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Crystal and Molecular Structure of *N*-Ferrocenylmethyl-*N*-methylaminomethylene(tetracarbonyl)manganese[1]

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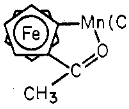
The crystal and molecular structure of *N*-ferrocenylmethyl-*N*-methylaminomethylene(tetracarbonyl)manganese, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2(CH_3)\overline{NCH_2Mn}(CO)_4$, has been determined by a three-dimensional x-ray diffraction study. The compound forms yellow crystals which are of the primitive space group $P2_12_12_1$, of the orthorhombic system, with $a = 10.152\ (2)$, $b = 21.348\ (4)$, and $c = 8.104\ (1)$ Å. Diffraction data were collected using Mo Kα radiation and a Syntex $P\bar{1}$ automated diffractometer. The structure was solved by use of Patterson and Fourier summations and was refined by full-matrix least-squares techniques to a conventional discrepancy factor $R = 0.057$ for 1271 unique nonzero reflections with $2\theta < 55°$. All atoms were located. The novel $\overline{Mn\text{–}N\text{–}C}$ metallocycle is best viewed as an aminomethylene group acting as a three-electron donor to the manganese atom. The principal distinguishing features are a C–N bond length of 1.42 (1) Å and a C–N–C bond angle of 110.4° for the groups bonded to the nitrogen atom. These parameters are similar to those found in the related $\overline{Ni\text{–}N\text{–}C}$ metallocycle obtained in the reaction of an iminium salt with a Ni^0 complex. The two cyclopentadienyl rings in the title compound are in an *eclipsed* conformation.

Introduction

A recent communication from these laboratories reported the metalation of acetylferrocene (**1**) and dimethylaminomethylferrocene (**2**) with pentacarbonylmethylmanganese (**3**) and -rhenium (**4**).[2] The product of each of these reactions, except that of **2** and **3**, was the homoannular metalation of ferrocene, i.e., product **5**. The metal–carbonyl infrared stretching vibrations and proton magnetic resonance indicated that the reaction of **2** with **3** had resulted in metalation of a methyl group to form a compound presumed to be **6**. Both prior and concurrent structural reports of metal–nitrogen–



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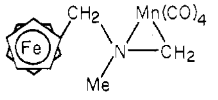
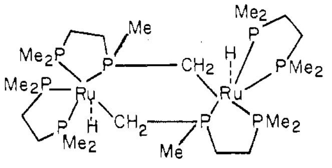


6

carbon rings[3,4] established precedents and analogues for structure **6**. However, since an early example of the metalation of a methyl group on phosphorus[5a] resulted not in the metal–phosphorus–carbon triangle but in the dimer **7**,[5b] an x-ray crystal study seemed advisable to demonstrate the structure of **6** conclusively. Recently, a compound of formula $Fe[P(CH_3)_3]_4$ has been isolated,[6] which on the basis of spectroscopic evidence is believed to contain a three-membered metallocyclic ring as shown in **8**.



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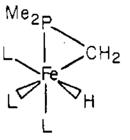


8, L = $P(CH_3)_3$

Experimental Section

A solution of the compound in hexane was cooled to −20 °C to obtain yellow crystals suitable for an x-ray structure determination. Since in air the compound slowly decomposed on exposure to x rays, crystals were sealed in glass capillaries for use in the x-ray study. Examination of preliminary oscillation and Weissenberg photographs showed orthorhombic symmetry and systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$. Thus the $P2_12_12_1$ space group was indicated.

The crystal chosen for intensity measurements was a fragment of a bar bounded by {100}, {010}, and {001}. Crystal dimensions normal to these faces were 0.30 × 0.20 × 0.15 mm. The crystal was mounted with the a axis close to the ϕ axis of a four-circle computer-controlled diffractometer (Syntex $P\bar{1}$ autodiffractometer) equipped with a scintillation counter and a graphite monochromator. Lattice parameters, determined by a least-squares fit of 15 accurately centered reflections, are $a = 10.152$ (2), $b = 21.348$ (4), and $c = 8.104$ (1) Å,[7] at room temperature, based on λ(Mo Kα) 0.71069 Å. The flotation density measured in bromobenzene–CCl_4 solution was 1.51 g/cm^3 at room temperature which compares with the calculated value of 1.55 g/cm^3 based on $Z = 4$. On this basis intensity data were collected using the θ–2θ scan technique, Mo Kα radiation, a scan rate of 2°/min, and a scan range from 1.0° below the Kα_1 peak to 1.0° above the Kα_2 peak. The takeoff angle was 4°, and background counts were recorded for half the scan time at each end of the scan range. The pulse-height analyzer was set at an 85% window for Mo Kα radiation.

Intensities of three reference reflections (0,12,0, 105, and 400) were checked after every 97 intensity measurements. The intensities of the standards showed only variations consistent with their respective $\sigma(I)$ values. A total of 2433 intensities accessible in one octant with $2\theta \leq 55°$ were collected. After eliminating 27 space group absences and 78 recordings of the reference reflections, those reflections for which $I \geq 3.0\sigma(I)$ were retained as observed data. Thus 1271 unique, observed reflections were used in the structural solution and refinement. Of the 560 reflections with $50 < 2\theta < 55°$, only 47 were retained as observed data.

