Structures of Two Mn(CO)₃[C₅H₄-X-C₅H₄]Mn(CO)₃ Molecules, where X = —C(CH₃)(OH)— and —C(O)CH=C(CH₃)—

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Abstract. (I) 1,1-Bis(η^5-cyclopentadienyl)ethanol-bis-(tricarbonyl-manganese), $C_{18}H_{12}Mn_2O_7$; (II) 1,4-bis-(η^5-cyclopentadienyl)-but-2-en-1-one-bis(tricarbonyl-manganese), $C_{20}H_{12}Mn_2O_7$, $M_r = 450 \cdot 2$ (I), $474 \cdot 2$ (II), triclinic, $P\bar{1}$, $a = 11 \cdot 921$ (3), $b = 12 \cdot 352$ (5), $c = 16 \cdot 831$ (4) Å, $\alpha = 62 \cdot 08$ (3), $\beta = 62 \cdot 66$ (2), $\gamma = 67 \cdot 85$ (3)°, $V = 1903 \cdot 4$ (7) Å³, $Z = 2$, $D_x = 1 \cdot 62$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 13 \cdot 1$ cm⁻¹, $F(000) = 928$, $T = 293$ K, $R = 0 \cdot 032$ for 3928 reflections with $F_o^2 > 3\sigma(F_o^2)$. There are two different molecules in the asymmetric portion of the unit cell: in one the bridging linkage between the two cyclopentadiene (cp) units is —C(CH₃)(OH)— and in the other it is (*trans*)—C(O)CH=C(CH₃)—. In the latter complex the organic ligand is planar within 0·16 Å with the two η^5-bonded Mn(CO)₃ units on the same side of the plane. In the complex with the CMeOH bridge the cp units form a dihedral angle of 106·7° and the Mn(CO)₃ units are on the outside of the ligand unit.

Experimental. A 50:50 mixture of the title complexes (I) and (II) was obtained by the incomplete reaction of (I) (Kolobova, Valueva, Anisimov & Suleimanov, 1978) with *n*-BuLi in THF. Yellow crystals obtained by slow evaporation of a pentane/benzene (2:1) solution. Data crystal 0·20 × 0·26 × 0·46 mm mounted with epoxy on a glass fiber. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4–16° min⁻¹ in θ. Unit cell determined from least-squares analysis of angle data for 25 reflections with $20 < 2\theta < 24°$. Analytical absorption correction varied from 0·90 to 1·00. Data collected to $(\sin\theta)/\lambda$ of 0·57 Å⁻¹, $-13 < h < 13$, $0 < k < 14$, $-19 < l < 19$. Three standard reflections ($\bar{2}50$, $\bar{4}03$, 625) indicated crystal decomposition of less than 0·5% over 54·4 h of data collection. 6275 reflections measured, 5952 unique ($R_{int} = 0 \cdot 03$), 2024 reflections with $I < 3\sigma(I)$ where $\sigma^2(I) = \sigma_{cs}^2(I) + (0 \cdot 05I)^2$; $\sigma_{cs}(I)$ is standard deviation of I based on counting statistics. Solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Full-matrix least squares minimized $\sum w(F_o - F_c)^2$. Methyl H-atom orientation determined from difference maps and all H atoms constrained to idealized positions (C—H = 0·95 Å) with fixed iso-

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

Label *A* refers to atoms of (I), label *B* to atoms of (II).

