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Studies on Interactions of Isocyanide with Transition Metal Complexes. XII.[1] The Crystal and Molecular Structure of π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$, a Complex Containing a Bidentate Ligand Bonding to an Iron Atom by a σ-Bonded Group and a Carbene Group

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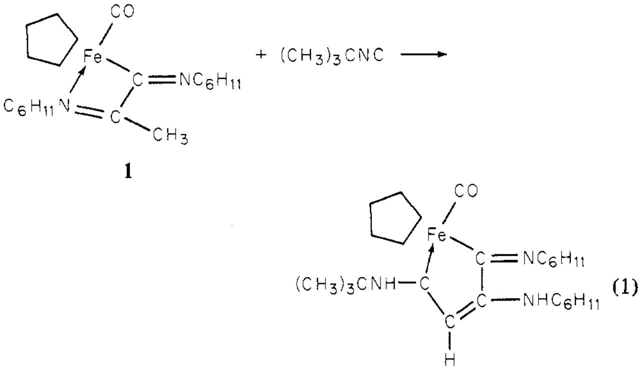
The structure of π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$ (**2**) produced by the reaction of π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_2(CH_3)]$ (**1**) with *tert*-butyl isocyanide has been elucidated by x-ray diffraction. Compound **2** crystallizes in space group $P2_1/c$ with four molecules in a unit cell of dimentions $a = 11.732$ (5) Å, $b = 10.380$ (5) Å, $c = 22.831$ (7) Å, and $\beta = 112.97$ (3)°. The observed and calculated densities are 1.21 and 1.208 g cm^{-3}, respectively. Block-diagonal least-squares refinement has resulted in $R_1 = 5.05\%$ for 3276 data with $F_o \geq 3\sigma(F_o)$. The Fe atom is coordinated by the CO and cyclopentadienyl ligands and by two carbon atoms (σ and carbene bonds) of the $[(C{=}NC_6H_{11})(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$ chelating ligand. Electron delocalization exists in the N(H)–C–C(H)–C–N(H) system of the chelating ligand.

Introduction

It is known that isocyanide reacts with transition metal alkyl complexes to give the imino type complexes.[2,3] The palladium and nickel alkyl complexes among them undergo the successive insertion of isocyanides to give the polyimino-type complexes. We have reported that the analogous reactions occur between benzyl derivatives of π-cyclopentadienyl(dicarbonyl)iron and cyclohexyl isocyanide. At that time the products were formulated as possessing the trisimino-type structure.[4] When our study on these systems was expanded in scope, it became evident that the trisimino-type formulations are not compatible with the proton NMR data. For instance no signal assignable to the methyl group was observed in the proton NMR spectrum of the product having the empirical formula π-$C_5H_5Fe(CO)(CH_3)(CNC_6H_{11})_3$, obtained by the reaction of bisimino-type complex **1**[5] with cyclohexyl isocyanide. The observed inconsistency of the spectrum prompted x-ray crystallographic examination of a compound **2** obtained from **1** and *tert*-butyl isocyanide, which revealed a novel type of metal carbene structure having the bidentate ligand bonding to an iron atom by a σ-bonded group and a carbene group (eq 1).



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We report here our investigation on the x-ray structural determination of **2**, and the revised structure for "trisimino-type complex" obtained from dicarbonyl-π-cyclopentadienylbenzyliron and cyclohexyl isocyanide.[4] A preliminary account has appeared previously.[6] Chemical studies of this compound and related reactions will be reported in the near future.

Experimental Section

The reaction was carried out under an atmosphere of nitrogen. *tert*-Butyl isocyanide was prepared as described in the literature.[7] The bisimino-type complex π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_2(CH_3)]$ (**1**) was prepared according to the described method.[5]

Preparation of the Cyclic Carbene Complexes, π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$. A mixture of **1** (0.50 g, 1.3 mmol) and $(CH_3)_3CNC$ (0.38 g, 4.6 mmol) in benzene (35 ml) was kept at 70° for 21 hr in a sealed tube. The solvent was removed in vacuo, and the residue was chromatographed on alumina. Elution with benzene gave a reddish brown solution. Removal of the solvent and recrystallization of the residue from a hexane–benzene mixture gave orange brown crystals **2** (0.27 g, 45%; mp 138–141° dec).

X-Ray Structure Determination. Recrystallization of the compound from *n*-hexane at −30° gave well-formed crystals suitable for x-ray studies. Precession and Weissenberg photography established that the crystals were monoclinic with the systematic absences of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with space group $P2_1/c$. Cell constants of $a = 11.732$ (5) Å, $b = 10.380$ (5) Å, $c = 22.831$ (7) Å, and $\beta = 112.97$ (3)° were determined from high-order reflections on a Rigaku four-circle automated diffractometer. The density, measured by flotation in an aqueous solution of potassium iodide, 1.21 g cm^{-3}, agrees well with 1.208 g cm^{-3} calculated for four molecules in the unit cell.

