Paramagnetic Transition-metal Carbonyls and Cyanides. Part 7.† Electron Addition to Pentacarbonyl Halides of Chromium, Molybdenum, Tungsten, and Rhenium induced by Ionizing Radiation. An Electron Spin Resonance Study

By **Martyn C. R. Symons,* Stephen W. Bratt,** and **Jane L. Wyatt,** Department of Chemistry, The University, Leicester LE1 7RH

Exposure of tetra-alkylammonium salts of $[Cr(CO)_5I]^-$, $[Mo(CO)_5I]^-$, and $[W(CO)_5I]^-$, and dilute solutions of $[Re(CO)_5Br]$ and $[Re(CO)_5I]$ in methyltetrahydrofuran (mthf), to ^{60}Co γ-rays at 77 K gave electron-addition products characterized by large hyperfine coupling to the halogen and metal nuclei. Orbital populations for the extra electrons estimated therefrom showed trends characteristic of antibonding electrons, and in all cases the extra electron appears to be accommodated in the metal–halogen σ^* orbital comprising primarily (d_{z^2}–p_z). For the tungsten complex, a species exhibiting additional hyperfine coupling to a single proton was also detected. A species previously assigned the formula $[Cr(CO)_5I]$ was prepared, but gave no detectable e.s.r. spectrum.

WE have maintained for some time that the use of ionizing radiation is a useful and valid process for adding electrons to, or removing electrons from, transition-metal complexes.[1-4] The method competes favourably with electrolytic or chemical redox processes and has the advantage that, by working at very low temperatures, unstable complexes can be studied that might not have been detectable by conventional procedures. Only low concentrations are produced, but that is ideal for e.s.r. studies since spin–spin broadening is thereby avoided.

Two types of complexes have given particularly interesting reduction products, those with metal–halogen bonds[1] and those with metal–metal bonds. In both cases, capture occurred in the σ^* orbital comprising mainly the metal d_{z^2} orbital and the halogen p_z orbital for the former and the metal–metal bond (d_{z^2}–d_{z^2}) for the latter. Our present aim was to extend our studies of $[(OC)_5Mn\dot{-}X]^-$ (X = halogen) anions[1] to the isostructural derivatives of Cr, Mo, W, and Re. A subsidiary aim was to prepare the species thought to be $[Cr(CO)_5I]$[5] for e.s.r. study.

EXPERIMENTAL

Preparation.—Purified samples of the rhenium pentacarbonyl halides were kindly supplied by Dr. John Holloway. Tetra-alkylammonium salts of $[M(CO)_5I]^-$ (M = Cr, Mo, or W) were prepared from tetra-alkylammonium iodides and the metal hexacarbonyl using the method of Abel *et al.*,[6] and were recrystallized from aqueous acetone before use. The compound thought to be $[Cr(CO)_5I]$ was prepared by the procedure of Bond and Colton.[5] Sealed tubes containing solutions in acetone, 2-methyltetrahydrofuran (mthf), or methylcyclohexane were prepared by vacuum distillation and kept below 190 K at all times.

Powdered salts and solutions in degassed mthf were cooled to 77 K, and irradiated in a Vickrad ^{60}C γ-ray source to doses of up to 2 Mrad.‡ E.s.r. spectra were measured at 77 K on Varian E3 or E109 spectrometers. Samples were annealed above 77 K until significant changes were detected in their spectra, and recooled to 77 K for study.

RESULTS AND DISCUSSION

The results are summarized in Table 1 and in Figures 1—5. Interpretation of the ^{127}I multiplets for the derivatives of Cr, Mo, and W was straightforward, and follows that for many other σ^* complexes containing iodine.[1,7] Hyperfine coupling constants to ^{127}I were extracted using the Briet–Rabi equation. Unfortunately, the task of extracting hyperfine coupling constants for the low abundant magnetic metal nuclei proved to be more difficult [^{53}Cr, 9.54% abundant, $I = \frac{3}{2}$, magnetic moment (μ_N) = −0.473 54; ^{95}Mo, 15.78% abundant, $I = \frac{5}{2}$, μ_N = −0.909 9; ^{97}Mo, 9.60% abundant, $I = \frac{5}{2}$, μ_N = −0.929; ^{183}W, 14.28% abundant, $I = \frac{1}{2}$, and μ_N = 0.115]. Some satellite features due to ^{53}Cr, flanking some of the perpendicular features, were clearly defined for the chromium complex [Figure 1(*b*)]. Unfortunately for most of the parallel features the satellites were below noise level: however, some features flanking the intense M_I (^{127}I) = $+\frac{1}{2}$ feature may be due to ^{53}Cr, in which case $|A_{\parallel}|$ (^{53}Cr) is *ca.* 15 G.

