Electronic Structure and Reactivity of Pentamethylcyclopentadienyl Complexes of Cobalt, Rhodium, and Iridium: He-I and He-II Photoelectron Spectroscopic Investigation *

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The He-I and He-II photoelectron spectra of $[Co(\eta\text{-}C_5Me_5)(CO)_2]$, $[Rh(\eta\text{-}C_5Me_5)(CO)_2]$, $[Ir(\eta\text{-}C_5Me_5)(CO)_2]$, $[Ir(\eta\text{-}C_5Me_5)Me_2(Me_2SO)]$, and $[Ir(\eta\text{-}C_5Me_5)Me_4]$ are reported and assigned on the basis of simple molecular orbital schemes. The highest occupied molecular orbital of the dicarbonyls is deduced to have more ring-carbon character in the case of the rhodium and iridium compounds than in the case of the cobalt compound. This is correlated with their differing behaviour on one-electron oxidation and their relative ease of CO substitution by two-electron donor ligands. For the series of iridium compounds the first ionization energy increases only very slightly with oxidation state, whereas the average *d*-orbital ionization energy is greatest for the iridium(I) compound. The ability of the $Ir(\eta\text{-}C_5Me_5)$ moiety to exist in a wide variety of oxidation states is understood in terms of the electron-releasing ability of the pentamethylcyclopentadienyl ligand which enables the metal *d* orbitals to maintain suitable energy and overlap for covalent bond formation.

Pentamethylcyclopentadienyl has been used widely as a protecting group in both *d*- and *f*-block transition metal chemistry.[1-3] One of the more extensively developed areas where this strategy has been employed, and which is still expanding, is the chemistry of cobalt, rhodium, and iridium. Substantial differences are found in the chemical behaviour of the cobalt and the rhodium and iridium complexes. There have been few investigations of the electronic structure of these compounds, although some model systems have been studied by theoretical calculations.[4-6]

We have obtained photoelectron (p.e.) spectra of the compounds $[M(\eta\text{-}C_5Me_5)(CO)_2]$, (M = Co, Rh, or Ir), $[Ir(\eta\text{-}C_5Me_5)Me_2(Me_2SO)]$, and $[Ir(\eta\text{-}C_5Me_5)Me_4]$, in order to obtain information on the orbital structure of derivatives in the oxidation states I, III, and V. The spectrum of $[Co(\eta\text{-}C_5Me_5)(CO)_2]$ has been reported previously,[7] along with those of $[Co(\eta\text{-}C_5Me_5)(CO)(PMe_3)]$, $[Co(\eta\text{-}C_5Me_5)(Me_2PCH_2CH_2PMe_2)]$, and $[Co(\eta\text{-}C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]$. These data are given here also in order to facilitate comparison down the group.

Experimental

The compounds were all synthesised by previously reported routes.[8]

Spectra were measured using a PES Laboratories 0078 photoelectron spectrometer, and a Perkin-Elmer 16/18 photoelectron spectrometer. Data were collected by two methods, one using a ratemeter and conventional scanning and recording on an *X*–*Y* recorder, the other by repeated scans and accumulation of counts using a Research Machines 380Z microprocessor. The latter spectra were then curve-fitted with asymmetric mixed Lorentzian–Gaussian functions in order to determine band areas. The areas were corrected by dividing by the kinetic energy of the electrons and normalized to 100%. In many cases bands overlapped too extensively to enable reliable area data to be obtained on individual bands (see Figure 2, for example). However, the trends in intensities found by this method, tended to reinforce those apparent to the eye on inspection of the spectra. The numbers quoted in the Table are for the He-II/He-I intensity ratios of the normalized bands.

No evidence for the release of free Me_2SO was found, either in the warm-up period, or during the measurement of $[Ir(\eta\text{-}C_5Me_5)Me_2(Me_2SO)]$.

Results

The spectra of the compounds are shown in Figures 1—4, 9, and 10, and ionisation and intensity data are given in the Table. In Figures 2—4, 9, and 10 the points represent the experimental accumulated counts and the line a least-squares fit to these data.

All spectra show a main band at *ca.* 14 eV which may be assigned to ionizations from ligand-based orbitals; these will not be discussed further. In the spectra of the dicarbonyls a shoulder appears on this band to low ionization energy (i.e.) (*ca.* 11.5 eV) which is characteristic of pentamethylcyclopentadienyl complexes and is associated with the ring methyl groups.[9] This shoulder decreases in relative intensity in the He-II spectra. The dimethyl and tetramethyl complexes, however, show more complex band structure, to rather lower i.e., which has different intensity characteristics suggesting that these bands should have other assignments.