The crystal with the following six planes, 100, $\bar{1}00$, 011, $0\bar{1}\bar{1}$, $0\bar{1}1$, and $01\bar{1}$, was mounted such that the c axis was nearly parallel to the ϕ axis of a Rigaku four-circle diffractometer. The perpendicular distances to each of these planes from an arbitrary origin within the crystal were 0.0082, 0.0082, 0.0174, 0.0174, 0.0192, and 0.0192 cm, respectively. Intensities were measured by the 2θ–ω scan method using Cu Kα radiation filtered through a nickel foil.[8] A scan rate of 4° min^{-1} was used. Ten-second stationary background counts were taken at the lower and upper limits of each scan. Three standard reflections were monitored before every 52 measurements. A total of 4713 independent intensities in the range $2\theta \leq 130°$ were measured. The 3276 reflections for which $F_o \geq 3\sigma(F_o)$ were used in the solution and refinement of the structure.

Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient of this compound for Cu Kα radiation is 52.9 cm^{-1}, and then absorption correction was made.[9] The calculated transmission factors varied from 0.200 to 0.481.

Solution and Refinement of Structure. The iron atom was located from a three-dimensional Patterson map. A subsequent Fourier map phased by the iron atom gave the positions of the remaining nonhydrogen atoms. Five cycles of a block-diagonal least-squares refinement of all the positional and isotropic thermal parameters resulted in the residual factors $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ of 12.3 and 13.0%, respectively. Further five cycles of a refinement with anisotropic thermal parameters converged to $R_1 = 8.1\%$ and $R_2 = 9.3\%$. A difference Fourier synthesis revealed clearly all of the 39 hydrogen atoms. Four more cycles of block-diagonal least-squares calculations completed the refinement, in which the 39 hydrogen atoms were included. The hydrogen atoms were given isotropic thermal parameters. This refinement converged to the lower residual factors $R_1 = 5.05\%$ and $R_2 = 4.00\%$. In these refinements,

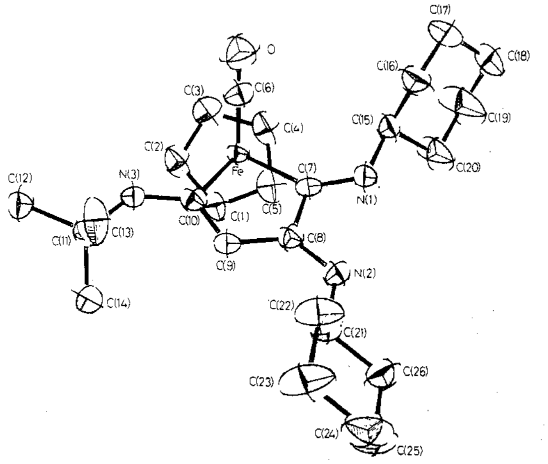


Figure 1. The anisotropic thermal ellipsoids of nonhydrogen atoms showing the numbering scheme. Ellipsoids are scaled to include 50% probability.

the $\sum w(|F_o| - |F_c|)^2$ function was minimized, where the weight, w, was $1/\sigma(F_o)$. No unusual trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of either $\sin\theta/\lambda$ or $|F_o|$. In the final cycle of a refinement, no positional parameters exhibited a shift of more than 0.58 times its estimated standard deviation. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.93, where the numbers of reflection (m) and refined parameters (n) were 3276 and 436, respectively. Anomalous dispersion effects were included in the calculation of F_c using $\Delta f'$ and $\Delta f''$ calculated by Cromer.[10] The atomic scattering factors for Fe, C, N, O, and H were from the usual tabulation.[11]

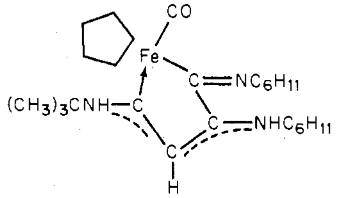
A list of observed and calculated structure factor amplitudes is available.[12] The final atomic coordinates and thermal parameters are listed in Table I.

Description of the Structure

Figure 1 is a perspective view of the π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$ molecule showing the numbering scheme and thermal ellipsoid of the atoms. Interatomic distances and angles with their estimated standard deviations are listed in Table II.

