

He I and He II Photoelectron Spectra of some Trifluorophosphine, Carbonyl, and Hydrido Transition Metal Complexes†

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The He I and He II gas-phase ultraviolet photoelectron (p.e.) spectra of $[M(PF_3)_5]$ ($M = Fe$ or Ru), $[ReH(PF_3)_5]$, and $[RuH_2(PF_3)_4]$, together with the He I spectrum of $[OsH_2(CO)_4]$, have been recorded and assigned empirically. The highest energy bands, corresponding to ionisation from the $\sigma(M-L)$ and ligand localised orbitals, are separated from the predominantly metal-based bands by bands associated with the metal-hydrogen bonding orbitals (where present). For the $[M(PF_3)_5]$ complexes, evidence is presented for significant phosphorus character in the e' (highest occupied molecular orbital) level, indicating a greater metal-phosphorus interaction than is found for the e'' (second highest occupied molecular orbital) level. The p.e. bands due to ionisation from the M-H localised orbitals of $[OsH_2(CO)_4]$ occur at 11.1 and 11.5 eV, values significantly lower than those found for the bridging hydrido moieties of $[Os_3(\mu-H)_2(CO)_{10}]$ and $[Os_4(\mu-H)_4(CO)_{12}]$ (12.1–12.8 eV). A comparison of the p.e. data reported herein with literature data reveals two trends: a trend towards increasing ionisation energy of the metal d bands in $[M(PF_3)_x]$ complexes with the atomic number of M , and a trend towards lower ionisation energy for the $\sigma(M-H)$ bands of PF_3 complexes on descending a Group. This latter trend contrasts with the approximately constant, or slightly increasing, ionisation energy associated with the analogous bands of the related hydrido carbonyl complexes.

Photoelectron spectroscopy is a well established technique for obtaining information regarding chemical bonding in molecules, and several critical reviews describing its applicability to transition-metal compounds of the d and f block elements have appeared.^{1–4} More data exist for the carbonyl complexes of the transition elements than for any other class of complexes, and the quantity and quality of the reported data upon this class of compounds are an accurate reflection of the importance that a clear understanding of the electronic basis of metal-CO bonding has upon the rationalisation of carbonyl complex reactivity and carbon monoxide chemisorption phenomena. It has long been accepted that the mechanism of CO and PF_3 bonding to transition metals is essentially similar^{5,6} and this has prompted the detailed study of the electronic structure of a range of monomeric trifluorophosphine transition-metal complexes. Thus, molecular-orbital (CNDO/2) calculations have been performed upon $[Cr(PF_3)_6]$ and $[Fe(PF_3)_5]$,⁷ and photoelectron spectral data have been reported for $[M(PF_3)_6]$ ($M = Cr, Mo, \text{ or } W$),^{8,9} $[MnH(PF_3)_5]$,⁹ $[M(PF_3)_5]$ ($M = Fe$ or Ru),^{8–10} $[FeH_2(PF_3)_4]$,¹¹ $[MH(PF_3)_4]$ ($M = Co, Rh, \text{ or } Ir$),^{8,9} $[M(PF_3)_4]$ ($M = Ni, Pd, \text{ or } Pt$),^{10,12–14} and for the mixed-ligand complexes $[Fe(CO)_x(PF_3)_{5-x}]$ ($x = 1–4$)^{10,15} and $[Cr(CO)_x(PF_3)_{6-x}]$ ($x = 3–5$).¹⁰ More recently a close link has been demonstrated between the mode of metal- PF_3 bonding in PF_3 chemisorbed upon single-crystal metal surfaces [*i.e.*, $Fe(111)$ and (110) , $Ru(001)$, $Ir(100)$, $Ni(111)$, $Pd(110)$, $Pt(111)$, or $Cu(110)$] and mononuclear $[M(PF_3)_x]$ ($x = 4$ or 5) complexes of the same metal where this is known.¹⁶

The results of the gas-phase photoelectron spectroscopic studies^{7–15} have been used as a basis for the interpretation of the

spectral data presented in this paper (N.B. as Koopmans' theorem has been shown to be invalid for several carbonyl hydride complexes, the assignments for this type of complex reported here may not reflect the ordering of the ground-state molecular energy levels). Included are the first He II photoelectron spectroscopic data for the trifluorophosphine compounds $[M(PF_3)_5]$ ($M = Fe$ or Ru), $[ReH(PF_3)_5]$, and $[RuH_2(PF_3)_4]$, and the He I photoelectron spectrum of the carbonyl compound, $[OsH_2(CO)_4]$. The interesting features and some of the trends which are now becoming established for transition-metal trifluorophosphine complexes are discussed.