In the spectra of the three dicarbonyls, the most striking feature of the low i.e. region is the first band, A, which lies close to subsequent bands in the case of the cobalt compound, but is well separated from them in the case of rhodium and iridium. In all three cases one band (X) has a significantly smaller He-II/He-I intensity ratio than the others and may be assigned to a cyclopentadienyl (e_1) type ionization. Band X is relatively more intense in the spectrum of the cobalt compound than in the other two dicarbonyl(η-pentamethylcyclopentadienyl)metal compounds. A similar band is apparent in the spectra of the tetramethyl compound (X). In the case of $[Ir(\eta\text{-}C_5Me_5)Me_2(Me_2SO)]$, there are a number of overlapping bands in the region 8—11 eV which are difficult to distinguish.

Discussion

Dicarbonyl(η-pentamethylcyclopentadienyl)metal Complexes.—The bonding in this type of molecule has been discussed by several authors.[4-6,10] In Figure 5 we give an energy level scheme indicating the allowed interactions. The scheme for the cobalt compound is consistent with the calculations of Hof-

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* *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

Table. Ionization energies (eV) and band intensity ratios (He-II/He-I) for [Co(η-C_5Me_5)$(CO)_2$] (1), [Rh(η-C_5Me_5)$(CO)_2$] (2), [Ir(η-C_5Me_5)$(CO)_2$] (3), [Ir(η-C_5Me_5)Me_2(Me_2SO)] (4), and [Ir(η-C_5Me_5)Me_4] (5)

Compound	Band	I.e.	He-II/He-I	Assignment
(1)	A	6.96	0.78	b_1
	B	7.33	1.6	a_1
	C	7.94	1.4	a_1
	X	8.87	0.84	$a_2 + b_1 + b_2$
		11.4		ring Me
		13.6		
(2)	A	6.84	0.7	b_1
	B	8.17	1.8	a_1
	X	8.68	0.67	$b_2 + (b_1\ ?)$
	C	9.00	1.0	a_1
	D	9.72	1.1	$a_2 + (b_1 ?)$
		11.4		ring Me
		13.9		
(3)	A	6.94	1.1	b_1
	B	8.22	1.2	a_1
	X	9.00	0.5	$b_2 + (b_1 ?)$
	C	9.25	1.4	a_1
	D	10.02	1.1	$a_1 + (b_1 ?)$
		11.62		
		14.0		
(4)	A	7.01		*d*
	B	7.24		*d*
	C	8.05		*d*
	D	8.51		
	E	8.88		
	F	9.40		
	G	10.15		Ir–C
		11.4		
		12.7		
		13.5		
(5)	A	7.37	1.9	a_1
	B	8.09	0.8	b_2
	X	8.42		*e*
	C	9.89		Ir–C
	D	10.08	0.9	Ir–C
	E	10.47		Ir–C
		11.4		
		12.8		

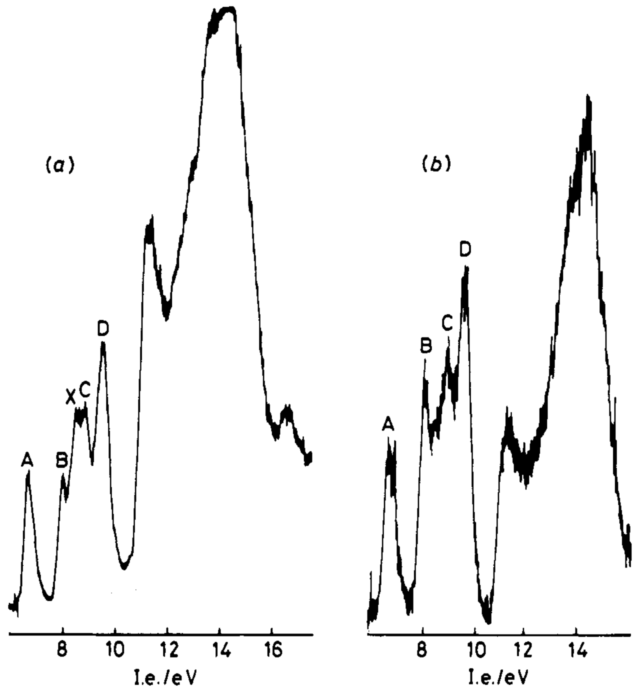

Figure 1. (*a*) He-I and (*b*) He-II spectra of [Rh(η-C_5Me_5)$(CO)_2$]

