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Transition-Metal Methylene Complexes. 19.[1] Studies on Metal–Metal Bonds. 7.[2] Crystal and Molecular Structure of μ-Methylene-bis[dicarbonyl(η^5-methylcyclopentadienyl)manganese](*Mn–Mn*)

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A full report on the crystal structure of μ-methylene-bis[dicarbonyl(η^5-methylcyclopentadienyl)manganese](*Mn–Mn*), the first μ-methylene (metal–metal) dimer ever synthesized, is presented. The compound crystallizes in the triclinic system with $a = 6.834$ (6) Å, $b = 9.602$ (2) Å, $c = 13.605$ (5) Å, $\alpha = 108.29$ (2)°, $\beta = 92.92$ (5)°, and $\gamma = 104.85$ (4)°, of space group $P\bar{1}$. The structure refined to $R = 0.0438$ and $R_w = 0.0484$, with 2910 reflections and 249 variable parameters. The molecule displays noncrystallographic C_2 symmetry. Bonding parameters for the bridging μ-methylene group are similar to those reported for other μ-methylene-bridged Mn, Fe, Co, Rh, and Ru dimers. The Mn–Mn distance (2.779 (1) Å) is within the wide range of previously reported Mn–Mn single-bond distances. Comments are included concerning the use of the effective atomic number (EAN) rule as a predictor of metal–metal distances.

Introduction

The discovery of μ-methylene (CH_2) transition-metal complexes[5] and their structural characterization has initiated intense research into the synthesis, spectroscopy, theory, and reactivity of this amazingly versatile class of compounds.[6,7] Much of the interest in these substances results from their potential as model systems for the further understanding, and eventual control, of important catalytic reactions such as the Fischer–Tropsch process.[8,9] Accurate determination of the molecular structures of methylene-bridged compounds ("metallacyclopropanes") has been of considerable importance in the development of synthetic methods and has set the scene for reactivity studies[6,7] and molecular orbital studies[10] as well. In this paper we give a full report on the crystal and molecular structure of $(\mu\text{-}CH_2)[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2$ (**1**), the original methylene-bridged manganese complex synthesized by Herrmann, Reiter, and Biersack[5] and partly described in our preliminary communication.[11]

Experimental Section

Preparation of the Crystal. Compound **1** was synthesized according to the published procedure given by Herrmann, Reiter, and Biersack.[14] Single crystals were grown by slow temperature decrease from +25 to −35 °C of a half-concentrated solution of **1** in pentane/diethyl ether. For this purpose, the solution was placed in a Schlenk tube with cooling jacket, the latter being connected with a LAUDA Kryostat, type K120W, equipped with a temperature program system P 250. The temperature decreased by a rate of 3.0 °C/h. Elemental analysis of the crystalline sample was used for the X-ray diffraction study. Anal. Calcd for $C_{17}H_{16}Mn_2O_4$: C, 51.80; H, 4.06; Mn, 27.87; N, 0.00. Found: C, 51.76; H, 4.11; Mn, 27.88, N, 0.04. Molecular weight for $C_{17}H_{16}Mn_2O_4$: calcd, 394.2; found (osmometrically in chloroform), 395. The spectroscopic data (IR, ^1H NMR) agreed with those reported in the original communication.

Data Collection. A crystal was mounted on an *xyz*-translation head and oriented on an Enraf-Nonius CAD-4 diffractometer operating under the OS/4 software package.[12] Molybdenum radiation was used throughout and in conjunction with a monochromatizing dense graphite crystal assumed, for all practical purposes, to be ideally imperfect.[13] A total of 25 reflections were automatically found and centered, and these defined an orientation matrix, a Niggli matrix,[14,15] and a set of cell constants. Data decoding and data reduction were carried out with a locally written program.[16]

Table I. Crystallographically Important Data Collection and Data Processing Information

empirical formula	$C_{17}H_{16}O_4Mn_2$
mol wt	394.19
cell constants	$a = 6.834$ (6) Å, $b = 9.602$ (2) Å, $c = 13.605$ (5) Å, $\alpha = 108.29$ (2)°, $\beta = 92.92$ (5)°, $\gamma = 104.85$ (4)°
unit cell V	807.60 Å^3
space group	$P\bar{1}$
density (measd)	1.588 g cm^{-3}
(calcd), $Z = 2$	1.621 g cm^{-3}
abs coeff (Mo Kα)	7.07 cm^{-1}
radiation	Mo Kα ($\lambda = 0.710\,69$ Å)
scanning range for 2θ	$4.0° < 2\theta < 60.0°$
crystal along	$[0\bar{3}1]$
stds for intens control (every 30 reflctns)	$[1\bar{2}7]$ and $[05\bar{4}]$
scan width for each reflctn	$\Delta\theta = (0.90 + 0.35 \tan \theta)°$
max scan time	4 min
prescan acceptance criterion for classifying "obsd" reflctns	$\sigma(I)/I < 1.90$
scan technique	θ:2θ
total no. of reflctns collected[a]	4458
no. of contributing reflctns in the last least squares[b]	2910
no. of variables	249
weighting scheme	unit weights
final $R(F)$[b]	0.0436
final $R_w(F)$[c]	0.0484

[a] A total of 4715 reflections were collected of which 257 were standards, and 2910 having $I > 2\sigma(I)$ were classified as "observed" with the remaining being omitted. [b] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|(F_o)|$. [c] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Solution and Refinement. The structure was solved by locating the two Mn atoms in a Patterson function. A series of Fourier maps revealed all of the heavier atoms but failed to show a number of the hydrogens at chemically sensible positions. Therefore, all hydrogen atoms were first calculated at ideal positions (C–H = 0.97 Å) and then refined. Since the methyl hydrogens were obviously affected by torsional motion, they were refined in the "riding mode" of SHELX-76.[17] The final cycles of refinement were carried out with

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Table II. Atomic Coordinates and Thermal Parameters (×1000; Mn ×10 000)