The data reduction was achieved by PI BAR[8a] and processed as previously described.[8b]

The calculated value of μ(Mo Kα radiation) is 16.6 cm^{-1}. The calculated maximum and minimum transmission factors are 0.80 and 0.72; absorption effects could have caused errors of no more than ~2.5% in the values of $|F_o|$. No corrections for the effects of absorption were made.

Determination and Refinement of the Structure

A three-dimensional Patterson summation[8] resulted in location of the heavy atoms (Fe and Mn). A Fourier synthesis[8] phased on these two atoms served to locate the other 22 nonhydrogen atoms. Two cycles of least-squares refinement with isotropic temperature parameters followed by three cycles of least-squares refinement in which the temperature factors for the iron atom, the manganese atom, and the carbon and oxygen atoms of the carbonyl groups were allowed to refine anisotropically resulted in discrepancy factors $R_1 = 0.077$ and $R_2 = 0.090$.[9]

Molecular geometry calculations[8] indicated the planarity of the five carbon atoms of each cyclopentadienyl ring. Further refinement treated each of the cyclopentadienyl rings (C_5H_4 and C_5H_5) as a rigid group, consisting of a regular pentagon of carbon atoms with C–C distances of 1.42 Å and C–H lengths of 1.00 Å. Each cyclopentadienyl hydrogen atom was assigned a thermal parameter one unit greater than that of the carbon to which it is attached. After another cycle of least-squares refinement, the methylene and methyl hydrogen atoms were located on a difference Fourier map. The positions of all seven hydrogen atoms were established with the aid of HPOSN.[8a] Temperature factors were assigned to these hydrogen atoms in the same manner as described above. The methyl group was treated as a rigid group with all H–C–H angles tetrahedral and all C–H lengths equal to 1.00 Å. In further least-squares refinement in which methylene hydrogen atom positions were fixed, the discrepancy factors converged to final values of $R_1 = 0.057$ and $R_2 = 0.061$. A cycle of least squares in which the thermal parameters of the nitrogen and the methylene carbons were allowed to vary anisotropically produced only minor changes (within 3σ) of the positional parameters and no change in the values of R_1 and R_2 cited above.

The refinement involved full-matrix least-squares procedures with anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) applied to the form factors of iron and manganese.[10] The atomic scattering factors used for all nonhydrogen atoms are those of Hanson et al.,[11] while those employed for hydrogen were derived from Stewart and co-workers.[12] Structure factors were calculated for all unique reflections on the basis of the final positional and thermal parameters. These are available as Table I.[13] In the final cycle of least-squares refinement the largest shift of a nongroup, nonhydrogen positional parameter was 0.34σ and of a thermal parameter was 0.32σ. The "goodness of fit" defined $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ was 1.84. In this expression $N_o = 1271$, the number of observed reflections used in the refinement, and $N_v = 132$, the number of parameters varied. The final difference Fourier map showed residuals in the range −0.33 to +0.54 e/Å^3, which were randomly dispersed throughout the map.

An analysis of the values of $d = ||F_o| - |F_c||/\sigma(F_o)$ for the 1057 unobserved reflections showed the following distribution: $d = 0$ to 1, 80.2%; $d = 1$ to 2, 14.0%; $d = 2$ to 3, 4.9%; $d = 3$ to 4, 0.7%. Two reflections had values of d greater than 4, with a maximum value of 4.40.

Results

The final least-squares positional and thermal parameters are given with their standard deviations in Tables II and III, respectively. The positional parameters for rigid groups are given in Table IV, and the thermal parameters and derived positions of the atoms of the rigid groups are given in Table V. Tables VI and VII list selected intramolecular distances and angles, respectively. In Table VIII the equations for a number of least-squares planes are given followed by some pertinent interplanar angles, and in Table IX the deviation of selected atoms from these various planes is given.

ORTEP plots in Figures 1 and 2 indicate the numbering system adhered to throughout these tables and the Discussion. They, with the packing diagram in Figure 3, graphically depict the molecular geometry described below. A stereoview of the unit cell is depicted in Figure 4, supplementary material. In addition it should be pointed out that C_5 and C_7 are methylene carbon atoms with hydrogen atoms H_{25} and H_{35} attached to C_5 and H_{27} and H_{37} to C_7. Also the methyl carbon atom C_6 is bonded to hydrogen atoms H_{26}, H_{36}, and H_{46}. Hydrogen