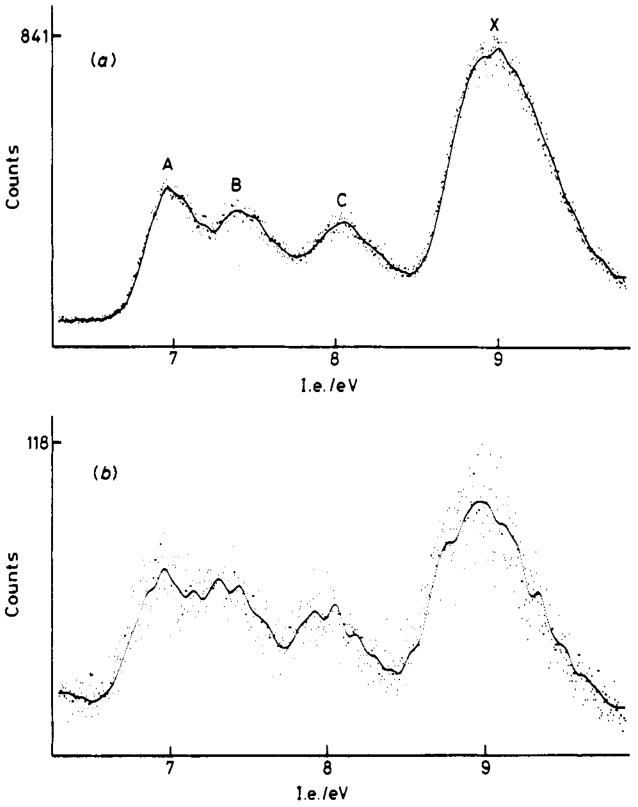

Figure 2. Low-energy region of (*a*) the He-I and (*b*) the He-II spectra of [Co(η-C_5Me_5)$(CO)_2$]

mann [4] and Albright and Hoffmann.[5] The left-hand diagram is derived by coupling a Co(η-C_5Me_5) unit with two CO ligands; the right-hand diagram is derived by joining a C_5Me_5 ring with a bent $Co(CO)_2$ fragment. For Rh and Ir interactions will be similar though *d*-orbital splittings are normally larger for second- and third-row transition metals. The levels correspond with the ionization energies of the bands and are not the result of a molecular orbital (m.o.) calculation.

The highest occupied molecular orbital (h.o.m.o.) of b_1 symmetry (see Figure 6) is metal–ring antibonding but metal–carbonyl bonding, the electrons being stabilized by back-donation to the carbonyl $2\pi^*$ orbitals. The b_2 orbital, which is also metal–ring antibonding, is destabilized by σ-donation from the CO 5σ orbitals and is consequently unoccupied. The differential interaction of the metal b_1 and b_2 orbitals with the ligand e_1 orbitals has been emphasised by Byers and Dahl [11] in their careful examination of the crystal structure of [Co(η-C_5Me_5)$(CO)_2$]. They observed a ring distortion consistent with greater electron density in the ring b_1 (e_1) orbital than the ring b_2 (e_1) orbital. This correlates directly with the proposition that both bonding and antibonding b_1 metal–ring orbitals are occupied whereas only the bonding b_2 orbital is occupied. (Both b_1 orbitals have bonding character with respect to some of the carbon atoms of the ring; see Figure 6.)

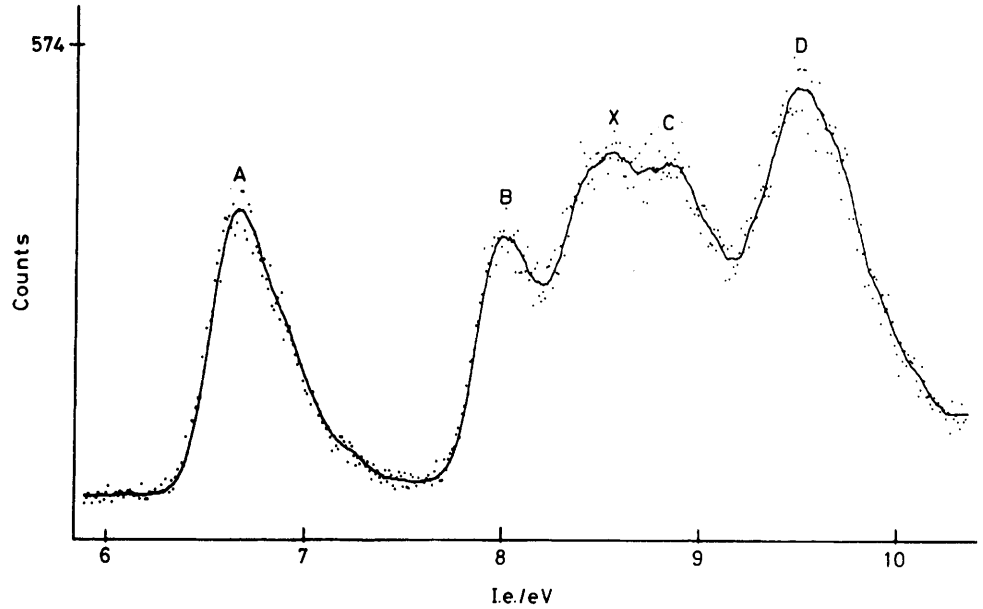

Figure 3. Low-energy region of the He-I spectrum of $[\mathrm{Rh}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$

