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## UV PHOTOELECTRON SPECTRA OF FIRST-ROW TRANSITION METAL HYDRIDOCARBONYL AND HYDRIDOTRIFLUOROPHOSPHINE COMPLEXES

ROBERT A. HEAD, JOHN F. NIXON \*

*School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)*

and RONALD J. CLARK

*Chemistry Department, Florida State University, Tallahassee, Florida (U.S.A.)*

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### Summary

The He(I) photoelectron spectrum of  $\text{FeH}_2(\text{PF}_3)_4$  is reported, and the bands are assigned and compared with those of the analogous carbonyl complex. Molecular orbital energies for the M—H  $\sigma$ -bonding orbitals, metal-3d orbitals and metal—phosphorus  $\sigma$ -bonding orbitals for the hydridocarbonyl and hydrido-trifluorophosphine complexes  $\text{MnHL}_5$ ,  $\text{FeH}_2\text{L}_4$  and  $\text{CoHL}_4$  (L = CO and  $\text{PF}_3$ ) are compared and correlations discussed.

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### Introduction

In recent years the technique of UV photoelectron (PE) spectroscopy has been applied to several classes of organometallic compounds [1–4]. Compounds studied include metal carbonyls [4–16], metal nitrosyls [8,17],  $\pi$ -arenes [18,19],  $\pi$ -allyls [20,21],  $\pi$ -cyclopentadienyls [4,19,22–24], and a series of trifluorophosphine metal complexes [25–29].

In certain cases comparison of the molecular orbital energy levels obtained by assignment of the PE spectra with results from ab initio calculations have raised questions [8,14,17,30–33] as to the reliability of Koopmans' theorem [34] when applied to compounds of this type. Very recently, however, support for the near validity of Koopmans' theorem has been reported [21].

In view of the known similarity [35–37] in coordinating ability of carbon monoxide and trifluorophosphine towards transition metals, it was of interest to compare the He(I) PE spectra of metal carbonyls and their analogous trifluorophosphine complexes. We have previously studied some complexes of this type and the recent report by Guest et al. [33] of the UV photoelectron spectrum of *cis*- $\text{FeH}_2(\text{CO})_4$  prompts us to describe our results on the related *cis*- $\text{FeH}_2(\text{PF}_3)_4$

complex, thus enabling a comparison to be made of the molecular orbital energy levels of the type M—H  $\sigma$ -orbitals, metal 3d-orbitals, and metal—phosphorus  $\sigma$ -bond orbitals for the series of compounds of the type  $MnHL_5$ ,  $FeH_2L_4$ , and  $CoHL_4$  ( $L = CO$  and  $PF_3$ ).

## Experimental

Photoelectron spectra were recorded as previously described [28].  $FeH_2(PF_3)_4$  was made by a modification of the vapour synthesis described by Timms [38] and details will be reported in full elsewhere [39]. Purification was carried out by trap to trap fractional condensation in the high vacuum line and the IR spectrum of the sample used in the PE study agreed with that reported in the literature [37].

## Results and discussion

The bands in the He(I) photoelectron spectrum of *cis*- $FeH_2(PF_3)_4$  shown in Fig. 1 fall into the characteristic energy regions discussed elsewhere [28] for a number of related transition metal trifluorophosphine complexes. The three high energy bands at 15.9, 17.4 and 19.6 eV can clearly be assigned to ionisations from fluorine lone-pair orbitals localised on the ligand atoms. These bands have been observed in the UV PE spectra of all metal trifluorophosphine complexes so far studied and their energies seem to be largely insensitive to changes in the metal or other attached ligands, differing by less than 0.1 eV from compound to compound.

By analogy with previous data and the discussion below, the band at 13.16 eV can be confidently assigned to ionisation from metal—phosphorus  $\sigma$ -molecular orbitals which in the idealised  $C_{2v}$  geometry of the *cis*-dihydrido complex transform as  $2a_1 + b_1 + b_2$ . The observation of a single band indicates that these orbitals are very similar in energy and this feature was also observed in other trifluorophosphine complexes of first-row elements [28]. The observed M—P  $\sigma$ -orbital energy represents a stabilisation of about 0.8 eV from the value of the phosphorus lone-pair orbital in  $PF_3$  itself.

The appearance of the two low energy bands at 9.78 eV and the broad composite band at 11.60 and 11.90 eV are strikingly similar in appearance to those observed by Guest et al. [33] in the related  $FeH_2(CO)_4$  complex (see Fig. 1). These authors assigned the lowest energy band in the dihydridotetracarbonyl complex as arising from the three essentially metal-3d orbitals ( $a_1$ ,  $b_2$  and  $a_2$ ), thus correlating the second band with the mainly Fe—H  $\sigma$ -bonding molecular orbitals ( $b_1$  and  $a_1$ ). *Ab initio* calculations [33] did not agree with this order, but suggested that the Fe—H  $\sigma$ -bonding molecular orbitals are the highest filled and the breakdown of Koopmans' theorem was attributed to orbital relaxation accompanying ionisation.