ATOM	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
MN1	.17605(10)	.32397(7)	.20262(5)	426(4)	380(3)	342(3)	112(3)	41(3)	151(3)
MN2	.39286(10)	.63294(7)	.29360(4)	404(3)	384(3)	335(3)	123(3)	16(3)	134(3)
O1	-.0099(7)	.3076(5)	-.0007(3)	78(3)	86(3)	47(2)	8(2)	-21(2)	32(2)
O2	.5502(6)	.3281(5)	.1053(3)	56(2)	67(3)	60(2)	27(2)	24(2)	15(2)
O3	.6372(6)	.4950(4)	.3983(3)	54(2)	65(2)	48(2)	24(2)	-6(2)	26(2)
O4	.2527(8)	.7435(6)	.4949(3)	132(4)	97(4)	45(2)	67(3)	39(3)	23(2)
C1	.0609(8)	.3155(6)	.0796(4)	49(3)	42(2)	40(2)	3(2)	-4(2)	18(2)
C2	.4096(7)	.3352(5)	.1460(3)	44(2)	37(2)	35(2)	13(2)	5(2)	11(2)
C3	.5330(7)	.5415(5)	.3552(3)	42(2)	41(2)	30(2)	14(2)	4(2)	12(2)
C4	.3051(9)	.6969(6)	.4152(4)	65(3)	48(3)	40(3)	28(3)	8(2)	16(2)
C5	.0932(8)	.5193(6)	.2470(5)	35(2)	38(2)	61(3)	11(2)	2(2)	17(2)
C6	.1380(9)	.0925(6)	.1968(4)	68(4)	39(2)	52(3)	21(2)	14(3)	25(2)
C7	.2549(10)	.1942(6)	.2931(5)	65(4)	48(3)	60(3)	13(3)	-2(3)	34(3)
C8	.1300(10)	.2789(7)	.3472(4)	73(4)	50(3)	33(2)	-2(3)	6(2)	21(2)
C9	-.0599(9)	.2297(6)	.2840(4)	55(3)	45(3)	47(3)	9(2)	20(2)	21(2)
C10	-.0560(8)	.1150(5)	.1910(4)	58(3)	35(2)	39(2)	4(2)	7(2)	19(2)
C11	-.2322(9)	.0242(6)	.1044(4)	65(4)	48(3)	54(3)	-9(3)	-2(3)	18(2)
C12	.4937(9)	.8667(6)	.2996(5)	61(3)	34(2)	54(3)	11(2)	3(3)	18(2)
C13	.3582(8)	.7807(6)	.2071(4)	44(3)	47(3)	62(3)	7(2)	-6(2)	34(3)
C14	.4418(8)	.6716(6)	.1471(4)	55(3)	50(3)	34(2)	-4(2)	-2(2)	23(2)
C15	.6301(8)	.6889(6)	.2028(4)	45(3)	45(3)	51(3)	9(2)	13(2)	23(2)
C16	.6644(8)	.8105(6)	.2978(4)	43(3)	40(2)	50(3)	-1(2)	-8(2)	22(2)
C17	.8523(9)	.8755(7)	.3785(5)	54(3)	70(4)	81(4)	-9(3)	-28(3)	33(3)
H51	.028(10)	.546(8)	.206(5)	8(2)					
H52	.008(9)	.530(6)	.300(4)	6(2)					
H6	.193(8)	.029(6)	.148(4)	6(2)					
H7	.394(10)	.205(8)	.311(5)	8(2)					
H8	.164(8)	.345(6)	.407(5)	6(2)					
H9	-.147(8)	.266(6)	.296(4)	4(2)					
H111	-.188(1)	-.048(1)	.049(0)	11(1)					
H112	-.280(1)	.094(1)	.077(0)	11(1)					
H113	-.343(1)	-.032(1)	.131(0)	11(1)					
H12	.487(8)	.940(6)	.347(4)	5(2)					
H13	.242(8)	.795(6)	.196(4)	5(2)					
H14	.386(9)	.603(7)	.090(5)	6(2)					
H15	.710(8)	.640(6)	.176(4)	4(1)					
H171	.947(1)	.815(1)	.358(1)	11(1)					
H172	.814(1)	.873(1)	.445(1)	11(1)					
H173	.918(1)	.981(1)	.384(1)	11(1)					

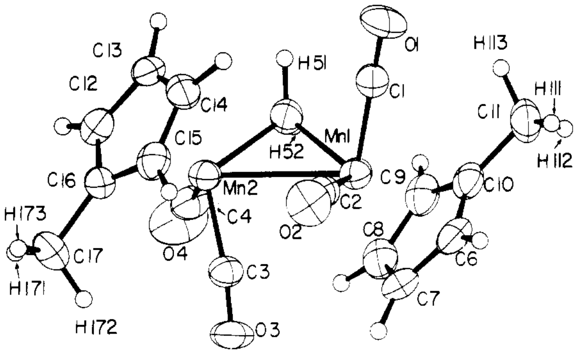

Figure 1. Single ORTEP[27] diagram of the title compound with atom numbering scheme displayed. Nonhydrogen atoms are represented by 50% probability ellipsoids, while hydrogen atoms are represented by spheres of convenient size.

anisotropic thermal parameters for the heavier atoms and with individual positional and thermal parameters for the hydrogens not associated with the two methyl groups. Details of important crystallographic data collection and processing parameters are given in Table I while Table II lists the final coordinates and thermal parameters.

Results and Discussion

Description of Structure. As shown in Figures 1–4, the $(\mu\text{-CH}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_4$ complex may be visualized as composed of two equivalent $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ fragments joined through a μ-methylene (CH_2) bridge, equidistant [2.013 (4) Å] from the two Mn atoms. If the $\mu\text{-CH}_2$ group is counted as a 2-electron donor, then each Mn atom will attain an 18-electron configuration upon formation of a Mn–Mn single bond. The Mn–Mn distance [2.779 (1) Å] is close to that found in two other μ-methylene-bridged Mn complexes (Table VI) and is actually shorter than distances found in many other complexes (Table VIII) for which Mn–Mn single bonds are postulated. From the nonbonding Mn···C(O) distances (2.96–3.61 Å) and from the MnC=O angles (173.7–173.8°), it appears that in the solid state all four carbonyls are terminal.[18] Within the π-bonded methylcyclopentadienyl rings, individual C–C distances show only minor deviations from their group mean value of 1.399 (8) Å. Both ring ligands are oriented trans to each other, with a (ring centroid 1)–Mn(1)–Mn(2)–(ring centroid 2) torsion angle of 170.20° and a Cp(1)–Cp(2) interplanar angle of 9.14°. Additional bond distances and angles are listed in Table III, while least-squares planes and angles between planes appear in Table IV.

