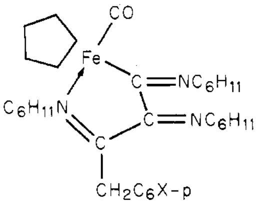
Table VI. Intermolecular Distances Less Than 3.5 Å

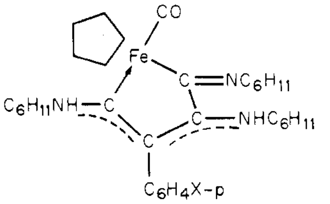
Bond from atom	Bond to atom[a]	Distance, Å	Bond from atom	Bond to atom[a]	Distance, Å
Fe	C(8)	2.882 (3)	C(4)	C(10)	2.906 (5)
Fe	C(9)	2.856 (3)	C(4)	N(3)	3.476 (5)
Fe	C(15)	3.466 (3)	C(5)	C(7)	2.870 (5)
Fe	N(1)	3.023 (3)	C(5)	N(1)	3.484 (5)
Fe	N(3)	2.869 (3)	C(6)	C(7)	2.607 (5)
Fe	O	2.876 (4)	C(6)	C(9)	3.490 (5)
C(1)	C(6)	3.154 (6)	C(6)	C(10)	2.621 (5)
C(1)	C(7)	3.290 (4)	C(6)	N(1)	3.373 (5)
C(1)	C(15)	3.494 (5)	C(6)	N(3)	3.311 (4)
C(2)	C(6)	2.939 (6)	C(7)	C(20)	3.461 (5)
C(3)	C(6)	3.372 (6)	C(7)	O	3.456 (5)
C(3)	C(10)	2.998 (5)	C(10)	O	3.495 (5)
C(3)	N(3)	3.176 (4)			
C(4)	C(7)	3.308 (5)			

[a] Of molecule I(000).

D_2O, attributable to two N–H groups. We reformulate the structure of the compounds (**4a** and **4b**) as **5a** and **5b**.



4a, X = H
b, X = Cl



5a, X = H
b, X = Cl

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Registry No. π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_2(CH_3)]$, 52346-55-1; π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$, 52346-57-3; $(CH_3)_3CNC$, 7188-38-7; **5a**, 57016-60-1; **5b**, 57016-61-2; **4a**, 35770-36-6; **4b**, 35770-37-7.

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

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(9) The absorption correction program ABS10 (by T. Ito) used the Gaussian integration method of Busing and Levy. The following programs were used during the course of the structural analyses: FANDFR, structure factor calculation and Fourier synthesis, Y. Iitaka; HBLS, structure factor calculation and block-diagonal least-squares refinement, T. Ashida; BOND, distances, angles, and least-squares planes, Y. Iitaka; ORTEP, thermal ellipsoid drawings, C. K. Johnson.
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Crystal Structure of 5-*exo*-CH_3-$C_5H_5Mn(CO)(NO)P(C_6H_5)_3$

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An accurate x-ray crystallographic structural study of a Mn–π-cyclopentadiene complex has been carried out. 5-*exo*-CH_3-$C_5H_5Mn(CO)(NO)P(C_6H_5)_3$ crystallizes in the space group $Pbca$ with $Z = 8$, $a = 17.969$ (53) Å, $b = 26.631$ (78) Å, and $c = 9.277$ (35) Å. Intensities of 2269 independent reflections were used in the refinement of the structure to an $R(F)$ of 0.057. The Mn is tetrahedrally coordinated to its ligands: PPh_3, CO, NO, and 5-*exo*-CH_3-C_5H_5. The PPh_3 fragment of the molecule is stereochemically well behaved, exhibiting no unusual distances or angles. The Mn–N–O and Mn–C–O groups are nearly linear with angles of 178.4 (5) and 174.8 (5)°, respectively. Observed Mn–C and Mn–N distances of 1.771 (7) and 1.674 (5) Å, respectively, are in good agreement with other unambiguous determinations of these parameters. The stereochemical consequence of the destruction of the aromaticity of the η^5-C_5H_5 ring by the introduction of the CH_3 group is a folding and shift of the ring in such a way that the Mn makes its closest approach (1.79 Å) to the newly created diene part of the ring and the newly introduced CH_3 group avoids steric interference with other parts of the molecule by acquiring the exo conformation.

Introduction

Brunner and Langer[2] have described the reactions of $[C_5H_5Mn(CO)(NO)P(C_6H_5)_3]PF_6$ with $LiCH_3$ and with $NaBH_4$. The former leads to the formation of a ring addition product, postulated[2] to be 5-*exo*-CH_3-$C_5H_5Mn(CO)(NO)$-$P(C_6H_5)_3$, and a carbonyl addition product $C_5H_5Mn(COCH_3)(NO)P(C_6H_5)_3$. The compounds were characterized by NMR and mass spectral measurements. In this report, we present structural proof that Brunner and Langer's postulate[2] of the exo-5 derivative for one of the two products of the reaction with $LiCH_3$ is correct. Furthermore, this study is the first example of a structural investigation of a Mn–π-cyclopentadiene complex.

Experimental Section

A well-shaped bright-red crystal suitable for x-ray diffraction studies was selected from material kindly supplied by Professor Henri Brunner.

