed to involve both donation of σ electrons (from the phosphorus lone-pair orbitals) into empty metal orbitals of appropriate symmetry and back donation from the metal *d* orbitals into the ligand π orbitals (in this case the phosphorus 3*d* levels).[11-14] The formation of low-valent complexes should lead to stabilisation both of the *d* orbitals with respect to the metal atoms and of the M–P σ-bonding orbital (strictly speaking, the weighted average of all the M–P σ orbitals) with respect to the phosphorus lone-pair orbital.

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[1] P. Burroughs, D. M. Gibson, B. R. Higginson, D. R. Lloyd, and A. F. Orchard, *J.C.S. Faraday II*, 1973, 1659.

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

[3] I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1974, **27**, 215.

[4] B. R. Higginson, D. R. Lloyd, J. A. Connor, and I. H. Hillier, *J.C.S. Faraday II*, 1974, 1418.

[5] S. Cradock, E. A. V. Ebsworth, and A. Robertson, *J.C.S. Dalton*, 1973, 22.

[6] S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, 1969, **47**, 112.

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

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

[9] P. J. Bassett, B. R. Higginson, D. R. Lloyd, N. Lynaugh, and P. J. Roberts, *J.C.S. Dalton*, 1974, 2316.

[10] J. F. Nixon, *J.C.S. Dalton*, 1973, 2226.

[11] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

[12] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

[13] J. F. Nixon, *Endeavour*, 1973, **32**, 19.

[14] R. J. Clark and M. A. Busch, *Accounts Chem. Res.*, 1973, **6**, 246.

EXPERIMENTAL

Samples of $[Fe(PF_3)_5]$ and $[Ru(PF_3)_5]$ were synthesised by the method of Clark *et al.*[15,16] from $[Fe(CO)_5]$ and $[Ru_3(CO)_{12}]$ respectively, $[Cr(PF_3)_6]$ (a gift from Dr. P. L. Timms) and $[HCo(PF_3)_4]$ by the technique of metal vaporisation developed by Timms,[17] $[HMn(PF_3)_5]$, $[Mo(PF_3)_6]$, and $[W(PF_3)_6]$ from the corresponding metal carbonyls by u.v. irradiation in the presence of PF_3 and separation by g.l.c. techniques described elsewhere,[14,15] and $[HRh(PF_3)_4]$ and $[HIr(PF_3)_4]$ by acidification of their metallate salts [18,19] which were synthesised from the corresponding $[\{MCl(PF_3)_2\}_2]$ complexes.[20-22] All the complexes were purified by trap to trap fractionation on a high-vacuum line and their purity checked by i.r. spectroscopy immediately prior to use.

Photoelectron (p.e.) spectra were recorded on a PS16 He(I) spectrometer, fitted with a modified high-intensity lamp. All complexes were vaporised into the machine remotely, from slush baths at suitable temperatures. This technique is generally preferred to the use of needle valves since the sample vapour pressure is more constant. Spectra were calibrated using methyl iodide, oxygen, and argon.

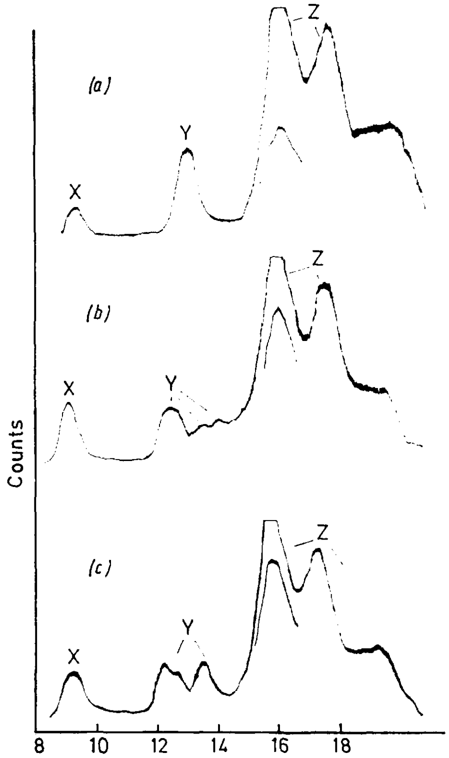

FIGURE 1 He(I) p.e. spectra of $[M(PF_3)_6]$ [M = Cr (*a*), Mo (*b*), and W (*c*)]

