Synthesis and Structure of Dicarbonyl(η^5-methylcyclopentadienyl)triphenylphosphine-manganese(I)

By Michael J. Zaworotko, Riz Shakir and Jerry L. Atwood*

Department of Chemistry, University of Alabama, University, Alabama 35486, USA

and Vijit Sriyunyongwat, Stephen D. Reynolds and Thomas A. Albright

Department of Chemistry, University of Houston, Houston, Texas 77004, USA

Abstract. $[(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2P(C_6H_5)_3]$, orthorhombic, *Pbca*, $a = 7 \cdot 755$ (3), $b = 16 \cdot 975$ (7), $c = 33 \cdot 091$ (11) Å, $Z = 8$, $D_c = 1 \cdot 38$ g cm^{-3}, $R = 0 \cdot 042$, $R_w = 0 \cdot 056$ for 1549 observed reflections. The major feature of interest lies in the *trans* orientation of the methyl group with respect to the phosphine ligand. The intramolecular distances and angles are typical for compounds of this type: the Mn—C(π) distances range from 2·132 (9) to 2·162 (8) Å, the Mn—C(carbonyl) distances are 1·76 (1) and 1·77 (1) Å, and the Mn—P distance is 2·232 (2) Å.

Introduction. During recent years compounds of the type $[(\eta^5\text{-}C_5H_5)Mn(CO)_2L]$ have been extensively studied structurally, but the same cannot be said of monosubstituted cyclopentadienyl analogues. The only examples of the latter are $[(\eta^5\text{-}C_5H_4CH_3)\text{-}Mn(CO)_2\{S(CH_3)_2(C_2H_5)\}]^+$ (Adams & Chodosh, 1978), $[(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(\text{anthronylketene})]$† (Herrmann, Plank, Ziegler & Weidenhammer, 1979), and more recently $[(\eta^5\text{-}C_5H_4CH_3)\text{-}Mn(CO)_2(\text{dibenzocycloheptenylketene})]$† (Rogers, Atwood & Herrmann, 1981, unpublished results). Our interest in such compounds has arisen through studies of the isoelectronic analogues of chromium, where $L = NO$ (Shakir & Atwood, 1981). In these systems we studied the electronic and steric effects of the cyclopentadienyl substituent on the orientation of the nitrosyl group. In order to expand the scope of the work we sought a comparison with the title compound.

The title compound was synthesized *via* the photochemical elimination of carbon monoxide from tricarbonyl(methylcyclopentadienyl)manganese and reaction of the resulting diethyl ether adduct with tri-

phenylphosphine. Suitable crystals for diffraction analysis were grown *via* slow evaporation of an ethanol solution of the product.

A yellow-orange air-stable crystal (a near-cube, 0·50 × 0·50 × 0·40 mm) of the title compound was mounted and sealed in a glass capillary and placed on

---

* To whom correspondence should be addressed.

† Anthronylketene ≡ 10-carbonyl-9(10*H*)-anthracenone and dibenzocycloheptenylketene ≡ 5-carbonyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene.

Table 1. *Final fractional coordinates with e.s.d.'s in parentheses and U_{eq} values*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

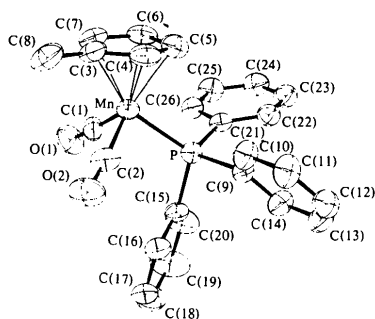|	x	y	z	U_{eq} (Å^2)
Mn	0·8186 (2)	0·67332 (7)	0·15555 (3)	0·034
P	0·6853 (3)	0·5807 (1)	0·11925 (6)	0·035
O(1)	0·9103 (9)	0·7633 (4)	0·0830 (2)	0·061
O(2)	0·5125 (9)	0·7692 (5)	0·1700 (2)	0·073
C(1)	0·870 (1)	0·7271 (5)	0·1113 (3)	0·043
C(2)	0·630 (1)	0·7292 (6)	0·1630 (3)	0·047
C(3)	0·935 (1)	0·7177 (6)	0·2102 (3)	0·050
C(4)	0·862 (1)	0·6427 (6)	0·2181 (2)	0·051
C(5)	0·938 (1)	0·5853 (6)	0·1927 (3)	0·052
C(6)	1·064 (1)	0·6235 (6)	0·1698 (3)	0·054
C(7)	1·062 (1)	0·7053 (6)	0·1804 (3)	0·050
C(8)	0·896 (1)	0·7925 (6)	0·2304 (3)	0·067
C(9)	0·526 (1)	0·5179 (5)	0·1447 (2)	0·035
C(10)	0·496 (1)	0·5237 (5)	0·1854 (3)	0·048
C(11)	0·372 (1)	0·4787 (6)	0·2042 (3)	0·054
C(12)	0·275 (1)	0·4268 (6)	0·1832 (3)	0·051
C(13)	0·297 (1)	0·4206 (6)	0·1419 (3)	0·054
C(14)	0·418 (1)	0·4662 (5)	0·1223 (3)	0·046
C(15)	0·556 (1)	0·6174 (5)	0·0764 (2)	0·038
C(16)	0·418 (1)	0·6654 (6)	0·0846 (3)	0·046
C(17)	0·315 (1)	0·6972 (5)	0·0539 (3)	0·051
C(18)	0·355 (1)	0·6808 (7)	0·0147 (3)	0·068
C(19)	0·489 (2)	0·6329 (8)	0·0059 (3)	0·080
C(20)	0·589 (1)	0·6000 (6)	0·0360 (3)	0·065
C(21)	0·832 (1)	0·5109 (5)	0·0948 (2)	0·036
C(22)	0·819 (1)	0·4294 (5)	0·0967 (2)	0·043
C(23)	0·930 (1)	0·3814 (6)	0·0743 (3)	0·053
C(24)	1·056 (1)	0·4136 (6)	0·0507 (3)	0·053
C(25)	1·075 (1)	0·4939 (6)	0·0494 (3)	0·051
C(26)	0·966 (1)	0·5423 (5)	0·0709 (2)	0·042

