

**Photolytic Homolysis of the Metal–Carbon ( $sp^3$  or  $sp^2$ ) Bond of Alkyl or Acyl Transition-metal Complexes: an Electron Spin Resonance Study using Spin Trapping; and a Note on Aminyl Oxides  $[ML_n\{N(\dot{O})R\}]$  [ $ML_n = Ru(CO)_4(SiMe_3)$ ,  $Os(CO)_4(SiMe_3)$ , or  $Fe(\eta-C_3H_5)(CO)_3$ ;  $R = aryl$ ]**

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Irradiation of the following metal alkyls has been carried out in  $CH_2Cl_2$  (or PhMe) in the presence of nitrosodurene, RNO ( $R = C_6HMe_4-2,3,5,6$ ), in the cavity of an e.s.r. spectrometer:  $[Mn(CO)_5R']$  ( $R' = CH_2Ph$  or  $CH_2SiMe_3$ ),  $[Fe(\eta-C_5H_5)(CO)_2R']$ ,  $[Mo(\eta-C_5H_5)(CO)_3R']$  ( $R' = Me, Et, or CH_2Ph$ ), *cis*- $[PtR'_2(PMe_2Ph)_2]$  ( $R' = CH_2SiMe_3$  or  $CH_2CMe_3$ ),  $[AuR'(PPh_3)]$  ( $R' = Me$  or  $CH_2SiMe_3$ ), and  $[CoR'L(oep)]$  ( $H_2oep = 2,3,7,8,12,13,17,18$ -octaethylporphyrin and  $R' = Me, L = NC_5H_5$ ; or  $R' = Et, L = OH_2$ ). Similar experiments have been performed on (i) the acylmetal complexes  $[Mn(CO)_5\{C(O)R''\}]$  ( $R'' = CH_2Cl, Me, Et, CH_2Ph, or CHPh_2$ ) or  $[Fe(\eta-C_5H_5)(CO)_2\{C(O)R''\}]$  ( $R'' = Me$  or  $CH_2Ph$ ), and (ii) the metal–metal bonded  $[M_2(CO)_8(SiMe_3)_2]$  ( $M = Ru$  or  $Os$ ). Finally, the dark reaction between the stable iron(II) complex  $[Fe(\eta-C_3H_5)(CO)_3]$  and RNO in  $CH_2Cl_2$  has been investigated. As a consequence, from the alkyls, metallo-aminyl oxides  $[ML_n\{N(\dot{O})R\}]$  were observed, except for  $ML_n =$  a platinum(I), gold(0), or cobalt(II) moiety, but the alkylaminyl oxides  $RN(\dot{O})R'$  were found in every case [although with the molybdenum(II) alkyls as substrates these were not detected at  $-30^\circ C$  but only at  $20^\circ C$ ]; two of these ( $R' = CH_2SiMe_3$  or  $CH_2CMe_3$ ) are new and show remarkably different  $\beta$ -proton hyperfine couplings, attributed in part to a conformational difference allowing for close  $Si \cdots O$  proximity for  $R' = CH_2SiMe_3$ , and also to the greater steric requirements of the neopentyl group. From the acyls, the corresponding metallo-aminyl oxide was invariably detected, but never the spin-trapped acyl radical  $RN(\dot{O})COR''$ ; however, the corresponding spin-trapped alkyl radical  $RN(\dot{O})R''$  was observed but only for the case of  $R'' = CH_2Ph$  or  $CHPh_2$ . The remaining experiments led to the e.s.r. characterisation of  $[ML_n\{N(\dot{O})R\}]$ ,  $ML_n = Ru(CO)_4(SiMe_3)$ ,  $Os(CO)_4(SiMe_3)$ , or  $Fe(\eta-C_3H_5)(CO)_3$ .

THE factors involved in thermal decomposition of transition-metal alkyls are now well understood and several pathways have been established.<sup>1</sup> In contrast, photolytic reactions involving metal–carbon bonds have only recently attracted attention for transition-metal alkyls,<sup>2,3</sup> with the notable exception of cobalt(III) alkyls related to coenzyme  $B_{12}$  which have been subjected to detailed scrutiny<sup>4</sup> because of the postulated importance of homolytic cleavage of the Co–C bond in  $B_{12}$  catalysed reactions.<sup>5</sup> These cobalamin and cobaloxime complexes are rather atypical of metal alkyls, having photochemical behaviour involving the corrin or oxime ligands<sup>4a</sup> and we will not discuss them further.

