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Crystal Structure and Molecular Geometry of (3,5-Dimethylaceheptylene)hexacarbonyldimanganese, $(C_{14}H_8Me_2)Mn_2(CO)_6$

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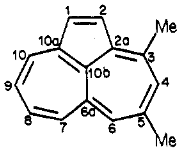
(3,5-Dimethylaceheptylene)hexacarbonyldimanganese, $(C_{14}H_8Me_2)Mn_2(CO)_6$, prepared previously by King and Harmon, has been the subject of a complete three-dimensional X-ray structural analysis. The complex crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ [D_2^4; No. 19] with $a = 9.678$ (1) Å, $b = 13.100$ (2) Å, $c = 15.639$ (3) Å, $V = 1982.6$ (5) Å^3, ρ(obsd) = 1.626 (10) g cm^{-3} and ρ(calcd) = 1.620 g cm^{-3} for mol wt 484.23 and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer using Mo Kα radiation. The structure was solved via direct methods and refined by difference-Fourier and least-squares refinement techniques. Final discrepancy indices are $R_F = 6.8\%$ and $R_{wF} = 5.3\%$ for 1079 independent reflections with $5° < 2\theta < 40°$ (*no* reflections rejected). The molecule consists of two $Mn(CO)_3$ groups bonded to opposite sides of a 3,5-dimethylaceheptylene ligand. One $Mn(CO)_3$ group interacts with the carbon atoms of the five-membered ring and participates in an η^5-cyclopentadienyl→metal bond, while the second $Mn(CO)_3$ is associated with the remaining five atoms of the dimethyl-substituted seven-membered ring via an η^5-dienyl→metal linkage in which individual manganese–carbon distances are (cyclically) 2.256 (15), 2.119 (14), 2.149 (13), 2.151 (13), and 2.404 (14) Å. The second (nonsubstituted) seven-membered ring retains a noncoordinated *cis*-diene system.

Introduction

We have been interested, for some time, in the bonding of transition-metal atoms to nonalternant aromatic hydrocarbons[1] and have previously reported the results of single-crystal X-ray structural analyses of complexes containing azulene,[2] acenaphthylene,[3] fulvalene,[4] heptafulvene,[5] and the bis(pentalenyl)[6] ligand.

We now report the results of an X-ray diffraction study of the species (3,5-dimethylaceheptylene)hexacarbonyldimanganese, $(C_{14}H_8Me_2)Mn_2(CO)_6$, prepared by King and Harmon from reaction of 3,5-dimethylaceheptylene[7] ($C_{14}H_8Me_2$, I) with dimanganese decacarbonyl.[8a] It should be noted that we have previously published a full account of the structure of the related species $(C_{14}H_8Me_2)Fe_3(CO)_8$.[8b]



I

Experimental Section

A. Collection and Reduction of X-ray Diffraction Data. Red crystals of $(C_{14}H_8Me_2)Mn_2(CO)_6$ were provided by Professor R. B. King of the University of Georgia. The complex appears to be air-stable and does not decompose upon exposure to X-rays. The crystals typically form extremely thin plates; despite many attempts at recrystallization, the best single crystal that we could obtain was a rather irregular plate of dimensions 0.50 mm × 0.38 mm × ~0.05 mm. This was mounted along its extended direction on a thin glass fiber which was then sealed into a 0.5-mm diameter thin-walled glass capillary and fixed into a eucentric goniometer. The crystal was centered in a random orientation (with $\phi \sim 3.3°$ from [122]) on a Syntex $P2_1$ four-circle diffractometer.

Approximate unit cell parameters were obtained via an autoindexing routine; axial photographs taken about each of the principal axes showed the crystal to be orthorhombic (D_{2h} or *mmm* Laue symmetry). Determination of the orientation matrix and accurate unit cell parameters, checks on peak profiles, and data collection were all carried out as described previously;[2] details are given in Table I.

Examination of the complete set of intensity data revealed the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$. The noncentrosymmetric orthorhombic space group $P2_12_12_1$ [D_2^4; No. 19] is thereby uniquely indicated.

Table I. Details of Data Collection for $(C_{14}H_8Me_2)Mn_2(CO)_6$

(A) Crystal Data[a]

cryst system: orthorhombic
space group: $P2_12_12_1$ [D_2^4; No. 19]
$a = 9.6777$ (14) Å
$b = 13.0999$ (20) Å
$c = 15.6385$ (26) Å
$V = 1982.6$ (5) Å^3
temp = 24 °C
mol wt = 484.23
ρ(obsd)[b] = 1.626 (10) g cm^{-3}
ρ(calcd) = 1.620 g cm^{-3}
$Z = 4$