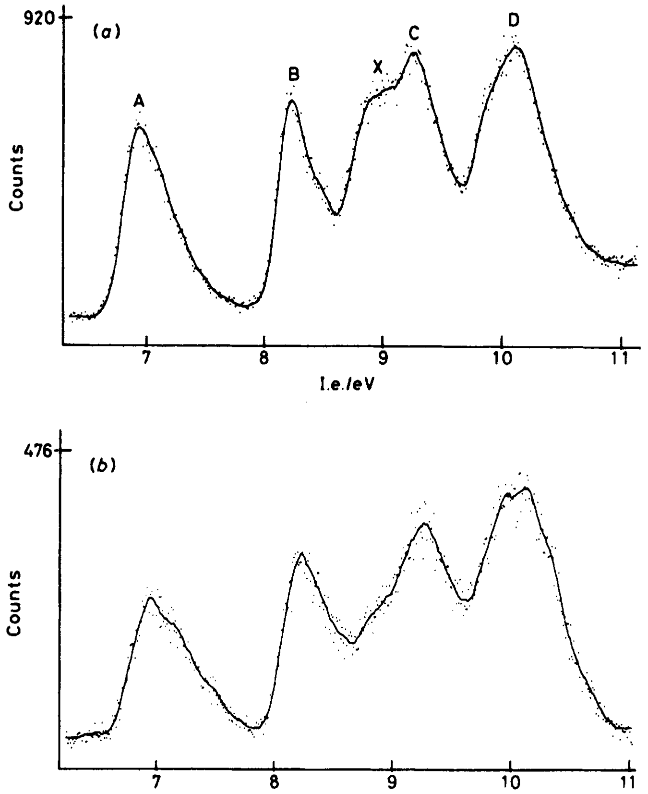

Figure 4. Low-energy region of (a) the He-I and (b) the He-II spectra of $[\mathrm{Ir}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$

The first band in all three spectra may be assigned to ionization from the upper b_1 orbital; the significantly greater separation of the first band from subsequent ones in the case of the rhodium and iridium complexes noted above suggests that this orbital is substantially more antibonding, for the heavier metal complexes, with the electrons being delocalised onto the cyclopentadienyl ring. This view is reinforced when the He-II/He-I intensity ratios are examined. In all three cases they are smaller than found for the other *d* bands as is evident by inspection of Figures 1, 2, and 4.

Assignment of the other *d* ionization bands is given in the Table and is based on the order given by calculation,[4,5] which seems reasonable as differential relaxation between these types of orbitals should be small. In the case of $[\mathrm{Co}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$ the highest *d* band lies under the cyclopentadienyl band; evidence that this is in fact the case is seen by extrapolation from the cobalt derivatives where CO is successively substituted by phosphines.[7] The rhodium and iridium complexes have the ionization bands associated with the most stable *d* orbitals lying at higher i.e. than the cyclopentadienyl band.

Though both the ring ionizations, b_1 and b_2, lie under band X in the cobalt case, the rather lower intensity of band X in the rhodium and iridium spectra and the high intensity of band D suggest that X may only consist of b_2 in these cases and that the ring b_1 ionization may comprise part of band D. The profile of band D in the spectrum of $[\mathrm{Ir}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$ is also suggestive of two bands. The alternative assignments are presented in the Table.

The average *d* i.e. increases in a regular manner on passing down the group (Co, 7.76; Rh, 8.43; Ir, 8.61 eV;). In contrast, the first i.e. *decreases* from cobalt to rhodium and then increases to iridium (Table). This reinforces the view that this orbital has substantially more ring character in the complexes of the heavier metals. A similar trend has been found in the case of (cyclopentadienyl)(diene)metal complexes.[12]

Species of the type $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_{2-n}\mathrm{L}_n]$ (M = Co or Rh, $n = 1$ or 2, L = phosphine) show markedly different behaviour on one-electron oxidation. A range of stable paramagnetic 17-electron cobalt salts of the type $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_{2-n}\mathrm{L}_n]\mathrm{X}$ ($n = 1$ or 2, L = phosphine, X = $\mathrm{BF_4}$ or $\mathrm{PF_6}$) have been isolated.[13] In contrast rhodium compounds such as $[\mathrm{Rh}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})]$ undergo chemical oxidation with $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{PF_6}$ or $[p\text{-}\mathrm{N_2C_6H_4F}]\mathrm{PF_6}$ or by controlled-potential electrolysis, to give a reactive radical cation which rapidly dimerizes to a fulvalene complex of the type $[\mathrm{Rh_2(CO)_2(PPh_3)_2}(\eta^5:\eta^{5'}\text{-}\mathrm{C_{10}H_8})]^{2+}$.[14-16] The implied radical coupling through the ring carbons in the latter case is fully consistent with the delocalized nature of the b_1 h.o.m.o. proposed above.

