Investigation of Paramagnetic Species formed during the Thermolysis, Photolysis, and Oxygenation of some Bi- and Tri-nuclear Organometallic Compounds of Chromium, Iron, and Molybdenum

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Oxygenation of the products derived thermally (−70 °C) from $[Cr_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (1a) or photochemically from $[Hg\{Cr(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (2a) or $[\{(\eta\text{-}C_5H_5)Cr(CO)_3Cu(phen)\}_n]$ (3; phen = 1,10-phenanthroline) gives rise to a paramagnetic species $[Cr(\eta\text{-}C_5H_5)(CO)_n(O_2)]$ ($n \leqslant 3$), most probably containing a peroxo-ligand and with $n = 2$. Evidence in support of the structure of this dioxygen complex is adduced from, among other things, experiments using ^2H- and ^{17}O-labelled precursors. Attempts to identify an intermediate in the reaction of (1a) by using the spin-trapping agents RNO (R = Bu^t or C_6Me_4H) have produced paramagnetic species believed to be side-on bonded nitroso-complexes $[Cr(\eta\text{-}C_5H_5)(CO)_2(ONR)]$ (4b); when R = Bu^t this complex decomposes thermally to form $Bu^t{}_2NO$ and a possible mechanism for this process is discussed.

The solution photolyses are described of derivatives (7), $[Fe(\eta\text{-}C_5H_5)(CO)(L)X]$ [L = CO, X = $Fe(\eta\text{-}C_5H_5)(CO)_2$, $HgFe(\eta\text{-}C_5H_5)(CO)_2$, $SnPh_3$, or $PbPh_3$; L = PPh_3 or alkene, X = $SnPh_3$], *in vacuo* with and without added nitrosodurene and also in the presence of air or dioxygen. E.s.r. parameters of the resulting paramagnetic products are reported and discussed. Iron–aminyl oxide complexes are formed with nitrosodurene at −40 °C but at higher temperatures (*ca.* −10 to +20 °C) photolyses of complexes (7d), (7e), and (7i) (L = CO or PPh_3, X = $SnPh_3$; L = CO, X = $PbPh_3$) form a nitroxide $(C_5H_5)NO(C_6Me_4H)$ resulting from $Fe\text{–}(\eta\text{-}C_5H_5)$ bond fission. Also, when X = $SnPh_3$ (7d) and (7f)—(7h) or X = $PbPh_3$(7i) photolysis *in vacuo* produces paramagnetic iron derivatives which contain the Group 4B metal and the nature of these products is discussed. Solution photolyses of complexes (11), $[Mo(\eta\text{-}C_5H_5)(CO)_2(L)X]$ [L = CO, X = $Mo(\eta\text{-}C_5H_5)(CO)_3$, $HgMo(\eta\text{-}C_5H_5)(CO)_3$, or $CdMo(\eta\text{-}C_5H_5)(CO)_3$; L = PPh_3, X = $HgMo(\eta\text{-}C_5H_5)(CO)(PPh_3)$], are described; e.s.r. data are presented for paramagnetic products arising from reaction with nitrosodurene *in vacuo* and from oxygenation.

THE interaction of dioxygen with transition-metal complexes is of considerable importance in understanding the mode of action of biological oxygen carriers, and extensive studies have been made on the structure and reactivity of dioxygen–metal complexes.[1] Also, there is continuing interest in the potential use of such complexes as selective oxidants for organic substrates.[2]

We have previously shown that the low-temperature u.v. photolysis and oxygenation of decacarbonyldimanganese gives rise to a paramagnetic species, $[Mn(CO)_n(O_2)]$, and have also presented evidence for a related species derived from the binuclear complex $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$.[3] We now describe the results of an e.s.r. study of the thermolysis or photolysis and oxygenation of several related bi- and tri-metallic complexes including examples where one metal is of main-group type; a preliminary communication of part of this work has appeared.[4]

EXPERIMENTAL

Reactions were carried out using Schlenk techniques and dried deoxygenated solvents either in an atmosphere of dioxygen-free dinitrogen or *in vacuo*. Photolytic preparations were performed in stoppered Pyrex tubes positioned 5—10 cm from a cooled, medium-pressure mercury lamp. E.s.r. experiments were carried out on *ca.* 10^{-3} mol dm^{-3} solutions using a JEOL PE1 *X*-band spectrometer under conditions previously described.[3]

Primary e.s.r. signals were all observed within 30 min under the conditions stated in the text and in Tables 1 and 2; chromium complexes gave relatively intense signals in shorter times (*ca.* 0—10 min) than iron (*ca.* 2—20 min) or molybdenum complexes ($\leqslant$30 min). Computer simulations were carried out using a program based on a simple isotropic spin Hamiltonian with first-order hyperfine splitting (Lorenztian lineshape, linewidth = first derivative peak–peak width). Parameters used are given in the text and Figures 1—3.