For more conventional transition-metal alkyls, detailed photolysis studies are only available<sup>6,7</sup> for the complexes  $[M(\eta-C_5H_5)(CO)_3R']$  ( $R' = Me$  or  $CH_2Ph$ ;  $M = Cr, Mo, or W$ ), alkyl and aryl derivatives of the type  $[M(\eta-C_5H_5)_2R'_2]$  from the titanium group,<sup>8,9</sup> and  $[M(\eta-C_5H_5)_2Me_2]$  ( $M = V$  or  $Nb$ ),<sup>10</sup> or  $[V(\eta-C_5H_5)_2Me]$ . Other scattered reports relate to photochemical syntheses.

In this paper we report the results of a spin-trapping study of a variety of transition-metal alkyls and acyls designed to give qualitative information concerning the effect of differing alkyl ligand and transition-metal group on the photolytic homolysis of the M–C bond. Some preliminary results have appeared previously.<sup>11</sup> We also present some further results on the spin-trapping of metal-centred radicals produced by the homolysis of metal–metal bonds. As spin-trap, nitrosodurene RNO ( $R = C_6HMe_4-2,3,5,6$ ) was used and the derived spin

adduct is an aminyl oxide (or nitroxide)  $RN(\dot{O})R'$ , and  $RN(\dot{O})R''$  where  $R'$  or  $R''$  is the carbon- or metal-centred radical.

#### EXPERIMENTAL

*General.*—The metal alkyl and acyl complexes used in this study were prepared by well known routes and were checked for purity by C,H analyses and i.r. spectroscopy. Nitrosodurene was synthesised by a published method.<sup>12</sup> Dichloromethane was distilled from  $P_4O_{10}$  under  $N_2$  immediately before use. Other experimental details have been described earlier.<sup>13</sup>

E.s.r. spectra were assigned by comparison of spectral parameters with those of nitrosodurene adducts of alkyl<sup>14</sup> or metal-centred radicals<sup>15</sup> reported previously except for the new aminyl oxides derived from  $\dot{C}H_2EMe_3$  ( $E = C$  or  $Si$ ) which were independently prepared by Cl abstraction from the appropriate compound  $Me_3ECH_2Cl$ .

*Photolysis Experiments.*—Equal volumes of  $CH_2Cl_2$  solutions of the metal alkyl or acyl (*ca.*  $10^{-2}$  mol  $l^{-1}$ ) and nitrosodurene (*ca.*  $10^{-3}$  mol  $l^{-1}$ ) were mixed in quartz e.s.r. tubes under  $N_2$ . The sample was then directly irradiated in the cavity of the e.s.r. spectrometer, using a 1-kW Hanovia Hg–Xe lamp.

*Preparation of Authentic Aminyl Oxides  $Me_3ECH_2N(\dot{O})R$  ( $E = C$  or  $Si$ ).*—A mixture of nitrosodurene,  $Me_3ECH_2Cl$ , and  $Sn_2Bu_6$  in  $CH_2Cl_2$  was irradiated.<sup>16</sup> The e.s.r. spectra of the resulting adducts  $Me_3ECH_2N(\dot{O})R$  were easily observed [ $E = C$ :  $a(^{14}N) = 1.34$ ,  $a(^1H) = 1.04$ ;  $E = Si$ :  $a(^{14}N) = 1.44$ ,  $a(^1H) = 1.59$  mT].

*Spin Trapping of the Phenylacetyl Radical,  $PhCH_2\dot{C}(O)$ .*—A mixture of the aldehyde  $PhCH_2C(O)H$ ,  $CH_2Cl_2$ ,  $(Bu^tO)_2$ , and nitrosodurene was photolysed in the cavity of the e.s.r. spectrometer at  $-30^\circ C$ . The only radical detected had

$a(^{14}\text{N}) = 0.71$  mT and was assigned  $^{14}$  to  $\text{PhCH}_2\text{C}(\text{O})\text{N}(\dot{\text{O}})\text{R}$ . At  $0^\circ\text{C}$  a significant amount of  $\text{PhCH}_2\text{N}(\dot{\text{O}})\text{R}$  was also present and this became the dominant species at  $25^\circ\text{C}$ .

## RESULTS

*Photolysis of Alkylmetal Complexes.*—The radical species detected during photolysis of metal alkyls or aryls are summarised in Tables 1 and 2 respectively. Some e.s.r. parameters are given in Table 3.

