carbonato ligand is bidentate, in contrast to the pair of monodentate acetate ligands reported here.

We thank SERC for a research grant and R. McLaughlan for technical assistance.

References

BARANIAK, E., FREEMAN, H. C., JAMES, J. M. & NOCKOLDS, C. E. (1970). *J. Chem, Soc. A*, pp. 2558–2566.
CATTERICK, J. & THORNTON, P. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1634–1640.
CLEGG, W. (1981). *Acta Cryst.* A**37**, 22–28.
HORROCKS, W. D. JR, ISHLEY, J. N., HOLMQUIST, B. & THOMPSON, J. S. (1980). *J. Inorg. Biochem.* **12**, 131–141.
HORROCKS, W. D. JR, ISHLEY, J. N. & WHITTLE, R. R. (1982*a*). *Inorg. Chem.* **21**, 3265–3269.
HORROCKS, W. D. JR, ISHLEY, J. N. & WHITTLE, R. R. (1982*b*). *Inorg. Chem.* **21**, 3270–3274.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributors Kluwer Academic Publishers, Dordrecht.)
SHELDRICK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, revision 5. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1989). C**45**, 1994–1996

Structure of $Mn(CO)_3[C_5H_4CHMeC_5H_4]Mn(CO)_3$ and its Benzene Solvate

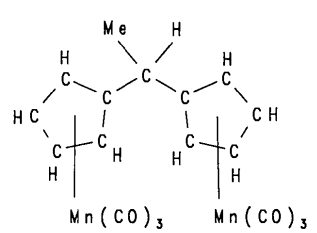
BY A. W. CORDES, B. DURHAM AND E. ASKEW

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA

(*Received* 12 *June* 1989; *accepted* 4 *July* 1989)

Abstract. (I) 1,1-Bis(η^5-cyclopentadienyl)ethanebis(tricarbonylmanganese), $C_{18}H_{12}Mn_2O_6$, $M_r = 434\cdot2$, monoclinic, $P2_1/c$, $a = 12\cdot045\ (2)$, $b = 14\cdot169\ (2)$, $c = 11\cdot468\ (4)$ Å, $\beta = 115\cdot91\ (2)^\circ$, $V = 1760\ (2)$ Å^3, $Z = 4$, $D_x = 1\cdot64$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14\cdot1$ cm^{-1}, $F(000) = 872$, $T = 293$ K, $R = 0\cdot043$ for 1251 reflections with $F_o^2 > 3\sigma(F_o^2)$. (II), the 0·5 benzene solvate of (I), $C_{18}H_{12}Mn_2O_6.\frac{1}{2}C_6H_6$, $M_r = 473\cdot2$, triclinic, $P\overline{1}$, $a = 7\cdot850\ (3)$, $b = 9\cdot205\ (4)$, $c = 14\cdot291\ (4)$ Å, $\alpha = 85\cdot42\ (3)$, $\beta = 85\cdot79\ (3)$, $\gamma = 75\cdot50\ (3)^\circ$, $V = 995\ (2)$ Å^3, $Z = 2$, $D_x = 1\cdot58$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 12\cdot5$ cm^{-1}, $F(000) = 478$, $T = 293$ K, $R = 0\cdot028$ for 1800 reflections with $F_o^2 > 3\sigma(F_o^2)$. These two crystals show large differences of conformation of the dicyclopentadiene ligand: in (I) the cp rings are each within 9·1° of being perpendicular to the central C(cp)—C—C(cp) plane and the $Mn(CO)_3$ units are both on the outside of the ligand unit, while in (II) one cp ring is perpendicular to the C(cp)—C—C(cp) plane while the other is twisted 32·6° away from the perpendicular orientation; the $Mn(CO)_3$ unit bonded to the latter cp ring is on the inside of the fold of the ligand.

