Syntheses, Structures, and Reactions of Trimeric and Tetrameric Alkoxotricarbonylmanganese Complexes

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Bromopentacarbonylmanganese reacts with $SnMe_3(OR)$ (R = Me, Et, Pr^n, Pr^i, Bu^n, C_6H_{11}, $CH_2CH{=}CH_2$, or CH_2Ph) to form the complexes $[\{Mn(OR)(CO)_3\}_3]$, and in the case of benzyl the tetramer $[\{Mn(OCH_2Ph)(CO)_3\}_4]$ is also formed. The structure of the trimers is based on a scalene triangle of manganese atoms, with face- and edge-bridging alkoxide groups. The tetramer is a cube of manganese and oxygen atoms with only face-bridging alkoxide groups. The complex $[\{Mn(OEt)(CO)_3\}_3]$ reacts with PMe_2Ph, PhOH, and PhSH to give respectively $[Mn_3(OEt)_3(CO)_8(PMe_2Ph)]$, $[Mn_3(OEt)_2(OPh)(CO)_9]$, and $[\{Mn(SPh)(CO)_3\}_4]$.

In contrast to the extensive range of alkylthiometal carbonyls that are known,[1] the corresponding alkoxometal carbonyls are rare.[2-5] Tetrameric alkylthiotricarbonyls of manganese have been reported from a number of reactions,[6-9] and they have the highly symmetrical structure [10] illustrated in Figure 1. No alkoxocarbonyls of manganese have been recorded to date, although neutral rhenium complexes $[\{Re(OR)(CO)_3\}_4]$ have been reported [4] from the action of diazoalkanes on the hydroxo-complex $[\{Re(OH)(CO)_3\}_4]$.

Treatment of bromopentacarbonylmanganese with ethanol and triethylamine produced deep red crystals of tricarbonylethoxomanganese. Similar products were

$$3ROH + 3[MnBr(CO)_5] + 3NEt_3 \longrightarrow [\{Mn(OR)(CO)_3\}_3] + 6CO + 3[NEt_3H]Br \quad (1)$$

$$R = Et,\ Pr^i,\ \text{or}\ Bu^n$$

obtained with isopropyl and n-butyl alcohol, but yields were not reproducible and other alcohols did not appear to undergo reaction. Infrared spectra of these complexes in the metal-carbonyl region were virtually identical, but remarkably complex, with nine stretching modes clearly resolved (see Figure 2 for the ethoxo-derivative). The ^1H n.m.r. spectrum indicated two different environments for the ethyl group, and mass spectrometry and solution molecular-weight measurements showed these substances to be trimeric $[\{Mn(OR)(CO)_3\}_3]$.

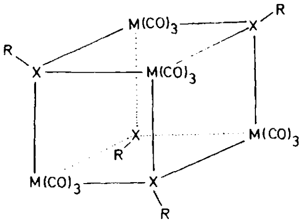

FIGURE 1 Cube-shaped structure of the tetrameric alkoxo- and alkylthio-tricarbonyls of manganese

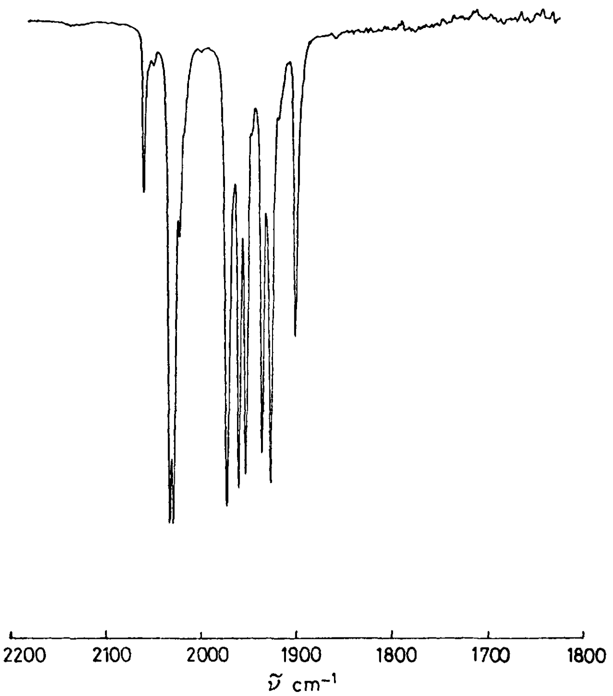

FIGURE 2 Infrared spectrum of $[\{Mn(OEt)(CO)_3\}_3]$ in the carbonyl-stretching region

