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Crystal and Molecular Structure of μ-(η^5:η^1-Cyclopentadienyl)-[(η^5-cyclopentadienyl)carbonylmolybdenum][tetracarbonylmanganese]

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The structure of the title compound, $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$, has been determined by a three-dimensional X-ray diffraction study. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.056$ (1) Å, $b = 9.322$ (3) Å, $c = 11.927$ (2) Å, $\alpha = 98.44$ (3)°, $\beta = 82.97$ (3)°, and $\gamma = 123.39$ (2)°. The density of 1.89 g cm^{-3} calculated on the basis of two molecules in the unit cell agrees with the measured density of 1.88 g cm^{-3}. Diffraction data to $2\theta_{max} = 65°$ (Mo Kα radiation) were collected on a Picker four-circle automated diffractometer. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a conventional discrepancy index $R = 0.045$ on the basis of 4900 unique reflections. The C_5H_4 ring has C–C bond distances of average value 1.424 Å and appears to be a cyclopentadienyl ring rather than a dienecarbenoid ring. One carbon atom in the C_5H_4 ring is rather close to the Mn atom, Mn–C = 2.005 (4) Å and Mo–Mn = 2.9605 (8) Å. The angle Mo–Mn–C involving these three atoms is 49°. Apart from this cis compression, the disposition of the four CO groups around Mn is approximately octahedral; i.e., angles involving C_{CO} and Mn are approximately 90°. The configuration around Mo is very similar to that in $(\eta^5\text{-}C_5H_5)_2MoH_2$.

Introduction

The title compound was obtained in 50% yield from the reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ with $CH_3Mn(CO)_5$ as described in the previous paper.[1b] Spectroscopic data indicated that one of the η^5-C_5H_5 rings of the starting material had been converted to an η^5-C_5H_4–X group representing an unusual ring substitution product. In this work we report an X-ray crystallographic study which verifies the structure of the new complex.[2]

Experimental Section

Collection and Reduction of X-ray Data. The compound was recrystallized from 1:1 diethyl ether/*n*-hexane at −30 °C. The crystals which formed were air- and X-ray-stable dark red parallelepipeds elongated along the *a* axis. Preliminary oscillation and Weissenberg (0*kl*, 1*kl*, *hk*0, and *hk*1) photographs (Cu Kα radiation) showed no symmetry, indicating the triclinic space groups $P1$ or $P\bar{1}$.[3] The latter was ultimately chosen on the basis of solution and refinement of the structure (see below). The crystal chosen for intensity measurements was a fragment 0.3 × 0.2 × 0.2 mm along *a*, *b*, and *c*, respectively. This crystal was sealed under nitrogen in a capillary; the rotation axis of the goniometer was coincident with the *a* axis.

Lattice parameters were determined from a least-squares fit[4] of 40 reflections (35° < 2θ < 55°, Mo Kα radiation) which were centered on a Picker four-circle automated diffractometer (FACS-1). The refined unit cell parameters and specifics related to collection of data are given in Table I. The intensities of three standard reflections were measured every 50 reflections. No significant fluctuation in any of these was observed.

In all, the intensities of 5354 reflections were measured, of which 4900 were considered to be observed; i.e., the net integrated intensity $I \geq 1.95\sigma_B$, where σ_B is the standard deviation due to counting statistics of the total background. Data reduction also utilized the equations

$$I = CT - (t_c/t_b)(B_1 + B_2)/2$$

$$\sigma_I = [CT + \tfrac{1}{4}(t_c/t_b)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$$

where I is the net integrated intensity, CT is the total scan count, B_1 and B_2 are the background counts, each taken for time t_b (s) on the low-2θ and high-2θ sides of the peak, and t_c (s) is the scan time.[5] The intensities were corrected for Lorentz and polarization effects, but not for absorption. The calculated absorption coefficient μ for the crystal is 17.5 cm^{-1} (Mo Kα radiation). The ratio of the maximum to the minimum transmission factors is 1.1:1.

Solution and Refiement of the Structure. The structure was solved by use of standard heavy-atom techniques. Scattering factors used for C, O, Mo, and Mn are those of Cromer and Waber.[6] The atomic scattering factor for H is that of Stewart, Davidson, and Simpson.[7] The real part, $\Delta f'$, of the anomalous dispersion correction for Mo and Mn was taken from the tabulation of Cromer.[8]

Table I. Experimental Data for Single-Crystal Study of $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$

A. Unit Cell Parameters at 21 ± 2 °C

$a = 8.056$ (1) Å	space group: $P\bar{1}$ (C_i^1, No. 2)
$b = 9.322$ (3) Å	$Z = 2$
$c = 11.927$ (2) Å	mol wt 420.12
$\alpha = 98.44$ (3)°	ρ(calcd) = 1.89 g cm^{-3}
$\beta = 82.97$ (3)°	ρ(obsd) = 1.88 g cm^{-3} (flotation in $CCl_4/CHBr_2CHBr_2$ mixture)
$\gamma = 123.39$ (2)°	
$V = 738.82$ Å^3	

