Paramagnetic Transition-metal Carbonyls and Cyanides. Part 10.† Electron Addition to Various Carbonyl(η^5-cyclopentadienyl)metal Halides; an Electron Spin Resonance Study

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Exposure of [Mo(cp)(CO)$_3$I], [W(cp)(CO)$_3$I], [Fe(cp)(CO)$_2$Cl], [Fe(cp)(CO)$_2$I], and [Mn(cp)(CO)$_3$] (cp = η^5-cyclopentadienyl) either as the pure compounds or as dilute solutions in solvents that facilitate electron capture, to ^{60}Co γ-rays at 77 K, gave the corresponding anions. All the halides had e.s.r. spectra dominated by large hyperfine coupling to the halogen nuclei, characteristic of electron capture into the metal–halogen σ^* orbitals. This is expected for the iron complexes, which are formally $3d^6$, but surprising for the Mo and W complexes which are formally $3d^4$. No hyperfine features from coupling to metal nuclei were observed for the iron or tungsten complexes, but well defined features from $^{95/97}$Mo nuclei were observed in spectra of irradiated single crystals of [Mo(cp)(CO)$_3$I]. Analysis of this coupling together with the g-tensor components supports the σ^* assignment, suggesting that the $3d_{z^2}$ orbital is the major metal orbital involved. On annealing, the molybdenum complex anion was converted into another complex, exhibiting smaller hyperfine coupling to iodine which is thought to be the relaxed structure for [Mo(cp)(CO)$_3$I]$^-$ with a π^* semi-occupied molecular orbital (s.o.m.o.) rather than the σ^* (s.o.m.o.). In contrast, [Fe(cp)(CO)$_2$Cl]$^-$ and the iodide gave an axially symmetric centre with no halogen hyperfine coupling, thought to be [Fe(cp)(CO)$_2$]. This was formed together with a more stable protonated species, possibly [FeH(cp)(CO)$_2$]$^+$, which exhibited well defined proton hyperfine coupling (^{2}H coupling when CD$_3$OD was the solvent). Possible structures for this species are considered. The manganese carbonyl complexes, studied for comparative purposes, gave well defined anions, but we were unable to obtain clear-cut results for the species [Mn(cp)(CO)$_2$]$^-$, isoelectronic with the corresponding iron derivative.

This is a continuation of our studies of paramagnetic complexes formed mainly by electron addition to diamagnetic precursors at 77 K in rigid matrices. The solvents 2-methyltetrahydrofuran (mthf) and [^{2}H$_4$]methanol (CD$_3$OD), which are ideal for this purpose, have been used. In principle, the pure compounds give, on irradiation, equal yields of electron-loss and electron-capture centres, and use of these solvents was expected to enable us to make unambiguous assignments. In practice, however, features from the pure compounds are frequently so poorly defined that analysis is impossible.

We have already studied [V(CO)$_6$],[1] [Mn(CO)$_5$],[2] [Co(CO)$_4$],[3] [Fe(CO)$_5$]$^-$, and [Fe(CO)$_4$]$^-$ [4] by e.s.r. spectroscopy. Preston and Morton and their co-workers have also studied [V(CO)$_6$] [5] and [Mn(CO)$_5$],[6] and have prepared [Fe(CO)$_5$]$^+$ using [Cr(CO)$_6$] crystals or sulphuric acid as matrices.[7]

Some time ago we established that electron addition to [Mn(CO)$_5$Cl], [Mn(CO)$_5$Br], and [Mn(CO)$_5$I] gave anions having (s.o.m.o.) semi-occupied molecular orbitals comprising the $3d_{z^2}$ metal orbital and the p_z halogen orbitals.[8] This work was recently extended to include [Cr(CO)$_5$I]$^{2-}$, [Mo(CO)$_5$I]$^{2-}$, [W(CO)$_5$I]$^{2-}$, [Re(CO)$_5$Br]$^-$, and [Re(CO)$_5$I]$^-$.[9]

The only paramagnetic mononuclear metal carbonyl containing a η^5-cyclopentadienyl (cp) ligand studied in this way, to our knowledge, is [Co(cp)(CO)$_2$]$^-$, formed by electron addition to the neutral complex in mthf at 77 K.[10] In the present study, we have attempted to prepare the anion of [Mn(cp)(CO)$_3$]. However, our major study was of mixed-ligand complexes containing both cyclopentadienyl and halide ligands. Here an added electron has the choice between being strongly associated with the organic ligand or with halogen, and we considered that e.s.r. spectroscopy would give us a clear-cut distinction between these alternatives. The study proved to be particularly interesting in that, not only was the metal–halide bond preferred, but, for the iron complexes, halide ions were lost thermally to give the new complex [Fe(cp)(CO)$_2$]. We have not previously been able to detect halide ion loss from such σ^* complexes.