Fig. 1. Molecular structure with the atoms represented by their 50% ellipsoids for thermal motion.

an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined from a least-squares fit of 15 reflections ($2\theta > 36°$) centered on the diffractometer, using graphite-crystal-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å).

One independent octant of data out to $2\theta = 44°$ was collected using the ω–2θ scan technique and 1549 reflections were considered observed [$I > 3\sigma(I)$]. An absorption correction was not applied ($\mu = 6.43$ cm^{-1}).

The structure was solved via application of the direct methods program MULTAN (Germain, Main & Woolfson, 1971), which afforded the positions of the Mn and P atoms. A difference Fourier map based on these placements revealed the coordinates of the remaining non-H atoms. After several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms, the H atoms of the methyl group were located from a difference Fourier map. The remaining H atoms were placed in calculated positions (C–H = 1.00 Å) and allowed to ride on the appropriate C atom for four more cycles of refinement. This resulted in final R values of $R = \sum [|F_o| - |F_c|]/\sum |F_o| = 0.042$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.056$. All least-squares refinements were carried out using the SHELX program package (Sheldrick, 1976). No corrections were made for extinction. Atomic scattering factors for Mn, P, O and C were taken from Cromer & Waber (1965), whereas those for H were taken from International Tables for X-ray Crystallography (1962). Corrections for the real and imaginary components of anomalous dispersion were carried out for Mn only, the values of Cromer & Liberman (1970) being used. Final atomic parameters are given for all non-H atoms in Table 1,* while a view of the molecular structure, showing the atom-numbering scheme is presented in Fig. 1.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36603 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Other crystallographic programs used on a Univac 1100/60 computer included ORTEP (Johnson, 1965) and BPL (W. E. Hunter, best least-squares planes).

Discussion. As is evidenced by Fig. 1, the methyl is oriented almost trans to the P atom. This suggests that the bulkiness of the phosphine has more than counteracted the natural electronic tendency for the methyl to place itself in a more electrophilic position: trans to a carbonyl. The same effect, but not as pronounced, was seen in [$(\eta^5$-$C_5H_4CH_3)Mn(CO)_2L$] for $L = [S(CH_3)_2(C_5H_5)]^+$, dibenzocycloheptenylketene and anthronylketene.

The bond distances are within previously observed ranges. The Mn–C(π) distances, with a range of 2·132 (9)–2·162 (8) Å, show perhaps surprisingly no trend that might be caused by either the bulkiness of the phosphine ligand or the inductive effects of the methyl group. The ring is planar to 0·01 Å, and the methyl C atom is 0·03 Å out of the plane (exo to the Mn atom). The equivalence of M–C(π) distances is seen in most other related compounds, with ranges of 2·14 (2)– 2·16 (2), 2·17 (2)–2·19 (2), 2·159 (8)–2·18 (1) and 2·07 (2)–2·11 (1) Å having been observed in [(η^5-$C_5H_5)Mn(CO)_2L$] for $L = $ methylmethoxycarbene (Fontana, Schubert & Fischer, 1978), tricarbonyl[1-3-η-(3-oxo-1-phenylpropane)]iron (Andrianov, Struchkov, Kolobova, Antonova & Obezyuk, 1976), bicyclo[2.2.1]hepta-2,5-diene (Granoff & Jacobson, 1968) and sulfur dioxide (Barbeau & Dubey, 1973), respectively. There have been several examples with extremely bulky ligands present: [{(η^5-$C_5H_5)Mn(CO)_2$}(diphenyldiarsane)]_2 (Huttner, Schmid & Lorenz, 1976), [(η^5-$C_5H_5)Mn(CO)_2${Co_2(CO)_2$-($\eta^5$-$C_5H_5)_2PCH_2C_6H_5$}] (De, Seyerl & Huttner, 1979), and [(η^5-$C_5H_4CH_3)Mn(CO)_2$(dibenzocycloheptenylketene)], where ranges of 2·10 (1)–2·15 (1), 2·12 (2)– 2·21 (1) and 2·109 (7)–2·190 (8) Å were observed, respectively.