Table I. Crystal Data[a]

$a = 17.969 \pm 0.053$ Å
$b = 26.631 \pm 0.078$
$c = 9.277 \pm 0.035$
$V = 4439.3$ Å^3
$d_{\text{measd}} = 1.355$ g cm^{-3}
$d_{\text{calcd}} = 1.362$ g cm^{-3}
$Z = 8$
$\mu = 7.18$ cm^{-1}

[a] 5-*exo*-CH_3-$C_5H_5Mn(CO)(NO)P(C_6H_5)_3$; fw = 455.37; space group P_{bca}; orthorhombic.

This crystal was bounded by seven faces with the following shapes and indices: two hexagonal faces, the $(\bar{1}00)$ and $(1\bar{1}0)$; two triangular faces, the $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$; two trapezoidal faces, the (011) and $(01\bar{1})$; and one rectangular face, the (010). The crystal faces were indexed by placing each in reflecting positions on a diffractometer so that observed values of 2θ, χ, and ϕ could be compared with the calculated values. Perpendicular distances from an origin chosen at the intersection of three faces, the $(1\bar{1}0)$, $(\bar{1}00)$ and $(0\bar{1}1)$, to the remaining faces were as follows: 0.223 mm to the (010); 0.342 mm to the $(01\bar{1})$; 0.235 mm to the $(0\bar{1}\bar{1})$; and, 0.061 mm to the (011). The volume of the data crystal was 0.00503 mm^3.

Preliminary Weissenberg and precession x-ray photographs established that the title compound is orthorhombic, belonging to space group P_{bca} as uniquely determined by the systematic extinctions, $0kl$ with $k = 2n + 1$, $h0l$ with $l = 2n + 1$, and $hk0$ with $h = 2n + 1$. Approximate unit-cell dimensions were refined by least-squares analysis using observed diffractometer data for 42 reflections, automatically centered under computer control. The crystal data are summarized in Table I.

Data Collection and Reduction

Using graphite monochromatized Mo Kα radiation (λ 0.71069 Å), intensity data were collected under computer control using the Brookhaven Multiple Spectrometer Control System.[3] The θ–2θ step-scan technique was used with the scan length determined by the function: $\Delta 2\theta = 1.2° (1 + 0.7 \tan \theta)$. The step size was chosen to give approximately 50 points in each scan. Data were collected out to $\sin \theta/\lambda = 0.668$ Å^{-1} and included measurements of many equivalent reflections over an entire hemisphere of reciprocal space. The total of 11080 integrated intensity measurements yielded a unique data set of 2297 observed intensities with $I > 3\sigma(I)$. I is the background corrected integrated intensity and $\sigma(I)$ is its esd based on counting statistics. Two standard reflections were measured at regular intervals to monitor the crystal and electronic stability. No corrective measures were required by the observed variations.

Background corrections were made using a method[4] which separates the peak and background in such a way that $\sigma(I)/I$ is minimized. Lorentz, polarization, and absorption corrections were applied to the data. Polarization due to the pyrolytic graphite monochromator crystal was neglected. The Gaussian integration method[5] with a grid of 512 points was used in the absorption correction calculations, where the crystal shape was represented by the seven rational boundary planes described above.

Structure Determination and Refinement

A three-dimensional sharpened Patterson map showed the position of the Mn atom in the unit cell. Subsequently, all other atoms in the molecule were revealed by Fourier and difference Fourier maps.

The full-matrix least-squares refinement of the structure proceeded in a straightforward manner. $R' = \sum w(|F_o| - |F_c|)^2$ was the quantity minimized, where F_o and F_c respectively are the observed and calculated structure amplitudes and $w = 1/\sigma_{(F_o)}{}^2$ is the weight for each reflection. $\sigma_{(F_o)}$ was given by $\sigma_{(F_o)} = (\sigma_{(F_o)}{}^2 + (0.075|F_o|)^2)^{1/2}$ with $\sigma_{(F_o)}{}^2$ based only on counting statistics.

During the isotropic refinement, the atomic position parameters and isotropic temperature factors for all atoms other than hydrogen were varied, together with a single scale factor. Following this, five anisotropic refinement cycles were computed in such a way that the number of variables did not exceed 270, the maximum for our least-squares program. Thus during these cycles, the atomic position parameters and anisotropic temperature factors were held fixed for some atoms while they were varied for others. All hydrogen atoms were kept isotropic ($B = 4.0$ Å^2) and their atomic positions were not varied. In fact, even though all hydrogen atoms were found in the difference Fourier maps, their positions were idealized in the structure factor calculations with all C–H distances set to 0.96 Å. In this way the hydrogen atoms were included in the structure factor calculation as a fixed contribution.

Table II. Summary of the Refinement

Cycle	No. of observations[a]	No. of variables	Error in an observation of unit wt[b]	R_1[c]	R_2[d]
1	2296	109	1.77	6.7	9.6
2	2297	217	1.67	6.2	8.8
3	2269	270	2.73	5.7	9.6
4	2269	1	2.56	5.7	9.6
5	2269	270	2.73	5.7	9.6

[a] Data were rejected if $|F_o - kF_c|/\sigma_{(F_o)} \geqslant 10.0$. [b] Error = $[\Sigma w(F_o - kF_c)^2/(m - n)]$ where m = total number of observations and n = total number of parameters varied. [c] $R_1 = \Sigma |F_o - kF_c|/\Sigma |F_o|$. [d] $R_2 = [\Sigma w(F_o - kF_c)^2]^{1/2}/(\Sigma w F_o{}^2)^{1/2}$.