	x	y	z	B_{eq}
Mn(1B)	−0·03457 (5)	0·58780 (5)	0·62168 (3)	3·33 (1)
Mn(1A)	−0·43271 (5)	0·60634 (5)	1·07800 (4)	3·23 (1)
Mn(2B)	0·52555 (5)	0·83132 (6)	0·39133 (4)	4·05 (2)
Mn(2A)	−0·12989 (5)	0·98706 (5)	0·91454 (3)	3·23 (1)
O(1B)	0·2337 (3)	0·5131 (3)	0·5069 (3)	8·3 (1)
O(1A)	−0·4993 (3)	0·7576 (3)	0·9037 (2)	5·67 (9)
O(2B)	0·0345 (3)	0·4705 (3)	0·7945 (2)	7·4 (1)
O(2A)	−0·5658 (3)	0·7947 (3)	1·1694 (2)	6·8 (1)
O(3B)	−0·1042 (3)	0·3556 (3)	0·6670 (2)	7·1 (1)
O(3A)	−0·6609 (3)	0·4988 (3)	1·1614 (2)	6·7 (1)
O(4B)	0·5231 (3)	0·6933 (3)	0·5885 (2)	7·3 (1)
O(4A)	−0·1345 (3)	1·0890 (2)	0·7196 (2)	5·16 (9)
O(5B)	0·5433 (5)	0·6038 (4)	0·3680 (3)	13·3 (2)
O(5A)	−0·1172 (3)	1·2285 (2)	0·9008 (2)	7·1 (1)
O(6B)	0·8074 (3)	0·7977 (4)	0·3087 (3)	9·6 (2)
O(6A)	0·1522 (3)	0·9038 (3)	0·8474 (2)	6·2 (1)
O(7B)	−0·0119 (3)	0·8397 (2)	0·6848 (2)	4·88 (8)
O(7A)	−0·2025 (2)	0·7593 (2)	0·8630 (1)	3·75 (7)
C(1B)	0·1285 (4)	0·5425 (4)	0·5513 (3)	5·2 (1)
C(1A)	−0·4718 (3)	0·7019 (3)	0·9714 (2)	3·9 (1)
C(2B)	0·0070 (4)	0·5170 (3)	0·7272 (3)	4·7 (1)
C(2A)	−0·5155 (4)	0·7222 (4)	1·1325 (3)	4·6 (1)
C(3B)	−0·0759 (4)	0·4460 (3)	0·6486 (3)	4·6 (1)
C(3A)	−0·5723 (4)	0·5417 (4)	1·1298 (3)	4·5 (1)
C(4B)	0·5260 (4)	0·7468 (4)	0·5109 (3)	4·7 (1)
C(4A)	−0·1314 (3)	1·0497 (3)	0·7949 (2)	3·6 (1)
C(5B)	0·5346 (5)	0·6917 (5)	0·3783 (3)	7·6 (2)
C(5A)	−0·1202 (4)	1·1350 (3)	0·9045 (3)	4·5 (1)
C(6B)	0·6971 (4)	0·8101 (5)	0·3407 (3)	6·2 (2)
C(6A)	0·0418 (4)	0·9370 (3)	0·8734 (3)	4·4 (1)
C(7B)	−0·0661 (3)	0·7814 (3)	0·5949 (2)	3·0 (1)
C(7A)	−0·2312 (3)	0·6080 (3)	1·0186 (2)	3·06 (9)
C(8B)	−0·0511 (3)	0·7671 (3)	0·5107 (2)	3·7 (1)
C(8A)	−0·2511 (3)	0·5166 (3)	0·9999 (2)	3·7 (1)
C(9B)	−0·1499 (3)	0·7117 (3)	0·5330 (2)	4·2 (1)
C(9A)	−0·3065 (4)	0·4267 (3)	1·0888 (3)	5·1 (1)
C(10B)	−0·2278 (3)	0·6916 (3)	0·6301 (3)	4·1 (1)
C(10A)	−0·3208 (4)	0·4608 (4)	1·1625 (3)	5·1 (1)
C(11B)	−0·1784 (3)	0·7341 (3)	0·6686 (2)	3·5 (1)
C(11A)	−0·2739 (3)	0·5717 (3)	1·1193 (2)	3·7 (1)
C(12B)	0·3320 (3)	0·9411 (3)	0·4309 (2)	3·5 (1)
C(12A)	−0·2001 (3)	0·8174 (3)	0·9795 (2)	2·71 (9)
C(13B)	0·3618 (3)	0·9214 (4)	0·3459 (2)	4·6 (1)
C(13A)	−0·3034 (3)	0·9228 (3)	0·9674 (2)	3·4 (1)
C(14B)	0·4678 (4)	0·9746 (5)	0·2739 (3)	5·7 (2)
C(14A)	−0·3187 (4)	0·9914 (4)	1·0196 (3)	5·2 (1)
C(15B)	0·5054 (4)	1·0284 (4)	0·3126 (3)	6·0 (2)
C(15A)	−0·2273 (4)	0·9303 (3)	1·0659 (2)	5·4 (1)
C(16B)	0·4250 (4)	1·0080 (4)	0·4087 (3)	4·6 (1)
C(16A)	−0·1538 (3)	0·8226 (3)	1·0417 (2)	3·9 (1)
C(17B)	0·2267 (4)	0·9215 (4)	0·6045 (3)	5·4 (1)
C(17A)	−0·0160 (3)	0·6623 (3)	0·9141 (3)	4·1 (1)
C(18B)	0·2249 (3)	0·9068 (3)	0·5215 (2)	3·2 (1)
C(18A)	−0·1619 (3)	0·7140 (3)	0·9425 (2)	2·90 (9)
C(19B)	0·1308 (3)	0·8699 (3)	0·5247 (2)	3·3 (1)
C(20B)	0·0169 (3)	0·8311 (3)	0·6074 (2)	3·3 (1)
H(O)	−0·1270	0·7793	0·8027	4·4*