Previous experience of the use of trimethyltin as a leaving group [11] in metathetical reactions prompted us to examine the reaction of a range of alkoxotrimethyltin compounds with $[MnBr(CO)_5]$. All the reactions gave a trimeric product, but in the case of benzyl there was also a tetramer, which was the major product. Monitoring the reaction by the i.r. spectra of the metal-carbonyl region suggested that tetramers may be formed as intermediates in some reactions other than the benzyl, but no intermediary products could be isolated. Tetrameric $[\{Mn(OCH_2Ph)(CO)_3\}_4]$ had a remarkably simple i.r. spectrum of only three bands in the carbonyl-stretching region, and the ^1H n.m.r. spectrum showed

$$nSnMe_3(OR) + n[MnBr(CO)_5] \longrightarrow [\{Mn(OR)(CO)_3\}_n] + 2nCO + nSnBrMe_3 \quad (2)$$

$$R = CH_2Ph,\ n = 4$$

$$R = Me,\ Et,\ Pr^n,\ Pr^i,\ Bu^n,\ C_6H_{11},\ CH_2CH{=}CH_2,\ \text{or}\ CH_2Ph,\ n = 3$$

that all the benzyl groups had the same environment. On this basis we believe the structure (Figure 1, R = CH_2Ph, X = O) to be exactly analogous to that of the corresponding alkylthio-complexes $[\{Mn(SR)(CO)_3\}_4]$.

The complex $[\{Mn(OEt)(CO)_3\}_3]$ underwent reaction with dimethylphenylphosphine to displace one carbon monoxide group, the resulting product being trinuclear with eight active CO-stretching modes in the i.r. spectrum.

$$[\{Mn(OEt)(CO)_3\}_3] + PMe_2Ph \longrightarrow [Mn_3(OEt)_3(CO)_8(PMe_2Ph)] + CO \quad (3)$$

The structure of this phosphine derivative as determined by *X*-ray crystallography [12] is illustrated in Figure 3(*a*), and from this we deduce the structure of the trimeric alkoxotricarbonyls of manganese to be as in Figure 3(*b*). This structure is completely in accord with the observations by ^{1}H n.m.r. of the two different types of alkoxide groups, and the large number of active CO-stretching modes. The three manganese atoms form a scalene triangle in which only one of the sides (Mn^1–Mn^3) is construed as a metal–metal bond. The notable difference in the non-bonded Mn^1–Mn^3 and Mn^2–Mn^3 distances is caused by the marked contraction of the Mn^2–Mn^3 distance resulting from an edge-bridging alkoxide group.

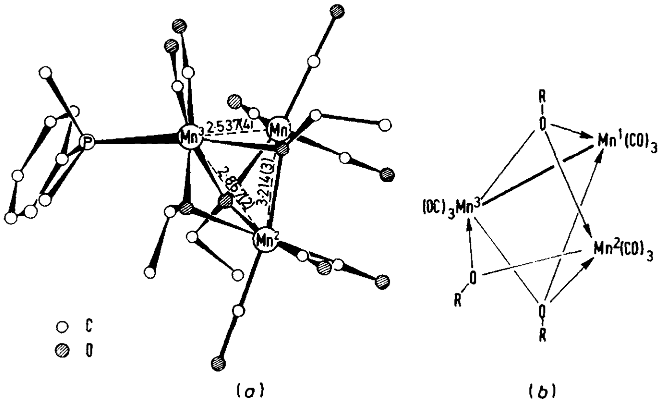

FIGURE 3 (*a*) Structure of the complex $[Mn_3(OEt)_3(CO)_8(PMe_2Ph)]$. (*b*) Representation of the structure of $[\{Mn(OR)(CO)_3\}_3]$ showing the unique nature of each $Mn(CO)_3$ group, and the noble-gas formalism for each Mn atom

Interaction of $[\{Mn(OEt)(CO)_3\}_3]$ with phenol brought about the displacement of one ethoxide group as illustrated in equation (4). Of the three alkoxide groups in

$$[\{Mn(OEt)(CO)_3\}_3] + PhOH \longrightarrow [Mn_3(OEt)_2(OPh)(CO)_9] + EtOH \quad (4)$$

$[\{Mn(OEt)(CO)_3\}_3]$ [see Figure 3(*b*), R = Et], the formally five-electron donor face-bridging groups will have no nucleophilic character, but the edge-bridging oxygen atom will formally still have one lone pair of electrons available for reaction. From this we deduce that the reaction with phenol replaces the edge-bridging ethoxide group only. This is confirmed by the ^{1}H n.m.r. spectrum of the complex.

