Electronic Structure of Transition-metal Indenyl Compounds: A He I and He II Photoelectron Spectroscopic Study of $[Mn(\eta^5-C_9H_7)(CO)_3]$, $[Fe(\eta^5-C_9H_7)_2]$, $[Ru(\eta^5-C_9H_7)_2]$, and $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$ †

Neil S. Crossley, Jennifer C. Green,* Attila Nagy, and Graham Stringer
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

He I and He II photoelectron spectra have been recorded for $[Mn(\eta^5-C_9H_7)(CO)_3]$, $[Fe(\eta^5-C_9H_7]_2$, $[Ru(\eta^5-C_9H_7)_2]$ and $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$ and assigned by comparison with the photoelectron-spectra of related cyclopentadienyl complexes and with the help of extended-Hückel molecular-orbital calculations. The indenyl complexes have lower first ionization energies than the cyclopentadienyl complexes showing the indenyl ligand to be electron releasing relative to cyclopentadienyl, and comparable to methylcyclopentadienyl in its donor power.

Transition-metal indenyl compounds have attracted interest for two main reasons. One is the possibility of ring slippage in the ground-state structure, whereby the indenyl ligand may become in extremis effectively η^3.[1–5] The other is the rate enhancement of ligand substitution in indenyl compounds in comparison to cyclopentadienyl compounds;[6] in this case ring slippage in the transition state of the indenyl compounds is assumed to be particularly facile as the unco-ordinated double bond is stabilized by conjugation within the six-membered ring. Though a similar mechanism has been proposed in the case of bimolecular substitution in cyclopentadienyl compounds,[7–13] the transition state is not so stable and a rate disparity results.

We have carried out an investigation of the photoelectron spectra of a number of transition-metal η^5-indenyl compounds in order to elucidate their ground-state electronic structure. In this paper we report the results on a series of d^6 indenyl complexes, namely $[Mn(\eta^5-C_9H_7)(CO)_3]$, $[Fe(\eta^5-C_9H_7)_2]$, $[Ru(\eta^5-C_9H_7)_2]$ and $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$. A series of d^8 indenyl compounds will be discussed subsequently.

Experimental

Bis(η-indenyl)iron and tricarbonyl(η-indenyl)manganese were synthesized by the literature methods.[14,15]

$[Ru(\eta^5-C_9H_7)_2]$.—Bis(η-indenyl)ruthenium was prepared by a modified version of the synthesis of $[Ru(\eta-C_5H_5)_2]$.[16] The compound $RuCl_3{\cdot}3H_2O$ (5.2 g, 19.8 mmol) was dissolved in ethanol (40 cm^3). Freshly distilled indene (30 cm^3, 0.25 mol) was added, and the mixture stirred thoroughly. Zinc dust (3.5 g) was added with vigorous stirring, and the colour changed from orange-brown to blue-grey. After 10 min, the colour changed back to orange-brown. The mixture was allowed to stir for 24 h to ensure complete reaction and was then concentrated under reduced pressure to *ca.* 10 cm^3. The oily residue was extracted with diethyl ether (*ca.* 20 cm^3). The extract obtained was passed through a column of alumina (25 cm), using diethyl ether as an eluant. Concentration of the orange solution under reduced pressure to *ca.* 50 cm^3 and cooling to −78 °C over a period of 24 h gave orange needles of $[Ru(\eta^5-C_9H_7)_2]$ (2.9 g, 44%).

$[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$.—The complex $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$ was prepared by a modification of a previous synthesis.[17] The compound $\{[Ru(\eta-C_5Me_5)Cl_2]_x\}$ was prepared as described.[18,19] $Na(C_9H_7)$ (0.60 g, 4.4 mmol) in tetrahydrofuran (*ca.* 10 cm^3) was added to a suspension of $\{[Ru(\eta-C_5Me_5)Cl_2]_x\}$ (0.51 g, 1.6 mmol) in tetrahydrofuran (*ca.* 15 cm^3) in a Young's ampoule. The reaction mixture was heated to 60 °C for a period of 72 h. The solvent was removed under reduced pressure, and the residue was extracted with toluene (3×15 cm^3). The volatiles were removed under reduced pressure, and the orange-brown residue was extracted with light petroleum (b.p. 40—60 °C, *ca*, 20 cm^3). The solution was passed through a column of alumina (20 cm), using light petroleum (b.p. 40—60 °C) as the eluant. The bright yellow band was collected and concentrated under reduced pressure to *ca.* 15 cm^3, and cooled to −80 °C for a period of 24 h. The bright yellow, air-stable needles were isolated by filtration, and dried *in vacuo*. Yield 0.42 g (75%), m.p. 61—63 °C (Found: C, 65.0; H, 6.5. Calc. for $C_{19}H_{22}Ru$: C, 64.95; H, 6.30%). ^1H N.m.r.: two multiplets at 7.11 and 6.84 (C_6 ring of indenyl), doublet at 4.67 and triplet at 4.43 (C_5 ring of indenyl), singlet at 1.65 (C_5Me_5).

Photoelectron Spectra.—He I and He II photoelectron (p.e.) spectra were recorded on a PES laboratories 0078 spectrometer at resolutions better than 0.05 eV. The data from 20—60 scans were accumulated using a Research Machines 380Z microcomputer; the typical intensity of the highest peak reached 4 000 counts in the He I spectra and 1 000 counts in the He II spectra. The spectra were calibrated using N_2, Xe, and He. The calibration error was no greater than 0.02—0.03 eV.

The low-ionization energy (i.e.) regions of all the spectra were fitted with asymmetric Gaussian curves. The band areas obtained were corrected for the analyser transmission factor by dividing by the electron kinetic energy. It was not always possible, due to substantial overlapping of bands, to obtain separate areas. In these cases joint areas were determined.

Molecular Orbital (M.O.) Calculations.—Extended-Hückel m.o. calculations, both with and without charge iteration, were performed in order to facilitate assignment of the p.e. spectra. Input data are listed in Table 1. The geometries assumed were based on structure determinations.[20–26]

Results

The p.e. spectra are given in Figures 1—4. The points represent the experimental data and the continuous line at least-squares fit to these points. Bands are labelled on the basis of the assignment that follows so that corresponding bands in different spectra bear the same labels. Table 2 contains the vertical i.e.s

---

† *Non-S.I. unit employed:* eV $\simeq 1.60 \times 10^{-19}$ J.

