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UV Photoelectron Spectra of $[Rh_2X_2L_4]$, (X = Cl, Br, I), (L = CO, PF_3) and $Ir_2Cl_2(PF_3)_4$

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He(I) photoelectron spectra of $[Rh_2Br_2(CO)_4]$, $[Rh_2X_2(PF_3)_4]$ (X = Br, I) and $[Ir_2Cl_2(PF_3)_4]$ are presented and discussed in relation to those of $[Rh_2Cl_2L_4]$ (L = CO, PF_3). The He(II) spectrum of $[Rh_2Cl_2(PF_3)_4]$ confirms previous band assignments made from the He(I) spectrum. UV spectroscopic data for $[M_2Cl_2(PF_3)_4]$ (M = Rh, Ir) are compared with other literature data for d^8 metal complexes.

Introduction

Previously, as part of a comparative study of transition metal trifluorophosphine complexes and their carbonyl analogues [1–4], we reported [5] the He(I) and He(II) photoelectron spectra of $[Rh_2Cl_2(CO)_4]$ and the He(I) photoelectron spectrum of $[Rh_2Cl_2(PF_3)_4]$. Detailed assignments of the observed ionisation potentials (i.p's) were proposed on the basis of He(I)/He(II) intensity variations [5] and SCF-Xα SW calculations on $[Rh_2Cl_2(CO)_4]$ [6].

The ordering of the molecular orbitals in both complexes was proposed to be as follows; $9b_1$,$11a_1$ (90% Rh-4d) < $10a_1$, $8b_1$, $9b_2$ (70% Rh-4d) < $7a_2$, $9a_1$, $7b_1$ (83% Rh-4d) ⩽ $8b_2$ (86% Cl-3p) < $6b_1$, $7b_2$, $8a_1$, $6a_2$ (70% Cl-3p) < $7a_1$ (Cl-3p) < Rh-ligand σ-orbitals < ligand based orbitals.

Recent studies of the UV and M.C.D. spectra [7] of $[Rh_2Cl_2(CO)_4]$ and an HFLCAO calculation [8] are in reasonable agreement with our assignments and the results of an independent photoelectron spectroscopic study of $[Rh_2Cl_2(CO)_4]$ have been recently reported by Dickson *et al.* [9].

TABLE I. Low Energy Ionisation Potentials (eV) and Assignments for $[M_2L_2L_4]$ Complexes (M = Rh, Ir, X = Cl, Br, I; L = CO, PF_3).

Band Type	A Metal orbitals			B Halogen orbitals			P M–P σ
	$9b_1$ $11a_1$	$10a_1$ $8b_1$ $9b_2$	$7a_2$ $9a_1$ $7b_1$	localised	bridging		
				$8b_2$	$6b_1$ $7b_2$ $8a_1$ $6a_2$	$7a_1$	
Complex							
$Rh_2Cl_2(CO)_4$[b]	9.0	9.8	10.7	11.3	12.4	13.4	–
$Rh_2Br_2(CO)_4$	9.0	9.7	10.9		12.1	–	–
$Rh_2Cl_2(PF_3)_4$[a]	9.0	10.0	11.2		12.4	13.3	14.5
$Rh_2Br_2(PF_3)_4$	8.9	9.7	10.8		12.1	–	14.2
$Rh_2I_2(PF_3)_4$	9.1		9.7	10.3	11.8	–	13.9
$Ir_2Cl_2(PF_3)_4$	8.9 9.5	10.3	11.1	11.5	12.8	13.9	15.3

[a]Data from Ref. 5. [b]For original calculation see Ref. 6.

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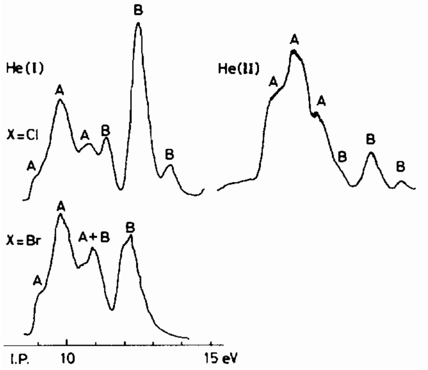

Fig. 1. Photoelectron spectra of $[Rh_2X_2(CO)_4]$ (X = Cl and Br).