Experimental. The title complex (I) was obtained by the procedure described by Kolobova, Valueva, Anisimov & Suleimanov (1978). Yellow crystals of (I) obtained from pentane/benzene (20:1) solution and of (II) from benzene solution by slow evaporation of the solvents. Data crystal was 0·08 × 0·26 × 0·32 mm for (I) and approximately 0·5 × 0·5 × 0·5 mm for (II); both were 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 for each determined from least-squares analysis of angle data for 25 reflections with $14 < 2\theta < 20^\circ$. Analytical absorption correction for (I) varied from 0·74 to 1·00; an absorption correction based on ψ scans for (II) varied from 0·95 to 1·00. Data collected to $(\sin\theta)/\lambda$ of 0·53 Å^{-1} for both crystals; $0 < h < 12$, $0 < k < 14$, $-12 < l < 12$ for (I) and $-8 < h < 8$, $0 < k < 9$, $-15 < l < 15$ for (II). Three standard reflections [40$\overline{4}$, 24$\overline{4}$, 160 for (I); 007, 040, 300 for (II)] indicated crystal decomposition of less than 2·5% over 20·1 h (I) and 12·7 h (II) of data collection. For (I): 2390 reflections measured, 2147 unique ($R_{\rm int} = 0\cdot033$), 896 reflections with $I < 3\sigma(I)$ where $\sigma^2(I) = \sigma_{\rm cs}^2(I) + (0\cdot05I)^2$; $\sigma_{\rm cs}(I)$ is standard deviation of I based on counting statistics. For (II): 2612 reflections measured, 2428 unique ($R_{\rm int} = 0\cdot014$), 628 with $I < 3\sigma(I)$. Both structures solved by direct methods using *MULTAN*11/82 (Main, Fiske,



(I)

0108-2701/89/121994-03\$03.00

Table 1. *Final fractional coordinates and B_{eq} thermal factors for non-*H *atoms*

E.s.d.'s in parentheses are in the units of the least-significant digit.