B. Measurement of Intensity Data

radiation: Mo Kα (graphite monochromated)
crystal-to-detector distance: 235 mm
counter aperture width: 13 mm × 13 mm
incident beam collimator diameter: 1 mm
takeoff angle: 2.5 °
scan technique: θ–2θ
scan rate: 10/min (calibrated brass attenuators used when counting rate exceeded 10 000 counts/s)
scan range: 2.0°
background: stationary crystal, stationary counter at each end of the scan; 10 s
range of data: 0° < 2θ(Mo Kα) < 65 °

Least-squares refinement[9] with anisotropic thermal parameters for Mo and Mn and isotropic parameters for the other atoms converged at $R = 0.141$.[10] Further refinement, using only reflections having 2θ < 45° and allowing all atoms to vibrate anisotropically, led to a conventional R value of 0.052. All nine hydrogen atoms were located on a difference Fourier map based on reflections having 2θ < 45°.

Secondary extinction corrections were applied to all data,[11] followed by further refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms and of the positional parameters of all hydrogen atoms. Isotropic thermal parameters for hydrogen atoms were fixed at 5.0 Å^2. The final value of R was 0.045. A final difference map contained no peaks greater than 0.38 e Å^{-3}; the largest peaks were near the Mo and Mn atoms. Final positional parameters are listed in Table II and thermal parameters are in Table III. The final values of the observed and calculated structure factors are shown in Table IV (supplementary material). Selected bond lengths and angles are given in Tables V and VI, respectively. Several least-squares planes and interplanar angles are listed in Table VII.

Results and Discussion

Overall Structure. The crystal consists of discrete molecular units of the title compound separated by normal van der Waals contacts. The overall geometry of an individual molecule and numbering of atoms are shown in Figure 1. A second projection of the molecule is given in Figure 2. The structure is composed of a bis(cyclopentadienylcarbonyl)molybdenum

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Table II. Final Positional Parameters[a] for $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$

atom	x	y	z
Mo	0.65996 (4)	0.25825 (3)	0.74077 (2)
Mn	0.76717 (8)	0.01165 (6)	0.77603 (4)
O(1)	0.9074 (6)	−0.1473 (5)	0.9014 (3)
O(2)	0.7894 (6)	−0.1537 (6)	0.5471 (3)
O(3)	1.1870 (5)	0.3028 (5)	0.7384 (5)
O(4)	0.3435 (5)	−0.2848 (4)	0.8025 (4)
O(5)	0.2277 (4)	−0.0418 (4)	0.6785 (3)
C(1)	0.8502 (6)	−0.0861 (5)	0.8531 (3)
C(2)	0.7815 (6)	−0.0883 (5)	0.6360 (3)
C(3)	1.0247 (6)	0.1934 (5)	0.7532 (4)
C(4)	0.5052 (6)	−0.1689 (5)	0.7927 (4)
C(5)	0.3843 (5)	0.0653 (5)	0.7018 (3)
C(6)	0.8056 (8)	0.5111 (5)	0.6596 (4)
C(7)	0.9410 (6)	0.4555 (5)	0.6408 (4)
C(8)	0.8540 (6)	0.3007 (5)	0.5696 (3)
C(9)	0.6634 (6)	0.2572 (5)	0.5463 (3)
C(10)	0.6330 (7)	0.3887 (6)	0.6006 (3)
C(11)	0.8378 (6)	0.3504 (5)	0.8974 (3)
C(12)	0.7230 (7)	0.4257 (5)	0.9124 (3)
C(13)	0.5207 (7)	0.2927 (6)	0.9171 (3)
C(14)	0.5137 (6)	0.1342 (5)	0.9047 (3)
C(15)	0.7106 (5)	0.1648 (4)	0.8873 (3)
H(1)	0.8071 (74)	0.5957 (64)	0.7220 (44)
H(2)	1.0463 (81)	0.5016 (67)	0.6756 (46)
H(3)	0.9377 (73)	0.2323 (64)	0.5305 (45)
H(4)	0.5545 (71)	0.1550 (62)	0.4880 (45)
H(5)	0.5091 (74)	0.4158 (67)	0.6129 (44)
H(6)	0.9839 (76)	0.4042 (66)	0.8851 (44)
H(7)	0.7919 (75)	0.5437 (67)	0.9136 (45)
H(8)	0.4153 (74)	0.3155 (65)	0.9346 (47)
H(9)	0.4069 (75)	0.0407 (66)	0.9148 (43)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit of the preceding number.

unit bonded to a *cis*-$Mn(CO)_4$ group through the molybdenum atom and through a carbon atom of one of the cyclopentadienyl rings.