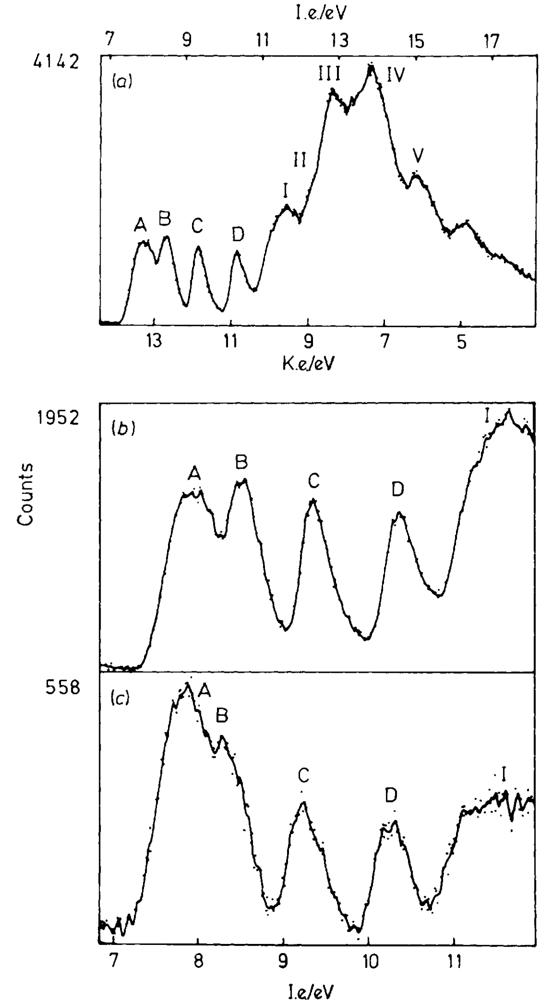

Figure 1. p.e. spectrum of [$Mn(\eta^5-C_9H_7)(CO)_3$]: (*a*) He I full range, (*b*) He I low i.e. range, and (*c*) He II low i.e. range

Table 1. Parameters used in the extended-Hückel calculations

Atom	Orbital	Exponent (ζ)[a]	Energy/eV[b]
H	1*s*	1.300	−13.6 (−13.26)
C	2*s*	1.625	−21.40 (−20.3)
	2*p*	1.625	−11.40 (−10.5)
O	2*s*	2.275	−32.30
	2*p*	2.275	−14.80
Mn	3*d*	5.15 (0.5139) 1.70 (0.6929)	−10.5
	4*s*	1.80	−9.75
	4*p*	1.80	−5.89
Fe	3*d*	5.35 (0.5505) 2.00 (0.6260)	−12.6 (−10.69)
	4*s*	1.9	−9.1 (−8.92)
	4*p*	1.9	−5.32 (−4.87)
Ru	4*d*	5.38 (0.5340) 2.30 (0.6365)	−14.90 (−11.06)
	5*s*	2.08	−10.40 (−8.64)
	5*p*	2.04	−6.87 (−3.65)

[a] Double ζ values were used for *d* orbitals. Coefficients are given in parentheses. [b] Values for the energies after charge iteration are given in parentheses. Those for C and H are averaged.

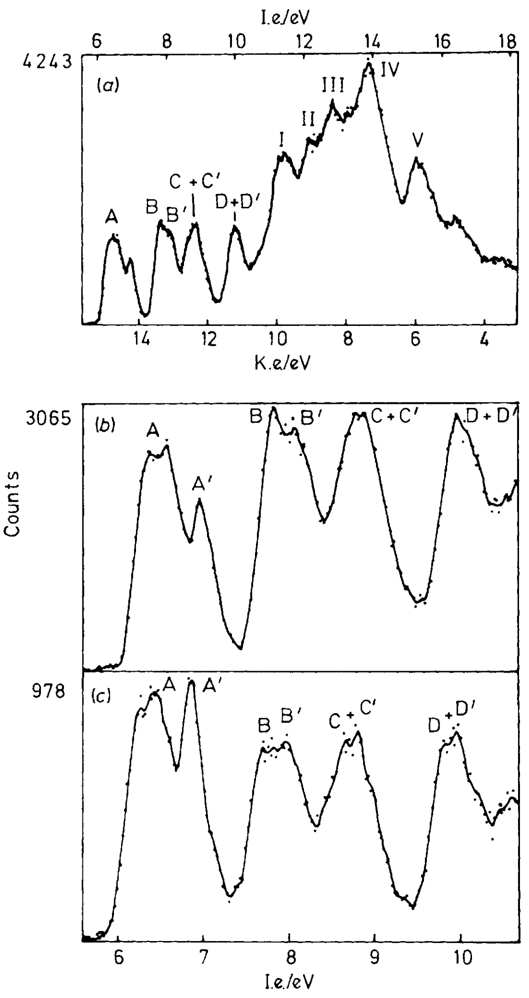

Figure 2. p.e. spectrum of [$Fe(\eta^5-C_9H_7)_2$]. Details as in Figure 1

and the corrected relative band areas. Band areas are normalized by dividing them by the area of the band with the lowest i.e. The relative He II/He I area ratio of a band is designated by $R_{2/1}$; it is a measure of the increase in the relative cross-section for the corresponding ionization when the ionizing radiation is changed from 21.22 to 40.81 eV. Obviously the $R_{2/1}$ values are also normalized to that of the band of lowest i.e. The area values are quite accurate (2—3%) for distinct bands but their accuracy quickly deteriorates with increasing overlap. Areas of overlapping bands were only measured separately when the differing behaviour of these bands in the He I and He II spectra was obvious to the naked eye.

Discussion

For the purpose of electronic structure description, all the molecules in question will be assumed to exist in their eclipsed conformations, which means that all possess at least one plane of symmetry, and for the bis(indenyl) compounds they possess two planes of symmetry (Figure 5). This is in accord with experimental evidence for the crystal structure of the ruthenium compounds;[24,25] bis(indenyl) iron is in fact staggered,[21] but this distortion was found to have minimal effect on the calculated orbital energies and is assumed to have none on the p.e. spectrum. The assumed symmetry groups are C_s for [$Mn(\eta^5-C_9H_7)(CO)_3$] and [$Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)$] and C_{2v} for [$Fe(\eta^5-C_9H_7)_2$] and [$Ru(\eta^5-C_9H_7)_2$]. However, in spite of the