The complexes $[Cr_2(\eta\text{-}C_5H_5)_2(CO)_6]$,[5] $[Hg\{Cr(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[5] $[\{(\eta\text{-}C_5H_5)Cr(CO)_3Cu(phen)\}_n]$ (phen = 1,10-phenanthroline),[6] $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[7] $[Hg\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$,[8] $[Fe(\eta\text{-}C_5H_5)(CO)_2(SnPh_3)]$,[9] $[Fe(\eta\text{-}C_5H_5)(CO)_2(PbPh_3)]$,[10] $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(SnPh_3)]$,[11] $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$,[7] $[Hg\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[12] $[Hg\{Mo(\eta\text{-}C_5H_5)(CO)_2(PPh_3)\}_2]$,[13] $[Cd\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[14] $[Mo(\eta\text{-}C_5H_5)(CO)_3(SnPh_3)]$,[15] and $[Mo(\eta\text{-}C_5H_5)(CO)_3(PbPh_3)]$ [15] were prepared and purified as described in the literature. The deuteriated derivative $[Hg\{Cr(\eta\text{-}C_5{}^2H_5)_2(CO)_3\}_2]$ was also formed by a standard method using $C_5{}^2H_5$(>95% ^2H) prepared by exchange of C_5H_6 with $NaO^2H\text{–}{}^2H_2O$ in hexamethylphosphoramide.[16] Isotopically enriched O_2 (71.47% ^{17}O) and 2-methyl-2-nitrosopropane were purchased from Miles Laboratories Inc. and Aldrich Chemicals respectively. Nitrosodurene (2,3,5,6-tetramethyl-1-nitrosobenzene) was prepared as described.[17]

Preparation of Carbonylcyclo-octene(η-cyclopentadienyl)(triphenylstannio)iron, $[Fe(\eta\text{-}C_5H_5)(C_8H_{14})(CO)(SnPh_3)]$.—A solution of dicarbonylcyclopentadienyl(triphenylstannio)iron (0.30 g, 0.57 mmol) and cyclo-octene (0.7 cm^3) in benzene (15 cm^3) was irradiated for 50 h. The solvent was then removed under high vacuum to leave a red oil. This oil was redissolved in benzene (2 cm^3) and addition of hexane (4 cm^3) precipitated the product as an orange solid which was isolated, washed (hexane), and dried under vacuum; yield 0.070 g (21%) (Found: C, 62.9; H, 5.8; Fe, 9.65. $C_{32}H_{34}FeOSn$ requires C, 63.1; H, 5.6; Fe, 9.2%); i.r. (CH_2Cl_2) ν(CO) 1 925 cm^{-1}.

The following complexes were prepared by similar photolytic reactions: $[Fe(\eta\text{-}C_5H_5)(C_7H_{10})(CO)(SnPh_3)]$ (C_7H_{10} = bicyclo[2.2.1]hept-2-ene), yellow-orange solid (32%)

(Found: C, 62.8; H, 5.3; Fe, 9.1. $C_{31}H_{30}FeOSn$ requires C, 62.8; H, 5.1; Fe, 9.4%), i.r. (CH_2Cl_2) ν(CO) 1 928 cm^{-1}; $[Fe(\eta\text{-}C_5H_5)(C_6H_{12})(CO)(SnPh_3)]$ (C_6H_{12} = hex-1-ene) (27%) (Found: C, 62.0; H, 5.5; Fe, 9.8. $C_{30}H_{32}FeOSn$ requires C, 61.8; H, 5.5; Fe, 9.6%), i.r. (CH_2Cl_2) ν(CO) 1 927 cm^{-1}, and $[Fe(\eta\text{-}C_5H_5)(C_8H_{16})(CO)(SnPh_3)]$ (C_8H_{16} = oct-1-ene) (25%), i.r. (CH_2Cl_2) ν(CO) 1 927 cm^{-1}.

RESULTS AND DISCUSSION

Chromium Complexes.—Solutions of the bimetallic chromium complex (1a), $[Cr_2(\eta\text{-}C_5H_5)(CO)_6]$, in degassed toluene (−70 to +90 °C) and in dichloromethane (⩽20 °C) are found to be e.s.r. inactive. When air or dioxygen (100—300 Torr *) is admitted to a toluene solution in the dark at −70 °C an e.s.r. signal is observed (Figure 1) as a sextet ($g_{iso.}$ = 1.9873 ± 0.0005, $a_{iso.}$ = 0.111 ± 0.005 mT) with quartet satellites ($a_{iso.}$ = 1.72 ± 0.02 mT) assignable to coupling with ^{53}Cr ($I = \frac{3}{2}$, 9.5% abundance) present at a single chromium centre. The signal intensity does not diminish during 1 h at −70 °C but at temperatures ⩾−40 °C decomposition is evident which is complete by −20 °C and other paramagnetic species are formed ($g_{iso.}$ ⩾ 2). Identical sextet e.s.r. spectra (Figure 1) are formed on u.v. photolysis of (2a); $[Hg\{Cr(\eta\text{-}C_5H_5)(CO)_3\}_2]$, in toluene at −50 °C or (3), $[\{(\eta\text{-}C_5H_5)Cr(CO)_3Cu(phen)\}_n]$, in dichloromethane at −70 °C [$g_{iso.}$ (in CH_2Cl_2) = 1.9867 ± 0.0005]. Using the deuteriated species (2b), $[Hg\{Cr(\eta\text{-}C_5{}^2H_5)(CO)_3\}_2]$, the sextet interaction is eliminated so that this coupling can be assigned unambiguously to five ^1H nuclei of one η-C_5H_5 group. Using $^{17}O_2$ (71.47% enriched) the e.s.r. spectrum shows additional hyperfine structure (see Figures 2 and 3) which can be assigned to coupling with *two* equivalent oxygen nuclei with $a_{iso.}(^{17}O)$ = 0.177 ± 0.005 mT, as illustrated by computer simulation.