(B) Collection of Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite (equatorial)
monochromator angle: 12.2°
2θ range: 5–40°
scan type: θ(crystal)-2θ(counter)
scan speed: 1.0° min^{-1}
scan range: $[2\theta(K\alpha_1) - 1.0]° \rightarrow [2\theta(K\alpha_2) + 1.0]°$
background measurement: at the beginning and end of each scan, each for half of the total scan time
standards: 3 every 47 reflections[c]
reflections collected: one octant (i.e., $+h$, $+k$, $+l$) giving a total of 1171 measurements of which 1079 were independent (75 check reflections and 17 systematic absences)

(C) Treatment of Intensity Data

ignorance factor: $P = 0.01$
reflections rejected: none
absorption coefficient: $\mu = 12.57$ cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 25 reflections with 2θ = 20–30°. [b] The density was measured by neutral buoyancy in aqueous zinc iodide. [c] Maximum deviations of intensities from their mean values were 0.76% for 002, 0.99% for 020, and 3.34% for 200.

Data were corrected for absorption by an empirical method, using the program TAPER.[9] Three carefully selected close-to-axial reflections were each measured at 10° intervals around their diffraction vectors (from $\psi = 0°$ to $\psi = 350°$). Each reflection was used to define a (normalized) transmission curve. The curve(s) nearest in 2θ to the Bragg angle of the intensity datum under consideration were interpolated both in 2θ and in ϕ to derive the transmission coefficient. The reflections used, their 2θ values, and their (maximum intensity):(minimum intensity) ratios were as follows: 122, $2\theta = 9.12°$, 1.27:1; 344, $2\theta = 20.59°$, 1.33:1; 457, $2\theta = 29.50°$, 1.33:1. These curves were found to be mutually consistent—i.e., maxima and minima were each observed at similar ϕ values, similar profiles vs. ϕ were observed (but with a characteristic broadening of features with increasing 2θ), etc.

Unscaled $|F_o|$ values and their associated esd's based solely upon counting statistics $[\sigma_c(|F_o|)]$ were generated following correction of the data for Lorentz, polarization, and absorption effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$ and was retained.

B. Solution of the Structure. All calculations were performed using the Syntex XTL system[10] which consists of (a) a Data General Nova 1200 computer with 24K of 16-bit word memory and with a parallel floating-point processor for 32- or 64-bit arithmetic, (b) a Diablo moving-head disk unit with 1.2 million 16-bit words, (c) a Versatec

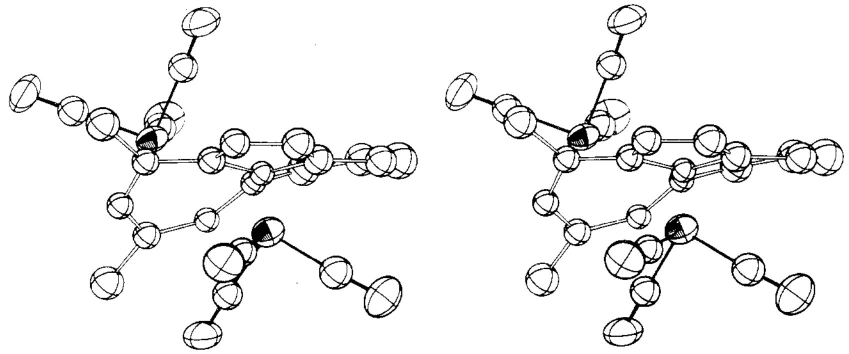


Figure 1. Stereoscopic view of the $(C_{14}H_8Me_2)Mn_2(CO)_6$ molecule.

electrostatic printer/plotter, and (d) a locally modified version of the XTL conversational crystallographic program package.

The function $w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement. The weights, w, are defined in eq 1. The discrepancy

$$w = [\{\sigma_c(|F_o|)\}^2 + \{P|F_o|\}^2]^{-1} \qquad (1)$$

indices, R_F and R_{wF}, and the "goodness-of-fit" are defined in eq 2–4.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100\ (\%) \qquad (2)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \qquad (3)$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \qquad (4)$$

The analytical form of the scattering factors for neutral manganese, oxygen, carbon, and hydrogen[11a] were used during the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[11b] were included in the calculations.

Data were placed on an (approximate) absolute scale by means of a Wilson plot which also provided the average overall thermal parameter ($\bar{B}$ = 3.49 Å^2).

The structure was solved by direct methods (using MULTAN, which resulted in the location of the two manganese atoms). Routine difference-Fourier and least-squares refinement techniques (using isotropic thermal parameters) led to the location of all nonhydrogen atoms and convergence with R_F = 8.6%, R_{wF} = 7.9%, and GOF = 3.69.

