

## Electron Spin Resonance Investigation of the Thermolysis, Photolysis, and Oxygenation of Bi- and Tri-metallic Organochromium Complexes

By LAURENCE CARLTON, W. EDWARD LINDSELL, and PETER N. PRESTON

(Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS)

**Summary** Oxygenation of the products derived thermally ( $-70\text{ }^{\circ}\text{C}$ ) from  $[\text{Cr}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$  or photochemically from  $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{Cu}(\text{phen})\}_n]$ ; (phen = 1,10-phenanthroline) and  $[\text{Hg}\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2]$  gives rise to an e.s.r. signal assigned to  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_n(\text{O}_2)]$  ( $n = 2$  or  $3$ ); evidence in support of this structure is adduced from experiments using the deuterium labelled complex  $[\text{Hg}\{\text{Cr}(\eta^5\text{-C}_5\text{D}_5)(\text{CO})_3\}_2]$  and by the use of  $^{17}\text{O}_2$ -enriched dioxygen.

We have concluded from e.s.r. spectral evidence that the photolysis and oxygenation of  $[\text{Mn}_2(\text{CO})_{10}]$  gives rise to  $[\text{Mn}(\text{CO})_5(\text{O}_2)]$  and we have shown that related binuclear complexes, *e.g.*  $[\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ , behave in similar fashion.<sup>1</sup> We now demonstrate that a chromium-dioxygen

complex is generated in a thermal reaction of  $[\text{Cr}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$  (1) in oxygenated solution and that the same complex is also generated by the photolysis and oxygenation of the bimetallic complex  $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{Cu}(\text{phen})\}_n]^2$  (2) (phen = 1,10-phenanthroline) and the trimetallic complex  $[\text{Hg}\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2]^3$  (3).

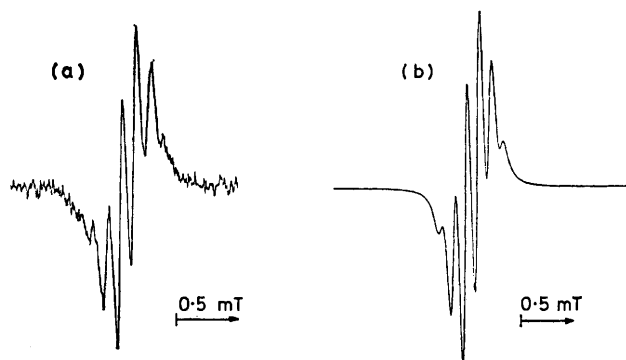
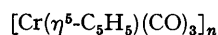
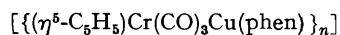


FIGURE 1. E.s.r. spectrum from (1) with  $\text{O}_2$  in toluene at  $-70\text{ }^{\circ}\text{C}$ : (a) experimental (9.38 GHz); (b) simulated using parameters given in text (line width = 0.07 mT).

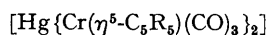


(1)  $n = 2$

(6)  $n = 1$

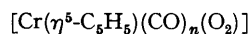


(2)



(3) R = H

(5) R = D



(4)

Degassed solutions of (1) in toluene or dichloromethane are e.s.r.-inactive<sup>4</sup> but when dioxygen (100–300 Torr) is admitted to a toluene solution in the dark at  $-70\text{ }^{\circ}\text{C}$  an e.s.r. signal is observed (Figure 1) as a sextet ( $g_{180} = 1.9873 \pm 0.0005$ ,  $a_{180} = 0.111 \pm 0.005$  mT) with quartet satellites