Molecular Symmetry. One interesting feature that the title compound shares with other μ-methylene-bridged Mn,[19,20]

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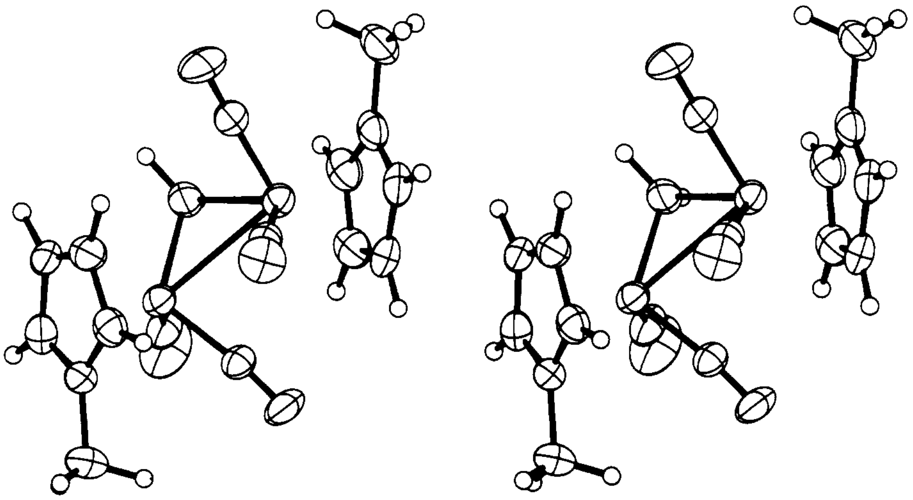

Figure 2. Stereoview of the title compound.

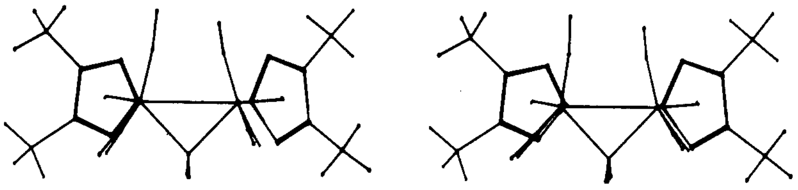

Figure 3. Stereoview of the title compound (larger circles) together with its rotated image (smaller circles).

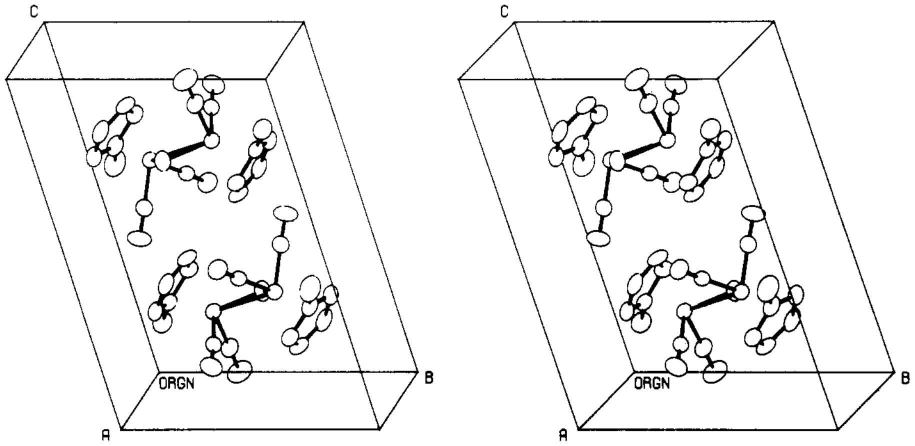

Figure 4. Stereopacking diagram showing unit cell contents.

Rh,[21a] and Co[22] dimers is a noncrystallographic nearly exact C_2 axis of molecular symmetry passing through the methylene carbon [C(5)] and the midpoint of the Mn(1)–Mn(2) bond. Figure 3 shows a BMFIT[26] diagram of the title compound compared with its C_2 rotated image. Aside from the methyl groups (which are not symmetrically related) the largest deviations between the two images occur between the following atoms: O(1) and O(4), 0.18 Å; C(1) and C(4), 0.09 Å; H(51) and H(52), 0.21 Å. The remaining carbonyl groups, Mn atoms, and Cp centroids all show deviations of less than 0.05 Å. Unlike the vinylidene-bridged Mn dimers reported recently,[19,20] the title compound also displays an equivalence of indivicual Cp carbon atoms upon 2-fold rotation; deviations between Cp carbon atoms and their rotated images are all less than 0.075 Å. Looking down the two Cp(centroid)–Mn vectors one would find the equivalent C(10)–Cp(1)–Mn(1)–C(1) and C(12)–Cp(2)–Mn(2)–C(4) torsion angles to be −0.75 and −2.04°, respectively. The two methyl groups are in different positions relative to the apparent C_2 axis and obviously (see Table IX) incur different nonbonding forces from neighboring carbonyls and from neighboring molecules; nonetheless, the ring carbons of the two Cp groups adopt identical orientations relative to the other Mn ligands. The orientation of the two Cp groups is identical with that recently found in $[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_2(\mu\text{-}CH_2)$,[23] where an absence of methyl groups allows the molecule to sit on a crystallographic C_2 axis (space group $C2/c$).

With or without molecular C_2 symmetry, individual molecules of the title compound would be chiral since the distribution of ligands about the metals makes each Mn center optically active (i.e., examine the Mn(2) site on Figure 1).

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Table III. Molecular Geometry

(a) Intramolecular Distances (Å)

Mn(1)-Mn(2)	2.779 (1)		
Mn(1)-C(1)	1.782 (5)	Mn(2)-C(3)	1.788 (4)
Mn(1)-C(2)	1.800 (5)	Mn(2)-C(4)	1.769 (5)
Mn(1)-C(5)	2.013 (5)	Mn(2)-C(5)	2.014 (4)
Mn(1)-C(6)	2.140 (5)	Mn(2)-C(12)	2.140 (5)
Mn(1)-C(7)	2.143 (7)	Mn(2)-C(13)	2.155 (7)
Mn(1)-C(8)	2.167 (5)	Mn(2)-C(14)	2.168 (5)
Mn(1)-C(9)	2.171 (5)	Mn(2)-C(15)	2.150 (5)
Mn(1)-C(10)	2.165 (4)	Mn(2)-C(16)	2.154 (5)
C(1)-O(1)	1.143 (5)	C(3)-O(3)	1.155 (5)
C(2)-O(2)	1.141 (5)	C(4)-O(4)	1.149 (6)
C(6)-C(7)	1.409 (8)	C(12)-C(13)	1.396 (7)
C(7)-C(8)	1.405 (9)	C(13)-C(14)	1.379 (8)
C(8)-C(9)	1.399 (8)	C(14)-C(15)	1.402 (7)
C(9)-C(10)	1.396 (7)	C(15)-C(16)	1.399 (7)
C(10)-C(6)	1.398 (7)	C(16)-C(12)	1.402 (7)
C(10)-C(11)	1.502 (7)	C(16)-C(17)	1.499 (7)
C(5)-H(51)	0.83 (6)	C(5)-H(52)	0.94 (6)
C(6)-H(6)	0.91 (5)	C(12)-H(12)	0.80 (5)
C(7)-H(7)	0.94 (5)	C(13)-H(13)	0.85 (5)
C(8)-H(8)	0.83 (6)	C(14)-H(14)	0.84 (6)
C(9)-H(9)	0.76 (5)	C(15)-H(15)	0.83 (5)
C(11)-H(111)	0.97 (–)	C(17)-H(171)	0.97 (–)
C(11)-H(112)	0.97 (–)	C(17)-H(172)	0.97 (–)
C(11)-H(113)	0.97 (–)	C(17)-H(173)	0.97 (–)

