Photolytic Homolysis of Metal–Metal Bonds of Some Binuclear Transition-metal carbonyls: an Electron Spin Resonance Investigation using Spin Trapping†

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Irradiation, using a 250-W high-pressure mercury lamp, of a solution of $[Mn_2(CO)_{10}]$ and an excess of nitrosodurene (RNO) in CH_2Cl_2 at $\leqslant -30$ °C in the cavity of an e.s.r. spectrometer produces an 18-line signal attributed to $[Mn(CO)_5\{\dot{N}(O)R\}]$. Similarly, aminyl oxides derived from spin trapping of $[Mn(CO)_4L]$ [L = $P(OPh)_3$, PPh_3, $PMePh_2$, PMe_2Ph, $PBu^n{}_3$, or $P(C_6H_{11})_3$], $[Re(CO)_5]$, $[Co(CO)_3\{P(OEt)_3\}]$, $[Mo(\eta\text{-}C_5H_5)(CO)_2L]$ [L = CO or PPh_3), or $[Fe(\eta\text{-}C_5H_5)(CO)_2]$ have been characterised by their e.s.r. solution spectra at *ca.* −30 °C, g = 2.005—2.01. The nitrogen hyperfine coupling [$a(^{14}N)$] is in the range 1.45—1.75 mT, while $a(^{55}Mn)$ = 0.82—0.89, $a(^{185,187}Re)$ = 4.09, $a(^{59}Co)$ = 1.39, $a(^{95,97}Mo)$ = 0.40—0.50, and $a(^{31}P)$ = 0.92—1.67 mT for the manganese complexes and 0.45 mT for $[Co(CO)_3\{\dot{N}(O)R\}\{P(OEt)_3\}]$. For photolysis of $[Mn(CO)_{10}]$: (*i*) formation of aminyl oxide requires light in the 300—400 nm region; (*ii*) using PhMe as solvent, or with CH_2Cl_2 but RNO as a minor component, a 31-line spectrum assigned to $[\{R(O)N\}(OC)_4MnMn(CO)_5]^{+\bullet}$ is obtained. A mechanism is proposed whereby initial formation of $[Mn(CO)_5]$ is followed by competitive processes leading either to $[Mn(CO)_5\{\dot{N}(O)R\}]$ or $[Mn(CO)_5]^-$ and $[Mn_2(CO)_{10}]^{+\bullet}$, which finally may disproportionate to Mn^{II}–Mn^{-I} or react with RNO to yield the binuclear metal aminyl oxide.

THE chemical reactivity of metal carbonyl complexes containing metal–metal bonds has been the subject of extensive study.[1] However, although many of the reactions involving these complexes are photochemical, there is little information concerning the primary photochemical changes (for a contemporary review see ref. 2). Until recently it was assumed that expulsion of a CO ligand [equation (1)] to give a co-ordinatively-unsaturated reactive intermediate is the most important

$$[M_2(CO)_xL_y] \xrightarrow{h\nu} [M_2(CO)_{x-1}L_y] + CO \qquad (1)$$

process. Further studies [3] have shown that photolytic cleavage of the metal–metal bond is common [equation (2)], and that the resulting paramagnetic species undergo

$$[M_2(CO)_xL_y] \xrightarrow{h\nu} 2[M(CO)_{x/2}L_{y/2}] \qquad (2)$$

various reactions characteristic of free radicals, as well as others in which the lability to substitution of CO ligands is demonstrated. These conclusions have been based on careful product analysis. Although they provide strong circumstantial evidence for the formation of metal-centred radicals by metal–metal bond homolysis, the reactive paramagnetic intermediates have not been detected.