The closest intermolecular contact in the crystal is 2.52 Å between H(7) and O(1)′; the sum of the van der Waals radii for H and O is 2.6 Å. The closest intermolecular contact for nonhydrogen atoms is 3.12 Å between O(1) and O(1)′; the sum of the van der Waals radii for two O atoms is 2.80 Å.

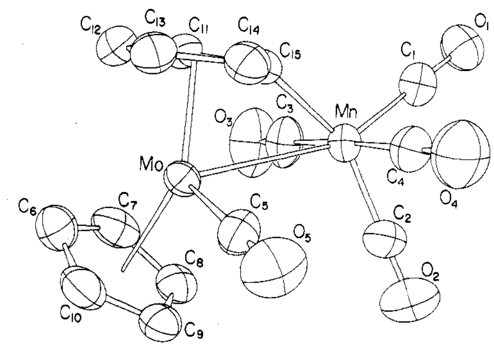


Figure 1. Side view of the structure of the title compound. Thermal ellipsoids are at 50% probability level.

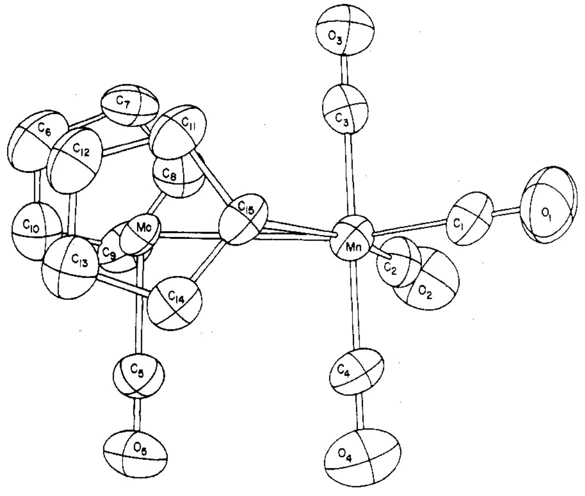


Figure 2. Top view of the structure of the title compound. Thermal ellipsoids are at 50% probability level.

The compound is quite clearly a monomer. A stereoview of the unit cell is given in Figure 3 (supplementary material).

Structural Parameters in the Cyclopentadienyl Rings. In the $\eta^5\text{-}C_5H_5$ ring the C–C bond distances vary from 1.403 (6) to 1.429 (8) Å (see Table V) with an average value of 1.416 Å. This is similar to average values reported for the C–C distances in the $\eta^5\text{-}C_5H_5$ rings in $(\eta^5\text{-}C_5H_5)_2MoH_2$, 1.43 Å,[12a] $(\eta^5\text{-}C_5H_5)(CO)_3MoMn(CO)_5$, 1.42 Å,[12b] and $[(\eta^5\text{-}C_5H_5)Mo\text{-}$

Table III. Final Thermal Parameters $(A^2)^{a,b}$ for $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4))(Mn(CO)_4$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	3.210 (12)	2.466 (8)	2.38 (1)	2.72 (4)	0.478 (12)	1.03 (2)
Mn	3.585 (22)	2.704 (14)	3.39 (2)	3.13 (7)	−0.494 (27)	0.759 (4)
O(1)	8.86 (24)	5.42 (12)	5.89 (1)	9.36 (8)	−3.36 (30)	1.5 (2)
O(2)	7.87 (24)	7.56 (16)	4.22 (10)	8.61 (8)	−1.2 (3)	−2.1 (2)
O(3)	3.77 (10)	4.75 (12)	12.2 (3)	3.48 (5)	0.54 (30)	2.6 (2)
O(4)	5.29 (12)	4.15 (12)	8.22 (12)	0.99 (5)	−1.4 (3)	1.2 (2)
O(5)	3.70 (9)	5.57 (12)	6.05 (15)	3.23 (5)	−0.82 (28)	0.2 (2)
C(1)	5.22 (12)	3.17 (10)	3.9 (1)	4.60 (6)	−0.85 (32)	0.3 (2)
C(2)	4.69 (16)	4.49 (12)	3.8 (1)	5.24 (6)	−0.98 (24)	0.58 (18)
C(3)	3.81 (14)	3.89 (12)	6.22 (15)	4.64 (6)	−0.51 (27)	0.73 (24)
C(4)	4.42 (16)	3.00 (10)	4.7 (1)	2.46 (5)	−1.2 (2)	0.40 (18)
C(5)	3.71 (10)	3.67 (10)	3.7 (1)	3.64 (5)	0.89 (24)	0.95 (18)
C(6)	6.97 (26)	3.10 (10)	3.9 (1)	4.39 (7)	0.82 (27)	2.37 (18)
C(7)	3.52 (14)	4.44 (14)	4.3 (1)	1.8 (3)	0.095 (21)	4.05 (21)
C(8)	4.77 (18)	4.85 (14)	3.2 (1)	5.14 (6)	2.22 (28)	3.3 (18)
C(9)	5.09 (15)	3.86 (12)	2.8 (1)	3.72 (6)	−0.032 (22)	1.8 (18)
C(10)	6.17 (22)	5.13 (16)	3.8 (1)	7.24 (8)	0.60 (30)	3.1 (21)
C(11)	5.13 (18)	3.31 (10)	3.0 (1)	3.77 (5)	−1.7 (2)	−0.37 (15)
C(12)	7.29 (24)	3.67 (12)	3.1 (1)	6.28 (7)	−0.32 (24)	−0.44 (18)
C(13)	6.19 (22)	5.18 (14)	3.2 (1)	7.49 (8)	2.1 (2)	1.3 (3)
C(14)	4.59 (16)	3.89 (12)	2.8 (1)	3.70 (6)	1.7 (2)	1.8 (2)
C(15)	4.48 (16)	3.14 (8)	2.6 (2)	3.83 (5)	−0.51 (18)	1.0 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.
[b] The hydrogen atoms were assigned isotropic thermal parameters with $B = 5.0\ A^2$, which were not allowed to refine.

