He(I) Photoelectron Spectra of Tricarbonyl-iron and -ruthenium Complexes of Cyclic Dienes, and of Tricarbonylcycloheptatriene- and Tricarbonylcyclo-octatetraene-iron

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The He(I) photoelectron spectra of the complexes [M·LM(CO)$_3$] [L = cyclohexa-1,3-diene and cyclohepta-1,3-diene (M = Fe or Ru); L = cyclo-octa-1,3-diene, cyclohepta-1,3,5-triene, and cyclo-octatetraene (M = Fe)] have been examined. The ionisation energies of the iron diene complexes show a regular variation with ring size, in contrast to those of the parent cyclic dienes.

THE photoelectron (p.e.) spectrum of butadienetricarbonyliron (1) has been reported previously.[1-3] The most recent paper[3] included both He(I) and He(II) spectra, which were assigned in the light of an *ab initio* SCF molecular-orbital calculation. The free ligands have also been studied.[4-6] The separation of the two bands of lowest ionisation energy in the spectra of the cyclic dienes has been correlated with the stereochemistry of the ring. We now report the spectra of complexes of the type [M(diene)(CO)$_3$] (M = Fe or Ru) and also of tricarbonylcycloheptatriene- and tricarbonylcyclo-octatetraene-iron.

EXPERIMENTAL

The complexes were prepared according to published methods.[7-12] The purity of the samples was confirmed by elemental analysis and by measurement of m.p., b.p., and i.r., ^{1}H n.m.r., and mass spectra, which agreed with reported values.[13,14]

The He(I) p.e. spectra were recorded on a Perkin-Elmer PS 16/18 instrument modified to take a heated insert. The spectra were calibrated using xenon and argon.

RESULTS AND DISCUSSION

Diene Complexes.—The spectra are summarised in the Table. Connor *et al.*[3] ascribed the first band (A) in the spectrum of butadienetricarbonyliron to the ionisation of electrons largely localised on the metal atom. The second peak (B) is assigned to an orbital which correlates with the higher filled π level of *cis*-butadiene ($1a_2$). The third band (C) arises through ionisation from a molecular orbital correlating with the lower filled π level ($1b_1$) of the free ligand. The bands (D) at higher ionisation energy (i.e.) are attributed to loss of electrons from σ levels of the diene, and from the carbonyl ligands.

The spectra of the tricarbonyl(diene)iron complexes [Fe(C$_6$H$_8$)(CO)$_3$] (2), [Fe(C$_7$H$_{10}$)(CO)$_3$] (3), and [Fe(C$_8$H$_{12}$)(CO)$_3$] (4) resemble that of the parent molecule, (1), and have been assigned similarly. In the former, however, band (B) was less well resolved from the metal '*a*' bands (A), and bands (C) occurred as shoulders on the low i.e. edge of the σ ionisations of the diene ligands. The i.e. values derived from bands (C) are therefore less well established than for the parent molecule.

Ionisation energies of the tricarbonyl complexes and the π levels of the free ligands

	Ionisation energy (eV)				
Compound	Band (A)		Band (B)	Band (C)	Band (D)
[Fe(C$_4$H$_6$)(CO)$_3$] (1)	8.16 (sh)	8.67	9.82	11.43	12.56
[Fe(C$_6$H$_8$)(CO)$_3$] (2)	7.98 (sh)	8.56	9.33	11.04	12.17
[Fe(C$_7$H$_{10}$)(CO)$_3$] (3)	7.78 (sh)	8.46	9.12	10.86	11.71
[Fe(C$_8$H$_{12}$)(CO)$_3$] (4)	7.45 (sh)	8.27	8.87	10.44	10.87
[Ru(C$_6$H$_8$)(CO)$_3$] (5)	8.01	8.91	9.39 (sh)	11.01	11.83
[Ru(C$_7$H$_{10}$)(CO)$_3$] (6)	7.96	8.94	9.40 (sh)	10.84	11.64
[Fe(C$_7$H$_8$)(CO)$_3$] (7)	7.76 (sh)	8.39	8.78 10.23	11.10	11.82
[Fe(C$_8$H$_8$)(CO)$_3$] (8)	7.84		8.74 10.61	11.63	
trans-Buta-1,3-diene[4]	9.08		11.34		
Cyclohexa-1,3-diene[5]	8.25		10.75		
Cyclohepta-1,3-diene[5]	8.31		10.63		
Cyclo-octa-1,3-diene[6]	8.68		10.00		
Cyclohepta-1,3,5-triene[5]	8.57		9.52	10.96	
Cyclo-octatetraene[5]	8.42		9.78	11.15	