Indeed, spectroscopic detection of neutral paramagnetic metal carbonyls is rare {but note the kinetic stability of the co-ordinatively saturated $[V(CO)_6]$}. With the exception of matrix isolation [4] and (indirectly) mass-spectrometric studies,[5] the only substantiated report of such a molecule derived from a bi- or oligonuclear precursor comes from e.s.r. investigation [6,7] of $[Co(CO)_4]$, prepared by sublimation of $[Co_2(CO)_8]$ on to a cold-finger (−196 °C) in the cavity of an e.s.r. spectrometer. Attempts to prepare $[Mn(CO)_5]$ by the same technique were initially thought successful,[8] but the spectrum obtained was later shown [6] to be that of $[Mn(CO)_5(O_2)]$ arising from incomplete degassing of the sublimation apparatus. The assignment of a persistent e.s.r. signal from photolysis of $[Mn_2(CO)_{10}]$ in tetrahydrofuran (thf) solution, originally attributed to $[Mn(CO)_5]$,[9] has been disputed [10,11] and is now attributed [11] to $[Mn(thf)_6]^{2+}$ with $[Mn(CO)_5]^-$ as counter ion.

Recently, we briefly reported [12] that spin-trapping methods,[13] coupled with e.s.r. spectroscopy, could be used to detect metal-centred radicals formed by photolytic homolysis of metal–metal bonds, and it is these results which are now presented in detail.

RESULTS AND DISCUSSION

When a solution of $[Mn_2(CO)_{10}]$ and 2,3,5,6-tetramethyl-1-nitrosobenzene (RNO) (400 mol %) in CH_2Cl_2 was irradiated below *ca.* −30 °C in the cavity of an e.s.r. machine an 18-line spectrum was obtained. (RNO was used as spin trap in preference to the more common Bu^tNO because it does not give rise to spurious e.s.r.

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† No reprints available.

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[6] S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567.

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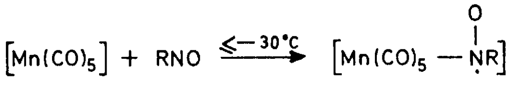
[12] A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1974, 966.

[13] (*a*) M. J. Perkins, *Chem. Soc. Special Publ.*, 1970, **24**, 97; (*b*) C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466; (*c*) E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; (*d*) S. Terabe, K. Kuruma, and R. Konaka, *J.C.S. Perkin II*, 1973, 1252.

signals on irradiation.[13d]) This spectrum is readily assigned to the aminyl oxide radical (1), showing coupling of the unpaired electron with a single ^{14}N nucleus (I 1, a 1.59 mT) and a single ^{55}Mn nucleus (I $\frac{5}{2}$, a 0.88 mT). The formation of (1) is attributed to initial homolysis of the Mn–Mn bond in $[Mn_2(CO)_{10}]$ and subsequent spin trapping of the $[Mn(CO)_5]$ radicals by RNO [equations (3) and (4)]. This process appears to be quite

$$[Mn_2(CO)_{10}] \xrightarrow[CH_2Cl_2]{h\nu} 2[Mn(CO)_5] \qquad (3)$$



$$[Mn(CO)_5] + RNO \xrightarrow{\leqslant -30\,°C} [Mn(CO)_5-\overset{\overset{\displaystyle O}{|}}{\underset{\bullet}{N}}R] \qquad (4)$$

(1)

general. Thus, from the corresponding dimers $[(ML_n)_2]$, radicals centred on Mo, Re, Fe, or Co were trapped, and identified by e.s.r. spectroscopy as the aminyl oxides $[ML_n\{\dot{N}(O)R\}]$ in Table 1. In each case, hyperfine coupling to the metal atom, and to the phosphorus atom when present, gave a characteristic splitting pattern. A typical spectrum is shown in Figure 1. The only metal–metal bonded dimer that did not appear to behave in this way was $[Co_2(CO)_8]$, which with RNO in a variety of solvents gave no e.s.r. signals on irradiation. As a cobalt-centred radical $[Co(CO)_3\{P(OEt)_3\}]$ was trapped from the dimer under these conditions, it appears that light-induced homolysis of the Co–Co bond in $[Co_2(CO)_8]$ does not occur readily. This may have some bearing on the observation[14] that the $[Co_2(CO)_8]$–CCl_4 system, unlike analogues using other metal carbonyl complexes, is inactive as a photolytic polymerisation catalyst for methyl methacrylate.