A complex π-$C_5H_5Fe(CO)[(CHNCH_3)BH_2(CHNCH_3)]$ (**3**) having a similar type of bidentate ligand was obtained in the reaction of $[\pi\text{-}C_5H_5Fe(CO)(CNCH_3)_2]PF_6$ with sodium borohydride.[13] The structure was confirmed by an x-ray structural analysis.[14]

The five-membered ring containing the iron atom is essentially coplanar with N(1), N(2), N(3), and H[C(9)] atoms. Distances from this plane are shown in Table III. The C(8)–N(2) (1.322 (4) Å) and C(10)–N(3) (1.336 (4) Å) distances are shorter than expected for normal single bonds, compared with the C–N bond lengths in the aminocarbene complexes of Pt (1.32 (3) Å),[15] Pd (ca. 1.33 Å),[16] Cr (1.32),[17,18] and Rh (1.328 (16) Å),[19] indicating the presence of the pπ–pπ double bond character in the C–N bonds. A salient feature of this compound is that the carbon–carbon distance of 1.407 (4) Å [C(9)–C(10)] is shorter than the single bond[20] (av = 1.51 Å) observed for the monoaminocarbene complexes, thus suggesting the presence of double bonding interaction, whereas the C(8)–C(9) bond length of 1.360 (5) Å is longer than expected for a normal C(sp²)–C(sp²) double bond. The C(7)–C(8) (1.533 (4) Å) and C(7)–N(1) (1.275 (4) Å) distances agree with the expected single and double bond lengths for the formally hybridized carbon–carbon and carbon–nitrogen bonds, namely C(sp²)–C(sp²), 1.48 Å, and C(sp²)–N(sp²), 1.28 Å, respectively. The aforementioned planarity and double bond character of the C–C and C–N bonds indicate that there exists considerable electron delocalization in the N(2)–C(8)–C(9)–C(10)–N(3) system. Thus the structure is best represented as follows.



The Fe–carbene carbon [C(10)] bond length of 1.932 (3) Å is slightly shorter than the Fe–C(7) σ-bonded length of 1.960 (3) Å and the Fe–C(sp²) distances observed for the alkyliron complexes. Relevant data are: Fe–(CH=) = 1.987 (5) Å in π-$C_5H_5Fe(CO)_2(CH{=}CHCH{=}CH)(CO)_2Fe(\pi\text{-}C_5H_5)$[21] and Fe–(C=) = 1.996 (8) Å in π-$C_5H_5Fe(CO)_2[\overline{C{=}C(CH_3)SO(O)C}H_2]$.[22] The Fe–C(carbene) distance is relatively longer than the average Fe–C(sp²) distance of 1.882 Å found for the carbene complex **3**. The carbene carbon has been known to have a slightly distorted sp² hybridized state from idealized hybrid orbitals in the monoaminocarbene complexes, e.g., 109.8, 126.0, and 124.2° for $(CO)_5Cr[C(NHC_6H_{11})C(OCH_3){=}CH_2]$[18] and 129.4, 114.3, and 116.3° for $(CO)_5Cr[C(CH_3)N(C_2H_5)_2]$.[17] However, the observed carbene carbon is considered to have relatively idealized hybrid orbitals, thus 121.7 (3), 121.5 (3), and 116.7 (3)°.

The arrangement of ligands about the iron atom is similar to that of π-$C_5H_5Fe(CO)[(CHNCH_3)BH_2(CHNCH_3)]$ (**3**). The angles C(7)–Fe–C(10), C(6)–Fe–C(7), and C(6)–Fe–C(10) are 82.6 (2), 89.8 (2), and 91.3 (2)°, respectively. The latter two angles are to be compared with the corresponding C–Fe–C angles (89.4 (6) and 92.5 (7)°) observed for **3**. Another angle, C(7)–Fe–C(10), differs by 7° (89.7 (7)° for complex **3**). This difference arises from the ring size containing the bidentate ligand and the iron atom.

The distribution of monodentate and bidentate ligands relative to the Cp[23]–Fe vector is regular as well as those of other alkyliron complexes π-$C_5H_5Fe(CO)_2R$; the angles are Cp–Fe–C(6) = 128.3 (1)°, Cp–Fe–C(7) = 125.7 (1)°, and Cp–Fe–C(10) = 125.7 (1)°. The maximum deviation of the π-cyclopentadienyl carbon atoms from their least-square plane is 0.005 Å (Table III). Carbon–carbon distances within the π-cyclopentadienyl group range from 1.395 (6) to 1.407 (5) Å (av = 1.400 Å) and are not significantly different from those for π-$C_5H_5Fe(CO)_2[C(CH_3)C(CN)_2C(CN)_2CH_3]$ (av = 1.403 and 1.410 Å)[24] and $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$ (av = 1.398 and 1.393 Å).[25] Individual C–C–C angles range from 107.5 (4) to 108.4 (4)° (av = 108.0 Å) and individual C–C–H angles range from 118 (2) to 134 (2)° (Tables I and IV). These values show a system of D_{5h} symmetry. Carbon–hydrogen distances within the π-cyclopentadienyl ligand range from 0.93 (3) to 0.97 (4) Å (av = 0.94 Å) and are in good agreement with other x-ray determined C–H distances (Table V).

The Fe–CO distance of 1.727 (4) Å is not significantly different from the corresponding distances found in the alkyliron complexes and is compared with that in **3** (1.718 (17) Å). The C–O bond length of 1.149 (6) Å is also normal for the metal–carbonyl complexes.