* Isotropic temperature factor, B_{iso}.

tropic B values of 1·2 times the B value of the attached atoms. All non-H atoms were refined anisotropically for a total of 505 parameters. $R = 0.032$, $wR = 0.041$, $GOF = 1.1$, where non-Poisson $w^{-1} = [\sigma^2(I) + (0.05I)^2]/4F^2$. Final $(\Delta/\sigma)_{max} < 0.02$, $\rho_{max} = 0.25$ (6) and $\rho_{min} = -0.46$ (6) e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP*.* Table 1 gives the atomic coordinates and Table 2 gives selected bond distances and angles. Figs. 1 and 2 show the complexes with the numbering scheme.

(I)   (II)
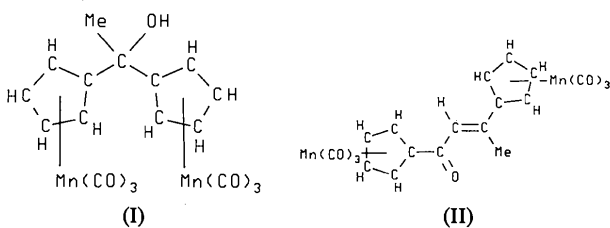
Related literature. The structure of a similar dimanganese complex with a C(Me)(OSiMe$_3$) unit bridging the two cp rings has been reported (Cordes, Durham & Askew, 1989). Related complexes of diiron (Weaver & Woodward, 1973) and ditungsten (Abriel & Heck, 1986) have been reported. The structure of a related monomeric manganese complex has been reported by Berndt & Marsh (1963).
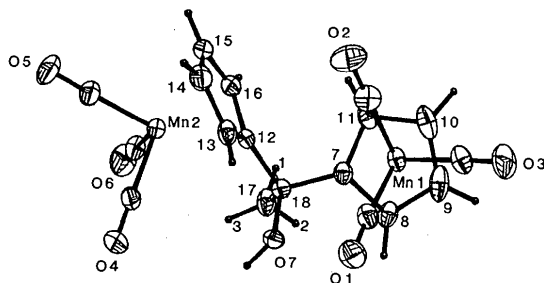
Fig. 1. *ORTEP* (Johnson, 1976) drawing and numbering scheme for (I); the A's of the atom labels have been omitted. Carbonyl C atoms have the same number as the attached O atom, and H atoms have the same number as the attached atom. The ellipsoids are drawn at the 30% probability surface and H atoms have been given arbitrary radii for figure clarity. The numbered atoms without labels are C atoms.