Experimental

The complex [Mo(cp)(CO)$_3$I] was prepared in quantitative yield by refluxing [{Mo(cp)(CO)$_3$}$_2$] (Strem Chemicals Inc., Danvers, Mass.) with iodine in an inert solvent. Single crystals were grown in the form of thin plates by evaporation of a solution in cyclopentanone over several days. The corresponding tungsten complex, [W(cp)(CO)$_3$I], was prepared by the iodination of the hydride, [WH(cp)(CO)$_3$] in ether. The iron complexes, [Fe(cp)(CO)$_2$I] and [Fe(cp)(CO)$_2$Cl] were prepared by halogenation of [{Fe(cp)(CO)$_2$}$_2$], purchased from Alfa Inorganics Inc., Beverly, Mass. Tricarbonyl(η^5-cyclopentadienyl)manganese, [Mn(cp)(CO)$_3$], was obtained from Strem Chemicals, and used without further purification.

Powdered samples and sealed tubes containing solutions of the complexes in degassed 2-methyltetrahydrofuran (mthf) and [^{2}H$_4$]methanol (CD$_3$OD) were cooled to 77 K and irradiated in a Vickrad ^{60}Co γ-ray source with doses up to *ca.* 2 Mrad. Single-crystal spectra in the case of [Mo(cp)(CO)$_3$I] were recorded over a wide range of orientations. For studies above 77 K, the liquid nitrogen was decanted and the spectrum continuously monitored as the temperature rose. The sample was recooled to 77 K whenever significant changes occurred.

The X-band spectra were measured with a Varian E-109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker BH 12E field probe, standardized with a sample of diphenylpicrylhydrazyl.

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† Part 9, M. C. R. Symons, B. M. Peake, and J. L. Wyatt, *J. Chem. Soc., Dalton Trans.*, 1983, 1171.