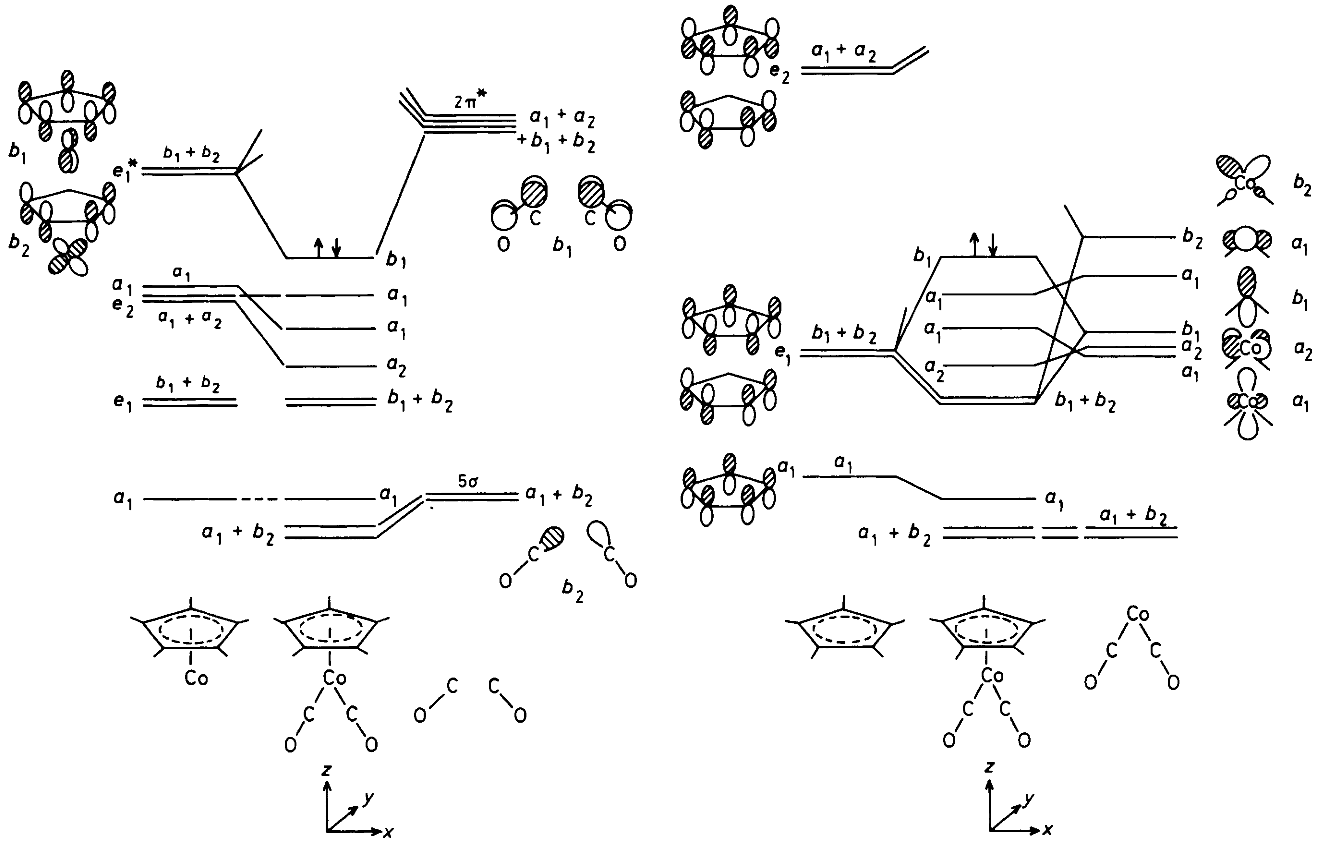

Figure 5. Interaction diagram for [Co(η-C_5Me_5)$(CO)_2$]. These level diagrams are constructed by considering the interaction of a metal–pentamethylcyclopentadienyl moiety with two carbonyl ligands and a $Co(CO)_2$ unit interacting with a C_5Me_5 ring. The Co–CO interaction is taken from ref. 6 and the scheme for the cobalt compound is similar to that given in refs. 4 and 5

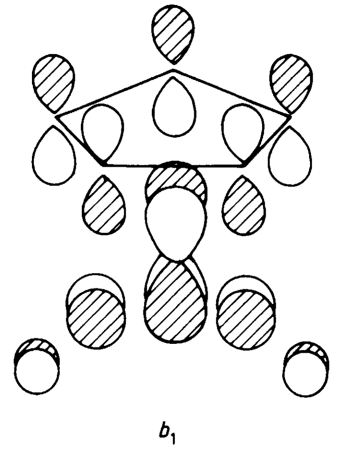

Figure 6. Representation of the b_1 h.o.m.o. showing the metal–ring antibonding character, the M–CO bonding character, and some C–C bonding character. Short C–C distances are found for the pairs of atoms which are bonding in the b_1 orbital and long distances for those which are antibonding (ref. 11)