For the molybdenum complex, each of the iodine features should exhibit six satellite lines from coupling to $^{95/97}Mo$ (lines from ^{95}Mo will be superimposed[9] on those for ^{97}Mo because of their similar magnetic moments). However, because of the wide range of separations between parallel and perpendicular lines (ΔA) for each iodine line, and the severe overlapping of features, only those with small ΔA values are well defined. Fortunately, such features were sufficient for us to estimate both the parallel and perpendicular coupling constants with confidence (Table 1). The same considerations apply to the tungsten complex.

For the two rhenium complexes there was no difficulty in picking out the parallel components, which exhibit very small second-order shifts, but the perpendicular components, exhibiting larger shifts, were much more difficult to assign. Our best fit is indicated in Figures 4 and 5.

Identification.—The similarity between the results, given in Tables 1 and 2, and those for $[Mn(CO)_5X]^-$ anions,[1] leaves little doubt that all the complexes under

---

† For Part 6 see ref. 4.

‡ Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

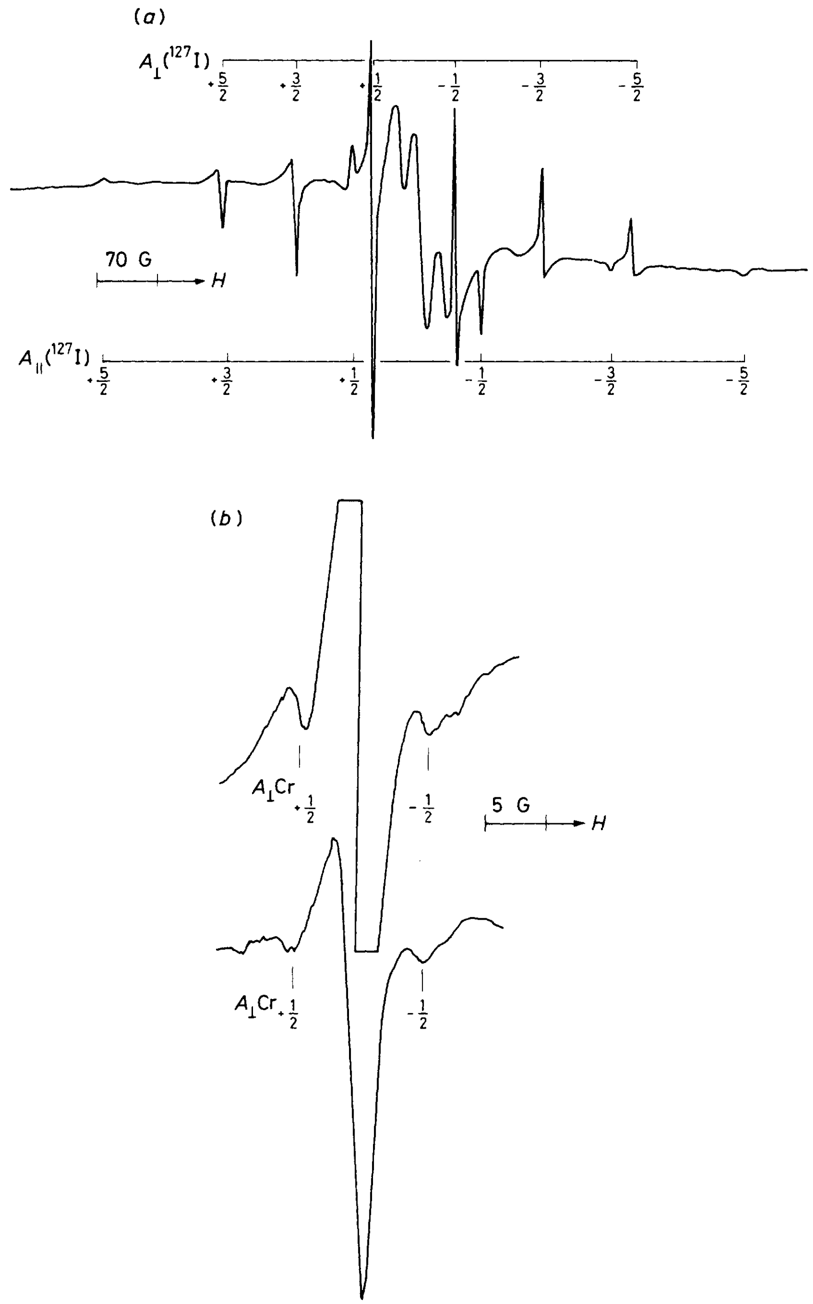

FIGURE 1 First-derivative X-band e.s.r. spectra for $[\mathrm{NEt_4}][\mathrm{Cr(CO)_5I}]$ after exposure to $^{60}\mathrm{Co}$ γ-rays at 77 K, showing (*a*) features assigned to $[(\mathrm{OC})_5\mathrm{Cr{-}I}]^{2-}$ anions (the central lines are assigned to organic radicals), and (*b*) possible $^{53}\mathrm{Cr}$ satellite lines on two of the perpendicular features

discussion are σ* anions. It is possible that with all these complexes the axial CO ligands are lost on electron addition. Unfortunately, these studies give no information about this possibility.