Non-S.I. units employed: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

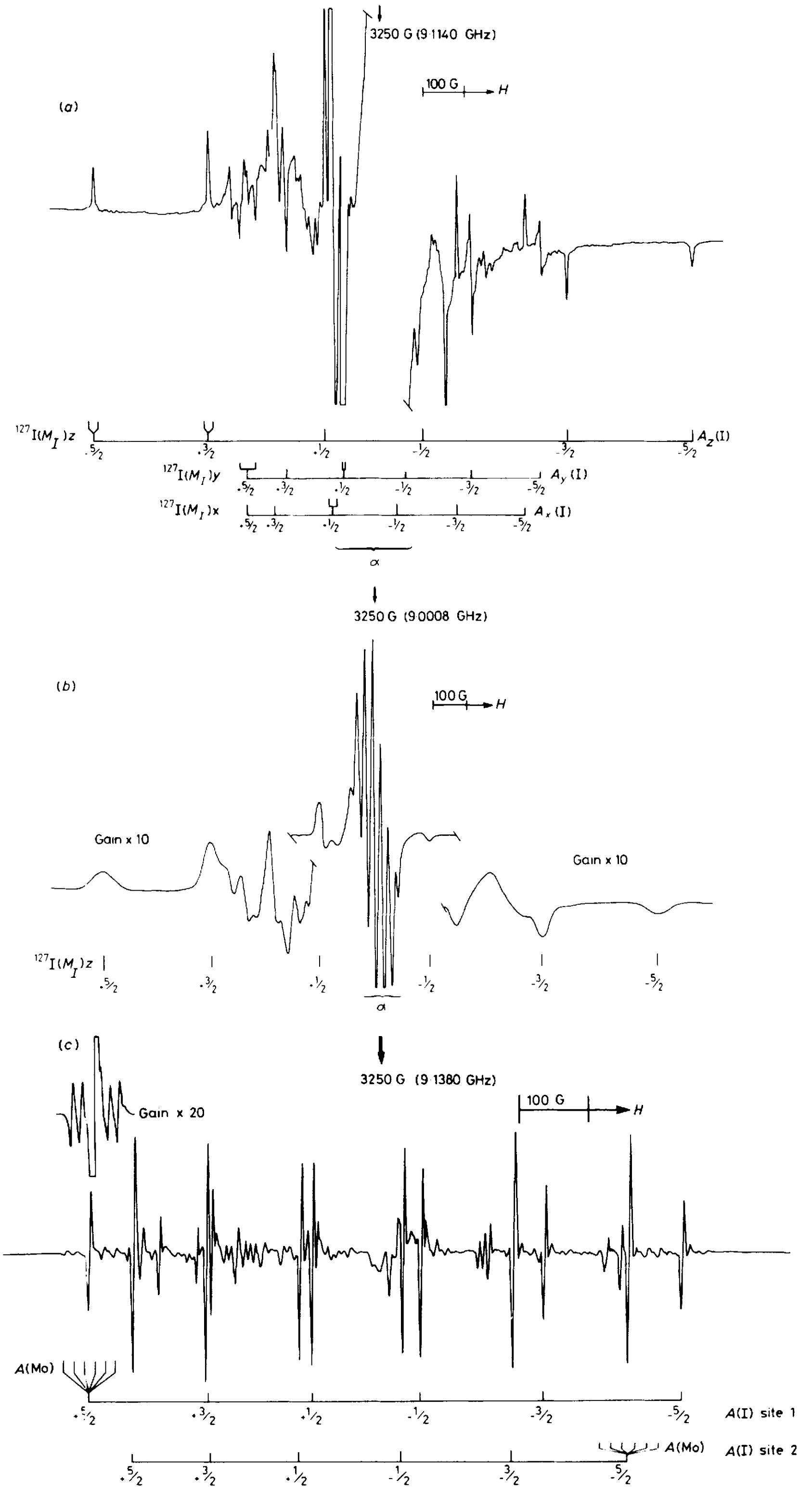

Figure 1. First derivative X-band e.s.r. spectra for [Mo(cp)(CO)$_3$I] after exposure to ^{60}Co γ-rays at 77 K showing features assigned to [Mo(cp)(CO)$_3$I]$^-$ anions: (*a*) powdered [Mo(cp)(CO)$_3$I]; note the molybdenum satellite lines appearing as shoulders especially on the *z* features. Many, but probably not all the small lines are due to ^{95}Mo and ^{97}Mo complexes. Note also the extra doublet splitting on some of the low-field *x* and *y* features and the marked Breit–Rabi shifts; (*b*) dilute solution in mthf; (*c*) single crystal in an arbitrary orientation, showing signals from complexes in the two sites and clear superhyperfine coupling to ^{95}Mo and ^{97}Mo

Table 1. Experimental e.s.r. parameters for metal halide complexes

		g Values			Hyperfine coupling (G)				
					Halogen		Metal		
Complex [a]	Solvent	g_x	g_y	g_z	$A_{\parallel}(z)$	$A_{\perp}$	A_x	A_y	A_z
$[Mo(cp)(CO)_3I]^-$		2.004	1.995	2.002	290	144	16	16	6
	mthf	2.004	1.996	2.002	270	123			
$[W(cp)(CO)_3I]^-$ [b]		2.031	1.997	2.000	335	145			
$[Fe(cp)(CO)_2Cl]^-$	mthf [c]			*ca.* 2.008	*ca.* 55				
$[Fe(cp)(CO)_2I]^-$	mthf	2.008	2.008	2.002	192	82			
$[Mo(CO)_5I]^{2-}$ [d]		2.000	2.000	1.990	235	153			18
$[W(CO)_5I]^{2-}$ [d]		2.001	2.001	1.999	256	164	0 ± 5	0 ± 5	36

[a] In all cases, the paramagnetic centres were formed by electron addition at 77 K. [b] In mthf only the $M_I = +\frac{1}{2}$ feature was detected. [c] Only the $M_I = +\frac{1}{2}$ features (^{35}Cl, ^{37}Cl) were detected. [d] From ref. 9.

Results and Discussion

$[Mo(cp)(CO)_3I]$.—The e.s.r. spectrum for the major species detected when the pure compound was irradiated as a fine powder at 77 K is shown in Figure 1. There are extra features in this spectrum which may be due to the electron-loss centres, including intense central features (α) possibly associated with radicals derived from cyclopentadiene. Unfortunately we have not been able to make any firm assignments. That the main features are due to electron-capture centres is confirmed by the similarity to the spectrum of the major species formed on irradiating solutions in mthf [Figure 1(*b*)]. In this case the features are much broader, indicating considerable variation in the parameters *g* and *A*, but there can be no doubt that the species are essentially the same (Table 1).

The spectra are dominated by an anisotropic sextet assigned to hyperfine coupling to ^{127}I (^{127}I has $I = \frac{5}{2}$, and is 100% abundant). Several extra features are apparent in the powder spectrum, some of which are clearly satellite lines from coupling to $^{95/97}Mo$ nuclei. [Both ^{95}Mo (15.78% abundant) and ^{97}Mo (9.60% abundant) have $I = \frac{5}{2}$: and such similar magnetic moments that these features are superimposed in our spectra.*] There are, however, further features which are not accounted for, as indicated in Figure 1. It is possible that these are two isomers with identical parallel (*z*) coupling but slightly different (*x*) and (*y*) couplings and *g* values, but at present we fail to understand the information contained in these extra features.

In order to check our assignments and the possibility of major deviation of the three tensors from a common set of axes, we have made a brief study of an irradiated single crystal. There were two magnetically distinct radicals per unit cell, and the spectra were so well defined that, in many cases, all the $^{95/97}Mo$ hyperfine components were resolved [Figure 1(*c*)]. A wide range of orientations was studied, and we have satisfied ourselves that the three tensors are indeed nearly coaxial, as expected for the σ* structure described below. Several spectra showed quite intense extra features which were not readily assigned to forbidden transitions made prominent by quadrupole effects. We think that they were due to the electron-loss species, but, as with the powder spectra, they were too poorly defined for a complete analysis.