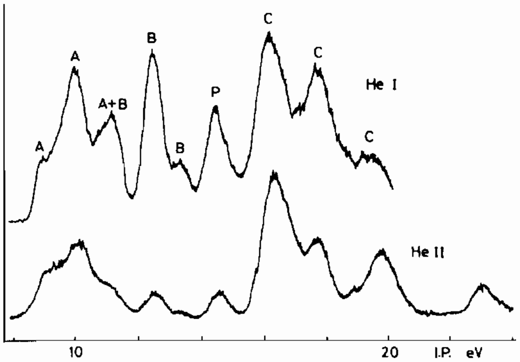

Fig. 2. He(I) and He(II) photoelectron spectra of $[Rh_2Cl_2(PF_3)_4]$.

We have now extended our studies to include the He(I) photoelectron spectra of $[Rh_2Br_2(CO)_4]$, $[Rh_2X_2(PF_3)_4]$ (X = Br, I) and $[Ir_2Cl_2(PF_3)_4]$ and the He(II) spectrum of $[Rh_2Cl_2(PF_3)_4]$ in order to confirm our previous assignments. The UV spectra of $[Rh_2Cl_2(PF_3)_4]$ and $[Ir_2Cl_2(PF_3)_4]$ are also presented and assigned by comparison with similar systems studied by Mason *et al.* [7, 10]. Attempts to record the p.e. spectrum of $[Rh_2I_2(CO)_4]$ and the UV spectrum in $[Rh_2I_2(PF_3)_4]$ were unsuccessful.

Results and Discussion

Photoelectron Spectra

The low energy part of the He(I) photoelectron spectrum of $[Rh_2Br_2(CO)_4]$ is shown in Fig. 1 together with the corresponding He(I) and He(II) spectra of $[Rh_2Cl_2(CO)_4]$ for comparison [5]. The experimental i.p's and the proposed assignments are listed in Table I.

Previously [5] the p.e. spectrum of $[Rh_2Cl_2(CO)_4]$ was considered in three different energy regions; (i) bands at lowest i.p. consisting of ionisations of predominantly Rh-4d character (A); (ii) three bands of higher i.p. derived from chlorine based orbitals (B) and (iii) metal carbonyl ionisations occurring at highest i.p. (C). Our assignments differ only slightly from those of Dickson *et al.* [9] who have been able to resolve the band at lowest i.p. (9.0 eV) into two components at 8.9 and 9.2 eV, but there is agreement that these bands derive from ionisations from the two orbitals of highest Rh-4d character. The other two 'A' type bands at *ca.* 9.8 and 10.7 eV, having approximate intensity ratio 2:1, are of high Rh-4d character as evidenced by their enhancement using He(II) irradiation. On the basis of SCF-Xα SW calculations we assigned [5] these bands as arising from the $8b_1$, $10a_1$, and $9b_2$ orbitals (approximately 70% Rh, 20% Cl and 10% O character) and the $7a_2$, $9a_1$, and $7b_1$ (approximately 83% Rh, 5% Cl 12% O). Other workers [9], on the basis of HFLCAO calculations of Serafini *et al.* [8], regard the lower energy band as arising from three Rh-4d orbitals and one Rh–Cl orbital ($11a_1$, $10a_1$, $8b_1$ and $7a_2$)† while the second band is assigned to one Rh-4d orbital ($7b_2$) and one Rh–Cl orbital ($8b_2$).

It should be noted that the HFLCAO calculation places the $7b_2$ orbital to higher i.p. which is inconsistent with the He(II) data. The three (B type) ionisations of relative intensity 1:4:1, which occur in the 11.3 → 13.4 eV region of the spectrum, are of high Cl-3p character and are well reproduced by both calculations.

In our previous paper we noted that the He(I) photoelectron spectrum of $[Rh_2Cl_2(CO)_4]$ was similar to that of $[Rh_2Cl_2(PF_3)_4]$ except for the presence of an extra band at 14.5 eV in the latter complex which is readily assigned to ionisations of Rh–PF_3 σ-orbitals (P). Furthermore the band corresponding to the chlorine $8b_2$ orbital was not observed in the spectrum of $[Rh_2Cl_2(PF_3)_4]$ and we suggested that this was due to the expected higher i.p's of the metal-d orbitals [1–5], causing overlap of the ionisations. At that time we were primarily concerned with assignment of the spectrum of the carbonyl complex and He(II) data for $[Rh_2Cl_2(PF_3)_4]$ were not available. We have now recorded this spectrum (Fig. 2) and the relative intensities of the He(I) and He(II) spectra clearly show that the first two A type bands at low i.p are enhanced using He(II) irradiation, confirming their Rh-4d character and those labelled [B] are greatly reduced, as expected for orbitals of high chlorine 3p character. Furthermore, the observation that the He(II) enhancement of the [A + B] band is not as great as the Rh-4d ionisations

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†The coordinate system of Serafini *et al.* [8] differs from that of Norman *et al.* [6] for the two calculations.