RESULTS AND DISCUSSION

The spectra are shown in Figures 1—4, and the measured vertical ionisation potentials (i.p.s) are listed for comparison, together with the appropriate assignment, in Table 1. Inclusion of the results from ref. 9 affords a useful comparison with the results described in this paper.

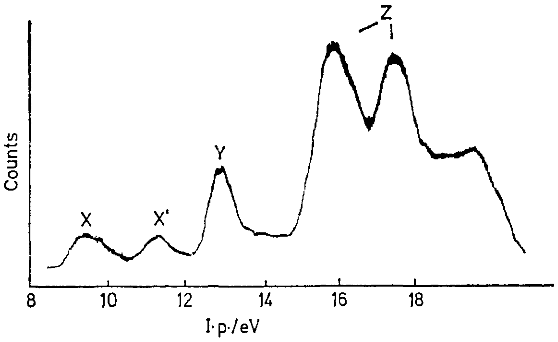

FIGURE 2 He(I) p.e. spectrum of $[HMn(PF_3)_5]$

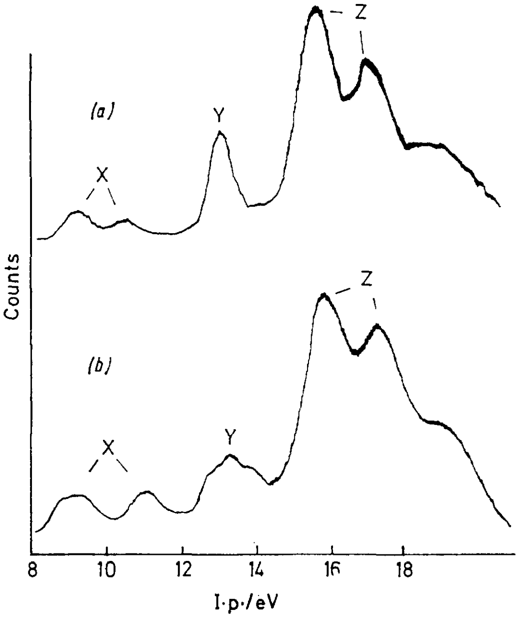

FIGURE 3 He(I) spectra of $[M(PF_3)_5]$ [M = Fe (*a*) and Ru (*b*)]

A major advantage of the present series is that trifluorophosphine complexes tend to be more thermally stable than the corresponding carbonyls. For example, while all complexes of the type $[HM(PF_3)_4]$ (M = Co, Rh, and Ir) are available for study by p.e. spectroscopy, the only analogous carbonyl complex is $[HCo(CO)_4]$. All the complexes studied obey the 18-electron rule, and they are all diamagnetic.† In order to facilitate the discussion the bands in the spectra are labelled. Bands of type (X)

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† Recent studies indicate that unusually high relaxation occurs on ionisation from metal *d* orbitals in some transition-metal complexes and that Koopmans' theory does not apply (M. M. Rohmer and A. Veillard, *Chem. Comm.*, 1973, 230; M. F. Guest, B. R. Higginson, I. H. Hillier, and D. R. Lloyd, *J.C.S. Faraday II*, 1975, 902). Koopman's theory is assumed to hold qualitatively for the PF_3 complexes described in this paper where in general the i.p.s. are well separated in energy from orbitals of predominantly ligand character.

[15] R. J. Clark, *Inorg. Chem.*, 1964, **3**, 1395.