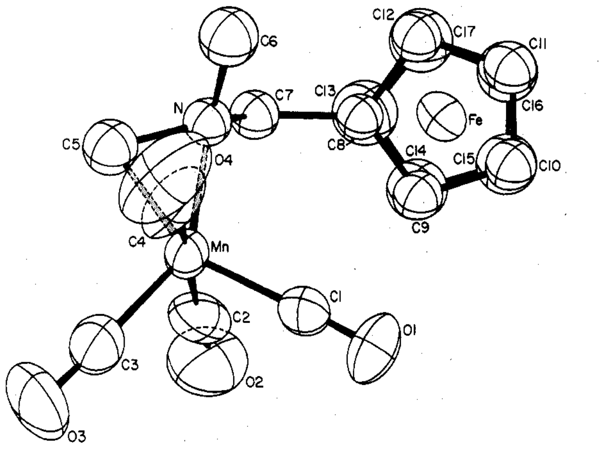


Figure 1. ORTEP plot of $FcCH_2(CH_3)\overline{NCH_2Mn}(CO)_4$, viewed perpendicular to the plane of the C_5H_4 ring and with its centroid as the focal point. Thermal ellipsoids represent 50% probability.

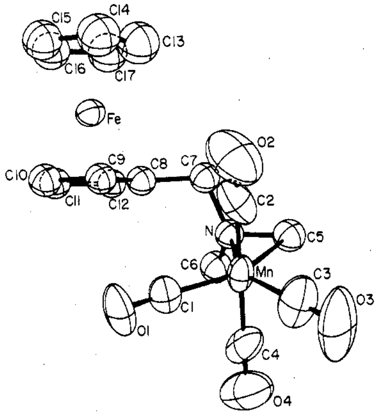


Figure 2. ORTEP plot of $FcCH_2(CH_3)\overline{NCH_2Mn}(CO)_4$, viewed parallel to the plane of C_5H_4 and with the nitrogen atom as the focal point. Thermal ellipsoids represent 50% probability.

atoms H_9 through H_{17} are attached to cyclopentadienyl carbon atoms C_9 through C_{17}, respectively.

Discussion

The most interesting feature of the *N*-ferrocenylmethyl-*N*-methylaminomethylene(tetracarbonyl)manganese molecule is the manganese–nitrogen–carbon (C_5) system for which two canonical structure types may be considered. The first would be to regard the C–N system as an iminium cation π bonded to a tetracarbonylmanganese anion. This would require

Table II. Atomic Positional Parameters[a]

Atom	*x*	*y*	*z*
Fe	0.4447 (1)	0.16542 (6)	0.4479 (2)
Mn	0.5000 (2)	−0.09496 (6)	0.4767 (2)
C_1	0.498 (1)	−0.0755 (4)	0.254 (1)
C_2	0.329 (1)	−0.0648 (6)	0.483 (2)
C_3	0.429 (2)	−0.1711 (5)	0.483 (2)
C_4	0.664 (2)	−0.1318 (5)	0.448 (2)
C_5	0.535 (1)	−0.0712 (5)	0.719 (1)
C_7	0.507 (1)	0.0383 (4)	0.629 (1)
N	0.579 (1)	−0.0223 (3)	0.613 (1)
O_1	0.495 (1)	−0.0664 (4)	0.119 (1)
O_2	0.223 (1)	−0.0502 (6)	0.479 (2)
O_3	0.393 (1)	−0.2212 (4)	0.488 (1)
O_4	0.759 (1)	−0.1572 (5)	0.421 (1)
H_{25}[b]	0.605	−0.097	0.783
H_{35}[b]	0.459	−0.064	0.797
H_{27}[b]	0.539	0.060	0.734
H_{37}[b]	0.411	0.030	0.642

[a] The numbers given in parentheses here and in succeeding tables are the estimated deviations in least significant digits. [b] These hydrogen positional parameters were not refined.

Table III. Atomic Thermal Parameters (×10^4)[a]

Atom	β_{11} (or B, Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	93 (2)	18.2 (3)	201 (3)	3.5 (7)	13 (2)	−0.5 (9)
Mn	162 (2)	18.7 (3)	112 (2)	−8.8 (8)	−13 (3)	1.7 (8)
C_1	146 (15)	22 (3)	157 (18)	−14 (6)	−9 (17)	−4 (6)
C_2	162 (18)	39 (4)	173 (25)	−31 (7)	34 (21)	−22 (8)
C_3	293 (24)	29 (3)	183 (23)	−21 (8)	−67 (21)	9 (8)
C_4	259 (24)	30 (3)	175 (25)	35 (8)	−90 (25)	−3 (8)
C_5	5.1 (3)					
C_7	4.3 (2)					
N	3.9 (2)					
O_1	249 (16)	53 (3)	105 (13)	−14 (6)	6 (15)	14 (5)
O_2	123 (12)	79 (4)	385 (30)	−19 (6)	35 (19)	1 (10)
O_3	547 (31)	35 (3)	348 (27)	−86 (8)	−55 (26)	21 (8)
O_4	313 (21)	54 (4)	306 (24)	71 (7)	−85 (19)	−27 (8)
H_{25}	5.8[b]					
H_{35}	5.8[b]					
H_{27}	5.2[b]					
H_{37}	5.2[b]					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] These values of B were assigned and were not refined.