Table III. Positional Parameters

Atom	x/a	y/b	z/c
Mn	0.08339 (5)	0.14288 (3)	0.08278 (10)
P	0.08699 (8)	0.10962 (6)	−0.14417 (17)
O(N)	0.2422 (3)	0.1521 (2)	0.1075 (6)
O(C)	0.0554 (4)	0.0563 (2)	0.2668 (7)
N	0.1760 (3)	0.1481 (2)	0.0952 (5)
C	0.0642 (4)	0.0894 (2)	0.1899 (8)
CC1	−0.0372 (4)	0.1727 (2)	0.2322 (7)
CC2	−0.0352 (4)	0.1613 (2)	0.0759 (7)
CC3	0.0100 (4)	0.1979 (2)	0.0075 (7)
CC4	0.0575 (4)	0.2173 (2)	0.1156 (8)
CC5	0.0396 (4)	0.1933 (2)	0.2453 (7)
C(Me)	−0.0987 (4)	0.2115 (3)	0.2736 (10)
CP1	−0.0039 (3)	0.1049 (2)	−0.2293 (6)
CP2	−0.0301 (4)	0.1412 (3)	−0.3236 (8)
CP3	−0.1042 (4)	0.1388 (3)	−0.3736 (9)
CP4	−0.1502 (4)	0.1012 (3)	−0.3275 (9)
CP5	−0.1237 (5)	0.0658 (3)	−0.2343 (9)
CP6	−0.0521 (4)	0.0674 (3)	−0.1835 (8)
CP7	0.1254 (3)	0.0467 (2)	−0.1639 (7)
CP8	0.1049 (4)	0.0147 (3)	−0.2803 (8)
CP9	0.1386 (6)	−0.0311 (3)	−0.2939 (11)
CP10	0.1934 (6)	−0.0457 (3)	−0.2018 (12)
CP11	0.2151 (5)	−0.0153 (3)	−0.0921 (11)
CP12	0.1806 (4)	0.0304 (3)	−0.0701 (8)
CP13	0.1438 (4)	0.1451 (2)	−0.2723 (6)
CP14	0.1532 (5)	0.1295 (3)	−0.4132 (9)
CP15	0.2003 (5)	0.1555 (4)	−0.5081 (9)
CP16	0.2371 (4)	0.1980 (4)	−0.4561 (10)
CP17	0.2284 (4)	0.2141 (3)	−0.3202 (9)
CP18	0.1812 (4)	0.1880 (3)	−0.2279 (7)

In the first of the five anisotropic cycles, the carbon atoms of the phenyl groups were not varied. In the second, the carbon atoms of the methylcyclopentadiene group were not varied. In the third cycle only the scale factor was not varied, while in the fourth only the scale factor was varied. Finally, in the fifth cycle again only the scale factor was not varied. Table II summarizes the refinement. All final results reported here are based on the parameter values at the end of cycle 5 of Table II. Throughout the refinement calculations, the atomic scattering curves of Cromer[6a] were used. The curves for Mn and P included corrections for anomalous dispersion.[6b]

During the refinement of the data, we had to make a choice as to which of the XO groups (X = C and N) was the carbonyl and which the nitrosyl. This is a standard problem in the case of x-ray diffraction work with molecules which contain these ligands and can only be resolved with certainty by neutron diffraction, where the scattering lengths of C and N are sufficiently different to permit a definite answer, provided no disorder exists. We have used the same criteria (thermal parameters, R factors) as Enemark and Ibers[7] to make a decision. In the spirit of these criteria, we differentiated between the C and N atoms of the CO and NO ligands. The fact that we find the Mn–N distance shorter than the Mn–C distance is very satisfying (see discussion).

Tables III, IV, and V respectively list the atomic position parameters, anisotropic temperature factors, and idealized hydrogen positions. Table VI (in the microfilm edition only) lists F_o, F_c, and $\sigma_{(F_o)}$ values. Bond lengths and angles are listed in Tables VII and VIII, respectively, and equations of least-squares planes through important groups of atoms are given in Table IX. The latter table also lists the deviations (in Å) of certain atoms from the plane.