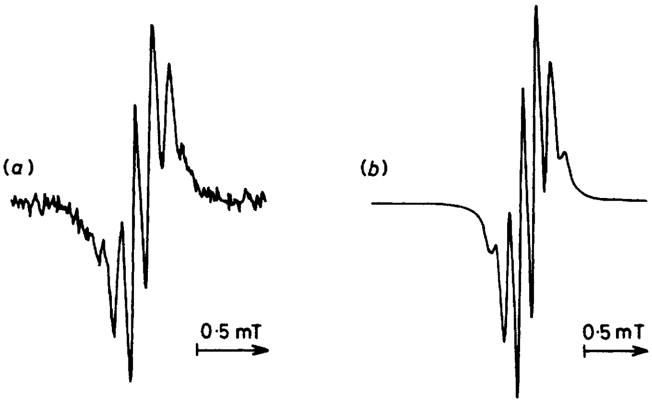

FIGURE 1 E.s.r. spectra from (1a) with O_2 in toluene at −70 °C: (*a*) experimental (9.38 GHz); (*b*) simulated using parameters given in text (linewidth = 0.07 mT)

The paramagnetic chromium species observed in solution at low temperatures must, therefore, be formulated as $[Cr(\eta^5\text{-}C_5H_5)(CO)_n(O_2)]$; the presence of the dioxygen ligand and a η^5-cyclopentadienyl group is supported by the isotopic labelling studies. The coordination of carbonyl groups has not been directly confirmed by e.s.r. spectroscopy but the conditions of formation of this species (*i.e.* thermally at −70 °C) and the known chemistry of the tricarbonyl(η-cyclopentadienyl)chromium system [18] strongly suggest that some carbonyl ligands remain. The value of *n* in the formulation must be ⩽3. It has previously been established that 17-electron carbonyl–metal fragments of the type $[M(CO)_5]$ (M = Mn or Re) [19a] or $[M(\eta\text{-}C_5H_5)(CO)_3]$ (M = Cr, Mo, or W) [19b] are labile to displacement of a carbonyl ligand so it is possible that *n* = 2.

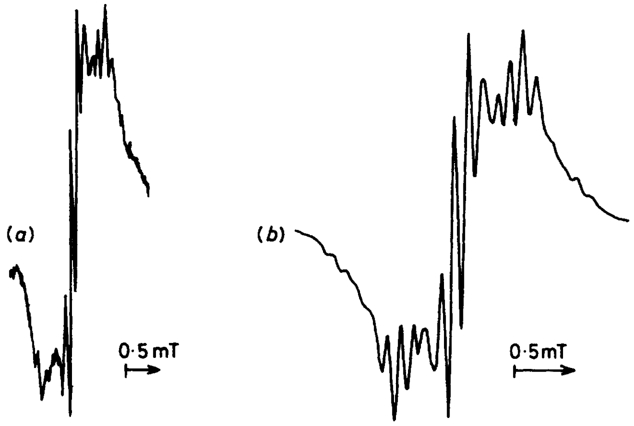

FIGURE 2 E.s.r. spectra from (2a) with $^{17}O_2$ in toluene at −50 °C with u.v. irradiation (medium-pressure mercury lamp): (*a*) experimental (9.38 GHz); (*b*) simulated using parameters given in text [linewidths = 0.07 mT for ^{16}O–^{16}O (8.1%), 0.08 mT for ^{16}O–^{17}O (40.8%), and 0.09 mT for ^{17}O–^{17}O (51.1%)]

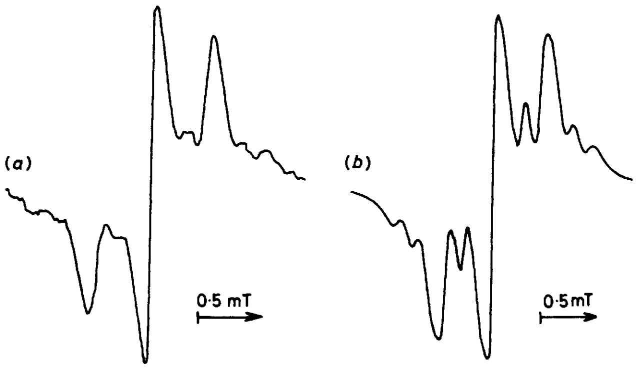

FIGURE 3 E.s.r. spectra from (2b) with $^{17}O_2$: (*a*) experimental (9.38 GHz) (conditions as for Figure 2); (*b*) simulated using parameters given in text (linewidths = 0.11, 0.13, and 0.15 mT for ^{16}O–^{16}O, ^{16}O–^{17}O, and ^{17}O–^{17}O respectively)

E.s.r. studies of (1a) in benzonitrile have shown the presence of *ca.* 1% of a paramagnetic species (*g* = 2.025);[20] also, broadening of the ^1H n.m.r. resonance of (1a) in toluene at temperatures above −10 °C has been interpreted in terms of a reversible formation of a small concentration of a paramagnetic entity.[21] The related phosphite complex $[Cr_2(\eta\text{-}C_5H_5)_2(CO)_4\{P(OMe)_3\}_2]$ is largely dissociated in non-polar solvents at 25 °C according to equation (1) [L = $P(OMe)_3$].[22] Thus, it may be

$$[Cr_2(\eta\text{-}C_5H_5)_2(CO)_4L_2] \rightleftharpoons 2[Cr(\eta\text{-}C_5H_5)(CO)_2L] \quad (1)$$

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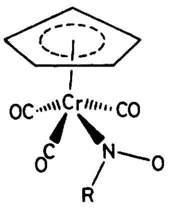
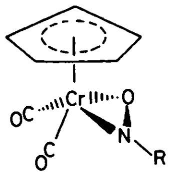
* Throughout this paper: 1 Torr = (101 325/760) Pa.

inferred that such a dissociation occurs to a smaller extent for (1a) [equation (1); L = CO]. Such a dissociation is also supported by studies of the photochemical conversion of $[M_2(\eta\text{-}C_5H_5)_2(CO)_6]$ into $[M_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (M = Cr, Mo, or W).[19b] The 17-electron mononuclear fragment should react readily with triplet O_2 to form $[Cr(\eta\text{-}C_5H_5)(CO)_3(O_2)]$ although CO loss from this species or its precursor is possible.