Refinement was continued using anisotropic thermal parameters for manganese and oxygen atoms and isotropic thermal parameters for carbon atoms; convergence was reached with R_F = 7.3%, R_{wF} = 5.9%, and GOF = 2.76. A difference-Fourier synthesis at this stage failed to provide definitive evidence for the positions of the hydrogen atoms. The eight hydrogen atoms associated with the aromatic system were therefore placed in calculated positions based upon d(C–H) = 0.95 Å;[12] the hydrogen atoms of the methyl groups, whose positions are indeterminate, were not included in our calculations. Refinement was continued, leading to R_F = 6.9%, R_{wF} = 5.4%, and GOF = 2.57.

Since $P2_12_12_1$ is a noncentrosymmetric space group, it was necessary to test the chirality of the particular crystal used in the analysis. We therefore inverted all atomic positional coordinates [i.e., $(x, y, z) \rightarrow (-x, -y, -z)$] and refined to convergence [$(\Delta/\sigma)_{\max} < 0.005$] once more. The resulting discrepancy indices (R_F = 6.8%, R_{wF} = 5.3%, and GOF = 2.54) indicate that the inverted structure is the correct one. A final difference-Fourier synthesis had, as its highest feature, a peak of height 0.52 e Å^{-3}; the structure was declared both correct and complete.

Note that the number of observations (NO) was 1079 and the number of parameters varied (NV) was 161. The observation:variable ratio has the rather low value of 6.70:1. Refinement of anisotropic thermal parameters for the carbon atoms was deemed to be unwise, since it would reduce the NO:NV ratio to an unacceptably low value of 3.98:1 (i.e., 1079:271).

Final positional and isotropic thermal parameters are collected in Table II; anisotropic thermal parameters are listed in Table III.

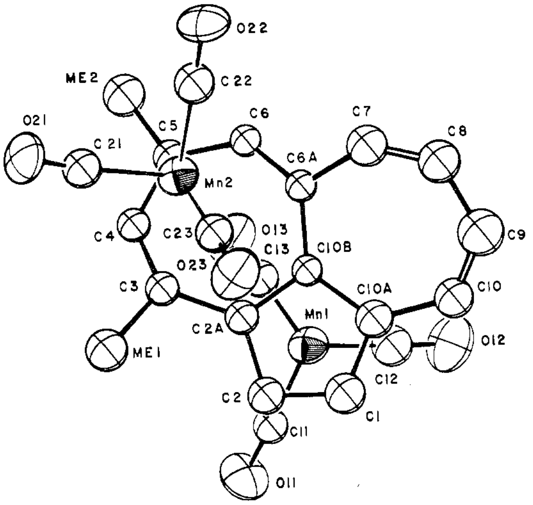


Figure 2. The $(C_{14}H_8Me_2)Mn_2(CO)_6$ molecule, projected onto its five-membered ring.

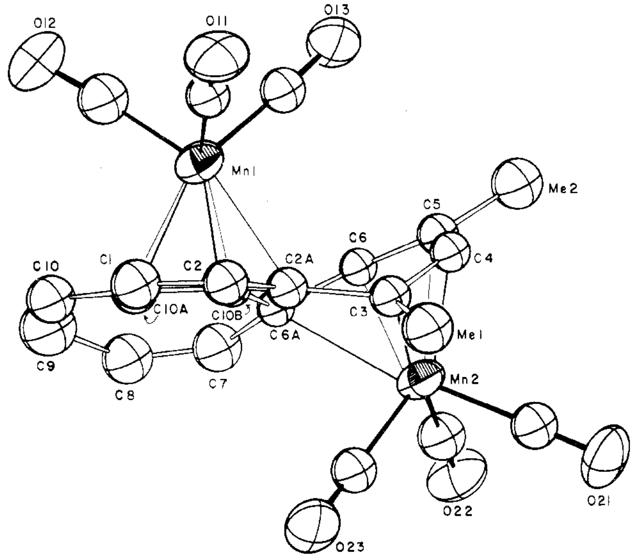


Figure 3. View of the $(C_{14}H_8Me_2)Mn_2(CO)_6$ molecule, showing the relative locations of the $Mn(CO)_3$ groups and the buckling of the aceheptylene system.

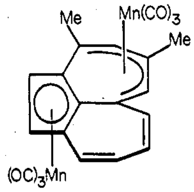
Results and Discussion

A stereoscopic view of the molecule appears as Figure 1. The labeling scheme and other facets of the molecular geometry are given in Figures 2 and 3, which show the molecule projected onto its five-membered ring and another approximately perpendicular view. Interatomic distances and angles are given in Tables IV and V; least-squares planes (and deviations of atoms therefrom) are listed in Table VI.