Table IV. Thermal Parameters ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	19.6 (3)	9.8 (1)	69.0 (10)	1.2 (2)	−1.6 (5)	−2.7 (3)
P	18.9 (5)	8.4 (2)	80.9 (19)	−0.3 (3)	−2.3 (8)	−1.7 (5)
O(N)	17 (2)	20 (1)	158 (9)	0 (1)	−13 (3)	−1 (2)
O(C)	69 (3)	15 (1)	220 (12)	−2 (1)	18 (5)	29 (3)
N	24 (2)	11 (1)	74 (6)	0 (1)	5 (3)	−2 (2)
C	32 (3)	8 (1)	102 (9)	2 (1)	5 (4)	6 (2)
CC1	27 (2)	12 (1)	84 (8)	−2 (1)	14 (3)	3 (2)
CC2	19 (2)	13 (1)	110 (9)	2 (1)	−4 (4)	−8 (3)
CC3	25 (2)	11 (1)	87 (8)	4 (1)	6 (4)	−1 (2)
CC4	28 (2)	10 (1)	122 (10)	0 (1)	9 (4)	−3 (3)
CC5	24 (2)	12 (1)	64 (7)	2 (1)	3 (3)	−7 (2)
C(Me)	31 (3)	15 (1)	165 (13)	2 (1)	30 (5)	−6 (3)
CP1	21 (2)	10 (1)	70 (8)	0 (1)	0 (3)	−9 (2)
CP2	28 (2)	13 (1)	88 (9)	0 (1)	−8 (4)	2 (2)
CP3	28 (3)	20 (2)	131 (11)	4 (2)	−18 (4)	−2 (3)
CP4	26 (2)	21 (1)	133 (12)	0 (2)	−16 (4)	−4 (4)
CP5	30 (3)	18 (1)	138 (12)	−7 (2)	0 (5)	−3 (3)
CP6	29 (3)	12 (1)	136 (11)	−4 (1)	−9 (4)	3 (3)
CP7	24 (2)	9 (1)	91 (8)	0 (1)	0 (3)	−3 (2)
CP8	36 (3)	11 (1)	137 (12)	2 (1)	4 (4)	−10 (3)
CP9	65 (5)	11 (1)	195 (16)	2 (2)	−6 (7)	−9 (3)
CP10	57 (4)	10 (1)	222 (17)	9 (2)	34 (7)	2 (4)
CP11	44 (3)	16 (1)	175 (14)	12 (2)	4 (6)	5 (4)
CP12	28 (2)	13 (1)	108 (10)	3 (1)	4 (4)	5 (3)
CP13	23 (2)	11 (1)	56 (7)	3 (1)	0 (3)	3 (2)
CP14	45 (4)	18 (1)	107 (10)	3 (2)	−1 (5)	−3 (3)
CP15	46 (4)	29 (2)	90 (1)	12 (2)	25 (5)	13 (4)
CP16	25 (3)	25 (2)	160 (15)	−4 (2)	13 (5)	16 (4)
CP17	33 (3)	23 (2)	109 (12)	−8 (2)	−1 (5)	23 (3)
CP18	27 (2)	13 (1)	110 (10)	−5 (1)	−13 (4)	8 (3)

[a] Anisotropic temperature factors of the form: $T_i = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table V. Idealized Hydrogen Positions[a]

Atom	x/a	y/b	z/c
HCC1[b]	−0.049	0.145	0.295
HCC2[c]	−0.060	0.134	0.029
HCC3	0.009	0.208	−0.092
HCC4	0.095	0.243	0.102
HCC5	0.071	0.191	0.328
HCP2	0.002	0.168	−0.355
HCP3	−0.122	0.164	−0.440
HCP4	−0.201	0.100	−0.361
HCP5	−0.156	0.039	−0.204
HCP6	−0.035	0.043	−0.116
HCP8	0.068	0.025	−0.348
HCP9	0.123	−0.053	−0.370
HCP10	0.217	−0.078	−0.214
HCP11	0.255	−0.026	−0.029
HCP12	0.195	0.051	0.010
HCP14	0.127	0.100	−0.447
HCP15	0.207	0.144	−0.606
HCP16	0.270	0.216	−0.520
HCP17	0.255	0.243	−0.287
HCP18	0.174	0.200	−0.131
HC1[d]	−0.097	0.217	0.377
HC2	−0.093	0.244	0.217
HC3	−0.150	0.200	0.241

[a] The positions of the hydrogen atoms were located in a difference Fourier and then idealized. The atoms were assigned an isotropic thermal parameter of 4.0 Å^2. The C-H distance in all cases was 0.96 Å. [b] The position of HCC1 was calculated using the positions of C(Me), CC1, CC2, and CC5. [c] The positions of HCC2 thru HCP18 were calculated from the positions of the carbon atom to which each is attached and the positions of the two other carbon atoms bonded to that central carbon atom. [d] The methyl hydrogen atoms were idealized to tetrahedral geometry.

Table VII. Bond Distance (Å)

Mn-N	1.674 (5)	CP1-CP2	1.386 (9)
Mn-C	1.771 (7)	CP2-CP3	1.410 (10)
Mn-P	2.285 (2)	CP3-CP4	1.366 (11)
Mn-CC1	2.693 (6)	CP4-CP5	1.365 (12)
Mn-CC2	2.188 (6)	CP5-CP6	1.372 (11)
Mn-CC3	2.092 (6)	CP6-CP1	1.387 (9)
Mn-CC4	2.059 (7)		
Mn-CC5	2.166 (6)	CP7-CP8	1.424 (9)
		CP8-CP9	1.367 (11)
N-O(N)	1.200 (7)	CP9-CP10	1.360 (14)
C-O(C)	1.144 (8)	CP10-CP11	1.357 (13)
		CP11-CP12	1.382 (10)
P-CP1	1.818 (6)	CP12-CP7	1.389 (9)
P-CP7	1.822 (6)		
P-CP13	1.830 (6)	CP13-CP14	1.382 (10)
		CP14-CP15	1.405 (12)
CC1-CC2	1.482 (9)	CP15-CP16	1.397 (13)
CC2-CC3	1.419 (9)	CP16-CP17	1.341 (12)
CC3-CC4	1.415 (10)	CP17-CP18	1.391 (9)
CC4-CC5	1.401 (9)	CP18-CP13	1.389 (9)
CC5-CC1	1.491 (9)		
CC1-C(Me)	1.560 (10)		