Table V. Interatomic Distances (Å)[a] in $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$

H(1)-C(6)	0.99 (6)	C(11)-C(12)	1.421 (9)
H(2)-C(7)	0.84 (6)	C(12)-C(13)	1.404 (6)
H(3)-C(8)	1.17 (7)	C(13)-C(14)	1.432 (8)
H(4)-C(9)	1.09 (4)	C(14)-C(15)	1.442 (7)
H(5)-C(10)	1.14 (7)	C(15)-C(11)	1.440 (5)
H(6)-C(11)	0.99 (6)	Mo-C(6)	2.284 (4)
H(7)-C(12)	0.91 (5)	Mo-C(7)	2.308 (4)
H(8)-C(13)	0.97 (7)	Mo-C(8)	2.355 (4)
H(9)-C(14)	0.83 (4)	Mo-C(9)	2.314 (4)
C(6)-C(7)	1.427 (9)	Mo-C(10)	2.302 (6)
C(7)-C(8)	1.403 (6)	Mo-C(11)	2.260 (4)
C(8)-C(9)	1.409 (7)	Mo-C(12)	2.309 (4)
C(9)-C(10)	1.429 (8)	Mo-C(13)	2.325 (4)
C(10)-C(6)	1.410 (6)	Mo-C(14)	2.269 (3)
Mn-C(15)	2.005 (4)	Mo-C(15)	2.234 (4)
Mo-Mn	2.9605 (8)	C(1)-O(1)	1.149 (8)
Mn-C(1)	1.786 (6)	C(2)-O(2)	1.156 (6)
Mn-C(2)	1.813 (4)	C(3)-O(3)	1.144 (4)
Mn-C(3)	1.838 (3)	C(4)-O(4)	1.153 (4)
Mn-C(4)	1.847 (3)	C(5)-O(5)	1.133 (4)
Mo-C(5)	1.998 (3)		

[a] Numbers in parentheses are the estimated standard deviations in the bond lengths and refer to the last significant digit of the preceding number.

Table VI. Bond Angles (deg)[a] in $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$

C(6)-C(7)-C(8)	108.4 (4)	C(1)-Mn-Mo	156.2 (1)
C(7)-C(8)-C(9)	107.5 (5)	C(2)-Mn-Mo	105.7 (2)
C(8)-C(9)-C(10)	109.0 (4)	C(3)-Mn-Mo	84.6 (2)
C(9)-C(10)-C(6)	106.8 (5)	C(4)-Mn-Mo	93.6 (2)
C(10)-C(6)-C(7)	108.1 (1)	C(5)-Mo-Mn	91.4 (2)
C(11)-C(12)-C(13)	108.4 (4)	C(1)-Mn-C(2)	97.6 (2)
C(12)-C(13)-C(14)	106.3 (5)	C(1)-Mn-C(3)	90.8 (2)
C(13)-C(14)-C(15)	111.4 (3)	C(1)-Mn-C(4)	91.8 (2)
C(14)-C(15)-C(11)	103.0 (4)	C(2)-Mn-C(3)	89.6 (2)
C(15)-C(11)-C(12)	110.7 (4)	C(2)-Mn-C(4)	88.9 (2)
		C(3)-Mn-C(4)	177.2 (2)
Mn-C(1)-O(1)	178.6 (4)	C(1)-Mn-C(15)	107.9 (2)
Mn-C(2)-O(2)	179.2 (4)	C(2)-Mn-C(15)	154.5 (2)
Mn-C(3)-O(3)	177.8 (5)	C(3)-Mn-C(15)	90.2 (2)
Mn-C(4)-O(4)	178.1 (5)	C(4)-Mn-C(15)	90.2 (2)
Mo-C(5)-O(5)	178.5 (5)		
		Mo-Mn-C(15)	49.0 (2)

[a] Numbers in parentheses are the estimated standard deviations of the bond angles and refer to the last significant digit of the preceding number.

