

Dicarbonyl(η^5 -methylcyclopentadienyl)- { η^2 -[tricarbonyl(η^6 -styrene)chromium(0)]}- manganese(I)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ (C–C) = 0.006 Å
R factor = 0.044
wR factor = 0.099
Data-to-parameter ratio = 13.4

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

The title compound, [CrMn(C₆H₇)(C₈H₈)(CO)₅], is a hetero-bimetallic complex in which the styrene ligand achieves a μ_2 -bridging function while providing η^6 and η^2 coordination of, respectively, the Cr and Mn atoms. However, the bond lengths and angles and, in particular, the coordination of the individual metal atoms is otherwise much as would be expected.

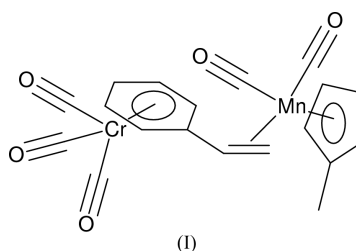
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Comment

The title compound, (I), is a further example of a compound containing η^2 -alkene coordination of Mn, such as those described by Crocock *et al.* (2003, and references therein). The case described here is, however, rather different, because the alkene involved is the double bond of the vinyl group of a styrene molecule, which is itself a component of tricarbonyl(η^6 -styrene)chromium(0), (II) [Khand *et al.*, 1978; Cambridge Structural Database (Version 5.24; Allen, 2002) refcode KAPDAU (Brown & Frazier, 1989)] and the formation of a hetero-bimetallic species is the inevitable consequence.



The molecule of (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. Both of these employ the centroids of the aromatic rings, unlabelled in Fig. 1 but designated in Table 1 as Cg1 and Cg2 for the cyclopentadienyl and benzene ring, respectively, and likewise Mb for the midpoint of the C18=C19 bond, in order to simplify the presentation. Both metal atoms are then readily seen to be effectively four-coordinate, with their coordination in the form of a trigonal pyramid with the aryl ring in the apical position in each case. The M–C_{aryl} distances are in the respective ranges 2.121 (4)–2.199 (4) Å for M = Mn and cyclopentadienyl, and 2.204 (4)–2.269 (4) Å for Cr and benzene. These ranges differ, as do the displacements of M from the ring planes, but now in the opposite sense, *i.e.* Mn1–Cg1 = 1.790 (2) Å and Cr1–Cg2 = 1.7295 (19) Å. The M–C_{CO} distances show the opposite trend to that of the displacements from the aryl rings, being 1.770 (5) and 1.785 (5) Å for Mn and in the range 1.823 (4)–1.841 (4) Å for Cr. The description of the coordination of Cr

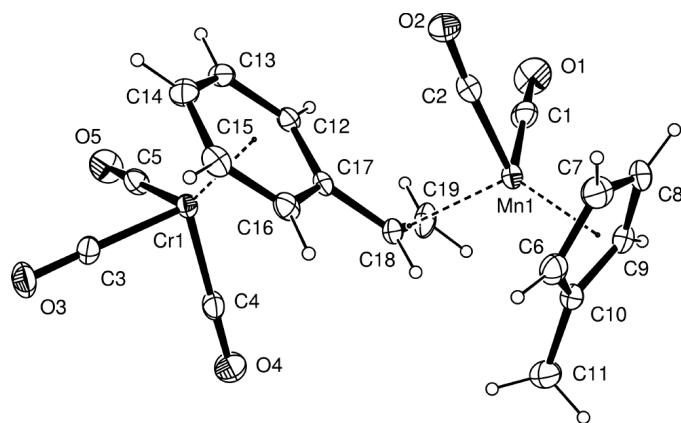


Figure 1
The molecule of (I), showing the labelling scheme. Non-H atoms are drawn as 20% probability displacement ellipsoids and H atoms as small circles of arbitrary radii. For clarity, dashed lines have been used to represent bonds between the metal atoms and the double bond and the aryl rings.

and Mn as trigonal pyramidal is justified by the fact that all of the $Cg-M-X$ angles, where X is a basal ligand atom, e.g. C1, C2 or Mb for $M = Mn$, or C3, C4 or C5 for $M = Cr$, are greater than 120° , while all angles of the form $X-M-X'$ are less than 100° . The wider range of $X-M-X'$ angles at Mn, viz. $87.83(19)$ – $99.35(19)^\circ$ as against $88.26(18)$ – $90.79(19)^\circ$ at Cr, is characteristic of the presence of the η^2 double-bond ligand in the coordination of Mn. Of interest in the coordination of the metal atoms are the positions of the aryl rings in terms of their rotation in their own planes about the vectors joining their centroids to the metal atoms. For the cyclopentadienyl ring associated with Mn1, the torsion angles of the form $C10-Cg1-Mn1-X$ ($X = Mb, C1$ or $C2$; Table 1) show that the methyl group in (I) is *cis* to the $C18=C19$ bond. In dicarbonyl(η^2 -*cis*-cyclooctene)(η^5 -methylcyclopentadienyl)-manganese(I) (Crockett *et al.*, 2003), however, the torsion angles corresponding by type to those given in Table 1 are $124.02(19)$, $2.5(2)$ and $-110.7(2)^\circ$, thus showing that in this case the methyl group is *cis* to one of the carbonyl groups. For the benzene ring associated with Cr1, the torsion angles of the form $X-Cr1-Cg2-Y$ ($X = C3, C4$ or $C5$; $Y = C15, C17$ or $C13$) reveal that the three atoms of the benzene ring almost eclipse the $Cr-C_{CO}$ bonds, but to a lesser extent than was found in KAPDAU, where the equivalent torsion angles were of the order of $8.7(2)^\circ$.