Rerek and Basolo[17] have studied the mechanism of substitution of the dicarbonyls where one CO group is readily replaced by a phosphine. They find the reaction to be first order in complex and first order in phosphine. This rules out a mechanism where the rate-determining step is ligand dissociation. The proposed mechanism for the reaction is that, on attack by a nucleophile, ring slippage occurs so that the

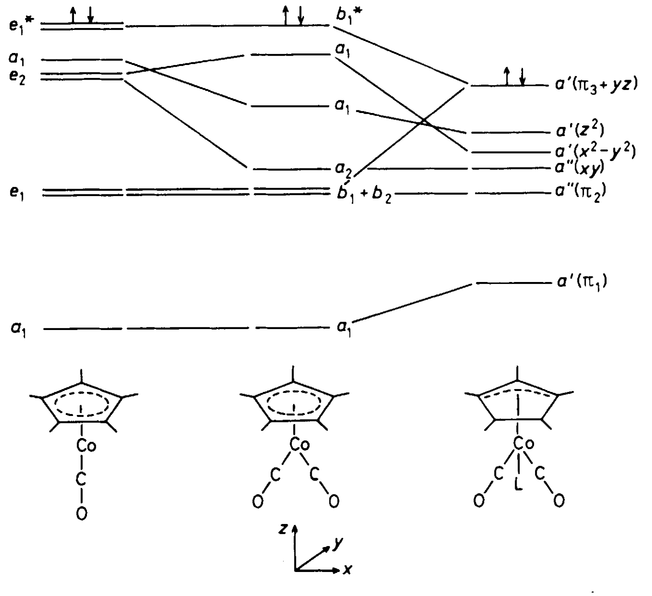

Figure 7. Correlation diagram for the 18-electron parent molecule [Co(η-C_5Me_5)$(CO)_2$] and two possible intermediates: 16-electron Co(η-C_5Me_5)(CO) (a pseudo-linear geometry is assumed) where the activating step is CO loss, and 18-electron Co(η^3-C_5Me_5)$(CO)_2$L where the activating step for substitution is ring slippage provoked by nucleophilic attack (for clarity, the unco-ordinated double bond has been omitted from the diagram)

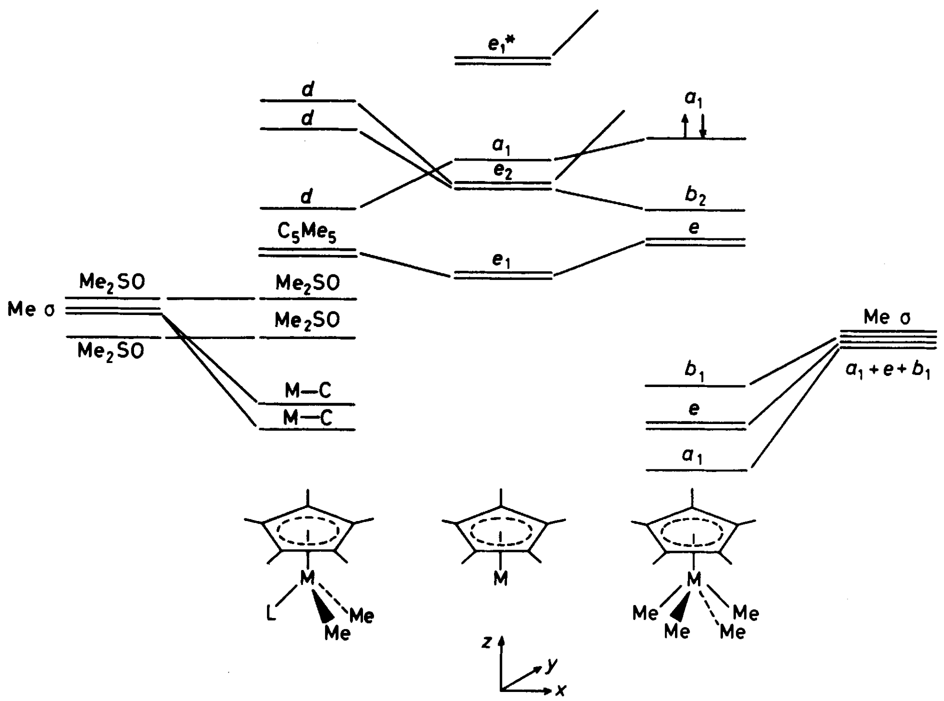

Figure 8. Interaction diagram for [Ir(η-C_5Me_5)Me_2(Me_2SO)] and [Ir(η-C_5Me_5)Me_4]

