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Tricarbonyl(η^5-formylcyclopentadienyl)manganese(I) and tricarbonyl(η^5-formylcyclopentadienyl)rhenium(I) containing short π(CO)···π(CO) and π(CO)···π interactions

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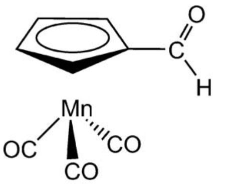
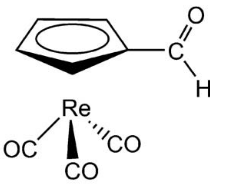
The structures of tricarbonyl(formylcyclopentadienyl)manganese(I), [Mn(C_6H_5O)(CO)$_3$], (I), and tricarbonyl(formylcyclopentadienyl)rhenium(I), [Re(C_6H_5O)(CO)$_3$], (II), were determined at 100 K. Compounds (I) and (II) both possess a carbonyl group in a *trans* position relative to the substituted C atom of the cyclopentadienyl ring, while the other two carbonyl groups are in almost eclipsed positions relative to their attached C atoms. Analysis of the intermolecular contacts reveals that the molecules in both compounds form stacks due to short attractive π(CO)···π(CO) and π(CO)···π interactions, along the crystallographic *c* axis for (I) and along the [201] direction for (II). Symmetry-related stacks are bound to each other by weak intermolecular C—H···O hydrogen bonds, leading to the formation of the three-dimensional network.

Comment

The field of organometallic chemistry dealing with derivatives of cymantrene and cyrhetrene is of considerable interest for materials chemistry. One of the eye-catching areas of organometallic chemistry is the introduction of organometallic labels for the immunoassay of proteins, for instance, bovin serum albumin, enkephalin and others (Hromadová *et al.*, 2003, 2006; Peindy N'Dongo *et al.*, 2008; Jaouen, 2008), due to the electron-withdrawing and IR-active nature of the carbonyl groups. Other examples include the synthesis of cymantrene-containing organometallic polymers (Setayesh & Bunz, 1996), incorporation into biological molecules to modify or provide new biological activities (for example, 17α-ethynylestradiol derivatives; Ferber *et al.*, 2006), synthesis of planar chiral derivatives for further use in the asymmetric synthesis (Loim *et al.*, 1994; Lyubimov *et al.*, 2006), and chemistry of fuels (Geivanidis *et al.*, 2003; Marsh *et al.*, 2005). Because of the significant interest in this area, we have focused our studies on structural investigations of the title compounds, (I) and (II) (Fig. 1), which are usually used as starting reagents for the above-mentioned applications. In spite of the great variety of monosubstituted (η^5-C_5H_4X)M(CO)$_3$ (where M is Mn or Re and X is any atom) complexes reported in the literature, the structures of such fundamental compounds as formylcymantrene and formylcyrhetrene have not yet been described. In this work, we report the first structural study of formyl derivatives of (η^5-C_5H_4CHO)M(CO)$_3$ [with M = Mn, (I), and M = Re, (II)].


(I)


(II)

The mean values of the geometric parameters for (I) and (II) are in accordance with those previously reported (Table 1) for 89 monosubstituted cymantrenes and 30 (η^5-C_5H_4X)Re(CO)$_3$ compounds, which were retrieved from the Cambridge Structural Database using *ConQuest* (CSD, Version 1.12; Allen, 2002), as well as the unsubstituted compounds (η^5-C_5H_5)M(CO)$_3$ (M = Mn or Re; Cowie *et al.*, 1990). Monosubstituted complexes (η^5-C_5H_4X)M(CO)$_3$ (where X is any atom and M = Mn or Re) were considered, with the following search criteria: (*a*) three-dimensional coordinates and R < 0.10; (*b*) no errors; (*c*) no crystallographic disorder; and (*d*) no polymer structures.

The formyl substituent of each of (I) and (II) is almost coplanar with the Cp ring [7.5 (3) and 8.6 (6)° for (I) and (II), respectively], thus allowing conjugation of the π–π electron

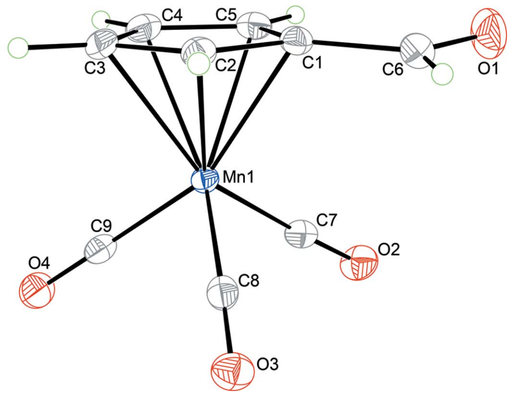


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The molecule of (II) is essentially identical.