17-Electron fragments including $[Mo(\eta\text{-}C_5H_5)(CO)_3]$ and $[M(CO)_5]$ (M = Mn or Re) resulting from metal–metal bond fission form spin adducts of the type $M(CO)_n$-L(NOR) (L = CO or $\eta\text{-}C_5H_5$) with monomeric nitroso-compounds.[23] Attempts were made in the present work to spin-trap the species (1b), $[Cr(\eta\text{-}C_5H_5)(CO)_3]$. Degassed solutions of (1a) *in vacuo* with nitrosodurene or 2-methyl-2-nitrosopropane in toluene or dichloromethane gave paramagnetic species exhibiting triplet e.s.r. spectra [*e.g.* with nitrosodurene in toluene ($h\nu$, −50 °C), $g_{iso.} = 1.9920 \pm 0.0005$, $a_{iso.}(^{14}N) = 0.56 \pm 0.02$ mT; with 2-methyl-2-nitrosopropane in CH_2Cl_2 (dark, room temperature), $g_{iso.} = 1.9851$, $a_{iso.}(^{14}N) = 0.62$ mT]. However, the low values of $a_{iso.}(^{14}N)$ and $g_{iso.} < 2$ are inconsistent with normal spin-trapped species RN(O)X (X = alkyl, metal, *etc.*) having unpaired electron density on the NO group.[23,24] Thus, structure (4a) is unlikely and (4b) involving a side-on bonded nitroso-group is a probable alternative. Such a η^2-bonding form is found for several diamagnetic complexes including the molybdenum derivatives $[MoO(S_2CNR_2)_2(PhNO)]$[25] and $[Mo(\eta\text{-}C_5H_5)(CO)_2(Me_2CNO)]$.[26] The paramagnetic nitroso-species (4) decomposes in solution at ambient temperature, and in the dark, when R = Bu^t, the nitroxide $Bu^t{}_2NO$ is progressively formed in the presence of excess of Bu^tNO. Also, the diamagnetic complex $[Cr(\eta\text{-}C_5H_5)(CO)_2(NO)]$ is identified as a major product in solution by i.r. spectroscopy. Thus, the reactions of equations (2)—(4) appear to take place.



(4a)



(4b)

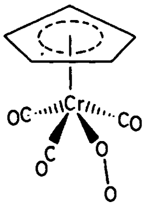
R = Bu^t or 2,3,5,6-Me_4C_6H

$$[Cr_2(\eta\text{-}C_5H_5)_2(CO)_6] \xrightarrow{RNO} 2[Cr(\eta\text{-}C_5H_5)(CO)_2(RNO)] + 2CO \quad (2)$$

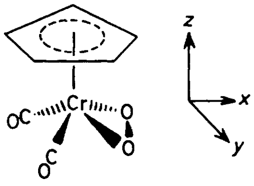
$$[Cr(\eta\text{-}C_5H_5)(CO)_2(Bu^tNO)] \longrightarrow [Cr(\eta\text{-}C_5H_5)(CO)_2(NO)] + Bu^{t\cdot} \quad (3)$$

$$Bu^{t\cdot} + Bu^tNO \longrightarrow Bu^t{}_2NO \quad (4)$$

The two most likely structures for the paramagnetic chromium dioxygen complex $[Cr(\eta\text{-}C_5H_5)(CO)_n(O_2)]$ are (5) and (6). The σ-superoxo-form (5) is not well supported by the spectroscopic data since the $g_{iso.}$, $a_{iso.}(^{53}Cr)$, and $a_{iso.}(^{17}O)$ parameters are typical for a species with unpaired electron density mainly in a *d* orbital of the Cr atom with negligible spin density on the O_2 ligand. Normally such paramagnetic σ-bonded O_2 species have a high proportion of spin on this ligand;[1,27] also the presence of equivalent ^{17}O atoms could only be explained by a rapid head-to-tail rearrangement of the Cr–O–O linkage in solution. On the other hand, the e.s.r. data are readily accommodated by structure (6); the oxygen atoms are equivalent and the species is formally a chromium(III) peroxo-complex with a low-spin d^3 electronic structure. Structure (6) is analogous to the proposed structure (4b) of the paramagnetic nitroso-complexes. It is relevant that related paramagnetic dicarbonyl *ortho*-quinone complexes $[M(\eta\text{-}C_5H_5)(CO)_2(O_2C_6H_2Bu^t{}_2)]$ [M = Cr, $g_{iso.} = 1.971$, $a_{iso.}(^{53}Cr) = 2.67$ mT; M = Mo, $g_{iso.} = 1.9688$] have been reported.[28]



(5)



(6)

E.s.r. spectra of the dioxygen–chromium complex in frozen toluene solution (< −140 °C) gave three principal values for the *g* tensor indicating the absence of axial symmetry: $g_1 = 1.997$, $g_2 = 1.986$, $g_3 = 1.976$ ($g_{av.} = 1.986$). This is consistent with the C_s symmetry of (6) for which the highest occupied molecular orbitals, based on previous calculations for compounds $[M(\eta\text{-}C_5H_5)(CO)_2L]$ by Hoffmann and co-workers,[29] are $(1a')^2(2a')$.[1] In the co-ordinate system of (6) the compositions of these orbitals are mainly d_{z^2} and $d_{x^2-y^2}$, although symmetry-allowed mixing must occur. Such an electronic ground state is consistent with all principal *g* values <2.002, arising from spin–orbit coupling with unoccupied d_{xy}, d_{yz}, and d_{xz} orbitals, but the differences from the free-spin value are relatively small and may partly reflect the covalent and substantial ligand nature of these orbitals.