TABLE 1

E.s.r. parameters for the aminyl oxides $[ML_n\{\dot{N}(O)R\}]$ [a]

Organometallic moiety	a(N) mT	a(M) mT	a(P) mT	g
$[Mn(CO)_5]$	1.59	0.88 (^{55}Mn)		2.006
$[Mn(CO)_5]$ [b]	1.66	0.69 (^{55}Mn)		2.006
$[Re(CO)_5]$	1.47	4.09 ($^{185,187}Re$)		2.01
$[Co(CO)_3\{P(OEt)_3\}]$	1.79	1.39 (^{59}Co)	0.45	2.007
$[Fe(\eta\text{-}C_5H_5)(CO)_2]$	1.75			2.005
$[Mo(\eta\text{-}C_5H_5)(CO)_3]$	1.45	0.40 ($^{95,97}Mo$)		2.005
$[Mo(\eta\text{-}C_5H_5)(CO)_2(PPh_3)]$	1.45	0.50 ($^{95,97}Mo$)	1.67	2.006
$[Mn(CO)_4\{P(OPh)_3\}]$	1.59	0.89 (^{55}Mn)	1.44	2.006
$[Mn(CO)_4(PPh_3)]$	1.59	0.82 (^{55}Mn)	1.29	2.006
$[Mn(CO)_4(PMePh_2)]$	1.59	0.84 (^{55}Mn)	1.31	2.006
$[Mn(CO)_4(PMe_2Ph)]$	1.59	0.86 (^{55}Mn)	0.99	2.006
$[Mn(CO)_4(PBu_3)]$	1.59	0.86 (^{55}Mn)	0.93	2.006
$[Mn(CO)_4\{P(C_6H_{11})_3\}]$	1.59	0.87 (^{55}Mn)	0.92	2.006

[a] In CH_2Cl_2 solution at *ca.* −30 °C. [b] Using Bu^tNO as spin-trap.

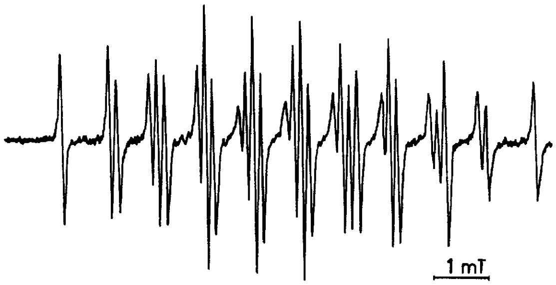


FIGURE 1 E.s.r. spectrum of $[Mn(CO)_4\{\dot{N}(O)R\}(PMe_2Ph)]$ in CH_2Cl_2 solution at *ca.* −30 °C

The radicals $[Fe(\eta\text{-}C_5H_5)(CO)_2]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_3]$ formed the most persistent adducts and were observed up to 20 °C in various solvents, including CH_2Cl_2, $CHCl_3$, thf, and toluene. The relative concentrations of metal complex and spin trap seem not to be critical for obtaining these species. On the other hand, the manganese-, rhenium-, and cobalt-centred radicals did not invariably give clean spectra. The solvents of choice were CH_2Cl_2 or $CHCl_3$ and, although thf was satisfactory, the use of diethyl ether or toluene led to more complicated radicals which were only identified for the $[Mn_2(CO)_{10}]$ system (see below). A large excess of spin trap was also necessary and spectra were only obtained at low temperatures (⩽ −30 °C). The intensity of irradiation can also have a marked effect because the aminyl oxides themselves are photosensitive and strong irradiation destroyed the e.s.r. signal.

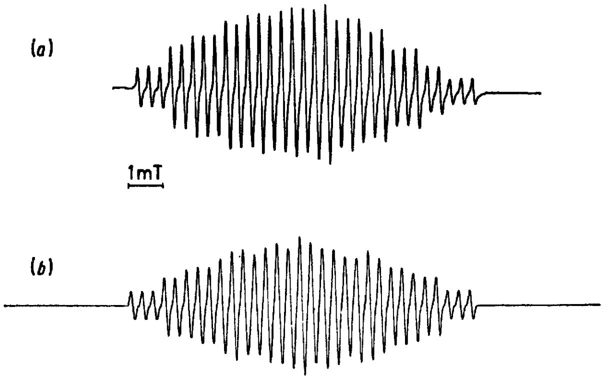


FIGURE 2 Experimental (*a*) and simulated e.s.r. spectra (*b*) of $[Mn_2(CO)_9\{\dot{N}(O)R\}]^+$ in toluene solution at *ca.* 0 °C