Description of the Molecule and Discussion

Figure 1 is an ORTEP[8] drawing showing the general appearance of the molecule and the numbering system used in the crystallographic study. Figure 2 is a stereo pair drawn with the same orientation as that in Figure 1, showing the heavier atoms represented by their anisotropic thermal ellipsoids. In Figure 1, the thermal parameters were isotropic and of an arbitrary size which was convenient for illustrative purposes (i.e., minimizing overlap of atoms aligned nearly along the line of sight). Finally, Figure 3 is a packing diagram showing the intermolecular arrangement in the unit cell.

Aside from being a convenient view of the molecule, Figure 1 was chosen because it emphasizes the nearly tetrahedral arrangements of ligands to the Mn and the P atoms. In the case of the manganese atom, if the assumption is made that the 5-*exo*-C_5H_5 moiety is counted as a single ligand, the geometry is tetrahedral. Otherwise, if every one of the four carbons (CC5, CC2, CC3, and CC4) is counted as an independent ligand, this molecule constitutes an example of a (4 and 3) sevenfold coordination found in molecules such as $(Ph_4C_4)Fe(CO)_3$,[9] $S_2Fe_3(CO)_9$,[10] and $Se_2Fe_3(CO)_9$.[11] In either case, the geometry is one that is well established in organometallic molecules.

As predicted by Brunner and Langer[2] from their NMR

Table VIII. Bond Angles (Degrees)

N-Mn-C	102.8 (3)	P-CP1-CP2	122.1 (5)
N-Mn-P	93.9 (2)	P-CP1-CP6	118.5 (5)
C-Mn-P	102.2 (2)	P-CP7-CP8	121.9 (5)
Mn-N-O(N)	178.4 (5)	P-CP7-CP12	119.6 (5)
Mn-C-O(C)	174.8 (5)	P-CP13-CP14	121.8 (6)
Mn-P-CP1	113.7 (2)	P-CP13-CP18	120.1 (5)
Mn-P-CP7	117.4 (2)	CP6-CP1-CP2	118.8 (6)
Mn-P-CP13	114.5 (2)	CP1-CP2-CP3	119.8 (7)
CP1-P-CP7	103.4 (5)	CP2-CP3-CP4	120.1 (7)
CP1-P-CP13	104.8 (5)	CP3-CP4-CP5	119.6 (7)
CP7-P-CP13	101.4 (5)	CP4-CP5-CP6	121.4 (7)
CC5-CC1-CC2	97.6 (5)	CP5-CP6-CP1	120.3 (7)
CC1-CC2-CC3	108.2 (6)	CP12-CP7-CP8	118.2 (6)
CC2-CC3-CC4	106.2 (6)	CP7-CP8-CP9	119.3 (8)
CC3-CC4-CC5	107.6 (6)	CP8-CP9-CP10	121.2 (8)
CC4-CC5-CC1	108.1 (6)	CP9-CP10-CP11	120.5 (7)
CC2-CC1-C(Me)	113.1 (6)	CP10-CP11-CP12	120.5 (8)
CC5-CC1-C(Me)	113.1 (6)	CP11-CP12-CP7	120.2 (7)
CP18-CP13-CP14	118.0 (7)		
CP13-CP14-CP15	121.2 (8)		
CP14-CP15-CP16	117.9 (8)		
CP15-CP16-CP17	122.0 (8)		
CP16-CP17-CP18	119.3 (8)		
CP17-CP18-CP13	121.6 (7)		

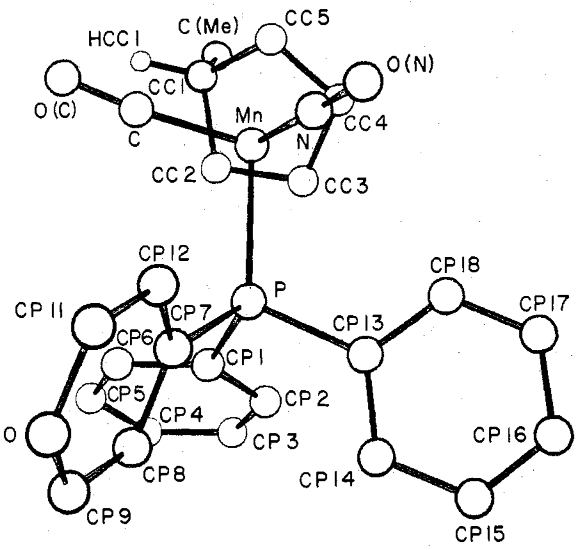

Figure 1. A general view of the molecule showing the numbering system used.