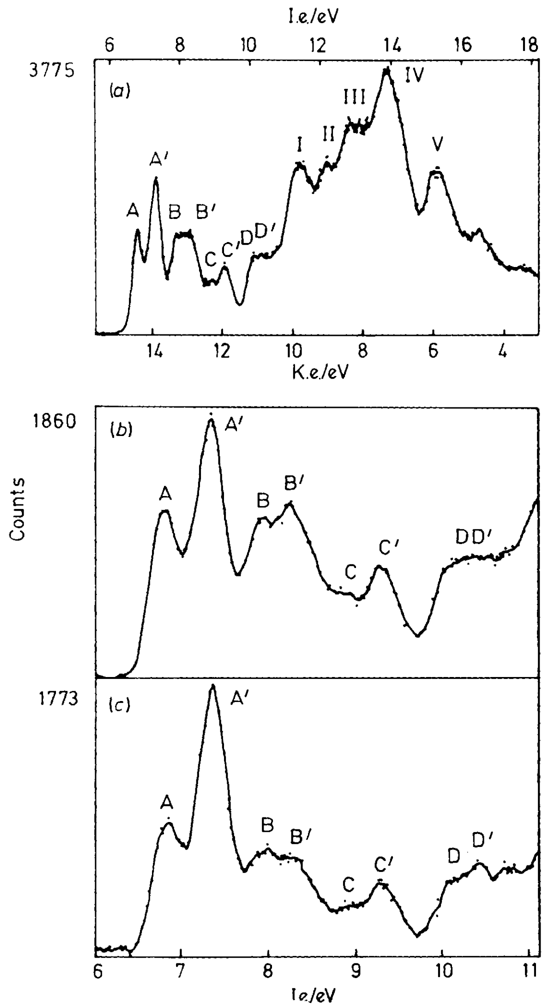

Figure 3. p.e. spectrum of $[Ru(\eta^5-C_9H_7)_2]$. Details as in Figure 1

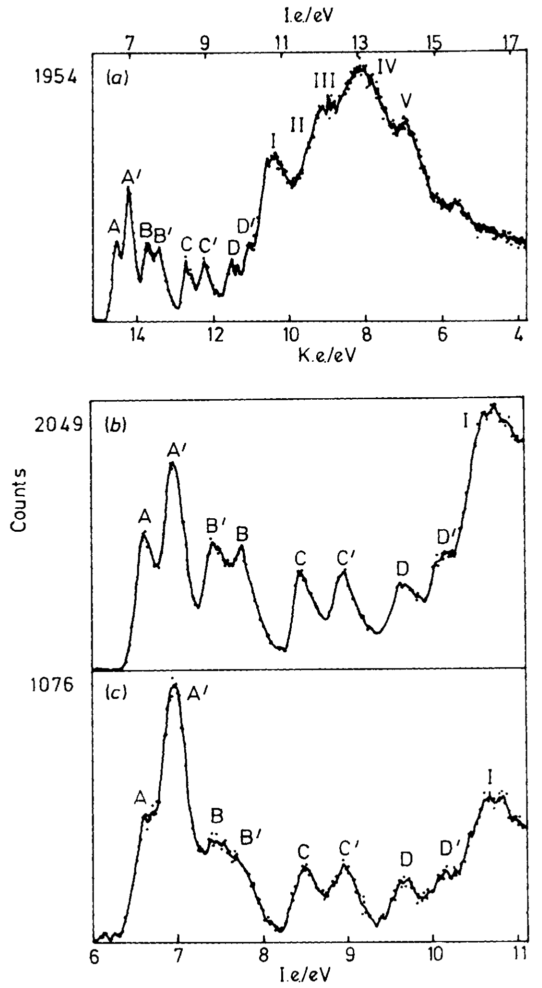

Figure 4. p.e. spectrum of $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$. Details as in Figure 1

different symmetries there are underlying similarities between the m.o.s of these molecules which are reflected in their p.e. ionization bands. We therefore assume a consistent set of cartesian axes throughout, with the z axis perpendicular to the ring plane and the x axis in the symmetry plane bisecting the indenyl ligand(s) (see Figure 5). Thus the z axis is unconventionally not a two-fold axis in the C_{2v} molecules.

General Spectral Assignment.—In general terms, the bonding in the indenyl d^6 compounds is similar to that in their cyclopentadienyl analogues, whose p.e. spectra and electronic structures have been thoroughly discussed.[27–32] The spectra can be divided into three main regions. The first region, that consisting of bands A and A′, is similar to that in the spectra of the analogous cyclopentadienyl compounds which results from the ionization of the metal d orbitals. As in the cyclopentadienyl compounds, the six d electrons occupy orbitals of z^2, $x^2 - y^2$, and xy character. The degree of mixing with ligand orbitals will be discussed separately for each compound but for sandwich compounds with two C_5 ring ligands the conditions for such overlap are generally poor so the mixing is very weak. Apart from the computational results giving very high metal d coefficients for these orbitals, this is also indicated by the high $R_{2/1}$ values which are significantly higher for these bands than for any other part of the spectrum. Though, in the indenyl complexes, there are evidently three metal-based ionizations in accord with the d^6 formalism for these molecules, the d-band structure differs in the iron and ruthenium compounds from that of the analogous cyclopentadienyl compound, indicating that there is a difference in the metal–ligand interaction which is independent of the molecular symmetry. It seems reasonable to look for a common cause for these differences.

The second region of the spectrum, that containing bands B to D, is, as in the case with the cyclopentadienyl compounds, assigned to ionization from orbitals of ligand π character. These bands in general have rather lower $R_{2/1}$ values than bands A and A′. It is apparent that three of the indenyl π orbitals ionize in this region.

The remaining region of the spectra consists of ionizations from the lower π levels of the rings, the ring σ electrons, and in the case of $[Mn(\eta^5-C_9H_7)(CO)_3]$ carbonyl ionizations.

More detailed spectral assignment will be carried out after discussion of the results of the calculations. Extended-Hückel calculations were carried out on the series of molecules in order to obtain an approximation to the m.o. composition. The sum of the squares of the d-orbital coefficients in particular m.o.s. was correlated with the $R_{2/1}$ value of the corresponding band, which is strongly dependent on the d content of the orbital from which it arises,[33,34] in order to aid assignment. Otherwise the calculations were used to devise schematic energy-level schemes and provide easily visualized orbitals.

Table 2. Vertical ionization energies (eV), band intensities, and assignments for $[Mn(\eta^5-C_9H_7)(CO)_3]$, $[Fe(\eta^5-C_9H_7)_2]$, $[Ru(\eta^5-C_9H_7)_2]$, and $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$

			Intensities			
Complex	Band	Vertical i.e.	He I	He II	$R_{2/1}$	Assignment
$[Mn(\eta^5-C_9H_7)(CO)_3]$	A	7.91	1	1	1	$xz–\pi_5, x^2-y^2, z^2$
	B	8.52	0.85	0.56	0.66	$\pi_5 + yz + xz$
	C	9.42	0.82	0.43	0.53	$\pi_4 + xz$
	D	10.48	0.97	0.40	0.41	π_3
	Other	11.44				
		11.89				
		12.48				
		13.10				
		14.23				
		15.44				
$[Fe(\eta^5-C_9H_7)_2]$	A	6.50, 6.65	1	1	1	$xy - \pi_5, x^2 - y^2$
	A′	6.97	0.40	0.57	1.43	z^2
	B	7.89	1.41	0.93	0.66	$\pi_5 + xy$
	B′	8.10				$\pi_5 + yz$
	C	8.90	1.77	1.01	0.57	$\pi_4, \pi_4 + xz$
	D	9.96	1.60	0.99	0.62	$\pi_3 \times 2$
	Other	11.38				
		12.09				
		12.76				
		13.78				
		15.14				
$[Ru(\eta^5-C_9H_7)_2]$	A	6.85	1	1	1	$xy - \pi_5$
	A′	7.34	1.44	1.88	1.31	$z^2, x^2 - y^2$
	B	7.92	2.30	1.59	0.69	$xy + \pi_5$
	B′	8.24				$yz + \pi_5$
	C	8.88	1.50	0.92	0.61	π_4
	C′	9.22				$xz + \pi_4$
	D	10.04	1.65	1.16	0.70	$\pi_3 \times 2$
	D′	10.24				
	Other	11.28				
		12.01				
		12.68				
		13.69				
		15.02				
$[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$	A	6.64	1	1	1	$xy - \pi_5$
	A′	6.98	1.53	2.36	1.54	$z^2, x^2 - y^2$
	B	7.53	2.10	1.43	0.68	$\pi_5 + e_1^- + xy$
	B′	7.82				$\pi_5 - e_1^- + yz$
	C	8.56	0.88	0.73	0.83	$\pi_4 + e_1^+$
	C′	9.09	1.27	0.71	0.56	$\pi_4 - e_1^+ + xz$
	D	9.85	1.02	0.64	0.63	π_3
	D′	10.32				C_5Me_5
	Other	11.03				
		11.73				
		12.34				
		13.40				
		14.23				
		15.44				