$[W(cp)(CO)_3I]$.—The spectra for the tungsten derivative were broader (Figure 2) and we were unable to detect well defined satellite features from ^{183}W. The spectra for solutions in mthf were remarkable in that the M_I (^{127}I) $= +\frac{1}{2}$ line was well defined, but all the other features were too broad to be detected. This arises because the $+\frac{1}{2}$ line is, fortuitously, almost isotropic. The result is important, since, if we only had the mthf spectrum available, we could never have recognised it for what it is, and might well have made a completely erroneous assignment.

$[Fe(cp)(CO)_2Cl]$ *and* $[Fe(cp)(CO)_2I]$.—In contrast with these results, the powder spectra for the iron derivatives were poorly defined, but solutions in mthf gave reasonably clear features for the electron-adducts (Figure 3). For $[Fe(cp)(CO)_2Cl]$ in mthf only two features were detected, on the low-field edge of the main spectrum due to solvent radicals. These had the form of parallel lines and their relative intensities were correct for ^{35}Cl and ^{37}Cl features. If we assume that the separation between these features is normal, we can use this and the magnetic moments of the isotopes to calculate an approximate value for $A_{\parallel}$. The result [$A_{\parallel}(^{35}Cl) = 55$ G] gives $g_{\parallel} \simeq 2.008$. Unfortunately, the high-field ($-\frac{3}{2}$) line was too weak to be resolved in the tail of the spectrum due to organic radicals. On annealing, this centre was lost and species (I) was formed as for the iodide discussed below.

The six parallel and perpendicular features for the iodide are readily analysed, giving the data included in Table 1. On careful annealing, these features, together with those due to solvent radicals were lost, and features due to two novel iron complexes appeared [(I) and (II) in Figure 3(*b*)]. Species (I) is axially symmetric, with $g_{\perp} \gg g_{\parallel} \simeq 2.0023$, as is normally observed for a species having a - - - $(d_{z^2})^1$ configuration [11] (Table 2). The other species (II) has a similar form for its *g*-tensor components, but the shift for $g_{\perp}$ is much smaller, and both parallel and perpendicular features show a well defined doublet splitting. That this is due to hyperfine coupling to a single proton was established by the appearance of a triplet centred on the same value for $g_{\perp}$, having a splitting exactly equal to that calculated for coupling to deuterium when solutions in CD_3OD were studied [Figure 3(*c*)].

In contrast, when the $[Mo(cp)(CO)_3I]^-$ complex in mthf was annealed, a new species (III), still exhibiting hyperfine coupling to ^{127}I, was formed (Figure 4). This spectrum is poorly defined, suggesting that the ^{127}I and *g* tensors are no longer coaxial. We suggest that species (III) is still $[Mo(cp)(CO)_3I]^-$, having a different electronic structure from that of the primary species.

Aspects of Mechanism.—That electron addition is responsible for the formation of the species detected in this study is strongly supported by general experience with these solvent

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* The magnetic moments for ^{95}Mo and ^{97}Mo are negative. This sign is ignored herein to avoid confusion with the ambiguities in sign that arise for the hyperfine coupling constants. In other words, we treat all magnetic moments as if they were positive.