measurements, the methyl group is in the 5-exo position. This result is consistent with a nucleophilic attack by CH_3^- on the outside of the delocalized system during the reaction, as has been found previously for nucleophilic attack on $[(\pi\text{-}C_5H_5)_2M]^+$ (M = Co and Rh) and $[(\pi\text{-}C_6H_6)M(CO)_3]^+$ (M = Mn, Tc, and Re) ions.[27] The phenyl groups are normal, planar, hexagonal, and oriented at arbitrary angles with one another so as to minimize steric hindrance among themselves. This is normal for such groups and has been frequently mentioned in the literature.[12]

Table IX. Least-Squares Planes[a]

Distance of atoms from the plane, Å

(a) Plane Based on CC2, CC3, CC4, CC5

$0.6785x - 0.7061y - 0.2025z = -3.6088$

CC1	−0.529	CC4	0.006
CC2	0.003	CC5	−0.003
CC3	−0.005		

(b) Plane Based on CP1, CP2, CP3, CP4, CP5, CP6

$0.2908x - 0.5671y - 0.7706z = 0.0292$

CP1	0.006	CP3	0.002	CP5	0.006
CP2	−0.005	CP4	−0.001	CP6	−0.008

(c) Plane Based on CP7, CP8, CP9, CP10, CP11, CP12

$0.6901x + 0.4273y - 0.5841z = 2.9749$

CP7	−0.001	CP9	−0.017	CP11	0.018
CP8	0.012	CP10	−0.003	CP12	−0.009

(d) Plane Based on CP13, CP14, CP15, CP16, CP17, CP18

$-0.7701x + 0.5687y - 0.2891z = 0.9434$

CP13	−0.006	CP15	0.001	CP17	−0.003
CP14	0.006	CP16	−0.003	CP18	0.008

[a] *xyz* are absolute coordinates in ångströms of a point from the origin of the unit cell.

The Mn–PPh_3 Fragment

This fragment of the molecule is well behaved stereochemically in that the structural parameters found resemble closely those found elsewhere in studies of related molecules. For example, our Mn–P distance is 2.285 (2) Å, which compares well with values of 2.278 (5) and 2.279 (5) Å found in $MnNO(CO)_2(PPh_3)_2$[7] and of 2.305 (4) Å found in $MnNO(CO)_3(PPh_3)$.[13] Both of these substances contain pentacoordinated (trigonal bipyramidal) Mn, whereas $(CH_3)Mn(CO)_4(PPh_3)$, which contains hexacoordinated (octahedral) Mn, has been reported to have a Mn–P bond of 2.311 Å.[14] Finally, Bennett et al.[15] reported values of 2.295 (3) and 2.299 (2) Å for the two isomers of $C_{25}H_{20}MnO_4P$, both of which contain $-(Ph_2)P-Mn$ fragments and both of which have hexacoordinated central Mn atoms.

The P–C bonds in our compound range in length from 1.818 (6) to 1.830 (6) Å and the Mn–P–C angles range from 113.7 (2) to 117.4 (2)°. However, there is no simple correlation among these quantities, and the differences probably are not significant. This same observation has been made regarding the P–C distances and metal–P–C angles in the triphenylphosphines of the two isomers of $(Ph_3P)_2Ru(CO)S_2C_2(CF_3)_2$ reported by Bernal et al.[12,16] However, one interesting feature of the geometry of the triphenylphosphine ligand found in this study is that, while all the angles at the head carbon of the phenyl rings deviate from 120.0°, the mean values (CP1 = 119.8; CP7 = 119.9, and CP13 = 120.0) add very closely to the ideal value for a planar hexagon. This result is in accord with the fact that the phenyl carbons are located in a very good plane, as shown by the results listed in Table IX, where deviations from the least-squares planes through such atoms are small. The mean value and the standard deviation from the mean for the C–C distances of the phenyl rings are 1.382 (21)

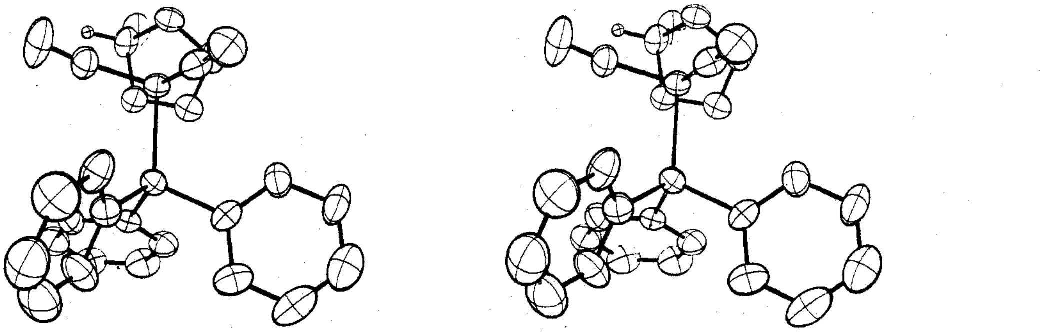

Figure 2. A stereoscopic view of the molecule.