Structure.—Again, by analogy with the $[(\mathrm{OC})_5\mathrm{Mn}\dot{-}\mathrm{X}]^-$ anions, the extra electrons are expected to be in metal d_{z^2} orbitals combined with p_z orbitals on the halogen. Approximate orbital populations can be estimated in the usual way, using calculated unit populations.[8] The results are given in Table 2. In deriving these data, it is assumed that, in common with other σ* halogen complexes,[7] $A_\parallel$ and $A_\perp$ ($^{127}\mathrm{I}$ or $^{79/81}\mathrm{Br}$) are both positive.

For the metal hyperfine tensor components, however, $A_\perp$ may be positive or negative. The results for $^{55}\mathrm{Mn}$ in $[(\mathrm{OC})_5\mathrm{Mn}\dot{-}\mathrm{X}]^-$ anions required that $A_\parallel$ be positive and $A_\perp$ negative.[1] This is likely to be the case for chromium also, but need not be the case for the other complexes. Both signs for $A_\perp$ have been used in deriving the results given in Table 3. However, in all cases, the higher anisotropic values ($2B$) obtained using

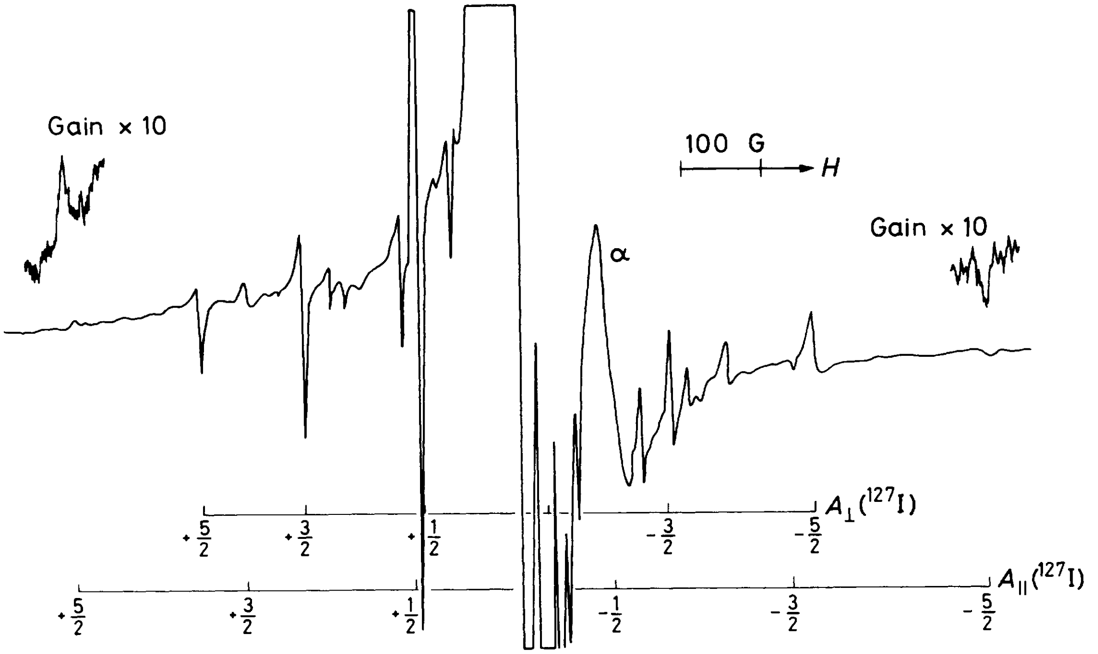

FIGURE 2 First-derivative X-band spectrum for $[NEt_4][Mo(CO)_5I]$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[(OC)_5Mo\dot{-}I]^{2-}$ anions (the central lines are assigned to organic radicals). The broad feature marked α is unassigned: other weak features are mainly $^{95/97}Mo$ satellites

negative values for $A_\perp$ are clearly preferable, as can be judged from the calculated orbital populations given in Table 3. These values are used in the following discussion.

The spin densities on the metal ions estimated from the metal hyperfine coupling constants at best only give rough indications of the true values. They confirm our previous conclusion[1] that the extra electron is remarkably confined to the metal–halogen σ-bonding region, delocalization onto axial or equatorial carbonyl groups being small. However, spin densities estimated from the halogen hyperfine parameters are more reliable, and are therefore used in considering trends in spin-density distributions. These trends are depicted in Figure 6, the horizontal axis being selected for display purposes only.