Two cyclohexyl rings adopt the chair form and the conformation which minimizes repulsive interactions between two cyclohexyl rings. The H(N2)---N(1) distance of 2.29 (3) Å is significantly shorter than that of van der Waals radii, 2.7 Å, indicating the presence of hydrogen bonding between both atoms. This bonding is supported from the planarity (Table III) of the five-membered ring system, N(1)–C(7)–C(8)–N(2)–H(N2). The slightly distorted sp²-hybridized state of the C(8) and C(7) atoms relative to the C(10) atom is probably the result of the hydrogen bonding.

Figure 2 shows the packing of molecules within the crystal as projected onto (010). The positions of the molecules are

Table I. Final Atomic Parameters and Standard Deviations[a]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
FE	−0.1564 (0)	0.2301 (1)	0.0569 (0)	0.0050 (0)	0.0062 (1)	0.0017 (0)	0.0001 (1)	0.0007 (0)	−0.0000 (0)
C(1)	−0.2729 (3)	0.2609 (4)	−0.0402 (2)	0.0104 (4)	0.0096 (5)	0.0018 (1)	0.0021 (4)	0.0004 (2)	−0.0004 (2)
C(2)	−0.2917 (3)	0.1367 (4)	−0.0224 (2)	0.0083 (4)	0.0106 (5)	0.0023 (1)	−0.0013 (4)	0.0005 (2)	−0.0014 (2)
C(3)	−0.1792 (4)	0.0694 (4)	−0.0035 (2)	0.0096 (4)	0.0072 (4)	0.0027 (1)	0.0000 (3)	0.0009 (2)	−0.0007 (2)
C(4)	−0.0911 (3)	0.1534 (4)	−0.0094 (2)	0.0090 (4)	0.0102 (5)	0.0025 (1)	0.0003 (4)	0.0020 (2)	−0.0011 (2)
C(5)	−0.1492 (4)	0.2719 (4)	−0.0327 (2)	0.0131 (5)	0.0094 (4)	0.0019 (1)	−0.0004 (4)	0.0023 (2)	−0.0001 (2)
C(6)	−0.2412 (3)	0.2493 (4)	0.1034 (2)	0.0076 (4)	0.0095 (5)	0.0023 (1)	−0.0006 (3)	0.0012 (2)	−0.0000 (2)
C(7)	−0.0707 (3)	0.3927 (3)	0.0899 (2)	0.0060 (3)	0.0071 (4)	0.0015 (1)	0.0005 (3)	0.0012 (1)	0.0001 (1)
C(8)	0.0593 (3)	0.3674 (3)	0.1403 (2)	0.0064 (3)	0.0071 (4)	0.0016 (1)	0.0004 (3)	0.0008 (1)	−0.0000 (2)
C(9)	0.0812 (3)	0.2423 (3)	0.1590 (2)	0.0062 (3)	0.0073 (4)	0.0020 (1)	0.0004 (3)	0.0004 (1)	0.0004 (2)
C(10)	−0.0187 (3)	0.1589 (3)	0.1277 (2)	0.0071 (4)	0.0068 (4)	0.0019 (1)	0.0002 (3)	0.0013 (2)	0.0003 (2)
C(11)	0.0809 (3)	−0.0420 (3)	0.1937 (2)	0.0079 (4)	0.0072 (4)	0.0018 (1)	0.0009 (3)	0.0008 (2)	0.0007 (2)
C(12)	0.0296 (4)	−0.1787 (4)	0.1878 (2)	0.0107 (5)	0.0072 (4)	0.0037 (1)	0.0004 (4)	0.0012 (2)	0.0012 (2)
C(13)	0.1027 (4)	0.0107 (4)	0.2590 (2)	0.0180 (6)	0.0115 (5)	0.0021 (1)	0.0016 (5)	0.0025 (2)	0.0008 (2)
C(14)	0.2000 (4)	−0.0466 (4)	0.1815 (2)	0.0083 (4)	0.0114 (5)	0.0033 (1)	0.0018 (4)	0.0017 (2)	−0.0002 (2)
C(15)	−0.2169 (3)	0.5577 (3)	0.0383 (2)	0.0066 (4)	0.0061 (4)	0.0028 (1)	0.0007 (3)	0.0002 (2)	−0.0000 (2)
C(16)	−0.2831 (4)	0.6210 (4)	0.0763 (2)	0.0087 (5)	0.0148 (6)	0.0037 (2)	0.0042 (4)	0.0020 (2)	0.0014 (3)
C(17)	−0.4059 (4)	0.6817 (4)	0.0332 (2)	0.0082 (4)	0.0135 (6)	0.0050 (2)	0.0020 (4)	0.0017 (2)	0.0005 (3)
C(18)	−0.3885 (4)	0.7738 (4)	−0.0149 (2)	0.0095 (5)	0.0107 (5)	0.0058 (2)	0.0036 (4)	0.0012 (2)	0.0023 (3)
C(19)	−0.3252 (5)	0.7107 (5)	−0.0511 (2)	0.0167 (7)	0.0226 (8)	0.0042 (2)	0.0093 (6)	0.0023 (3)	0.0054 (3)
C(20)	−0.2004 (4)	0.6524 (5)	−0.0088 (2)	0.0118 (5)	0.0194 (7)	0.0032 (1)	0.0069 (5)	0.0026 (2)	0.0035 (3)
C(21)	0.2638 (3)	0.4586 (3)	0.2064 (2)	0.0059 (3)	0.0077 (4)	0.0022 (1)	−0.0001 (3)	0.0003 (2)	−0.0000 (2)