(b) Intramolecular Angles (Deg)

C(1)-Mn(1)-Mn(2)	102.5 (1)	C(4)-Mn(2)-Mn(1)	105.6 (2)
C(2)-Mn(1)-Mn(2)	77.2 (1)	C(3)-Mn(2)-Mn(1)	77.2 (1)
C(1)-Mn(1)-C(2)	85.9 (2)	C(3)-Mn(2)-C(4)	85.8 (2)
O(1)-C(1)-Mn(1)	178.1 (5)	O(4)-C(4)-Mn(2)	177.6 (5)
O(2)-C(2)-Mn(1)	173.7 (4)	O(3)-C(3)-Mn(2)	173.8 (4)
C(5)-Mn(1)-Mn(2)	46.4 (1)	C(5)-Mn(2)-Mn(1)	46.4 (1)
Mn(1)-C(5)-Mn(2)	87.3 (2)	H(51)-C(5)-H(52)	98 (5)
C(6)-C(7)-C(8)	107.3 (5)	C(12)-C(13)-C(14)	108.2 (5)
C(7)-C(8)-C(9)	107.7 (4)	C(13)-C(14)-C(15)	107.7 (5)
C(8)-C(9)-C(10)	109.1 (5)	C(14)-C(15)-C(16)	108.9 (5)
C(9)-C(10)-C(6)	107.2 (5)	C(15)-C(16)-C(12)	106.3 (4)
C(10)-C(6)-C(7)	108.8 (5)	C(16)-C(12)-C(13)	108.8 (5)
C(6)-C(10)-C(11)	126.3 (5)	C(12)-C(16)-C(17)	126.5 (5)
C(9)-C(10)-C(11)	126.4 (5)	C(15)-C(16)-C(17)	127.1 (5)

(c) Selected Torsion Angles

A	B	C	D	angle, deg
C(1)	Mn(1)	Mn(2)	C(3)	−153.52
C(1)	Mn(1)	Mn(2)	C(4)	124.51
C(2)	Mn(1)	Mn(2)	C(3)	−70.82
Cp(1)[a]	Mn(1)	Mn(2)	Cp(2)	170.20
Cp(1)	Mn(1)	Mn(2)	C(5)	−93.61
Cp(2)	Mn(1)	Mn(2)	C(5)	−96.19

[a] Cp(1) and Cp(2) denote the centroids of the two cyclopentadienyl rings.

Table IV. Equations of Least-Squares Planes[a] and Distances (Å) of Atoms from Those Planes

(a) Plane Based on Mn(1), Mn(2), and C(5)

$$0.1187x + 0.4013y + -0.9082z = -1.4945$$

C(1)	1.548 (5)	C(2)	0.994 (4)	C(3)	−1.033 (4)
C(4)	−1.500 (5)	H(51)	0.61 (6)	H(52)	−0.76 (5)

(b) Plane Based on C(5), H(51), and H(52)

$$-0.2673x + -0.8486y + -0.4566z = -4.3282$$

Mn(1)	1.3311 (6)	Mn(2)	−1.4430 (6)

(c) Plane Based on C(6), C(7), C(8), C(9), and C(10)

$$0.1718x + 0.8913y + -0.4196z = -1.0062$$

C(6)	−0.004 (5)	C(7)	0.004 (6)	C(8)	−0.002 (6)
C(9)	−0.001 (5)	C(10)	0.003 (5)	Mn(1)	1.7986 (6)
C(11)	−0.078 (6)				

(d) Plane Based on C(12), C(13), C(14), C(15), and C(16)

$$0.3220x + 0.8406y + -0.4356z = 4.2357$$

C(12)	−0.001 (6)	C(13)	−0.002 (6)	C(14)	0.004 (6)
C(15)	−0.004 (5)	C(16)	0.003 (5)	Mn(2)	−1.7970 (6)
C(17)	0.084 (7)				

(e) Equation of Line Based on Mn(1) and Mn(2)

$L(1) = I = 0.5866 + 0.2356T$
$L(2) = J = 3.2762 + 0.8772T$
$L(3) = K = 3.1697 + 0.4184T$

(f) Equation of Line Based on Mn(1) and C(1)

$L(1) = I = -0.0784 + -0.3787T$
$L(2) = J = 2.2040 + 0.2765T$
$L(3) = K = 1.8009 + -0.8833T$

(g) Equation of Line Based on Mn(1) and C(2)

$L(1) = I = 1.0622 + 0.8928T$
$L(2) = J = 2.2405 + 0.2035T$
$L(3) = K = 2.2271 + 0.4018T$

(h) Equation of Line Based on Mn(2) and C(3)

$L(1) = I = 1.4843 + 0.6049T$
$L(2) = J = 3.9287 + -0.6040T$
$L(3) = K = 3.2576 + 0.5231T$

(i) Equation of Line Based on Mn(2) and C(4)

$L(1) = I = 0.4917 + -0.4774T$
$L(2) = J = 4.5088 + 0.0158T$
$L(3) = K = 4.5270 + 0.8785T$

(j) Angles between Planes and/or Lines

plane 1	plane 2	angle, deg	plane 1	plane 2	angle, deg
(a)	(b)	87.57	(c)	(f)	133.01
(a)	(c)	139.39	(c)	(g)	98.08
(a)	(d)	140.22	(d)	(e)	128.50
(c)	(d)	9.14	(d)	(h)	122.73
(c)	(e)	124.46	(d)	(i)	121.54

[a] Planes are expressed in the form $ax + by + cz = d$ in orthogonal space where vectors x, y, and z are parallel to unit cell vectors a, b, and c^*, respectively.