Results and Discussion

$[Fe(PF_3)_5]$ and $[Ru(PF_3)_5]$ are proposed (on the basis of n.m.r. and vibrational spectroscopic evidence¹⁷) to have trigonal-bipyramidal geometries in solution. In the absence of any gas-phase structural data, this geometry has been assumed for the isolated molecules. Under D_{3h} symmetry (*i.e.*, free rotation of the PF_3 groups has been assumed), the d atomic orbitals transform as $a_1'(d_z^2)$, $e'(d_{x^2-y^2}, d_{xy})$, and $e''(d_{xz}, d_{yz})$ and calculations (upon several ML_5 species and at various levels of sophistication) have predicted an orbital energy ordering of $a_1' > e' > e''$.¹⁸ The eight valence electrons of the zerovalent metals, iron and ruthenium, are therefore predicted to occupy the e'' and e' levels and ionisations from these levels are expected to give rise to two photoelectron bands which may have additional structure due to spin-orbit interactions or Jahn-Teller distortion. Although the spin-orbit coupling constant for iron is small ($\zeta_{Fe\ 3d}$ ca. 0.05 eV¹⁹), Hubbard and Lichtenberger²⁰ have observed a Jahn-Teller splitting of 0.38 eV (at 298 K) on the lowest ionisation energy band of the He I spectrum of $[Fe(CO)_5]$ {a Jahn-Teller splitting of <0.2 eV was calculated

† Non-S.I. units employed: eV $\approx 1.60 \times 10^{-19}$ J, mmHg $\approx 13.6 \times 9.8$ Pa.

Table 1. Assignments, ionisation energies, and intensity data^a for [Fe(PF₃)₅] and [Ru(PF₃)₅]

Assignment	Band label	[Fe(PF ₃) ₅]			[Ru(PF ₃) ₅]		
		I.e./eV	Relative intensities		I.e./eV	Relative intensities	
			He I	He II		He I	He II
Metal <i>d e'</i> <i>e''</i>	X ₁	9.11	7.8	3.5	9.14	5.6	4.4
	X ₂	10.47	4.0	4.0	11.01	4.0	4.0
M-P (<i>e'</i> , 2 <i>a</i> ₁ ', <i>a</i> ₂ '')	Y	13.07	22.7	8.4	12.76	17.6	6.0
					13.32		
					13.97		
					15.97		
Fluorine lone-pair and P-F σ-bonding	Z	15.88			17.33		
		17.44			19.6 ^b		
		19.7 ^b			22.7 ^b		
		22.7 ^b					

^a Values corrected for the perturbation in intensity caused by the presence of the He IIβ spectrum and for the analyser sensitivity variation with electron kinetic energy. ^b Values obtained from the He II spectrum.

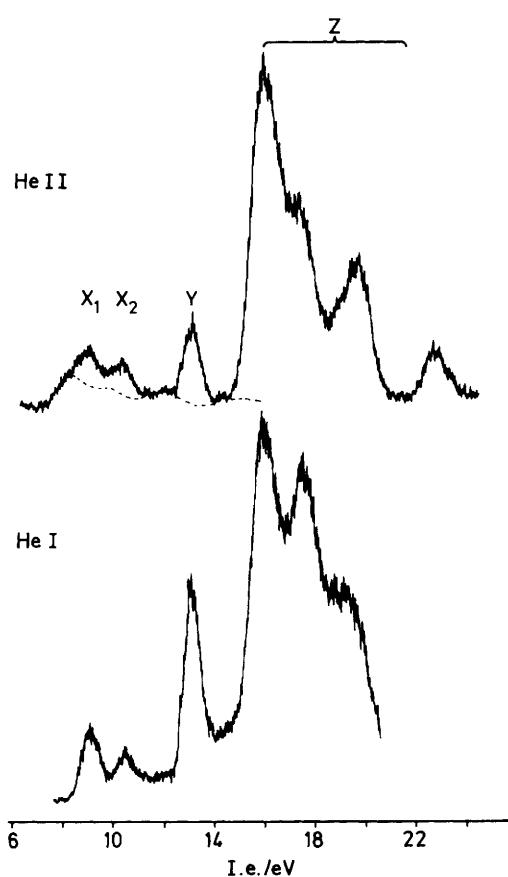


Figure 1. He I and He II p.e. spectra of [Fe(PF₃)₅], (---) estimated profile of the He IIβ spectrum