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å^2)
(I)				
Mn(1)	0·53295 (9)	0·35137 (9)	0·1385 (1)	2·83 (3)
Mn(2)	1·11814 (9)	0·40139 (9)	0·2838 (1)	3·25 (3)
O(1)	0·5509 (5)	0·3700 (4)	−0·1063 (5)	4·6 (1)
O(2)	0·4446 (6)	0·1569 (4)	0·0793 (6)	6·9 (2)
O(3)	0·2780 (5)	0·4224 (5)	0·0243 (6)	6·6 (2)
O(4)	1·3093 (5)	0·5285 (6)	0·2834 (7)	10·4 (2)
O(5)	0·9871 (6)	0·3882 (5)	0·0015 (5)	6·2 (2)
O(6)	1·2592 (6)	0·2327 (5)	0·2892 (6)	8·6 (2)
C(1)	0·5418 (6)	0·3630 (5)	−0·0119 (7)	3·1 (2)
C(2)	0·4785 (6)	0·2335 (6)	0·1034 (7)	3·9 (2)
C(3)	0·3789 (7)	0·3941 (6)	0·0708 (7)	4·4 (2)
C(4)	1·2335 (7)	0·4767 (7)	0·2824 (9)	6·0 (3)
C(5)	1·0392 (7)	0·3949 (6)	0·1108 (7)	3·9 (2)
C(6)	1·2046 (7)	0·2991 (7)	0·2888 (8)	5·3 (3)
C(7)	0·6678 (6)	0·4573 (5)	0·2365 (7)	2·9 (2)
C(8)	0·5895 (7)	0·4502 (6)	0·2969 (7)	3·8 (2)
C(9)	0·5998 (6)	0·3567 (6)	0·3447 (7)	3·7 (2)
C(10)	0·6857 (6)	0·3069 (5)	0·3146 (6)	3·1 (2)
C(11)	0·7290 (6)	0·3688 (5)	0·2472 (6)	2·7 (2)
C(12)	0·8262 (6)	0·3485 (6)	0·1999 (6)	3·1 (2)
C(13)	0·9481 (6)	0·3881 (5)	0·3004 (6)	2·9 (2)
C(14)	1·0423 (6)	0·3403 (6)	0·4034 (7)	3·8 (2)
C(15)	1·1346 (7)	0·4049 (7)	0·4772 (7)	4·5 (2)
C(16)	1·0994 (6)	0·4946 (6)	0·4215 (7)	4·2 (2)
C(17)	0·9844 (6)	0·4852 (6)	0·3124 (7)	3·6 (2)
C(18)	0·8353 (7)	0·2450 (6)	0·1727 (7)	4·2 (2)
(II)				
Mn(1)	0·54290 (7)	0·61080 (6)	0·26810 (4)	3·30 (1)
Mn(2)	1·12654 (7)	0·15203 (6)	0·13086 (4)	3·10 (1)
O(1)	0·1692 (4)	0·7383 (3)	0·2373 (2)	5·60 (8)
O(2)	0·4640 (5)	0·3982 (4)	0·4188 (2)	8·1 (1)
O(3)	0·5536 (4)	0·8439 (4)	0·3938 (2)	7·47 (9)
O(4)	0·9185 (4)	0·3225 (3)	−0·0223 (2)	6·03 (8)
O(5)	1·3182 (4)	−0·0883 (3)	0·0126 (2)	6·43 (8)
O(6)	0·8423 (4)	0·0072 (3)	0·1954 (2)	5·63 (8)
C(1)	0·3155 (5)	0·6891 (4)	0·2503 (3)	3·84 (9)
C(2)	0·4941 (6)	0·4835 (5)	0·3603 (3)	5·0 (1)
C(3)	0·5479 (5)	0·7514 (5)	0·3453 (3)	4·6 (1)
C(4)	1·0006 (5)	0·2533 (4)	0·0364 (3)	4·1 (1)
C(5)	1·2393 (5)	0·0058 (4)	0·0591 (3)	4·09 (9)
C(6)	0·9543 (5)	0·0621 (4)	0·1693 (3)	3·83 (9)
C(7)	0·6737 (5)	0·4326 (4)	0·1837 (3)	3·93 (9)
C(8)	0·5894 (5)	0·5562 (5)	0·1255 (3)	4·6 (1)
C(9)	0·6614 (5)	0·6777 (5)	0·1383 (3)	4·4 (1)
C(10)	0·7930 (5)	0·6279 (4)	0·2047 (3)	3·83 (9)
C(11)	0·8024 (4)	0·4759 (4)	0·2333 (2)	3·11 (8)
C(12)	0·9297 (5)	0·3744 (4)	0·2984 (3)	3·19 (8)
C(13)	1·0963 (4)	0·2960 (4)	0·2447 (2)	2·92 (8)
C(14)	1·1833 (5)	0·3555 (4)	0·1664)3)	3·39 (9)
C(15)	1·3410 (5)	0·2491 (4)	0·1435 (3)	3·98 (9)
C(16)	1·3560 (5)	0·1256 (5)	0·2090 (3)	4·4 (1)
C(17)	1·2056 (5)	0·1526 (4)	0·2712 (3)	3·85 (9)
C(18)	0·9768 (5)	0·4553 (4)	0·3783 (3)	4·2 (1)
C(19)	0·8324 (6)	1·0364 (5)	0·4684 (3)	5·6 (1)
C(20)	0·9474 (6)	0·9046 (5)	0·4470 (3)	5·7 (1)
C(21)	1·1156 (6)	0·8674 (5)	0·4788 (3)	5·6 (1)

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 isotropic B values of 1·2 times the B value of the attached atoms. For (I) all non-H atoms were refined anisotropically for a total of 235 parameters. $R = 0{\cdot}043$, $wR = 0{\cdot}052$, GOF = 1·1, where non-Poisson $w^{-1} = [\sigma^2(I) + (0{\cdot}05I)^2]/4F^2$; final $(\Delta/\sigma)_{max} < 0{\cdot}02$, $\rho_{max} = 0{\cdot}39\,(9)$ and $\rho_{min} = -0{\cdot}63\,(9)$ e Å^{-3} on final difference map. For (II) all non-H atoms

