Cyclometallation Reactions. VIII*  
Binuclear Manganese Carbonyl Complexes Derived from Azobenzene

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Abstract

The binuclear bis-ortho-metallated complex

\[(\text{OC})_2\text{MnC}_6\text{H}_4\text{N=NC}_6\text{H}_4\text{Mn(CO)}_4\]

has been obtained from a reaction between \(\text{MnMe(CO)}_5\) and \(\text{Mn(C}_6\text{H}_4\text{N=NPh)(CO)}_4\); the reaction between azobenzene and \(\text{MnPh(CO)}_4\) affords \((\text{PhN=NH}_2\text{C}_6\text{H}_4)\text{Mn}_2(\text{CO})_6\).

The reaction between nickelocene and 2,2' dichloroazobenzene affords the metallated complex (1) and, in a separate reaction, (1) reacts further with nickelocene to give the binuclear complex (2). However, to our knowledge there have been no further reports of dimetallated azobenzenes containing transition metals. Herein we describe two such complexes of differing structure, containing manganese.

† Direct mercuration of azobenzene affords small amounts (c. 3%) of dimercurated products.

The thermal reaction between \( \text{Mn(C}_6\text{H}_4\text{N=NPh)(CO)}_3 \) (3) and excess penta-carbonylmethylmanganese affords the dark green binuclear complex (4), readily identified by the usual methods. Thus the i.r. spectrum of (4) shows the characteristic four-band \( v(\text{CO}) \) pattern expected for a cis-LL'M(\text{CO)}_4 complex, while the mass spectrum contains a molecular ion, which fragments by successive loss of eight carbonyl groups. In the proton n.m.r. spectrum, the two equivalent \( \text{C}_6\text{H}_4 \) groups gave four resonances, with a fine structure consistent with a four-spin AMPX system. The appearance of the spectrum is typical of the metallated phenyl ring in complexes containing ortho-metallated ligands, and is similar to that of \( \text{Mn(C}_6\text{H}_4\text{N=NC}_6\text{F}_5)(\text{CO)}_4 \).4

The formation of (4) shows that the donor properties of one nitrogen of azobenzene are not seriously affected by coordination of the second nitrogen to a metal, and further suggests that reactions between MnMe(\text{CO)}_5 and various 2-(phenylazo)-phenylmetal complexes might give rise to other related, mixed metal complexes. Initial investigations using Pd(\text{C}_6\text{H}_4\text{N=NPh})(\text{C}_2\text{H}_3) and [RhCl(\text{C}_6\text{H}_4\text{N=NPh)})_2] were, however, unsuccessful, ligand transfer reactions occurring to give (3) in good yield.

A second binuclear manganese complex has been obtained in poor yield from reactions between azobenzene and several alkyl or aryl pentacarbonylmanganese derivatives. For example, the reaction using MnPh(\text{CO)}_5 gave a product which on chromatography afforded initially Mn(\text{C}_6\text{H}_4\text{N=NPh})(\text{CO)}_3 (3), followed by a deep red compound (5). Analyses and mass spectral evidence were consistent with the formula Mn_2(\text{C}_{12}\text{H}_{10}\text{N}_2)(\text{CO)}_6, and the six carbonyl groups were lost in stepwise fashion from the molecular ion at m/e 460. In addition, ions at m/e 292 ([Mn_2\text{C}_6\text{H}_4\text{N=NC}_6\text{F}_5]+), 237 ([Mn\text{C}_6\text{H}_4\text{N=NC}_6\text{F}_5]+) and 160 ([MnNNHC\text{C}_6\text{H}_4]+) were present.

The i.r. spectrum contained six \( v(\text{CO}) \) bands, with a pattern similar to that found for the ferrole–Fe(\text{CO)}_5 complex C\text{C}_4\text{H}_4\text{Fe}_2(\text{CO)}_6,5 suggesting the presence of two Mn(\text{CO)}_3 moieties bonded to each other. A sharp \( v(\text{NH}) \) absorption was found at 3365 cm\(^{-1}\). In addition, bands at 1550, 753 and 697 cm\(^{-1}\) resemble those assigned to vibrations of the ortho-metallated ring in (1) (at 1548, 772 and 720 cm\(^{-1}\)). Rapid decomposition in solution precluded obtaining satisfactory \( ^1\text{H} \) n.m.r. spectra.

We suggest that complex (5) has the benzodiazamanganoline structure shown. In this the conventional metallated azobenzene ligand interacts with a second manganese atom through a bond from the nitrogen adjacent to the metallated ring and a two-electron interaction from this ring. Formally, the hydrogen displaced by metallation may be considered to have undergone a 1,3-migration to the adjacent nitrogen atom.

Several complexes having related structures have been described. The product from reactions between Fe\text{CO}_5 and benzylideneaniline has structure (6),6 and a

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similar cyclic structure has been suggested for $\text{H}_2\text{C}_2\text{S}_2\text{Mn}_2(\text{CO})_6$ (7), obtained from MnBr(CO)$_5$ and disodium (Z)-ethene-1,2-dithiolate.$^5$

**Experimental**

Spectra were obtained with Perkin–Elmer 257 (i.r.), Varian Associates HA 100 ($^1$H n.m.r.) and AEI MS 902 (m.s.) instruments. Reactions were run under nitrogen, but no special precautions were taken to exclude oxygen during workup. Chromatography was with columns of Florisil, initially packed in light petroleum (b.p. 40–60$^\circ$).

**Reaction between MnMe(CO)$_3$ and Mn(C$_6$H$_4$N=NPh)(CO)$_4$**

A mixture of MnMe(CO)$_3$ (315 mg, 1·5 mmol) and Mn(C$_6$H$_4$N=NPh)(CO)$_4$ (522 mg, 1·5 mmol) was refluxed in toluene (50 ml) for 20 h. Chromatography of the concentrated solution gave a black band (eluted with 19 : 1 light petroleum–ether), which afforded deep green crystals of complex (4), m.p. 133–135$^\circ$ (55 mg, 7·2%) (Found: C, 46·8; H, 1·7; N, 5·4; mol. wt (mass spectrometry), 514. C$_{20}$H$_5$Mn$_2$N$_2$O$_8$ requires C, 46·7; H, 1·6; N, 5·5%; mol. wt, 514). I.r. (cyclohexane): $\nu$(CO) at 2080m, 2016vs, 1999m, 1996sh, 1961s cm$^{-1}$. $^1$H n.m.r. (CS$_2$): $\delta$ 1·44q (H$_6$), 1·88q (H$_3$), 2·70m (H$_4$, H$_5$).

**Synthesis of Complex (5)**

An equimolar mixture of PhMn(CO)$_5$ and azobenzene was refluxed in methylcyclohexane for 2 h, and the concentrated solution was chromatographed. Azobenzene and complex (1) were eluted with light petroleum–ether (99/1) mixtures; increasing the ether concentration to 10% resulted in elution of a deep red band, which was crystallized (hexane) to give air-sensitive crystals of complex (5), m.p. 117–118$^\circ$ (14% conversion) (Found: C, 47·2; H, 2·3; N, 6·1; mol. wt (mass spectrometry), 460. Calc. for C$_{18}$H$_{18}$Mn$_2$N$_2$O$_6$: C, 47·0; H, 2·2; N, 6·0%; mol. wt, 460). I.r. (cyclohexane): $\nu$(NH) at 3365 cm$^{-1}$; $\nu$(CO) at 2043m, 2003vs, 1959s, 1948s, 1943sh, 1927m cm$^{-1}$.

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