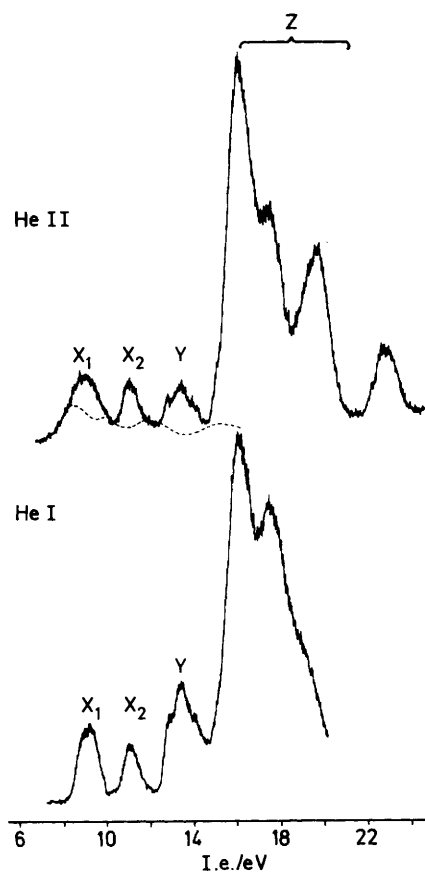


Figure 2. He I and He II p.e. spectra of [Ru(PF₃)₅], (---) estimated profile of the He IIβ spectrum

for the (*e''*)⁻¹ band of [Fe(CO)₅] and no splitting was observed in the experimental spectrum}. The spin-orbit coupling constant for ruthenium has an estimated value of *ca.* 0.1 eV¹⁹ and [Ru(PF₃)₅] would be expected to show a Jahn-Teller splitting of comparable magnitude. Thus, the lowest ionisation energy bands of both [Fe(PF₃)₅] and [Ru(PF₃)₅] are expected to show some vibronic structure (probably of a complex nature in the ruthenium case) but none is expected on the (*e''*)⁻¹ bands. The M-P σ-bonding orbitals transform as *e'*, 2*a*₁', and *a*₂' in *D*_{3h} symmetry, giving rise to the possibility of a maximum of four photoelectron bands.

The observed He I and He II photoelectron spectra of [Fe(PF₃)₅] and [Ru(PF₃)₅] are illustrated in Figures 1 and 2 respectively, and the ionisation energy (i.e.), peak intensity data, and assignments are presented in Table 1. The He II peak areas have been corrected for the perturbation in intensity caused by the superposition of low-intensity bands present as a result of ionisation by He IIβ radiation (see Experimental section): this effect is particularly severe for PF₃ compounds in general as the fluorine 2*p* cross-section is large relative to *d* orbital cross-sections at He II energies, but it is also apparent in the He II spectra of carbonyl complexes. Although the assignments of the