Experimental

Compound (I) was synthesized by the photochemical substitution of a carbonyl ligand of $(\eta^5-C_5H_4CH_3)Mn(CO)_3$ in tetrahydrofuran (THF) and subsequent reaction of the THF adduct with (II). In the solid state, the compound is relatively stable on exposure to air and light, but it decomposes rapidly in solution. For this reason, crystals suitable for analysis were grown from a diethyl ether/hexane solution at 298 K in the dark over a period of 3–5 d.

Crystal data

$[CrMn(C_6H_7)(C_8H_8)(CO)_5]$
 $M_r = 430.25$
 Monoclinic, $P2_1/c$
 $a = 7.281(4) \text{ \AA}$
 $b = 23.637(14) \text{ \AA}$
 $c = 10.502(5) \text{ \AA}$
 $\beta = 99.19(4)^\circ$
 $V = 1784.2(17) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.602 \text{ Mg m}^{-3}$
 $D_m = 1.6(1) \text{ Mg m}^{-3}$

D_m measured by density-gradient method
 Mo $K\alpha$ radiation
 Cell parameters from 14 reflections
 $\theta = 7.5$ – 10.5°
 $\mu = 1.34 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Block, red-brown
 $0.50 \times 0.50 \times 0.20 \text{ mm}$

Data collection

Nicolet P3 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.561$, $T_{\max} = 0.764$
 3422 measured reflections
 3167 independent reflections
 2247 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.075$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 28$
 $l = -12 \rightarrow 12$
 2 standard reflections every 50 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.099$
 $S = 1.01$
 3167 reflections
 236 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths and angles ($^\circ$) for (I).

Mn1–Cg1	1.790 (2)	Cr1–Cg2	1.7295 (19)
Mn1–C1	1.770 (5)	Cr1–C3	1.823 (4)
Mn1–C2	1.785 (5)	Cr1–C4	1.827 (5)
Mn1–Mb	2.043 (4)	Cr1–C5	1.841 (4)
Mn1–C18	2.163 (4)		
Mn1–C19	2.155 (4)		
C1–O1	1.160 (5)	C3–O3	1.154 (4)
C2–O2	1.142 (5)	C4–O4	1.158 (5)
C18–C19	1.397 (6)	C5–O5	1.147 (4)
Cg1–Mn1–C1	121.24 (16)	Cg2–Cr1–C3	127.63 (15)
Cg1–Mn1–C2	122.23 (16)	Cg2–Cr1–C4	125.51 (15)
Cg1–Mn1–Mb	124.11 (15)	Cg2–Cr1–C5	124.67 (15)
C1–Mn1–C2	87.83 (19)	C3–Cr1–C4	88.26 (18)
C1–Mn1–Mb	93.30 (19)	C3–Cr1–C5	88.11 (18)
C2–Mn1–Mb	99.35 (19)	C4–Cr1–C5	90.79 (19)
Mn1–C1–O1	178.9 (5)	Cr1–C3–O3	179.3 (4)
Mn1–C2–O2	176.1 (3)	Cr1–C4–O4	178.4 (4)
C18–Mn1–C19	33.75 (16)	Cr1–C5–O5	178.54 (4)
C10–Cg1–Mn1–Mb	17.0 (3)	C3–Cr1–Cg2–C15	18.0 (3)
C10–Cg1–Mn1–C1	–102.5 (3)	C4–Cr1–Cg2–C17	18.0 (3)
C10–Cg1–Mn1–C2	148.3 (3)	C5–Cr1–Cg2–C13	17.0 (3)

Note: Cg1, Cg2 and Mb are, respectively, the centroids of the cyclopentadienyl and benzene rings and the mid-point of the $C18=C19$ bond.

H atoms were placed in calculated positions and refined with a riding model, with $C-H = 0.96$ and 0.93 \AA , and $U_{\text{iso}} = 1.5$ and 1.2 times U_{eq} of the parent C atom, for methyl and all other H atoms, respectively. The rotational orientation of the rigid body methyl group was also refined.

Data collection: P3 Software (Nicolet, 1980); cell refinement: P3 Software; data reduction: RDNIC (Howie, 1980); program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2003).

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