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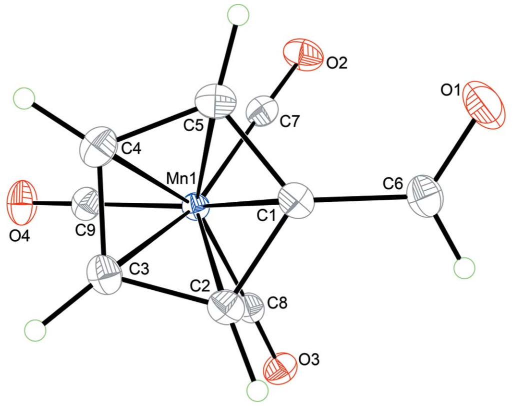

Figure 2
A view of the conformation of (I).

systems of the C═O bond and of the aromatic cyclopentadienyl ring. The existence of CO—Cp conjugation is supported by the C1—C6 bond lengths of 1.4631 (19) and 1.466 (5) Å for (I) and (II), respectively, which are between the typical values for single- and double-bond distances (1.54 and 1.40 Å, respectively). The C═O bond lengths are 1.2142 (17) and 1.208 (4) Å, and the C1—C6—O1 angles are 124.09 (12) and 124.0 (3)° for (I) and (II), respectively; these angles are significantly smaller than those reported for formylferrocene (142.5°; Lousada *et al.*, 2008). The (O)C—*M*—C(O) angle is in accord with a tendency for decreasing pyramidality of the *M*(CO)$_3$ fragment with increasing π-donor capacity of the cyclic polyene (Fitzpatrick, Le Page, Sedman & Butler, 1981): (η^6-C_6H_6)Cr(CO)$_3$ = 88.22 (8)° (Rees & Coppens, 1973), (η^5-C_5H_5)Re(CO)$_3$ = 90.0 (2)° (Fitzpatrick, Le Page & Butler, 1981), (η^5-C_5H_5)Mn(CO)$_3$ = 92.02 (5) (Cowie *et al.*, 1990), (η^4-C_4H_4)Fe(CO)$_3$ = 95.6 (Hall *et al.*, 1975) and (η^4-C_4Ph_4)Fe(CO)$_3$ = 97.03 (3)° (Dodge & Schomaker, 1965). The *M*—C—O angles do not differ significantly from 180°.

The coordination to the (η^5-C_5H_4X) ring of the *M*(CO)$_3$ (*M* = Mn or Re) fragment, which possesses C_{3v} molecular symmetry, lowers the molecular symmetry to C_1 (Fig. 2). Compounds (I) and (II) show the same mutual dispositions of the carbonyl groups and (η^5-C_5H_4X) rings: the carbonyl C9≡O4 group for (I) and (II) is in a *transoid* position relative to substituted atom C1 of the (η^5-C_5H_4CHO) ring, while the C7≡O2 and C8≡O3 carbonyl groups are in almost eclipsed postions relative to atoms C5 and C2, respectively (Fig. 2).

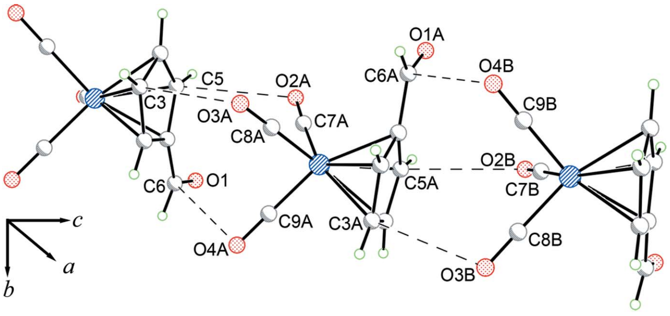

Figure 3
A view of a stack for (I). Dashed lines indicate the π(CO)···π(CO) and π(CO)···π interactions. [Symmetry codes: (A) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (B) $x, y, z + 1$.]