$[C_9H_7]^-$.—The indenyl anion possesses nine π orbitals, five of which are filled. They are shown in projection in Figure 6. The three highest-lying occupied π m.o.s, π_5, π_4, and π_3, resemble the degenerate e_1 highest occupied molecular orbital (h.o.m.o.) of the cyclopentadienyl anion in that they possess one nodal plane cutting through the C_5 ring, thus they are of appropriate symmetry to interact with the d_{xz} and d_{yz} orbitals of a metal fragment. Orbital π_5 is more localized on the C_5 ring than orbital π_3, consequently it is likely to have greater overlap with metal orbitals when the metal is positioned to bond to the C_5 ring. Together with its closer proximity in energy to the metal orbitals, we anticipate that π_5 will mix more strongly with d_{yz} than with π_3.

An important distinction between π_5 and the corresponding $[C_5H_5]^-$ orbital is that π_5 has very little density on the bridgehead atoms 8 and 9 of the five-membered ring.

$[Mn(\eta^5-C_9H_7)(CO)_3]$.—The bonding in this molecule is discussed in terms of the combination of a $[Mn(CO)_3]^+$ unit with an indenyl ion $[C_9H_7]^-$. The electronic structure of the $[Mn(CO)_3]^+$ fragment has been discussed for the compound $[Mn(\eta-C_5H_5)(CO)_3]$.[31,32] In this d^6 fragment the metal electrons occupy orbital of e and a_1 symmetry (principally d_{xy}, $d_{x^2-y^2}$, and d_{z^2}) which are involved in back donation to the carbonyl groups; there are available two low-lying empty orbitals of e symmetry, primarily d_{xz} and d_{yz} in character, which

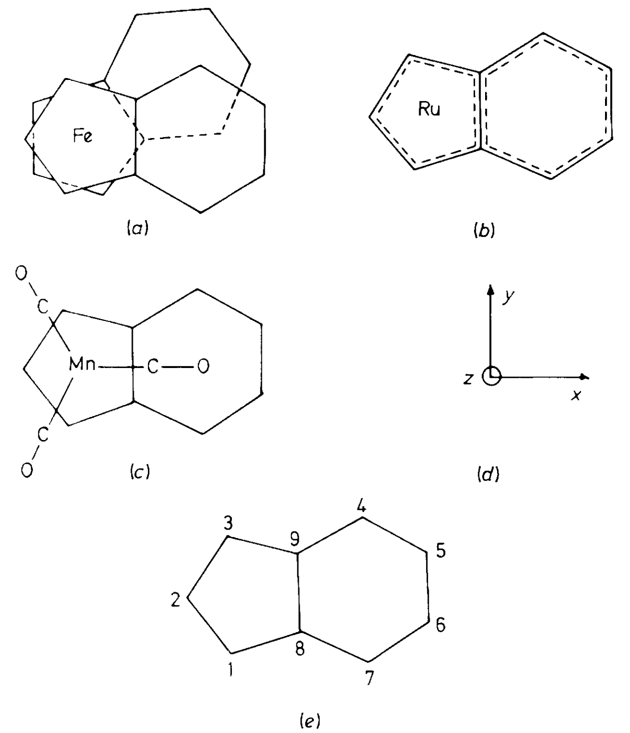

Figure 5. Structures of (*a*) [Fe(η^5-C_9H_7)$_2$], (*b*) [Ru(η^5-C_9H_7)$_2$], and (*c*) [Mn(η^5-C_9H_7)(CO)$_3$]; (*d*) co-ordinate system assumed for calculations; (*e*) labelling of carbon atoms on the indenyl ligands

have the ability to act as acceptor orbitals. The remaining orbitals, mainly of carbonyl character, are either lower or higher in energy and unlikely to be perturbed by further bonding of the [Mn(CO)$_3$]$^+$ unit.

Figure 7 shows the orbital-energy sequence predicted by the calculations for [Mn(η^5-C_9H_7)(CO)$_3$] and Figure 8 presents key m.o.s. The bonding interaction between the [Mn(CO)$_3$]$^+$ fragment and the indenyl ion mainly involves the unoccupied orbitals of Mn d character and the top two orbitals (π_5 and π_4) of the indenyl anion, π_3 being involved to a smaller extent. The d_{xy} orbital, of a'' symmetry, is also significantly perturbed by the interaction, whereas the d_{z^2} and $d_{x^2-y^2}$ orbitals, of a' symmetry, are less affected. The calculaton places the three a'' basis orbitals, d_{xy}, d_{yz}, and π_5, close in energy and consequently they mix strongly; orbital 40 has bonding interactions between π_5 and a hybrid of d_{xy} and d_{yz}, whereas orbital 37 appears weakly anti-bonding with respect to metal–ring interaction but retains metal carbonyl bonding characteristics. This is in contrast to the bonding in [Mn(η-C_5H_5)(CO)$_3$] where the d_{xy} and $d_{x^2-y^2}$ orbitals remain effectively degenerate in the higher local rotational symmetry of this molecule.

We can trace this mixing back to the interaction between d_{xy} and π_5. The absence of significant probability density on atoms 4 and 5 of the C_5 ring results in d_{xy} having a significant overlap with π_5. In an M–C_5H_5 interaction, the corresponding overlap is zero, as the analogous ligand orbital is of e_1 symmetry whereas the d_{xy} orbital is e_2.

Orbitals 38 and 39 involve back donation from the metal $d_{x^2-y^2}$ and d_{z^2} orbitals to the carbonyl π orbitals, and are similar to those of the Mn(CO)$_3$ fragment.

Orbital 41, of a' symmetry, consists of a bonding interaction between the metal d_{xz} orbital and π_4 or the indenyl ligand. The next lowest π orbital, π_3, does not appear to mix much with the metal and contributes to orbitals 43 and 44; σ π separability having been lifted in the complex, the calculation mixes arbitrarily the π orbital with a nearby σ orbital.