According to the extention of the *R*,*S* system[28a,b] to *polyhapto* ligands, we proposed previously,[28c] the η^5-MeCp group on Mn(2) would be assigned the highest priority. If each of the four remaining atoms bounded to Mn(2) were considered as individual monodentate ligands, then Mn(1) (high atomic number) would be assigned second priority, followed by CH_2 (bonded to Mn(1)). If either of the low-ranking carbonyl groups were directed away from the reader (as shown at the Mn(2) site in Figure 1), then, in tracing the priority sequence [η^5-MeCp > Mn(1) > CH_2(Mn) > CO], the reader would follow a counterclockwise rotation. As depicted in Figure 1, both Mn sites would be assigned the symbol *S*. Regardless of whether one accepts the above priority sequence or some alternate sequence, both Mn sites would be assigned identical chirality symbols. As shown in Figure 4, one pair of enantiomers (*R*; *R* and *S*; *S*) is present in the solid state, as dictated

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(28) (a) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem.* **1966**, *78*, 423; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385. (b) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *97*, 6599. (c) Bernal, I.; LaPlaca, S. J.; Korp. J.; Brunner, H.; Herrmann, W. A. *Inorg. Chem.* **1978**, *17*, 382. Reisner, M. G.; Bernal, I.; Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1977**, *137*, 329.

(29) Although the average Mn—C(O) and C=O distances in the (μ-CCHPh)-bridged dimer deviate from those for (μ-CH_2)- and (μ-CCH_2)-bridged compounds, the sum (Mn—C(O) + C=O) remains constant in these three compounds (2.92, 2.92, and 2.93 Å). In their preliminary communication on the (μ-CCHPh)-bridged species, Nesmeyanov et al.[19] stated that data collection was limited by the decomposition of crystals in the X-ray beam. One way in which a lack of sufficient data may manifest itself is in the location of lighter atoms (i.e., carbons in C=O). Also, it is known that the effect of using scattering curves calculated on the basis of spherically distributed electrons will be most pronounced in linear fragments containing light atoms.

Table V. Comparison of $\text{CpMn(CO)}_2\text{L}$ and Related Fragments

compd	av dist, Å				angle, deg C(O)–Mn–C(O)	ref
	Mn–C(Cp)	Mn–Cp	Mn–C(O)	C=O		
$(\eta^5\text{-Cp})\text{Mn(CO)}_3$	2.15	1.794	1.80	1.13	92.0	32a
$(\eta^5\text{-Cp})\text{Mn(CO)}_2\text{PPh}_3$	2.15	1.775	1.75	1.17	92.4	32b
$(\eta^5\text{-Cp})\text{Mn(CO)}_2\text{CC(H)Ph}$	2.16		1.74	1.18	89.1	19
$(\eta^5\text{-Cp})_2\text{Mn}_2(\text{CO})_4(\eta^2\text{-}\eta^2\text{-C}_5\text{H}_5)$	2.15	1.785	1.77	1.16	89.4	33a
$(\eta^5\text{-Cp})\text{Mn(CO)}_2(\eta^2\text{-C}_8\text{H}_8)$	2.16	1.791	1.79	1.15	88.8	33b
$(\eta^5\text{-Cp})\text{Mn(CO)}_2(\eta^2\text{-C}_7\text{H}_7)$	2.17	1.814	1.79	1.15	91.9	33c
$[(\eta^5\text{-MeCp})\text{Mn(CO)}_2]_2(\mu\text{-CH}_2)$	2.15	1.798	1.79	1.15	85.8	this work
$[(\eta^5\text{-Cp})\text{Mn(CO)}_2]_2(\mu\text{-CCHPh})$	2.14	1.782	1.75	1.17	86.4	19
$[(\eta^5\text{-Cp})\text{Mn(CO)}_2]_2(\mu\text{-CCH}_2)$	2.15	1.785	1.79	1.14	89.0	20
$[(\eta^5\text{-MeCp})\text{Mn(CO}_2)]_2(\mu\text{-SC}_2\text{H}_5)]\cdot\text{ClO}_4$	2.16	1.800	1.81	1.14	83.8	30
$(\eta^5\text{-Cp})\text{Mn}_2(\text{CO})_6(\mu\text{-AsMe}_2)$	2.17		1.81	1.17	86.4	31a

Table VI. Additional Bonding Parameters for μ-Bridged Mn Dimers

μ ligand	av dist, Å				Mn-L-Mn, deg	ref
	Mn-Mn	*trans*-Mn–C(O)	*cis*-Mn–C(O)	Mn–L		
		$[\text{CpMn(CO)}_2]$ or $[(\text{MeCp})\text{Mn(CO)}_2]$				
CCHPh	2.734 (2)	1.745	1.770	1.97 (2)	88.0	19
CCH_2	2.759 (2)	1.806	1.781	1.973 (3)	88.6	20
CH_2	2.779 (1)	1.794	1.776	2.013 (1)	87.3	this work
SC_2H_5	2.930 (1)	1.815	1.815	2.26 (3)	81.0	30
		$[\text{CpMn(CO)}_2\text{Mn(CO)}_4]$				
AsMe_2	2.912 (4)	1.81	1.73 (1.81)	2.36 (1)	76.3	31a
$\text{C(C}_6\text{H}_4\text{Me)CO}$	2.735 (1)				87.2	31b

Table VII. Comparison of μ-Methylene Compounds

compd	dist, Å		M–C–M, deg	methylene radius, Å	ref
	M–M	M–C			
$[(\eta^5\text{-Cp})\text{Fe(CO)}]_2(\mu\text{-CO})(\mu\text{-CHCO}_2\text{-}t\text{-C}_4\text{H}_9)$	2.505 (5)	1.96	79.4	0.708	24
	2.512 (5)	1.92	85.3	0.664	
$[(\eta^5\text{-Cp})\text{Fe(CO)}]_2(\mu\text{-CO})(\mu\text{-C(H)CH}_3)$	2.520 (1)	1.986	78.8	0.726	25a
$[(\eta^5\text{-Cp})\text{Co(CO)}]_2(\mu\text{-C}_9\text{H}_4\text{O}_2)$	2.475 (1)	1.945	79.0	0.707	22a
$[(\eta^5\text{-Cp})\text{Co(CO)}]_2(\mu\text{-C(H)C(O)OC}_2\text{H}_5)$	2.499 (1)	1.937	80.4	0.700	22b
$[(\eta^5\text{-Cp})\text{Rh(CO)}]_2(\mu\text{-CH}_2)$	2.6649 (4)	2.037	81.7	0.704	21a
$[(\eta^5\text{-Cp})\text{Rh(CO)}]_2[\mu\text{-C(CO}_2\text{CH}_3)_2]$	2.663 (1)	2.076	79.9	0.745	21b
$[(\eta^5\text{-Cp})\text{Ru(CO)}]_2(\mu\text{-CO})(\mu\text{-CCH}_2)$	2.695 (1)	2.029	83.2	0.682	25b
average			80.9	0.704	

by space group ($P\bar{1}$) symmetry.