TABLE 1

Experimental e.s.r. parameters

			Hyperfine coupling/G			
			Halogen		Metal	
Complex	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$
$[Re(CO)_5Br]^-$	1.999	2.002	320	160	180	±80
$[Re(CO)_5I]^-$	2.002	2.003	425	223	225	±50
$[Cr(CO)_5I]^{2-}$	2.000	1.997	145	93	15	±11
$[Mo(CO)_5I]^{2-}$	1.999	2.000	235	153	18	±7
$[W(CO)_5I]^{2-}$	1.999	2.001	256	164	36	0 ± 5
$[Mn(CO)_5Cl]^-$ *	2.000	2.001	38.8	19.4	52.5	− 51.3
$[Mn(CO)_5Br]^-$ *	2.003	2.003	240	119	48	− 50
$[Mn(CO)_5I]^-$ *	2.000	2.004	292	155	51	− 48

* Ref. 1.

TABLE 2

Derived e.s.r. parameters and calculated orbital populations for halogen atoms

Complex	$A_{iso.}$/G	$2B$/G	a_s^2/% [a]	a_p^2/% [b]
$[Re(CO)_5Br]^-$	213	107	1.7	22
$[Re(CO)_5I]^-$	290	134.5	2.0	28
$[Cr(CO)_5I]^{2-}$	110	45	0.7	9.9
$[Mo(CO)_5I]^{2-}$	180	55	1.2	12.1
$[W(CO)_5I]^{2-}$	195	61	1.3	13.5
$[Mn(CO)_5Cl]^-$	26	13	1.2	13.0
$[Mn(CO)_5Br]^-$	159	81	1.3	16.0
$[Mn(CO)_5I]^-$	201	91	1.5	20.0

[a] Estimated from data in ref. 9. [b] Estimated from data in ref. 8.

TABLE 3

Derived e.s.r. parameters and calculated orbital populations for metal atoms

Complex [a]		$A_{iso.}$/G	$2B$/G	a_s^2/% [b]	$a^2_{d_{z^2}}$ [c]
$[Re(CO)_5Br]^-$	α	+67	+113	5.3	34
	β	+6.7	+173	4.7	87
$[Re(CO)_5I]^-$	α	+108	+117	5.5	63
	β	+42	+183	5.1	92
$[Cr(CO)_5I]^{2-}$	α	+12.3	+2.7	8.2	14
	β	−2.3	+17.3	4.0	86
$[Mo(CO)_5I]^{2-}$	α	+10.7	+7.3	6.2	26
	β	−1.8	−16.7	5.0	60
$[W(CO)_5I]^{2-}$	α β	+12	+24	5.6	79
$[Mn(CO)_5Cl]^-$	β	−17	+69	1.3	63
$[Mn(CO)_5Br]^-$	β	−17	+65	1.3	59
$[Mn(CO)_5I]^-$	β	−15	+66	1.2	60

[a] α signifies $A_\parallel$ and $A_\perp$ of like signs; β, $A_\parallel$ and $A_\perp$ of opposite signs. [b] Using parameters from ref. 9. [c] Using parameters from ref. 8.

Trends in Halogen Hyperfine Coupling.—The higher the electronegativity of the metal, for a given halogen, the higher the spin density on the halogen [Figure 6(*b*)]. Therefore, the upward trend on going from Cr to W implies an increase in effective electronegativity for these metals. A similar trend is observed on going from Mn

