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Dicarbonyl(η^2-*cis*-cyclooctene)(η^5-methylcyclopentadienyl)manganese(I)

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The intramolecular distances in the title compound, $[Mn(C_8H_{14})(C_6H_7)(CO)_2]$, are typical for this type of complex, with Mn—C$_{Cp}$ in the range 2.128 (3)–2.166 (3) Å, Mn—C$_{double\ bond}$ 2.203 (3) and 2.211 (3) Å, and Mn—C$_{CO}$ 1.768 (3) and 1.778 (3) Å. The methyl substituent of the cyclopentadienyl ring eclipses a carbonyl ligand.

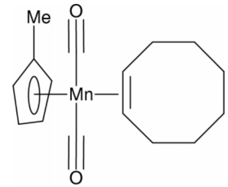
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.132
Data-to-parameter ratio = 24.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The molecule of the title compound, (I), is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The *cis*-cyclooctene ring coordinates Mn in (I) in an η^2 mode *via* the ring double bond, with Mn—C distances of 2.203 (3) and 2.211 (3) Å. Similar distances of 2.193 (2) and 2.202 (2) Å are found in CpMn(CO)$_2$(η^2-cyclooctatetraene), (II) [Cambridge Structural Database (Allen, 2002) refcode CPTOMN10; Benson *et al.*, 1981]. Non-equivalent Mn—C bond distances, *e.g.* 1.976 (6) and 2.242 (6) Å in (MeCp)Mn(CO)$_2$(η^2-anthronylketene), (III) (MCANKM; Hermann *et al.*, 1979), arise from the presence of a bulky substituent on one of the ring C atoms.



(I)

The C═C bond length in the cyclooctene ligand of (I) [1.378 (3) Å] is shorter and the C—Mn—C angle [36.37 (9)°] is smaller than in other Mn complexes with η^2 ligands, *e.g.* 1.448 (8) Å and 39.5 (2)° in (III), 1.404 (4) Å and 38.0 (1)° in CpMn(CO)$_2$(η^2-norbornadiene) (COCPMN01; Vella *et al.*, 1981), 1.398 (2) Å and 37.1 (1)° in (II), but comparable with 1.390 (12) Å and 37.5 (3)° in CpMn(CO)$_2$(η^2-methylvinylketone) (CMNMVK; le Borgne *et al.*, 1975). This is indicative of a decrease in the strength of binding of the η^2 ligand through the series from (III) to (I). For the conformation of the cyclooctene ligand with major (C4/C5) occupancy (see later), the C—C bond lengths are in the range 1.495 (4)–1.546 (4) Å, with an average value of 1.518 (6) Å. For the conformation of lower occupancy (C4*A*/C5*A*), the range is extended to 1.56 (3) Å and the average increased to 1.531 (12) Å.

The Mn—C$_{Cp}$ bond lengths in (I), in the range 2.128 (3)–2.166 (3) Å, with an average value of 2.147 (3) Å, are typical of complexes of this type. The comparatively narrow range for (I) contrasts, however, with that observed [2.117 (6)–

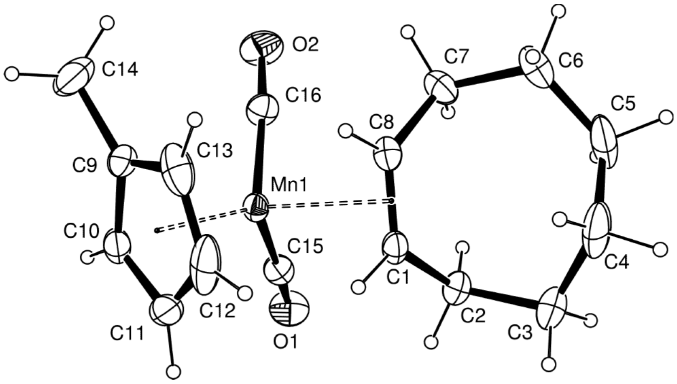


Figure 1
The molecule of (I). Non-H atoms are drawn as 20% probability displacement ellipsoids and H atoms as small circles of arbitrary radius. Dashed lines represent the bonding between Mn1 and the π-systems of the cyclopentadienyl and cyclooctene ligands. The lower occupancy disordered atoms have been omitted.