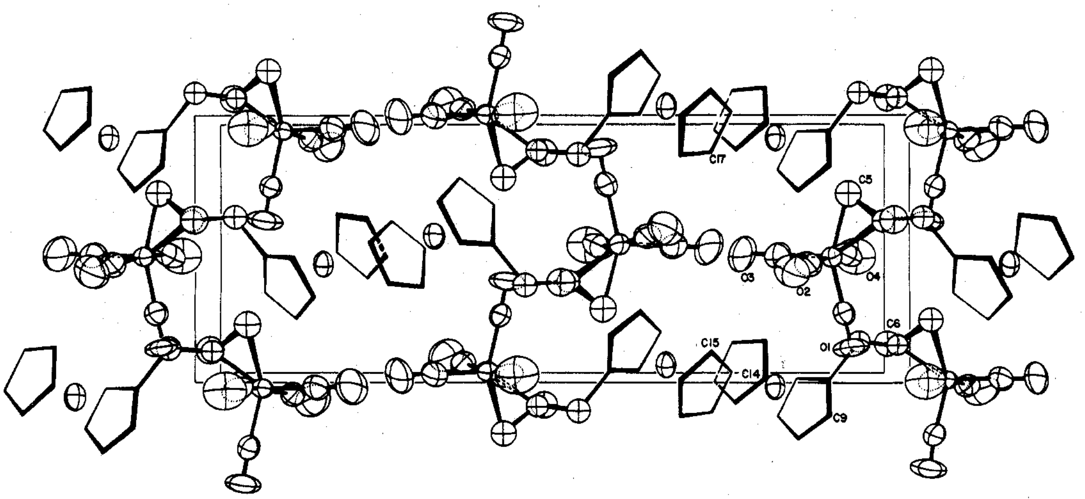


Figure 3. Unit cell, viewed along the *a* axis. Thermal ellipsoids represent 50% probability but for clarity have not been included for the cyclopentadienyl carbons. Oxygen atoms and carbon atoms bearing hydrogen atoms involved in close intermolecular contacts are labeled (see text).

Table IV. Group Parameters[a]

Group	x	y	z	ϕ	θ	ρ
Cp 1 (C_5H_4)	0.5314 (7)	0.0808 (3)	0.4824 (7)	−0.259 (7)	2.267 (4)	0.928 (7)
Cp 2 (C_5H_5)	0.3217 (10)	0.1826 (4)	0.6429 (10)	−0.245 (10)	2.227 (6)	0.921 (11)
Me (CH_3)	0.7212 (11)	−0.0119 (6)	0.6173 (15)	−1.8 (5)	1.8 (1)	1.8 (5)

[a] Definitions of these parameters are given by C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

Table V. Derived Positional and Isotropic Thermal Parameters for Group Atoms

Group	Atom	x	y	z	B, Å^2
Cp 1	C_8	0.5314	0.0808	0.4824	3.9 (2)
	C_9	0.4615	0.0813	0.3307	4.2 (2)
	C_{10}	0.5153	0.1296	0.2308	4.5 (2)
	C_{11}	0.6182	0.1588	0.3206	4.7 (2)
	C_{12}	0.6282	0.1286	0.4761	4.3 (2)
	H_9	0.388	0.053	0.300	5.3[a]
	H_{10}	0.486	0.141	0.117	5.6[a]
	H_{11}	0.674	0.194	0.281	6.0[a]
	H_{12}	0.692	0.139	0.566	5.2[a]
Cp 2	C_{13}	0.3217	0.1826	0.6429	8.5 (4)
	C_{14}	0.2502	0.1807	0.4926	7.3 (3)
	C_{15}	0.3018	0.2277	0.3870	8.6 (3)
	C_{16}	0.4051	0.2586	0.4720	7.0 (3)
	C_{17}	0.4175	0.2308	0.6302	7.8 (4)
	H_{13}	0.307	0.155	0.741	9.5[a]
	H_{14}	0.176	0.151	0.466	8.5[a]
	H_{15}	0.271	0.237	0.273	7.7[a]
	H_{16}	0.460	0.294	0.428	8.1[a]
	H_{17}	0.482	0.243	0.717	8.8[a]
				Group	5.8 (3)
Me	C_6	0.7212	−0.0119	0.6173	+0.0
	H_{26}	0.733	−0.009	0.740	+1.0
	H_{36}	0.764	−0.051	0.575	+1.0
	H_{46}	0.763	0.026	0.565	+1.0

[a] These values of B were assigned and not allowed to refine.