TABLE 1

Radicals spin-trapped during photolysis of transition-metal alkyl complexes in  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$  <sup>a</sup>

Alkylmetal complex, $[\text{ML}_n\text{R}']$	Aminyl oxide, $\text{RN}(\dot{\text{O}})\text{R}'$	Metallo-aminyl oxide, $[\text{ML}_n\{\text{N}(\dot{\text{O}})\text{R}\}]$
$[\text{Mn}(\text{CO})_5(\text{CH}_2\text{Ph})]$	s	s
$[\text{Mn}(\text{CO})_5(\text{CH}_2\text{SiMe}_3)]$	s	s
$[\text{Mn}(\text{CO})_5\text{Me}]$	w	w
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CH}_2\text{Ph})]$	s	s
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CH}_2\text{SiMe}_3)]$	s	s
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Me}]$	w	w
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{CH}_2\text{Ph})]$	n.o. <sup>b</sup>	m
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{Me}]$	n.o. <sup>b</sup>	m
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{Et}]$	n.o. <sup>b</sup>	m
<i>cis</i> - $[\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_2\text{Ph})_2]$	s	n.o.
<i>cis</i> - $[\text{Pt}(\text{CH}_2\text{CMe}_3)_2(\text{PMe}_2\text{Ph})_2]$	s <sup>c</sup>	n.o.
$[\text{AuMe}(\text{PPh}_3)]$	s	n.o.
$[\text{Au}(\text{CH}_2\text{SiMe}_3)(\text{PPh}_3)]$	s	n.o.
$[\text{CoMe}(\text{oep})(\text{py})]$	w	n.o.
$[\text{CoEt}(\text{oep})(\text{OH}_2)]$	s	n.o.

<sup>a</sup> Abbreviations: s = strong, m = medium, w = weak, n.o. = not observed. <sup>b</sup>  $\text{R}'\cdot$  observed at  $20^\circ\text{C}$ . <sup>c</sup>  $\text{Bu}^+$  adduct also trapped.

TABLE 2

Radicals spin-trapped during photolysis of transition-metal acyl complexes in  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$  <sup>\*</sup>

Acylmetal complex, $[\text{M}_n\text{L}(\text{COR}')]$	Aminyl oxide, $\text{RN}(\dot{\text{O}})\text{R}'$	Metallo-aminyl oxide, $[\text{ML}_n\{\text{N}(\dot{\text{O}})\text{R}\}]$
$[\text{Mn}(\text{CO})_5(\text{COCH}_2\text{Ph})]$	s	s
$[\text{Mn}(\text{CO})_5(\text{COCHPh}_2)]$	s	s
$[\text{Mn}(\text{CO})_5(\text{COMe})]$	n.o.	w
$[\text{Mn}(\text{CO})_5(\text{COEt})]$	n.o.	w
$[\text{Mn}(\text{CO})_5(\text{COCH}_2\text{Cl})]$	n.o.	w
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COCH}_2\text{Ph})]$	w	s
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COMe})]$	n.o.	w

<sup>\*</sup> See footnote a, Table 1.

TABLE 3

Electron spin resonance parameters for some aminyl oxides  $\text{RN}(\dot{\text{O}})\text{R}'$

Radical $\text{R}'\cdot$	$a(^{14}\text{N})/\text{mT}$	$a(^1\text{H})/\text{mT}$
$\text{Me}_2\text{CCH}_2$ <sup>a</sup>	1.34	1.04
$\text{Me}_2\text{SiCH}_2$ <sup>a</sup>	1.44	1.59
$\text{Me}$ <sup>b</sup>	1.37	1.22
$\text{MeCH}_2$ <sup>b</sup>	1.37	1.10

<sup>a</sup> This work. <sup>b</sup> From ref. 14.

(a)  $[\text{Mn}(\text{CO})_5\text{R}']$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{R}']$ . Photolysis of these alkyls gave strong clean e.s.r. signals assignable to adducts derived from both  $\text{R}'\cdot$  and  $\cdot\text{Mn}(\text{CO})_5$  or  $\cdot\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2$  ( $\text{R}' = \text{CH}_2\text{Ph}$  or  $\text{CH}_2\text{SiMe}_3$ ). When  $\text{R}' = \text{Me}$ , much weaker peaks, from  $\text{MeN}(\dot{\text{O}})\text{R}$  and the corresponding Mn- or Fe-centred radical, could only just be distinguished from other unidentified signals.

(b)  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{R}']$ . At  $-30^\circ\text{C}$ , photolysis ( $\text{R}' = \text{Me}$ ,  $\text{Et}$ , or  $\text{CH}_2\text{Ph}$ ) gave weak signals from a single species attributed to  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\{\text{N}(\dot{\text{O}})\text{R}\}]$ , with no evidence

for the expected  $\text{R}'\cdot$  adduct. However, at  $20^\circ\text{C}$  the reverse was found,  $\text{R}'\text{N}(\dot{\text{O}})\text{R}$  being clearly detected but no metal-containing radicals observed.