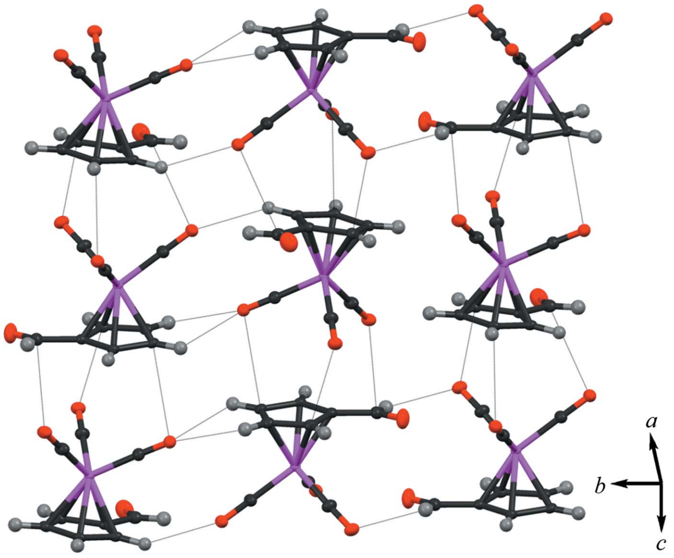

Figure 4
A view of the crystal packing for (I). Fine lines indicate the π(CO)···π(CO), π(CO)···π and C—H···O interactions.

According to a systematic CSD analysis of interactions between ketonic (C_2—C═O) carbonyl groups, three types of interaction motifs were identified, *viz.* a predominant slightly sheared antiparallel motif, a perpendicular motif and a highly sheared parallel motif (Allen *et al.*, 1998). For transition metal carbonyls, a higher percentage of the perpendicular motif has been reported (Allen *et al.*, 2006).

The molecules of both (I) and (II) form stacks due to the presence of short intermolecular interactions involving CO groups. These stacks are observed along the crystallographic *c* axis for (I) and the [201] direction for (II), and they involve short perpendicular π(CO)···π(CO) and π(CO)···π interactions (Fig. 3 and Table 2). Comparison of the parameters obtained for (I) and (II) with distances and angles reported for similar interactions in other transition metal carbonyls (2.95–3.60 Å and 80–135°) indicate that the π(CO)···π(CO) interactions are relatively strong in (I) (Allen *et al.*, 2006). Intermolecular π(CO)···π(CO) interactions are not rare; sheared antiparallel and perpendicular motifs were found for 14 of the 89 hits for monosubstituted cymantrenes and for three of the 30 hits for (η^5-C_5H_4X)Re(CO)$_3$ compounds in the above CSD search.

The C7≡O2 and C8≡O3 carbonyl groups are involved in π(CO)···π interactions between C atoms of the Cp ring and carbonyl groups of neighbouring molecules (see Table 2). Such weak noncovalent inter- and intramolecular interactions of the type CO···π(aromatic system) have been experimentally deduced in a noticeable number of compounds (Bitterwolf *et al.*, 1997). They are an important factor for crystal packing and hence for molecular physical properties and chemical reactivities (Boldyrev, 1996; Desiraju, 1997; Tanaka & Toda, 2000; Yang *et al.*, 2005). The distances between the carbonyl O atoms and the C atoms of the aromatic systems are in the range 3.10–3.55 Å (Bitterwolf *et al.*, 1997). Also, it is assumed that π(CO)$\cdots\pi$ interactions are attractive and can probably be described as charge-transfer interactions, with energies between -3.5 and -1.8 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) (Bitterwolf *et al.*, 1997).

Symmetry-related stacks of molecules in both (I) and (II) are bound to each other by weak intermolecular C—H$\cdots$O hydrogen bonds (Table 3). These two supramolecular motifs generate a three-dimensional network (Fig. 4). The sets of C—H$\cdots$O hydrogen bonds are similar between (I) and (II). The mean van der Waals radii used to identify intermolecular interactions and contacts were taken as C = 1.70 Å and O = 1.52 Å (Bondi, 1964).

Experimental

Compounds (I) and (II) were prepared according to a standard literature procedure (Kolobova *et al.*, 1981). Crystals of (I) and (II) were obtained by slow evaporation of hexane solutions at room temperature.

Compound (I)

Crystal data

[Mn(C_6H_5O)($CO)_3$]
M_r = 232.07
Monoclinic, $P2_1/c$
a = 7.9011 (10) Å
b = 11.4482 (15) Å
c = 12.4541 (12) Å
β = 129.220 (6)°
V = 872.74 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.49 mm^{-1}
T = 100 K
0.51 × 0.50 × 0.40 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.517, $T_{\max}$ = 0.587
12874 measured reflections
2115 independent reflections
2023 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.053
S = 1.00
2115 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\min}$ = -0.34 e Å^{-3}

Compound (II)

Crystal data

[Re(C_6H_5O)($CO)_3$]
M_r = 363.33
Monoclinic, $P2_1/c$
a = 8.0768 (6) Å
b = 11.5037 (8) Å
c = 12.3457 (7) Å
β = 127.860 (3)°
V = 905.63 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.40 mm^{-1}
T = 100 K
0.21 × 0.20 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.165, $T_{\max}$ = 0.414
9983 measured reflections
2189 independent reflections
2044 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.034

Table 1
Mean values of the geometric parameters (Å, °) for (I) and (II), and from the CSD.