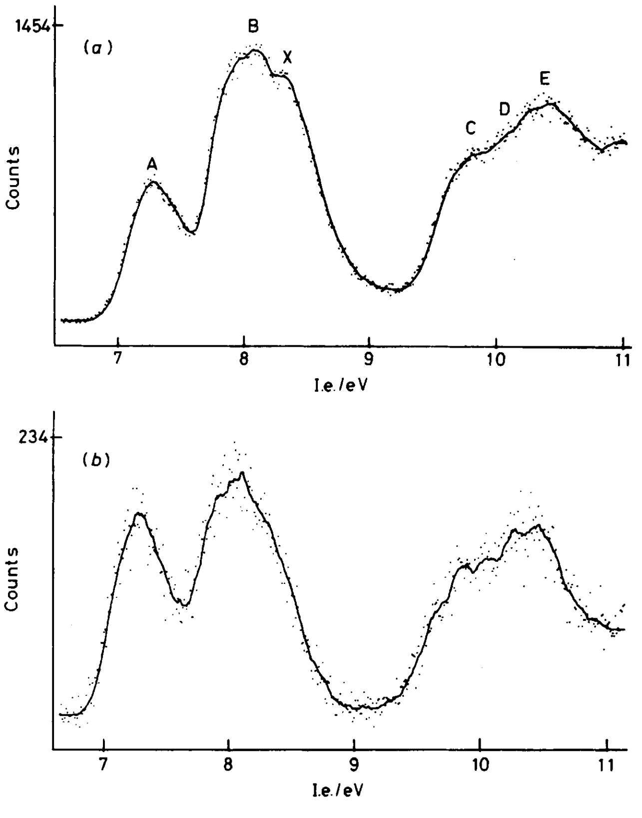

Figure 9. Low-energy region of (a) the He-I and (b) the He-II spectra of [Ir(η-C_5Me_5)Me_4]

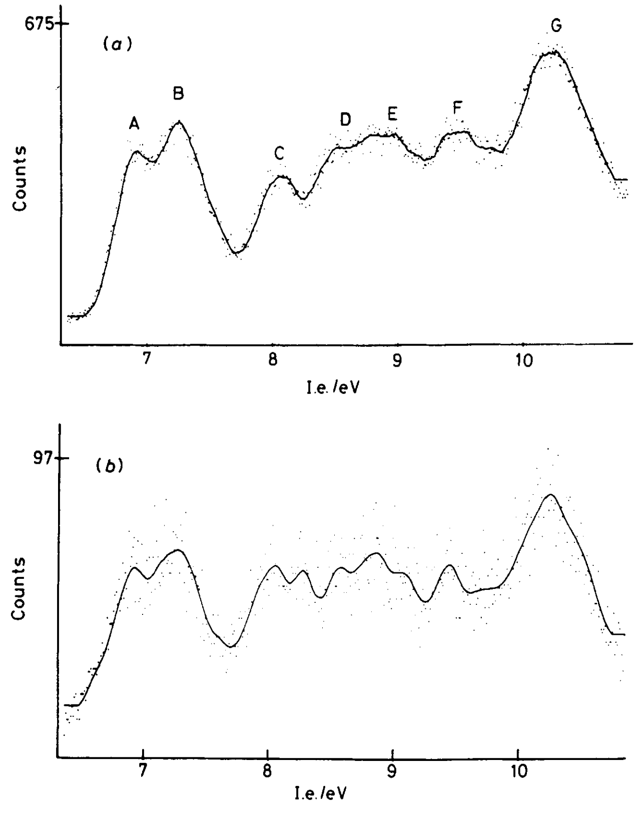

Figure 10. Low-energy region of (a) the He-I and (b) the He-II spectra of [Ir(η-C_5Me_5)Me_2(Me_2SO)]

cyclopentadienyl ligand becomes η^3- rather than η^5-bonded. The reactions tend to proceed at a greater rate for Rh complexes than for Co complexes. The 16-electron d^8 species M(η-C_5H_5)L has been implicated as a reactive intermediate in other reactions (summarized in ref. 18) and Walsh diagrams for a variety of species have been generated.[18] Hofmann proposes that the ground-state geometry of the [M(η^5-C_5H_5)L] intermediate is likely to be bent whether in a triplet or singlet state. However, in any geometry two electrons occupy orbitals related to e_1* and thus possess metal–ring antibonding character. The specific example of a linear geometry is represented by a level diagram in Figure 7. Hofmann[18] did not calculate the energy associated with ring slippage in a molecule such as [M(η-C_5H_5)$(CO)_2$]. In Figure 7 we also give a level scheme for a possible intermediate of the type proposed by Rerek and Basolo[17] where this unfavourable bonding situation has been partially relieved by deco-ordination of the double bond. An intermediate of the latter type may well provide the lower energy pathway.