TABLE II. UV Data for $[M_2Cl_2(PF_3)_4]$ (M = Rh, Ir) and $[Rh_2Cl_2(CO)_4]$.

Complex	Band	λ_{max} (Å)	ϵ_{max} (m^{-1} cm^{-1})	Assignment	Reference
$[Rh_2Cl_2(PF_3)_4]$[a]	I	3760	(940)[c]	triplet, $dz^2 \rightarrow L\pi^*$	This work
	II	2840	12,500	singlet, $dz^2 \rightarrow L\pi^*$	
	III	–		–	
	IV	2390	9,650	singlet, dxz, yz $\rightarrow L\pi^*$	
$[Ir_2Cl_2(PF_3)_4]$[a]	I	3570	(1,800)	triplet, $dz^2 \rightarrow L\pi^*$	This work
	II	3090	5,140	singlet, $dz^2 \rightarrow L\pi^*$	
	III	2970 (sh)	–	triplet, dxz,yz $\rightarrow L\pi^*$	
	IV	2360	6,920	singlet dxz,yz $\rightarrow L\pi^*$	
$[Rh_2Cl_2(CO)_4]$[b]	I	3650	–	triplet, $dz^2 \rightarrow L\pi^*$	
	II	3180	8,300	singlet, $dz^2 \rightarrow L\pi^*$	
	III	–	–	–	
	IV	2600	13,400	singlet, dxz,yz $\rightarrow L\pi^*$	

[a] In cyclohexane. [b] CH_2Cl_2 and Et_2O solution (Ref. 7). [c] Tentative assignment.

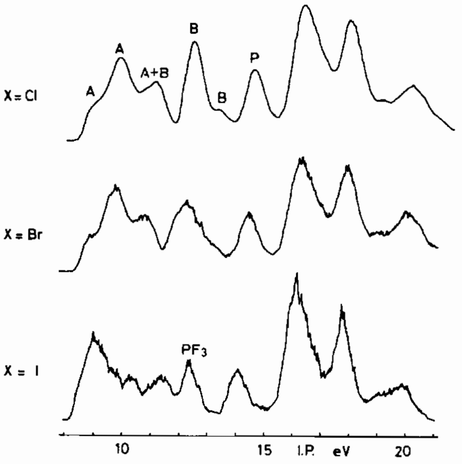

Fig. 3. He(I) photoelectron spectra of $[Rh_2X_2(PF_3)_4]$ (X = Cl, Br, I).

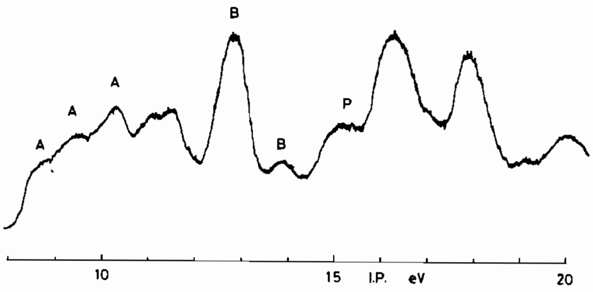

Fig. 4. He(I) photoelectron spectra of $[Ir_2Cl_2(PF_3)_4]$.

nor is it reduced as greatly as the chlorine 3p bands [B], supports our previously suggested orbital assignments for $[Rh_2Cl_2L_4]$ (L = CO, PF_3).

The He(I) photoelectron spectrum of $[Rh_2Br_2(CO)_4]$ (Fig. 1) is also readily understood since substitution of chlorine for bromine leads to the expected lowering in energy of those orbitals of high halogen character, resulting in the $8b_2$ orbital overlapping with the highest energy metal-d ionisations.