Iron Complexes.—It is known that photolysis of the iron complex (7a) in solution in the presence of nitroso-compounds, RNO, gives rise to aminyl oxide complexes (7b),[23a] possibly *via* spin trapping of the 17-electron

$[Fe(\eta\text{-}C_5H_5)(CO)(L)X]$
(7)

	X	L
(7a)	$Fe(\eta\text{-}C_5H_5)(CO)_2$	CO
(7b)	ONC_6Me_4H	CO
(7c)	$HgFe(\eta\text{-}C_5H_5)(CO)_2$	CO
(7d)	$SnPh_3$	CO
(7e)	$SnPh_3$	PPh_3
(7f)	$SnPh_3$	Oct-1-ene
(7g)	$SnPh_3$	Cyclo-octene
(7h)	$SnPh_3$	Norbornene
(7i)	$PbPh_3$	CO

species $[Fe(\eta\text{-}C_5H_5)(CO)_2]$ (8). These paramagnetic complexes (7b) gave $g_{\mathrm{iso.}}$ and $a_{\mathrm{iso.}}(^{14}N)$ parameters typical of nitroxide radicals. We have previously reported that low-temperature photolytic oxygenation of (7a) in toluene gives rise to paramagnetic oxygen-containing species, one of which has the probable formula $[Fe(\eta\text{-}C_5H_5)(CO)_n(O_2)]$.[3] In the present work we have extended these studies to photolytic reactions of related iron substrates containing Fe–M [M = Hg (7c), Sn (7d)—(7h), or Pb (7i)] bonds with both nitrosodurene * and dioxygen.

TABLE 1

E.s.r. data for paramagnetic species formed photochemically from organoiron complexes

		E.s.r. data ($g_{\mathrm{iso.}}$,[b] $a_{\mathrm{iso.}}$[c])		
Compound	Solvent [a]	*in vacuo*	*in vacuo* + nitrosodurene	With O_2 or air
(7a)	PhMe	No signal	*d*	(A) [e] 2.025, $a_{\mathrm{iso.}}(^{17}O)$ = 2.1 ± 0.2 (B) [e] 2.043
(7a)	CH_2Cl_2	No signal	2.0053, $a_{\mathrm{iso.}}(^{14}N) = 1.74$	2.025
(7c)	CH_2Cl_2	No signal	2.0053, $a_{\mathrm{iso.}}(^{14}N) = 1.74$	2.0664
(7d)	PhMe	2.074	*d*	2.044
(7d)	CH_2Cl_2	2.079,[f] $a_{\mathrm{iso.}}(Sn) = 2.8 \pm 0.2$	2.0050, $a_{\mathrm{iso.}}(^{14}N) = 1.72$	2.067
(7e)	CH_2Cl_2	No signal	2.0054, $a_{\mathrm{iso.}}(^{14}N) = 1.74$	No signal
(7f)—(7h)	CH_2Cl_2	2.078,[f] $a_{\mathrm{iso.}}(Sn) = 2.8 \pm 0.2$	2.0053, $a_{\mathrm{iso.}}(^{14}N) = 1.74$	2.066
(7i)	PhMe	2.068	*d*	2.043
(7i)	CH_2Cl_2	2.085, $a_{\mathrm{iso.}}(Pb) = 9.5 \pm 0.2$ [g]	2.005, $a_{\mathrm{iso.}}(^{14}N) = 1.73$	2.053 [h]

[a] Reaction temperatures are PhMe (−70 °C) and CH_2Cl_2 (−40 °C). [b] Estimated errors: $g \leqslant \pm 0.002$ (four significant figures), $g \leqslant \pm 0.0002$ (five significant figures). [c] Values in mT; estimated errors ±0.02 unless otherwise stated. [d] Not measured. [e] (A) precedes (B) (from ref. 3). [f] A quartet signal is also observed: $g_{\mathrm{iso.}} = 2.011$, $a_{\mathrm{iso.}}(^{35}/^{37}Cl) = 0.61$ mT. [g] Main signal, especially at temperatures ⩾ −40 °C; a second signal, $g = 2.067 \pm 0.003$, of variable intensity may also be observed. [h] Other signals present: $g = 2.085$, 2.067 (±0.003) (*cf.* photolysis *in vacuo*, see text).

