Reactions of Manganese Atoms with Cyclic Dienes and Cycloheptatriene: Crystal Structure of Carbonylbis(1—4-η-cyclohexa-1,3-diene)manganese †

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Condensation of manganese atoms with cyclopentadiene, cyclohexa-1,3-diene, cycloheptatriene, and cyclo-octa-1,3-diene at −196 °C, followed by warming to 20 °C in the presence of CO, has given organomanganese carbonyl complexes in yields of 5—10% based on Mn. The new compounds $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$, $[Mn(\eta^4\text{-}C_7H_8)_2(CO)]$, and $[Mn(\eta^3\text{-}C_8H_{13})(CO)_4]$ have been isolated. A single-crystal *X*-ray diffraction study of $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$ shows that the manganese atom adopts a square-pyramidal configuration with the carbonyl ligand in the axial position. The two hexadiene rings are each folded equatorially away from the Mn atom and the molecule has C_{2v} symmetry. As in other diene complexes, the two inner C atoms are slightly closer to the metal [Mn–C (mean) 2.078(8) Å] than are the outer C atoms [Mn–C (mean) 2.159(7) Å]. The crystals are orthorhombic, space group $P2_12_12_1$ (no. 19) with $Z = 4$ in a unit cell with $a = 8.570(1)$, $b = 17.220(1)$, and $c = 7.562(1)$ Å. The structure has been refined to R 0.045.

A wide range of organometallic compounds of Ti, V, Cr, Fe, Co, and Ni has been synthesised from reactions between the atoms of the metals and organic ligands at low temperatures.[1,2] By comparison, manganese atom chemistry seems sparse, with only scattered references in the literature to the formation of organometallic compounds.[3-5] The reason is that manganese atoms tend to react with themselves rather than with organic ligands and if reactions are carried out with manganese as with the other transition-metal atoms the yields of organomanganese products are commonly negligible. The lower reactivity of the manganese atoms is probably a consequence of the stability of the half-filled 3*d* shell in the ground state of the atoms. We have found that by carefully controlling the rate of condensation of the metal atoms and the metal : ligand ratio, we can isolate modest yields of organomanganese products in many cases. Here we describe reactions of manganese atoms with cyclic dienes and with cycloheptatriene.

Results and Discussion

Our results are summarised in the Scheme. Isolable products were generally obtained by condensing the organic ligands with manganese atoms at −196 °C and allowing the condensate to warm to room temperature under *ca.* 10^5 Pa CO. To optimise the yields, we found it necessary to limit the rate of evaporation of manganese to about 0.2 μg s^{-1} per cm^2 of condensing surface and to have a ligand : metal mol ratio of at least 30 : 1. Even then, only a maximum of 10% of the evaporated metal was recovered as organometallic products.

The six-, seven-, and eight-membered ring ligands showed an increasing tendency to undergo hydrogen-transfer reactions in addition to simple complexation. Thus, cyclohexa-1,3-diene gave only $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$ (see discussion of crystal structure below) but cycloheptatriene gave two products: the new compound $[Mn(\eta^4\text{-}C_7H_8)_2(CO)]$ which has properties closely akin to those of $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$, and the known $[Mn(1—5\text{-}\eta\text{-}C_7H_9)(CO)_3]$.[6] Cyclo-octa-1,3-diene underwent an effective disproportionation, giving the known $[Mn(1—5\text{-}\eta\text{-}C_8H_{11})(CO)_3]$[7] and a little of a yellow, air-sensitive oil which appears from our i.r. and mass spectra to be $[Mn(\eta^3\text{-}C_8H_{13})(CO)_4]$. Intra- and inter-molecular hydrogen-transfer reactions are well documented in metal-atom reactions.[1]

A brown air-sensitive solid, stable at room temperature, was obtained from the manganese atom–cyclopentadiene reaction in the absence of CO. We were unable to characterise this properly because of its high reactivity and the difficulty of separating organic impurities. It reacted with CO to give the known compounds $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ and $[Mn(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_{10}H_{12})(CO)_2]$,[8] and on heating it evolved a little manganocene.