$(CO)_3]_2$, 1.42 Å.[12c] The bond angles in the η^5-C_5H_5 ring average to 108.0° and fall within abut 1° of this value. The five carbon atoms in the η^5-C_5H_5 ring are coplanar within 0.01 Å; see Table VII.

For the bridging ($\eta^5{:}\eta^1$-C_5H_4) ring a distinct departure from fivefold symmetry in the C–C distances and internal angles is observed as well as a slight departure from coplanarity of all of the atoms. A pattern of one short, two medium, and two long bonds is seen; the data are given in Table V and illustrated schematically in Figure 4. Data for corresponding ($\eta^5{:}\eta^1$-C_5H_4) groups in three other complexes whose structures have been reported in full[13] since the completion of the present work are also shown in Figure 4. Although individual differences are around one or two esd's and thus not significant in and of themselves, as a group the data follow a consistent pattern worth noting: there are one short, two average, and two longer than average bonds in all derivatives but the ferrocenyldigold cation. The average C–C distances in these derivatives are as follows (Å): title compound, 1.424; Ti_2 derivative, 1.42;[13b] Nb_2 derivative, 1.418;[13a] $FeAu_2$ derivative, 1.45.[13c]

Table VII. Results of Least-Squares Planes Calculations

A. Distances of Atoms from Least-Squares Planes (Å)[a]

atom	plane 1	plane 2	plane 3	plane 4	plane 5
Mo	−1.940	1.974	0.000*	−1.955	−0.067*
Mn	−1.180	3.370	0.000*	−1.018	0.028*
C(1)	−0.090	4.548	−0.194	0.157	−0.072*
O(1)	0.598	5.285	−0.343	0.901	−0.162
C(2)	−2.737	2.384	0.095	−2.515	0.036*
O(2)	−3.725	1.767	0.166	−3.465	0.052
C(3)	−1.392	2.259	−1.822	−1.236	−1.805
O(3)	−1.526	1.576	−2.959	−1.371	−2.948
C(4)	−1.046	4.416	1.841	−0.881	1.874
O(4)	−0.965	5.075	2.987	−0.796	3.024
C(5)	−2.469	2.515	1.921	−2.480	1.816
O(5)	−2.786	2.800	3.006	−2.796	2.878
C(6)	−3.020	−0.001*	−1.403	−3.121	−1.560
C(7)	−3.064	0.006*	−2.017	−3.085	−2.154
C(8)	−3.842	−0.010*	−1.219	−3.810	−1.394
C(9)	−4.252	0.009*	−0.096	−4.266	−0.314
C(10)	−3.762	−0.005*	−0.211	−3.861	−0.419
C(11)	0.000*	3.096	−1.111	0.000*	−1.044
C(12)	0.000*	2.959	−0.656	−0.084	−0.612
C(13)	0.000*	3.655	0.748	−0.086	0.788
C(14)	0.000*	4.223	1.144	0.000*	1.205
C(15)	−0.056	3.847	0.000*	0.000*	0.075*

B. Interplanar Angles: Planes 1 and 4, 176.41°; Planes 1 and 2, 34.3°

[a] Atoms used to define the least-squares planes are indicated by asterisks. Plane 1 contains the four C atoms of the $\eta^5{:}\eta^1$-C_5H_4 ring which are not bonded to Mn. Plane 2 contains the five C atoms of the η^5-C_5H_5 ring bonded to Mo. Plane 3 contains the ring C atom omitted from plane 1 and Mo and Mn. Plane 4 contains the three C atoms of C_5H_4 nearest Mn. Plane 5 gives some indication of the deviation from idealized octahedral symmetry about the manganese atom.