It has been established (see Table 1) that the photolysis of (7a) and nitrosodurene in CH_2Cl_2 solutions at −40 °C gives the spin adduct [$g_{\mathrm{iso.}} = 2.0053$, $a_{\mathrm{iso.}}(^{14}N) = 1.74$ mT] previously assigned structure (7b) [23a] and that paramagnetic species with essentially the same parameters are formed from species (7c)—(7i) under identical conditions. Hence, photolytic cleavage of Fe–M (M = Hg, Sn, or Pb) bonds must occur in the presence of the nitroso-compound and it is possible that a 17-electron intermediate related to (8) is produced. However, the monocarbonyl complexes (7e) and (7f)—(7h) can only form the dicarbonyl adduct (7b) by a process involving replacement of ligand L by CO. If such replacement does not occur it is possible that all species $[Fe(\eta\text{-}C_5H_5)(CO)L(NOR)]$ (L = CO, alkene, or PPh_3; R = aryl) have the same e.s.r. parameters, even though significant coupling to ^{31}P would be expected from (7e) {*cf.* $[Mn(CO)_4(PR_3)(NOR)]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_2(PPh_3)(NOR)]$}.[23] Alternatively, the species formed in all cases could be $[Fe(\eta\text{-}C_5H_5)(CO)(NOR)]$ since the number of carbonyl groups has not been established with certainty.

Photolysis of complexes (7d), (7e), and (7i) at temperatures above −40 °C in the presence of nitrosodurene leads to the observation of additional nitroxide e.s.r. signals. The intensity of the metal–aminyl oxide resonances decreases but in the temperature range *ca.* −10 to +20 °C a quartet [$g_{\mathrm{iso.}} = 2.006$, $a_{\mathrm{iso.}} = 1.41 \pm 0.02$ mT (CH_2Cl_2)] dominates. This can be assigned to the cyclopentadienyl nitroxide, $(C_5H_5)NO(C_6Me_4H)$, with $a_{\mathrm{iso.}}(^{14}N) = a(^1H) = 1.41$ mT. This has been previously observed in photolysis of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ [30] and confirmed by ourselves; the slight discrepancy of parameters is not easily explained although the different solvents, $CHCl_3$ compared to CH_2Cl_2, may be the cause. In the temperature range above +10 °C a second signal, a doublet of triplets [$g_{\mathrm{iso.}} = 2.0061$, $a_{\mathrm{iso.}}(^{14}N) = 1.38 \pm 0.02$, $a_{\mathrm{iso.}}(^1H) = 0.65 \pm 0.01$ mT (in CH_2Cl_2)] is observed; this can also be obtained as a weak signal from photolysis of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ and probably arises from a differing interaction of the cyclopentadienyl group with nitrosodurene. These results indicate that photolysis of derivatives (7d)—(7i) causes Fe–(η-C_5H_5) bond fission, particularly at high temperature.

The product of photo-oxygenation of (7a) in toluene described earlier [3] and tentatively assigned the formula $[Fe(\eta\text{-}C_5H_5)(CO)_n(O_2)]$ is also observed ($g_{\mathrm{iso.}} = 2.025$) when dichloromethane solutions are photolysed in the presence of air or dioxygen but degassed solutions of (7a) are e.s.r. inactive under conditions of photolysis. In contrast, u.v. photolysis of degassed evacuated solutions of (7d) and (7f)—(7h) gives rise to paramagnetic species with the same e.s.r. parameters [$g_{\mathrm{iso.}} = 2.079$, doublet satellites 2.8 mT apart (in CH_2Cl_2)]. The broad doublet can be assigned to combined coupling with ^{119}Sn (8.68%), ^{117}Sn (7.67%), and ^{115}Sn (0.35%) ($I = \frac{1}{2}$). An additional signal observed on photolyses of (7d) and (7f)—(7h) in dichloromethane, but not in toluene, *in vacuo* is a 1 : 1 : 1 : 1 quartet ($g_{\mathrm{iso.}} = 2.011$, $a_{\mathrm{iso.}} = 0.62$ mT) which must arise from a $^{37/35}Cl$-containing species. In toluene a weak signal ($g_{\mathrm{iso.}} = 1.983$) is also observed with three main 1 : 1 : 1 peaks (splitting = 1.76 mT).

It is also found that photolysis of (7i) *in vacuo* in the temperature range −40 to 0 °C gives an e.s.r. signal [$g_{\mathrm{iso.}} = 2.085 \pm 0.002$ (CH_2Cl_2)] with doublet satellites ($a_{\mathrm{iso.}} = 9.5 \pm 0.2$ mT) attributable to coupling with ^{207}Pb (21.11%, $I = \frac{1}{2}$). This species may be related to

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* Blank photolytic experiments with nitrosodurene in the absence of complexes gave no e.s.r. signals.

the above mentioned paramagnetic iron–tin species but unlike the resonance from the tin compounds (7d) and (7f)—(7h) the signal from the lead–iron complex (7i) may also be observed as a prominent species in the presence of air or dioxygen.

A common paramagnetic entity ($g_{\text{iso.}}$ *ca.* 2.066) is formed when dichloromethane solutions of mercury (7c) and tin (7d) and (7f)—(7h) complexes are subjected to photolysis in the presence of dioxygen or air. No evidence for coupling to ($I = \frac{1}{2}$) tin isotopes is observed [from (7d), (7f)—(7h)]. Experiments using ^{17}O-enriched dioxygen gave no detectable hyperfine splitting so that the product is unlikely to be a simple σ-superoxo-complex, although the width of the singlet resonance [ΔH(peak-to-peak) = 1.4 mT] may obscure smaller coupling. In air, photolysis of the lead complex (7i) gives a paramagnetic species with $g_{\text{iso.}} = 2.053$ but a less intense signal ($g_{\text{iso.}} = 2.067$), possibly from the same species as formed by photo-oxidation of (7c), (7d), (7f)—(7h), is also evident and on prolonged photolysis at higher temperatures (−20 to 0 °C) the signal [$g_{\text{iso.}}$ = 2.085, $a_{\text{iso.}}(^{207}\text{Pb})$ = 9.5 mT] which is also observed *in vacuo* dominates the spectrum. In toluene solutions exposed to air, photolysis of (7d) or (7i) affords a singlet with $g_{\text{iso.}} = 2.044$; this is analogous to the secondary signal obtained from the homobimetallic compound (7a). Thus it appears that the nature of the photo-oxidation products of species (7c)—(7i) are solvent dependent and probably involve direct interaction of solvent with these iron species. At this stage it is not possible to formulate structures for these oxidation species.