Crystal Structure of $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$.—The overall configuration of the molecule and the atom-numbering system are shown in the Figure, while the crystallographic results are summarised in Table 1. The manganese atom occupies a site of square-pyramidal co-ordination, the carbonyl group occupying the apical site and the two cyclohexadiene rings each occupying two *cis* equatorial sites. The rings fold equatorially so that the saturated portion of each ring [C(15) and C(16), C(25) and C(26)] bends away from the metal atom centre. The diene portion of each ring is planar and is bonded to the metal atom with, characteristically, slightly shorter Mn–C distances to the inner C atoms C(12) and C(13), C(22) and C(23) [mean Mn–C, 2.078(8) Å] than to the outer C atoms C(11) and C(14), C(21) and C(24) [mean Mn–C 2.159(7) Å]. On the standard deviations given, there are no significant differences in the bonding of the two rings, so that the molecule as a whole attains C_{2v} symmetry. The four outer atoms of the diene, C(11), C(14), C(21), and C(24) (*i.e.* the atoms on the folds of the cyclohexadiene rings), are approximately coplanar with the Mn atom. Within the diene fragment extensive delocalisation has occurred; as compared with the bond lengths in the free molecule,[9] the former double bonds (1.348 Å) have lengthened by about 0.05 Å and the single bond (1.468 Å) has shortened.

A crystallographic study [10] of the closely similar compound $[Fe(\eta^4\text{-}C_6H_8)_2(CO)]$ has revealed a slight asymmetry in the bonding of the cyclohexadiene rings to the iron atom. This is not evident in the present structure, although small differences could be concealed by the relatively high standard deviations in the C–C bond lengths. However, we suspect that the difference in the structure is real and arises from the more

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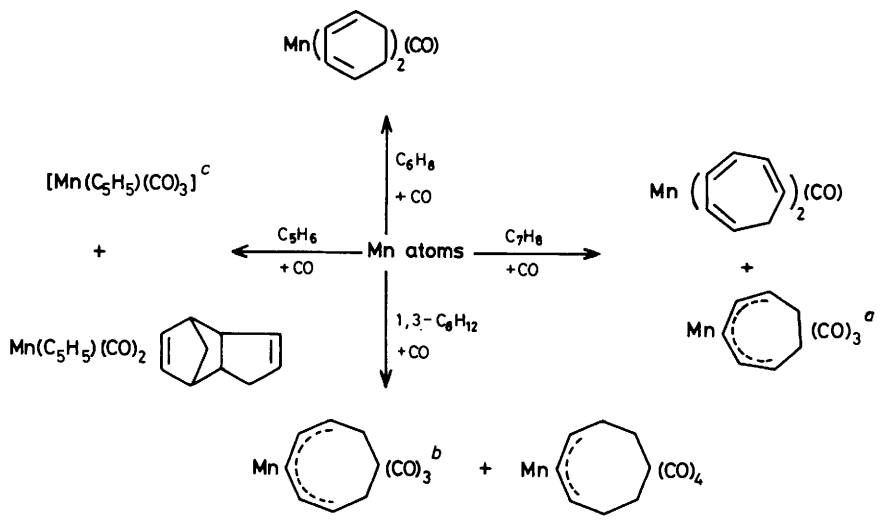

Scheme. Some reactions of manganese atoms. [a] See ref. 6. [b] See ref. 7. [c] See ref. 8

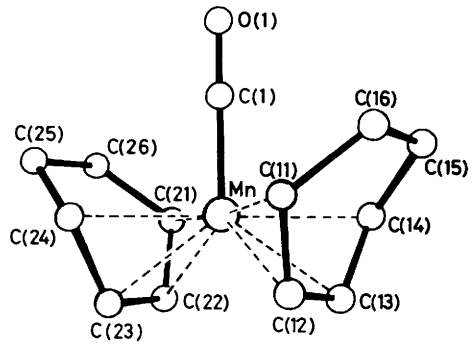

Figure. Molecular structure of $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$

favourable distribution of orbitals in square-pyramidal geometry for a d^7 metal (Mn) compared with a d^8 metal (Fe).[11] The metal–carbon distances are somewhat longer for Mn than Fe due to the greater covalent radius of Mn (1.39 *vs.* 1.25 Å). The bond angles at the central carbon atoms of the diene unit (mean 115.3°) and at the terminal carbon atoms (mean 120.2°) agree closely with those in the iron compound.