( $a_{180} = 1.72 \pm 0.02$  mT) assignable to  $^{53}\text{Cr}$  ( $I = 3/2$ , 9.5% natural abundance).<sup>5</sup> This signal does not diminish in intensity over 1 h at  $-70^\circ\text{C}$  but at  $\geq -40^\circ\text{C}$  decomposition occurs and other paramagnetic species ( $g_{180} > 2.0$ ) are formed. Identical sextet signals are formed by u.v. photolysis of (3) in toluene at  $-50^\circ\text{C}$  [ $g_{180} = 1.9873$ ,  $a_{180}(\text{sextet}) = 0.111 \pm 0.005$  mT,  $a_{180}(^{53}\text{Cr}) = 1.70 \pm 0.01$  mT] or (2) in dichloromethane at  $-70^\circ\text{C}$  ( $g_{180} = 1.9867$ ). From these data it was surmised that a paramagnetic  $\eta^5$ -cyclopentadienylchromium dioxygen complex such as  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_n(\text{O}_2)]$  (4) was produced from (1–3) during the initial phase of oxidation. The value of  $n$  is uncertain but could probably be determined by the use of  $^{13}\text{C}$ -labelled precursors.

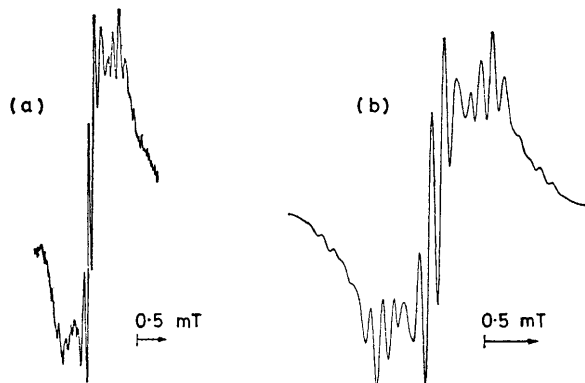


FIGURE 2. E.s.r. spectrum from (3) with  $^{17}\text{O}_2$  in toluene at  $-50^\circ\text{C}$  with u.v. irradiation (medium-pressure Hg lamp): (a) experimental (9.38 GHz); (b) simulated using parameters given in text [line widths = 0.07 mT for  $^{16}\text{O}$ – $^{18}\text{O}$  (8.1%), 0.08 mT for  $^{16}\text{O}$ – $^{17}\text{O}$  (40.8%), and 0.09 mT for  $^{17}\text{O}$ – $^{17}\text{O}$  (51.1%)].

The presence of  $\eta^5$ -cyclopentadienyl and dioxygen ligands in species (4) was confirmed by labelling procedures. Thus, u.v. irradiation of a toluene solution of  $[\text{Hg}\{\text{Cr}(\eta^5\text{-C}_5\text{D}_5)(\text{CO})_3\}_2]$  (5) (D enrichment  $> 95\%$ )<sup>6</sup> at  $-50^\circ\text{C}$  in the presence of dioxygen gave an e.s.r. spectrum in which the sextet ( $5\text{ }^1\text{H}$ ) hyperfine structure was absent. Also, the e.s.r. spectra observed when (3) (Figure 2) and (5) (Figure 3) were subjected to photolysis and oxygenation in  $^{17}\text{O}_2$  (enrichment 71.4%) can be analysed unambiguously in terms of hyperfine structure arising from two equivalent O atoms ( $a_{180} = 0.177 \pm 0.005$  mT). These data support the formulation (4). A frozen-solution e.s.r. spectrum in toluene ( $g_1 = 1.997$ ,  $g_2 = 1.986$ ,  $g_3 = 1.976$ ) indicates a low symmetry.

Possible structures are either (4,  $n = 2$ ) with a peroxo-type  $\text{Cr}-\text{O}_2$  bond with equivalent oxygens or (4,  $n = 2$  or 3) with

