# Synthesis of the Unsymmetrical Tricarbonylalkoxymanganese Trimers and *X*-Ray Crystal Structure of Dimethylphenylphosphineoctacarbonyltriethoxytrimanganese

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*Summary* The synthesis of the trimeric tricarbonylalkoxymanganese trimers [$\{ROMn(CO)_3\}_3$] is reported; these complexes have two face-bridging alkoxy groups and a single edge-bridging alkoxy group, together with a scalene triangle of manganese atoms, which appears to contain only one manganese–manganese bond.

Despite the remarkably wide range of alkylthiometal carbonyl derivatives that have been reported,[1] the analogous class of alkoxymetal carbonyls remains rare.[2]

The interaction of bromopentacarbonylmanganese with alkoxytrimethyltin compounds produces a series of nonacarbonyltrialkoxytrimanganese complexes [equation (1)].

$$3Mn(CO)_5Br + 3Me_3SnOR \rightarrow 6CO + 3Me_3SnBr + [\{ROMn(CO)_3\}_3] \text{ (ca. 60\% yield)} \qquad (1)$$

(R = Me, Et, Pr$^n$, Pr$^i$, Bu$^n$, cyclohexyl, or allyl)

All these complexes have nine distinct CO stretching modes in their i.r. spectra, and two different types of alkyl group environment are indicated by their $^1$H and $^{13}$C n.m.r. spectra. Such observations suggested a remarkably unsymmetrical structure for these [$(RO)_3Mn_3(CO)_9$] species. The trimeric nature of the series was determined by both vapour pressure osmometry and mass spectrometry.

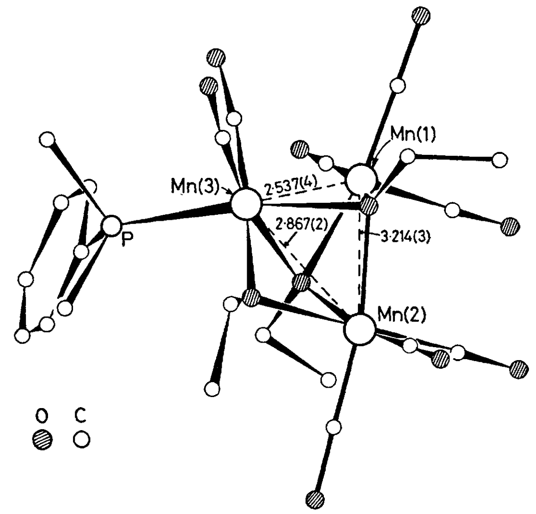

Figure 1. The structure of [$(EtO)_3Mn_3(CO)_8PMe_2Ph$].

Phenyldimethylphosphine reacted with [$(EtO)_3Mn_3(CO)_9$] to displace one carbonyl group producing [$(EtO)_3Mn_3(CO)_8$-$PMe_2Ph$]. This complex retained eight i.r. bands in the carbonyl stretching region, and two different alkoxy group environments, and its structure has been determined by *X*-ray diffraction.†

*Crystal data*: $(EtO)_3Mn_3(CO)_8PMe_2Ph$, monoclinic, $a = 17{\cdot}609$, $b = 21{\cdot}319$, $c = 9{\cdot}220$ Å, $\gamma = 127{\cdot}16°$, space group $P2_1/b$, $Z = 4$, $D_c = 1{\cdot}594$ g cm$^{-3}$, Cu-$K_\alpha$ radiation ($\lambda = 1{\cdot}54051$ Å), four-circle diffractometry, 1666 independent observable reflections. The structure was solved by Patterson and Fourier methods and refined by 'large' block least-squares. The conventional $R$ is 0·08 with anisotropic temperature factors on all atoms. The hydrogen atoms have not yet been located. The molecule, which is shown in Figure 1, is constructed from three manganese atoms in a triangle with unequal sides [3·214(3), 2·867(2), and 2·538(4) Å]. On one face of this triangle the oxygen atom of an $EtO^-$ group is bonded to all three manganese atoms and another $EtO^-$ is similarly bonded on the reverse face; the Mn–O bond lengths and Mn–O–Mn bond angles are in the ranges 2·005—2·081 Å and 77—104° with a mean of 2·042 Å and 90°, respectively. A third $EtO^-$ group is bonded to two manganese atoms along the edge of the triangle with an Mn(3)–O–Mn(2) bond angle of 92° and a mean Mn–O bond length of 1·989(6) Å. The Mn–P distance is 2·290(5) and the Mn–C and C–O bond lengths are in the ranges 1·71—1·83, and 1·10—1·22 Å, respectively.

It seems reasonable on the basis of their i.r. and n.m.r. spectra to suppose that the parent nonacarbonyls are structurally analogous to the phosphine derivative.

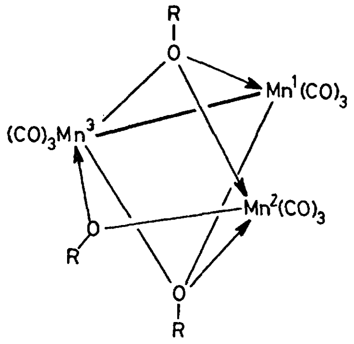

FIGURE 2. Diagramatic representation of $[\{ROMn(CO)_3\}_3]$ structure, showing the unique nature of each $Mn(CO)_3$ group and the rare gas formalism for each Mn atom.

Figure 2 illustrates the way in which each manganese atom in the cluster can be regarded as attaining a rare-gas outer shell of electrons.

As a result of the presence of the two nominally five-electron donor face-bridging alkoxy groups, only the shortest of the Mn–Mn distances [Mn(1)–Mn(3)] in the scalene triangle is regarded as a formal metal–metal bond.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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