Experimental

Manganese metal (99.8% pure) was sublimed from a resistance-heated, wire-wound alumina crucible at *ca.* 950 °C in a liquid-nitrogen-cooled, evacuated glass reactor (diameter 150 mm) of design described elsewhere (see Figure 2, ref. 2). Vapours of the organic ligands were condensed on the cold walls of the reactor at the same time as the metal atoms. Typically, 0.4 g (7.3 mmol) of manganese was evaporated over 1.5 h and condensed with 20 g (200—250 mmol) of ligand. In most experiments, the reactor was then filled with dry CO to *ca.* 10^5 Pa and allowed to warm to room temperature over 1—2 h. Carbon monoxide and excess of ligand were then pumped away and products extracted from the reactor with degassed hexane under N_2. The total yield of organomanganese compounds isolated in each of the reactions carried out this way was 6—10% based on the metal evaporated.

Manganese Atoms + Cyclohexa-1,3-diene + CO.—The compound $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$, recrystallised from pentane as slightly air-sensitive green needles, was the only organometallic product (Found: C, 63.4; H, 6.80. $C_{13}H_{16}MnO$ requires C, 64.2; H, 6.65%), m.p. 138—140 °C (decomp.), sublimes at 50 °C at 10^{-2} Pa; *m/e* 243 (P^+, 1.1%), 215 ($MnC_{12}H_{16}^+$, 4.3%), 133 ($MnC_6H_6^+$, 47%), and 55 (Mn^+, 100%). E.s.r. (toluene solution): six-line spectrum from coupling of the single electron with Mn ($I = \frac{5}{2}$), $g = 2.019$, $A = 7.3 \times 10^{-3}$ T. I.r. (pentane): ν_{CO} at 1 949 cm^{-1}.

Table 1. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Mn–C(11)	2.156(7)	Mn–C(21)	2.165(7)
Mn–C(12)	2.074(8)	Mn–C(22)	2.074(7)
Mn–C(13)	2.078(8)	Mn–C(23)	2.088(7)
Mn–C(14)	2.157(6)	Mn–C(24)	2.159(6)
Mn–C(15)	3.008(9)	Mn–C(25)	3.033(7)
Mn–C(16)	3.015(9)	Mn–C(26)	3.0297(7)
Mn–C(1)	1.791(6)	C(1)–O(1)	1.148(7)
C(11)–C(12)	1.395(10)	C(21)–C(22)	1.409(10)
C(12)–C(13)	1.435(11)	C(22)–C(23)	1.402(10)
C(13)–C(14)	1.403(11)	C(23)–C(24)	1.423(11)
C(14)–C(15)	1.509(11)	C(24)–C(25)	1.508(11)
C(15)–C(16)	1.533(13)	C(25)–C(26)	1.529(10)
C(16)–C(11)	1.503(12)	C(26)–C(21)	1.514(11)
C(1)–Mn–C(11)	87.7(3)	C(1)–Mn–C(21)	88.2(3)
C(1)–Mn–C(14)	91.4(3)	C(1)–Mn–C(24)	90.5(3)
C(11)–C(12)–C(13)	114.7(6)	C(21)–C(22)–C(23)	116.3(6)
C(12)–C(13)–C(14)	115.7(6)	C(22)–C(23)–C(24)	114.5(6)
C(13)–C(14)–C(15)	119.0(7)	C(23)–C(24)–C(25)	120.3(6)
C(14)–C(15)–C(16)	112.1(7)	C(24)–C(25)–C(26)	110.8(6)
C(15)–C(16)–C(11)	110.5(7)	C(25)–C(26)–C(21)	111.4(6)
C(16)–C(11)–C(12)	121.4(7)	C(26)–C(21)–C(22)	120.0(6)
Mn–C(1)–O(1)	179.8(7)		