The M–(CO) distances of 1·76 (1) and 1·77 (1) Å compare closely to those observed in the aforementioned analogues and also to the 1·74 (1) and 1·77 (1) Å seen in [(η^5-$C_5H_5)Mn(CO)_2P(C_6H_5)_3$] (Barbeau, Dichmann & Ricard, 1973).

The Mn–P distance, 2·232 (2) Å, compares closely with the 2·236 (3) Å seen in the (η^5-C_5H_5) analogue and the 2·246 (3) Å in [(η^5-$C_5H_5)Mn(CO)_2${Co_2(CO)_2$-($\eta^5$-$C_5H_5)_2PCH_2C_6H_5$}].

The angles within the Mn(CO)$_2L$ 'tripod' are normal: 91·3 (3), 94·1 (3) and 91·5 (4)° for P–Mn–C(1), P–Mn–C(2) and C(1)–Mn–C(2), respectively.

No significant intermolecular interactions were observed.

References

ADAMS, R. D. & CHODOSH, D. F. (1978). *J. Am. Chem. Soc.* **100**, 812–817.

ANDRIANOV, V. G., STRUCHKOV, YU. T., KOLOBOVA, N. E. ANTONOVA, A. B. & OBEZYUK, N. S. (1976). *J. Organomet. Chem.* **122**, C33–C36.

BARBEAU, C., DICHMANN, K. S. & RICARD, L. (1973). *Can. J. Chem.* **51**, 3027–3031.

BARBEAU, C. & DUBEY, R. J. (1973). *Can. J. Chem.* **51**, 3684–3689.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DE, R. L., SEYERL, J. V. & HUTTNER, G. (1979). *J. Organomet. Chem.* **178**, 319–324.

FONTANA, S., SCHUBERT, U. & FISCHER, E. O. (1978). *J. Organomet. Chem.* **146**, 39–44.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GRANOFF, B. & JACOBSON, R. A. (1968). *Inorg. Chem.* **7**, 2328–2333.

HERRMANN, W. A., PLANK, J., ZIEGLER, M. L. & WEIDENHAMMER, K. (1979). *J. Am. Chem. Soc.* **101**, 3133–3135.

HUTTNER, G., SCHMID, H. G. & LORENZ, H. (1976). *Chem. Ber.* **109**, 3741–3748.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SHAKIR, R. & ATWOOD, J. L. (1981). *Acta Cryst.* B**37**, 1656–1659.

SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

catena-Acetato(di-2-pyridylamine)-μ-perchlorato-copper(II) Monohydrate

By NOEL RAY, SURESH TYAGI AND BRIAN HATHAWAY*

Chemistry Department, University College, Cork, Ireland

Abstract. $[Cu(C_{10}H_9N_3)(C_2H_3O_2)(ClO_4)].H_2O$, $C_{12}H_{14}ClCuN_3O_7$, $M_r = 411.3$, monoclinic, $P2_1/c$, $Z = 4$, $a = 7.309$ (3), $b = 16.363$ (4), $c = 13.646$ (4) Å, $\beta = 103.085$ (3)°, $U = 1589.65$ Å^3, $D_m = 1.75$ (2), $D_c = 1.72$ Mg m^{-3}. $R = 0.0517$ for 2518 observed reflections. The local molecular $CuN_2O_2O_2'$ chromophore involves an elongated rhombic octahedral structure with near symmetrically bonded di-2-pyridylamine (dpyam) and acetate groups bonding in the plane and bridging semi-coordinate perchlorate groups completing the six coordination.

Introduction. In a programme to examine the bonding role of the acetate ligand (Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980) in ternary complexes of the Cu^{II} ion with bis-nitrogen chelate ligands, dark-green crystals of the title complex (1) were obtained. As the

IR spectrum (Hathaway & Underhill, 1961) suggested that the perchlorate group was bonded to Cu^{II}, but failed to establish the bonding of the acetate and water molecules, the structure of (1) was determined. (1) was prepared by mixing 0.01 mol of $[Cu(CH_3CO_2)_2]H_2O$ and 0.01 mol of $[Cu(H_2O)_6](ClO_4)_2$, both in 60 ml of (1:2) aqueous ethanol, and adding 0.022 mol of dpyam in 60 ml of (1:2) aqueous ethanol. The solution was boiled, filtered, and allowed to stand and the dark-green crystals were deposited overnight.

Found: C, 35.00; H, 3.70; Cl, 8.63; Cu, 14.41; N, 9.91%; calculated for $C_{12}H_{14}ClCuN_3O_7$: C, 35.04; H, 3.41; Cl, 8.63; Cu, 15.46; N, 10.22%. Intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reflections with $3.0 < \theta < 32°$ in one quadrant were examined in the θ–2θ scan mode with constant scan speed of $0.05°$ s^{-1}, and a variable scan width of $(0.7 + 0.1 \tan \theta)°$. 2518 unique reflections were retained $[I >$

---

* To whom correspondence should be addressed.