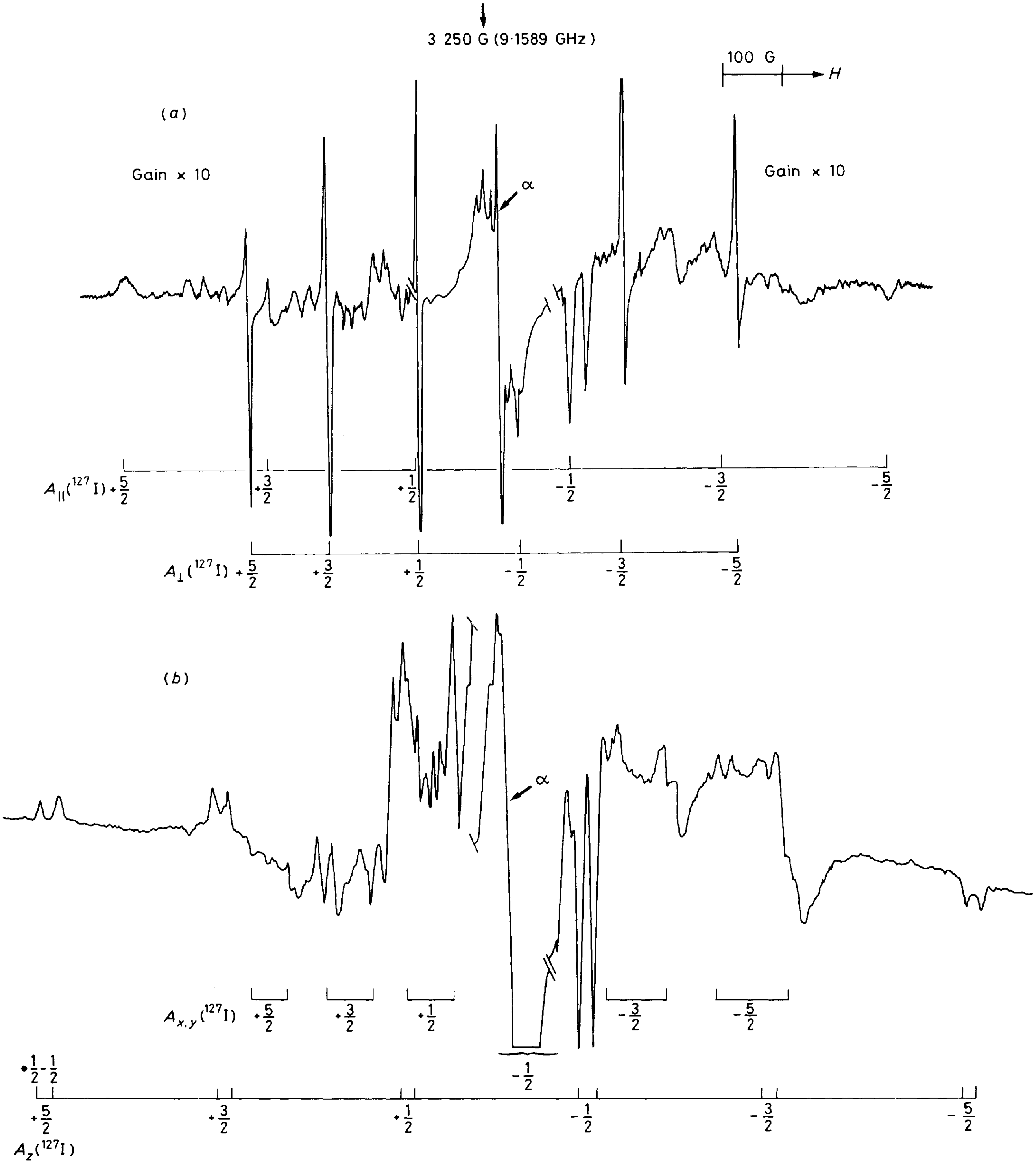

FIGURE 3 First-derivative *X*-band e.s.r. spectra for $[NBu_4][W(CO)_5I]$ after exposure to ^{60}Co γ-rays at 77 K, showing features (*a*) assigned to $[(OC)_5W\dot{-}I]^{2-}$ anions (the central lines marked α are assigned to organic radicals), and (*b*) after annealing, assigned to the protonated anion