(c) *cis*- $[\text{PtR}'_2(\text{PMe}_2\text{Ph})_2]$ . Photolysis of the platinum(II) alkyl ( $\text{R}' = \text{CH}_2\text{SiMe}_3$  or  $\text{CH}_2\text{CMe}_3$ ) gave strong signals due to  $\text{R}'\text{N}(\dot{\text{O}})\text{R}$  but no Pt-containing paramagnetic species were found. For  $\text{R}' = \text{CH}_2\text{CMe}_3$ , a weaker signal, assigned to  $\text{Bu}^+\text{N}(\dot{\text{O}})\text{R}$ , was also observed.

(d)  $[\text{AuR}'(\text{PPh}_3)]$ . When  $\text{R}' = \text{Me}$  or  $\text{CH}_2\text{SiMe}_3$ , photolysis gave clean, strong spectra of the spin-trapped alkyl radicals but no Au-containing adducts.

(e)  $[\text{CoR}'(\text{L})(\text{oep})]$  ( $\text{H}_2\text{oep} = \text{octaethylporphyrin}$ ). Two complexes of this type were studied ( $\text{R}' = \text{Me}$ ,  $\text{L} = \text{pyridine}$ ;  $\text{R}' = \text{Et}$ ,  $\text{L} = \text{OH}_2$ ); each gave, on photolysis, clear signals arising from  $\text{RN}(\dot{\text{O}})\text{R}'$ , but again no metal-centred adduct was found.

*Photolysis of Acylmanganese(II) Complexes.*—Various complexes  $[\text{Mn}(\text{CO})_5\{\text{C}(\text{O})\text{R}'\}]$  were irradiated in  $\text{CH}_2\text{Cl}_2$ . For  $\text{R}'' = \text{CH}_2\text{Ph}$  or  $\text{CHPh}_2$ , clean signals from  $\text{R}''\text{N}(\dot{\text{O}})\text{R}$  and  $[\text{Mn}(\text{CO})_5\{\text{N}(\dot{\text{O}})\text{R}\}]$  were readily observed. However, for  $\text{R}'' = \text{CH}_2\text{Cl}$ ,  $\text{Me}$ , or  $\text{Et}$  only weak  $\cdot\text{Mn}(\text{CO})_5$  adducts were detectable at  $-30^\circ\text{C}$ . The iron system behaved similarly,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{C}(\text{O})\text{R}'\}]$  giving strong  $\text{R}''\cdot$  and  $\cdot\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2$  adducts for  $\text{R}'' = \text{CH}_2\text{Ph}$  but not for  $\text{R}'' = \text{Me}$ . In no instance were signals arising from spin-trapped acyl radicals observed at  $-30^\circ\text{C}$ .

*Homolysis of Compounds containing Metal-Metal Bonds.*—In our earlier work <sup>13</sup> on the trapping of metal-centred radicals we have reported results for adducts containing  $\text{Mn}^0$ ,  $\text{Fe}^I$ ,  $\text{Mo}^I$ ,  $\text{Re}^0$ , or  $\text{Co}^0$ . However, not all metal-centred radicals are trapped by nitrosodurene; no aminyl oxides containing  $\text{Au}^0$  or  $\text{Pt}^I$  have been detected in the present investigation.\* We have, however, obtained some additional information on metal-metal bond homolysis which is included here as a supplement to our previous report.<sup>13</sup>

(a) *Spin trapping of*  $[\text{Fe}(\eta\text{-C}_3\text{H}_5)(\text{CO})_3]$ . The title allyl and related complexes are examples of stable transition-metal organometallic radicals produced by homolysis.<sup>3</sup> In an attempt to substantiate the authenticity of spin-trapping experiments where the homolysis was photo-induced, we have trapped this radical in the absence of light.