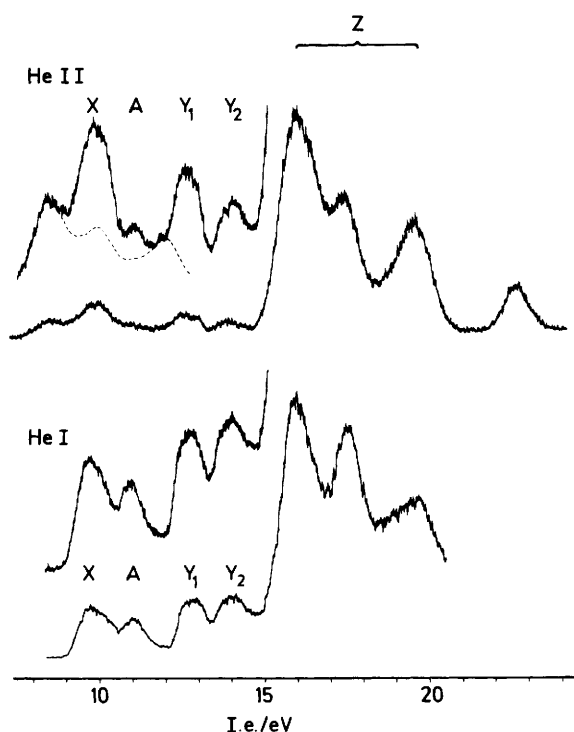


Figure 3. He I and He II p.e. spectra of $[\text{ReH}(\text{PF}_3)_5]$, (---) estimated profile of the He II β spectrum

spectra of $[\text{Fe}(\text{PF}_3)_5]$ and $[\text{Ru}(\text{PF}_3)_5]$ (*viz.*, bands X_1 and X_2 to the metal based e' and e'' levels, band Y to the M–P σ -bonding levels, and bands Z to the fluorine lone-pair and P–F σ -bonding levels) are uncontentious, several features of these photoelectron spectra merit comment. First, the ratio of the areas of bands X_1 and X_2 in the He I spectra of both compounds deviates from 1:1, the expected ratio, given that the bands are attributed to $(e')^{-1}$ and $(e'')^{-1}$ ionisations. A possible explanation is that the intensity of peak X_1 is enhanced relative to that of peak X_2 by admixture of some phosphorus orbital character, *i.e.* the highest occupied molecular orbital (h.o.m.o.; e'), although principally metal, may have significant phosphorus character, and the second highest occupied molecular orbital (s.h.o.m.o.; e'') may have much purer metal character. Although precise differential cross-section data are not yet available to test this proposal, two aspects of the spectra and the results of CNDO/2 calculations upon $[\text{Fe}(\text{PF}_3)_5]$ lend support to it. Considering the experimental evidence first, if it is assumed that the s.h.o.m.o. has the purer metal character and has an intensity of four units, then the He I intensities of bands Y in the spectra of both complexes {23 units for $[\text{Fe}(\text{PF}_3)_5]$; 18 units for $[\text{Ru}(\text{PF}_3)_5]$ } are far greater than expected on purely orbital occupation grounds. This is true even if Y is assigned to all of the available $\sigma(\text{M}–\text{P})$ bonding orbitals (*i.e.*, 10 units). It indicates that the phosphorus cross-section is greater than the metal d cross-section and suggests that the order of He I cross-sections is $\text{P} > \text{Ru}(4d) > \text{Fe}(3d)$. The second piece of experimental evidence is that, for both $[\text{Fe}(\text{PF}_3)_5]$ and $[\text{Ru}(\text{PF}_3)_5]$, the bands X_1 and Y clearly decrease in intensity (relative to band X_2) on changing from He I to He II radiation (see Table 1) and the percentage decrease is greater for Y than for X_1 . Finally, calculations upon $[\text{Fe}(\text{PF}_3)_5]$ ⁷ using the CNDO/2 formalism indicate that the e' level has only 38% iron and 41% phosphorus character whilst the e'' level has 66% iron but only 21% phosphorus character. These data are all consistent with X_1

Table 2. Vertical ionisation energies (eV) and assignments for $[\text{ReH}(\text{PF}_3)_5]$, $[\text{RuH}_2(\text{PF}_3)_4]$, and $[\text{OsH}_2(\text{CO})_4]$

Assignment	Band label	$[\text{ReH}(\text{PF}_3)_5]$	$[\text{RuH}_2(\text{PF}_3)_4]$	$[\text{OsH}_2(\text{CO})_4]$
Metal d	X	e	9.74	a_1
		b_2		a_2
M–H	A	a_1	10.98	a_1
				a_2
M–P	Y	a_1	12.76	a_1
		e		a_1
		e	13.98	a_1
		e		b_1
Ligand	Z	15.98	16.01	14.75
		17.5	17.5	15.8
		19.6	19.6	
		22.7	22.7	

* A precise ordering is not implied here.

having mixed metal–phosphorus character, X_2 having purer metal character, and Y having principally phosphorus character.