[Ir(η-C_5Me_5)Me_2(Me_2SO)] *and* [Ir(η-C_5Me_5)Me_4].—The spectrum of [Ir(η-C_5Me_5)Me_2(Me_2SO)] is too complex to assign fully but some interesting data may be gained on several of the ion states. M.o. schemes for [Ir(η-C_5Me_5)Me_2(Me_2SO)] and [Ir(η-C_5Me_5)Me_4] which form the basis of both assignments are given in Figure 8.

The He-I spectrum of [Ir(η-C_5Me_5)Me_4] (see Figure 9) shows two bands (A and B + X) below 9 eV, whereas one might expect three ionizations: two from the four *d* electrons and one from the degenerate pair of ring orbitals. The intensity ratio of the first two bands is approximately 1 : 3, the first band increasing in relative intensity in the He-II spectrum and the second band decreasing especially on the high i.e. side. This suggests that the first band (A) is a *d* ionization (probably a_1) and the second (B + X) comprises both the b_2 *d*-band and the ring *e* ionization. A survey of M–C ionization bands of transition metal alkyls shows them to lie in the range 8.5—10.5 eV.[19] We observe two bands at C and D eV which have intensity characteristics incompatible with ionization from the pentamethylcyclopentadienyl ring, which may reasonably be assigned to ionizations of the Ir–Me bonds (a_1, *e*, and b_1 symmetry).

In the case of the p.e. spectra of [Ir(η-C_5Me_5)Me_2(Me_2SO)] (Figure 10), the first two overlapping bands at 7.01 and 7.24 eV and the third band at 8.05 eV are of approximately equal intensities suggesting that they arise from ionization of the six *d* electrons. The band at 10.15 eV, by analogy with the spectrum of [Ir(η-C_5Me_5)Me_4], may be assigned to Ir–Me ionizations. The poorly resolved structure between 8.3 and 9.7 eV should contain the cyclopentadienyl *e* band and possibly two ionization bands from the Me_2SO ligand; these occur in free Me_2SO at *ca.* 9 and 10 eV.

It has been remarked that a wide range of oxidation states are accessible to the Ir(η-C_5Me_5) moiety.[20] However, it is not necessarily the case that the charge on the iridium varies widely in this series of compounds. The thesis that the charge on a metal atom increases with increasing oxidation state is a difficult one to test as both a definition of charge on an atom in a molecule and a method of measuring it remain elusive. Nevertheless that this is the case remains a widely held expectation. Valence-shell p.e. studies, though unable to measure charge, can give a direct measurement of the binding energies of valence electrons which can lead to an understanding of relative stability and reactivity of complexes.

In this context, the first i.e. and the average *d* i.e. values of the three iridium complexes are as follows: [Ir(η-C_5Me_5)$(CO)_2$], 6.94 and 8.61; [Ir(η-C_5Me_5)Me_2(Me_2SO)], 7.01 and 7.43; [Ir(η-C_5Me_5)Me_4], 7.37 and 7.73 eV.

The first i.e. is remarkably constant throughout the series though slightly higher for the Ir^V compound than for the others. The Ir^I compound, however, has the highest average i.e., its rather low first i.e. being due to the antibonding nature of the orbital from which the electron was ejected. The trends found are understandable in terms of the electron-*withdrawing* nature of CO as a ligand and the electron-*donating* nature of Me.

Maitlis[20] has observed that [Ir(η-C_5Me_5)Cl_4] has proved elusive to synthesise whereas [Ir(η-C_5Me_5)Me_4] is a readily formed thermally stable compound. Four electron-withdrawing chlorine ligands would substantially stabilize the *d* orbitals, pulling them into the core. (For an example of this compare the first i.e. of $ReCl_5$, 9.5 eV, and $ReMe_6$, 7.9 eV.[21,22]) This could have two consequences; the *d* orbitals become less effective at covalent bond formation, and the energy of the lowest unoccupied molecular orbital becomes such that the complex is readily reduced. In a similar vein, permethylation of the cyclopentadienyl ring lowers the i.e. of *d* orbitals by *ca.* 0.6 eV. Thus in having both a pentamethylcyclopentadienyl ring and electron-donating ligands such as methyl bound to the iridium, stabilization and contraction of the *d* orbitals is prevented, and effective covalent bond formation by the high oxidation state metal is maintained. These considerations differ from those which apply to more ionic compounds, where the stabilization of high oxidation states is primarily dependent on high lattice energies. However, for the primarily covalent species with which we are dealing here, the role of the pentamethylcyclopentadienyl group in stabilizing these high oxidation states is seen to depend on its electron-releasing ability.

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