The nature of the paramagnetic species formed by photolysis *in vacuo* of (7d) and (7f)—(7i) is of interest. The $g_{\text{iso.}}$ values are significantly greater than 2.0023 and, although the observation of doublet satellites proves the presence of a Group 4 atom, the relatively low values of coupling to tin or lead support the formulation of these species as iron-centred paramagnetic derivatives with low unpaired electron density on the main-group metal. Possible modes of formation for these species are electron-transfer reactions or homolytic bond cleavage.

The formation of ionic species by electron transfer seems a plausible explanation of these e.s.r. observations. Such a process is supported by the recently decribed photolysis of [Mn(η-C$_5$H$_5$)(CO)$_3$Me] (M = Cr or Mo) which affords a paramagnetic entity, tentatively assigned the anionic structure [M(η-C$_5$H$_5$)(CO)$_2$Me]$^{\bullet -}$ formed *via* primary M–C bond homolysis and ensuing electron transfer.[31] A related anionic derivative [Mn(CO)$_4$(PbPh$_3$)]$^{\bullet -}$ [$g_{\text{iso.}}$ = 2.017, $a_{\text{iso.}}(^{207}\text{Pb})$ *ca.* 9.0 mT] is apparently generated by radiolysis of [Mn(CO)$_5$(PbPh$_3$)] in the solid state.[32] Several paramagnetic anions of binary iron carbonyls, including [Fe$_2$(CO)$_8$]$^{\bullet -}$ ($g_{\text{iso.}}$ = 2.0385), have been characterised by e.s.r. spectroscopy using ^{57}Fe and ^{13}C labelling.[33] Electrochemical reduction of alkene–iron complexes has also produced related paramagnetic anions.[34] It should also be noted that electrochemical oxidation may form cations such as [Fe(η-C$_5$H$_5$)(CO)$_2$(SMe)]$^+$ ($g_{\text{iso.}}$ = 1.9978) [35] and it is possible that related cations could be formed by photolytically induced electron transfer *in vacuo*. Thus, possible reaction pathways involving Fe–M bond cleavage (established by trapping experiments) are outlined by equations (5) and (6), M = Sn or Pb.

$$[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{MPh_3})] \xrightarrow{h\nu} [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^{\bullet} + \mathrm{MPh_3}^{\bullet} \qquad (5)$$

$$[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^{\bullet} + [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_n(\mathrm{MPh_3})] \longrightarrow \left[\begin{array}{l} \xrightarrow{(a)} \left\{\begin{array}{c} [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_n(\mathrm{MPh_3})]^{\bullet +} \\ (9) \\ + [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^{-} \end{array}\right. \\ \xrightarrow{(b)} \left\{\begin{array}{c} [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_n(\mathrm{MPh_3})]^{\bullet} \\ (10) \\ + [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^{+} \end{array}\right. \end{array}\right. \qquad (6)$$

In this work attempts were made to generate paramagnetic ions such as (9) or (10) (M = Sn or Pb) and observe their e.s.r. spectra. Reduction of (7d) with sodium films (1,2-dimethoxyethane, −40 °C) gave a weak broad e.s.r. signal ($g_{\text{iso.}}$ = 2.039), possibly due to the related anion, but different from those of species formed on photolysis. Sodium reduction of (7i) provided no e.s.r. signals. Electrolytic reduction in the e.s.r. cavity at various temperatures using a mercury electrode, 1,2-dimethoxyethane solvent, and NBu$_4$PF$_6$ supporting electrolyte produced no e.s.r.-active species. It may be noted that a previous polarographic study showed reduction waves for (7d) and (7i) but Fe–Sn or Fe–Pb bond cleavage was also reported.[36] Electrolytic oxidation *in situ* likewise provided no e.s.r. signals. Tetracyanoethylene (tcne) was added as an electron acceptor in attempts to produce paramagnetic cations such as (9). It has previously been reported [37] that tcne reacts with some bimetallic carbonyl compounds causing homolytic fission of the metal–metal bond to form derivatives X–N=C=C(CN)C(CN)$_2^{\bullet}$ [X = M(η-C$_5$H$_5$)(CO)$_n$ (M = Cr or Mo, n = 3; M = Fe, n = 2) or Mn(CO)$_5$] but the primary step is electron transfer producing tcne$^{\bullet -}$ and an unstable organometallic cation. In this work we found that tcne reacts in the dark with (7d) or (7i) *in vacuo* at *ca.* −40 °C giving tcne$^{\bullet -}$, identified by its e.s.r. spectrum,[38] but no other e.s.r.-active species. This observation supports the initial formation of related organometallic cations but, at least in the presence of tcne, such products are not stable paramagnetic species and are not identifiable with products of photolysis *in vacuo*. Thus we have adduced no evidence for electron-transfer processes as proposed in equations (5) and (6).