The same ordering of ionisations (Table I) is proposed for the $[Rh_2X_2(PF_3)_4]$ (X = Br, I) and $Ir_2Cl_2(PF_3)_4$ photoelectron spectra (Fig. 3 and Fig. 4). In $[Rh_2Br_2(PF_3)_4]$ substitution of chlorine for bromide leads to the expected decrease in energy of the halogen orbitals, a small decrease in the i.p. of one metal-d band and a similar decrease is noted for the Rh–PF_3 σ orbitals (P). The He(I) photoelectron spectrum of $[Rh_2I_2(PF_3)_4]$ always shows the presence of traces of free PF_3 as evidenced by the observation of a band at 12.3 eV. The intensity of this band increased markedly as the temperature was raised and for this reason the spectrum was recorded at the lowest practical temperature. The relative intensities of the bands in the spectrum other than PF_3 recorded under different conditions were reproducible and the i.p. data continue the trends of the halogen orbitals and Rh–PF_3 σ orbitals to lower energies. In the metal-d region (A), however, a broad asymmetric peak centered at 9.1 eV is observed, which may be analogous to the first two Rh-4d bands in $[Rh_2X_2(PF_3)_4]$ (X = Cl, Br), while bands at 9.7 and 10.3 eV are tentatively assigned to Rh-4d and the $8b_2$ halogen ionisations respectively.

The He(I) photoelectron spectrum of $[Ir_2Cl_2(PF_3)_4]$ (Fig. 4) shows similarities to that of $[Rh_2Cl_2(PF_3)_4]$. A general move to higher energy of the

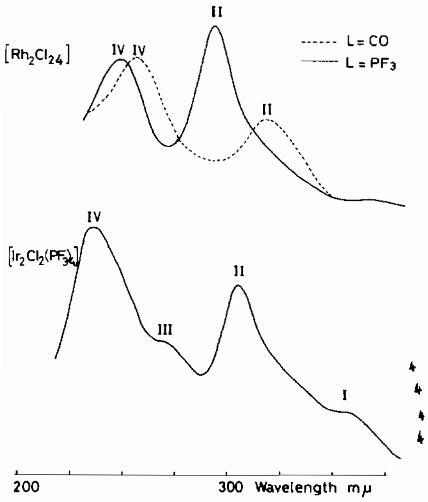

Fig. 5. Ultraviolet spectra of $[M_2Cl_2(PF_3)_4]$ (M = Rh, Ir).

M–PF_3 and $[MCl_2M]$ orbitals is observed for the iridium complex. This trend has been noted previously for a number of other trifluorophosphine complexes of second and third row transition metals [1–4]. In the metal-d region of the spectrum, however, the pattern of bands for $[Ir_2Cl_2(PF_3)_4]$ is more complex than found for the rhodium analogue. We assign (Table I) the first four low energy bands in the spectrum (8.9, 9.5, 10.3 and 11.1 eV) to metal-d ionisations and the band at 11.5 eV to the $8b_2$ orbital localised on chlorine, consistent with the move to higher energy noted above.

The complex nature of the metal-5d ionisations may conceivably arise from some *intra* molecular metal–metal interaction not present in $[Rh_2Cl_2(PF_3)_4]$. The latter type of interactions have been observed during UV spectroscopic studies of Rh(I) an Ir(I) dimeric complexes [7]. Thus, whereas the UV spectra of $[Rh_2Cl_2(CO)_4]$ and $[Rh_2Cl_2(olefin)_4]$ have been interpreted in terms of two non-interacting chromophores, those of $[Ir_2Cl_2(COD)_2]$ (COD = cyclooctadiene) and $[Rh_2Cl_2(CO)_4]$ in a glass at 77 K show evidence for significant M–M interactions. This interaction may be enhanced when certain ligands are used to bridge the metal atoms [7, 11]. It should be noted however that in the p.e. spectrum of $ML(C_5R_5)$ (M = Rh, Ir; R = H, Me; L = diene), more bands are visible in the d-region for M = Ir* and spin orbit coupling seems the most likely cause.

Ultraviolet Spectra

The UV spectra of $[M_2Cl_2(PF_3)_4]$ (M = Rh, Ir), are shown in Fig. 5 and proposed assignments, extinction coefficients and values of λ_{max} are listed in Table II. To our knowledge these are the first UV spectroscopic data for transition-metal PF_3 complexes, although extensive studies have been made of analogous carbonyl complexes.