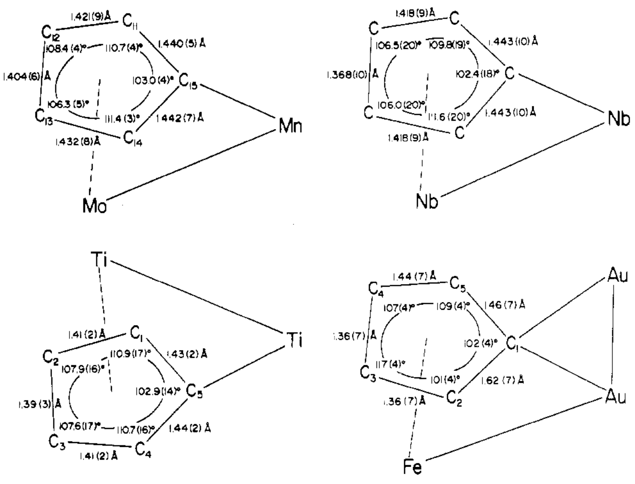


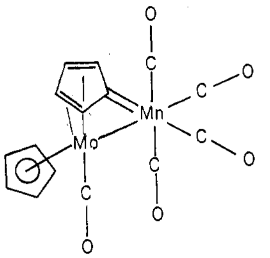
Figure 4. Comparison of parameters for the bridging $\eta^5{:}\eta^1$-C_5H_4 group in the title compound and related derivatives: $[(\eta^5\text{-}C_5H_5)(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))(H)Nb]_2$,[13a] $(\eta^5\text{-}C_5H_5)(C_4H_8O)Ti(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Ti(\eta^5\text{-}C_5H_5)$,[13b] and $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Au_2(PPh_3)_2][BF_4]$.[13c] The data for the niobocene dimer are the average of the parameters for six bridging units in the three crystallographically unique molecules observed in the unit cell.[13a]

The distortion in the C–C bond lengths of the bridging $\eta^5{:}\eta^1$-C_5H_4 groups is accompanied by distortions in the internal bond angles. In the title compound, the angle whose vertex is at the carbon bonded to manganese, namely, C(14)–C(15)–C(11), is 103.0(4)°. This is significantly smaller than the other internal angles; the average value for all five angles is 108.0°. The smallest angle is found to be adjacent to the two that are larger than average. This pattern is repeated in the other bridging $\eta^5{:}\eta^1$-C_5H_4 rings depicted in Figure 4. These distortions are also accompanied by a small departure from coplanarity of the carbon atom η^1-bonded to the metal. In the title compound this carbon atom, C(15), is displaced toward the metal atoms by 0.06 Å out of plane 1 (the plane defined by the other four carbon atoms in the bridging ring (see Table VII)). The dihedral angle between plane 1 and plane 4 (the plane defined by carbon atoms C(11), C(15), and C(14) (see Table VII)) is 3.6°. A similar distortion of the carbon atom η^1-bonded to niobium in the niobocene dimers was also observed; a maximum of 3.7° is reported for the analogous dihedral angle.[13a] By contrast, the unique carbon atom of the bridging $\eta^5{:}\eta^1$-C_5H_4 ring in the ferrocenyl digold complex is displaced 0.28 Å out of the plane *away* from the iron atom.[13c] The presence of the third metal atom in this structure is no doubt responsible for this difference.

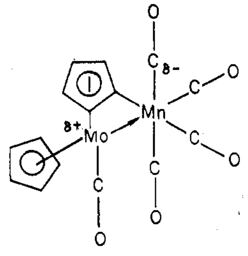
Structural Features around the Mo Atom. The geometry around the Mo atom in the title compound is similar to that in the parent compound, $(\eta^5\text{-}C_5H_5)_2MoH_2$.[12a] Around the molybdenum atom the CO group, the Mn atom of the $Mn(CO)_4$ group, and the normals to each of the two η^5 rings from the Mo atom are in a pseudotetrahedral configuration. The two rings deviate from being parallel by 34.3°. In the parent compound, this angle is 34 (1)°,[12a] while in the niobocene dimer it is 39.6°.[13a] In the ferrocenyldigold complex, by contrast, this angle is much smaller, only 16°.[13c]

The two rings in the title compound are observed in an eclipsed configuration, readily seen in Figure 2. Owing to the known low barrier for rotation in metallocene derivatives[14] no great significance should be attributed to this feature. The CO group on Mo, C(5)O(5), is located 18.4° away from an eclipsed configuration with C(4)O(4), the nearest CO group on Mn. The $Mn(CO)_4$ group is twisted slightly away from C(5)O(5), as indicated by the angles C(5)–Mo–Mn = 91.4 (2)°, C(4)–Mn–Mo = 93.6 (2)°, and C(3)–Mn–Mo = 84.6 (2)° (see Table VI).

Two possible modes of bonding based on two contrasting types of metallocene derivatives of molybdenum should be considered for the title compound, namely, structures A and B In structure A, the bonding around molybdenum would be like that in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.[12c] This would require the bridging unit to be a cyclopentadienylidene ring containing two short and three long bonds. This would also require a distinctly longer separation of the carbenoid carbon to the molybdenum atom as compared to the separation of the other carbon atoms in the bridging ring to the molybdenum atom. None of these features are observed in the crystal structure. The parameters within the bridging ring have been discussed above; these do not depart significantly from those of a η^5 ring, and not in any case toward those expected for a cyclopentadienylidene ring. Furthermore, the Mo–C(15) distance of 2.234 (4) Å is the shortest of all the molybdenum atom to ring-carbon atom distances in the molecule (see Table V). The average Mo–C distance to the bridging ring is 2.279 Å while that to the η^5-C_5H_5 ring is 2.313 Å.