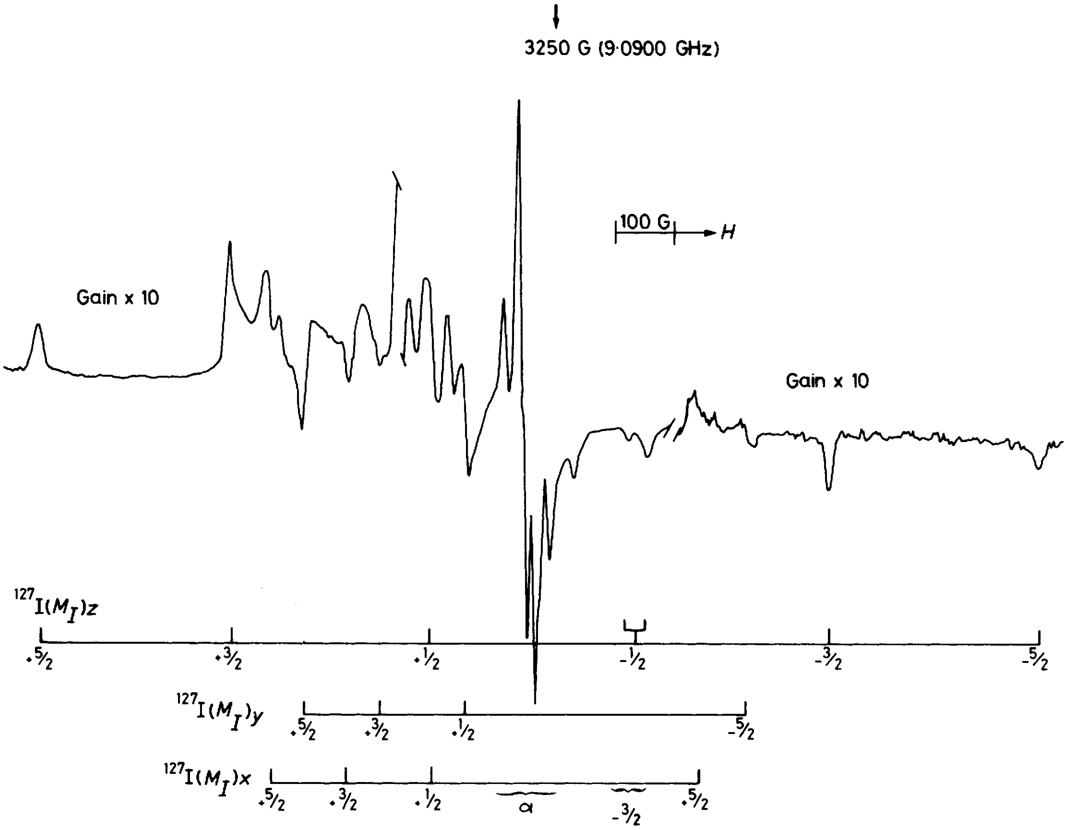


Figure 2. First derivative *X*-band e.s.r. spectrum for [W(cp)(CO)$_3$I] after exposure to ^{60}Co γ-rays at 77 K showing features assigned to [W(cp)(CO)$_3$I]$^-$ complexes. The central lines are due to radicals derived from the cp ligands. The extra components in the $M_I = +\frac{1}{2}$ region may be due to ^{183}W. There is some ambiguity regarding the location of the $M_I = -\frac{3}{2}$ features

Table 2. Experimental e.s.r. parameters for certain carbonyl(η^5-cyclopentadienyl)metal complexes

		g Values		Hyperfine coupling (G)		
Complex	Solvent	$g_\parallel$	$g_\perp$	Nucleus	$A_\parallel$	$A_\perp$
[Fe(cp)(CO)$_2$]	mthf or CD$_3$OD	2.003	2.144			
[FeH(cp)(CO)$_2$]$^+$	mthf	2.000	2.045	^{1}H	45	20
[FeD(cp)(CO)$_2$]$^+$	CD$_3$OD	*a*	2.045	^{2}H	7	*a*
[Mn(cp)(CO)$_3$]$^-$	mthf	2.004	1.99	^{55}Mn	74	36
[Co(cp)(CO)$_2$]$^-$ [b]	mthf	2.005	2.004	^{59}Co	172	45
[Mn(CO)$_5$] [c]	Argon	2.004	2.043	^{55}Mn	65	(−)33.5

[a] Features obscured by solvent radical signals. [b] Ref. 9. [c] Ref. 2.

systems, and by the fact that the intense violet-blue colour characteristic of trapped electrons in these systems was largely suppressed. The form and magnitude of the hyperfine coupling to iodine is characteristic of σ* structures, which again indicates electron addition.

Unfortunately, we cannot be sure that all the carbonyl ligands are retained on electron addition. In the absence of any information to the contrary we assume that CO is not lost, but it must be borne in mind that this is a possibility. Since species (I) was formed from [Fe(cp)(CO)$_2$Cl] and [Fe(cp)(CO)$_2$I] they must have been formed by loss of Cl$^-$ and I$^-$ from the corresponding anions. The fact that these iron derivatives undergo dissociative electron capture with clear loss of halide ion strongly supports our surmise that CO was not initially lost since there would then be no strong driving force for the additional loss of halide ions.

Species (II) is clearly a proton adduct. In mthf it may have been formed by hydrogen atom attack, but in CD$_3$OD it was probably formed by protonation of the parent anion prior to loss of halide ion. The ^{1}H hyperfine coupling is large, as also is the anisotropy (Table 2). We think it is probable that an Fe–H bond has been formed, but the evidence is not definitive.

Aspects of Structure.—Some idea of electron distribution in the s.o.m.o. of these species can be derived from the hyperfine coupling data. For the halogens the results are fairly unambiguous since there can be little doubt that both $A_\parallel$ and $A_\perp$ are positive. The resulting values for the isotropic and dipolar coupling constants have been used to derive approximate orbital populations, by using the one-electron parameters of Morton and Preston [12] for a_s^2 and those quoted by Symons [11] for a_p^2 (Table 3).[13] These results show that the *s*-orbital population is low, as expected, and that the *p*-orbital population is normal for σ* complexes.[13]