Table II. Final Positional and Isotropic Thermal Parameters (with Esd's) for $(C_{14}H_8Me_2)Mn_2(CO)_6$

atom	x	y	z	B, Å^2
Mn(1)	−0.34884 (20)	−0.41418 (20)	−0.86916 (13)	*a*
Mn(2)	−0.80996 (19)	−0.41298 (18)	−0.75942 (13)	*a*
C(11)	−0.2311 (16)	−0.3110 (10)	−0.8746 (12)	3.0 (9)
O(11)	−0.1624 (11)	−0.2424 (9)	−0.8776 (8)	*a*
C(12)	−0.2219 (17)	−0.5031 (14)	−0.8938 (12)	4.1 (10)
O(12)	−0.1438 (12)	−0.5666 (10)	−0.9123 (8)	*a*
C(13)	−0.3251 (13)	−0.4276 (13)	−0.7554 (11)	3.3 (8)
O(13)	−0.3058 (12)	−0.4363 (10)	−0.6846 (7)	*a*
C(21)	−0.9260 (17)	−0.3187 (13)	−0.7136 (11)	3.5 (10)
O(21)	−1.0041 (14)	−0.2668 (9)	−0.6832 (7)	*a*
C(22)	−0.9338 (18)	−0.5052 (13)	−0.7273 (11)	3.8 (10)
O(22)	−1.0182 (12)	−0.5641 (9)	−0.7058 (7)	*a*
C(23)	−0.8701 (14)	−0.3945 (12)	−0.8675 (11)	3.3 (8)
O(23)	−0.9045 (11)	−0.3771 (9)	−0.9371 (8)	*a*
C(1)	−0.4549 (15)	−0.4022 (14)	−0.9848 (9)	3.9 (4)
C(2)	−0.4943 (16)	−0.3199 (11)	−0.9353 (10)	3.2 (4)
C(2A)	−0.5653 (15)	−0.3625 (11)	−0.8636 (10)	2.7 (3)
C(3)	−0.6376 (16)	−0.3052 (10)	−0.7951 (9)	2.7 (3)
C(4)	−0.6371 (15)	−0.3338 (11)	−0.7092 (9)	2.6 (3)
C(5)	−0.6386 (13)	−0.4309 (11)	−0.6733 (8)	2.8 (3)
C(6)	−0.6507 (14)	−0.5197 (10)	−0.7246 (9)	2.3 (3)
C(6A)	−0.6445 (16)	−0.5342 (10)	−0.8127 (9)	2.3 (3)
C(7)	−0.6858 (17)	−0.6331 (11)	−0.8432 (10)	4.0 (4)
C(8)	−0.6510 (16)	−0.6923 (12)	−0.9059 (9)	4.2 (4)
C(9)	−0.5421 (19)	−0.6757 (13)	−0.9716 (11)	5.2 (5)
C(10)	−0.4770 (15)	−0.5944 (13)	−0.9899 (8)	3.7 (3)
C(10A)	−0.4965 (19)	−0.4958 (13)	−0.9508 (10)	3.4 (4)
C(10B)	−0.5610 (14)	−0.4693 (10)	−0.8705 (10)	2.2 (3)
Me(1)	−0.6692 (19)	−0.1932 (11)	−0.8206 (10)	4.1 (4)
Me(2)	−0.6382 (15)	−0.4407 (11)	−0.5745 (9)	4.3 (4)
H(1)[b]	−0.4046	−0.3958	−1.0367	5.0[b]
H(2)	−0.4777	−0.2497	−0.9465	5.0
H(4)	−0.6355	−0.2790	−0.6694	5.0
H(6)	−0.6658	−0.5806	−0.6929	5.0
H(7)	−0.7564	−0.6623	−0.8088	5.0
H(8)	−0.7013	−0.7543	−0.9105	5.0
H(9)	−0.5179	−0.7340	−1.0045	5.0
H(10)	−0.4089	−0.5991	−1.0335	5.0

[a] See Table III for anisotropic thermal parameters. [b] Hydrogen atoms are in idealized positions and were assigned isotropic thermal parameters of 5.0 Å^2.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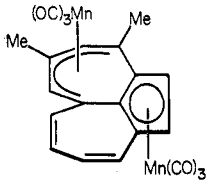
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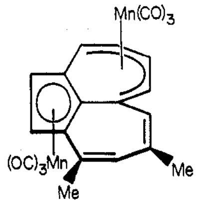
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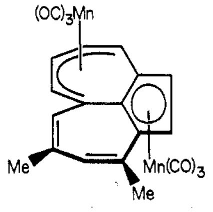
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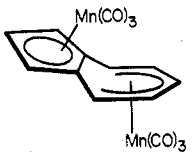
The molecule consists of two $Mn(CO)_3$ groups bonded to opposite sides of a 3,5-dimethylaceheptylene ligand. One $Mn(CO)_3$ group interacts with the carbon atoms of the five-membered ring via an η^5-cyclopentadienyl→metal linkage; the second $Mn(CO)_3$ is linked to the remaining five atoms of the dimethyl-substituted seven-membered ring via an acyclic η^5-dienyl→metal bond. (3,5-Dimethylaceheptylene)hexacarbonyldimanganese exists as two enantiomeric forms II and III. Since the space group $P2_12_12_1$ contains no operations of the second kind (i.e., no S_n axes), it follows that each crystal contains only one enantiomer and is therefore optically active. The particular crystal we selected for the analysis contained molecules of type II only. It is interesting to note that the *dimethyl-substituted* seven-membered ring is the one involved in the η^5-dienyl→manganese bonding. There is no evidence for the formation of isomers IV and V from the reaction of 3,5-dimethylaceheptylene with dimanganese decarbonyl.