A



B

Thus η^5 bonding of Mo to the bridging ring is indicated as represented by structure B. In this, the manganese atom is attached to the bridging ring by a σ bond Mn–C(15). The features of the bonding around manganese as well as the shortness of the Mn–C(15) bond are discussed further below. The electronic requirements around the manganese atom require an electron-pair donation from molybdenum, as indicated in structure B. The presence of this semipolar bond would account for the special solvent interactions that have been observed in the solution ^{1}H NMR spectra of this and the related W–Mn and Re–Mn derivatives.[1b] In other metal carbonyls the presence of atoms of inequivalent charge distribution has given rise to what Cotton has called the "semibridging" CO group.[15] Since C(5)O(5) is the only CO group bonded to Mo, this would be a candidate for semibridging to manganese to relieve charge density built up through the donor–acceptor metal–metal bond. The parameters for this CO group however clearly indicate it is not semibridging. First we have a separation of 3.6 Å between Mn and C(5) and also too little bend in the Mo–C(5)–O(5) angle of 178.5 (5)° to indicate any such interaction. This apparent exception can be understood on the grounds that there are factors mitigating the charge buildup of the semipolar bond. On the molybdenum atom, the cyclopentadienyl groups are on balance more electron donating than withdrawing, and on the manganese atom, the carbonyl groups are able to disperse negative charge.[15]

Structural Features around the Mn Atom. The four CO groups around the Mn atom define an approximate octahedral environment. The atoms Mo, C(15), C(1), O(1), C(2), and O(2) are essentially coplanar (see plane 5, Table VII). Carbonyl groups C(3)O(3) and C(4)O(4) are nearly perpendicular to this plane with deviations of 0.57 and 1.31°, respectively, from the perpendicular to this plane. Atoms C(15) and Mo, however, show a considerable departure from octahedral geometry with the Mo–Mn–C(15) angle at 49°. We may thus assume that the Mn–C(15) and Mn–Mo bonds are considerably "bent" and this is reflected in their atomic separations: Mn–C(15) = 2.005 (4) Å and Mo–Mn = 2.960 (5) Å. The first is significantly shorter than 2.19 Å, the value expected for an Mn–C_{sp^2} σ bond.[16] The shortness of the Mn–C(15) bond however is not enough to support a cyclopentadienylidene structure (A). The value expected for a manganese to carbon multiple bond is 1.96 Å.[17] Considering the "bent" nature of the Mn–C(15) interaction, an even shorter separation should be expected if this model was to be accepted. The Mo–Mn separation is also somewhat shortened over what might have been expected. This value is to be compared to 3.083 (5) Å in $(\eta^5\text{-}C_5H_5)(CO)_3MoMn(CO)_5$[12b] or the value of 3.073 Å calculated from the mean of the Mo–Mo separation of 3.222 (5) Å in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$[12c] and the Mn–Mn separation of 2.923 (3) Å in $Mn_2(CO)_{10}$.[18] The shortening of the Mo–Mn and Mn–C(15) bonds over the expected values is typical of systems with bridging constraints.[19] The facile disruption of this system by hydrogen gas[1b] would tend to support the idea that the $\overline{\text{Mo–Mn–C(15)}}$ system is somewhat strained. On the other hand, reaction of these bridged derivatives with CO or phosphine ligands[1b] does not lead to ring-enlarged acyl products which might have been produced by migration of the $\eta^5{:}\eta^1$-C_5H_4 group to coordinated CO.[1b] In this connection it may be worth noting that the bridging cyclopentadienyl group is a member of a class of σ–π-bonded hydrocarbons,[20] and other aspects of its chemistry might be interesting to investigate on this basis.

We conclude by pointing to a considerable trans influence[21] exerted by the Mo and C(15) atoms on the Mn–C distances of the CO groups attached in approximately trans positions: Mn–C(1) and Mn–C(2) are significantly shorter than Mn–C(3) and Mn–C(4) (see Table V), indicating considerable back-acceptance of charge by the C(1)O(1) and C(2)O(2) groups.

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Registry No. $(\eta^5\text{-}C_5H_5)(CO)\overline{Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn}(CO)_4$, 71411-08-0.

Supplementary Material Available: Figure 3 (unit cell of the title compound) and Table IV (structure factor amplitudes) (25 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) The present work has been taken in part from the dissertation of R. J. Hoxmeier, UCLA, 1972. This is part 15 of a series of papers on the metalation reactions. (b) Part 14: R. J. Hoxmeier, J. R. Blickensderfer, and H. D. Kaesz, *Inorg. Chem.*, preceding paper in this issue.

(2) A preliminary communication of this work was presented by R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Am. Chem. Soc.*, **93**, 536 (1971).