Table VI. Selected Intramolecular Distances (Å)

Mn–Fe	5.573 (2)	N–C_6	1.46[b]
Mn–C_1	1.85 (1)	N–C_7	1.49 (1)
Mn–C_2	1.84 (2)	C_7–C_8	1.52[b]
Mn–C_3	1.79 (1)	C_5–H_{25}	1.04[b]
Mn–C_4	1.87 (2)	C_5–H_{35}	1.01[b]
Mn–C_5	2.05 (1)	C_7–H_{27}	1.02[b]
Mn···C_6	3.07 (1)	C_7–H_{37}	1.00[b]
Mn–N	2.05 (1)	C–C for Cp's[a]	1.42[b]
C_1–O_1	1.11 (1)	C–H for Cp's[a]	1.00[b]
C_2–O_2	1.12 (1)	C–H for Me[a]	1.00[b]
C_3–O_3	1.13 (1)	Cent 1[a]–Fe	1.64[b]
C_4–O_4	1.12 (1)	Cent 2[a]–Fe	1.64[b]
N–C_5	1.42 (1)	Cent 1–Cent 2[a]	3.29[b]

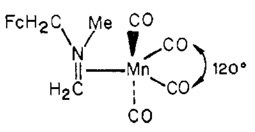
[a] Key: Cp = cyclopentadienyl; Me = methyl; Cent 1 = centroid of plane for Cp 1; Cent 2 = centroid of plane for Cp 2. [b] Standard deviations are not given for distances involving atoms treated as rigid groups.

Table VII. Selected Intramolecular Angles (deg)

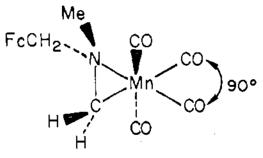
C_1–Mn–C_2	87.0 (6)	Mn–N–C_7	120.4 (6)
C_1–Mn–C_3	102.9 (5)	C_5–N–C_6	114[a]
C_1–Mn–C_4	88.8 (6)	C_5–N–C_7	115.7 (8)
C_1–Mn–C_5	152.1 (4)	C_6–N–C_7	110[a]
C_1–Mn–N	111.7 (4)	N–C_7–C_8	112[a]
C_2–Mn–C_3	86.2 (6)	Mn–C_5–H_{25}	118[a]
C_2–Mn–C_4	171.9 (5)	Mn–C_5–H_{35}	120[a]
C_2–Mn–C_5	93.1 (5)	N–C_5–H_{25}	118[a]
C_2–Mn–N	95.6 (4)	N–C_5–H_{35}	121[a]
C_3–Mn–C_4	88.0 (6)	H_{25}–C_5–H_{35}	106[a]
C_3–Mn–C_5	104.9 (5)	N–C_6–H_{26}	98[a]
C_3–Mn–N	145.4 (4)	N–C_6–H_{36}	107[a]
C_4–Mn–C_5	93.9 (5)	N–C_6–H_{46}	122[a]
C_4–Mn–N	92.4 (5)	H–C_6–H(Me)	109[a]
C_5–Mn–N	40.5 (3)	N–C_7–H_{27}	109[a]
Mn–C_1–O_1	177 (1)	N–C_7–H_{37}	110[a]
Mn–C_2–O_2	175 (1)	H_{27}–C_7–H_{37}	108[a]
Mn–C_3–O_3	176 (2)	C_8–C_7–H_{27}	109[a]
Mn–C_4–O_4	175 (1)	C_8–C_7–H_{37}	110[a]
Mn–C_5–N	69.8 (6)	C_7–C_8–Cent 1	178[a]
Mn–N–C_5	69.7 (5)	C_8–Cent 1–Fe	89[a]
Mn–N–C_6	121[a]	Cent 1–Fe–Cent 2	176[a]
Mn–C_5–N–C_7[b]	115.3	Mn–C_5–N–C_6[b]	115.5

[a] Standard deviations are not given for angles involving atoms which are members of rigid group. [b] Torsion angles.

trigonal-bipyramidal (tbp) geometry about manganese (structure I). In the second extreme, we would regard the N-disubstituted aminomethylene group as a three-electron donor to a neutral tetracarbonylmanganese group with a dative bond from nitrogen to manganese and a σ bond between carbon (C_5) and manganese. This would require octahedral geometry about manganese (structure II) with possible distortion due to the angle strain in the three-membered metallocycle.



I

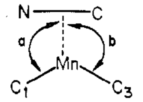


II

Fc = ferrocenyl

Octahedral geometry is the most common for manganese carbonyl derivatives, and structural examples of distorted octahedral configuration about manganese exist. Most of these do not possess three-membered rings and thus are expected to be less distorted than the present case. Nitrosyltetracarbonylmanganese is an example of trigonal-bipyramidal (tbp) geometry at manganese;[14] also, the isoelectronic (olefin)tetracarbonyliron[15-17] compounds offer prototypes for tbp geometry, and their structure elucidations[15-17] (see ref 17 in particular) indicate that a coordinated π system is expected to be coplanar with the equatorial carbonyl groups (here C_3O_3 and C_1O_1).