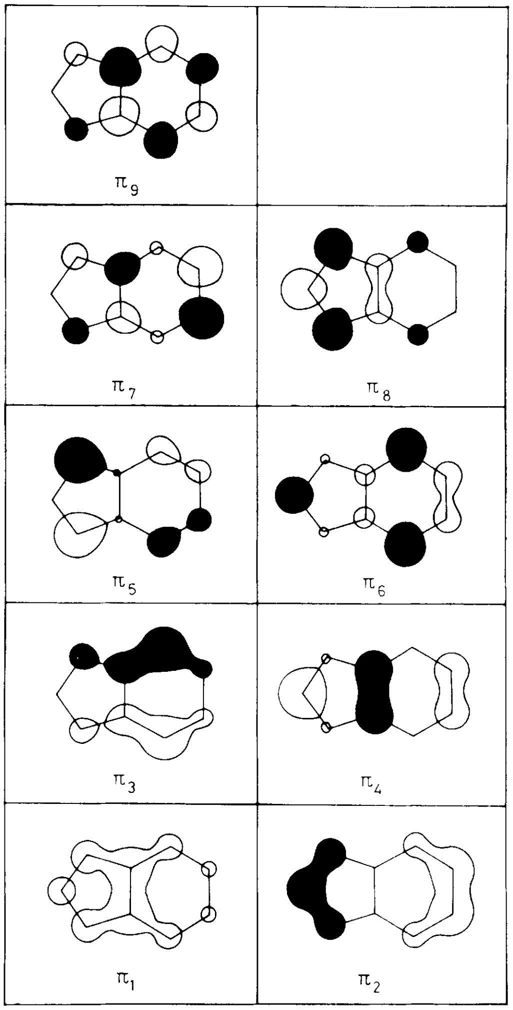

Figure 6. Projection on xy plane of the indenyl π orbitals

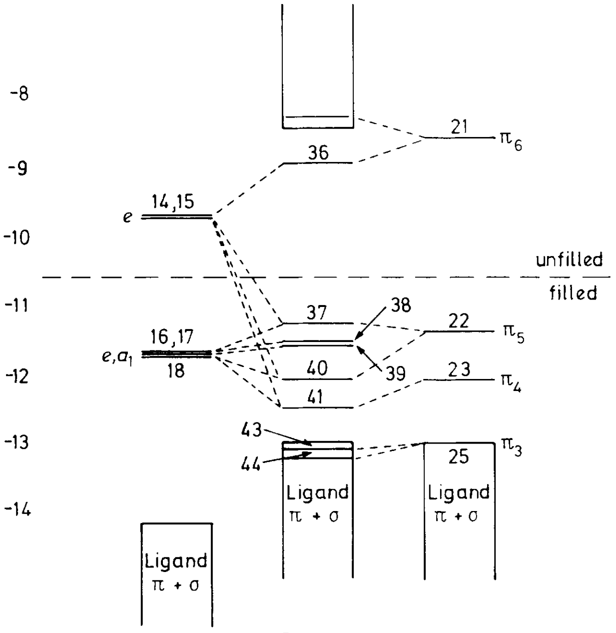

Figure 7. Schematic m.o. diagram for [Mn(η^5-C_9H_7)(CO)$_3$]. Energy scale in eV

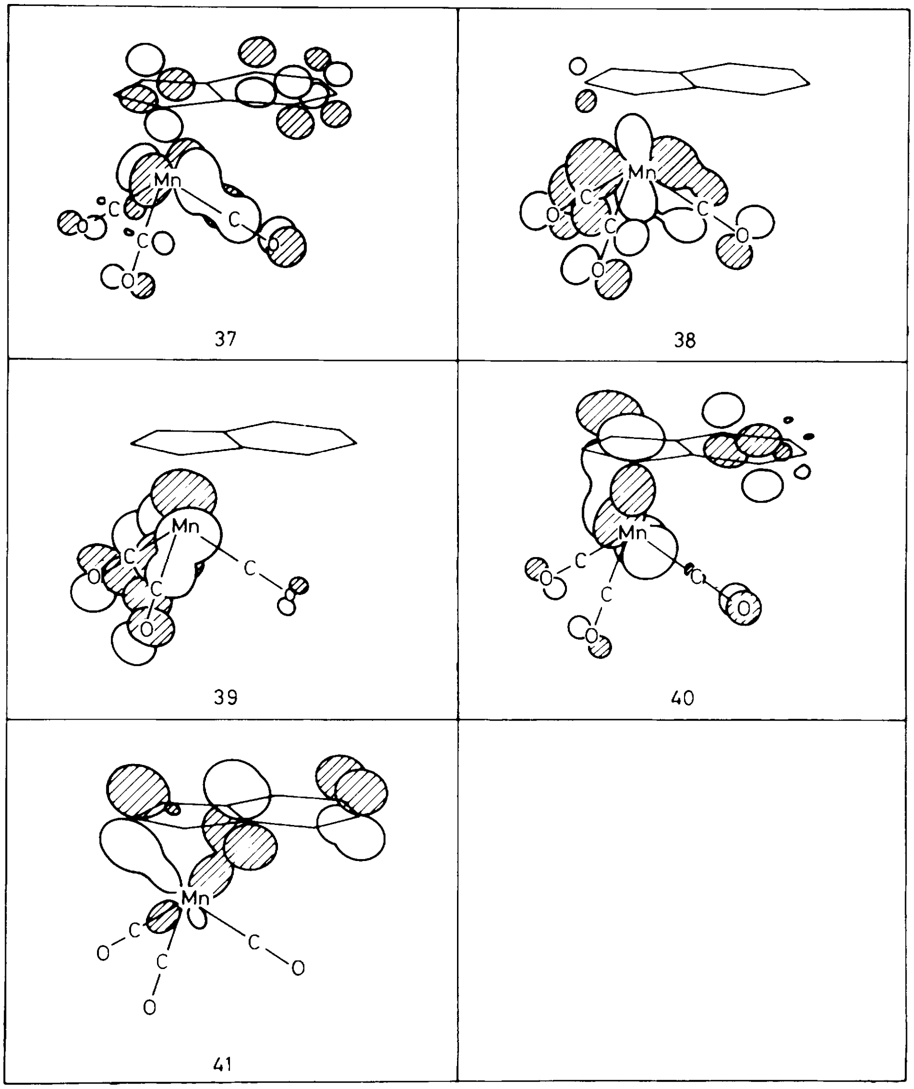

Figure 8. The five top filled m.o.s of [Mn(η^5-C_9H_7)(CO)$_3$]

In assigning the spectrum we assume that all three metal ionizations, *i.e.* those from orbitals 37, 38, and 39, comprise band A. Band B is assigned to orbital 40 (π_5), C to orbital 41 (π_4), and D to ionization of π_3. Part of the reason for this assignment is that we expect, on passing from C_5H_5 to C_9H_7, π_3 to be more stable and π_5 less stable than the top filled π levels of the cyclopentadienyl anion; π_4 should be rather similar in energy. Extended Hückel calculations on the two anions place π_4 within 0.1 eV of the C_5H_5 e_1 orbitals. The first ligand band of [Mn(η-C_5H_5)(CO)$_3$] has an i.e. of 9.90 eV, making the assignments of bands at 8.52, 9.42, and 10.48 eV to π_5, π_4, and π_3 respectively the most acceptable choice. This assignment also fits best with the intensity data and with energy shifts of ionization bands between related complexes as is discussed later.