Within the present $(C_{14}H_8Me_2)Mn_2(CO)_6$ molecule, the five-membered ring has a root-mean-square deviation from planarity of 0.022 Å. The pattern of deviations of atoms from the least-squares plane [i.e.: −0.011 (14) Å for C(1) and −0.006 (16) Å for C(2); +0.021 (15) Å for C(2A) and +0.023 (17) Å for C(10A); −0.027 (14) Å for C(10B)] suggests that the ring bends slightly about the C(2A)···C(10A) axis. Unfortunately, this effect is on the border line of statistical significance. Distances within the five-membered ring are equivalent and are consistent with its being regarded as a (substituted) η^5-cyclopentadienyl system. Individual carbon–carbon distances (cyclically) are C(1)–C(2) = 1.382 (22) Å, C(2)–C(2A) = 1.429 (22) Å, C(2A)–C(10B) = 1.403 (20) Å, C(10B)–C(10A) = 1.445 (22) Å, and C(10A)–C(1) = 1.395 (24) Å; the average value is 1.411 Å. In contrast to this, there is a considerable range of Mn(1)–C(ring) distances. Cyclically, these are as follows: Mn(1)–C(1) = 2.085 (14) Å, Mn(1)–C(2) = 2.139 (15) Å, Mn(1)–C(2A) = 2.203 (14) Å, Mn(1)–C(10B) = 2.177 (14) Å, and Mn(1)–C(10A) = 2.194 (17) Å. We ascribe these variations to crystal packing forces, since Mn–C distances for the five-membered ring in $(azulene)Mn_2(CO)_6$ (VI) range only from 2.151 (10) to 2.186 (9) Å,[13] while in $[(azulene)Mn(CO)_3]_2$ (VII), Mn–C distances show an intermediate range—from 2.127 (3) to 2.178 (2) Å and from 2.128 (3) to 2.191 (2) Å for the two independent five-membered rings.[2] There is certainly no *electronic* explanation for these observations.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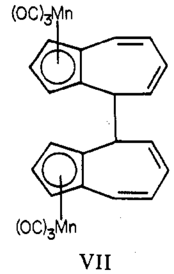
VII

Table III. Anisotropic Thermal Parameters[a] (with Esd's) for $(C_{14}H_8Me_2)Mn_2(CO)_6$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	2.36 (10)	3.97 (11)	3.99 (11)	−0.12 (13)	0.29 (9)	0.16 (13)
Mn(2)	2.21 (9)	4.02 (10)	3.80 (11)	0.34 (12)	0.04 (9)	0.27 (12)
O(11)	3.6 (6)	4.8 (6)	7.3 (7)	−1.6 (6)	−0.4 (6)	−0.5 (7)
O(12)	4.2 (7)	7.7 (8)	7.3 (7)	1.6 (8)	1.0 (6)	−0.8 (8)
O(13)	4.8 (6)	7.1 (8)	3.6 (6)	1.9 (7)	−0.6 (6)	0.7 (7)
O(21)	5.6 (8)	5.1 (7)	5.5 (7)	2.6 (7)	1.1 (6)	0.1 (6)
O(22)	3.3 (6)	5.9 (8)	5.8 (7)	−0.8 (6)	1.1 (5)	1.2 (6)
O(23)	5.4 (7)	6.7 (8)	4.1 (6)	2.6 (6)	−0.4 (5)	1.0 (6)

[a] The anisotropic thermal parameters (Å^2) enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Table IV. Intramolecular Distances and Esd's for $(C_{14}H_8Me_2)Mn_2(CO)_6$ (Å)