[16] C. A. Udovich and R. J. Clark, *J. Organometallic Chem.*, 1972, **36**, 355.

[17] P. L. Timms, *J. Chem. Soc.* (*A*), 1970, 2526.

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

[19] Th. Kruck, W. Lang, N. Derner, and M. Stadler, *Chem. Ber.*, 1968, **101**, 3816.

[20] M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, 1971, **10**, 2387.

[21] D. A. Clement and J. F. Nixon, *J.C.S. Dalton*, 1972, 2553.

[22] J. F. Nixon and J. R. Swain, *J.C.S. Dalton*, 1972, 1044.

refer to d-orbital ionisations, (X') to M–H σ ionisation (where applicable), (Y) to M–P σ ionisations, and (Z) to pure ligand (fluorine lone-pair) ionisations.

TABLE 1

Ionisation potentials (eV) of transition-metal trifluorophosphine and hydridotrifluorophosphine complexes. Data for analogous carbonyl complexes are given in parentheses where applicable

		$[M(PF_3)_6](O_h)$				$[HMn(PF_3)_5](C_{4v})$		$[M(PF_3)_5](D_{3h})$			$[HM(PF_3)_4](C_{3v})$				$[M(PF_3)_4](T_d)$ [a]		
Orbital		Cr	Mo	W				Fe	Ru		Co	Rh	Ir		Ni	Pd	Pt
Metal d	e_g				a_1		a_1'			a_1				t_2	9.69	9.9	9.83
															(8.93)		
	t_{2g}	9.29	9.17	9.30	b_1		e'	9.15	9.17	e	9.58	9.70	9.82	e	10.74	12.2	12.45
		(8.40)	(8.50)	(8.56)				(8.60)			(8.90)				(9.76)		
					e	(8.85)	e''	10.43	11.07	e	10.56	11.79	11.95				
					b_2	9.47 (9.14)		(9.86)			(9.90)						
M–H					a_1	11.30				a_1	12.12						
						(10.55)					(11.5)						
M–P [b]	t_{1u}		12.94	12.26	a_1		a_1			a_1				t_2	13.17	13.7	14.54
	a_{1b}	12.84	13.48	12.64	e	12.93	a_1	13.08	12.8	a_1	13.25	13.83	14.18	a_1	14.65		
	e_g		13.93	13.52	e		e'		13.25	e							
							a_2''		13.65								
Fluorine lone-pair [b]		15.80	15.80	15.85		15.85		15.83	15.75		16.00	15.90	16.01		15.97	15.8	15.87
		17.36	17.36	17.44		17.43		17.24	17.18		17.46	17.42	17.42		17.48	17.4	17.53
		19.3	19.1	18.7		19.4		19.1	18.9		19.4	19.3	19.4				

[a] From ref. 9. [b] In PF_3, phosphorus lone-pair i.p. = 12.27 eV, intense fluorine lone-pair i.p.s. = 15.88 and 17.46 eV.[24]

The He(I) p.e. spectra of the complexes $[M(PF_3)_6]$ (M = Cr, Mo, and W), like their carbonyl counterparts, showed a single band (band X) in the region below 12 eV, with an almost invariant vertical i.p. (9.29, 9.17, and 9.30 eV for Cr, Mo, and W respectively).* This band is clearly associated with ionisation from the filled t_{2g} orbital, which arises from splitting of the metal d orbitals in the presence of the octahedral field. In all cases the observed bands were symmetrical, and surprisingly the band showed no sign of further splitting, even for the tungsten complex. This is in contrast to results obtained by Lloyd and his co-workers [4] on $[W(CO)_6]$ where spin–orbit splitting was observed.[23] It is interesting to note that the energies of the t_{2g} orbitals in the metal hexacarbonyls $[M(CO)_6]$ are 8.40, 8.52, and 8.56 eV for M = Cr, Mo, and W respectively,[1] reflecting the slightly smaller overall electron-withdrawing ability of CO compared with PF_3.