The e.s.r. spectrum of  $[\text{Fe}(\eta\text{-C}_3\text{H}_5)(\text{CO})_3]$  in tetrahydrofuran (thf) consists of a broad singlet with  $g_{\text{av.}} = 2.045$  (cf., the published value <sup>16</sup> of 2.042 in benzene). Upon addition of nitrosodurene in the dark a low-intensity 1 : 1 : 1 triplet appeared which grew in intensity as the solution was warmed. This is assigned to the spin adduct (Table 4). The e.s.r. parameters are very similar to those found in the M-M bond

TABLE 4

Electron spin resonance parameters for some new spin-trapped metal-centred radicals  $[\text{ML}_n\{\text{N}(\dot{\text{O}})\text{R}\}]$

Organometallic moiety, $\text{ML}_n$	$a(^{14}\text{N})/\text{mT}$	$a(\text{M})/\text{mT}$	$g_{\text{av.}}$
$[\text{Fe}(\eta\text{-C}_3\text{H}_5)(\text{CO})_3]$ <sup>a</sup>	1.48		2.0051
$[\text{Ru}(\text{CO})_4(\text{SiMe}_3)]$ <sup>b</sup>	1.62	ca. 0.5 (av. <sup>99,101</sup> Ru)	2.0048
$[\text{Os}(\text{CO})_4(\text{SiMe}_3)]$ <sup>c</sup>	1.65	0.38 ( <sup>189</sup> Os)	2.0066

<sup>a</sup> Formed by addition of  $\text{RNO}$  to the stable monomer  $[\text{Fe}(\eta\text{-C}_3\text{H}_5)(\text{CO})_3]$  in tetrahydrofuran at  $20^\circ\text{C}$ . <sup>b</sup> Formed by warming  $[\text{Ru}_2(\text{CO})_8(\text{SiMe}_3)_2]$  in toluene at  $40^\circ\text{C}$  in the presence of  $\text{RNO}$ . <sup>c</sup> Formed by photolysing  $[\text{Os}_2(\text{CO})_8(\text{SiMe}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  at  $10^\circ\text{C}$  in the presence of  $\text{RNO}$ .

\* Platinum(II) has been spin-trapped using  $\text{PhCH}=\text{N}(\text{O})\text{Bu}^+$  (cf., H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, 1977, **99**, 7073; T. L. Hall, M. F. Lappert, and P. W. Lendnor, *J. Chem. Soc., Dalton Trans.*, 1980, 1448).

homolysis studies.<sup>13</sup> These observations demonstrate that nitrosodurene can intercept transition-metal-centred carbonyl radicals in the absence of light, supporting a simple trapping role for RNO.

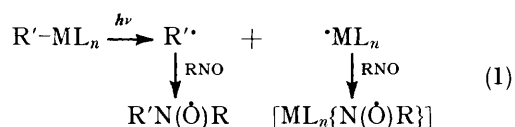
(b) *Spin trapping of*  $[M(\text{CO})_4(\text{SiMe}_3)]$  ( $M = \text{Ru}$  or  $\text{Os}$ ). The complexes  $[M_2(\text{CO})_8(\text{SiMe}_3)_2]$  ( $M = \text{Ru}$ <sup>17</sup> or  $\text{Os}$ <sup>18</sup>) formed by heating  $\text{SiMe}_3\text{H}$  with  $[M_3(\text{CO})_{12}]$  have an axially disubstituted structure containing a metal-metal bond. The cleavage reactions of the ruthenium complex are extremely facile; for example there is a rapid reaction<sup>19</sup> with  $\text{I}_2$  at 0 °C for which it has been suggested that the first step is thermolysis of the metal-metal bond. The osmium analogue has a stronger M-M bond and is thermally stable. However, homolysis is believed to occur on irradiation.

When  $[\text{Ru}_2(\text{CO})_8(\text{SiMe}_3)_2]$  in toluene was warmed to 50 °C in the presence of nitrosodurene, a clear 1 : 1 : 1 triplet e.s.r. signal was obtained which is assigned to the aminyl oxide radical  $[\text{Ru}(\text{CO})_4\{\text{N}(\dot{\text{O}})\text{R}\}(\text{SiMe}_3)]$ . The e.s.r. parameters (Table 4) compare well with those for previously established metallo-aminyl oxide radicals.<sup>13</sup> Isotope structure from <sup>99</sup>Ru (12.8%,  $I = \frac{5}{2}$ ) and <sup>101</sup>Ru (17%,  $I = \frac{5}{2}$ ) was detectable and we estimate the ruthenium coupling constant to be ca. 0.5 mT.

A similar 1 : 1 : 1 e.s.r. signal was obtained on photolysis of  $[\text{Os}_2(\text{CO})_8(\text{SiMe}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  at 10 °C in the presence of RNO. However, the signal intensity was much lower than for the ruthenium spin adduct, indicating either a less stable aminyl oxide, less efficient spin trapping, or possibly a lower steady-state concentration of metal-centred radicals. The e.s.r. parameters for the two new metallo-aminyl oxides show close similarity. Osmium satellites (<sup>189</sup>Os, 16.1%,  $I = \frac{3}{2}$ ) were detectable with a coupling constant of 0.38 mT.