The form of the *g* tensor components is typical of complexes

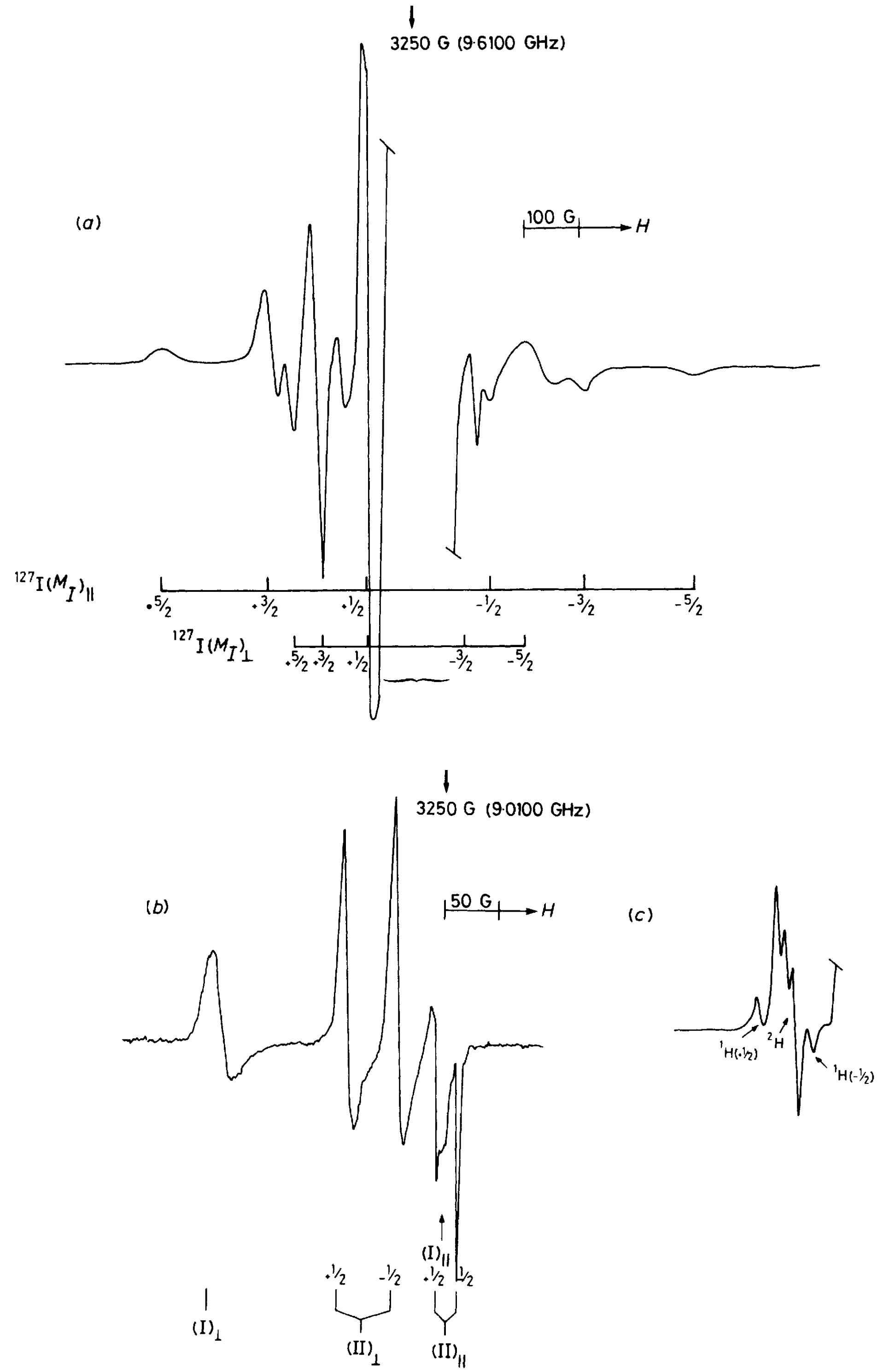


Figure 3. First derivative X-band e.s.r. spectra for $[Fe(cp)(CO)_2I]$ after exposure to ^{60}Co γ-rays at 77 K; (*a*) in mthf, showing features assigned to $[Fe(cp)(CO)_2I]^-$; (*b*) after annealing, showing features for species (I) $[Fe(cp)(CO)_2]$ and (II) $[FeH(cp)(CO)_2]^+$; and (*c*) in CD_3OD, showing (II) $[FeD(cp)(CO)_2]^+$, together with the protonated species in low concentration