C(22)	0.2718 (4)	0.4612 (5)	0.2744 (2)	0.0092 (5)	0.0184 (7)	0.0025 (1)	−0.0011 (5)	0.0005 (2)	−0.0002 (2)
C(23)	0.4074 (4)	0.4518 (6)	0.3220 (2)	0.0108 (5)	0.0293 (10)	0.0020 (1)	−0.0022 (6)	−0.0004 (2)	−0.0003 (3)
C(24)	0.4819 (4)	0.5600 (5)	0.3102 (2)	0.0075 (4)	0.0215 (8)	0.0042 (2)	−0.0007 (5)	0.0000 (2)	−0.0035 (3)
C(25)	0.4741 (4)	0.5591 (5)	0.2427 (2)	0.0076 (5)	0.0173 (7)	0.0047 (2)	−0.0029 (5)	0.0008 (2)	0.0004 (3)
C(26)	0.3387 (4)	0.5650 (4)	0.1947 (2)	0.0083 (4)	0.0144 (6)	0.0036 (1)	−0.0025 (4)	0.0007 (2)	0.0015 (2)
N(1)	−0.0943 (2)	0.5128 (3)	0.0814 (1)	0.0064 (3)	0.0061 (3)	0.0022 (1)	0.0003 (2)	0.0007 (1)	0.0004 (1)
N(2)	0.1360 (2)	0.4661 (3)	0.1601 (1)	0.0061 (3)	0.0063 (3)	0.0026 (1)	−0.0003 (2)	0.0002 (1)	0.0002 (1)
N(3)	−0.0148 (2)	0.0347 (3)	0.1437 (1)	0.0066 (3)	0.0071 (3)	0.0023 (1)	−0.0005 (3)	0.0006 (1)	0.0006 (1)
O	−0.2957 (3)	0.2644 (3)	0.1352 (1)	0.0140 (4)	0.0184 (5)	0.0038 (1)	−0.0026 (4)	0.0048 (2)	−0.0009 (2)
H(C1)	−0.329 (2)	0.329 (2)	−0.055 (1)	4.3 (0.8)					
H(C2)	−0.367 (2)	0.104 (3)	−0.023 (1)	4.7 (0.8)					
H(C3)	−0.167 (3)	−0.014 (3)	0.013 (1)	6.3 (1.0)					
H(C4)	−0.006 (3)	0.128 (3)	0.001 (1)	7.8 (1.0)					
H(C5)	−0.121 (3)	0.354 (3)	−0.040 (1)	6.1 (0.9)					
H(C9)	0.154 (2)	0.217 (2)	0.190 (1)	3.7 (0.7)					
H1(C12)	−0.054 (3)	−0.175 (3)	0.196 (1)	6.5 (1.0)					
H2(C12)	0.090 (3)	−0.234 (3)	0.216 (1)	7.1 (1.0)					
H3(C12)	0.002 (2)	−0.211 (3)	0.142 (1)	5.8 (0.9)					
H1(C13)	0.032 (3)	0.019 (3)	0.266 (1)	7.3 (1.1)					
H2(C13)	0.146 (3)	−0.045 (3)	0.289 (1)	8.7 (1.2)					
H3(C13)	0.138 (3)	0.103 (3)	0.266 (1)	7.0 (1.0)					
H1(C14)	0.258 (2)	−0.104 (3)	0.213 (1)	5.5 (0.9)					
H2(C14)	0.235 (3)	0.039 (3)	0.176 (1)	8.3 (1.1)					
H3(C14)	0.186 (3)	−0.092 (3)	0.146 (1)	5.9 (0.9)					
H(C15)	−0.263 (3)	0.491 (3)	0.022 (1)	6.0 (0.9)					
H1(C16)	−0.231 (3)	0.688 (3)	0.102 (1)	7.4 (1.1)					
H2(C16)	−0.294 (3)	0.548 (3)	0.108 (1)	7.9 (1.1)					
H1(C17)	−0.455 (3)	0.726 (4)	0.060 (2)	11.6 (1.4)					
H2(C17)	−0.456 (3)	0.614 (3)	0.010 (1)	7.1 (1.0)					
H1(C18)	−0.342 (3)	0.856 (3)	0.017 (1)	9.8 (1.3)					
H2(C18)	−0.468 (3)	0.798 (3)	−0.046 (1)	7.5 (1.1)					
H1(C19)	−0.298 (3)	0.773 (4)	−0.069 (2)	11.6 (1.4)					
H2(C19)	−0.382 (3)	0.630 (3)	−0.079 (1)	7.9 (1.1)					
H1(C20)	−0.160 (3)	0.620 (3)	−0.030 (1)	7.0 (1.0)					
H2(C20)	−0.148 (3)	0.719 (3)	0.021 (1)	9.1 (1.2)					
H(C21)	0.302 (2)	0.374 (2)	0.199 (1)	2.2 (0.6)					
H1(C22)	0.233 (3)	0.556 (3)	0.274 (1)	6.3 (1.0)					
H2(C22)	0.229 (3)	0.381 (3)	0.283 (1)	9.0 (1.2)					
H1(C23)	0.399 (3)	0.446 (4)	0.365 (2)	10.9 (1.4)					
H2(C23)	0.452 (4)	0.340 (4)	0.306 (2)	12.7 (1.5)					
H1(C24)	0.445 (3)	0.652 (3)	0.318 (1)	9.7 (1.3)					
H2(C24)	0.571 (2)	0.552 (3)	0.337 (1)	5.5 (0.9)					
H1(C25)	0.515 (3)	0.642 (3)	0.231 (1)	7.4 (1.1)					
H2(C25)	0.507 (3)	0.466 (3)	0.233 (1)	8.7 (1.2)					
H1(C26)	0.304 (3)	0.653 (3)	0.204 (1)	6.6 (1.0)					
H2(C26)	0.335 (2)	0.552 (3)	0.151 (1)	6.1 (0.9)					
H(N2)	0.108 (2)	0.547 (3)	0.149 (1)	5.1 (0.9)					
H(N3)	−0.077 (2)	−0.010 (2)	0.120 (1)	4.2 (0.8)					