## DISCUSSION

If photolysis of a transition-metal alkyl  $\text{R}'\text{-ML}_n$  resulted in efficient homolytic cleavage of the M-C bond then aminyl oxides derived from both alkyl- and metal-centred radicals should be observable by e.s.r. spectroscopy, equation (1). This straightforward behaviour was



only found in the present study for  $[\text{Mn}(\text{CO})_5\text{R}']$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{R}']$  when  $\text{R}' = \text{CH}_2\text{Ph}$  or  $\text{CH}_2\text{SiMe}_3$ ; these gave approximately equal intensity signals from both  $\text{R}'\cdot$  and  $\cdot\text{ML}_n$  adducts. However, when  $\text{R}' = \text{Me}$ , weak peaks from both fragments were observed, suggesting that Me-Mn or Me-Fe homolysis occurs, although comparatively inefficiently.

It appears that photolysis of  $[\text{AuR}'(\text{PPh}_3)]$  ( $\text{R}' = \text{Me}$  or  $\text{CH}_2\text{SiMe}_3$ ) also efficiently generates  $\text{R}'\cdot$  since strong, clean signals due to the adducts  $\text{R}'\text{N}(\dot{\text{O}})\text{R}$  were observed. Apparently  $\cdot\text{Au}(\text{PPh}_3)$ , which is presumably the other fragment generated, is not spin-trapped by nitrosodurene. A similar situation is probable for the cobalt(III) alkyls studied. Nitroso-compounds are not universal spin traps and several other metal-centred radicals do not form adducts with RNO.<sup>13,20</sup> For all the other systems investigated more complicated behaviour than simple

homolysis is indicated although radical species were found.

For the complexes  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{R}']$ , photolysis at -30 °C gave only the adduct derived from the metal-centred fragment  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\{\text{N}(\dot{\text{O}})\text{R}\}]$ . Free  $\text{R}'\cdot$  radicals are apparently not formed since these would be trapped efficiently under the conditions of the experiment. In their detailed study of the photolysis of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{Me}]$  Samuel *et al.*<sup>7</sup> showed that several processes occurred. In particular, one-electron transfer led to detectable levels of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_n\text{Me}]^-$  ( $n = 2$  or  $3$ ). A similar process is presumably operating in our system with subsequent decay (at -30 °C) of the radical anion giving  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$  but not  $\cdot\text{CH}_3$ . Interestingly at 25 °C the reverse result was obtained: photolysis gave  $\text{R}'\cdot$  adducts but no molybdenioaminyl oxide suggesting that fragmentation processes are temperature dependent.

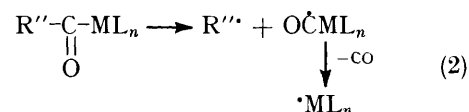
A quite different behaviour was noted for platinum alkyls. Photolysis of *cis*- $[\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_2\text{Ph})_2]$  gave rise to strong  $\text{Me}_3\text{SiCH}_2\text{N}(\dot{\text{O}})\text{R}$  signals, indicative of relatively facile Pt-C homolysis, although no paramagnetic Pt species were seen. Similar Pt-C homolysis was found for the neopentyl analogue, but in addition a signal attributable to  $\text{Me}_3\text{CN}(\dot{\text{O}})\text{R}$  was also clearly visible. The *t*-butyl radical can only arise from homolysis of the C-C bond  $\beta$  to the Pt atom giving presumably  $\cdot\text{CH}_2\text{Pt}(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$  as the other fragment which however was not detected by e.s.r. spectroscopy. A similar Pt-containing radical,  $\cdot\text{CH}_2\text{Pt}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_2\text{Ph})_2$ , was previously observed directly<sup>3</sup> (*i.e.*, in absence of RNO) by e.s.r. upon photolysis of *cis*- $[\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_2\text{Ph})_2]$  with  $(\text{Bu}^t\text{O})_2$ , which suggests that formation of a  $\cdot\text{CH}_2\text{-Pt}^{\text{II}}$  or  $\text{CH}_2\text{-Pt}^{\text{I}}$  grouping is favoured.

For acylmetal complexes it is apparent that photolysis does *not* give rise to M-C homolysis. Irradiation of  $[\text{Mn}(\text{CO})_5(\text{COR}'')]$  or  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{COR}'')]$  gave strong signals due to  $\text{R}''\text{N}(\dot{\text{O}})\text{R}$  ( $\text{R}'' = \text{CH}_2\text{Ph}$  or  $\text{CHPh}_2$ ) and  $[\text{Mn}(\text{CO})_5\{\text{N}(\text{O})\text{R}\}]$  or  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{N}(\text{O})\text{R}\}]$ ; no  $\text{R}''\dot{\text{C}}\text{O}$  radical adducts were observed. The formation of alkyl but not acyl radicals is surprising. Possible explanations include (a)–(c).