For complexes (2)—(4) all bands show a decrease in i.e. with increase in ring size. This is not so, however, for the two π ionisations of the parent dienes.[5] Although the average of the first two i.e.s of the latter decreases with increase in ring size, the difference between them is irregular. The separation between these two bands has been correlated with the angle of twist between the conjugated double bonds. This correlation, however, does not agree well with a recent value of 0° twist in cycloheptadiene derived from i.r. spectroscopic data.[15]

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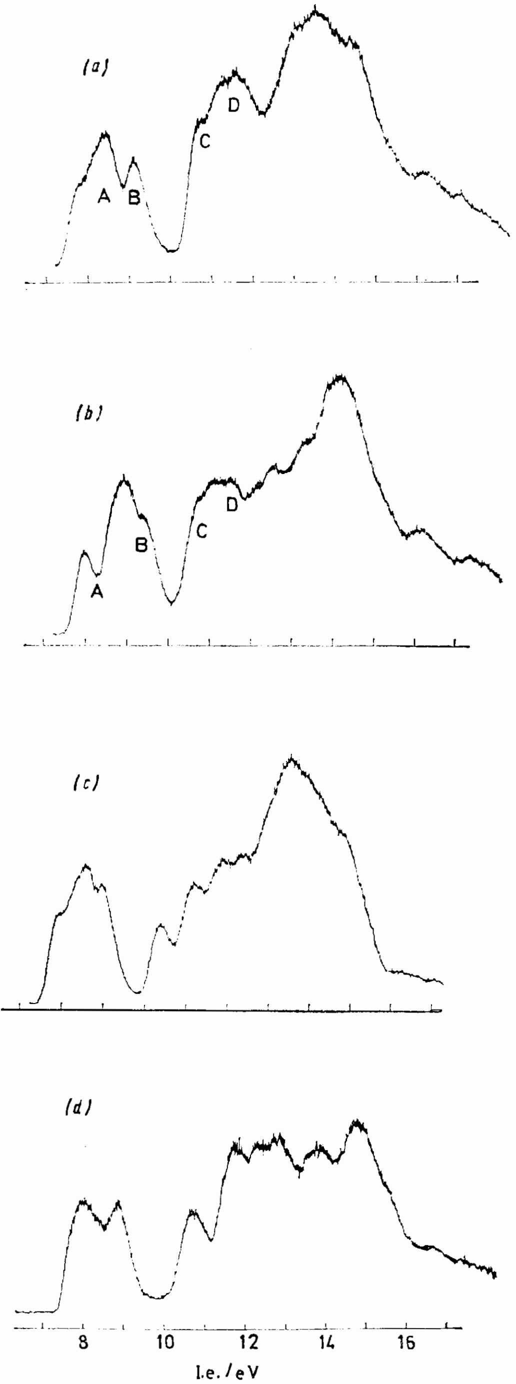
It is interesting nonetheless that the separation between bands (B) and (C) in all the iron and ruthenium complexes is almost constant (1.7 ± 0.1 eV).* This is consistent with the suggestion that the dienes when complexed are constrained to assume an essentially *cis*-planar conformation in which the twist angle is close to 0°. If one assumes that free cycloheptadiene has this conformation, one can estimate the change of the π-ionisation energies on complexing by comparing the spectrum of cycloheptadiene itself with that of its tricarbonyliron complex. The ‘$1a_2$’ i.e. is increased by 0.81 eV and the ‘$1b_2$’ i.e. by 0.23 eV. If a similar change in i.e. occurs with other dienes we can predict the i.e.s for dienes in the *cis*-planar conformation. *cis*-Butadiene, for example, would be expected to show i.e.s of 9.01 and 11.20 eV. Worley[2] calculated values of 9.19 and 11.18 eV.

