Homolysis of Metal–Carbon and Metal–Metal Bonds: Spin-trapping of the Resulting Carbon- and Metal-centred Radicals

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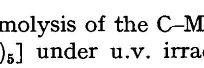
Summary Homolysis of the C–Mn bond of $[\mathrm{RMn(CO)_5}]$ or $[\mathrm{RCOMn(CO)_5}]$ under u.v. irradiation has been studied using nitrosodurene as a spin-trap for *both* the radicals formed; irradiation of various metal–metal bonded compounds (LM–ML, M = Mn, Re, Fe, Mo, or Co) gives rise to metal-centred radicals which can similarly be trapped.

We have used the spin-trapping technique to determine the radical species formed by u.v. irradiation of organometallic compounds in solution. In this way we have demonstrated (i) C–Mn bond homolysis in alkylpentacarbonylmanganese(I) compounds, and (ii) M–M bond homolysis in dimeric organometallic species. In each case the transient metal-centred free radical has been identified by spin-trapping with nitrosodurene[1] (ArNO, Ar = 2,3,5,6-$\mathrm{Me_4C_6H}$).

Irradiation with u.v. light of $[\mathrm{RMn(CO)_5}]$ (R = Me or $\mathrm{PhCH_2}$) in solution leads to homolytic cleavage of the C-Mn bond [reaction (1)]. Evidence was provided by spin-trapping *both* radical fragments with ArNO to give the

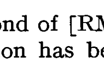
$$[\mathrm{RMn(CO)_5}] \xrightarrow[\mathrm{CHCl_3}]{h\nu,\ ca.\ -30^\circ} \mathrm{R\cdot} + \mathrm{\cdot Mn(CO)_5} \qquad (1)$$

derived nitroxides (I) and (II), identified by e.s.r. spectroscopy.


$\mathrm{Ar{-}N(O\cdot){-}Mn(CO)_5}$

(I)

and


$\mathrm{Ar{-}N(O\cdot){-}R}$

(II)

Homolysis of C–M (M = Sn, Pb, or Hg) bonds has been studied previously[2] using spin-trapping methods. However, we believe this is the first time that *both* radical fragments have been directly detected.

The acylpentacarbonylmanganese(I) compounds $[\mathrm{R'C(O)Mn(CO)_5}]$($\mathrm{R'} = \mathrm{PhCH_2}$ or $\mathrm{Ph_2CH}$) undergo similar homolysis although the spin-adduct formed is generally derived from R'· rather than from R'CO. This may arise from decarbonylation of an acyl radical prior to trapping, cleavage of the $\mathrm{R'{-}C(O)Mn(CO)_5}$ bond, or cleavage of an R'–Mn bond after decarbonylation of the parent compound. Studies are underway to distinguish between these possibilities.

Table

E.s.r. parameters for nitroxides,[a] ArN(ML)O·

ML	*a* (N)	*a* (M)	*a* (P)	*g*
$[\mathrm{Mn(CO)_5}]$	1·59	0·86 (^{55}Mn)		2·006
$[\mathrm{Re(CO)_5}]$	1·47	4·09 (^{185,187}Re)		2·01
$[\mathrm{Mn(CO)_4PPhMe_2}]$	1·59	0·86 (^{55}Mn)	0·99	2·006
$[\mathrm{Co(CO)_3P(OEt)_3}]$	1·79	1·39 (^{59}Co)	0·45	2·007
$[\mathrm{Fe(CO)_2Cp}]$	1·75			2·005
$[\mathrm{Mo(CO)_3Cp}]$	1·45	0·40 (^{95,97}Mo)		2·005

[a] In $\mathrm{CHCl_3}$ solution at *ca.* −30°. Coupling constants in mT. Radicals generated by the reaction LM–ML + ArNO $\xrightarrow{h\nu}$ ArN(ML)O· Cp = η-$\mathrm{C_5H_5}$.

The spin-adduct (I) is of particular interest. An alternative synthesis involves irradiation of $[\mathrm{Mn_2(CO)_{10}}]$ and ArNO (400 mol%) in $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$, or THF below −30°. It is readily identified by its 18 line e.s.r. spectrum (see Figure). {The relatively stable nitroxides $[\mathrm{(NC)_5MN(R)O\cdot}]^{3-}$ (M = Co or Fe) have been studied by e.s.r. spectroscopy,[3] but there is no precedent for the addition of reactive transition metal-centred radicals to nitroso-compounds to give nitroxides}. The large excess of spin-trap proved necessary since at lower ratios of ArNO:$[\mathrm{Mn_2(CO)_{10}}]$ a different radical is formed. The 31-line spectrum obtained for this species is consistent with a radical containing a nitroxide N atom [*a*(N) 1·67 mT] and two magnetically inequivalent Mn atoms [*a*(Mn) 0·99 mT and 0·33 mT], but the complete structure has yet to be determined.

The use of ArNO as a spin-trap for metal-centred radicals formed by M–M bond cleavage of the appropriate dimers under u.v. irradiation has proved quite general. Thus the radicals $\mathrm{\cdot Mn(CO)_4PPhMe_2}$, $\mathrm{\cdot Re(CO)_5}$, $\mathrm{\cdot Fe(CO)_2Cp}$, $\mathrm{\cdot MoCp(CO)_3}$ and $\mathrm{\cdot Co(CO)_3P(OEt)_3}$ all form spin-adducts (see Table).

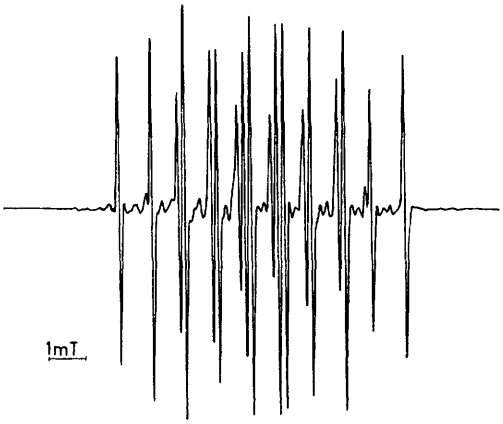


FIGURE. E.s.r. spectrum of Ar–N(–O·)–Mn(CO)$_5$ in CHCl$_3$ at *ca.* −30°. Note asymmetric line broadening effects expected for nitroxides.

The similarity of the ^{14}N coupling constants and *g*-factors to those normally found for spin-adducts suggests that these compounds are best regarded as nitroxide radicals with no substantial spin density in the metal *d*-orbitals (*cf.* ref. 3).

It is interesting to note that in control experiments with no spin-trap present, irradiated solutions of the dimers gave no e.s.r. signals. This suggests that spin relaxation times are too rapid for direct detection of these metal-centred radicals in solution. An e.s.r. spectrum attributed to the ·Mn(CO)$_5$ radical in THF solution has been reported,[4] but the Mn hyperfine coupling constant (*ca.* 9·3 mT) is similar to that expected for an Mn^{II} species. Furthermore the solid state spectrum at 77 K shows fine structure effects characteristic of a sextet spin state.

The results presented in this report suggest that spin-trapping of metal-centred radicals may provide a simple method of determining their involvement in chemical reactions.

(*Received, 24th September* 1974; *Com.* 1194.)

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