(a) Initial formation of an acyl radical which decarbonylates prior to trapping. This can be excluded since authentic  $\text{PhCH}_2\dot{\text{C}}(\text{O})$  [prepared by H abstraction from  $\text{PhCH}_2\text{C}(\text{O})\text{H}$ ] gives the acyl adduct with RNO at -30 °C in  $\text{CH}_2\text{Cl}_2$  and only above 0 °C is extensive decarbonylation observed (using the same light source).

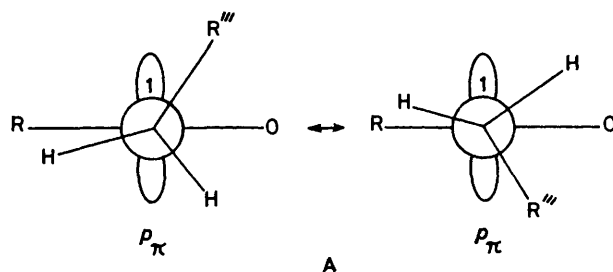
(b) Carbonyl elimination from  $[\text{ML}_n(\text{COR}'')]$  to give  $[\text{ML}_n\text{R}'']$  precedes homolysis of the resulting alkyl to give  $\text{R}''\cdot$ . This is also unlikely since signal strength reaches a maximum rapidly on irradiation whereas appreciable  $[\text{ML}_n\text{R}'']$  would form relatively slowly.

(c) Cleavage of the C-C bond of  $[\text{ML}_n(\text{COR}'')]$ , equation (2).

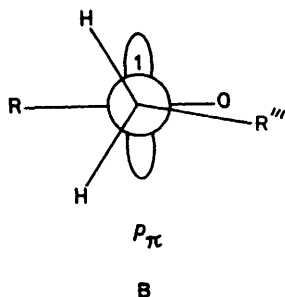


Explanation (c) appears to be the most probable and is supported by further evidence. First, this cleavage is analogous to well known photolytic scission of C-C bonds adjacent to ketonic carbonyl.<sup>21</sup> Second, cleavage of a C-C bond  $\beta$  to a metal centre is also implicated for a neopentyl platinum complex, see above. Third, photolysis of  $[\text{Mn}(\text{CO})_5(\text{COCH}_2\text{Ph})]$  at  $-70^\circ\text{C}$  in the presence of nitrosodurene gives [in addition to  $\text{R}'\text{N}(\dot{\text{O}})\text{R}$ ] an aminyl oxide containing both N [ $a(^{14}\text{N}) = 1.66\text{ mT}$ ] and Mn [ $a(^{55}\text{Mn}) = 0.98\text{ mT}$ ] which is not  $[\text{Mn}(\text{CO})_5\{\text{N}(\dot{\text{O}})\text{R}\}]$ , (I) [ $a(\text{N}) = 1.59, a(^{55}\text{Mn}) = 0.89\text{ mT}$ ]. An alternative might be  $[\text{Mn}(\text{CO})_5\{\text{C}(\text{O})\text{N}(\dot{\text{O}})\text{R}\}]$ , (II), arising from trapping of the  $\text{OCML}_n$  fragment of equation (2), but this might have been expected to have had a lower  $a(^{14}\text{N})$  and a higher  $a(^{55}\text{Mn})$  value. In the temperature range  $-70^\circ\text{C}$  to  $30^\circ\text{C}$  the signal due to (II) decreases in intensity while that of (I) increases, suggesting that decarbonylation of  $\text{OCML}_n$  to  $\text{ML}_n$  is facile (if the acyl nitroxide assignment is accepted).

