Ultraviolet Photoelectron Spectra of Cyclohepta-1,3,5-triene and Mesitylene Tricarbonyl Complexes of the Group 6A Metals

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The He(Iα) photoelectron spectra of [M($C_6H_3Me_3$-1,3,5)(CO)$_3$] and [M(C_7H_8)(CO)$_3$] (M = Cr, Mo, or W) are reported. The metal *d*-orbital and ligand π orbital ionization energies are assigned and discussed.

THE u.v. photoelectron (p.e.) spectra of several Group 6A organometallic complexes have been reported.[1-7] Of these studies, two report the p.e. spectra for the complete triad with a given set of ligands, [M(PF$_3$)$_6$] [1] and [M(CO)$_6$].[2] In both cases the first ionization energy (i.e.) corresponds to ionization from metal *d* orbitals, and has only a very slight dependence on the metal. Herein we present the He(Iα) p.e. spectra of η-cyclohepta-1,3,5-triene- and η-mesitylene-tricarbonylmetal complexes for M = Cr, Mo, and W. These complexes allow a comparison of the metal *d* i.e.s as well as the effect of the metal on the i.e.s of the hydrocarbon π orbitals.

EXPERIMENTAL

The p.e. spectra were obtained on a spectrometer of the Turner type,[8] incorporating a $\pi/2^{\frac{1}{2}}$ (10-cm) electrostatic cylindrical condenser analyzer. The spectra were excited with He(1α) (21.22 eV) † photon radiation. The ionization energies ($\pm$0.05 eV) were inferred from internal calibration with xenon and argon. Mass spectra were recorded on a Varian CH-5D instrument using a Varian combined field desorption–electron impact (f.d.–e.i.) source. Acetone was used as solvent and the source temperature was 80 °C. Infrared spectra were recorded on a Perkin-Elmer 257 instrument.

The [M(C_7H_8)(CO)$_3$] (M = Cr, Mo, or W) complexes were synthesized by published methods [9,10] and purified by recrystallization from light petroleum (Cr and Mo) or by sublimation at 0.1 Torr and 80 °C (W). Infrared spectra agreed with published ones.[9,10] The [M($C_6H_3Me_3$-1,3,5)(CO)$_3$] (M = Cr, Mo, or W) complexes were also prepared by known methods [10,11] and purified *via* sublimation at 0.1 Torr and 80 °C (Cr and Mo) or 110 °C (W). The i.r. spectra agreed with those of Fischer.[12] The identity of all the metal complexes was confirmed by recording field-desorption (f.d.) mass spectra. The only appreciable mass peaks were those due to isotopes of the parent ion. The temperatures (°C) at which the p.e. spectra were recorded for the [M(C_7H_8)(CO)$_3$] complexes were 57 (Cr), 61 (Mo), and 82 (W) and for the mesitylene complexes were 95 (Cr), 97 (Mo), and 108 (W).

RESULTS AND DISCUSSION

The p.e. spectra are presented in Figures 1 and 2 and some band assignments are in Tables 1 and 2.

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† Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J; 1 Torr = (101 325/760) Pa.

[1] R. A. Head, J. F. Nixon, G. J. Sharp, and R. J. Clark, *J.C.S. Dalton*, 1975, 2054.

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

[3] M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.

[4] S. Evans, J. C. Green, and S. E. Jackson, *J.C.S. Faraday II*, 1972, 249.

[5] J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1975, 403.

[6] S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1974, 304.

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

[8] D. W. Turner, *Proc. Roy. Soc.*, 1967, **A307**, 15.

[9] R. B. King, *Organometallic Synth.*, 1965, **1**, 123.

[10] R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

[11] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.

[12] R. D. Fischer, *Chem. Ber.*, 1960, **93**, 165.

The p.e. spectra of $[M(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$ are very similar for all the three metals, and in particular the spectrum of the chromium complex is very similar to that of $[Cr(C_6H_6)(CO)_3]$ reported previously.[3] The first p.e. band clearly corresponds to ionization from metal *d* orbitals, which transform as $a_1 + e$ in the C_{3v} point group. Guest *et al.*[3] showed that the calculated i.e.s of the a_1 and e orbitals are separated by 2.7 eV in $[Cr(C_6H_6)(CO)_3]$ when Koopmans' theorem is applied to the results of an all-electron *ab initio* SCF molecular-orbital (m.o.) calculation. However, the calculated i.e.s are the same when orbital relaxation is included. Thus Koopmans' theorem is violated for *d*-orbital ionization in this complex, and Figure 1 shows that this is true of the $[M(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$ complexes as well, *i.e.* the first p.e. band correlates with the metal $a_1 + e$ orbitals which are probably not accidently degenerate in the neutral molecule. Unfortunately, in many metal complexes relaxation energies