In the corresponding reaction with thiophenol, all the ethoxide groups are displaced and the familiar tetrameric organothio-product (Figure 1, R = Ph, X = S) was produced. Here it seems likely that an initial exchange

$$4\ [\{Mn(OEt)(CO)_3\}_3] + 12\ PhSH \longrightarrow 3\ [\{Mn(SPh)(CO)_3\}_4] + 12\ EtOH \quad (5)$$

takes place to produce $[Mn_2(OEt)_2(SPh)(CO)_9]$, but then the new edge-bridging sulphur atom probably moves to a preferred face-bridging position, displacing a face-bridging oxygen atom to an edge-bridging position, where it can then undergo reaction with further thiophenol. In addition to such sequential replacement reactions, a redistribution reaction from trimer to tetramer must also take place at some point in the reaction.

The action of carbon monoxide on $[\{Mn(OCH_2Ph)(CO)_3\}_4]$ and $[\{Mn(OEt)(CO)_3\}_3]$ did not produce any new products, other than a small amount of decacarbonylmanganese in each case.

EXPERIMENTAL

All the reactions were carried out routinely under an atmosphere of dry nitrogen, and solvents for reactions were dried by distillation from potassium diphenylketyl. Infrared spectra were recorded in hexane solution using calcium fluoride (0.1-mm path length) cells on a Perkin-Elmer 257 spectrophotometer. Hydrogen-1 n.m.r. spectra were obtained in deuteriochloroform on a JEOL MH100 spectrometer, mass spectra on a Perkin-Elmer–Hitachi RMU-6 spectrometer, and molecular weights with a Knauer vapour-pressure osmometer.

Interactions.—Bromopentacarbonylmanganese, triethylamine, and ethanol. Equimolar quantities (*ca.* 4 mmol) of the reagents in hexane (10 cm^3) were stirred at 45 °C for 7 h. After cooling to room temperature the deposited solid was filtered off. The solution was concentrated (*ca.* 3 cm^3) and cooled to −20 °C. The dark red crystals deposited were recrystallised from hexane to yield pure tris(tricarbonylethoxomanganese) (yield varied from 7—70% erratically in a series of preparations), m.p. 142—143 °C (decomp.) (Found: C, 32.6; H, 2.65. $C_{15}H_{25}Mn_3O_9$ requires C, 32.6; H, 2.75%). In similar experiments using isopropyl and n-butyl alcohol the corresponding tris(alkoxotricarbonylmanganese) complexes were obtained in low and erratic yields.

Ethoxotrimethyltin and bromopentacarbonylmanganese. To a stirred suspension of $[MnBr(CO)_5]$ (0.5 g) in hexane (15 cm^3) at 55 °C was added ethoxotrimethyltin (0.4 g). After 1 h, solvent was removed (20 °C, 10 mm, Hg)* and the by-product, bromotrimethyltin, was removed (26 °C, 0.01 mmHg) from the resulting red mass. The residue was recrystallised from hexane to produce deep red crystals of $[\{Mn(OEt)(CO)_3\}_3]$ (0.2 g, 65%), (*M* 545 in $CHCl_3$) (required 552). By similar reactions the other alkoxotricarbonyls of manganese recorded in the Table were prepared in yields of 55—75%.

Benzyloxotrimethyltin and bromopentacarbonylmanganese. To a stirred suspension of $[MnBr(CO)_5]$ (0.5 g, 1.8 mmol) in hexane (15 cm^3) at 65 °C was added benzyloxotrimethyltin (0.47 g, 1.8 mol). Solvent was removed (20 °C, 15 mmHg) after 30 min, and the resulting solid pumped (25 °C, 0.01 mmHg) for 2 h to remove $SnBrMe_3$. The red residue was then dissolved in benzene, filtered, and chromatographed on basic alumina, using a 30 × 25 cm column eluting with benzene. A broad red-orange band was collected and the benzene removed (30 °C, 10 mmHg). The residue was extracted with hexane (2 cm^3 at 0 °C), and cooling of the filtered extract (−20 °C) produced red crystals of di-μ_3-benzyloxo-μ_2-benzyloxo-nonacarbonyltrimanganese (0.1