[Fe(η^5-C_9H_7)$_2$] *and* [Ru(η^5-C_9H_7)$_2$].—In the bis(indenyl) complexes the π orbitals of the two indenyl fragments may be combined in symmetric and antisymmetric combinations with respect to the mirror plane, *xy*. In the hypothetical absence of the metal atom, the symmetric combinations are slightly more stable than the antisymmetric ones, but in the bis(indenyl) molecule this situation is reversed as it is the antisymmetric ones which can combine with the metal d_{xz} and d_{yz} orbitals, which are the best directed *d* orbitals for overlap with the ligand π set. An energy-level diagram for the molecule is given in Figure 9 and seven of the resultant orbitals for [Fe(η^5-C_9H_7)$_2$] are shown in Figure 10. Again we find that the calculation predicts mixing of the d_{xy} orbital with π_5; in this case it is the symmetric combination of the two π_5 orbitals, of b_1 symmetry, that is involved. The d_{xy} orbital remixes the carbon p_π orbitals; orbital 52, which is bonding between d_{xy} and the ligand, has contributions mainly from carbons 1 and 3, whereas orbital 53, has a higher weight from carbons 4—7 than in π_5 itself. The orbitals calculated for [Ru(η^5-C_9H_7)$_2$] are similar, but they differ slightly in the energy ordering in that the d_{z^2} orbital lies below the antibonding combination of d_{xy} with the π_5 orbitals.

It is clear from the $R_{2/1}$ values, as noted above, that the first three ionizations are from orbitals largely localized on the metal. The first band, A, shows a splitting (for ferrocene the two e_2 orbitals are degenerate and we have a single band). The ionization at 6.50 eV is assigned to orbital 50, the d_{xy} orbital being destabilized by interaction with the ligand. That at 6.65 is assigned to $d_{x^2-y^2}$, orbital 51, and A′ to d_{z^2}, orbital 49. The assignment of A′ to d_{z^2} is made on the basis of its characteristically high $R_{2/1}$ value and by analogy with the i.e. ordering found in ferrocene. The order of ionization energies differs from the order of orbital energies: d_{z^2} is calculated to have the highest orbital energy. A similar inversion occurs in ferrocene, where the

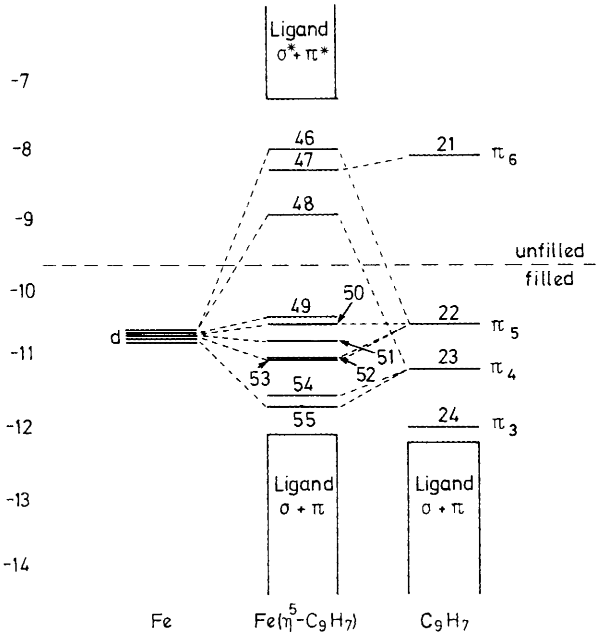

Figure 9. Schematic m.o. diagram for $[Fe(\eta^5-C_9H_7)_2]$. Energy scale in eV.

e_2 orbitals have lower i.e. than d_{z^2}, though calculation places the d_{z^2} orbital above the d_{xy} and $d_{x^2-y^2}$ orbitals.

In the i.e. region where the upper ligand π orbitals ionize assignment is straightforward. Band B + B′ is assigned to orbitals 52 and 53, band C + C′ to 54 and 55; D + D′ is assigned to ionizations from the π_3 levels of the indenyl ligands. In the case of the p.e. spectrum of $[Fe(\eta-C_5H_5)_2]$ the ionization bands arising from the symmetric and antisymmetric orbitals overlap.

The p.e. spectrum of $[Ru(\eta^5-C_9H_7)_2]$ is assigned in a similar manner (see Table 2). However, in this case, interaction between metal and ligand is more marked than in the case of $[Fe(\eta^5-C_9H_7)_2]$. The separation between the ionizations of d_{xy} and $d_{x^2-y^2}$ is greater, as is the splitting of B from B′ and C from C′. This has its analogy in the metallocene spectra, where the $e_{1''}/e_{1'}$ splitting is greater for ruthenocene than ferrocene. Ruthenium's more extended 4*d* orbitals are capable of greater interaction with the ligand orbitals than the relatively contracted 3*d* orbitals of iron.

$[Ru(\eta^5-C_9H_7)(C_5Me_5)]$.—The main bonding orbitals of the pentamethylcyclopentadienyl group are the e_1 pair of degenerate orbitals. One component e_1^+ is symmetric with respect to the symmetry plane of the whole molecule, as is π_4 of the indenyl ligand. The other component e_1^- is antisymmetric in this sense as are π_3 and π_5. The amount orbitals from the two rings mix is not symmetry determined in contrast to the bis(indenyl) sandwiches so assignment is less straightforward.

The *d* bands of the p.e. spectrum of $[Ru(\eta^5-C_9H_7)(\eta-C_5Me_5)]$ are similar in structure to those of $[Ru(\eta^5-C_9H_7)_2]$ though they occur at lower ionization energy. We assign A to ionization from an antibonding combination of d_{xy} with π_5, and A′ to ionization from d_{z^2} and $d_{x^2-y^2}$. The splitting of A from A′ is less than in the bis(indenyl) compound presumably because the d_{xy} orbital is interacting with one indenyl ligand rather than two.

Bands B and B′ and C and C′ are more separated from each other than in the spectrum of $[Ru(\eta^5-C_9H_7)_2]$. This results from unequal contributions from the two ligands. Band B we assign to ionization from an in-phase combination of π_5 and e_1^- *and* d_{xy}; band B′ is assigned to an out-of-phase combination of π_5 and e_1^- and d_{yz}. They have very similar shifts from their corresponding i.e. in the spectrum of $[Ru(\eta^5-C_9H_7)_2]$ (B by 0.39 eV and B′ by 0.42 eV) suggesting rather similar contributions from the C_5Me_5 ligand, if anything that to the orbital giving rise to B′ being the larger. Band C we assign to an in-phase contribution of π_4 and e_1^+ and C′ to an out-of-phase combination of π_4 and e_1^+ combined with the d_{xz} orbital. We must recognize that, because of the low symmetry, the d_{xz} orbital can mix with both in-phase and out-of-phase contributions; the $R_{2/1}$ values indicate a larger metal contribution to the orbital giving rise to C. In the case of C and C′ the shifts in i.e. from $[Ru(\eta^5-C_9H_7)_2]$ differ from one another (C shifts by 0.32 eV and C′ by 0.13 eV). This suggests that the orbital giving rise to C is predominantly C_5Me_5 in character while that giving rise to C′ is more indenyl in character.