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

	(I)	(II)
Mn(1)—C(1)	1·782 (9)	1·779 (4)
Mn(1)—C(2)	1·775 (10)	1·777 (5)
Mn(1)—C(3)	1·776 (10)	1·775 (5)
Mn(2)—C(4)	1·757 (11)	1·789 (4)
Mn(2)—C(5)	1·789 (9)	1·771 (4)
Mn(2)—C(6)	1·771 (11)	1·787 (4)
O(1)—C(1)	1·139 (8)	1·147 (4)
O(2)—C(2)	1·150 (9)	1·154 (5)
O(3)—C(3)	1·164 (9)	1·152 (5)
O(4)—C(4)	1·168 (11)	1·146 (4)
O(5)—C(5)	1·134 (9)	1·158 (4)
O(6)—C(6)	1·146 (10)	1·145 (4)
C(11)—C(12)	1·517 (9)	1·506 (5)
C(12)—C(13)	1·523 (10)	1·513 (5)
C(12)—C(18)	1·514 (10)	1·526 (5)
C(cp)—C(cp)	1·40 (1) – 1·43 (1)	1·400 (5) – 1·426 (5)
Mn—C(cp)	2·135 (7) – 2·154 (8)	2·119 (5) – 2·150 (5)
C(benz.)—C(benz.)		1·360 (7) – 1·380 (7)
C(1)—Mn(1)—C(2)	92·3 (4)	92·0 (2)
C(1)—Mn(1)—C(3)	92·2 (4)	91·8 (2)
C(2)—Mn(1)—C(3)	90·5 (4)	93·8 (2)
C(4)—Mn(2)—C(5)	93·4 (5)	92·7 (2)
C(4)—Mn(2)—C(6)	92·4 (5)	91·1 (2)
C(5)—Mn(2)—C(6)	90·8 (4)	94·1 (2)
C(11)—C(12)—C(13)	107·4 (6)	111·0 (3)
C(11)—C(12)—C(18)	113·2 (6)	113·5 (3)
C(13)—C(12)—C(18)	112·3 (6)	109·6 (3)
C(cp)—C(cp)—C(cp)	106·4 (7) – 109·2 (8)	106·5 (3) – 108·7 (4)
Mn—C—O	177·7 (9) – 178·8 (8)	177·6 (4) – 178·8 (4)
C(benz.)—C(benz.)—C(benz.)		119·6 (4) – 120·6 (4)

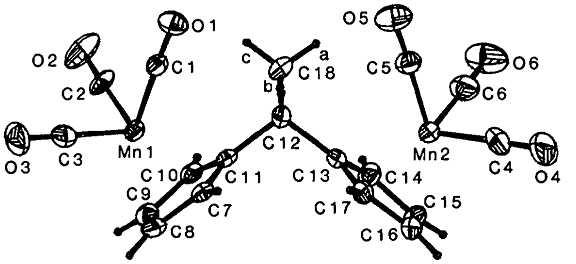


Fig. 1. *ORTEP* (Johnson, 1976) drawing and numbering scheme for (I); H atoms have the same number as the attached atom. The ellipsoids are drawn at the 30% probability surface and H atoms have been given arbitrary radii for figure clarity.

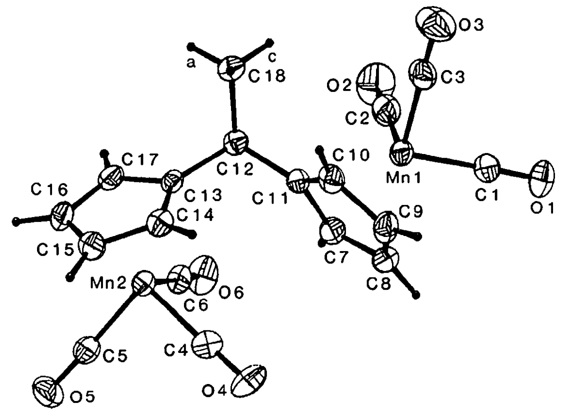


Fig. 2. *ORTEP* (Johnson, 1976) drawing and numbering scheme for (II). Drawing and labeling as in Fig. 1.

were refined anisotropically for a total of 262 parameters. $R = 0\cdot028$, $wR = 0\cdot035$, GOF = 1·2, where non-Poisson $w^{-1} = [\sigma^2(I) + (0\cdot04I)^2]/4F^2$; final $(\Delta/\sigma)_{\max} < 0\cdot01$, $\rho_{\max} = 0\cdot24\,(5)$ and $\rho_{\min} = -0\cdot21\,(5)$ 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 schemes.