With this knowledge various intramolecular angles and lengths can be predicted for each of the possible idealized geometries. In both geometries the axial carbonyl groups (C_2O_2 and C_4O_4) are expected to be mutually collinear and perpendicular to the plane of the other ligands on manganese. The equatorial carbonyl groups, C_1O_1 and C_3O_3, however, would ideally form a 90° angle at manganese for octahedral coordination, instead of 120° expected for trigonal-bipyramidal coordination. Likewise, the angles formed by the midpoint of C_5–N and either C_1 or C_3 at manganese (angles a and b, structure III) should each be 120° in the trigonal bipyramidal case, but 135° for the octahedron. Finally, a coordinated iminium ion would be expected to have a C_5–N distance slightly longer than the typical carbon–nitrogen double bond and an angle of 120° for C_7–N–C_6, while an amine acting as



III

Table VIII. Least-Squares Planes

Planes[a] Determined

Plane	*A*	*B*	*C*	*D*	Description of plane
A	−0.901 13	0.429 94	0.055 81	5.222 49	$Mn–C_5–N$
B	−0.911 21	0.400 49	0.096 46	5.057 50	$C_3–Mn–C_1$
C	−0.212 36	−0.651 25	0.728 54	−3.044 04	$C_2–Mn–C_4$
D	−0.005 99	−0.103 87	0.994 57	−4.957 89	$C_6–N–C_7$
E	−0.655 69	0.649 69	0.384 66	0.913 30	Cp 1[b]
F	−0.656 52	0.657 85	0.369 07	−2.343 33	Cp 2[c]

Interplanar Angle between Planes

A and B	2.99°	A and D	89.07°
A and C	92.75°	E and F	0.82°
B and C	89.83°		

Angle between normals to Planes through C_3, C_5, Mn and C_1, Mn, N: 1.06°

Angle between C-N and Normal to Plane through C_6, C_7, N: 47.2°

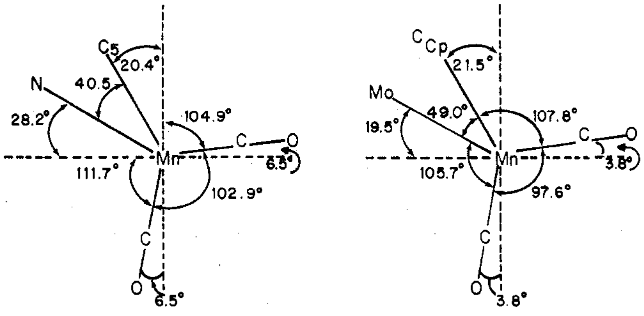
[a] Plane equation: $AX + BY + CZ + D = 0$. *X, Y,* and *Z* are in angstroms and refer to the orthogonal coordinates along *a, b,* and *c; D* is the distance of the plane from the origin, in angstroms. [b] Cp 1 = C_5H_4; position of centroid of Cp 1 = Cent, $x = 0.5509$, $y = 0.1158$, $z = 0.3681$. [c] Cp 2 = C_5H_5; position of centroid of Cp 2 = Cent 2, $x = 0.3392$, $y = 0.2161$, $z = 0.5249$.

Table IX. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

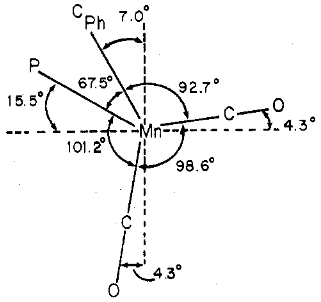
	Plane[b]			
Atom	A(C_5-MnN)	B(C_1-C_3Mn)	E(Cp 1)[c]	F(Cp 2)[c]
Mn	0	0		
C_1	85	0		
C_3	−58	0		
O_1	138	4		
O_3	−181	−86		
N	0	−8		
C_5	0	62		
Fe			1644	−1644
C_8			0	−3308
C_9			0	−3288
C_{10}			0	−3268
C_{11}			0	−3275
C_{12}			0	−3300
C_{13}			3309	0
C_{14}			3290	0
C_{15}			3268	0
C_{16}			3275	0
C_{17}			3300	0

[a] A negative deviation from a plane indicates that the atom with the coordinates given in Table II lies between that plane and the origin. [b] Least-squares planes described in Table VIII. [c] Both Cp 1 and Cp 2 have been constrained to be planar; they have been refined as rigid groups.

Scheme I



a. equatorial plane of **6** b. equatorial plane of **15a**



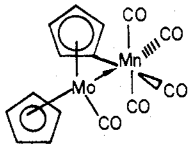
c. equatorial plane of **15b**

a three-electron donor should have a C_5–N distance comparable to a carbon–nitrogen single bond and a 109.5° angle for C_6–N–C_7. Table XII summarizes the idealized features and cites some structurally determined parameters for species which are exemplary of near ideal geometry.

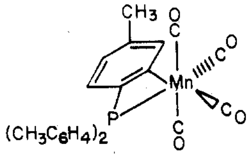
Comparison of the distances and angles in Table X indicates that compound **6** is intermediate between each of the given extremes. The bonding about nitrogen, however, indicates that it is closer to sp^3 hybridization than to sp^2. Also the C_5–N bond length in **6** (1.42 Å) is shorter than that of a carbon–nitrogen single bond (1.50 Å, see Table XI) but is much longer than a carbon–nitrogen double bond (1.24 Å, see Table X). In addition the C_6–N–C_7 angle here (110.4°) is quite close to the 109.5° expected for sp^3 hybridization. The equatorial C_1–Mn–C_3 angle of 102.9° is larger than that for idealized octahedral geometry but further still from idealized tbp. It is clear that the constraint of the 40.1° C_5–Mn–N angle might cause enlarging of the other equatorial angles in octahedral geometry but should *not* result in such a decreased angle for tbp geometry since the C–Fe–C angles of the olefin–carbon systems above are 39°,[15] 36–41 (1)°,[16b] and 38.6 (1)°[17] in compounds **9a**, **9b**, and **10**, respectively, while the corresponding angles between the opposing radial carbonyl groups are *108.1* (*6*)°,[15] *112* (*2*)°,[16b] *113.7* (*9*)°,[16a] and *115.1* (*2*)°,[17] respectively (see Table X).