Returning to the general features of the spectra of $[\text{Fe}(\text{PF}_3)_5]$ and $[\text{Ru}(\text{PF}_3)_5]$, no evidence was found for any splitting of band X_1 in the spectra of $[\text{Fe}(\text{PF}_3)_5]$ but that of $[\text{Ru}(\text{PF}_3)_5]$ exhibited splitting that was only just detectable. Also the separation of bands X_1 and X_2 increases from 1.36 to 1.87 eV on going from the iron to the ruthenium compound. This latter increase is due essentially to the larger ligand-field splitting of the metal levels in the ruthenium case. The ionisation energy of the e'' level, which is non-bonding with respect to the sigma skeleton, is an approximate measure of the relative d orbital ionisation energy of the free metal atoms.

It is of interest that bands X_1 and X_2 in the spectrum of $[\text{Ru}(\text{PF}_3)_5]$ are not appreciably more intense (relative to the Z ligand bands) than those in the spectrum of $[\text{Fe}(\text{PF}_3)_5]$ although a 'heavy-atom effect' was clearly observed in related carbonyl complexes, *e.g.* $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$).²¹ In the particular case of $[\text{Fe}(\text{PF}_3)_5]$ and $[\text{Ru}(\text{PF}_3)_5]$, given the above arguments, attention should perhaps be restricted to the He I intensities of bands X_2 and Z. Band X_2 in fact exhibits an extremely small increase in intensity, relative to the Z bands, on going down the Grbup from $[\text{Fe}(\text{PF}_3)_5]$ to $[\text{Ru}(\text{PF}_3)_5]$.

On the basis of the experimental evidence alone, it is impossible to assign with any degree of certainty the features apparent on band Y of the spectrum of $[\text{Ru}(\text{PF}_3)_5]$. Although it has been assigned to ionisation from all of the M–P σ -bonding orbitals, it is possible that one or more of the bands derived from these orbitals lie obscured under the bands at > 15 eV.

The assignment for $[\text{Fe}(\text{PF}_3)_5]$ presented in Table 1, although consistent with all the available experimental evidence, is in conflict with an assignment proposed by Savariault *et al.*⁷ on the basis of a CNDO/2 calculation. Their assignment, but with band labels in line with this study, was: X_1 , e' ; X_2 , $e'' + a_1'$; Y, $a_2'' + e'$. This assignment of bands X_2 and Y is clearly unacceptable given the intensity data presented in Table 1.

The He I and He II photoelectron spectra of $[\text{ReH}(\text{PF}_3)_5]$ are depicted in Figure 3 and the vertical ionisation energies and proposed assignments are listed in Table 2. Infrared spectroscopic data for $[\text{ReH}(\text{PF}_3)_5]$ indicate that the molecule possesses C_{4v} symmetry in the gas phase with the hydrogen atom occupying an apical position.²² Under C_{4v} symmetry the rhenium d orbitals transform as $a_1(d_{z^2}) + b_1(d_{x^2-y^2}) + b_2(d_{xy}) + e(d_{xz}, d_{yz})$, the hydrogen orbital transforms as a_1 and the phosphorus lone-pair orbitals transform as $2e + a_1$. The e

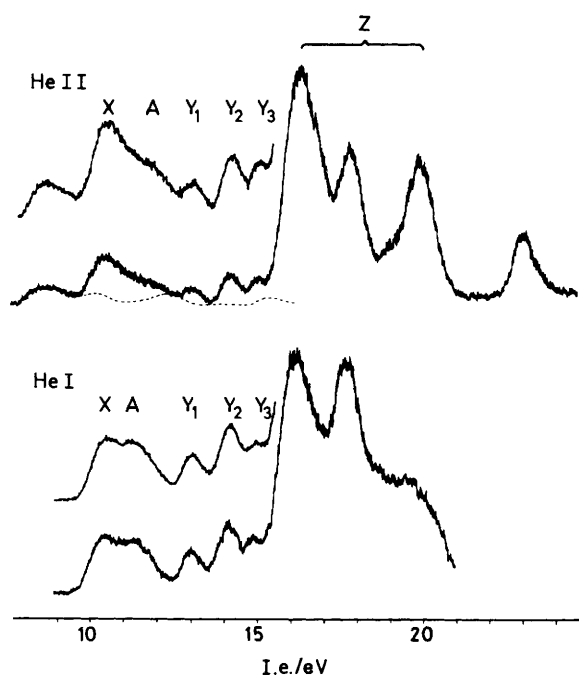


Figure 4. He I and He II p.e. spectra of $[\text{RuH}_2(\text{PF}_3)_4]$, (---) estimated profile of the He II β spectrum