Related literature. The structures of three similar dimanganese complexes have been reported recently: one with a —C(Me)(OSiMe$_3$)— unit bridging the two cp rings (Cordes, Durham & Askew, 1989*a*), one with a —C(CH$_3$)(OH)— bridge (Cordes, Durham & Askew, 1989*b*) and one with a —C(O)CH=C(CH$_3$)— bridge (Cordes, Durham & Askew, 1989*b*). The structure of a related monomeric manganese complex has been reported by Berndt & Marsh (1963).

We thank the National Science Foundation and the State of Arkansas for financial support.

References

Berndt, A. F. & Marsh, R. E. (1963). *Acta Cryst.* **16**, 118–123.
Cordes, A. W., Durham, B. & Askew, E. (1989*a*). *Acta Cryst.* C**45**, 1231–1232.
Cordes, A. W., Durham, B. & Askew, E. (1989*b*). *Acta Cryst.* C**45**, 1229–1231.
Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kolobova, N. E., Valueva, Z. P., Anisimov, K. N. & Suleimanov, G. Z. (1978). *Bull. Acad. Sci. USSR Div. Chem. Sci.* **27**, 787–790.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

---

* Tables of anisotropic temperature factors, H-atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52089 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1989). C**45**, 1996–1998

Structure of Acetonitriletris(triphenylphosphine)rhodium(I) Tetraphenylborate

By William Clegg

Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

and C. David Garner and Susan Heyworth

Department of Chemistry, The University, Manchester M13 9PL, England

(*Received* 28 *June* 1989; *accepted* 6 *July* 1989)

Abstract. $[Rh(C_2H_3N)\{P(C_6H_5)_3\}_3][B(C_6H_5)_4]$, $M_r = 1250\cdot1$, triclinic, $P\overline{1}$, $a = 12\cdot095\,(1)$, $b = 15\cdot594\,(2)$, $c = 18\cdot482\,(2)$ Å, $\alpha = 105\cdot971\,(5)$, $\beta = 93\cdot856\,(8)$, $\gamma = 99\cdot580\,(6)°$, $V = 3281\cdot0$ Å^3, $Z = 2$, $D_x = 1\cdot265$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1\cdot54184$ Å, $\mu = 3\cdot17$ mm^{-1}, $F(000) = 1300$, $T = 295$ K, $R = 0\cdot0402$ for 7864 unique observed reflections. The structure consists of discrete cations and anions. The Rh atom in the cation has essentially square-planar coordination, with the Rh—P bond *trans* to the acetonitrile ligand [2·262 (1) Å] significantly shorter than those *cis* to it [2·315 (1) and 2·361 (1) Å]. The Rh—N bond length is 2·045 (3) Å. There is a small distortion of the square-planar coordination towards tetrahedral, with deviations of atoms from the RhP_3N mean plane of: Rh −0·027 (1), P(1) −0·146 (1), P(2) 0·134 (1), P(3) −0·140 (1), N(4) 0·180 (4) Å, and with in-plane compression of P—Rh—N angles and expansion of P—Rh—P angles from ideal values of 90°. The acetonitrile ligand is essentially linearly coordinated [Rh—N—C = 171·8 (3)°].

Experimental. The compound was obtained in an attempt to prepare a salt of the $[Rh(PPh_3)_3(\text{pyridine})]^+$ cation; pyridine was replaced by acetonitrile during recrystallization from this solvent. Crystal size 0·13 × 0·23 × 0·27 mm, Stoe–Siemens diffractometer, unit-cell parameters from 2θ values

0108-2701/89/121996-03$03.00