Whereas band D is assigned to π_3, D′ lies in a region where the C_5Me_5 ligand ionizes[30] and is probably due to such a process.

Table 3. Ionization energies (eV) of the *d* bands and average i.e. of the ligand π bands in d^6 cyclopentadienyl and indenyl compounds

	d i.e.				
Compound	*xy*	$x^2 - y^2$	z^2	Average π i.e.	Ref.
$[Fe(\eta-C_5H_5)_2]$	6.88	6.88	7.23	9.03	14
$[Fe(\eta-C_5H_4Me)_2]$	6.72	6.72	7.06	8.85	14
$[Fe(\eta-C_5Me_5)_2]$	5.88	5.88	6.28	7.69	30
$[Fe(\eta^5-C_9H_7)_2]$	6.50	6.65	6.97	8.95	
$[Ru(\eta-C_5H_5)_2]$	7.45	7.45	7.45	9.39	14
$[Ru(\eta-C_5H_4Me)_2]$	7.25	7.25	7.25	9.00	14
$[Ru(\eta-C_5Me_5)_2]$	6.78	6.78	6.78	8.15	*
$[Ru(\eta^5-C_9H_7)_2]$	6.85	7.34	7.34	9.09	
		Average *d* i.e.			
$[Mn(\eta-C_5H_5)(CO)_3]$		8.17		9.90	32
$[Mn(\eta-C_5H_4Me)(CO)_3]$		8.00		9.57	32
$[Mn(\eta-C_5Me_5)(CO)_3]$		7.58		8.72	32
$[Mn(\eta^5-C_9H_7)(CO)_3]$		7.91		9.47	

* T. P. Chadwick, J. C. Green, and D. O'Hare, unpublished work

Conclusions

The main bonding interaction in the indenyl compounds investigated can be visualized as electron transfer from the filled π orbitals of the indenyl anion to the empty *d* orbitals of the central metal ion. All the studied compounds are d^6 complexes in which the d_{xz} and d_{yz} orbitals are ready to accept electron density from the indenyl group acting as a π donor.

In addition to these bonding interactions, there is a repulsive interaction between the filled d_{xy} orbital and the ligand h.o.m.o., π_5. This interaction is absent in cyclopentadienyl compounds as the higher symmetry forbids overlap between the analogous orbitals. It results in the indenyl compounds showing larger *d*-band splittings than the corresponding cyclopentadienyl compounds and is partly the reason why the indenyl compounds exhibit lower first ionization energies. A general comparison of i.e. for the indenyl and related compounds is given in Table 3.

It is also the case that the non-bonding *d* orbitals (z^2 and $x^2 - y^2$) ionize at lower energies in the indenyl compounds than the cyclopentadienyl compounds (Table 3). Indenyl can therefore be regarded as more electron donating than cyclopentadienyl in these d^6 compounds. It is clearly a weaker donor than pentamethylcyclopentadienyl and appears to be electronic-

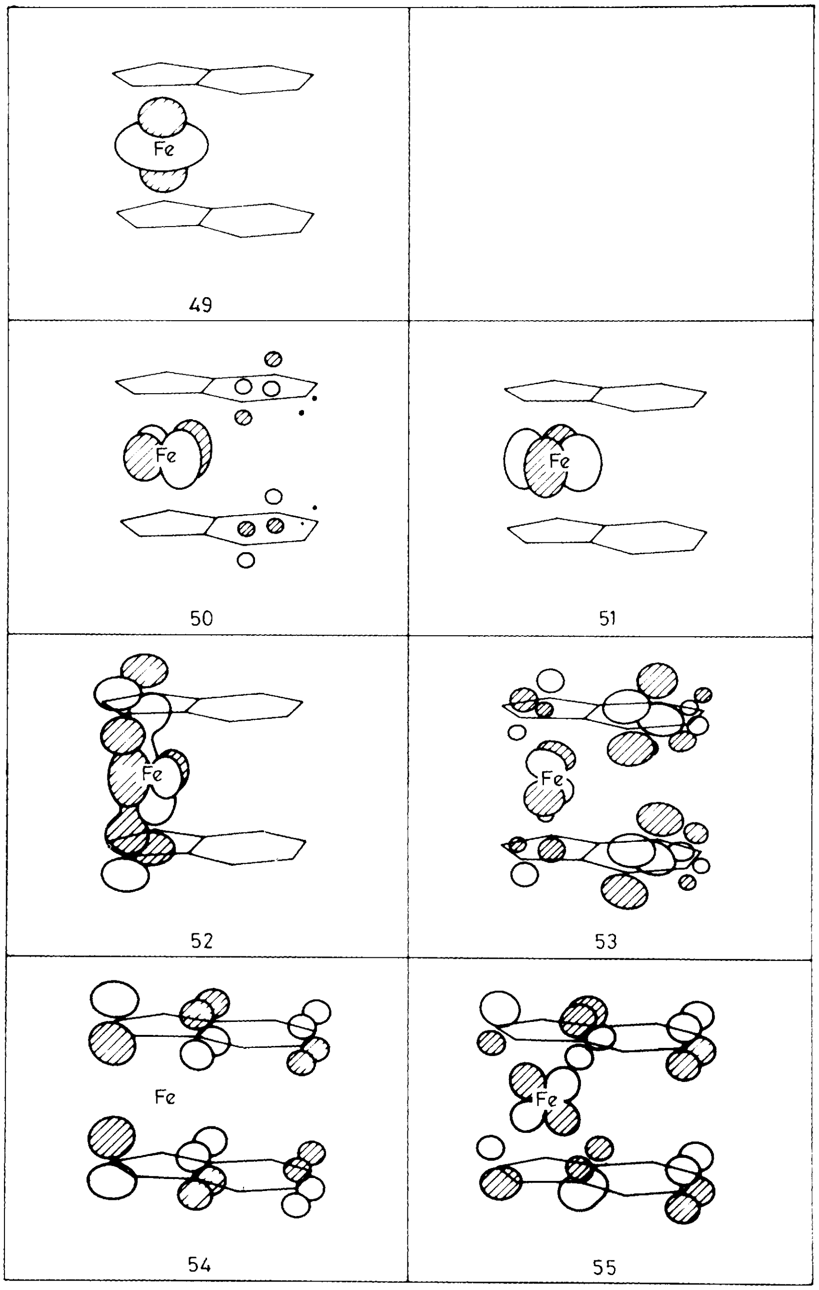

Figure 10. The seven top filled m.o.s of [$Fe(\eta^5\text{-}C_9H_7)_2$]

ally most similar to methylcyclopentadienyl in its electron-releasing ability. In [$Ru(\eta^5\text{-}C_9H_7)_2$], however, the extra *d*-orbital splitting brings the first i.e. quite close to that of [$Ru(\eta\text{-}C_5Me_5)_2$].