TABLE III. Solvent Dependence of $dz^2 \rightarrow L\pi^*$ Excitations of $[Rh_2Cl_2(PF_3)_4]$.[†]

Solvent	λ_{nm}	$\bar{\nu}$ μm^{-1}
CH_2Cl_2	294	3.40 (3.14)[a]
CCl_4	297	3.38 (3.13)[a]
Toluene	298	3.36 (3.11)[a]
Et_2O	293	3.41 (3.06)[a]
Cyclohexane	284	3.52 (3.20)[b]

[†] Values in parentheses are those for $[Rh_2Cl_2(CO)_4]$.
[a] Ref. 1. [b] This work.

Mason *et al.* [7, 10, 12, 13] have interpreted UV spectra for an extensive series of d^8 square planar complexes in terms of singlet and triplet components of $dz^2 \rightarrow L\pi^*$ and dxz, yz $\rightarrow L\pi^*$ excitations (L = ligand) and similar assignments (Table II) can be made for $[M_2Cl_2(PF_3)_4]$ (M = Rh, Ir). Mason also reports a solvent dependence for the UV spectrum of $[Rh_2Cl_2(CO)_4]$, and since this effect was absent for $[RhCl_2(CO)_4^-]$ the authors attribute this to differing M·····M interactions in different solvents [7]. We observe a similar solvent dependence for $[Rh_2Cl_2(PF_3)_4]$, although the effect is less marked than that for $[Rh_2Cl_2(CO)_4]$ (Table III). Reproducible spectra for $[Ir_2Cl_2(PF_3)_4]$ could only be obtained in hydrocarbon solvents.

In Table IV are listed the parameters dσ, defined by Mason [7] as $\bar{\nu}_{max}$ for the excitation from the approximately non-bonding $dz^2 \rightarrow L\pi^*$ and $\Delta\pi$-σ which is the energy difference between $dz^2 \rightarrow L\pi^*$ and dxz,yz $\rightarrow L\pi^*$ excitations. The dσ value for $[Rh_2Cl_2(PF_3)_4]$ suggests that the empty π^* orbitals of PF_3 lie at higher energy than those of CO in $[Rh_2Cl_2(CO)_4]$. The parameter $\Delta\pi$-σ, in the limit of approximately equal electron repulsions, is the difference in energy between the metal-d orbitals involved and can also be obtained from the photoelectron spectrum, being the difference in i.p. between the first two Rh-4d bands. The data for the two spectroscopic techniques are listed in Table IV, however it should be noted that a strict comparison is only possible if the electron repulsions for the two excitations and orbital relaxations for the two ionisations cancel.

Experimental

He(I) photoelectron spectra were recorded on the Sussex Perkin-Elmer PS16 instrument with a modifi-

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*J. C. Green, unpublished observations.

TABLE IV. UV Spectroscopic Parameters for some Rh(I) and Ir(I) Complexes*.

Complex	d_σ [a]	$\Delta_{\pi\text{-}\sigma}$ [a]	$\Delta_{\pi\text{-}\sigma}$ [b]	$\Delta_{\pi\text{-}\sigma}$ [b] (PES)	Ref.
$[Rh(EtNC)_4]^+$	2.63	0.62	0.77	–	7
$[Rh(diphos)_2]^+$	2.48	0.71	0.88	–	10
$[Rh_2Cl_2(C_2H_4)_4]$	2.63	1.03	1.23	–	7
$[Rh_2Cl_2(CO)_4]$	3.14	0.71	0.88	0.8	7
$[Rh_2Cl_2(PF_3)_4]$	3.52	0.66	0.82	1.0	This work
$[Ir_2Cl_2(PF_3)_4]$	3.24	1.0	1.24	–	This work

*For definition of values, see text.
[a]In μm^{-1}. [b]In eV.

ed inlet system and the He(II) spectra using the Oxford PS 16/18 spectrometer. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer.

$[Rh_2X_2(CO)_4]$ complexes (X = Br, I) were prepared by halogen exchange from $[Rh_2Cl_2(CO)_4]$ by treatment with an excess of KX in refluxing hexane and purified by recrystallisation from hexane. $[Rh_2X_2(PF_3)_4]$ (X = Cl, Br, I) were obtained from $[Rh_2X_2(CO)_4]$ by treatment with a large excess of PF_3 [14]. Prior to recording the photoelectron spectra the complexes were further purified by high vacuum sublimation. $[Ir_2Cl_2(PF_3)_4]$ was prepared from $[Ir_2Cl_2(C_8H_{14})_4]$ and purified by sublimation [15].

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