[a] The temperature factors for heavier atoms are of the form, $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and those for the hydrogen atoms are, $T = \exp[-\beta(\sin\theta/\lambda)^2]$.

denoted as follows; I at x, y, z; II at $x, {}^1/_2 - y, {}^1/_2 + z$; III at $-x, -y, -z$; IV at $-x, -{}^1/_2 + y, -{}^1/_2 - z$, with the x, y, and z coordinates as given in Table I. The translations along the three edges of the unit cell are indicated in parentheses. A list of intermolecular contacts (to 3.5 Å) is summarized in Table VI. The molecules are separated by normal van der

Table II. Bond Lengths and Angles with Their Standard Deviations

Bond lengths		Bond angles	
Bond	Length, Å	Bond	Angle, deg
Fe-C(1)	2.125 (3)	C(7)-Fe-C(10)	82.6 (2)
Fe-C(2)	2.119 (3)	C(7)-Fe-C(6)	89.8 (2)
Fe-C(3)	2.114 (4)	C(7)-Fe-Cp	125.7 (1)
Fe-C(4)	2.104 (5)	C(10)-Fe-C(6)	91.3 (2)
Fe-C(5)	2.124 (4)	C(10)-Fe-Cp	125.7 (1)
Fe-C(6)	1.727 (4)	C(6)-Fe-Cp	128.3 (1)
Fe-C(7)	1.960 (3)	Fe-C(6)-O	178.4 (4)
Fe-C(10)	1.932 (3)	Fe-C(7)-C(8)	110.6 (2)
Fe-Cp[a]	1.755	Fe-C(7)-N(1)	137.4 (3)
C(6)-O	1.149 (6)	Fe-C(10)-C(9)	116.7 (3)
C(1)-C(2)	1.395 (6)	Fe-C(10)-N(3)	121.7 (3)
C(2)-C(3)	1.404 (5)	C(1)-C(2)-C(3)	108.2 (4)
C(3)-C(4)	1.397 (6)	C(2)-C(3)-C(4)	107.6 (4)
C(4)-C(5)	1.407 (5)	C(3)-C(4)-C(5)	108.3 (4)
C(5)-C(1)	1.398 (6)	C(4)-C(5)-C(1)	107.5 (4)
C(7)-C(8)	1.533 (4)	C(5)-C(1)-C(2)	108.4 (4)
C(8)-C(9)	1.360 (5)	C(7)-C(8)-C(9)	114.2 (3)
C(9)-C(10)	1.407 (4)	C(8)-C(9)-C(10)	114.2 (3)
C(11)-C(12)	1.527 (5)	C(12)-C(11)-C(13)	109.4 (3)
C(11)-C(13)	1.513 (6)	C(12)-C(11)-C(14)	108.2 (3)
C(11)-C(14)	1.529 (6)	C(13)-C(11)-C(14)	112.1 (3)
C(15)-C(16)	1.522 (7)	C(15)-C(16)-C(17)	111.9 (4)
C(16)-C(17)	1.528 (5)	C(16)-C(17)-C(18)	111.4 (4)
C(17)-C(18)	1.529 (7)	C(17)-C(18)-C(19)	111.4 (4)
C(18)-C(19)	1.464 (8)	C(18)-C(19)-C(20)	113.1 (4)
C(19)-C(20)	1.530 (6)	C(19)-C(20)-C(15)	110.3 (4)
C(20)-C(15)	1.523 (7)	C(20)-C(15)-C(16)	111.0 (3)
C(21)-C(22)	1.518 (6)	C(21)-C(22)-C(23)	110.8 (4)