Cotton–Kraihanzel force contants for the CO stretching frequencies have been compared for [$Mn(\eta\text{-}C_5H_5)(CO)_3$] ($K = 15.75$, $K_c = 0.35$) and [$Mn(\eta\text{-}C_9H_7)(CO)_3$] ($K = 15.73$, $K_c = 0.46$).[15] The difference in the stretching force constant is small indicating little difference in the back-donating ability of the Mn in these two compounds though the direction of what change there is does indicate a greater electron density on the metal in the case of the indenyl compound.

The electrochemistry of [$Fe(\eta^5\text{-}C_9H_7)_2$][35] [$E_{\frac{1}{2}} = 0.21$ *vs.* saturated calomel electrode (s.c.e.)] shows that it is easier to oxidize than ferrocene ($E_{\frac{1}{2}} = 0.49$ *vs.* s.c.e.). Electrochemical measurements of the oxidation potential of [$Ru(\eta\text{-}C_5H_5)_2$] indicate that it undergoes a two-electron, one-step, irreversible oxidation in acetonitrile at *ca.* 0.65 V (*vs.* s.c.e.).[36] Cyclic voltammetric studies on [$Ru(\eta^5\text{-}C_9H_7)_2$] in ethanol indicate an irreversible oxidation at 0.41 V[37] again indicating a relative ease of oxidation of the bis(indenyl) complex over the metallocene analogue. This is in part due to the greater electron density on the metal, but also, it should be noted, that it is the d_{xy} orbital from which an electron is being removed, and this is destabilized by the antibonding interaction with π_5.

It is also of interest to compare the ligand π-ionization energies for the various compounds. The average i.e., for the three bands, B, C, and D, are given in Table 3 together with the i.e. of the cyclopentadienyl e_1 orbitals in the analogous compounds. The averages are higher for the compounds of Ru than of Fe, in accord with the general observation that ruthenium-ligand interactions are stronger than iron–ligand interactions. Both the cyclopentadienyl and indenyl ligand levels are more stabilized in the 'half-sandwich' manganese carbonyl compounds than in the full sandwich compounds. The π-acceptor ability of the carbonyl groups enhances the electron-withdrawing capacity of the metal; the $Mn(CO)_3$ fragment is a better electron acceptor than either $M(\eta-C_5H_5)$ or $M(\eta-C_9H_7)$ and this is well reflected in the ionization energies of ligand orbitals donating electron density into these fragments.

However these results contrast with an earlier interpretation of the i.r. spectra of bis(indenyl)iron and bis(indenyl)ruthenium.[38] It was suggested that the metal–ring force constants were lower for these compounds than for their cyclopentadienyl analogues, and this was attributed to the electron-withdrawing character of the arene ring in the indenyl group. Our results, suggest, to the contrary, that the arene ring is able to contribute to some extent to the flow of electron density from the five-membered ring of the indenyl group to the metal atom.

References

1 J. W. Faller, R. H. Crabtree, and A. Habib, *Organometallics*, 1985, **4**, 929.

2 A. N. Nesmeyanov, U. S. Ustynyuk, L. G. Makarova, V. G. Adrianov, Y. T. Struchkov, S. Andrae, Y. A. Ustynyuk, and S. G. Malyunga, *J. Organomet. Chem.*, 1978, **159**, 189.

3 R. M. Kowaleski, A. L. Rheingold, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.*, 1986, **108**, 2461.

4 T. C. Forschner, A. R. Cutler, and R. K. Kullnig, *Organometallics*, 1987, **6**, 889.

5 R. T. Baker and T. Tulip, *Organometallics*, 1986, **5**, 839; J. S. Merola, R.-T. Kacmarcik, and D. Van Engen, *J. Am. Chem. Soc.*, 1986, **108**, 329; T. B. Marder, J. C. Calabrese, D. C. Roe, and T. H. Tulip, *Organometallics*, 1987, **6**, 2012.

6 M. E. Rerek, L-N. Ji, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 1983, 1208.

7 H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, 1966, **88**, 1657.

8 M. E. Rerek and F. Basolo, *Organometallics*, 1983, **2**, 372.

9 J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.

10 O. Crickton, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 167.

11 M. E. Rerek and F. Basolo, *J. Am. Chem. Soc.*, 1984, **106**, 5908.

12 O. Crickton, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 1208.

13 D. L. Kerschner and F. Basolo, *J. Am. Chem. Soc.*, 1987, **109**, 7397.

14 J. H. Osiecki, C. J. Hoffman, and D. P. Hollis, *J. Organomet. Chem.*, 1965, **3**, 107.

15 R. B. King and A. Efraty, *J. Organomet. Chem.*, 1970, **23**, 527.

16 P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.

17 A. R. Kudinov, M. I. Rybinskaya, Yu. T. Strukov, A. I. Yanovskii, and P. V. Petrovskii, *J. Organomet. Chem.*, 1987, **336**, 187.

18 T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, 1984, **3**, 274.

19 N. Oshima, K. Mukai, and Y. Moro-Oka, *Chem. Lett.*, 1984, 1611.

20 J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, 1956, **9**, 373.

21 J. Trotter, *Acta Crystallogr.*, 1958, **11**, 355.

22 A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, 1963, **16**, 118.

23 M. B. Honan, J. L. Atwood, I. Bernal, and W. A. Herrmann, *J. Organomet. Chem.*, 1979, **179**, 403.

24 G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, 1959, **12**, 28.

25 N. C. Webb and R. E. Marsh, *Acta Crystallogr.*, 1967, **22**, 382.

26 D. P. Freyberg, J. L. Robbins, K. N. Raymond, and J. C. Smart, *J. Am. Chem. Soc.*, 1979, **101**, 892.

27 S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, 1972, 1847.

28 J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, M. Husain, and K. Siegbahn, *J. Chem. Phys.*, 1972, **57**, 1185.

29 S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, 1974, 356.

30 C. Cauletti, J. C. Green, M. R. Kelly, P. Powell, J. van Tilborg, J. Robbins, and J. Smart, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **19**, 327.

31 D. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, 1976, **98**, 50.

32 D. C. Calabro, J. L. Hubbard, C. H. Blevins II, A. C. Campbell, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1981, **103**, 6839.

33 J. C. Green, *Struct. Bonding (Berlin)*, 1981, **43**, 37.

34 G. Cooper, J. C. Green, and M. P. Payne, *Mol. Phys.*, 1988, **63**, 1031.

35 P. M. Treichel, J. W. Johnson, and K. P. Wagner, *J. Organomet. Chem.*, 1975, **88**, 227.

36 T. Kuwna, D. E. Bublitz, and G. Hoh, *J. Am. Chem. Soc.*, 1960, **82**, 5811; D. E. Bublitz, G. Hoh, and T. Kuwana, *Chem. Ind. (London)*, 1959, 635.

37 D. N. Hendrickson, Y. Sohn, W. H. Morrison, and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 808.

38 E. Samual and M. Bigorgne, *J. Organomet. Chem.*, 1971, **30**, 235.

Received 20th February 1989; Paper 9/00786E