and b_2 orbitals (which correlate with the t_{2g} orbitals of a metal atom in an octahedral ligand environment) are expected to be occupied for rhenium(I) (d^6). The assignment of the photoelectron spectrum of $[\text{ReH}(\text{PF}_3)_5]$ presented in Table 2 was achieved by qualitative consideration of the He I/He II intensity changes and by analogy with the spectra of $[\text{ReH}(\text{CO})_5]$ and $[\text{MnH}(\text{PF}_3)_5]$.^{9,23}

The low intensity of band A relative to band X in the He II spectrum of $[\text{ReH}(\text{PF}_3)_5]$ precludes the assignment of significant metal character to the former band, A. Thus both the e and b_2 metal levels are assigned to X and the a_1 hydrogen-based level is assigned to A. Band X might have been expected to show some structure, especially as the corresponding region of the photoelectron spectrum of $[\text{ReH}(\text{CO})_5]$ clearly exhibits three partially resolved bands with a similar overall band width at half maximum. A similar effect was observed in the spectra of $[\text{MnH}(\text{CO})_5]$, which exhibits a d band that is partially resolved into two components, and of $[\text{MnH}(\text{PF}_3)_5]$, which exhibits a broad, symmetric, featureless d band. The absence of detectable splitting in the PF_3 complexes {although note the asymmetry of the band X in the spectrum of $[\text{ReH}(\text{PF}_3)_5]$ } may be the result of a reduction of the symmetry of the metal centre, in either the neutral molecule or some of the ion states, from C_{4v} .

Turning now to the M–P σ -bonding region of the photoelectron spectrum of $[\text{ReH}(\text{PF}_3)_5]$, two bands Y_1 and Y_2 are observed, in contrast to the same region of the photoelectron spectrum of $[\text{MnH}(\text{PF}_3)_5]$ ⁹ which only exhibits a single featureless band. An increase in structure in this region as the Group is descended is not unexpected {cf. the M–P σ -bonding region of the spectra of $[\text{Cr}(\text{PF}_3)_6]$ as compared with $[\text{W}(\text{PF}_3)_6]$ ⁹. However it is not possible, on the basis of the experimental evidence alone, to assign unequivocally the two observed bands.

The He I and He II photoelectron spectra of $[\text{RuH}_2(\text{PF}_3)_4]$ are depicted in Figure 4, and the He I spectrum of $[\text{OsH}_2(\text{CO})_4]$ {together with the He I spectrum of $[\text{FeH}_2(\text{CO})_4]$,²⁴ for comparison} is presented in Figure 5. The vertical ionisation energies and assignments of the compounds are given in Table 2.

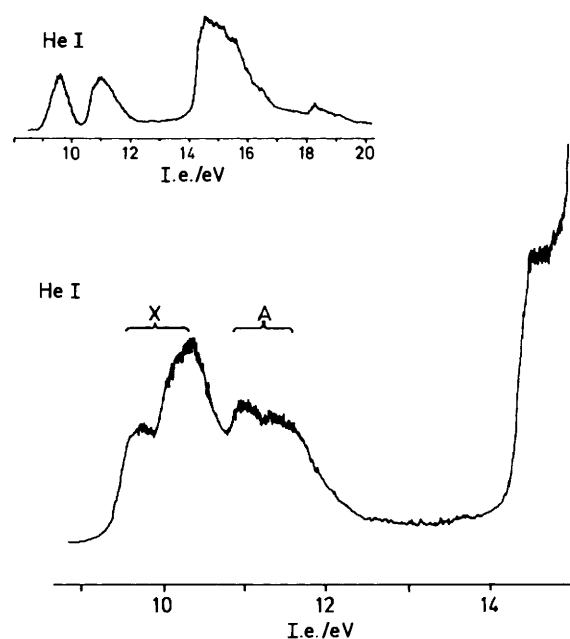


Figure 5. He I p.e. spectrum of $[\text{OsH}_2(\text{CO})_4]$ with that of $[\text{FeH}_2(\text{CO})_4]$ (inset) for comparison