Interestingly in the analogous dihydridotetrakis(trifluorophosphine)iron complex reported here, assignment of the 9.78 eV band to metal 3d-orbitals and the bands at 11.60 and 11.90 eV to the Fe—H  $\sigma$ -bonding orbitals not only agrees with the assignments of Guest et al. for the carbonyl derivative, but also supports several trends previously noted by us [28] when comparing the orbital

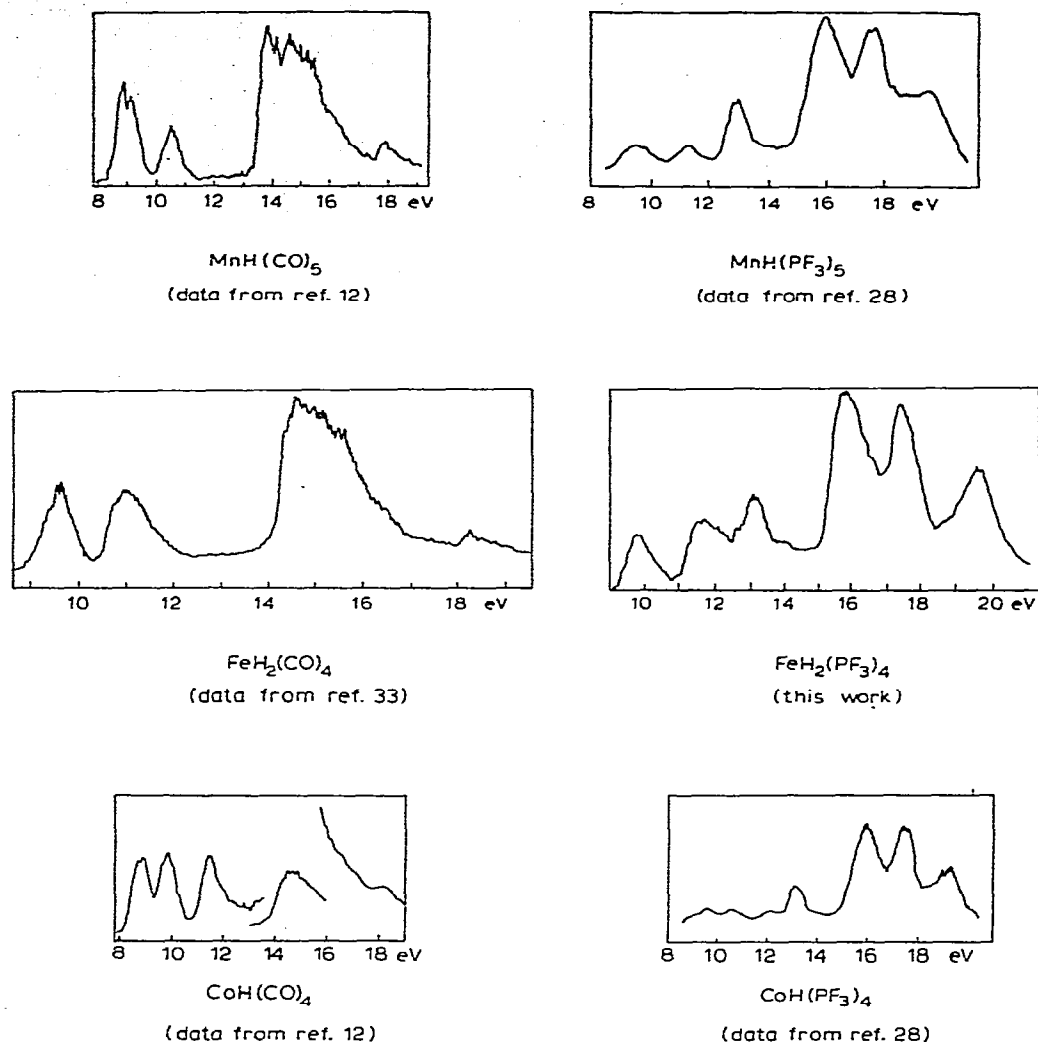


Fig. 1. He(I) photoelectron spectra of hydridocarbonyl and hydridotrifluorophosphine complexes of Mn, Fe, and Co.

energies of metal carbonyls and metal trifluorophosphine complexes. It is noticeable that as in the case of  $\text{FeH}_2(\text{CO})_4$ , the band arising from ionisation of the electrons in Fe—H bonding orbitals has greater intensity than expected on degeneracy grounds. This has been observed in other transition metal hydrido compounds.