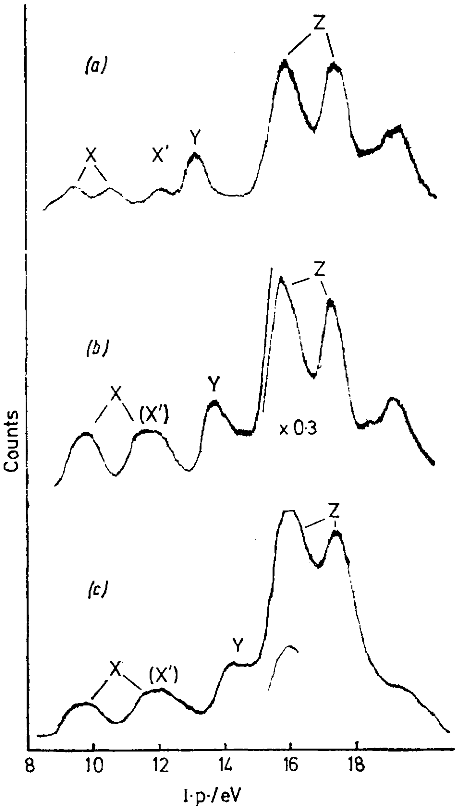

FIGURE 4 He(I) p.e. spectra of $[HM(PF_3)_4]$ [M = Co (a), Rh (b), and Ir (c)]

The remaining bands in the spectra of the $[M(PF_3)_6]$ complexes are assigned to ionisations from orbitals predominantly localised on the PF_3 ligands, since the t_{2g} orbital contains all of the central-atom valence electrons. The other regions of the spectra therefore represent perturbations of the spectrum of PF_3.[24] The phosphorus lone-pair orbitals [i.p.(PF_3) 12.27 eV] are likely to be affected most since these are substantially responsible for the M–P σ bonding. In O_h symmetry the six phosphorus lone pairs transform as a_{1g}, e_g, and t_{1u} and, although these orbitals should be observed as separate bands in the p.e. spectrum, it is likely that they will remain in the same region as the phosphorus lone-pair i.p. in PF_3. In this respect, the p.e. spectra of the PF_3 complexes are easier to interpret than the corresponding carbonyl derivatives, since there is only a single band in this region for the free ligand. Only one band was observed in the spectrum of $[Cr(PF_3)_6]$, whilst both $[Mo(PF_3)_6]$ and $[W(PF_3)_6]$ showed three bands in this region [bands (Y)]. For all these complexes the bands (Z) were very similar and there was no suggestion of a low-energy shoulder in the case of $[Cr(PF_3)_6]$. The band (Y) in $[Cr(PF_3)_6]$ was separated from the bands (Z) by at least 3 eV, so that the implication is that in $[Cr(PF_3)_6]$ the t_{1u}, e_g, and a_{1g} orbitals are

* 1 eV ≈ 1.60×10^{-19} J.

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

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

degenerate. The spectra of [Mo(PF_3)$_6$] and [W(PF_3)$_6$] on the other hand showed three bands in this region. Calculations on the analogous metal hexacarbonyl complexes[25] indicate that the t_{1u} orbital has the lowest i.p. and qualitatively this is acceptable since the e_g and a_{1g} orbitals are likely to be somewhat stabilised by interactions with the empty *d* and *s* orbitals on the central metal atom. The bands at lowest i.p. in region (Y) for [Mo(PF_3)$_6$] and [W(PF_3)$_6$] are assigned accordingly to ionisations from the M–P t_{1u} σ orbitals.