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

Characterisation of alkoxotricarbonyls of manganese

	Analysis (%) [a]			
Complex	C	H	I.r. carbonyl-stretching bands (cm^{-1}) [b]	^{1}H N.m.r. (δ/p.p.m. from $SiMe_4$)
[{Mn(OMe)$(CO)_3\}_3$]	27.8 (28.2)	1.65 (1.75)	2 065 (1), 2 037 (10), 2 033 (9.6), 1 979 (8.7), 1 965 (7.5), 1 958 (6.7), 1 944 (5.6), 1 931 (8), 1 909 (2.9)	3.59 (s, Me, 2 H) 4.52 (s, Me 1 H)
[{Mn(OEt)$(CO)_3\}_3$]	32.6 (32.6)	2.65 (2.70)	2 063 (1.3), 2 034 (9), 2 030 (10), 1 974 (8.6), 1 962 (7.5), 1 954 (7.2), 1 938 (6.4), 1 930 (7.8), 1 903 (3.9)	1.60 (m, Me, 9 H) 3.65 (q, CH_2, 4 H) 4.65 (q, CH_2, 2 H)
[{Mn(OPr^n)$(CO)_3\}_3$]	34.7 (36.4)	3.40 (3.55)	2 063 (1.3), 2 034 (9), 2 030 (10), 1 974 (8.6), 1 962 (7.5), 1 954 (7.2), 1 938 (6.4), 1 930 (7.8), 1 930 (3.9)	Not well resolved
[{Mn(OPr^i)$(CO)_3\}_3$]	35.8 (36.4)	3.30 (3.55)	2 061 (1.2), 2 033 (8.6), 2 027 (10), 1 969 (7.5), 1 963 (5.8), 1 955 (4.1), 1 933 (4.8), 1 929 (6.9), 1 899 (2.2)	1.57 (Me, 18 H) 3.75 (spt, CH, 2 H), 4.80 (spt, CH, 1 H)
[{Mn(OBu^n)$(CO)_3\}_3$]	39.5 (39.6)	4.20 (4.25)	2 063 (1.3), 2 034 (9), 2 033 (10), 1 975 (8.6), 1 962 (7.5), 1 954 (7.2), 1 938 (6.4), 1 930 (7.8), 1 903 (3.9)	Not well resolved
[{Mn(OC_6H_{11})$(CO)_3\}_3$]	45.2 (45.4)	4.60 (4.60)	2 055 (1.8), 2 026 (8.1), 2 020 (10), 1 961 (7.8), 1 957 (5.6), 1 949 (3.6), 1 925 (6.7br), 1 893 (2.3)	1.00—2.60 (m, CH_2 30 H), 3.15 (q, CH, 2 H), 4.10 (q, CH, 1 H)
[{Mn(OC_3H_5)$(CO)_3\}_3$]	36.1 (36.7)	2.50 (2.55)	2 057 (1.4), 2 036 (9.1), 2 032 (10), 1 977 (7.1), 1 963 (6.3), 1 953 (6.4), 1 935 (4.7), 1 929 (6.9), 1 901 (3.7)	3.9 (d, CH_2, 4 H), 4.93 (d, CH_2, 2 H), 5.46 (m, $=CH_2$, 6 H), 6.25 (m, $=CH-$, 3 H)
[{Mn(OCH_2Ph)$(CO)_3\}_3$]	48.4 (48.8)	2.40 (2.85)	2 061 (1), 2 034 (10), 2 030 (10), 1 976 (7), 1 965 (4.3), 1 950 (5), 1 937 (5), 1 929 (5), 1 901 (2.8)	4.35 (s, CH_2, 4 H), 5.37 (s, CH_2, 2 H), 7.20—7.60 (m, Ph, 15 H)
[{Mn(OCH_2Ph)$(CO)_3\}_4$]	47.5 (48.8)	2.85 (2.85)	2 031 (10), 1 941 (6.7), 1 933 (10)	5.35 (s, CH_2, 2 H), 7.4—8.1 (m, Ph, 5 H)

[a] Calculated values are given in parentheses. [b] Spectra were run at concentrations where the most intense peak gave *ca.* 75% absorbance, and was assigned a relative height of 10. Relative peak heights are given in parentheses.

g, 22%) (see Table). The residue left after the hexane extraction was washed with more cold hexane (2 × 2 cm^3), and the remaining yellow solid was then dissolved in hexane–dichloromethane (80 : 20). Cooling to −20 °C produced yellow crystals of tetrakis(μ_3-benzyloxo-tricarbonylmanganese) (0.27 g, 60%) (see Table), M 995 (in $CHCl_3$) (required 984).