$(\eta^5$-MeCp)Mn(CO)$_2$ Fragments. Table V has been prepared as a comparison of $(\eta^5\text{-Cp})\text{Mn(CO)}_2$ and $(\eta^5\text{-MeCp})\text{Mn(CO)}_2$ fragments from a variety of Mn complexes, while Table VI lists additional parameters for μ-bridged Mn dimers. Aside from the deviant Mn—C(O) and C═O distances listed for the (μ-CCHPh)-bridged complex, the three μ-methylene-bridged Mn dimers show similarities in all parameters listed. For the (μ-CH$_2$)-, (μ-CCHPh)-, and (μ-CCH$_2$)-bridged complexes the average values of Mn–C(Cp), Mn–Cp(centroid), and Mn–C(O) are 2.15, 1.778, and 1.785 Å, respectively. Although steric factors play an obvious role in determining individual C(O)–Mn–C(O) angles, all three compounds have angles close to the mean value of 87.1°. By contrast, this angle in the (μ-SEt)-bridged species[30] is 83.8°. Tables V and VI both show that for the (μ-sEt)-[30] and (μ-AsMe$_2$)-bridged[31] complexes all distances associated with the Mn atom are greater than for the three μ-methylene-bridged complexes.

Comparison of the μ-methylene-bridged compounds with other complexes in Table V shows that there is very little variation throughout the table so far as the $(\eta^5\text{-Cp})\text{Mn(CO)}_2$ and $(\eta^5\text{-MeCp})\text{Mn(CO)}_2$ fragments are concerned. Among the first three compounds, some variation in Mn–C(O) and Mn–Cp(centroid) distances can be attributed to differences in electronegativity and π-acceptor character of the η^1-substituents; thus, both (μ-PPh$_2$) and (μ-CCHPh) substituents lead to decreased Mn–C(O) and Mn–Cp distances. If all of the bonding parameters in Table V are considered equally accurate, a closer resemblance can be found between the μ-methylene-bridged complexes and *other* η^2-substituted complexes than between the bridged complexes and any of the other compounds listed. The similarities between the bridged complexes and the η^2 complexes indicate that the combined inductive influence of a methylene group plus a second Mn atom upon $(\eta^5\text{-Cp})\text{Mn(CO)}_2$ or $(\eta^5\text{-MeCp})\text{Mn(CO)}_2$ is comparable to the influence exerted by an η^2-substituted ethylene group.

μ-CH$_2$ Fragment. As already stated, and as shown in Table II, the methylene hydrogens H(51) and H(52) are not precisly located in the present refinement and will not be discussed here.[34] In many respects, the μ-CH$_2$ group in the title com-

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(34) A low-temperature data set of the title compound has been collected by R. Lalancette of Rutgers University, the results of which will be published at a later date.

Table VIII. Comparison of Mn–Mn Distances

(a) $Mn_2(CO)_8L_1L_2$: L_1,L_2 Axial

		av dist, Å		
L_1	L_2	Mn–Mn	Mn–$C(O)_{eq}$	ref
PMe_2Ph	PMe_2Ph	2.90 (1)	1.75	37a
C=O	$Mn(CO)_5$	2.883 (4)	1.81	37b
		2.906 (5)	1.82	
C=O	PMe_2Ph	2.904	1.76	37c
C=O	C=O	2.9038 (6)	1.856 (7)	37d

(b) $Mn_2(CO)_8L_1L_2$: L_1,L_2 Equatorial

		av dist, Å			
L_1	L_2	Mn–Mn	Mn–$C(O)_{ax}$	Mn–$C(O)_{eq}$	ref
C=O	C(Ph)OMe	2.909 (3)	1.80	1.85	41a
$AsMe_2Ph$	$AsMe_2Ph$	2.94 (1)		1.78	37a
$[AsPh_2(C_4F_4)AsPh_2]$		2.971 (2)		1.80	41b

(c) $Mn_2(CO)_8(\mu\text{-}L_1)(\mu\text{-}L_2)$

		av dist, Å			
L_1	L_2	Mn–Mn	Mn–$C(O)_{cis}$	Mn–$C(O)_{trans}$	ref
C=O	$GeMe_2$	2.854 (2)	1.850	1.805	45a
$SiPh_2$	$SiPh_2$	2.871 (2)	1.852	1.805	45b
H	PPh_2	2.937 (5)	1.84	1.78	45c

(d) Additional Doubly Bridged Complexes

compd	Mn–Mn, Å	ref
$(\eta^5\text{-}Cp)_2(\eta^1\text{-}Cp)Mn_2(NO)_3$	2.520 (1)	45d
$Cp_2Mn_2(CO)_2(NO)_2$	2.571 (1)	45e

(e) Triply Bridged Complexes

compd	Mn–Mn, Å	ref
$Mn_2(CO)_6(\mu\text{-}CO)[\mu\text{-}NN(CF_3)_2]_2$	2.518 (2)	47

(f) Trimeric Complexes

compd	Mn–Mn, Å	ref
$Cp_3Mn_3(\mu_3\text{-}NO)(\mu\text{-}NO)_3$	2.502 (1)	48a
$Mn_3(CO)_8(PMe_2Ph)(\mu_3\text{-}Et)(\mu\text{-}Et)_2$	2.538 (4)	48b
	2.867 (2)	
	3.214 (3)	
$Mn_3(CO)_{12}[\mu\text{-}\eta^1\text{-}NNMe]$	2.807 (3)	48c
	2.826 (4)	
$Mn_3(CO)_{12}(\mu\text{-}H)_3$	3.099 (2)	48d
	3.107 (2)	
	3.126 (2)	

(g) Additional Mn Compounds

compd	EAN bond order	Mn–Mn, Å	ref
$Cp_2Mn_2[\mu\text{-}NN(SiMe_3)_2]_2$	2	2.393 (2)	51a
$Mn_2[CH_3\text{-}m\text{-}C_6H_4NMe_2]_4$	0	2.810 (3)	51b
$Mn_2(CO)_8(\mu\text{-}NNPh)_2$	0	3.235 (1)	51c
$Mn_2(CO)_8(\mu\text{-}Br)_2$	0	3.74	51d
$Mn_2(CO)_8(\mu\text{-}SeCF_3)_2$	0	3.793	51e
$Mn_2(CO)_6(PPh_2)_4(\mu\text{-}Br)_2$	0	3.661 (1)	52
$Mn_2(CO)_6(TePh_2)_2(\mu\text{-}Br)_2$	0	3.66	53

Table IX. Selected Nonbonding Contacts

(a) Intramolecular

atom 1	atom 2	dist, Å	atom 1	atom 2	dist, Å
Mn(1)	C(3)	2.96	Mn(2)	C(2)	2.96
O(1)	H(112)	2.83	O(4)	H(12)	3.38
O(1)	H(51)	2.95	O(4)	H(52)	2.89
O(2)	H(15)	2.70	O(3)	H(7)	2.71
C(1)	H(51)	2.40	C(4)	H(52)	2.35
C(1)	C(10)	2.80	C(4)	C(12)	2.75
C(1)	H(112)	2.68	C(4)	H(12)	2.81
C(2)	H(7)	2.91	C(3)	H(173)	2.73
C(2)	H(6)	2.97	C(3)	H(15)	3.01