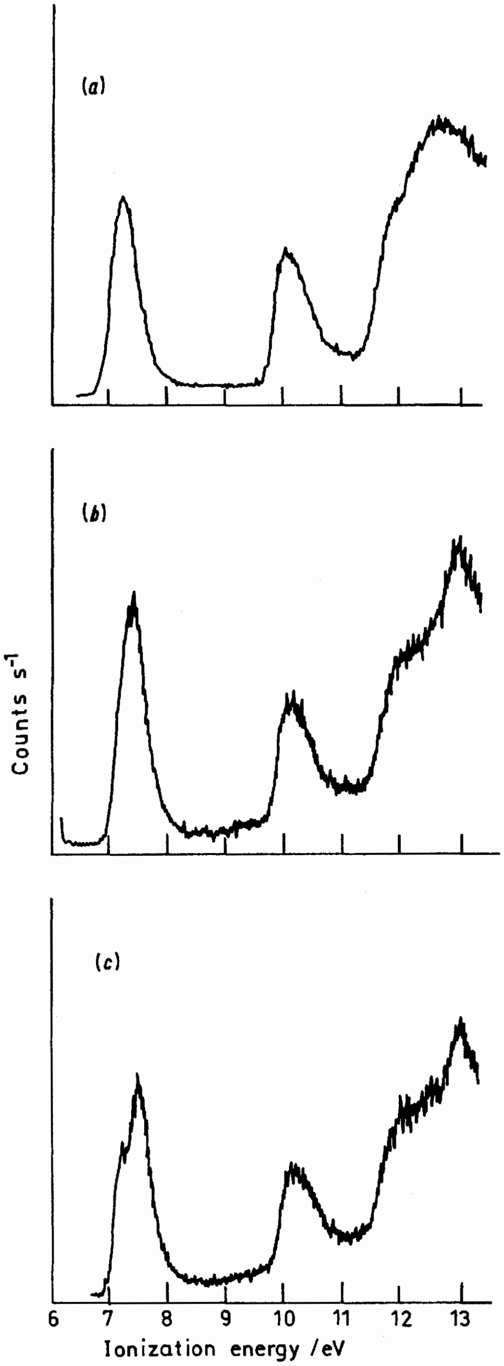

FIGURE 1 He(Iα) p.e. spectra of $[M(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$: M = Cr (*a*), Mo (*b*), and W (*c*)

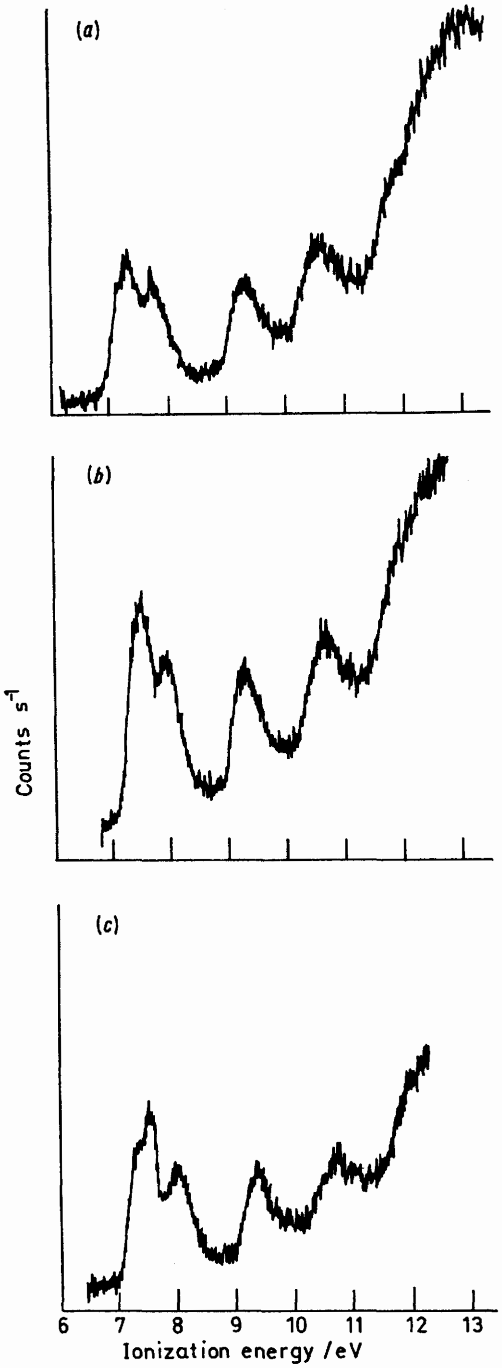

FIGURE 2 He(Iα) p.e. spectra of $[M(C_7H_8)(CO)_3]$: M = Cr (*a*), Mo (*b*), and W (*c*)

seem to be very different for ligand orbitals and those containing significant metal character, with the result that Koopmans' theorem is of dubious value.[3,13-22]

TABLE 1

Ionization-energy assignments for the mesitylene complexes [a]

Compound	Orbital	
	Metal *d* (a_1, *e*)	Ligand $\pi(e)$
$C_6H_3Me_3$-1,3,5		8.45
$[Cr(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$	7.20	10.08
$[Mo(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$	7.35	10.08
$[W(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$	7.20, 7.45	10.17
C_6H_6		9.25
$[Cr(C_6H_6)(CO)_3]$ [b]	7.42	10.70

[a] Symmetry taken to be C_{3v}; the i.e.s are in eV units. [b] Data from ref. 3.