Assignment of the remaining two bands in region (Y) for these two complexes poses a greater problem. Initially it was considered that the band at 12.26 eV in [W(PF_3)$_6$] might arise from PF_3 possibly present as an impurity, but this was discounted since the relative intensity of the peaks remained unchanged even when the temperature of the target chamber was varied from *ca.* 30 to 250 °C. Furthermore the gas-phase i.r. spectrum of the sample showed no detectable PF_3 in accord with the known high thermal stability of the complex.[11]

We therefore conclude that all the observed bands arise from genuine ionisations from the [W(PF_3)$_6$] complex. The peak at 12.64 eV appeared only as a shoulder on the band assigned to ionisation from the t_{1u} orbital. The intensity ratio of the two separate bands in region (Y) for [W(PF_3)$_6$] was much closer to 2:1 [implying the assignment ($t_{1u} + a_{1g}$): e_g] than 5:1 [corresponding to the alternative ordering ($t_{1u} + e_g$):a_{1g}] and we accordingly propose the former assignment. By analogy we tentatively suggest that the same ordering occurs in the molybdenum complex. It should be noted here that our spectrum differs in detail in this region from that recently obtained by Eland.[26] To summarise it is proposed that the M–P σ-bonding orbitals are degenerate for [Cr(PF_3)$_6$], but split in both [Mo(PF_3)$_6$] and [W(PF_3)$_6$]. Since the extent of splitting of the phosphorus lone pairs is directly related to the degree of σ bonding in the molecules, the implication is that within the [M(PF_3)$_6$] triad M–P σ bonding is weakest in the chromium complex. A similar effect is observed with other complexes in this series (see below).

In the next vertical group, Group 7B, the only analogous compound available to us was [HMn(PF_3)$_5$]. This complex is thought to have C_{4v} symmetry, with the hydrogen atom occupying an apical position. The manganese atom has a d^6 configuration and we expect to observe two bands corresponding to ionisation from the *e* and b_2 orbitals in order of increasing i.p. If the distortion of the four equatorial PF_3 groups towards the H atom is large, the b_2 orbital should be significantly stabilised with respect to the *e*. In fact just three bands [(X), (X′), and (Y)] were observed in the p.e. spectrum in the region below the fluorine lone-pair bands. The highest (in i.p.) of these, which occurred at 12.93 eV, clearly corresponds to ionisation from Mn–P σ-bonding orbitals. The band (X′) at 11.30 eV is assigned to the a_1 Mn–H σ-bonding orbital. Cradock *et al.*[5] observed an analogous band in the p.e. spectrum of [HMn(CO)$_5$], although at lower i.p., due to the smaller overall electron-withdrawing ability of the CO ligand. The observation of a single band (X) at lowest i.p. implies that the b_2 and *e* orbitals are approximately degenerate with only a minor distortion from O_h symmetry. The observation of a single band (Y) in the M–P σ-bonding region suggests that, as found for [Cr(PF_3)$_6$], all the ionisations from orbitals derived from the phosphorus lone pairs are contained in this band. This appears to be a feature of all the first-row complexes {with the possible exception of [Ni(PF_3)$_4$][9]} while of the second- and third-row complexes studied only [Mo(PF_3)$_6$], [W(PF_3)$_6$], and [Ru(PF_3)$_5$] showed clear splitting of the M–P σ orbitals. It is likely that these orbitals are also split in [Pd(PF_3)$_4$], [Pt(PF_3)$_4$], [HRh(PF_3)$_4$], and [HIr(PF_3)$_4$], but the M–P bands in these complexes are close to those arising from fluorine lone-pair ionisations.

