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He(I) PHOTOELECTRON SPECTRA OF MIXED CARBONYLTRIFLUOROPHOSPHINE COMPLEXES OF ZEROVALENT IRON

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Summary

The UV PE spectra of complexes of the type $Fe(CO)_x(PF_3)_{5-x}$ are presented and discussed.

Results and discussion

Previous UV photoelectron spectroscopic studies on transition metal carbonyl complexes and their trifluorophosphine analogues [1—4] have shown the similarity in ligand field strengths of the two ligands and established that the ionisation potentials of metal *d*-orbitals (and metal—hydride σ-orbitals in hydrido complexes) are always slightly larger for the PF_3 compounds.

Here we present data on the He(I) photoelectron spectra of several mixed iron carbonyl trifluorophosphine complexes of the type $Fe(CO)_x(PF_3)_{5-x}$ (x = 4, 3, and 1) which support these earlier conclusions and also confirm the trends in first ionisation potentials obtained from mass spectroscopic studies on this series of compounds by Müller et al. [5].

The photoelectron spectrum of $Fe(CO)_4(PF_3)$ shown in Fig. 1, which is typical, shows two low energy bands of roughly equal intensity similar in appearance to those observed in $Fe(CO)_5$ [6] and $Fe(PF_3)_5$ [1], which are readily assigned to ionisations from orbitals essentially of metal 3*d*-character. The remaining bands in increasing order of energy arise from excitations from Fe—P σ-bonding orbitals and carbonyl and fluorine lone pair orbitals respectively. As expected, there is considerable overlap of the highest energy bands.

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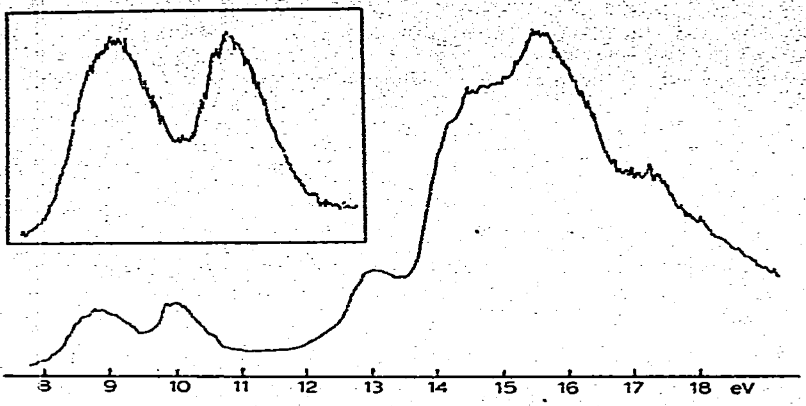

Fig. 1. He(I) PE spectrum of $Fe(CO)_4(PF_3)$.

TABLE 1

METAL *d*-ORBITAL ENERGIES FOR $M(CO)_x(PF_3)_{5-x}$ COMPLEXES

Complex	First adiabatic *IP* [5] (eV)	Vertical *IP* (eV)	Ref.
$Fe(PF_3)_5$	8.83	9.15, 10.45	[1]
$Fe(CO)(PF_3)_4$	8.62	9.18, 10.32	This work
$Fe(CO)_2(PF_3)_3$	8.61	—	—
$Fe(CO)_3(PF_3)_2$	8.47	8.95, 10.23	This work
$Fe(CO)_4(PF_3)$	—	8.75, 9.88	This work
$Fe(CO)_5$	7.96	8.60, 9.86	[6]

The band (Fe—P-σ) at 12.99 eV in $Fe(CO)_4(PF_3)$ lies close to the value found previously for $Fe(PF_3)_5$ [1], while broader bands of similar energy are observed for $Fe(CO)_x(PF_3)_{5-x}$ ($x = 1, 3$).

Inspection of the data listed in Table 1, which also includes the first adiabatic *IP* [5], shows that there is an overall increase in the iron 3*d*-orbital energies along the series from $Fe(CO)_5$ to $Fe(PF_3)_5$, presumably reflecting the slightly greater overall electron-withdrawing effect of the trifluorophosphine ligand.

The complexes were prepared by literature methods [7] and carefully purified by chromatography. Their purity was established by IR spectroscopy.

Acknowledgements

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