Infrared spectroscopic data for $[\text{RuH}_2(\text{PF}_3)_4]$ ^{25,26} and electron-diffraction data for $[\text{MH}_2(\text{CO})_4]$ ($M = \text{Fe}$ or Os)^{27,28} indicate that a *cis*- C_{2v} distorted octahedral geometry is adopted. Elementary group theory predicts that the metal levels split into $2a_1 + a_2 + b_1 + b_2$ and for $M^{II} d^6$, the three metal orbitals of a_1 , a_2 , and b_2 symmetry are fully occupied.²⁴ In addition to these levels, two M–H σ -bonding levels (of a_1 and b_1 symmetry) and four M–L σ -bonding levels (of $2a_1$, b_1 , and b_2 symmetry) are predicted.

The photoelectron spectra of $[\text{RuH}_2(\text{PF}_3)_4]$ have been assigned (see Table 2) by consideration of the qualitative He I/He II intensity changes apparent in the spectra and by analogy with the assignment of the spectra of $[\text{FeH}_2(\text{CO})_4]$ ²⁴ and $[\text{FeH}_2(\text{PF}_3)_4]$.¹¹ Thus the two overlapping bands at 10.5 and 11.3 eV are assigned to ionisation from the metal d and metal–H σ -bonding levels respectively, the three bands between 12 and 15 eV are assigned to ionisation from metal–P σ -bonding levels, and the bands at greater than 16 eV are attributed to ionisation from the fluorine lone pair and P–F σ -bonding orbitals. Without the benefit of the results of a detailed molecular-orbital calculation upon $[\text{RuH}_2(\text{PF}_3)_4]$, it is impossible to assign the metal and metal–H levels more precisely. Although the He II photoelectron spectra of a number of hydridocarbonyl cluster compounds have been reported,^{29,30} He II photoelectron spectra of mononuclear transition-metal hydrido complexes are relatively scarce.

The He I photoelectron spectrum of $[\text{OsH}_2(\text{CO})_4]$ (Figure 5) can be assigned by analogy with the wealth of data that already exist for carbonyl compounds. Thus, the two lowest ionisation energy bands, at 9.7 and 10.4 eV, are due to ionisation from the metal d orbitals (a_1 , a_2 , and b_2), the partially resolved bands at 11.1 and 11.5 eV are assigned to ionisation from the Os–H σ -bonding orbitals (a_1 and b_1) and the bands at greater than 14 eV are attributed to ionisation from the M–C σ -bonding and CO localised orbitals.

Although the metal d to metal–H band intensity ratio is greater for $[\text{OsH}_2(\text{CO})_4]$ than $[\text{FeH}_2(\text{CO})_4]$, consistent with the well known 'heavy-atom effect', it is interesting that there is

an apparent decrease in intensity of the *d* bands relative to the carbonyl based bands on going from iron to osmium. It is apparent that the Os–H bands in $[\text{OsH}_2(\text{CO})_4]$ occur at significantly lower ionisation energy than the analogous bands in the photoelectron spectra of the polynuclear carbonylhydridoosmium clusters, $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$ (*viz.*, 11.1 and 11.5 eV as compared with 12.1–12.8 eV).^{29,30} This indicates a stronger bonding interaction is in operation for the two-electron three-centre unit, $\text{Os}(\mu\text{-H})\text{Os}$, than for the two-centre two-electron unit, Os–H.