Table 2. *Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Mn(1A)–C(1A)	1·789 (4)		C(7A)–C(8A)	1·426 (6)
Mn(1A)–C(2A)	1·787 (5)		C(7A)–C(11A)	1·414 (6)
Mn(1A)–C(3A)	1·784 (4)		C(7A)–C(18A)	1·520 (6)
Mn(1B)–C(1B)	1·783 (4)		C(7B)–C(8B)	1·432 (7)
Mn(1B)–C(2B)	1·786 (4)		C(7B)–C(11B)	1·435 (6)
Mn(1B)–C(3B)	1·794 (4)		C(7B)–C(20B)	1·472 (6)
Mn(2A)–C(4A)	1·793 (5)		C(8A)–C(9A)	1·414 (6)
Mn(2A)–C(5A)	1·798 (5)		C(8B)–C(9B)	1·399 (6)
Mn(2A)–C(6A)	1·787 (6)		C(9A)–C(10A)	1·410 (5)
Mn(2B)–C(4B)	1·782 (5)		C(9B)–C(10B)	1·412 (5)
Mn(2B)–C(5B)	1·796 (5)		C(10A)–C(11A)	1·410 (5)
Mn(2B)–C(6B)	1·784 (5)		C(10B)–C(11B)	1·394 (6)
O(1A)–C(1A)	1·148 (5)		C(12A)–C(13A)	1·423 (6)
O(1B)–C(1B)	1·146 (5)		C(12A)–C(16A)	1·423 (5)
O(2A)–C(2A)	1·149 (6)		C(12A)–C(18A)	1·507 (7)
O(2B)–C(2B)	1·145 (5)		C(12B)–C(13B)	1·424 (6)
O(3A)–C(3A)	1·149 (6)		C(12B)–C(16B)	1·439 (5)
O(3B)–C(3B)	1·148 (5)		C(12B)–C(18B)	1·467 (6)
O(4A)–C(4A)	1·140 (7)		C(13A)–C(14A)	1·400 (6)
O(4B)–C(4B)	1·145 (5)		C(13B)–C(14B)	1·404 (5)
O(5A)–C(5A)	1·141 (5)		C(14A)–C(15A)	1·404 (5)
O(5B)–C(5B)	1·138 (7)		C(14B)–C(15B)	1·402 (6)
O(6A)–C(6A)	1·150 (10)		C(15A)–C(16A)	1·415 (5)
O(6B)–C(6B)	1·148 (5)		C(15B)–C(16B)	1·406 (5)
O(7A)–C(18A)	1·424 (5)		C(17A)–C(18A)	1·531 (6)
O(7B)–C(20B)	1·232 (5)		C(17B)–C(18B)	1·501 (8)
O(7A)–H(O)	1·00		C(18B)–C(19B)	1·333 (7)
O(7B)–H(O)	1·81		C(19B)–C(20B)	1·463 (6)