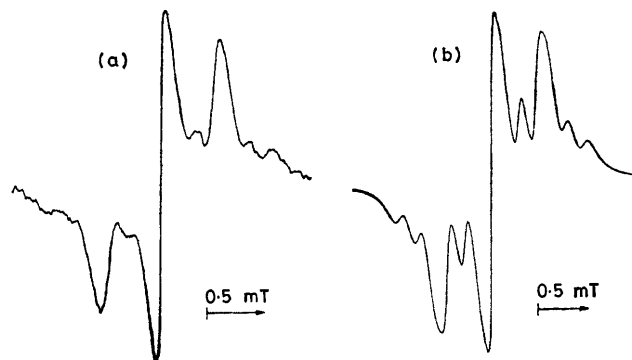


FIGURE 3. E.s.r. spectrum from (5) with  $^{17}\text{O}_2$ : (a) experimental (9.38 GHz) (conditions as for Figure 2); (b) simulated using parameters given in text (line widths = 0.11, 0.13, and 0.15 mT for  $^{16}\text{O}$ – $^{18}\text{O}$ ,  $^{16}\text{O}$ – $^{17}\text{O}$ , and  $^{17}\text{O}$ – $^{17}\text{O}$ , respectively).

a superoxo-type  $\text{Cr}-\text{O}_2$  bond but involving a dynamic equilibrium in which oxygen atoms are interchanged. However the e.s.r. data [ $g$  tensors,  $a_{180}(^{53}\text{Cr})$ ] are consistent with a Cr species having essentially a metal-centred unpaired electron and low unpaired spin density on  $\text{O}_2$ ; in this sense species (4) is different from superoxo-type complexes of group 4 metals<sup>7</sup> or cobalt<sup>8</sup> for which  $a_{180}(^{17}\text{O}) = \text{ca. } 2.0$  mT. A structure of the type shown in Figure 4 is therefore suggested as being the most probable.

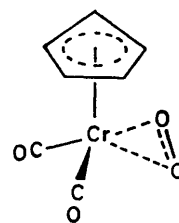


FIGURE 4. Probable structure of (4).

It is probable that species (4) arises from (1–3) via  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$  (6) but this is not proven: an attempt to spin-trap<sup>10</sup> species (6) by nitrosodurene or 2-methyl-2-nitrosopropane gave rise to uncharacterised paramagnetic complexes with relatively low values of nitrogen hyperfine splitting [e.g. PhMe solvent, ArNO trap,  $g_{180} = 1.9920$ ,  $a_{180}(^{14}\text{N}) = 0.56$  mT].<sup>11</sup>

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<sup>1</sup> W. E. Lindsell and P. N. Preston, *J. Chem. Soc., Dalton Trans.*, 1979, 1105.

<sup>2</sup> P. Hackett and A. R. Manning, *J. Chem. Soc. Dalton Trans.*, 1975, 1606.

<sup>3</sup> R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, 7, 104.

<sup>4</sup> Cf. T. Madach and H. Vahrenkamp, *Z. Naturforsch., Teil B*, 1978, 33, 1301.

<sup>5</sup> For comparison of  $g$  factors and  $^1\text{H}$  hyperfine interaction in paramagnetic Cr complexes, see Ch. Elschenbroich and F. Gerson, *J. Organomet. Chem.*, 1973, 49, 445.

<sup>6</sup> The deuterated analogue of (3) was synthesised in an identical manner to (3) but with the use of  $\text{C}_5\text{D}_6$  (cf. E. Gallinella and P. Mirone, *J. Labelled Comp. Radiopharm.*, 1971, 7, 183).

<sup>7</sup> J. A. Howard, J. C. Tait, and S. B. Tong, *Can. J. Chem.*, 1979, 57, 2761; J. A. Howard and J. C. Tait, *J. Am. Chem. Soc.*, 1977, 99, 8349.

<sup>8</sup> E. Melamud, B. L. Silver, and Z. Dori, *J. Am. Chem. Soc.*, 1974, 96, 4689.

<sup>9</sup> Ready loss of CO from (6) would be expected: cf. D. S. Ginley, C. R. Buck, and M. S. Wrighton, *Inorg. Chim. Acta.*, 1977, 23, 85; B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, 1975, 97, 3260.

<sup>10</sup> Spin-trapping experiments were conducted on (1) in dichloromethane or toluene solutions in the dark at  $-40^\circ\text{C}$ ; cf. A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1977, 551.

<sup>11</sup> Cf. side-on bonding of the nitroso-function in  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{ONCMe}_2)(\text{CO})_2]$ : G. P. Khare and R. J. Doedens, *Inorg. Chem.*, 1977, 16, 907.