In accordance with the structure, **6** is best viewed as containing an aminomethylene group acting as a three-electron donor to manganese, and the unusually small C_5–Mn–N angle results in considerable distortions of what otherwise could be regarded as an octahedron of ligands about manganese.

The structures of $(\eta^5\text{-}C_5H_5)(CO)\overline{Mo\text{-}\mu\text{-}(\eta^5\text{-}\eta^1\text{-}C_5H_4)\text{-}Mn}(CO)_4$, **15a**,[22] and $(CH_3C_6H_4)_2\overline{PC_6H_3(CH_3)Mn}(CO)_4$, **15b**,[8b] offer convenient examples of distorted octahedral geometry with which **6** can be compared. The relevant angles

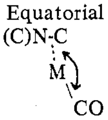
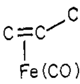
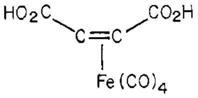
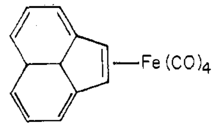
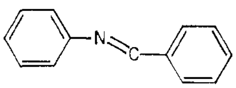
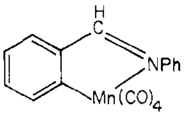
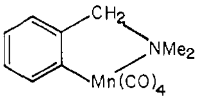


15a



15b

Table X. Ideal and Observed Intramolecular Distances (Å) and Angles (deg)

	Equatorial OC-M-CO angle	Equatorial  angle[a]	C-N bond length	C-N-C angle	Ref
(Iminium + Mn(CO)$_4^-$) idealized trigonal bipyramid	120	120	C=N	120	
Idealized octahedron (amine + Mn(CO)$_4$)	90	135	C−N	109.5	
 (9a)[b]	108.1 (6)				15
 (9b)[b]	(av) 112 (2) 113.7 (9)				16a (optically active form) 16b (racemic form)
 (10)[b]	115.1 (2)	124.1 121.5			17
NO(CO)$_4$Mn (11)[b]	118.9 (5)	120.6 (2)			14
			1.237 (3) (for C=N)		18
 (12)[c]	94.2 (4)	135.3 132.9	1.285 (10) (σ bound C=N)		19
 (13)[c]	93.1 (2)	132.7 134.2	1.489 (5) (-CH$_2$N)	108.5 (4) (Me-N-Me angle)	20
18			1.392 (6)	112.6 (4) (Me-N-Me)	4b
6	102.8 (5)	125.1 131.9	1.42 (1) (C$_5$-N)	110.4 (C$_6$-N-C$_7$)	This work

[a] Angles a and b in structure III. [b] Molecules of tbp geometry. [c] Molecules of octahedral geometry.

Table XI. Carbon-Nitrogen Single Bonds (Å)

	N-Me	N-CH$_2$-	Ref
13	1.496 (6) 1.509 (5)	1.489 (5)	20
$\mathrm{FcCH_2\overset{+}{N}H(Me)_2}$	1.50 (4), 1.53 (3)	1.51 (3), 1.53 (3)	21
14	1.48 (3), 1.54 (3)		

in the equatorial planes of the three compounds are presented in Scheme I.

In **15a** the C(Cp)–Mn–Mo angle of 49.0 (2)° and in **15b** the C(Ph)–Mn–P angle of 67.5 (3)° are both larger than the corresponding C$_5$–Mn–N angle of 40.5 (3)° in **6**. The former two are accompanied by smaller distortions in the opposite C(CO)–Mn–C(CO) angles, 97.6 and 98.6°, respectively, as that of 102.9° observed in **6**.

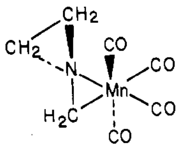
The axial carbonyl groups in **6** form angles at Mn of 86–89° with the equatorial carbonyl groups and of 92–96° with C$_5$ and N. Thus they too indicate a distortion from octahedral geometry, probably as a result of the rather gross distortion in the equatorial plane. This effect is not observed for compound **15**.

The three-membered C$_5$–Mn–N ring in **6** is symmetrical with equivalent C$_5$–Mn and N–Mn bonds, 2.05 Å, and Mn–C$_5$–N and Mn–N–C$_5$ angles, 69.7°. In the related compounds **16**,[3] **17**,[4a] and **18**,[4b] the M–C distance is at least 0.1 Å longer than the M–N length, while in all four examples the C–N distance is comparable (see Table XII).