(3) "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

(4) The programs used in this work included the following: locally written data reduction programs (based on the program of E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971)); LATPAR, least-squares refinement of lattice parameters (R. Sparks); UCLAFOUR, Fourier program (P. Gantzel and H. Hope); UCLALS4, full-matrix least-squares refinement program ACA No. 317 (modified) (P. Gantzel, R. Sparks, R. Long, and K. N. Trueblood); SECEXT, secondary extinction (Christensen and H. Hope); ORTEP, figure plotting (C. K. Johnson); MGTL, least-squares planes and dihedral angles (P. Gantzel and K. N. Trueblood); ORFFE, distance, angle, and error computations (W. R. Busing, K. O. Martin, and H. A. Levy).

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(10) The index, R, is defined as $\sum||F_o| - |F_c||\sum|F_o|$.

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Sulfur Ligand–Transition Metal Complexes. 4.[1] Dinuclear Mercapto Complexes of Iron(II) with the Tridentate Ligand Bis[2-(diphenylphosphino)ethyl]phenylphosphine: Synthesis and X-ray Crystal Structure

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Received March 9, 1979

Stable trimercapto dinuclear complexes of iron(II) are formed with the tris(tertiary phosphine) bis[2-(diphenylphosphino)ethyl]phenylphosphine (ppp). The X-ray structure determination of the compound $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4{\cdot}CO(CH_3)_2$ (triclinic, $P1$, $a = 13.989$ (5) Å, $b = 13.270$ (4) Å, $c = 12.020$ (6) Å, $\alpha = 109.23$ (4)°, $\beta = 120.93$ (3)°, $\gamma = 63.93$ (2)°) has shown that the coordination geometry is confacial bioctahedral. Each metal atom is bonded to the three phosphorus atoms of one ppp molecule and to the three sulfur atoms of the bridging SH groups.

Introduction

In previous papers[1,2] we have shown that some poly(tertiary phosphines) such as tris[2-(diphenylphosphino)ethyl]amine, np_3, tris[2-(diphenylphosphino)ethyl]phosphine, pp_3, and bis[2-(diphenylphosphino)ethyl]phenylphosphine, ppp, form stable mercapto complexes of 3d metals. In this manner many complexes of cobalt and nickel were added to the scanty list of the thiol–metal complexes so far obtained.

In this paper we wish to report two iron–mercapto complexes obtained by reaction of a mixture of the ppp ligand and $[Fe(H_2O)_6]X_2$ salts ($X = BF_4$, ClO_4) with hydrogen sulfide. The compounds so obtained have the formula $[Fe_2(\mu\text{-}SH)_3(ppp)_2]X$. They have been characterized by means of the usual chemical and physical measurements. The structure of the perchlorate has been elucidated by means of a complete X-ray diffraction analysis.

Experimental Section

All solvents were of reagent quality. The ligand ppp was purchased from Strem Chemicals Inc., Danvers, Mass., and was used without further purification. All the reactions were carried out under nitrogen by using deoxygenated solvents.

Preparation of the Complexes $[Fe_2(\mu\text{-}SH)_3(ppp)_2]X$ ($X = ClO_4$, BF_4). The ligand ppp (1 mmol) in 20 mL of acetone was added to a solution of $[Fe(H_2O)_6](ClO_4)_2$ (or $[Fe(H_2O)_6](BF_4)_2$) (1 mmol) in 15 mL of ethanol. When hydrogen sulfide was bubbled into the solution, at room temperature, a deep red color appeared. After bubbling of H_2S for a further 3 min, the resulting solution was concentrated in a stream of nitrogen. The deep red crystals that formed were filtered off and washed with ethanol and then with petroleum ether. Anal. Calcd for $[Fe_2(\mu\text{-}SH)_3(ppp)_2](ClO_4){\cdot}(CH_3)_2CO$, $C_{71}H_{75}ClFe_2O_5P_6S_3$: C, 59.32; H, 5.26; Fe, 7.77; S, 6.69. Found: C, 59.85; H, 5.51; Fe, 7.55; S, 6.36. Calcd for $[Fe_2(\mu\text{-}SH)_3(ppp)_2](BF_4){\cdot}(CH_3)_2CO$, $C_{71}H_{75}BF_4Fe_2OP_6S_3$: C, 59.84; H, 5.30; Fe, 7.84; P, 13.04; S, 6.75. Found: C, 60.44; H, 5.97; Fe, 7.45; P, 12.77; S, 6.53.

Physical Measurements. The physical measurements were executed by the previously described methods.[3]

X-ray Data Collection and Reduction. Crystals of the compound belong to the $P1$ space group of the triclinic system. Lattice constants, obtained by least-squares refinement of the setting angles of 24 reflections are $a = 13.989$ (5) Å, $b = 13.270$ (4) Å, $c = 12.020$ (6) Å, $\alpha = 109.23$ (4)°, $\beta = 120.93$ (3)°, and $\gamma = 63.93$ (2)°. The value

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