The spectra of the two ruthenium complexes [Ru(C_6H_8)(CO)$_3$] (5) and [Ru(C_7H_{10})(CO)$_3$] (6) resemble those of their iron analogues, and may be assigned similarly. The first band (A) lay to higher i.e., as do the metal orbital ionisations in [Ru(η-C_5H_5)$_2$] compared with [Fe(η-C_5H_5)$_2$].[16] Ionisation-energy data for both neutral and singly ionised atomic species similarly indicate an increase from Fe to Ru.[17] As a consequence of the shift in band (A), (B) was no longer so clearly resolved as in the spectra of the iron complexes, and appeared as a shoulder. It is interesting that the separation between bands (B) and (C) is still 1.7 ± 0.1 eV.

The intensity of the first group of bands (A) and (B) relative to (C) and (D) increases for both pairs of complexes from Fe to Ru. Similar increases in metal *d*-orbital cross section with principal quantum number have previously been noted, *e.g.* for [M(η-C_5H_5)$_2$] (M = Fe, Ru, and Os).[16]

Tricarbonylcycloheptatrieneiron.—Comparison between the spectra of [Fe(C_7H_{10})(CO)$_3$] (3) and [Fe(C_7H_8)(CO)$_3$] (7) shows that an additional band is present in the latter at 10.23 eV. To a first approximation the bonding in complex (7) can be considered as comprising a [Fe(diene)(CO)$_3$] system and a free $>$C=C$<$ unit. We assign the band at 10.23 eV to ionisation from the π system of the uncomplexed double bond. Moreover the bands which correlate with the π molecular orbitals of the complexed *cis*-diene system have a greater separation (2.32 eV) than in the spectra of [Fe(diene)(CO)$_3$] (1.7 eV). This suggests that there is some interaction between the complexed diene system and the uncomplexed π bond.

Tricarbonylcyclo-octatetraeneiron.—The p.e. spectrum of the free ligand (C_8H_8, D_{2d} symmetry) has been discussed by Batich *et al.*[5] The first three ionisations correspond to loss of an electron from π orbitals of b_2, e, and a_1 symmetry respectively. In the crystal the ligand assumes a dihedral conformation,[18] and the molecule is fluxional in solution.[19]



He(I) Photoelectron spectra of (*a*) [Fe(C_7H_{10})(CO)$_3$], (*b*) [Ru(C_7H_{10})(CO)$_3$], (*c*) [Fe(C_7H_8)(CO)$_3$], and (*d*) [Fe(C_8H_8)(CO)$_3$]

If the bonding were composed of a [Fe(diene)(CO)$_3$] unit plus a free diene system, with little or no interaction between them, the spectrum would appear as the sum of the spectra of the two parts. On this basis, the first broad band with maxima at 7.84 and 8.74 eV

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* 1 eV ≈ 1.60×10^{-19} J.

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(Figure) would correspond to bands (A) and (B) of the [Fe(diene)$(CO)_3$] unit together with the lower-energy π ionisation of the diene. The next band at 10.6 eV could be assigned to the higher π ionisation of the diene. This suggestion is supported by relative intensities. The ratio of the intensities of the first group of bands to the peak at 10.61 eV is *ca.* 6 : 1. The corresponding ratio in the spectrum of (7) is 4.8 : 1. The greater relative intensity of the first band in the spectrum of (8) is consistent with the inclusion of the ' $1a_2$ ' ' free-diene ' ionisation. It is likely, however, that there is significant interaction between the diene residue and the complexed diene unit. This is supported by the large ring angles (135°) in the unbound portion of the ring, and by SCF molecular-orbital calculations.[18]

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