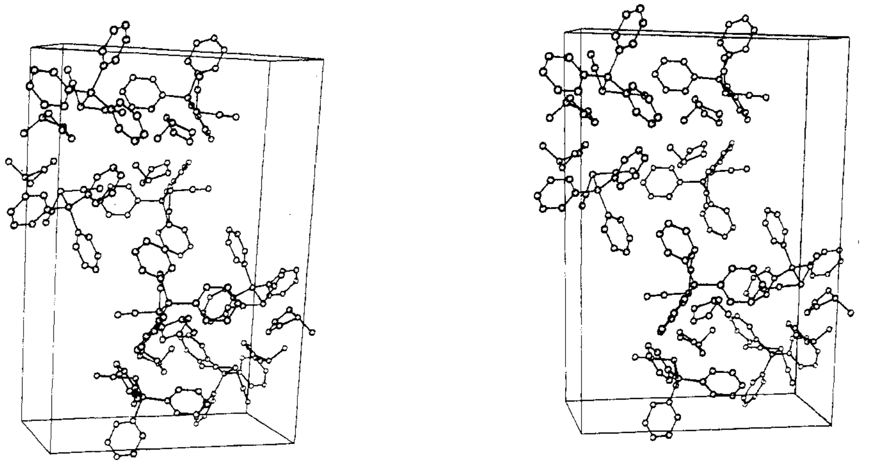

Figure 3. A packing diagram.

Å, which makes these normal rings.

The Mn–CO and the Mn–NO Fragments

Although there are large numbers of accurate and unambiguous determinations of the bonding parameters of the Mn–CO fragment, the stereochemistry of the Mn–NO group has been, until recently, almost exclusively described for compounds in which there were carbonyl groups present.[7,13] Consequently, there always has been uncertainty about which group was which and even as to the possibility of crystallographic disorder leading to a molecular "averaging" of the interatomic distances and angles in these fragments. Fortunately for us there were seven independent determinations of the interatomic distances and angles in the Mn–NO fragment during 1974, all of which were unambiguous in their results.[17,18] With respect to our molecule, the results are as follows. (A) The Mn–C and C–O distances are respectively 1.771 (7) and 1.144 (8) Å, while the Mn–C–O angle is 174.8 (5)°. Gaines et al.[19] determined the structure of 8-$[(C_2H_5)_3N(CH_2)_4O]$-6-$(CO)_3$-6-MnB_9H_{12} in which the three independent Mn–C distances were 1.773 (7), 1.791 (8), and 1.793 (7) Å; the three C–O distances were 1.147 (7), 1.150 (6), and 1.161 (7) Å; and the three Mn–C–O angles were 178.4 (5), 178.4 (6), and 178.7 (7)°. Churchill and Scholer,[20] studying a substance more closely related to ours, $(C_6H_7)Mn(CO)_3$, found average Mn–C, C–O, and Mn–C–O parameters of 1.789 (9) Å, 1.158 (12) Å, and 177.5 (9)°, respectively. We conclude, therefore, that this fragment of our molecule is well behaved. (B) Our Mn–N–O fragment has Mn–N and N–O distances of 1.674 (5) and 1.200 (7) Å, respectively, and the Mn–N–O angle is 178.4 (5)°. In the octahedral $Mn(CN)_5NO^{3-}$ anion, the Mn–N and N–O distances are[21] 1.66 (1) and 1.21 (2) Å, respectively, while the Mn–N–O angle is 174.3 (1.3)°. In the determination of the structure of a Mn–NO tetraphenylporphine derivative, Scheidt et al.[17] gave Mn–N and N–O distances of 1.644 (5) and 1.176 (7) Å and a Mn–N–O angle of 176.2 (5)°. Finally, Laing et al.[18] gave details of six independent determinations of the bonding parameters of the Mn–NO fragment. They reported values of the Mn–N distance ranging from 1.62 (1) to 1.64 (1) Å and N–O distances ranging from 1.19 (1) to 1.20 (1) Å. Interestingly enough, they found Mn–N–O angles ranging from 164 (1) to 166 (1)° (average 165 (1)°) and concluded that their results "confirm the suspicion that the apparent linearity of the Mn–N–O groups observed in the previous crystal structure determinations was indeed caused by disorder". In view of the results reported for $Mn(CN)_5NO^{3-}$ and the tetraphenylporphine study of Scheidt et al.,[17] the opinion voiced by Laing et al.[18] seems hardly justified. However, all of the data currently available on molecules containing the Mn–N–O fragment, which are neither disordered nor contain CO groups to cloud the conclusions, give excellent agreement with the assignment made for the NO group in our molecule.