(A) Distances from the Manganese Atoms			
Mn(1)-C(11)	1.770 (14)	Mn(2)-C(21)	1.817 (17)
Mn(1)-C(12)	1.736 (18)	Mn(2)-C(22)	1.774 (17)
Mn(1)-C(13)	1.802 (17)	Mn(2)-C(23)	1.803 (16)
Mn(1)-C(1)	2.085 (14)	Mn(2)-C(3)	2.256 (15)
Mn(1)-C(2)	2.139 (15)	Mn(2)-C(4)	2.119 (14)
Mn(1)-C(2A)	2.203 (14)	Mn(2)-C(5)	2.149 (13)
Mn(1)-C(10A)	2.194 (17)	Mn(2)-C(6)	2.151 (13)
Mn(1)-C(10B)	2.177 (14)	Mn(2)-C(6A)	2.404 (14)
(B) Distances within the Carbonyl Ligands			
C(11)-O(11)	1.118 (18)	C(21)-O(21)	1.222 (21)
C(12)-O(12)	1.160 (22)	C(22)-O(22)	1.173 (21)
C(13)-O(13)	1.129 (20)	C(23)-O(23)	1.162 (20)
(C) Carbon-Carbon Distances within Aceheptylene Ligand			
C(1)-C(2)	1.382 (22)	C(5)-Me(2)	1.552 (19)
C(1)-C(10A)	1.395 (24)	C(6)-C(6A)	1.393 (20)
C(2)-C(2A)	1.429 (22)	C(6A)-C(7)	1.437 (20)
C(2A)-C(3)	1.483 (21)	C(6A)-C(10B)	1.481 (20)
C(2A)-C(10B)	1.403 (20)	C(7)-C(8)	1.294 (21)
C(3)-C(4)	1.395 (20)	C(8)-C(9)	1.488 (23)
C(3)-Me(1)	1.550 (20)	C(9)-C(10)	1.269 (24)
C(4)-C(5)	1.390 (19)	C(10)-C(10A)	1.442 (23)
C(5)-C(6)	1.417 (19)	C(10A)-C(10B)	1.445 (22)

Table V. Interatomic Angles (with Esd's) for $(C_{14}H_8Me_2)Mn_2(CO)_6$ (deg)

(A) Angles Involving the Manganese Atoms			
C(11)-Mn(1)-C(12)	92.7 (8)	C(21)-Mn(2)-C(22)	86.2 (8)
C(11)-Mn(1)-C(13)	92.3 (7)	C(21)-Mn(2)-C(23)	94.5 (7)
C(12)-Mn(1)-C(13)	93.6 (8)	C(22)-Mn(2)-C(23)	98.0 (8)
(B) Mn-C-O Angles			
Mn(1)-C(11)-O(11)	176.4 (14)	Mn(2)-C(21)-O(21)	174.4 (15)
Mn(1)-C(12)-O(12)	175.6 (16)	Mn(2)-C(22)-O(22)	178.2 (15)
Mn(1)-C(13)-O(13)	177.8 (14)	Mn(2)-C(23)-O(23)	175.9 (14)
(C) Angles within the Five-Membered Ring			
C(10A)-C(1)-C(2)	113.1 (14)	C(2A)-C(10B)-C(10A)	108.6 (13)
C(1)-C(2)-C(2A)	105.5 (13)		
C(2)-C(2A)-C(10B)	108.3 (13)	C(10B)-C(10A)-C(1)	104.2 (14)
(D) Angles within Seven-Membered Rings			
C(10B)-C(2A)-C(3)	125.1 (13)	C(10A)-C(10)-C(9)	126.3 (15)
C(2A)-C(3)-C(4)	123.9 (13)		
C(3)-C(4)-C(5)	129.4 (13)	C(10)-C(9)-C(8)	129.0 (16)
C(4)-C(5)-C(6)	121.6 (12)	C(9)-C(8)-C(7)	128.3 (15)
C(5)-C(6)-C(6A)	131.9 (13)	C(8)-C(7)-C(6A)	136.0 (15)
C(6)-C(6A)-C(10B)	123.3 (13)	C(7)-C(6A)-C(10B)	117.8 (13)
C(6A)-C(10B)-C(2A)	120.6 (13)		
C(10B)-C(10A)-C(10)	129.8 (15)	C(6A)-C(10B)-C(10A)	128.9 (13)
(E) External Angles Involving Methyl Groups Etc.			
C(2A)-C(3)-Me(1)	112.7 (13)	C(4)-C(5)-Me(2)	118.5 (12)
C(4)-C(3)-Me(1)	120.2 (13)	C(6)-C(5)-Me(2)	119.7 (12)
C(2)-C(2A)-C(3)	126.5 (13)	C(1)-C(10A)-C(10)	126.0 (15)
C(6)-C(6A)-C(7)	116.1 (13)		