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C(1A)–Mn(1A)–C(2A)	94·8 (2)		C(8A)–C(9A)–C(10A)	108·2 (4)
C(1A)–Mn(1A)–C(3A)	89·9 (2)		C(8B)–C(9B)–C(10B)	108·2 (3)
C(2A)–Mn(1A)–C(3A)	92·8 (2)		C(9A)–C(10A)–C(11A)	107·8 (3)
C(1B)–Mn(1B)–C(2B)	91·1 (2)		C(9B)–C(10B)–C(11B)	108·8 (3)
C(1B)–Mn(1B)–C(3B)	93·0 (2)		C(7A)–C(11A)–C(10A)	108·8 (4)
C(2B)–Mn(1B)–C(3B)	90·2 (2)		C(7B)–C(11B)–C(10B)	108·1 (3)
C(4A)–Mn(2A)–C(5A)	92·1 (2)		C(13A)–C(12A)–C(16A)	106·7 (3)
C(4A)–Mn(2A)–C(6A)	91·3 (3)		C(13A)–C(12A)–C(18A)	125·0 (4)
C(5A)–Mn(2A)–C(6A)	92·4 (3)		C(16A)–C(12A)–C(18A)	128·0 (4)
C(4B)–Mn(2B)–C(5B)	91·9 (2)		C(13B)–C(12B)–C(16B)	106·0 (3)
C(4B)–Mn(2B)–C(6B)	93·2 (2)		C(13B)–C(12B)–C(18B)	127·6 (4)
C(5B)–Mn(2B)–C(6B)	90·3 (2)		C(16B)–C(12B)–C(18B)	126·4 (4)
Mn(1A)–C(1A)–O(1A)	176·1 (4)		C(12A)–C(13A)–C(14A)	108·8 (3)
Mn(1B)–C(1B)–O(1B)	179·3 (4)		C(12B)–C(13B)–C(14B)	109·4 (4)
Mn(1A)–C(2A)–O(2A)	177·5 (4)		C(13A)–C(14A)–C(15A)	108·3 (4)
Mn(1B)–C(2B)–O(2B)	179·3 (4)		C(13B)–C(14B)–C(15B)	107·6 (4)
Mn(1A)–C(3A)–O(3A)	178·3 (4)		C(14A)–C(15A)–C(16A)	108·0 (4)
Mn(1B)–C(3B)–O(3B)	178·9 (4)		C(14B)–C(15B)–C(16B)	109·1 (3)
Mn(2A)–C(4A)–O(4A)	178·8 (4)		C(12A)–C(16A)–C(15A)	108·2 (3)
Mn(2B)–C(4B)–O(4B)	178·4 (5)		C(12B)–C(16B)–C(15B)	108·0 (3)
Mn(2A)–C(5A)–O(5A)	177·8 (4)		O(7A)–C(18A)–C(7A)	106·1 (4)
Mn(2B)–C(5B)–O(5B)	178·2 (4)		O(7A)–C(18A)–C(12A)	109·6 (4)
Mn(2A)–C(6A)–O(6A)	179·4 (6)		O(7A)–C(18A)–C(17A)	110·5 (3)
Mn(2B)–C(6B)–O(6B)	179·0 (6)		C(7A)–C(18A)–C(12A)	110·2 (3)
C(8A)–C(7A)–C(11A)	107·0 (4)		C(7A)–C(18A)–C(17A)	109·0 (4)
C(8A)–C(7A)–C(18A)	124·7 (4)		C(12A)–C(18A)–C(17A)	111·2 (4)
C(11A)–C(7A)–C(18A)	127·9 (4)		C(12B)–C(18B)–C(17B)	116·6 (4)
C(8B)–C(7B)–C(11B)	106·5 (3)		C(12B)–C(18B)–C(19B)	119·2 (5)
C(8B)–C(7B)–C(20B)	128·3 (4)		C(17B)–C(18B)–C(19B)	124·3 (4)
C(11B)–C(7B)–C(20B)	125·2 (4)		C(18B)–C(19B)–C(20B)	127·7 (4)
C(7A)–C(8A)–C(9A)	108·0 (5)		O(7B)–C(20B)–C(7B)	119·9 (4)
C(7B)–C(8B)–C(9B)	108·4 (4)		O(7B)–C(20B)–C(19B)	122·9 (4)
C(18A)–O(7A)–O(H)	108·8		C(7B)–C(20B)–C(19B)	117·1 (4)
O(7A)–O(H)–O(7B)	169·4			
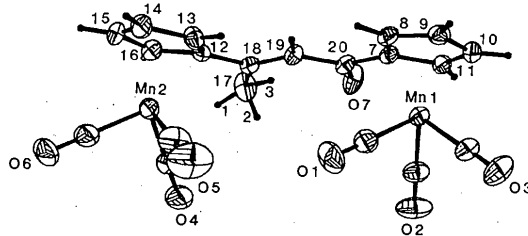
Fig. 2. *ORTEP* (Johnson, 1976) drawing and numbering scheme for (II) (the B's of the atom labels omitted). Drawing and labeling as in Fig. 1.