C(22)-C(23)	1.541 (5)	C(22)-C(23)-C(24)	109.7 (4)
C(23)-C(24)	1.510 (8)	C(23)-C(24)-C(25)	111.7 (4)
C(24)-C(25)	1.507 (8)	C(24)-C(25)-C(26)	111.2 (4)
C(25)-C(26)	1.539 (5)	C(25)-C(26)-C(21)	111.0 (4)
C(26)-C(21)	1.499 (6)	C(26)-C(21)-C(22)	111.3 (3)
C(7)-N(1)	1.275 (4)	C(8)-C(7)-N(1)	112.0 (3)
C(15)-N(1)	1.467 (4)	C(7)-C(8)-N(2)	118.0 (3)
C(8)-N(2)	1.322 (4)	C(9)-C(8)-N(2)	127.8 (3)
C(21)-N(2)	1.462 (4)	C(9)-C(10)-N(3)	121.5 (3)
C(10)-N(3)	1.336 (4)	C(12)-C(11)-N(3)	106.1 (3)
C(11)-N(3)	1.483 (4)	C(13)-C(11)-N(3)	110.5 (3)
		C(14)-C(11)-N(3)	110.3 (3)
		C(7)-N(1)-C(15)	120.7 (3)
		C(8)-N(2)-C(21)	125.1 (3)
		C(10)-N(3)-C(11)	131.6 (3)
		N(1)-C(15)-C(16)	109.8 (3)
		N(1)-C(15)-C(20)	108.5 (3)
		N(2)-C(21)-C(22)	112.1 (3)
		N(2)-C(21)-C(26)	109.8 (3)

[a] Cp is the center of gravity of the π-cyclopentadienyl ring.

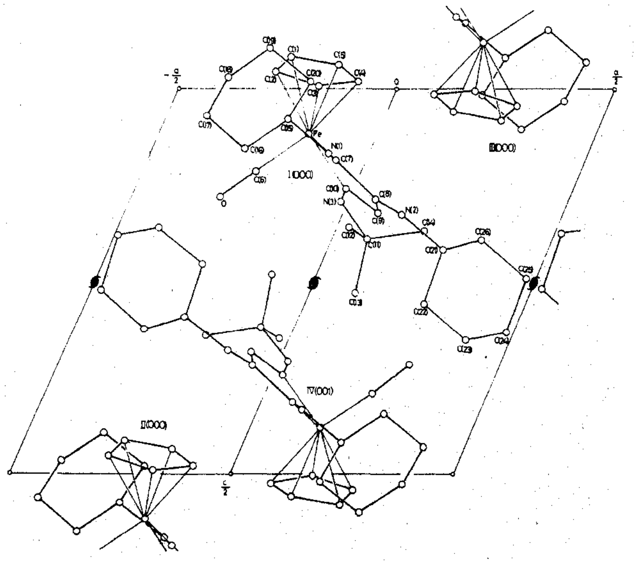


Figure 2. Projection of the crystal structure along the *b* axis.

Table III. Least-Squares Planes and Distances of Atoms from Their Respective Planes[a]

Atom	Distance, Å	Atom	Distance, Å
(1) Plane Through the π-Cyclopentadienyl Ring			
Equation: $0.2402x + 0.3134y + 0.9187z = 0.4442$			
C(1)	0.002	Fe	1.750
C(2)	0.001	H(C1)	0.00
C(3)	−0.004	H(C2)	0.00
C(4)	0.005	H(C3)	0.05
C(5)	−0.004	H(C4)	0.00
		H(C5)	0.06
(2) Plane Through Fe, C(7), C(8), C(9), and C(10) Atoms			
Equation: $0.4236x - 0.1341y - 0.8959z = -2.9176$			
Fe	0.076	N(1)	−0.279
C(7)	−0.081	N(2)	0.174
C(8)	0.050	N(3)	−0.197
C(9)	0.033	C(11)	−0.283
C(10)	−0.079	C(15)	−0.523
		C(21)	0.346
		H(C9)	0.07
		H(N2)	0.05
		H(N3)	−0.19
(3) Plane Through C(7), C(8), N(1), N(2), and H(N2) Atoms			
Equation: $-0.2942x + 0.0689y + 0.9533z = 2.8204$			
C(7)	−0.050		
C(8)	0.050		
N(1)	0.029		
N(2)	−0.028		
H(N2)	0.00		

[a] The equation of each plane is defined by $Ax + By + Cz = D$, where x, y, and z are the orthogonal coordinates measured in Å units along the crystallographic a^*, b, and c axes, respectively.