For most of the work described here, unfiltered u.v. light was used. However, for the $[Mn_2(CO)_{10}]$ system, experiments were carried out to determine the effect of varying the wavelength. Using suitable filters, it was found that the 300—400 nm region of the spectrum was the one that led to the formation of the $[Mn(CO)_5]$ radicals. The u.v.–visible spectrum of $[Mn_2(CO)_{10}]$ has been investigated[15] and the strong absorption at 340 nm was assigned to the excitation of a M–M σ-bonding electron into the corresponding antibonding orbital. It is this $\sigma(M\text{–}M) \longrightarrow \sigma^*(M\text{–}M)$ transition which clearly leads to the formation of $[Mn(CO)_5]$ radicals. Hence our result lends support to the mechanism of formation outlined in equations (3) and (4).

Under certain conditions, irradiation of $[Mn_2(CO)_{10}]$ in the presence of RNO gave a different aminyl oxide. Thus in toluene, or in CH_2Cl_2 with RNO as a minor component, a 31-line spectrum (Figure 2) was obtained.

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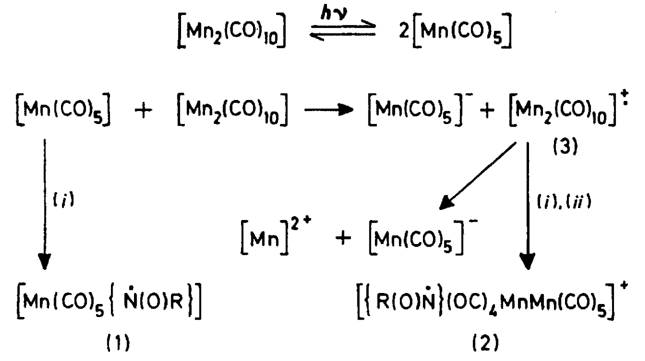
[14] C. H. Bamford in ' Reactivity, Mechanism and Structure in Polymer Chemistry,' eds. A. D. Jenkins and A. Ledwith, Wiley, New York, 1974, ch. 3.

[15] R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem. Soc.*, 1970, **92**, 3653.

This is assigned to a species containing a single ^{14}N nucleus (*a* 1.67 mT) and two magnetically inequivalent ^{55}Mn nuclei (*a* 0.99 and 0.33 mT); a possible structure for this species is (2). Although the mechanism of formation is not obvious, a possible sequence is shown in Scheme 1. In the presence of an excess of spin trap



SCHEME 1 (*i*) +RNO; (*ii*) −CO

RNO the $[Mn(CO)_5]$ radicals are removed as the aminyl oxide (1). However, if there is a deficiency of spin trap then we suggest that the $[Mn(CO)_5]$ radicals undergo one-electron reduction by $[Mn_2(CO)_{10}]$ to give the radical cation (3). Displacement of CO by RNO then accounts for the formation of (2). In the complete absence of RNO, (3) would be expected to disproportionate to Mn^{II} and $[Mn(CO)_5]^-$. The existence of a species such as (3) has been postulated by Krusic *et al.*,[16] and its further disproportionation to Mn^{II}–Mn^{-I} provides a plausible mechanism for the formation[11] of $[Mn(thf)_6]^{2+}$-$[Mn(CO)_5]^-_2$ by irradiation of a thf solution of $[Mn_2(CO)_{10}]$. The complex $[Re_2(CO)_{10}]$ also gave a complicated spectrum when irradiated in the presence of RNO in toluene, but this could not be assigned to a similar species.