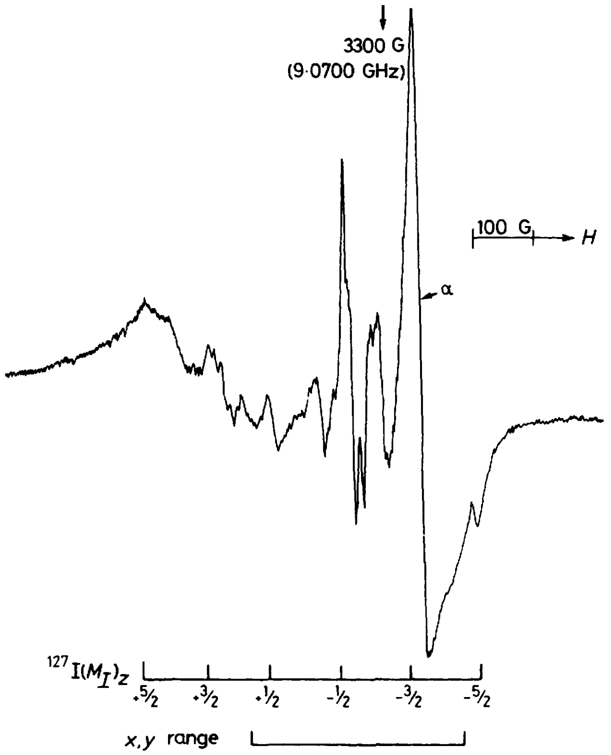


Figure 4. As for Figure 1(*a*) after annealing, showing features tentatively assigned to $[Mo(cp)(CO)_3I]^-$ anions with a π^* structure. Precise assignment of features is uncertain, but a possible stick-diagram is included. The line in the $g = 2$ region (α) is probably due to other species

having a $(d_{z^2})^1$ configuration (*z* is the metal–halogen bond direction). This has invariably been our experience with such σ^* complexes.[8,9] Unfortunately, only the molybdenum complex gave information from the metal nucleus and, as usual, there is a sign ambiguity which we were unable to resolve. If we take $A_\parallel = +6$ and $A_\perp = -16$ we get the parameters listed in Table 3, footnote *c*. These results are more reasonable than those obtained from other sign combinations, and are accepted herein. The only acceptable alternative, that both $A_\parallel$ and $A_\perp$ are negative, gives a d_{z^2} population of only 24%, remarkably low for such a somplex.

It is instructive to compare data for these complexes with those previously reported.[9] In that work we established that as the effective electronegativity of the metal increased so a_p^2 for the halogen ligands increased, as expected for an antibonding orbital. Similarly, as the electronegativity of the halogen increased, its spin density fell. The former trend is in accord with the increase noted here on going from the molybdenum to the tungsten complex (Table 3). In terms of this argument it might have been expected that there would be an increase in spin density on iodine on going from these complexes to the iron complex, whereas we obtain a clear decrease. However, the molybdenum and tungsten anions are formally seventeen-electron d^5 complexes whilst the latter are nineteen-electron d^7 complexes. The effect of these extra electrons is to reduce the effective electronegativity of the metal. This is clearly seen by comparing the spin density on iodine for $[Mo(CO)_5I]^{2-}$ and $[Mo(cp)(CO)_3I]^-$, the former being in the d^7 and the latter the d^5 category. There is a change from *ca.* 12.1 to 21.5% and the change is even larger for the tungsten complexes. However, on going from $[Mo(CO)_5I]^{2-}$ to $[Fe(cp)(CO)_2I]^-$ the increase predicted on electronegativity grounds is indeed observed (Table 3).

Table 3. Derived e.s.r. parameters and calculated orbital populations for halogen ligands

Complex	A_{iso}/G	2*B*/G	a_s^2 (%) [a]	a_p^2 (%) [b]
$[Mo(cp)(CO)_3I]^-$ [c]	193	97	1.3	21.5
$[W(cp)(CO)_3I]^-$	208	127	1.4	28.1
$[Fe(cp)(CO)_2I]^-$	119	73	0.8	16.2
$[Mo(CO)_5I]^{2-}$ [d]	180	55	1.2	12.1
$[W(CO)_5I]^{2-}$	195	61	1.3	13.5

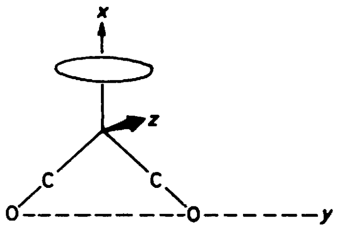
[a] Estimated from data in ref. 12. [b] Estimated from data in ref. 11. [c] $^{95/97}Mo$ $A_{iso} = -8.7$, $2B = +14.7$, $a_d^2 = 53\%$. [d] $^{95/97}Mo$ $A_{iso} = +1.8$, $2B = +16.6$, $a_d^2 = 60\%$.

An interesting aspect of this study is that the molybdenum and tungsten complexes react with electrons to give the σ^* $(d_{z^2})^1$ complexes. It might have been expected that one of the orbitals with greater π^* character would have been selected in these cases, rather than the same type of orbital as that selected by the d^6 complexes $[Mo(CO)_5I]^{2-}$ and $[W(CO)_5I]^{2-}$. We suggest that this is a kinetically controlled process and that the relaxation required to capture the electron in the σ^* orbital occurs more readily than that required for capture into the appropriate π^* orbital. Such behaviour is often observed in electron-capture processes in rigid matrices.[14] It is for this reason that we suggest that the secondary species formed from $[Mo(cp)(CO)_3I]^-$ on annealing is probably the thermodynamically favoured π^* complex. Unfortunately, the spectra (Figure 4) were never well enough defined to warrant full interpretation. However, we can deduce that the maximum coupling to ^{127}I is less than *ca.* 100 G, there being a large positive *g* shift associated with these components. If there is a component having a *g* value close to 2.00, the hyperfine coupling for this feature cannot be greater than *ca.* 40 G. These approximate data are clearly quite different from those characteristic of σ^* radicals, but are reasonably associated with a low-symmetry π radical of the type envisaged.