Tris(*tricarbonylethoxomanganese*) *and dimethylphenylphosphine.* To a stirred solution of the trimer (0.2 g) in hexane (15 cm^3) at 20 °C was added the phosphine (0.5 g, excess). After stirring for 3 h, solvent was removed (20 °C, 1 mmHg) and the resulting residue pumped (40 °C, 0.01 mmHg) for 3 h to remove excess of phosphine. The remaining red solid was recrystallised from hexane to give a very dark red, air-stable, crystalline product (0.19 g, 80%) [Found: C, 39.1; H, 3.80%; M 658 (in chloroform solution). $C_{22}H_{26}Mn_3O_{11}P$ requires C, 39.8; H, 3.95%; M 662]; metal carbonyl-stretching modes (with relative peak heights) at 2 043 (6.5), 2 027 (8.7), 1 955 (4.7sh), 1 951 (10), 1 943 (8.5), 1 929 (6), 1 921 (7.7), and 1 841 (2.2) cm^{-1}.

Tris(*tricarbonylethoxomanganese*) *and phenol.* To a stirred solution of the trimer (0.2 g, 0.36 mmol) in hexane (15 cm^3) at 20 °C was added phenol (0.04 g, 0.4 mmol). Solvent was removed (20 °C, 15 mmHg) and after 1 h the resulting red solid was pumped (25 °C, 0.01 mmHg) for 1 h to remove the last traces of phenol. The residue was recrystallised from hexane to give di-μ_3-ethoxo-μ_2-phenoxo-nonacarbonyltrimanganese (0.15 g, 70%) as deep red crystals (Found: C, 37.8; H, 2.50. $C_{19}H_{15}Mn_3O_{12}$ requires C, 38.0; H, 2.50%). The highest peak in the mass spectrum was at m/e 544, corresponding to the parent ion (M^+) for [$Mn_3(OEt)_2(OPh)(CO)_9$], and $[M - nCO]^+$ ions were observed for n = 1—9; metal carbonyl-stretching modes (with relative peak heights) were at 2 070 (1.2), 2 041 (8.9), 2 037 (10), 1 986 (7.3), 1 967 (6.9), 1 960 (7.6), 1 953 (4.5), 1 934 (7.2), and 1 912 (3.1) cm^{-1}.

Tris(*carbonylethoxomanganese*) *and thiophenol.* To a stirred solution of the trimer (0.3 g, 0.54 mmol) in hexane (15 cm^3) at 20 °C was added thiophenol (1 g, excess). After 4 h, stirring was stopped and the precipitate formed was allowed to settle. After decanting, the residual solid was washed with hexane (2 × 15 cm^3). It was then dissolved in benzene and chromatographed on basic alumina, using a 30 × 2.5 cm column eluted with benzene. The yellow-orange fraction was collected, and after evaporation of the eluate the residue was recrystallised from dichloromethane–hexane (50 : 50) to produce tetrakis(μ_3-phenylthio-tricarbonylmanganese) (0.02 g, 10%) as orange crystals (Found: C, 43.3; H, 2.05. $C_{36}H_{20}Mn_4O_{12}S_4$ requires C, 43.6; H, 2.00%); metal carbonyl-stretching modes (with relative peak heights) were observed at 2 031 (10) and 1 955 (5.3) cm^{-1}.

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REFERENCES

[1] E. W. Abel and B. C. Crosse, *Organometallic Chem. Rev.*, 1967, **2**, 443.

[2] W. Hieber and L. Schuster, *Z. anorg. Chem.*, 1956, **285**, 205; B. F. G. Johnson, J. Lewis, and P. A. Kilty, *Chem. Comm.*, 1968, 180; A. Vizi-Orosz, G. Palyi, and L. Markó, *J. Organometallic Chem.*, 1973, **57**, 379.

[3] V. G. Albano, G. Ciani, M. Freni, and P. Romiti, *J. Organometallic Chem.*, 1975, **96**, 259.

[4] M. Herberhold and G. Süss, *Angew. Chem. Internat. Edn.*, 1975, **14**, 700; M. Herberhold, G. Süss, J. Ellerman, and H. Gabelein, *Chem. Ber.*, 1978, **111**, 2931.

[5] A. P. Ginsberg and M. J. Hawkes, *J. Amer. Chem. Soc.*, 1968, **90**, 5930.

[6] E. W. Abel and B. C. Crosse, *J. Chem. Soc.* (*A*), 1966, 1141.

[7] A. G. Osborne and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1143.

[8] B. F. G. Johnson, P. J. Pollick, I. G. Williams, and A. Wojcicki, *Inorg. Chem.*, 1968, **71**, 831.

[9] M. Ahmad, G. R. Knox, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1967, 138.

[10] E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *Chem. Comm.*, 1970, 1531.

[11] E. W. Abel, *Ann. New York Acad. Sci.*, 1974, **239**, 306.

[12] E. W. Abel, I. D. H. Towle, T. S. Cameron, and R. E. Cordes, *J.C.S. Chem. Comm.*, 1977, 285.