TABLE 2

Ionization-energy assignments for the cycloheptatriene complexes [a]

Compound	Orbital		
	Metal *d*	Ligand $\pi(a')$	$\pi(a'')$
C_7H_8 [b]		8.57	9.52
$[Cr(C_7H_8)(CO)_3]$	7.30, 7.73	9.32	10.60
$[Mo(C_7H_8)(CO)_3]$	7.46, 7.94	9.29	10.68
$[W(C_7H_8)(CO)_3]$	7.55, 8.05	9.40	10.70

[a] Symmetry is C_s; i.e.s are in eV units. [b] Data from ref. 22.

Figure 1 and Table 1 show that the *d*-orbital i.e.s are almost independent of the metal. This is also true of other Group 6A complexes, $[M(CO)_6]$ [2] and $[M(PF_3)_6]$.[1] A splitting in the first p.e. band of $[W(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$ is evident in Figure 1. This is probably due to spin–orbit splitting of the ^2E state, although it is possible that the a_1 and *e* orbitals are resolved in this case. Photoelectron spectra of the Group 6A hexacarbonyls show a similar splitting of the *d*-orbital band for $[W(CO)_6]$ and this is ascribed to spin–orbit splitting.[2]

The second band in the p.e. spectra of the mesitylene complexes must be due to the degenerate orbital localized on the arene. The i.e. of this $\pi(e)$ orbital is raised by *ca.* 1.7 eV compared to free mesitylene, showing clearly the substantial interaction between the arene and the metal. It is seen that all the three metals exert nearly the same effect. The i.e. of the $\pi(e)$ orbital of benzene in $[Cr(C_6H_6)(CO)_3]$ is raised by 1.45 eV compared to free benzene.[3]

In the $[M(C_7H_8)(CO)_3]$ complexes the symmetry is lowered to C_s from the C_{3v} symmetry of $[M(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$. The filled *d* orbitals transform as $2a' + a''$ and are responsible for the first two bands in the p.e. spectra (Figure 2). That two bands are seen (area ratio 2 : 1) for the cycloheptatriene complexes while only one is present in the mesitylene analogues is probably due to the lower symmetry in the former complexes. Figure 2 shows that partial resolution of the *d*-orbital ionizations into three bands occurs for the tungsten complex since the lowest i.e. band contains a shoulder that is not, however, present for molybdenum or chromium. This shoulder is probably due to spin–orbit splitting which is not completely quenched by the low symmetry of the complex. If this splitting were simply due to the three non-degenerate orbitals having different i.e.s, one would expect to see it in the p.e. spectra of the molybdenum and chromium complexes. The *d*-orbital i.e.s are similar for all the three metals (Table 2), but there are greater differences between the three metals than seen in $[M(CO)_6]$, $[M(PF_3)_6]$, or $[M(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$.

The third and fourth p.e. bands in the spectra of $[M(C_7H_8)(CO)_3]$ correlate with the two lowest-i.e. π orbitals of the cycloheptatriene ring. These are the b_1 and a_2 (C_{2v} point group) which transform as a' and a'' in the metal complex. The substantial interaction of both $\pi(a')$ and $\pi(a'')$ with the metal is shown by the increase in the i.e. of these orbitals compared to free cycloheptatriene (Table 2). The three metals have similar effects. The $\pi(a')$ i.e. is raised by *ca.* 0.75 eV while $\pi(a'')$ is raised by *ca.* 1.1 eV, indicating that the metal–ligand interaction is greater for the $\pi(a'')$ orbital even though the energy separation between the metal *d* orbitals and the ligand π orbitals is greater for $\pi(a'')$ by *ca.* 1 eV.

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

[14] M. M. Coutiere, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, 1972, **27**, 281.

[15] M. M. Rohmer and A. Villard, *J.C.S. Chem. Comm.*, 1973, 250.

[16] M. F. Guest, B. R. Higginson, D. R. Lloyd, and I. H. Hillier, *J.C.S. Faraday II*, 1975, 902.

[17] B. R. Higginson, D. R. Lloyd, S. Evans, and A. F. Orchard, *J.C.S. Faraday II*, 1975, 1913.

[18] S. Evans, M. F. Guest, I. H. Hillier, and A. F. Orchard, *J.C.S. Faraday II*, 1974, 417.

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

[20] J. A. Connor, L. M. R. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1974, **28**, 1193.

[21] M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest, and D. R. Lloyd, *Mol. Phys.*, 1975, **30**, 839.

[22] C. Batich, P. Bischof, and E. Heilbronmer, *J. Elect. Specl. Rel. Phenom.*, 1972, **1**, 333.