An analysis of the reported data upon trifluorophosphine complexes^{8–15} and their carbonyl analogues² (where these exist) has revealed a number of interesting features. There is a trend of gradually increasing ionisation energy with increasing atomic number of M, for the complexes $[\text{M}(\text{PF}_3)_x]$, for the average ionisation energy from the metal-based *d* orbitals, both crossing the first-row transition metals {*e.g.* $[\text{Cr}(\text{PF}_3)_6]$, 9.29 eV; $[\text{Ni}(\text{PF}_3)_4]$, 10.3 eV} and descending a Group {*e.g.* $[\text{Fe}(\text{PF}_3)_5]$, 9.79 eV; $[\text{Ru}(\text{PF}_3)_5]$, 10.08 eV}. A similar trend is also observed for the metal hydrido complexes, $[\text{MH}_x(\text{PF}_3)_y]$, but this is complicated by the change in formal oxidation state {*e.g.* $[\text{Ru}(\text{PF}_3)_5]$, 10.08 eV; $[\text{RuH}_2(\text{PF}_3)_4]$, 11.27 eV}. There is a slight decrease (*ca.* 0.3–0.45 eV) in the $\sigma(\text{M-H})$ ionisation energies of trifluorophosphine compounds on descending a vertical Group {*viz.* for $[\text{MnH}(\text{PF}_3)_5]$ to $[\text{ReH}(\text{PF}_3)_5]$, $\Delta_{\text{M-H}} = -0.3$ eV; for $[\text{FeH}_2(\text{PF}_3)_4]$ to $[\text{RuH}_2(\text{PF}_3)_4]$, $\Delta_{\text{M-H}} = -0.45$ eV}. This compares with approximately constant values {for $[\text{MH}(\text{CO})_5]$ (M = Mn or Re)} or slightly increasing values {for $[\text{MH}_2(\text{CO})_4]$ (M = Fe or Os)} for the analogous M–H bands in the related carbonyl compounds. Perhaps a more important observation is the difference between the M–H ionisation energies for monomeric and cluster complexes (see above). The trends in the $\sigma(\text{M-P})$ and $\sigma(\text{P-F})$ ionisation energies are more subtle, and have been discussed elsewhere.^{8,11,31}

Experimental

The He I spectra were recorded on a Perkin-Elmer PS16 spectrometer with a modified inlet system. The He II spectra were recorded on a PS16/18 instrument, fitted with an Helectros lamp capable of producing high intensity He I and He II radiation. Liquid and solid samples of sufficient vapour pressure were condensed into a 'Rotaflo' ampoule under a static vacuum. The ampoule was attached to a 'volatile inlet' probe and, with the ampoule held at -196°C , the probe, connecting glassware and ampoule were evacuated to a pressure of *ca.* 10^{-3} mmHg. Slush-baths of gradually increasing temperature were employed until sufficient vapour pressure for a photoelectron spectrum was achieved. This method of controlling the vapour pressure of the sample gave better results than the use of needle valves. All photoelectron spectra were calibrated by reference to the He self-ionisation band (4.991 eV), MeI (9.538 eV), N_2 (15.570 eV), or Ar (15.759 eV). Corrected intensities for the low-ionisation energy bands of the He II spectra were obtained by assuming a linear sloping baseline and perturbation by a He II β spectrum 10% of the intensity of the He II α spectrum. No correction was made for the He II γ or higher contributions to the total band intensities. The reproducibility of the spectra was checked by recording each one several times; the sample containers were also checked for involatile decomposition products after recording the spectra. The bath temperatures and spectral count rates for each compound are given in Table 3.

The following compounds were prepared by previously published literature procedures: $[\text{Fe}(\text{PF}_3)_5]$,³² $[\text{Ru}(\text{PF}_3)_5]$,³³ $[\text{ReH}(\text{PF}_3)_5]$,²⁵ and *cis*- $[\text{RuH}_2(\text{PF}_3)_4]$.²⁵ All of the samples were purified by trap-to-trap distillation and their purity was established by i.r. spectroscopy prior to recording their

Table 3. Experimental operating conditions

Compound	Temp./ $^\circ\text{C}$	Counts s^{-1}	
		He I	He II
$[\text{Fe}(\text{PF}_3)_5]$	–28	<i>ca.</i> 10^3	$(3-4) \times 10^2$
$[\text{Ru}(\text{PF}_3)_5]$	–28	<i>ca.</i> 10^3	$(3-4) \times 10^2$
$[\text{ReH}(\text{PF}_3)_5]$	24.5	10^3	$(3-4) \times 10^2$
$[\text{RuH}_2(\text{PF}_3)_4]$	23–24	<i>ca.</i> 8×10^2	$(3-4) \times 10^2$
$[\text{OsH}_2(\text{CO})_4]$	–24	<i>ca.</i> 10^3	—

photoelectron spectra. *cis*- $[\text{OsH}_2(\text{CO})_4]$ was prepared by the procedure of Stone and co-workers,³⁴ *i.e.*, reduction of a liquid ammonia suspension of $[\text{Os}_3(\text{CO})_{12}]$ followed by treatment with 90% H_3PO_4 .

Acknowledgements

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