Alternative reactions by which paramagnetic species may be formed on photolysis of (7d)—(7i) *in vacuo* involve homolytic bond fission. In the presence of nitrosodurene no Ph• radicals are trapped so that M–Ph (M = Sn or Pb) bond cleavage seems unlikely. As mentioned previously it has been established that $C_5H_5^{\bullet}$ radicals are observed in trapping experiments carried out around 0 °C although at −40 °C the only signal observed with nitrosodurene is the aminyl oxide–iron complex, formed by Fe–M bond fission.* However, the primary product of Fe–(η-C_5H_5) fission, *i.e.* $[Fe(CO)L(MPh_3)]^{\bullet}$, is unlikely to be stable, even if solvated, unless reaction with solvent causes a significant chemical modification. Since Fe–M bond fission has been established but both Fe and M atoms are present in the observed paramagnetic species formed by photolysis *in vacuo*, a more likely formulation for these products is a di-iron species as in equation (7) (M = Sn or Pb). It

$$[Fe(\eta\text{-}C_5H_5)(CO)L]^{\bullet} + [Fe(\eta\text{-}C_5H_5)(CO)(MPh_3)] \longrightarrow [L(CO)(C_5H_5)Fe\text{–}Fe(C_5H_5)(CO)(MPh_3)]^{\bullet} \quad (7)$$

would be highly desirable to confirm this proposal using ^{57}Fe labelling, as applied to $[Fe_2(CO)_8]^{\bullet}$.[33]

Molybdenum Complexes.—E.s.r. signals produced by photolysis of several molybdenum-containing bi- and tri-metallic complexes (11a)—(11d) are listed in Table 2.

$[Mo(\eta\text{-}C_5H_5)(CO)_2(L)X]$
(11)

	L	X
(11a)	CO	$Mo(\mu\text{-}C_5H_5)(CO)_3$
(11b)	CO	$HgMo(\eta\text{-}C_5H_5)(CO)_3$
(11c)	CO	$CdMo(\eta\text{-}C_5H_5)(CO)_3$
(11d)	PPh_3	$HgMo(\eta\text{-}C_5H_5)(CO)_2(PPh_3)$
(11e)	CO	$SnPh_3$
(11f)	CO	$PbPh_3$

Spin-trapping experiments using nitrosodurene *in vacuo* of (11a)—(11c) produce the same aminyl oxide (11g), $[Mo(\eta\text{-}C_5H_5)(CO)_n(NOC_6Me_4H)]^{\bullet}$, previously observed from (11a),[23a] by Mo–M (M = Mo, Cd, or Hg) bond fission. Species (11g) is also observed in photolysis of (11d) as well as the previously reported $[Mo(\eta\text{-}C_5H_5)(CO)_2(PPh_3)(NOC_6Me_4H)]^{\bullet}$ which exhibits a doublet of triplets in its e.s.r. spectrum.[23a] This raises the question of the value of *n* in (11g). No aminyl oxides were observed from (11e) and (11f) under the conditions of our experiments.

No e.s.r. signals were produced *in vacuo* on photolysis of complexes (11a)—(11f) but in dioxygen or air complexes (11a)—(11c) in toluene or dichloromethane gave observable paramagnetic species. Complexes (11d)—(11f) failed to produce simple paramagnetic oxygenation products at −40 °C under the conditions of our experiments. Complexes (11a) and (11b) reacted similarly with O_2 giving products with slightly solvent-dependent e.s.r. signals. Complex (11c) gave two distinctly different products. At this stage it is not possible to identify these molybdenum oxygenation products.

TABLE 2

E.s.r. parameters for paramagnetic species formed photochemically from organomolybdenum complexes

Compound	Solvent [a]	E.s.r. data ($g_{iso.}$,[b] $a_{iso.}$[c])	
		in vacuo + nitrosodurene	With O_2 or air
(11a)	PhMe	*d*	1.927 (1.965,[e] 1.912[e])
	CH_2Cl_2	2.0056, $a_{iso.}(^{14}N) = 1.44$, $a_{iso.}(^{95/97}Mo) = 0.40$	1.914
(11b)	PhMe	*d*	1.927
	CH_2Cl_2	2.0056, $a_{iso.}(^{14}N) = 1.44$, $a_{iso.}(^{95/97}Mo) = 0.40$	1.914
(11c)	PhMe	*d*	1.970, 1.951
	CH_2Cl_2	2.0055, $a_{iso.}(^{14}N) = 1.44$, $a_{iso.}(^{95/97}Mo) = 0.40$	1.969, 1.950
(11d)	CH_2Cl_2	(A) 2.0055, $a_{iso.}(^{14}N) = 1.44$, $a_{iso.}(^{95/97}Mo) = 0.40$ (B) 2.0053, $a_{iso.}(^{14}N) = 1.45$, $a_{iso.}(^{95/97}Mo) = 0.50$, $a_{iso.}(^{31}P) = 1.67$	No signal

[a] Reactions temperatures PhMe (*ca.* −10 to −20 °C) and CH_2Cl_2 (*ca.* −40 °C). [b] Estimated errors: $g \leqslant \pm 0.003$ (four significant figures), $g \leqslant \pm 0.0002$ (five significant figures). [c] Values in mT; estimated errors $\leqslant \pm 0.02$. [d] Not measured. [e] Weaker signals.

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* It is also interesting that analysis of solutions of (7d) after photolysis *in vacuo* by gas chromatography–mass spectroscopy has identified ferrocene (<1%) as a product so that some cyclopentadienyl transfer does occur.

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