Table VI. Least-Squares Planes and Deviations of Atoms Therefrom

atom	dev, Å	atom	dev, Å
Plane I: Five-Membered Ring ($\chi^2 = 8.43$)			
$-0.8720X + 0.0467Y - 0.4873Z - 11.109 = 0$[a]			
C(1)*	−0.011 (14)	Mn(1)	−1.795 (2)
C(2)*	−0.006 (16)		
C(2A)*	0.021 (15)	C(3)	0.145 (15)
C(10B)*	−0.027 (14)	C(6A)	0.197 (15)
C(10A)*	0.023 (17)	C(10)	0.096 (14)
Plane II: Dienyl System ($\chi^2 = 20.10$)			
$0.9994X - 0.0345Y - 0.0036Z + 5.973 = 0$			
C(3)*	−0.012 (16)	Me(1)	−0.366 (18)
C(4)*	0.002 (15)	C(2A)	0.717 (14)
C(5)*	0.029 (13)	Me(2)	0.031 (15)
C(6)*	−0.045 (13)		
C(6A)*	0.026 (15)	C(7)	−0.327 (16)
Mn(2)	−1.632 (2)	C(10B)	0.808 (14)
Plane III: Noncoordinated Diene System ($\chi^2 = 20.14$)			
$-0.7327X + 0.3394Y - 0.5899Z - 9.489 = 0$			
C(7)*	−0.021 (16)	C(6A)	−0.157 (14)
C(8)*	0.046 (15)		
C(9)*	−0.046 (18)		
C(10)*	0.022 (14)	C(10A)	0.239 (17)
		C(10B)	0.074 (14)
Plane IV: C(3)-C(2A)-C(10B)-C(6A) System ($\chi^2 = 9.29$)			
$-0.7944X + 0.0641Y - 0.6040Z - 12.170 = 0$			
C(3)*	−0.014 (15)	C(4)	−0.854 (14)
		Me(1)	0.564 (17)
C(2A)*	0.029 (15)	C(2)	0.196 (16)
C(10B)*	−0.028 (14)	C(10A)	0.211 (17)
C(6A)*	0.013 (15)	C(7)	0.536 (16)
		C(6)	−0.760 (14)
Dihedral Angles of Note			
plane I-plane II	150.61°	plane II-plane IV	142.56°

[a] Equations are in orthonormal coordinates ($X = ax$, $Y = by$, $Z = cz$).

The manganese atom Mn(1) lies −1.795 (2) Å from the plane of the five-membered ring. All substituents on the ring are bent *away* from the metal atom, individual deviations from planarity being +0.145 (15) Å for C(3), +0.197 (15) Å for C(6A), and +0.096 (14) Å for C(10).

Carbon–carbon distances within the (noncyclic) η^5-dienyl system are C(3)–C(4) = 1.395 (20) Å, C(4)–C(5) = 1.390 (19) Å, C(5)–C(6) = 1.417 (19) Å, and C(6)–C(6A) = 1.393 (20) Å. This system has a root-mean-square deviation from planarity of 0.030 Å. Individual manganese–carbon distances show a considerable range, with Mn(2)–C(3) = 2.256 (15) Å, Mn(2)–C(4) = 2.119 (14) Å, Mn(2)–C(5) = 2.149 (13) Å, Mn–C(6) = 2.151 (13) Å, and Mn–C(6A) = 2.404 (14) Å. The manganese atom Mn(2) lies −1.632 (2) Å from the least-squares plane calculated through the five atoms of the η^5-dienyl system. The substituent Me(2) is displaced only slightly from the least-squares plane, having a deviation of 0.031 (15) Å. Substituents at the ends of the η^5-dienyl system are subjected to systematic but symmetrical distortions. The "outer" terminal substituents of the η^5-dienyl system, Me(1) and C(7), are each displaced toward the manganese atom, with deviations of −0.366 (18) and −0.327 (16) Å, respectively; the "inner" substituents, C(2A) and C(10B), are displaced away from the manganese atom, with deviations of +0.717 (14) and +0.808 (14) Å, respectively.

The η^5-dienyl system makes a dihedral angle of 142.56° with the remainder of this seven-membered ring (i.e., with the system C(3)–C(2A)–C(10B)–C(6A)) and a dihedral angle of 150.61° with the η^5-cyclopentadienyl system. We note here that the dihedral angle between the η^5-dienyl and η^5-cyclopentadienyl planes in (azulene)$Mn_2(CO)_6$ (VI) is 141.2°.

The remaining seven-membered ring retains a noncoordinated *cis*-diene system in which bond distances are C(7)–C(8) = 1.294 (21) Å, C(8)–C(9) = 1.488 (23) Å, and C(9)–C(10) = 1.269 (24) Å.

The $Mn(CO)_3$ group associated with the five-membered ring is fairly symmetrical (close to C_{3v} symmetry) with OC–Mn–CO angles ranging from 92.3 (7) to 93.6 (8)°. The $Mn(CO)_3$ group linked to the η^5-dienyl system is far less symmetrical, individual angles being C(21)–Mn(2)–C(22) =

86.2 (8)°, C(21)–Mn(2)–C(23) = 94.5 (7)°, and C(22)–Mn(2)–C(23) = 98.0 (8)°. The (η^5-dienyl)Mn(CO)$_3$ moiety has close to C_s symmetry; the carbonyl group C(23)–O(23) lies almost between (and below) the ends of the η^5-dienyl system and the reduced OC–Mn–CO angle is between the other two carbonyl groups. A similar situation occurs both in (azulene)Mn$_2$(CO)$_6$[13] and in (η^5-cyclohexadienyl)tricarbonylmanganese.[14]

Finally we note that Mn–CO and C–O distances are normal and that the Mn–C–O systems are each close to linear.