2.201 (5) Å in one molecule in the bimolecular asymmetric unit and 2.119 (6)–2.209 (5) Å in the other] in (MeCp)Mn(CO)$_2$(pyridine) (VOXCOA; Crocock *et al.*, 1992), where significant ring tilt is attributed to either or both of steric interaction between the methyl group and the pyridine ligand and electronic effects arising from increased electron density on the Mn atom. The C—C bond lengths within the cyclopentadienyl ring, in the range 1.384 (4)–1.391 (4) Å, with an average of 1.388 (4) Å, are again typical of a system of this type. In (I), the methyl substituent of the cyclopentadienyl ring eclipses a carbonyl ligand. In complexes of the type (MeCp)Mn(CO)$_2$*L*, this is the preferred arrangement when *L* is a good π-acceptor, as distinct from the methyl group *cis* to *L* when *L* is a poor π-acceptor. The displacement of the methyl C atom (C14) from the least-squares cyclopentadienyl plane [0.110 (6) Å on the opposite side of the plane from Mn] in (I) is as expected from the report of Chinn & Hall (1983).

With respect to the carbonyl groups of (I), the Mn—C$_{\rm CO}$ bond lengths and Mn—C—O angles (Table 1) are as expected. The coordination of the Mn atom is most readily summarized if the disposition of the cyclopentadienyl ring and the cyclooctene ligands around the Mn atom is expressed in terms of the cyclopentadienyl ring centroid (*Cg*) and the mid-point of the cyclooctene C1═C8 bond (*Mb*), respectively. Thereby the four-coordination of Mn (Table 1) takes the form of a trigonal pyramid with the cyclopentadienyl ring, due to its bulk and orientation, at the apex. The nominal tetrahedral coordination of Mn is further distorted by variation in the angles at Mn, involving pairs of basal atoms due to the bulk of the cyclooctene ligand. These types of distortion are well established, *e.g.* in the case of (II).

Experimental

Compound (I) was synthesized by the photochemical substitution of a carbonyl ligand of (η^5-$C_5H_4CH_3$)Mn(CO)$_3$ in tetrahydrofuran and subsequent reaction of the THF adduct with *cis*-cyclooctene. Crystals suitable for analysis were obtained by recrystallization from methanol.

Crystal data

[Mn(C_8H_{14})(C_6H_7)(CO)$_2$]
M_r = 300.27
Monoclinic, $P2_1/n$
a = 6.198 (5) Å
b = 19.476 (13) Å
c = 12.273 (10) Å
β = 94.21 (6)°
V = 1478 (2) Å^3
Z = 4

D_x = 1.350 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
θ = 10.5–11.6°
μ = 0.89 mm^{-1}
T = 298 (2) K
Block, yellow
0.60 × 0.58 × 0.34 mm

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: none
4669 measured reflections
4318 independent reflections
3177 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016

$\theta_{\rm max}$ = 30.0°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 27$
$l = -17 \rightarrow 17$
2 standard reflections
every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.133
S = 1.05
4318 reflections
180 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.2713P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.38 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.53 e Å^{-3}

Table 1
Selected bond lengths and angles (Å,°) for (I)..

Mn1—*Cg*[a]	1.793 (3)	Mn1—C15	1.778 (3)
Mn1—*Mb*[a]	2.097 (3)	Mn1—C16	1.768 (3)
Mn1—C1	2.203 (2)	Mn1—C8	2.211 (3)
C15—O1	1.150 (3)	C16—O2	1.158 (3)
C1—C8	1.378 (3)		
Cg—Mn—*Mb*	123.74 (8)	*Mb*—Mn—C15	96.42 (12)
Cg—Mn—C15	122.07 (10)	*Mb*—Mn—C16	95.14 (12
Cg—Mn—C16	120.79 (10)	C15—Mn—C16	90.86 (13)
Mn—C15—O1	177.2 (2)	Mn—C16—O2	176.1 (3)
C1—Mn—C8	36.37 (9)		

Note: (*a*) *Cg* and *Mb* are, respectively, the centroid of the cyclopentadienyl ring and the mid-point of the C1═C8 bond.

Anisotropic displacement parameters were refined for all non-H atoms except the lower occupancy [0.313 (8)] C4*A* and C5*A*, which were refined in an isotropic manner, with their $U_{\rm iso}$ constrained to be equal to the $U_{\rm eq}$ of the disorder major component alternatives C4 and C5. H atoms were placed in calculated positions and refined with a riding model, with C—H = 0.96, 0.97 and 0.93 Å, and $U_{\rm iso}$ = 1.5, 1.2 and 1.2 times $U_{\rm eq}$ of the parent C atom, for methyl, CH$_2$ and H atoms of sp^2 C atoms, respectively. The displacement ellipsoids associated with atoms C12 and C13 of the cyclopentadienyl ring are indicative of a degree of disorder in this part of the model also but, in the absence of any indication as to how these atoms might be split, no attempt was made to model this in detail.

Data collection: *Nicolet P*3 *Software* (Nicolet, 1980); cell refinement: *Nicolet P*3 *Software*; data reduction: *RDNIC* (Howie, 1980); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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