Crystal-structure Determination of $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$.—Crystals of $[Mn(\eta^4\text{-}C_6H_8)_2(CO)]$ grow as bright green needles elongated along *c*. Diffracted intensities were collected, from a crystal of dimensions 0.15 × 0.16 × 1.10 mm mounted in a Lindemann glass capillary under nitrogen, on a Syntex $P2_1$ four-circle diffractometer with Mo-K_α *X*-radiation according to methods described earlier.[12] Of the total 1 366 independent reflections (complete for $2.9 \leqslant 2\theta \leqslant 50.0°$), 1 140 satisfied the criterion $I > 1.0\sigma(I)$ and only these were used in the

Table 2. Atomic positional parameters (fractional co-ordinates) with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn	0.899 41(11)	0.122 90(5)	0.201 69(11)	H(161)	0.6715	0.3055	0.3620
				H(162)	0.7642	0.2506	0.5033
Carbonyl group				C(21)	0.948 1(8)	0.000 1(4)	0.174 9(11)
C(1)	0.905 3(8)	0.110 3(4)	0.436 8(7)	C(22)	0.970 0(8)	0.041 5(4)	0.016 1(9)
O(1)	0.908 5(8)	0.102 3(4)	0.587 5(6)	C(23)	1.078 9(9)	0.102 2(4)	0.021 0(9)
				C(24)	1.150 4(7)	0.113 7(4)	0.188 8(11)
Cyclohexadiene rings				C(25)	1.205 9(7)	0.045 1(4)	0.295 7(12)
C(11)	0.854 4(9)	0.244 4(4)	0.248 3(10)	C(26)	1.087 2(9)	−0.021 2(3)	0.288 2(12)
C(12)	0.827 7(9)	0.223 1(4)	0.072 9(9)	H(21)	0.8413	−0.0125	0.2161
C(13)	0.713 9(9)	0.162 8(4)	0.049 6(9)	H(22)	0.9062	0.0283	−0.0956
C(14)	0.648 5(7)	0.132 9(4)	0.205 5(11)	H(23)	1.1067	0.1340	−0.0846
C(15)	0.601 6(10)	0.188 4(5)	0.350 5(10)	H(24)	1.1591	0.1677	0.2373
C(16)	0.722 3(11)	0.253 0(4)	0.377 5(11)	H(251)	1.3073	0.0270	0.2444
H(11)	0.9633	0.2546	0.2915	H(252)	1.2215	0.0615	0.4205
H(12)	0.8829	0.2472	−0.0294	H(261)	1.1351	−0.0679	0.2339
H(13)	0.6826	0.1442	−0.0696	H(262)	1.0477	−0.0327	0.4082
H(14)	0.6332	0.0764	0.2235				
H(151)	0.5023	0.2140	0.3176				
H(152)	0.5918	0.1602	0.4635				

solution and refinement of the structure. Scan rates varied from 2.5° min^{-1} for the weakest reflections to 29.0° min^{-1} for the strongest, and three check reflections (012, 120, and $3\bar{1}0$) were remeasured every 40 reflections to monitor the stability of the system. The data were corrected for Lorentz and polarisation effects but not for *X*-ray absorption [μ(Mo-K_α) = 12.3 cm^{-1}].

Crystal data. $C_{13}H_{16}MnO$, $M = 243.2$, Orthorhombic, $a = 8.570(1)$, $b = 17.220(1)$, $c = 7.562(1)$ Å, $U = 1\,115.9$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $F(000) = 508$, space group $P2_12_12_1$ (no. 19), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å.

The structure was solved by conventional heavy-atom methods, and in the final refinement (by full-matrix least squares) anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were incorporated at positions calculated on an idealised model (C–H 1.00 Å) but neither their positional nor thermal parameters ($U = 7.6 \times 10^{-2}$ Å^2) were refined. Weights were applied according to the scheme $w^{-1} = xy$, where $x = F_o/a$ if $F_o > a$, $x = 1$ if $F_o \leqslant a$, and $y = b/\sin\theta$ if $\sin\theta < b$, $y = 1$ if $\sin\theta \geqslant b$; $a = 17.0$, $b = 0.32$. The refinement converged to R 0.045 (R' 0.056). Atomic scattering factors were from ref. 13 for hydrogen and ref. 14 for all other atoms. In the case of Mn these were corrected for the real and imaginary parts of anomalous dispersion [15] which in turn enabled the correct crystal enantiomorph to be assigned. The atomic fractional co-ordinates given in Table 2 correspond, we believe, to the actual crystal investigated; reversal of the signs of these gives less good refinement and less accurate bond lengths and angles.