(b) Intermolecular

atom 1	atom 2	sym	operation	dist, Å
O(2)	H(112)	1	(1 0 0)	2.63
O(3)	H(8)	2	(−1 −1 −1)	2.70
O(1)	H(13)	2	(0 −1 0)	2.76
O(4)	H(171)	2	(1 2 1)	2.84
O(4)	H(173)	1	(−1 0 0)	2.96
Cp(1)	H(172)	1	(−1 −1 1)	3.02
Cp(2)	H(113)	1	(1 1 0)	2.64

[a] Contact distances were calculated with the program ORFFE[56] and have esd's of 0.10 or less. [b] The second atom has been moved through a rotation +(*x*, *y*, *z*) translation, prior to distance calculation. Rotation operators: 1 (*x*, *y*, *z*); 2 (−*x*, −*y*, −*z*).

pound resembles the same group in $[(\eta^5\text{-}Cp)Rh(CO)_2]_2(\mu\text{-}CH_2)$, we which reported earlier.[21a] In that paper, we compared the μ-CH_2 group to μ-CO groups in other Rh dimers and found them to be similar in many respects. Since that time, μ-CHR and μ-CRR′ groups have been incorporated into Mn, Fe–Co, and Ru dimers (Tables VI and VII), and in all cases, comparison of the methylene group to bridging carbonyls has shown the μ-methylene group to have slightly longer M–C distances and smaller M–C–M angles. In valence-bond terms, both ligands may be considered as 2-electron donors, bonding through two separate metal-directed orbitals. A molecular orbital description of $[(\eta^5\text{-}Cp)Rh(CO)]_2(\mu\text{-}CH_2)$ has been presented recently.[10]

Among the Fe, Co, and Rh dimers listed in Table VII, individual M–C–M angles do not deviate appreciably from their group mean value of 80.9°; the mean value in Mn complexes (Table VI) is 84.7°. Although some of the divergence in M–C–M angles within both groups may be explained in terms of individual ligand radii and donor/acceptor properties (vide infra), the greater divergence in this angle between the two classes of compounds is more probably the result of differences in metal–metal bonding.

The EAN Rule and Mn–Mn Distances

Table VI shows that there is little variation in Mn–Mn distances among the three μ-methylene-bridged Mn dimers whose structures have been reported, indicating that minor changes in the methylene group do not appreciably change Mn–Mn bonding. Among the Fe, Co, and Rh complexes in Table VII, the sp^3-methylene radii [calculated from $d(M\text{–}C) - {}^1/_2 d(M\text{–}M)$] fall close to their mean value of 0.704 Å. Using this mean value and the observed Mn–C(methylene) distances listed on Table VI, one would calculate an effective Mn single-bond radius of 1.28 Å, which is 0.11 Å larger than that listed by Pauling.[40] The Mn–Mn bond distance (2.56 Å) predicted from this mean radius is shorter than that observed in any of the μ-methylene-bridged Mn complexes (Table VI) though it is within the range of some previously reported Mn–Mn "single bond" distances (Table VIII).

In a recent note[36] we called attention to the fact that observed "single bond" metal–metal distances for manganese

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(35) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 221.

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complexes span a much wider range (2.50–3.23 Å) than those for any other element. Although a complete explanation for the wide range of Mn–Mn distances still cannot be offered, some variations in Mn–Mn distances can be explained when compounds are categorized according to the nature of their ligand groups. Among the many factors that may influence Mn–Mn bond distances are the following.

Trans Influence of Axial Ligands. When ligands are substituted trans to a metal–metal bond, as in $Mn_2(CO)_8L_1L_2$, the ligands about one metal act toward the second metal as they would with any other ligand, competing for electron density. Variations in metal–metal distances have been observed by Christoph and Kuh[38,39] in quadruply bonded Rh dimers, in which σ and π influences of the ligands lead to variations of 0.07 Å in metal–metal bond distances. In these cases, ligand-induced variations have been correlated with ligand σ-donor/π-acceptor properties given by Graham[40] for a series of $Mn(CO)_5L$ and $Mo(CO)_5L$ complexes. We have attempted to do likewise with dinuclear Mn complexes available in the literature, including the very recent redetermination of the structure of $Mn_2(CO)_{10}$ by Churchill et al.,[37d] and the results are summarized in Table VIII. It is clear that within the estimated standard deviation, it is not possible to observe any such trans influences in this class of compounds.

Influence of Equatorial Ligands. In $Mn_2(CO)_{10}$,[37d] some of the attractive influence between the two $Mn(CO)_5$ fragments was attributed to partial overlap of nonbonding metal orbitals with π^* orbitals on adjacent carbonyls. Such interaction was expected to help overcome the repulsive forces[42] between filled metal orbitals and helped to explain the observed geometry; i.e., equatorial carbonyls are bent slightly toward adacent metal atoms. More recent molecular orbital calculations[43] suggest that the interaction between equatorial carbonyls and adjacent Mn atoms in $Mn_2(CO)_{10}$ may account for as much as 60% of the total attractive force between $Mn(CO)_5$ fragments. Consistent with this thinking, Table VIII, part b, shows that when equatorial carbonyls in $Mn_2(CO)_{10}$ are substituted with weaker π acceptors (such as AsR_3), the Mn–Mn distance increases, by as much as 0.062 Å.

Influence of Bridging Groups. Using a bonding model based upon molecular orbital calculations of Teo et al.,[44] Triplett and Curtis[45a] have correlated bonding properties of bridging ligands to observed Mn–Mn distances in compounds such as those listed on Table VIII, part c. Their findings suggested that the increased Mn–Mn distance in $Mn_2(CO)_8(\mu\text{-H})(\mu\text{-PPh}_2)$,[45c] as compared to $Mn_2(CO)_8(\mu\text{-CO})(\mu\text{-GeMe}_2)$,[45a] may be due to the decreased π-acceptor properties of μ-H and μ-PPh_2, leading to a decreased interaction with antibonding metal orbitals. In a more recent and more extensive MO study of bridged metal dimers, Hoffmann et al.[46] concluded that both M–M bond lengths and M–L–M angles are strongly determined by the π-acceptor character of bridging carbenoids. The variation in Mn–Mn distances for compounds in Table VIII, part c (0.083 Å), is only slightly greater than that observed for semibridging ligands in Table VIII, part b.