It is interesting to note that, in control experiments with no spin trap present, irradiated solutions of dimeric metal carbonyl complexes gave no e.s.r. signals assignable to $[ML_n]$ radicals. This may be due to two factors. First, the metal-centred radicals are likely to be highly reactive with respect to dimerisation or other reactions, and it may be that their lifetimes are too short in solution to enable detectable concentrations to be built up. Secondly, in such radicals there will be low-energy excited states which would lead to rapid spin-relaxation times with a concomitant broadening of the spectral lines. In support of this it is interesting to note[17] that the monomeric species $[Mn(CO)_3(PPh_3)_2]$ fails to give an e.s.r. spectrum even at −196 °C.

E.s.r. Spectra of the Aminyl Oxides.—The e.s.r. parameters of the new complexes are listed in Table 1, and selected values are compared with those of related radicals in Table 2. The *g* values and *N*-coupling constants of the metal-containing species are close to those found[13] for organic aminyl oxides, so there is no doubt that these are true aminyl oxides with the unpaired electron centred mainly on the NO group and with little electron density associated with the metal atom. This is also borne out by the relatively small metal-hyperfine interaction, which for the cobalt and manganese species is very similar to those of the $[M(CO)_n(O_2)]$ radicals ($M = Mn$, $n = 5$; $M = Co$, $n = 4$) (shown by Fieldhouse *et al.*[6] to have the unpaired electron mainly on the O_2 moiety); the latter radicals may be regarded as isoelectronic with O_2, rather than RNO, as spin trap. Other aminyl oxides have been prepared by chemical synthesis[18,19] [*e.g.* as in equation (5)] and their e.s.r. spectra have been analysed in detail to show that there is little unpaired electron density associated with the metal *d* orbitals, although this is theoretically possible.[20a] Our results are in full accord with these conclusions, although there is obviously some delocalisation of the unpaired spin over at least three bonds as shown by the significant phosphorus coupling constants in the $[Mn(CO)_4\{N(O)R\}(PR'_3)]$ radicals. The overall trend in the phosphorus coupling constants of the series of related manganese derivatives (Table 1) is readily understood in terms of the electronegativities of the substituents on the phosphorus atom. Thus the greater the electron-withdrawing ability of the phosphine, the larger the phosphorus coupling constant. The e.s.r. spectra of the aminyl oxides showed regular linewidth variations (*e.g.* Figure 1) which were strongly temperature dependent. This behaviour is well documented in related compounds[18,19] and reports giving detailed analysis of this phenomenon are available.[20]

TABLE 2

Some comparative e.s.r. parameters for RNO or O_2 spin adducts

Radical	*a*(N)	*a*(M)	*g*
	mT		
$[Mn(CO)_5\{\dot{N}(O)R\}]$	1.59	0.88 (^{55}Mn)	2.006
$[Co(CO)_3\{\dot{N}(O)R\}\{P(OEt)_3\}]$	1.79	1.39 (^{59}Co)	2.007
$MeR\dot{N}O$	1.37		2.006
$[Mn(CO)_5(O_2)]$ *		0.78 (^{55}Mn)	2.006
$[Co(CO)_4(O_2)]$ *		1.25 (^{59}Co)	2.008

* From ref. 6.

$$K_3[Co^{II}(CN)_5] + R''NO \xrightarrow{(R'' = \text{alkyl or aryl})} [Co^{III}(CN)_5\{\dot{N}(O)R''\}]^{3-} \quad (5)$$

In the preceding discussion it has been assumed that the spin adducts observed have been formed by photolysis of the organometallic complex to give radicals which are then trapped by RNO. However, it is impossible to rule out completely the possibility that the spin trap interferes with the photolysis, either by photosensitisation or by reaction with the organometallic substrate. One possible mechanism must be considered in the light

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[16] P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Amer. Chem. Soc.*, 1975, **97**, 667.

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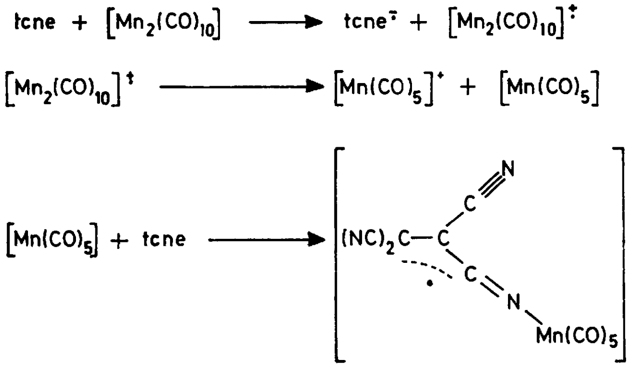
[18] M. G. Swanwick and W. A. Waters, *J. Chem. Soc.* (*B*), 1971, 1059; D. Mulvey and W. A. Waters, *J.C.S. Perkin II*, 1974, 666.