Vibrational spectroscopic studies on [Fe(PF_3)$_5$] and [Ru(PF_3)$_5$] suggest that these complexes have trigonal-bipyramidal structures.[27] By analogy with [Fe(CO)$_5$],[2] the *d* orbitals are expected to split into a_1', e', and e'' in order of increasing i.p. Since the metals are in the zero oxidation state they both have a d^8 configuration. Thus two bands are predicted and observed (X), although for the iron complex the intensities were unequal. It is difficult to accept that the assignment $e''^4e'^4$ is incorrect, and it seems probable that this is an example of misleading intensity ratios in p.e. spectroscopy.* The splitting of the two bands was markedly greater for the ruthenium complex (1.9 as against 1.28 eV), an effect which has previously been observed in the series [Ni(PF_3)$_4$], [Pd(PF_3)$_4$], and [Pt(PF_3)$_4$].[9] The e'' orbital, which is non-bonding, is likely to reflect the i.p. of the central atom. The calculation of the i.p. of a *d* electron from $(n-1)d^8 \rightarrow (n-1)d^7$ requires the weighting of a formidable number of configurations, some of which are not reported in Moore.[28] It seems almost certain, however, that the greater *d*-orbital splittings observed in the second and third-transition series reflect the increasing atomic i.p. of the formally non-bonding *d* orbital in the heavier complexes, as found by Lloyd and his co-workers[9] in the rather simpler case of the Ni, Pd, and Pt series. The iron complex, like those of chromium and manganese, showed only one band (Y) in the M–P σ-bonding region, implying that the M–P σ orbitals are degenerate. In the p.e. spectrum of the ruthenium complex, on the other hand, this band was complex and at least three vertical i.p.s were discerned. Group theory dictates that the M–P σ orbitals transform as $2a_1'$, e', and a_2'' in D_{3h} symmetry so that four bands should be observed. While it is possible that the fourth band is concealed by the fluorine lone-pair bands, it is probable that all ionisations from the M–P σ orbitals are observed in one complex band with only a limited splitting into the constituent orbitals.

Finally the spectra of the hydrido-complexes of Group 8,

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* See, for example, ch. 1 of ref. 26.

[25] I. H. Hillier and V. R. Saunders, *Mol. Phys.*, 1971, **22**, 1025.

[26] J. H. D. Eland, 'Photoelectron Spectroscopy,' Butterworths, 1974.

[27] Th. Kruck and A. Prasch, *Z. anorg. Chem.*, 1968, **356**, 118.

[28] C. E. Moore, 'Atomic Energy Levels,' Nat. Bureau Stand., Circular 467, U.S. Government Printing Office, Washington D.C., 1958.

[$HM(PF_3)_4$] (M = Co, Rh, or Ir) will be considered. These complexes have C_{3v} local symmetry, and the *d* orbital stransform as a_1', e, and e. Of these, the a_1, which is directed along the H–M–P axis, will again be the least stable on simple crystal-field grounds. The eight metal *d* electrons which are available should therefore just fill the two *e* orbitals. This is nicely reflected in the spectrum of the cobalt complex which exhibited two low-energy bands (X) of almost equal intensity. The third band in the spectrum (X′) may be assigned to excitation from the H–Co σ-bonding orbital. This band appeared at higher i.p. than the corresponding band in the manganese complex, reflecting the increasing i.p. of the metal on moving across the transition series. The observed trend in *d*-orbital splitting (the highest i.p. band undergoes a large increase in i.p. on moving down a Group) is again apparent in these complexes, and it is noted that the trend is less marked on going from the second to the third transition series than from the first to the second. This greater similarity of the second- to the third-row elements is a general feature of transition-metal chemistry.[29] As a result of this the band at lower energy is at significantly higher i.p. in the Rh and Ir complexes, and masks the band due to ionisation from the M–H σ orbital. This is supported by the fact that this band has a greater integrated intensity than the first, thus reversing the 'dropping-off' effect of intensities normally observed. In the M–P σ-bonding region the cobalt complex showed a single band (Y), which must accordingly be assigned to all the M–P σ orbitals ($2a_1$ and e). The corresponding bands for the rhodium and iridium complexes were less symmetric, but it is difficult to determine whether they are actually split since they occurred at higher i.p. close to the low-i.p. side of the intense ionisations from the fluorine lone-pair orbitals.

With the spectra assigned, and by comparison with published data, it is possible to draw some interesting conclusions regarding the bonding in the complexes and the comparative behaviour of CO and PF_3 as ligands.