Influence of Cp Groups. Throughout Tables VI and VIII, compounds with Cp groups exhibit shorter Mn–Mn distances than similar compounds having three carbonyl groups, instead of the Cp. The effect is similar to that observed in the structures of $Cr(CO)_6$ vs. $(\eta^5\text{-C}_5H_4SMe_2)Cr(CO)_3$,[49b] where substitution of three carbonyls by η^5-$C_5H_4SMe_2$ leads to a 0.077-Å decrease in Cr–C(O) bond lengths. One way in which Cp's may influence metal–metal bonding directly is through their interaction with metal–metal orbitals: In their description of $Cp_2Cr_2(CO)_4$, Curtis and Butler[50] noted that when Cp's are placed at a Cp–M–M angle of ca. 135°, the ligands seem to interact with metal–metal σ^* orbitals; one may note that in the title compound, as well as in a number of other bridged complexes listed in Table VI, Cp rings are ideally situated for such interaction. One may also reason that, in the competition between Cp and carbonyls, the latter groups would have a greater influence on the M–M σ^* orbitals, leading to longer M–M distances.

Additional Factors and Conclusions. While each of the above arguments may help to explain small deviations in Mn–Mn distances *within individual classes of compounds*, they share a common failing in that they do not explain the larger deviations in Mn–Mn distances between classes. One may imagine a number of additional factors (such as the presence of bridging nitrosyls[50e] or hydrides,[48d] the number of bridging groups,[47] the electronegativities of bridging groups,[54] etc.) which may be correlated with observed deviations in Mn–Mn distances; however, it is doubtful that any additional factors would make significant contributions toward explaining the full range of observed Mn–Mn distances.

It has long been held that the effective atomic number rule may be used to predict metal–metal bond orders and that bond order/bond length relationships, similar to those proposed by Pauling[35] for main-group elements, may be used to correlate EAN calculated bond orders with observed bond distances in transition-metal compounds.[55] For example, Mason and Mingos,[54] in their MO description of bridged polynuclear metal complexes, pointed out the 0.8-Å deviation in Mn–Mn distances, found between $Mn_2(CO)_8(\mu\text{-H})(\mu\text{-PPh}_2)$ (BO = 1) and $Mn_2(CO)_8(\mu\text{-Br})_2$ (BO = 0), as proof that the EAN rule successfully predicts bond distances. With the list of more recent Mn complexes in Tables VI and VIII, one may make

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additional observations on the question of bond order/bond length, so far as manganese complexes are concerned. For example, when one compares the shortest[51c] Mn–Mn distance for a compound with BO = 0 with the longest[48b] distance for BO = 1, the difference is only 0.021 Å. A larger (0.109 Å) deviation is observed when the shortest[48a] BO = 1 distance is compared with that recently reported for $Cp_2Mn_2[\mu\text{-NN(SeMe}_3)_2]_2$[51a] (BO = 2). By comparison, the overall range of Mn–Mn distances for compounds with EAN BO = 1 is 0.712 Å. This is the broadest range in single-bond distances that we know of, and it indicates (at least to us) a need for caution in using simple rules (such as the EAN rule) to explain metal–metal distances.

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Supplementary Material Available: A listing of observed and calculated structure factors for the Mn dimer (18 pages). Ordering information is given on any current masthead page.

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Molybdenum Complexes Containing Catecholate Ligands. Structural Studies on Complexes of the Pentaoxobis(quinone)dimolybdate($n-$) (n = 0, 1, 2) Redox Series

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Members of the $Mo_2O_5(\text{quinone})_2^{n-}$ (n = 0, 1, 2) series have been synthesized. The neutral complex prepared with 9,10-phenanthrenequinone, $Mo_2O_5(9,10\text{-phenSQ})_2$, has been characterized in a previous structural study. The dianion containing 3,5-di-*tert*-butylcatechol has been prepared and reported previously. We now report the results of a structural investigation on this dianion, obtained as the tetra-*n*-butylammonium salt. Structural features of the $Mo_2O_5^{2+}$ region of the complex closely resemble those of the neutral molecule. This result together with the features of the quinone ligands in both structures shows that the charge difference is contained entirely within the quinones. The monoanion formulated as the mixed-ligand complex $Mo_2O_5(3,5\text{-DBCat})(3,5\text{-DBSQ})^-$ has been prepared by Ag^+ oxidation of the dianion. The EPR spectrum of this $S = {}^1/_2$ complex is virtually identical with that of a free semiquinone, indicating that spin density is localized on only one of the two quinone ligands at room temperature. Oxygen atom transfer reactions involving molybdenum–catecholate complexes are also discussed.

Introduction

Among the earliest reports of transition-metal complexes prepared with catecholate ligands are a series of compounds prepared with molybdate ion.[1–4] These compounds and the solution chemistry of Mo(VI)–catechol systems have become of particular importance as a photometric analytical method for the determination of molybdenum.[5,6] In neutral solution a red-orange complex with a Mo:catechol ratio of 1:2 is formed, while at pH values below 2 a 1:1 complex is observed.[7] Atovmyan has characterized products of early synthetic reactions crystallographically, and found them to contain the $MoO_2(Cat)_2^{2-}$ and $Mo_2O_5(Cat)_2^{2-}$ ions.[8,9] These reports were the first structural studies carried out on transition-metal complexes containing catecholate ligands. More recently kinetic studies have been carried out on the molybdate–catechol system[10] and the redox chemistry of molybdenum–catecholate complexes has been investigated in detail.[11–13]

Table I. Crystallographic Data for $(n\text{-}Bu_4N)_2[Mo_2O_5(3,5\text{-DBCat})_2]$

fw	1197.6	Z	4
space group	$P2_12_12_1$ (D_2^4, No. 19)	μ, cm^{-1}	4.41
		Mo Kα radiation	$\lambda = 0.71069$ Å
		scan rate, deg min^{-1}	4
a, Å	14.293 (2)	max 2θ, deg	50
b, Å	17.515 (2)	scan range, deg	±0.7
c, Å	28.218 (5)	data collected	7035
V, Å^3	7064.3	unique data, $I > 3\sigma(I)$	3494
d_{calcd}, g cm^{-3}	1.126		
d_{exptl}, g cm^{-3}	1.13		

Research carried out in our laboratory, which has been directed at investigation of the coordination chemistry of quinone ligands, has also included work with molybdenum. Procedures used to synthesize complexes of molybdenum in aprotic media have involved oxidation of Mo(0) in $Mo(CO)_6$ by the *o*-benzoquinone form of the ligand. Results obtained by this procedure have shown a surprising ligand dependence (1).[14–16] Each product has been characterized structurally;

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