[19] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 243.

[20] (*a*) M. C. R. Symons and J. G. Wilkinson, *J.C.S. Faraday II*, 1972, 1265; (*b*) N. M. Atherton and D. Waldram, *ibid.*, p. 413.

of a recent report by Krusic *et al.*[16] They showed that $[Mn_2(CO)_{10}]$ (and related complexes) reacted with tetracyanoethylene (tcne) according to Scheme 2. Organic nitroso-compounds are oxidising agents (although much weaker than tcne) and it is conceivable that a similar mechanism is operative in the systems we have studied, although in our system there is no evidence of a reaction in the dark.



SCHEME 2

Nevertheless we believe that the reactions reported here are not initiated by the spin trap for the following reasons. First, none of the results or interpretations is inconsistent with evidence based on product analysis in systems containing no spin trap. Secondly, some of the results obtained with RNO could be replicated (albeit less conveniently, see Table 1) with Bu^tNO and it is unlikely that these two spin traps would behave identically towards a large range of organometallic complexes in any reaction more complicated than spin trapping. Thirdly, the aminyl oxides were also obtained by photolytic homolysis of C–M bonds of corresponding metal alkyl derivatives, *e.g.* $[Mn(CO)_5\{\dot{N}(O)R\}]$ from $[Mn(CH_2Ph)(CO)_5]$ in the presence of RNO.[12] Finally, there is no evidence, from i.r. or n.m.r. studies, of any interaction between RNO and $[Mn_2(CO)_{10}]$.

One final reservation concerning spin trapping must be mentioned. The intensity of the e.s.r. signal obtained depends on a number of factors, including the rate of production of radicals, efficiency of trapping, and the stability of the aminyl oxides formed.[13] For these reasons, no quantitative conclusions can be drawn, and there is always a possibility that the processes detected in spin-trapping studies are minor ones and do not reflect the major paths.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian Associates E3 spectrometer with a V-4557 variable-temperature unit. Irradiation of samples *in situ* was achieved with an Osram ME/D 250-W high-pressure mercury lamp. The intensity of light focused on the cavity was varied using a quartz lens system. Samples were examined in quartz e.s.r. tubes fitted with Pyrex T pieces so that solutions could be made up and maintained in an atmosphere of dry nitrogen. Coupling constants were obtained directly from the spectra after calibration of the field sweep using Fremy's salt, and *g* values were measured with respect to diphenylpicrylhydrazyl (dpph).

Solvents were dried before use by distillation under nitrogen from the following drying agents: CH_2Cl_2 and $CHCl_3$ from P_4O_{10}, thf and Et_2O from sodium diphenylketyl, and toluene from sodium metal. The nitroso-compounds RNO [13d] and Bu^tNO [21] were prepared by published procedures. The complexes $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$, and $[Co_2(CO)_8]$ were purchased from Strem Chemicals Inc. and were resublimed prior to use. Other organometallic reagents were synthesised by well known methods, and were characterised by comparison of their physical properties with those in the literature.

Solutions of the organometallic substrate and of the spin trap were prepared separately under nitrogen. Equal volumes of each were transferred by syringe to an e.s.r. tube which had been flushed with dry nitrogen. The sample was placed in the cavity of the e.s.r. machine and left to equilibrate at the required temperature before the irradiation was commenced. For the manganese, rhenium, and cobalt systems the concentrations of the solutions were adjusted so that the molar ratio of metal substrate : spin trap was *ca.* 1 : 4; typical concentrations were 0.015 and 0.060 mol dm^{-3} respectively. Other samples were prepared so that the spin trap was *ca.* 30 mol % with respect to the organometallic complex.

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[21] J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.