Comparison with Carbonyl Complexes.—Where results are available for both transition-metal carbonyl and trifluorophosphine complexes (see Table 1), *d*-orbital, and where applicable M–H σ-orbital, i.p.s are always found to be higher for the PF_3 complexes, implying that the electron-withdrawing effect of PF_3 is greater than that of CO. This has been suggested previously [10] but the result is confirmed here for an extensive series of complexes.

(ii) d-*Orbital Energy Levels.*—Since the u.v.–visible electronic spectra of most of the PF_3 complexes have not been published, it is not yet possible to obtain the energy of the unoccupied *d* levels and hence a baricentre *d*-orbital energy. It seems clear, however, that there is a tendency for the i.p. of the *d* orbitals to increase both on moving across a transition series (reflecting the weak shielding effect of valence *d* electrons) and on moving down a vertical Group. The change in i.p. between the *d* levels in the second- and third-row metal complexes is less than for the change between the first- and second-row complexes.

The relative constancy of the t_2 energy in the series [$M(PF_3)_4$] (M = Ni, Pd, or Pt) has been attributed [9] to a balance between the atomic *d*-orbital energy and the antibonding interaction with the phosphorus lone-pair orbital. The *e* orbital is non-bonding and reflects the atomic i.p. Support for this proposal comes from the spectra of [$M(PF_3)_5$] (M = Fe or Ru) where the i.p. of the e' orbital (which can interact with the MP_5 σ system) is virtually the same for Fe and Ru, while the e'' orbital increases in i.p. by 0.64 eV. This is the only new group of complexes where the comparison is valid, since both the occupied levels in [$HM(PF_3)_4$] (M = Co, Rh, or Ir) have *e* symmetry and will interact among themselves as well as with the MP_4 σ system. It is interesting to note that whereas the occupied *d* orbitals (*e* and b_2) are observed separately in [$HMn(CO)_5$] [5] they occur as a single band in [$HMn(PF_3)_5$].

However, this correlation cannot be extended easily to the Group 6 complexes since the t_{2g} orbital, which cannot interact with the M–P σ framework, has an almost constant i.p. for all three metals despite the variation in atomic i.p.

(iii) *The* M–P σ *Region.*—The most outstanding feature of the M–P σ-bonding region is that in most of the spectra a single band is observed which is attributed to M–P σ ionisations. Since a definite splitting is observed in the molybdenum, tungsten, rhodium, and nickel complexes, with the component bands well separated from the fluorine orbitals, this assignment is satisfactory, with the exception of the Pd and Pt complexes where the M–P t_2 σ ionisation occurs close to the fluorine lone-pair ionisations. As we believe that all components of the M–P σ orbital are observed, it is possible to estimate a weighted average i.p. for this orbital and to examine the variation in i.p. across and down the transition series (Table 2).

TABLE 2

Weighted averages of σ M–P ionisation energies (eV)

Cr	Mn	Fe	Co	Ni
12.84	12.93	13.08	13.25	13.54
Mo		Ru	Rh	Pd
13.11		13.25	13.83	>14.0 *
W			Ir	Pt
12.74			14.18	>14.8 *

* Estimated from published data.[9]

The two observable trends are (*a*) a shift to higher i.p. on moving from left to right across a series, and (*b*) with the exception of the Group 6 complexes the weighted average moves to higher i.p. on going down a Group. Trend (*a*) supports Lloyd's assignment [9] of the small band on the low-i.p. side of the fluorine lone-pair bands in [$Ni(PF_3)_4$] to the a_1 M–P σ orbital. If ionisations from all the M–P σ orbitals were contained in the high-energy M–P band the trend of the weighted average of the M–P σ i.p.s would be reversed at nickel and since this is inherently unlikely the assignment is likely to be valid.