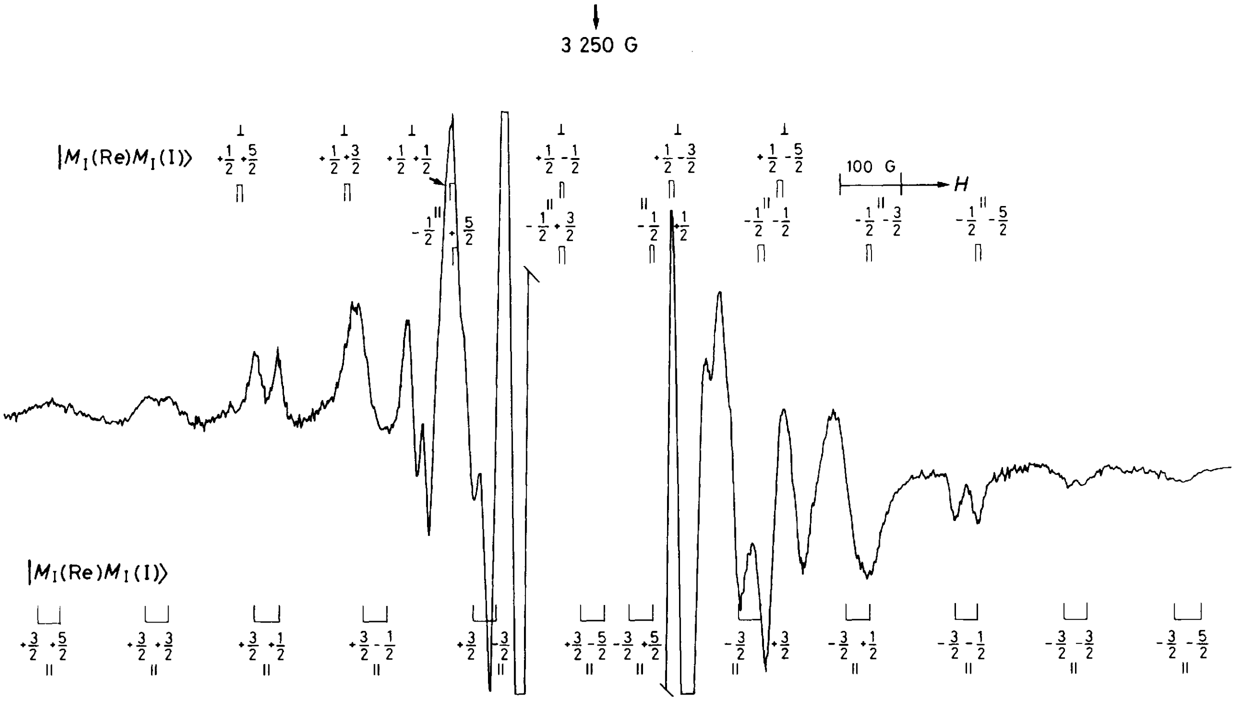

FIGURE 4 First-derivative *X*-band e.s.r. spectrum for $[Re(CO)_5Br]$ in mthf, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[(OC)_5Re\dot{-}Br]^-$ anions (central features are due to solvent radicals)

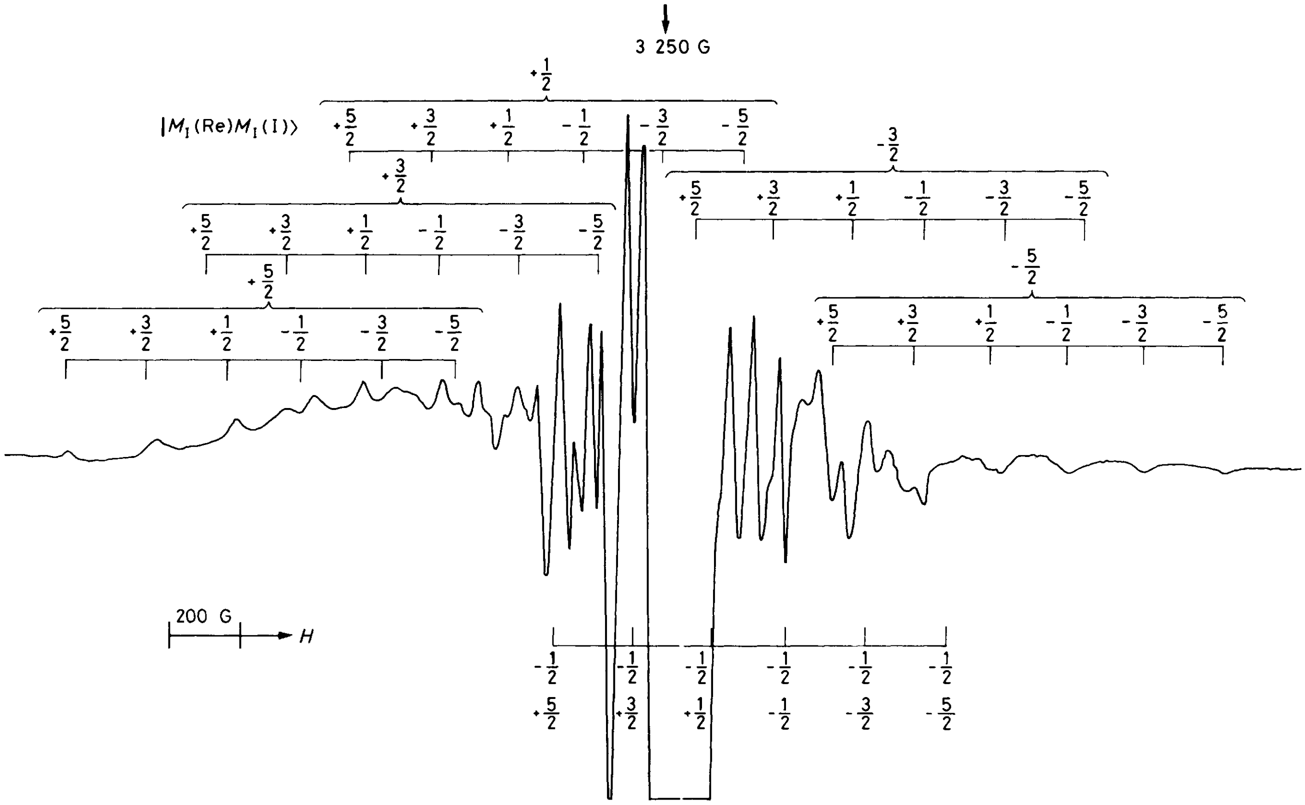

FIGURE 5 First-derivative *X*-band e.s.r. spectrum for $[Re(CO)_5I]$ in mthf, after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[(OC)_5Re\dot{-}I]^-$ anions (central features are due to solvent radicals). Only the parallel features are indicated