*E.S.R. Spectra of the Neopentyl-type Aminyl Oxides,  $\text{Me}_3\text{ECH}_2\text{N}(\dot{\text{O}})\text{R}$  (E = C or Si).*—Most of the nitrosodurene adducts detected have been discussed previously<sup>13,14</sup> and need no further comment. However, two new aminyl oxides,  $\text{Me}_3\text{ECH}_2\text{N}(\dot{\text{O}})\text{R}$ , (III) [(IIIa), E = C; (IIIb), E = Si], prepared in this study for the first time, show interesting hyperfine coupling constants. These are given in Table 3, together with typical values for related species. It is apparent that  $a(^{14}\text{N})$  does not vary greatly for different values of R' in  $\text{R}'\text{N}(\dot{\text{O}})\text{R}$ . However, large variations in  $a(^1\text{H}_\beta)$  are observed. In general for aryl alkyl nitroxides  $\text{R}'''\text{CH}_2\text{N}(\dot{\text{O}})\text{R}$ ,  $a(^1\text{H}_\beta)$  decreases as the steric bulk of the alkyl ligand increases.<sup>22</sup>



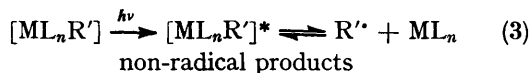
This may be rationalised in terms of the conformation A becoming more stable with increasing bulk so decreasing the average C-H- $p_\pi$  dihedral angle. Thus for  $\text{Me}_3\text{CCH}_2\text{N}(\dot{\text{O}})\text{R}$  the e.s.r. parameters are those expected for a bulky alkyl substituent. However, for  $\text{Me}_3\text{SiCH}_2\text{N}(\dot{\text{O}})\text{R}$ ,



(IIIb), the  $a(^1\text{H}_\beta)$  value is much larger than usual and suggests that for this radical conformation B is favoured. The neopentyl group is certainly more sterically demanding than the trimethylsilyl analogue, *cf.* the compounds  $[\text{M}(\text{CH}_2\text{EMe}_3)_4]$  (M = Ti, Zr, or Hf).<sup>23</sup> The different behaviour for (IIIa) and (IIIb) may thus be ascribed to steric factors, although such a gross discrepancy is unexpected. A possible contributory factor may involve an attractive interaction between the silicon atom and the nitroxyl oxygen in (IIIb) in the B conformation, which thus over-rides the steric preference for A expected for a bulky group R''' system. Simple calculations, using chemically reasonable bond lengths, suggest that the  $\text{Si} \cdots \text{O}$  distance is *ca.*  $2.8\text{ \AA}$  in B which lies well within the sum of the van der Waals radii for the two atoms. However, a definitive explanation must await a more detailed study of a range of nitroxides with  $\beta$ -silicon substituents.

*Solvent Effects.*—The experiments here reported were carried out in dichloromethane as solvent, because  $\text{CH}_2\text{Cl}_2$  is transparent to the wavelengths of light (*ca.*  $300\text{ nm}$ ) which induces M-C homolysis; furthermore, previous work<sup>13</sup> has shown  $\text{CH}_2\text{Cl}_2$  to be the solvent of choice for spin-trapping metal-centred radicals. Photolysis of metal alkyls was also carried out in toluene, giving essentially similar results except that, as expected,<sup>13</sup>  $\text{Mn}(\text{CO})_5$  was not trapped in this solvent. It therefore appears that the solvent does not play a critical role in the photolytic process. However, published work<sup>24</sup> on the photodecomposition of platinum and palladium alkyls indicates that a reaction occurs in  $\text{CHCl}_3$  to yield a metal chloride and a solvent-derived radical. The radical  $\text{W}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3$  also reacts with chlorinated solvents but it has been shown<sup>25</sup> that  $\text{CH}_2\text{Cl}_2$  is a much less effective trapping agent than  $\text{CCl}_4$  or  $\text{CHCl}_3$ .

*Conclusions.*—Spin trapping is not a reliable quantitative technique since signal strength depends on the relative trapping efficiencies of different radicals and on the stabilities of the resulting aminyl oxides. However, *qualitatively* we recognise the following trends in the efficiency of photolytic homolysis of M-C bonds in the metal alkyls  $[\text{ML}_n\text{R}']$ : (a)  $\text{ML}_n = \text{Au}(\text{PPh}_3) > \text{PtR}'(\text{PMe}_2\text{Ph})_2 > \text{Mn}(\text{CO})_5 \approx \text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2 > \text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3$ , and (b)  $\text{R}' = \text{CH}_2\text{Ph} \approx \text{CHPh}_2 > \text{CH}_2\text{Si-Me}_3 > \text{Et} > \text{Me}$ . These trends are reasonable. Thus, if the photolysis process is summarised by equation (3), then it is to be expected that (i) homolysis is favoured if



alternative pathways are unlikely [*e.g.* for  $\text{Au}(\text{PPh}_3)$  derivatives], unless the latter are energetically facile [*e.g.* CO elimination from  $\text{Mn}(\text{CO})_5$ ], and (ii) homolysis is preferred if the radical  $\text{R}'\cdot$  is stable. As for (ii), we note that the sequence (b) follows that of radical stability.

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