If we consider the *IP*'s of the two series of complexes  $\text{MnHL}_5$ ,  $\text{FeH}_2\text{L}_4$  and  $\text{CoHL}_4$  ( $\text{L} = \text{CO}$  and  $\text{PF}_3$ ) (see Figs. 1 and 2 and Table 1) it can be seen that the M—H and metal-*d* orbital energies are always found to be slightly higher for the  $\text{PF}_3$  complexes than the CO derivative. This presumably is indicative of the greater net transfer of electron density from the transition metal to the ligand in the former series. Likewise there is a steady increase in the M—H  $\sigma$ -bonding orbital energies along both the carbonyl and trifluorophosphine series in the

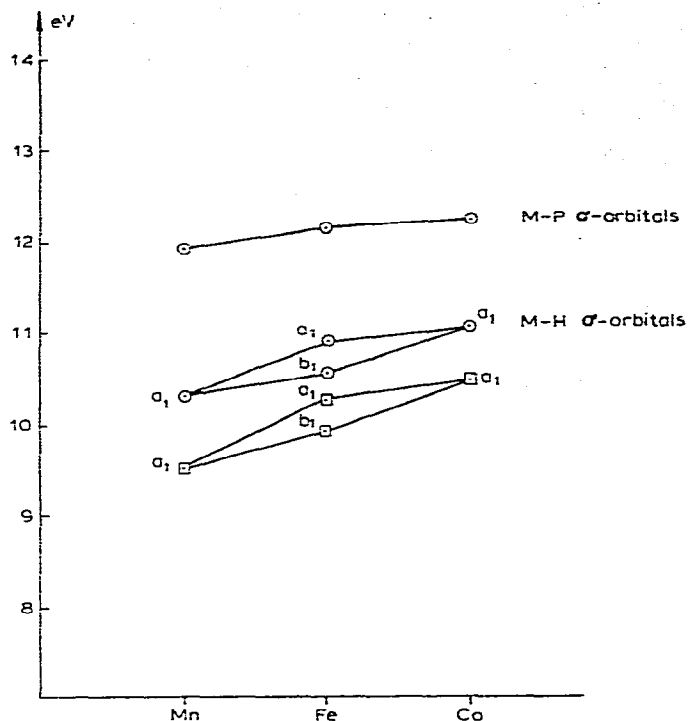


Fig. 2. Variation in M-H and M-P  $\sigma$ -orbital energies for carbonyl (C) and trifluorophosphine (P) complexes  $MnHL_5$ ,  $FeH_2L_4$ , and  $CoHL_4$  ( $L = CO$  and  $PF_3$ ).

order  $Mn < Fe < Co$  (see Table 1 and Fig. 2)\*. As expected, the metal-phosphorus  $\sigma$ -bonding orbitals also increase slightly in energy along the series  $Mn < Fe < Co$ .

We are currently studying related hydrides of the type  $MH_2(PF_3)_4$  ( $M = Ru, Os$ ) to see if these trends are borne out and also the PE spectra of mixed car-

TABLE 1

METAL- $d$ , METAL-H AND METAL-PHOSPHORUS ORBITAL IONISATION POTENTIALS (eV) OF SOME FIRST-ROW TRANSITION METAL HYDRIDOCARBONYL AND HYDRIDOTRIFLUOROPHOSPHINE COMPLEXES

Orbital	$MnH(CO)_5^a$	$MnH(PF_3)_5^b$	$FeH_2(CO)_4^d$	$FeH_2(PF_3)_4^c$	$CoH(CO)_4^a$	$CoH(PF_3)_4^b$
Metal- $d$	8.85 9.14	9.47	9.65	9.78	8.90 9.90	9.58 10.56
M-H	10.55	11.30	10.95 11.30	11.60 11.90	11.5	12.12
M-P	—	12.93	—	13.16	—	13.25

<sup>a</sup> Data from ref. 12. <sup>b</sup> Data from ref. 28. <sup>c</sup> This work. <sup>d</sup> Data from ref. 33.

\* In a footnote to ref. 33 unpublished calculations on  $CoH(CO)_4$  also give an incorrect ordering of IP's of the Co-3d and Co-H  $\sigma$ -bonding molecular orbitals compared with PE spectroscopic data.

bonyl trifluorophosphine systems, e.g.,  $\text{FeL}_x(\text{CO})_{5-x}$  and  $\text{MoL}_x(\text{CO})_{6-x}$  ( $\text{L} = \text{PF}_3$ ).

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