to Re, and, as expected, on going from Cr to Mn. The sharp fall in halogen spin density on going from iodine to bromine or chlorine again follows the expected behaviour for a σ* electron [Figure 6(*b*)]. Absence of good electronegativity parameters for the heavy elements precludes any attempt to quantify these results.

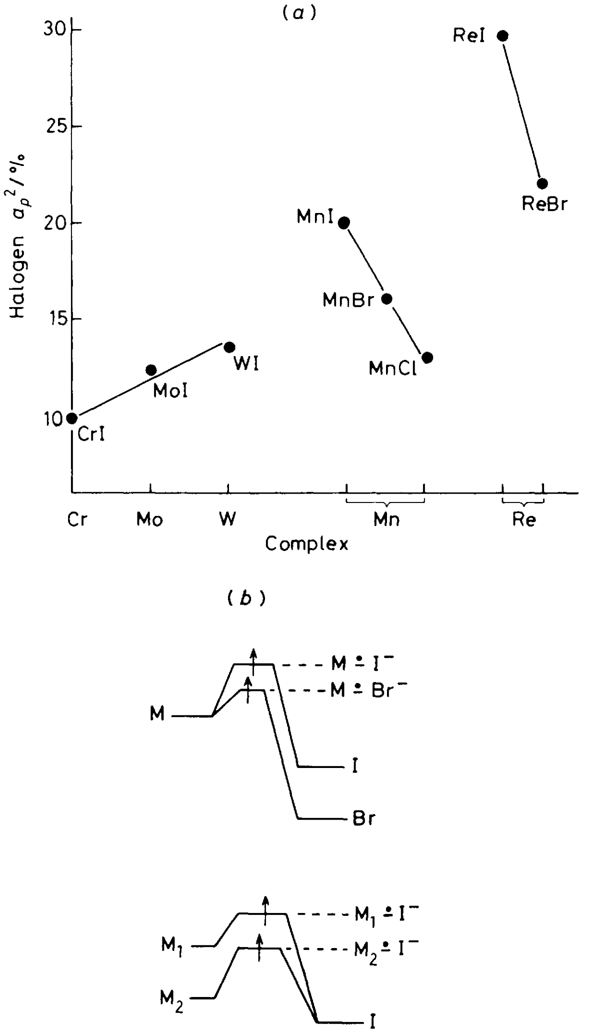

FIGURE 6 Trends in halogen spin densities (% p_z character). (*a*) as a function of the metal atom, and (*b*) as expected for singly occupied σ* orbitals

In general, as the *p* character increases on the halogen so does the estimated *s* character [Figure 7]. Indeed, there is a reasonably good linear correlation through the origin, when the A^0 values recommended by Morton and Preston[9] are used. The slope of this correlation (the *p* : *s* ratio) of 13.8 is remarkably close to that of *ca.* 15 derived from a wide range of other σ* radicals containing Cl, Br, or I.[10] Thus it seems that the degree of *s*–*p* admixture for the halogens is almost constant in such radicals, and is independent of the group to which the halogen is bound.

Results derived from the metal hyperfine parameters are given in Table 3. The *s* characters (a_s^2) were derived as follows. Normal spin-polarization values were subtracted from the experimental isotropic coupling constants to give the positive contributions assigned to admixtures of outer *s* orbitals. This procedure has been discussed elsewhere.[8] As mentioned above, in most cases, taking opposite signs for $A_\parallel$ and $A_\perp$ gives a more satisfactory result except for $[Re(CO)_5I]^-$ where a *d*-orbital population of 92% is too high. The lack of trend in the manganese results is surprising since these results are the most accurate, and the trend in halogen spin density is large. Possibly there is a compensatory shift between the different ligands, leaving the metal relatively unaffected.