(iv) π-*Bonding Considerations.*—The position of the

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[29] F. A. Cotton and G. Wilkinson in 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, 1972.

bands in the high-energy region of the p.e. spectra (15—19 eV) of all the PF_3 complexes studied is essentially the same and little different from PF_3 itself. These bands are assigned to fluorine lone-pair orbitals and previously it has been suggested [8,9] that any changes in energy of the non-bonding fluorine orbitals should reflect the net result of σ and π bonding between the metal and phosphorus. Since, as discussed above, the greatest change in the phosphorus lone-pair energy on complex formation occurs for the heavier metals in a particular group, acceptance of this viewpoint suggests that the importance of π bonding is greater for Pt than Ni in the $[M(PF_3)_4]$ complexes and also decreases in importance in the order $Ir > Rh > Co$ for $[HM(PF_3)_4]$.

It should be noted, however, that results of thermochemical,[30] kinetic,[31] and structural studies [32-34] on various PF_3 complexes all lead to an *opposite* conclusion from the above. In view of the general acceptance of π bonding in metal carbonyls, it is interesting to note that recent microcalorimetric studies on $[Cr(PF_3)_6]$ and $[Ni(PF_3)_4]$ show that their mean bond-dissociation energies $\bar{D}(Ni{-}PF_3)$ and $\bar{D}(Cr{-}PF_3)$ are very similar to $\bar{D}(Ni{-}CO)$ and $\bar{D}(Cr{-}CO)$ in $[Ni(CO)_4]$ and $[Cr(CO)_6]$.[30] Similarly mass-spectroscopic studies on the complexes $[HCo(CO)_x(PF_3)_{4-x}]$ have shown that the Co–CO and Co–PF_3 bond energies are very similar.[35] The results of kinetic studies on the mechanism of substitution reactions of $[M(PF_3)_4]$ ($M = Ni$ or Pt) together with related data on metal phosphite complexes [31] imply that the stability of Ni^0 complexes seems to be essentially due to π bonding while that of the Pt^0 derivatives is due to σ bonding. This is consistent with Nyholm's earlier proposal,[36] based on the i.p of the metal atom in the spin-paired states ($d^{10} \rightarrow d^9$), that the abilities to form d_π bonds decrease in the order Ni (5.81) $\gg$ Pt (8.20) $\geqslant$ Pd (8.33 eV).

The existence of $[Pt(PF_3)_4]$ and $[Pd(PF_3)_4]$ and non-existence of the analogous carbonyls * presumably implies a better σ-donor capacity for PF_3 than CO. Structural parameters are available for both $[Ni(PF_3)_4]$ and $[Pt(PF_3)_4]$ from electron-diffraction studies.[32,33] The geometry of PF_3 is essentially the same in the free ligand and in $[Ni(PF_3)_4]$, whereas there is a contraction of the P–F distances in $[Pt(PF_3)_4]$. In $F_3P{\cdot}BH_3$, where a marked shortening of the P–F bond has been observed, the σ contribution is, of course, dominant.[37] The metal–phosphorus bond lengths found so far in PF_3 complexes also support the view that any π bonding is likely to be more important for the first-row transition metals. For example, the Ni–P distance (2.116 Å) in $[Ni(PF_3)_4]$ and the Co–P distance in $[HCo(PF_3)_4]$ (2.052 Å) are exceptionally short and are in fact the shortest known for phosphine complexes of these metals. On the other hand, the Pt–P distance in $[Pt(PF_3)_4]$ is not particularly different from other values observed in platinum–phosphorus complexes.

Although clearly more structural data for a series of PF_3 complexes would be desirable in any discussion of their p.e. spectra, we conclude that, whereas at present the variation in energy of the phosphorus lone pair on co-ordination no doubt reflects the extent of σ donation in these complexes, the degree of π bonding is not as yet as readily ascertained from p.e. spectroscopic studies.

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* The complex $[Pd(CO)_4]$ has been identified by i.r. spectroscopy at 20 K.[38]

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