Cp′ is the C_5H_4X ring, M is Mn or Re and Cg1 is the centroid of the C_5H_4CHO ring.

Distance/angle	(I)	CSD (M = Mn)	(II)	CSD (M = Re)
C—C for Cp′	1.4255 (18)	1.415	1.426 (6)	1.419
M—C for Cp′	2.1436 (12)	2.138	2.303 (3)	2.299
M–C(O)	1.8033 (12)	1.790	1.920 (3)	1.902
C—O	1.1452 (16)	1.148	1.159 (4)	1.156
$M1\cdots Cg1$	1.7678 (6)	1.771	1.957 (1)	1.957
(O)C—M—C(O)	92.31 (5)	91.94	90.1 (1)	89.8
M—C—O	178.34 (11)	178.2	177.1 (3)	177.1

Table 2
Intermolecular π(CO)$\cdots\pi$(CO) and π(CO)$\cdots\pi$ interactions (Å, °) in (I) and (II).

Compound (I)	C$\cdots$C	C—O$\cdots$C
π(CO)$\cdots\pi$(CO) C9$A^{\rm i}$—O4$A^{\rm i}\cdots$C6	3.212 (2)	101.71 (7)
π(CO)$\cdots\pi$ C7$A^{\rm i}$—O2$A^{\rm i}\cdots$C5	3.114 (2)	103.67 (6)
π(CO)$\cdots\pi$ C8$A^{\rm i}$—O3$A^{\rm i}\cdots$C3	3.221 (3)	102.26 (6)
Compound (II)		
π(CO)$\cdots\pi$(CO) C9$A^{\rm ii}$—O4$A^{\rm ii}\cdots$C6	3.242 (6)	99.78 (7)
π(CO)$\cdots\pi$ C7$A^{\rm ii}$—O2$A^{\rm ii}\cdots$C5	3.052 (4)	104.97 (7)
π(CO)$\cdots\pi$ C8$A^{\rm ii}$—O3$A^{\rm ii}\cdots$C3	3.263 (5)	98.63 (7)

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$.

Table 3
Intermolecular C—H$\cdots$O hydrogen bonds (Å, °) in (I) and (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
Compound (I)				
C2—H2$\cdots$O2$A^{\rm iii}$	1.00	2.59	3.305 (3)	128
C2—H2$\cdots$O4$A^{\rm iv}$	1.00	2.58	3.415 (2)	141
C3—H3$\cdots$O1$A^{\rm v}$	1.00	2.48	3.355 (3)	146
C3—H3$\cdots$O3$A^{\rm vi}$	1.00	2.69	3.215 (2)	113
C4—H4$\cdots$O3$A^{\rm vi}$	1.00	2.71	3.224 (2)	113
C6—H6$\cdots$O2$A^{\rm vii}$	1.00	2.65	3.366 (3)	133
Compound (II)				
C2—H2$\cdots$O2$A^{\rm iii}$	1.00	2.52	3.279 (6)	133
C2—H2$\cdots$O4$A^{\rm viii}$	1.00	2.63	3.402 (4)	134
C3—H3$\cdots$O1$A^{\rm ix}$	1.00	2.48	3.330 (5)	143
C3—H3$\cdots$O3A^{x}	1.00	2.71	3.189 (4)	110
C4—H4$\cdots$O3A^{x}	1.00	2.70	3.187 (4)	110
C6—H6$\cdots$O2$A^{\rm xi}$	1.00	2.60	3.329 (4)	134

Symmetry codes: (iii) $x - 1, y, z$; (iv) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (vi) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + 1, -y, -z + 1$; (viii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (x) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (xi) $-x, -y + 1, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.042
S = 1.01
2189 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.90 e Å^{-3}
$\Delta\rho_{\min}$ = -1.53 e Å^{-3}

Despite crystallizing in the same space group with similar unit-cell dimensions, the closely analogous complexes (I) and (II) are not isomorphous. Although there are many structural similarities between them, molecules of (I) and (II) differ significantly in their orientation within the unit cell. All H atoms were positioned geometrically, with C—H = 1.00 Å, and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$.

For both compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3162). Services for accessing these data are described at the back of the journal.

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