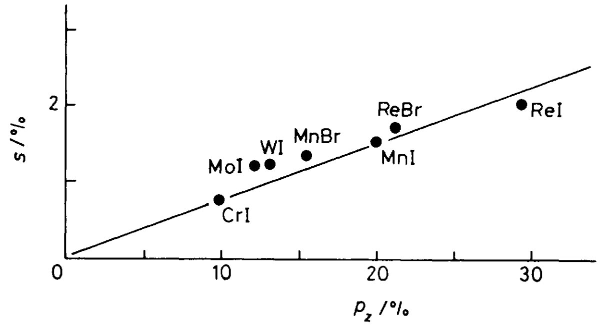

FIGURE 7 Link between the estimated *s* and *p* character for a change of $[(OC)_5M\dot{-}X]^{n-}$ σ* complexes

In all cases, whatever signs are selected, there is a relatively high outer *s*-orbital admixture. One problem with all these complexes relates to the axial carbonyl ligand. It is quite possible that this is lost on electron addition. Attempts to detect ^{13}C hyperfine coupling for enriched samples of $[Mn(CO)_5Cl]$[11] gave no extra hyperfine features. This means either that the coupling to the axial carbon is very small or that the CO ligand has been lost. This problem, together with further evidence, will be discussed fully elsewhere.[12]

Other Paramagnetic Centres.—In all cases, we have endeavoured to detect loss of halide anions on annealing, but to no avail. In general, the σ* anions decayed uniformly without giving any detectable paramagnetic products. The only well defined centre besides those already described was a species derived from $[W(CO)_5I]^-$ ions displaying a well defined doublet splitting on all features. This is almost certainly due to hyperfine coupling from a single proton [Figure 3(*b*)]. The hyperfine coupling of 23.5 ± 1 G is nearly isotropic. A similar proton coupling of *ca.* 13 G was observed in our study of $[Co(cp)(CO)_2]$ (cp = cyclopentadienyl). In that case electron addition was clearly followed by protonation, and we suggest that this occurred at one of the CO groups giving a HCO ligand.[4] In the present case, the source of hydrogen is less clear. There was clear evidence for the growth of the protonated species as the primary radical anion decayed, but in the absence of any proton donor it is not clear why this occurs. There is clear evidence for hyperfine coupling to ^{127}I and to ^{183}W. The former coupling $A_\parallel = 325$ $A_\perp = 165$ G leads to a spin density of *ca.* 24% on iodine. Thus there has been a 10.5% increase in spin density on iodine. A parallel coupling to ^{183}W of 28 G indicates a corresponding fall in spin on tungsten. We were unable to measure the ' perpendicular ' coupling, but if it is small, as with the parent radical anion, then the fall in spin density is *ca.* 18%.

As well as somehow causing the unpaired electron to migrate from tungsten towards iodine, the extra proton has caused a descent in symmetry, as indicated in Figure 3(*b*). The charge shift shows that the effective electronegativity of the metal atom has increased markedly. The descent in symmetry shows that one of the equatorial ligands has been modified or replaced. These deductions taken together with the relatively large proton coupling may be showing that one of the CO ligands has been replaced by H. Why this should occur uniquely for the tungsten complex is not clear to us.

If the axial CO ligand is lost on electron addition, to give $[W(CO)_4I]^{2-}$, then it is possible that this is protonated on tungsten to give $[WH(CO)_4I]^{-}$. However, we have recently shown that hydrogen atoms which form part of a σ^* unit give extremely large ^{1}H hyperfine coupling constants,[13] typically in the region of 170 G. The coupling of 23.5 G seems to be too small for this structure. Also this would not explain the loss of axial symmetry.

The $[Cr(CO)_5I]$ *Complex.*—The blue compound assigned this formula by Bond and Colton[5] gave no e.s.r. signal under any conditions. It was therefore thought to be of no relevance to the present study and no further investigations were undertaken.

We thank S.E.R.C. for a grant (to S. W. B.) and Leicester University for a grant (to J. L. W.).

[1/1678 *Received, 28th October,* 1981]

REFERENCES

[1] O. P. Anderson, S. A. Fieldhouse, C. E. Forbes, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 1329.

[2] O. P. Anderson, S. A. Fieldhouse, C. E. Forbes, and M. C. R. Symons, *J. Organomet. Chem.*, 1976, **110**, 247.

[3] S. W. Bratt and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1977, 1314.

[4] Part 6, M. C. R. Symons and S. W. Bratt, *J. Chem. Soc., Dalton Trans.*, 1979, 1739.

[5] A. M. Bond and R. Colton, *Inorg. Chem.*, 1976, **15**, 446.

[6] E. W. Abel, I. S. Butler, and I. G. Reid, *J. Chem. Soc.*, 1963, 2068.

[7] See, for example, S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1981, 185.

[8] M. C. R. Symons, ' Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand–Reinhold, Wokingham, 1978.

[9] J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.

[10] M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1981, 783.

[11] S. W. Bratt, Ph.D. Thesis, Leicester University, 1979.

[12] B. Peake, J. L. Wyatt, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, submitted for publication.