Finally it should be noted that the cyclopentadienyl rings of the ferrocenyl portion of molecule **6** are nearly parallel and eclipsed. They show less than 1° of tilt from parallel and are only about 2° skewed from an eclipsed configuration. Small rotations from an eclipsed position have been noted for other monosubstituted ferrocenes, i.e., 7° in **14**[21] and 7° in FcCH=C(CN)$_2$.[23] Owing to the known low barrier for rotation in metallocene derivatives,[24] no great significance should be attributed to these observations.

Table XII. Structural Parameters for CMN Systems

Compd	M-C, Å	M-N, Å	C-N, Å	C-Mn-N, deg	Ref
16	2.09 (0.9)	1.98 (0.9)	1.45 (1.5)	Not reported	3
17	1.917 (14)	1.867 (10)	1.43 (2)	40.5 (5)	4a
18	1.884 (5)	1.920 (4)	1.392 (6)	42.9 (2)	4b
6	2.05 (1)	2.05 (1)	1.42 (1)	40.5 (3)	This study



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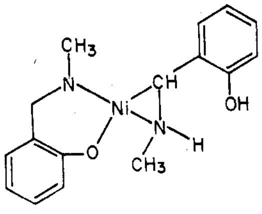

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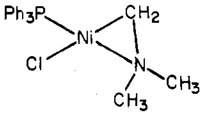

18

The structure of **6** indicates no unusual intermolecular contacts. The shortest intermolecular distances occur for O_1–H_{35} ($x, y, -1 + z$) 2.64 Å, O_1–H_{46} ($1.5 - x, -y, 0.5 + z$) 2.66 Å, O_1–H_{14} ($0.5 - x, -y, -0.5 + z$) 2.80 Å, O_2–H_9 ($0.5 - x, -y, 0.5 + z$) 2.83 Å, O_3–H_{17} ($1 - x, -0.5 + y, 1.5 - z$) 2.81 Å, and O_4–H_{15} ($1 - x, -0.5 + y, 0.5 - z$) 2.76 Å which compare with the sum of the van der Waals radii for oxygen and hydrogen of 2.6 Å.[25] These contacts are indicated in Figure 3. All intermolecular hydrogen–hydrogen distances are more than 0.20 Å greater than the value of 2.4 Å for the sum of the van der Waals radii of two hydrogen atoms.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Professor E. K. Barefield for a preprint of the study by himself and co-workers cited in this work.[4b] Computer time was furnished by the UCLA Campus Computing Network. The authors thank Dr. B. T. Huie for help in use of the diffractometer.

Registry No. **6**, 56725-20-3.

Supplementary Material Available: Figure 4, stereoview of unit cell, and Table I, the observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Taken in part from the dissertation of S. A. S. Crawford, UCLA, 1975. (b) This is part 13 in a series on metalation reactions; for part 12 see S. S. Crawford and H. D. Kaesz, *Inorg. Chem.*, preceding paper in this issue.

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(7) Numbers given in parentheses throughout this paper are the estimated standard deviations and refer to the last digit given. The automatic centering, indexing, and least-squares programs of the diffractometer were used to obtain these parameters and their estimated standard deviations.

(8) (a) The programs used in this work included locally written data reduction programs; JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs written by J. Blount; local version of ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; HPOSN (Hope) to calculate tentative hydrogen positions; ORTEP (Johnson) figure plotting; distances, angles, and error computations; all calculations were performed on the IBM 360-91 computer operated by the UCLA Campus Computing Network. (b) The reduction of diffractometer data is described in part 9 of this series: R. J. McKinney, C. B. Knobler, B. T. Huie, and H. D. Kaesz, *J. Am. Chem. Soc.*, **99**, 2988 (1977).

(9) Conventional R index, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; weighted residual factor $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where the weight $w = [1/\sigma(F_o)]^2$. The function $\sum w||F_o| - |F_c||^2$ was minimized.

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Spectroscopic Investigation of Aluminum Trihalide–Tetrahydrofuran Complexes. 1. Structure and Force Fields of the 1:1 and 1:2 Solid Compounds Formed by Aluminum Chloride or Bromide

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The infrared and Raman spectra of AlX_3·THF and AlX_3·2THF (X = Cl or Br) have been recorded. The vibrational analysis is based on the deuterium-isotope effect and on the halogen substitution. The 1:1 compounds have a molecular structure while the 1:2 derivatives correspond to the ionic arrangement $[AlX_2(THF)_4^+, AlX_4^-]$. A complete valence force field has been derived for each 1:1 complex, and a valence force field limited to the AlX_2O_4 part of each 1:2 complex has been estimated. The F(AlO) stretching force constants differ largely between the two types of complex and are consistent with known chemical properties. The main effect of coordination upon the force field is a decrease in the force constant of CO bonds.

Introduction

A structural investigation of coordination compounds formed between aluminum halides and various organic Lewis bases is in progress at the laboratory. The general purpose of this study is to describe the state of coordination of the aluminum atom in donor–acceptor complexes and to provide a way of