Table IV. Selected Bond Angles Involving Hydrogen Atoms

Bond	Angle, deg	Bond	Angle, deg
C(2)-C(1)-H	129 (2)	C(4)-C(5)-H	134 (2)
C(5)-C(1)-H	122 (2)	C(1)-C(5)-H	118 (2)
C(1)-C(2)-H	126 (2)	C(8)-C(9)-H	122 (2)
C(3)-C(2)-H	126 (2)	C(10)-C(9)-H	124 (2)
C(2)-C(3)-H	124 (2)	C(8)-N(2)-H	120 (2)
C(4)-C(3)-H	128 (2)	C(21)-N(2)-H	115 (2)
C(3)-C(4)-H	123 (2)	C(10)-N(3)-H	115 (2)
C(5)-C(4)-H	129 (2)	C(11)-N(3)-H	113 (2)

Table V. Bond Lengths Involving the Hydrogen Atoms

Bond	Length, Å	Bond	Length, Å
C(1)-H	0.93 (3)	C(18)-H1	1.11 (4)
C(2)-H	0.94 (3)	C(18)-H2	0.96 (3)
C(3)-H	0.93 (3)	C(19)-H1	0.90 (5)
C(4)-H	0.97 (4)	C(19)-H2	1.11 (4)
C(5)-H	0.95 (4)	C(20)-H1	0.87 (4)
C(9)-H	0.91 (2)	C(20)-H2	0.99 (4)
C(12)-H1	1.06 (4)	C(21)-H	1.03 (3)
C(12)-H2	0.94 (3)	C(22)-H1	1.08 (4)
C(12)-H3	1.04 (3)	C(22)-H2	1.02 (4)
C(13)-H1	0.91 (4)	C(23)-H1	1.03 (5)
C(13)-H2	0.89 (4)	C(23)-H2	1.38 (5)
C(13)-H3	1.03 (4)	C(24)-H1	1.10 (4)
C(14)-H1	0.98 (3)	C(24)-H2	0.98 (3)
C(14)-H2	1.01 (4)	C(25)-H1	1.07 (4)
C(14)-H3	0.89 (3)	C(25)-H2	1.10 (4)
C(15)-H	0.87 (3)	C(26)-H1	1.06 (4)
C(16)-H1	0.96 (3)	C(26)-H2	0.99 (4)
C(16)-H2	1.09 (4)	N(2)-H	0.90 (3)
C(17)-H1	1.10 (5)	N(3)-H	0.86 (3)
C(17)-H2	0.94 (3)		

Waals distances, the closest contact being C(6)---C(7) = 2.607 (5) Å.

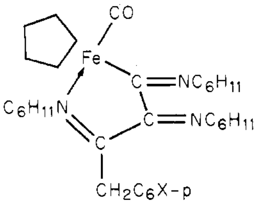
The x-ray crystallographic study of **2** prompted us to reexamine the aforementioned complexes (**4a** and **4b**), identified as the "trisimino-type structure".[4] We found that the resonances at τ 3.27 (broad doublet) for X = H and at τ 3.38 (bd) for X = Cl assigned incorrectly as the benzylic methylene protons, respectively, disappear on treatment with

Table VI. Intermolecular Distances Less Than 3.5 Å

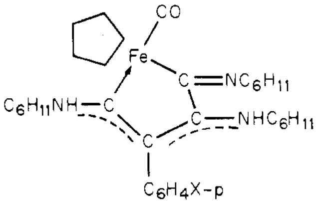
Bond from atom	Bond to atom[a]	Distance, Å	Bond from atom	Bond to atom[a]	Distance, Å
Fe	C(8)	2.882 (3)	C(4)	C(10)	2.906 (5)
Fe	C(9)	2.856 (3)	C(4)	N(3)	3.476 (5)
Fe	C(15)	3.466 (3)	C(5)	C(7)	2.870 (5)
Fe	N(1)	3.023 (3)	C(5)	N(1)	3.484 (5)
Fe	N(3)	2.869 (3)	C(6)	C(7)	2.607 (5)
Fe	O	2.876 (4)	C(6)	C(9)	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

Acknowledgment. We are grateful to Dr. H. Yamazaki of this Institute for helpful discussions and Dr. T. Ito of this Institute for his permission to use the absorption correction program.

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.