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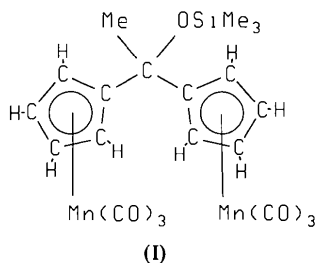
Structure of Mn(CO)₃[C₅H₄C(Me)(OSiMe₃)C₅H₄]Mn(CO)₃

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Abstract. 1,1-Bis(η^5-cyclopentadienyl)-1-(trimethylsiloxy)ethane-bis(tricarbonyl-manganese), $C_{21}H_{20}Mn_2$-O_7Si, $M_r = 522.4$, monoclinic, $P2_1/c$, $a = 12.729 (3)$, $b = 8.112 (3)$, $c = 22.432 (6)$ Å, $\beta = 96.51 (2)°$, $V = 2301 (2)$ Å^3, $Z = 4$, $D_x = 1.51$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 11.4$ cm^{-1}, $F(000) = 1064$, $T = 293$ K, $R = 0.044$ for 1637 reflections with $F_o^2 > 3\sigma(F_o^2)$. The dihedral angle between the two planar cyclopentadiene (cp) units is 99.0° and the two Mn(CO)₃ units are pentahapto bonded to these cp rings on the outside of the cp₂C(Me)OSiMe₃ molecule.

Experimental. Title compound (I) obtained by the

(I)

reaction of KH with a THF solution of Mn(CO)₃-C₅H₄C(Me)(OH)C₅H₄Mn(CO)₃ (Kolobova, Valueva, Anisimov & Suleimanov, 1978) followed by the addition of ClSiMe₃. Data crystal obtained by slow evaporation of a pentane–benzene (20:1) solution. Colorless platelet crystal $0.08 \times 0.24 \times 0.46$ mm mounted on a glass fiber with epoxy. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4–16° min^{-1} in θ. Unit cell

determined from least-squares analysis of angle data for 25 reflections with $13 < 2\theta < 19°$. Absorption correction based on ψ scans varied from 0.95 to 1.00. Data collected to $(\sin\theta)/\lambda$ of 0.59 Å^{-1}, $0 < h < 15$, $-9 < k < 0$, $-26 < l < 26$. Three standard reflections (008, $1\bar{2}6$, 500) decreased 1.7% over 34.2 h of data collection; a linear correction was applied. 4239 reflections measured, 4044 unique ($R_{int} = 0.03$), 2407 reflections with $I < 3\sigma(I)$ where $\sigma^2(I) = \sigma_{cs}^2(I) + (0.05I)^2$; $\sigma_{cs}(I)$ is standard deviation of I based on counting statistics. Solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Full-matrix least squares minimized $\sum w(F_o - F_c)^2$. H atoms were constrained to idealized positions (C—H = 0.95 Å) with fixed isotropic B values of 1.2 times the B value of the attached C atoms; the orientations of the methyl H atoms were determined from difference maps. The non-H atoms were refined anisotropically for a total of 280 parameters. $R = 0.044$, $wR = 0.049$, GOF = 1.1, where non-Poisson $w^{-1} = [\sigma^2(I) + (0.05I)^2]/4F^2$. Final $(\Delta/\sigma)_{max} < 0.1$, $\rho_{max} = 0.33 (7)$ and $\rho_{min} = -0.32 (7)$ e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP.** Table

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* Tables of H-atom positions, anisotropic temperature factors and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51829 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.