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Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Notes

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Intervalence Transfer in the Pyrimidine-Bridged Dimer $[(bpy)_2ClRu(pym)RuCl(bpy)_2]^{3+}$

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In earlier work[1-5] we have shown that in mixed-valence complexes of the type $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$ (bpy is 2,2′-bipyridine, L = pyrazine (pyr), 4,4′-bipyridine (4,4′-bpy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE)) there are localized Ru(II) and Ru(III) sites, at least on the vibrational time scale. The optical spectra of these complexes include low-energy absorption bands which have been assigned to intervalence transfer (IT)[6] transitions (eq 1). In an IT transition,

$$[\mathrm{Ru(II)\text{–}Ru(III)}] \xrightarrow{h\nu} [\mathrm{Ru(III)\text{–}Ru(II)}]^* \qquad (1)$$

long-range optical electron transfer occurs between localized redox sites.[6] IT transitions have been treated theoretically by Hush[6] and the Ru(bpy) complexes have been used experimentally to demonstrate the predicted dependence of E_{op} (the energy of the IT band at λ_{max}) on solvent properties[2,4,5] and of E_{op} on the distance between redox sites.[4] The same experimental results using the Ru(bpy) complexes have also been valuable in pointing out the close relationship between inner-sphere electron transfer between redox sites where the extent of delocalization is slight and related outer-sphere electron-transfer processes.[2,4]

Since the dimeric Ru(bpy) systems have well-defined mixed-valence properties and a well-developed synthetic chemistry, they can be modified chemically in ways which allow for the study of the effects of relatively subtle molecular changes on mixed-valence properties. One of the most important variations is in the nature of the bridging ligand.[7] In the dimers $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$, the most likely orbital pathways for Ru(II)–Ru(III) interaction are through the mixing of dπ(Ru(II)) with π^*(L) orbitals which "carries" the excess electron across the bridging ligand to Ru(III) or the mixing of dπ(Ru(III)) and filled π(L) levels which leads to electron hole delocalization. If this view is correct, the electronic structure of the bridging ligand should play an important role in determining the extent of electron delocalization from Ru(II) to Ru(III) in the ground state.

We have prepared the dimeric complex $[(bpy)_2ClRu(pym)RuCl(bpy)_2]^{2+}$ where the bridging ligand is pyrimidine (pym) and have generated the 3+, mixed-valence ion in solution. The point of interest was the expected appearance of an IT band for the mixed-valence ion and then a comparison of its properties with the IT band for the pyrazine (pyr)-bridged dimer $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$. The Ru–Ru separation is shorter in the pyrimidine-bridged complex, but earlier work using pyrimidine as a ligand had suggested that the transmission of electronic effects between groups bound to meta-nitrogen atoms through the π^* system of the diazine ring can be relatively ineffective.[8,9]

Experimental Section

Measurements. Ultraviolet–visible spectra were obtained using Cary Model 14, Cary Model 17, and Bausch and Lomb Spectronic 210 spectrophotometers at room temperature. Near-infrared spectra were recorded on a Cary Model 17 spectrophotometer. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C using Pt bead electrodes and are uncorrected for junction potential effects. The measurements were made using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetric experiments.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[1,10] recrystallized twice from hot ethanol–water mixtures and vacuum dried at 70 °C for 10 h. Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Pyrimidine was purchased commercially and used without further purification. Elemental analyses were carried out by Integral Microanalytical Inc., Raleigh, N.C.

Preparations. $[(bpy)_2ClRu(pym)RuCl(bpy)_2](PF_6)_2\cdot H_2O$ (bpy Is 2,2′-Bipyridine and pym Is Pyrimidine). This complex was prepared using methods described earlier[1-3,11] for similar bis(bipyridine)ruthenium dimers. $[(bpy)_2ClRu(pym)](PF_6)$ was prepared from $[(bpy)_2ClRu(NO)](PF_6)_2$ (0.483 g, 0.628 mmol) by dissolving the nitrosyl complex in ~30 mL of acetone and adding, dropwise, KN$_3$ (0.051 g, 0.629 mmol) dissolved in a minimum (~5 mL) of methanol. After ~15 min of stirring in the dark, excess pyrimidine was added to the burgundy-colored solution and it was heated at reflux for 20 h. The acetone solution was then filtered through a glass frit to remove

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