The Stereochemistry of the 5-*exo*-CH_3-C_5H_5–Mn Fragment

This fragment is the most important portion of the molecule for the following reasons: (a) since the molecule is derived from the reaction of $LiCH_3$ with the η^5-C_5H_5–Mn moiety, it is interesting to have an opportunity to describe the effect of destroying the aromaticity of the η^5-C_5H_5 ring on the stereochemistry of the molecule; and (b) the geometry, stereochemistry, bond lengths, angles, etc., ..., of a metal derivative of a 1,3-cyclopentadiene have never been accurately described before. Although the structures of $(\eta^5$-$C_5H_5)Co(\eta^4$-C_5H_5–$C_6H_5)$[22] and of $(\eta^5$-$C_5H_5)Re(CH_3)_2[\eta^4$-$C_5H_4(CH_3)_2]$[23] have been reported previously, the data were collected using film methods and the data sets were limited, typical of the conditions prevailing in crystallography at the times in question. Consequently, it seems fair to quote here one of the authors:[25] "the standard deviations of the carbon–carbon distances are too large for useful conclusions to be drawn about the distances in either of the rings". As a result, we feel that our study is the first truly accurate description of the bonding in a metal–$(\eta^4$-C_5H_5–R; R = H, alkyl, aryl, etc., ...) moiety. With respect to point (a) above, the results of methylating the cyclopentadienyl ring can best be described by recalling the stereochemical properties of a typical η^5-C_5H_5 fragment, such as that found by Berndt and Marsh[24] for $(\eta^5$-$C_5H_5)Mn(CO)_3$, by Ziegler[25] for $[(\eta^5$-$C_5H_5)Mn(CO)_2](trans$-$C_4H_6)$, and by Haedicke and Hoppe[26] for $(\eta^5$-$C_5H_5)Mn(CO)_2(OCPh)$. Mn–(ring centroid) in these compounds is approximately 1.80 Å while the individual Mn–C distances range from about 2.10 to 2.20 Å and the metal is directly above the ring centroid. That is, the perpendicular from the metal to the mean plane of the ring coincides almost exactly with the metal–(ring centroid) vector. Methylation of the cyclopentadienyl ring causes the following changes from that picture: (1) the metal is approximately equidistant from a conjugated set of four carbons (CC2, CC3, CC4, CC5) which define the diene fragment of an η^4-5-*exo*-methyl-1,3-cyclopentadiene; and (2) the cyclopentadiene ring is folded at the CC2 and CC5 carbons, both of which are slightly closer to the metal than the other two (CC3 and CC4) carbons of the diene. Individual distances are listed in Table VII. However, the effect can be summarized by noting that the midpoints between CC2 and CC5 and between CC3 and CC4 lie 1.87 and 2.06 Å, respectively, from the Mn atom. The midpoint of the four carbons of the diene fragment lies 1.79 Å away from the central Mn atom and the Mn–CC1 distance is 2.693 (6) Å, which is considerably longer than the other four Mn–C distances. The distance from Mn to HCC1 is 3.11 Å, which should result in little or no effect on the proton NMR of this particular hydrogen, as was found in the studies of Brunner and Langer.[2] The folding of the ring at CC2 and CC5 is such that CC1 lies 0.529 Å away from the plane of the four carbons of the diene and the dihedral angle between the planes defined by CC2, CC3, CC4, and CC5 and by CC2, CC5, and CC1 is 147.3°. As a result of these observations, we can describe the effect of methylating the η^5-C_5H_5–Mn fragment as follows: the ring slips up so the closest metal–ring contact is approximately at the midpoint of the newly created diene system; this metal–ring contact (1.79 Å) remains remarkably close to the distance of closest approach (1.80 Å) found in various molecules containing η^5-C_5H_5–Mn moieties. The 1,3-cyclopentadiene ring then tilts slightly toward the metal at the folding point of the ring (the line joining CC2 and CC5). There are drastic changes in the C–C distances, as expected. They are as follows: within the diene portion of the ring, the distances range from 1.401 (9) Å, for the CC4–CC5 bond of the diene, to 1.415 (10) and 1.419 (9) Å, for the other two C–C bonds of the diene. However, these three C–C distances are more uniform than those found by Ziegler[25] for a (*trans*-1,3-butadiene)–Mn fragment for which he reported values of 1.43 and 1.50 Å respectively for the outer and inner C–C distances of the butadiene. These differences may be associated with two factors: (1) his butadiene ligand is trans, whereas the conformation of our diene system is cis; and (2) the C–C–C angles of his butadiene are reported as 116.1°, whereas ours are 106.2 (6) and 107.6 (5)°. As a result of this, apparently, we have Mn–(diene C) distances which are about 0.1 Å shorter. That is, our shortest and longest Mn–(diene C) distances are 0.1 Å shorter than the shortest and longest distances reported by Ziegler.[25] Another relevant molecule with which to compare our results is $(\eta^5$-$C_6H_7)Mn(CO)_3$[20] which, with respect to our molecule, can be regarded as the product of the reaction of LiH with $[(C_6H_6)Mn(CO)_3]^+$. In $(\eta^5$-$C_6H_7)Mn(CO)_3$ the relationship of the Mn to the conjugated carbons of the (C_6H_7) moiety is described by the values of the five Mn–C distances which range from 2.141 (9) to 2.219 (7) Å. Given the change from a η^4-C_5H_5–Mn to a η^5-C_6H_7–Mn fragment, there is a remarkably small change in the Mn–C distances.

In our compound, the long Mn–CC1 distance is 2.693 (6) Å while that for the $(\eta^5$-$C_6H_7)Mn(CO)_3$ compound[20] is 2.757 (11) Å. This is quite reasonable since the six-membered ring is larger than the ring in our compound and the increase in the Mn–(aliphatic carbon) distance is as expected. Also this is consistent with the fact that the Mn in our compound seems to be closer to the conjugated carbons. Furthermore, it seems that in the compound studied by Churchill and Scholer[20] destruction of the aromaticity of the C_6H_6 ring leads to a similar sliding down of the Mn to that observed in our system.

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Registry No. 5-*exo*-CH_3-$C_5H_5Mn(CO)(NO)P(C_6H_5)_3$, 43135-67-7.

Supplementary Material Available: Table VI, a listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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