Radical Anions of Metal Carbonyls

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Summary A number of radical anions of metal carbonyl compounds have been prepared and their e.s.r. spectra studied; temperature-dependent phenomena may be indicative of non-rigid behaviour.

Theoretical studies[1] indicate that metal carbonyls with a metal–metal backbone have empty low-lying molecular orbitals associated with the metal–metal system; one-electron reduction of these compounds is therefore expected to be relatively easy. The addition or removal of an electron from a closed shell configuration of polynuclear metal carbonyls is also known to cause structural distortion[2] and this may prove to be a method for expanding or contracting metal polyhedra in cluster carbonyls.

In order to test these hypotheses we have characterized and studied a number of new radical anions of the type, $M(CO)_x^{\cdot -}$, $M_2(CO)_y^{\cdot -}$, $M_3(CO)_{12}^{\cdot -}$, $M_4(CO)_{12}^{\cdot -}$ and their heterometal and substituted analogues. The procedure involves alkali-metal and/or electrochemical reduction of the appropriate metal carbonyl compound in dry, O_2-free, ether solvents. A number of substituted metal carbonyl radical anions have previously been studied by electrochemical methods by Dessy and his co-workers[3] and the radical anions, $YCCo_3(CO)_9^{\cdot -}$,[4] $Mn_2(CO)_{10}^{\cdot -}$, $Mn(CO)_5Br^{\cdot -}$ [5] have been reported, but the anions shown in the Table (with *g* values at 223 K in tetrahydrofuran) show the generality of one-electron reduction in solution. With most compounds reduction is rapid and reversible and there is no accompanying colour change although prolonged reduction of the polynuclear iron derivatives results in the formation of mononuclear species. Solutions of the radical anions are remarkably stable, the most stable being the heavy-metal anions which have lifetimes of at least several hours; attempts to isolate solid salts have so far failed. Quantitative yields of the parent carbonyls are obtained when the solutions are quenched by MeI, indicating that no gross structural changes have occurred on reduction, while the *g* values and spectral profiles are independent of the ether. This argues against specific solvation of a particular metal atom. In general *g* values of polynuclear radical anions having bridging carbonyl groups are to higher field than those with non-bridged structures.

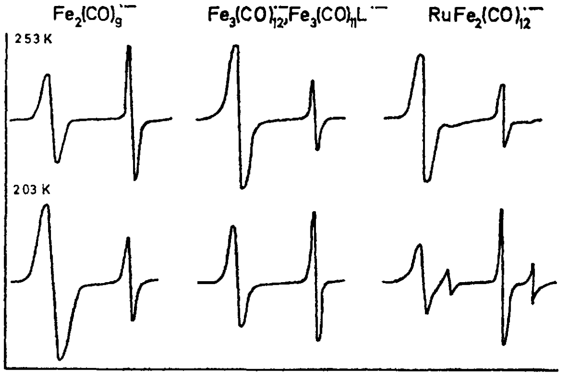

FIGURE. Temperature variation of e.s.r. spectra. Reproducible and reversible over the temperature range 253—193K.

The temperature dependence of the $Fe_3(CO)^{\cdot -}_{12}$, $Fe_3(CO)_{11}{}^{\cdot -}$ $P(OPh)^{\cdot -}_3$ and $RuFe_2(CO)^{\cdot -}_{12}$ spectra, (Figure), can be interpreted in terms of a dynamic equilibrium between an asymmetric carbonyl bridged structure [the solid-state $Fe_3(CO)_{12}$ structure[6]] and a non-bridged form. The mechanism of interconversion is presumably similar to that proposed for the neutral species.[6] It is reasonable to assign the low-field signals to the non-bridged form since the *g* values are close to those of $M_3(CO)^{\cdot -}_{12}$ (M = Ru, Os). The extra signal at low temperatures in the $RuFe_2(CO)^{\cdot -}_{12}$ spectra (and also in the spectrum of $Ru_3(CO)^{\cdot -}_{12}$) split by hyperfine coupling (a_{Ru} = 10G) must be due to a species where the electron is associated with only one ruthenium atom. It is significant that there was a marked temperature dependence of the two signals in the spectrum of $Fe_2(CO)_9$ (Figure) as investigations of its solution behaviour have previously been hindered by its insolubility. Nevertheless it is sufficiently soluble in ether solvents for e.s.r. investigation and the radical anion is quite soluble even at 173 K. In view of Cotton's work on substituted $Fe_2(CO)_9$ derivatives[7] we suggest that the dynamic equilibrium is between the triply-bridged ground-state structure[8] (high-field signal) and an asymmetrically-bridged form with one bridging carbonyl group.

TABLE

$Fe(CO)^{-}_{5}$	2·041
$Fe_2(CO)^{\cdot -}_{9}$	2·040, 2·002
$Fe_3(CO^{\cdot -}_{12}$	2·051, 2·003
$Fe_3(CO)_{11}P(OPh)^{\cdot -}_{3}$	2·052, 2·003
$RuFe_2(CO)^{\cdot -}_{12}$	2·053, 2·004
$Pt[P(OPh)_3]_2Fe_2(CO)^{\cdot -}_{8}$	2·054
$Ru_3(CO)^{\cdot -}_{12}$	1·982
$Os_3(CO)^{\cdot -}_{12}$	2·001
$Ir_4(CO)^{\cdot -}_{12}$	2·002
$Ru_6C(CO)^{\cdot -}_{17}$	2·001

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