The Complexes $[Fe(cp)(CO)_2]$ *and* $[Mn(cp)(CO)_3]^-$.—Less can be said about these species because of the absence of hyperfine information from the ligands. We cannot be sure that there was no loss of carbon monoxide from the manganese complex, but the very marked difference in *g* values on going from the iron complex to the isoelectronic $[Mn(cp)(CO)_2]^-$ complex would be most surprising, so we reject this formulation (Table 2). We had hoped to detect $[Mn(cp)(CO)_2]^-$ on annealing the primary anions, but were unable to detect any secondary product prior to complete loss.

It is nevertheless of interest to compare our results for $[Mn(cp)(CO)_3]^-$ with those for $[Mn(CO)_5]$.[2,5] If we assume that, as for $[Mn(CO)_5]$, $A_\perp(^{55}Mn)$ is negative, the results show that the s.o.m.o. is more confined to manganese in the cyclopentadienyl complex (the d_{z^2} population increases from *ca.* 58 to *ca.* 69% when two CO ligands are replaced by cp^-). This suggests that delocalisation from the d_{z^2} orbital into the cyclopentadienyl ring is small, which in turn implies that donation from cp^- into this orbital is small. This accords with normal expectation which suggests that bonding involving the π levels ($E_1 : d_{xz}, d_{yz}$) is strong, but that for the σ level ($A_1 : d_{z^2}$) is weak.

Our results for $[Fe(cp)(CO)_2]$ suggest that the s.o.m.o. is largely d_{z^2} on iron. Hofmann,[15] with extended Hückel-type m.o. calculations on $[Mn(cp)(CO)_2]$, concluded that the highest occupied molecular orbital for the ' planar ' form of this sixteen-electron species is a largely non-bonding $3d_{z^2}$ orbital on manganese [see (A)], whilst the lowest occupied molecular orbital (l.u.m.o.) is $3d_{xz}$ on the metal with consider-



(A)

able π* (CO) character. On pyramidization at manganese, the l.u.m.o. and s.o.m.o., which are calculated to be very close in the ' planar ' system, rapidly diverge.

Our $[Fe(cp)(CO)_2]$ species is isoelectronic with $[Mn(cp)(CO)_2]^-$, which, according to these calculations, should have its unpaired electron in the $3d_{xz}$ orbital. We can see no way in which the g-tensor components can be satisfied by such a configuration, and we suggest that, at least for the iron complex, the two frontier orbitals are inverted $[3(d_{xz})^2\ 3(d_{z^2})^1]$. In that case the complex has probably relaxed to a near-planar configuration, since such an inversion seems improbable for the strongly pyramidised complex.[15] Even if these suggestions are correct, it remains surprising that structure (A) should have an exactly axial g tensor.

The radical $[Co(cp)(CO)_2]^-$, recently studied by e.s.r. spectroscopy,[10] has two extra electrons relative to the iron complex. Our analysis of the e.s.r. data suggested a $3(d_{xz})^1$ structure for this complex [using the axes selected in (A)]. We conclude from our results that the order for the metal orbitals is $d_{xz}(\pi^*) > d_{z^2}$(weakly σ^*) $> d_{xy}(\sigma^*)$, where the π and σ bonding nomenclature relates to the carbonyl ligands.

References

1 S. W. Bratt, A. Kassyk, R. N. Perutz, and M. C. R. Symons, *J. Am. Chem. Soc.*, 1982, **104**, 490.
2 M. C. R. Symons and R. L. Sweany, *Organometallics*, 1982, **1**, 834.
3 S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1974, 567.
4 M. C. R. Symons, J. L. Wyatt, B. M. Peake, J. Simpson, and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, 1982, 2037.
5 M. P. Boyer, Y. Le Page, J. R. Morton, K. F. Preston, and M. Vuolle, *Can. J. Spectrosc.*, in the press.
6 J. A. Howard, J. R. Morton, and K. F. Preston, *Chem. Phys. Lett.*, 1981, **83**, 226.
7 T. Lionel, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1982, **76**, 234.
8 O. P. Anderson, S. A. Fieldhouse, C. E. Forbes, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 1329.
9 M. C. R. Symons, S. W. Bratt, and J. L. Wyatt, *J. Chem. Soc., Dalton Trans.*, 1982, 991.
10 M. C. R. Symons and S. W. Bratt, *J. Chem. Soc., Dalton Trans.*, 1979, 1739.
11 M. C. R. Symons, ' Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold, Wokingham, Berkshire, 1978.
12 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.
13 M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1981, 783.
14 M. C. R. Symons, *Pure Appl. Chem.*, 1981, **53**, 223.
15 P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 536.

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