Manganese Atoms + Cycloheptatriene + CO.—The hexane extract from the reactor gave two equal fractions when chromatographed on alumina under N_2. The first fraction yielded, after recrystallisation from pentane, very air-sensitive, green needles of [Mn(η^4-C_7H_8)$_2$(CO)] (Found: C, 68.4; H, 6.60. $C_{15}H_{16}MnO$ requires C, 67.4; H, 6.05%), sublimes at 75 °C (10^{-2} Pa) with decomposition; *m/e* 267 (P^+, 0.7%), 239 ($MnC_{14}H_{16}^+$, 25%), 147 ($MnC_7H_8^+$, 53%), and 91 ($C_7H_7^+$, 100%). E.s.r.: six-line spectrum as for [Mn(η^4-C_6H_8)$_2$(CO)], $g = 2\,019$, $A = 8 \times 10^{-3}$ T. I.r. (pentane): ν_{CO} at 1 972 cm^{-1}. The second fraction gave yellow crystals identified as the known [6] [Mn(1—5-η-C_7H_9)(CO)$_3$] by mass spectrometry {P^+ and [P-(1—3)CO]$^+$} and i.r. spectroscopy [ν_{CO} (pentane) at 2 013, 1 945, and 1 931 cm^{-1}; lit.[6] (CCl_4) 2 010 and 1 950 cm^{-1}].

Manganese Atoms + Cyclo-octa-1,3-diene + CO.—The hexane extract from the reactor was separated into three fractions on an alumina column. The first was shown by its i.r. spectrum to be [$Mn_2(CO)_{10}$]. The second was a small yield of an air-sensitive yellow oil which we believe to be [Mn(η^3-C_8H_{13})(CO)$_4$]; *m/e* 276 ($MnC_{12}H_{13}O_4^+$, 0.4%), 248 ($MnC_{11}H_{13}O_3^+$, 0.3%), 220 ($MnC_{10}H_{13}O_2^+$, 6.5%), 192 ($MnC_9H_{13}O^+$, 1.7%), and 164 ($MnC_8H_{13}^+$, 29.0%). I.r. (pentane): ν_{CO} at 2 056s, 1 977m, 1 963vs, and 1 952vs cm^{-1} {compare [Mn(η^3-C_8H_{11})(CO)$_4$],[7] ν_{CO} at 2 071, 1 990, 1 973, and 1 959 cm^{-1}}. The third fraction, a yellow solid, was found to be the known [Mn(1—5-η-C_8H_{11})(CO)$_3$].[7] I.r. (pentane): ν_{CO} at 2 013, 1 945, and 1 931 cm^{-1} (lit.[7] 2 020, 1 936, and 1 930 cm^{-1}); *m/e* 246 ($MnC_{11}H_{11}O_3^+$, 41.5%), 218 ($MnC_{10}H_{11}O_2^+$, 27.4%), 190 ($MnC_9H_{11}O^+$, 24.6%), and 162 ($MnC_8H_{11}^+$, 100%).

Manganese Atoms + Cyclopentadiene + CO.—The hexane extract from the reactor was separated into two equal fractions on an alumina column. These proved from their mass, i.r., and n.m.r. spectra to be known compounds: [Mn(η^5-C_5H_5)(CO)$_3$] [i.r., ν_{CO} (hexane) at 2 025 and 1 943 cm^{-1}; lit.,[8] 2 030 and 1 949 cm^{-1}]; yellow [Mn(η^5-C_5H_5)(η^2-$C_{10}H_{12}$)(CO)$_2$] [i.r., ν_{CO} at 1 963 and 1 905 cm^{-1}; lit.,[8] 1 972 and 1 912 cm^{-1}; *m/e* 308 ($MnC_{17}H_{17}O_2^+$, 4.3%), 252 ($MnC_{15}H_{17}^+$, 14.0%), 186 ($MnC_{10}H_{11}^+$, 39.1%), 132 ($C_{10}H_{12}^+$, 9.0%), and 66 ($C_5H_6^+$, 100%)].

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