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Structure of the Complex Obtained from the Addition of Acetamidine to Hexakis(methyl isocyanido)iron(II)

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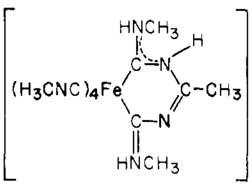
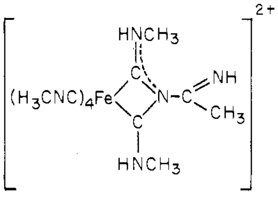
The structure of the cationic complex formed by the reaction of hexakis(methyl isocyanido)iron(II) with acetamidine has been determined by X-ray diffraction methods. The hexafluorophosphate salt, $Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$, crystallizes in the triclinic space group $P\bar{1}$, with cell dimensions $a = 10.301$ (8) Å, $b = 15.338$ (9) Å, $c = 8.494$ (7) Å, $\alpha = 105.73$ (5)°, $\beta = 104.65$ (5)°, $\gamma = 96.83$ (8)°, and $V = 1224$ Å^3. The unit cell contains two formula units. Intensity data were collected with the crystal at a temperature of about 85 K. The structure was solved by Patterson methods and refined by full-matrix least squares with isotropic temperature factors to an R index of 0.092. The cation has the structure



Introduction

In 1973 Doonan and Balch[1] reported the addition of acetamidine to a six-coordinate methyl isocyanide complex of Fe(II). Two possible structures, **1** and **2**, were proposed.



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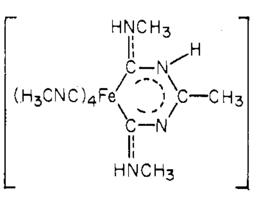

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Precedent for **1** is found in the structure of $[(CNCH_3)_4Fe(CHNCH_3)][PF_6]_2$.[2] From spectroscopic data they were unable to make a definite assignment of either structure to the complex, although they interpreted infrared data to favor **1**. In 1975 Bancroft and Sears[3] reported a study of a number of iron(II) carbene complexes including the above compound by ^{57}Fe Mössbauer spectroscopy; their study favored **2**.

It seemed that the structure could be determined quickly and unequivocally by an X-ray study. We now report our results for the complex.

Experimental Section

$Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$ was obtained from Doonan and Balch, and recrystallization was attempted. However, it was found that the compound deteriorated significantly in a matter of weeks in limited contact with the air, presumably because of hydrolysis of the PF_6^- ions. Once impurities are present, large crystals will not grow. Since the compound we had was over 1 year old, we decided to synthesize fresh compound. Synthesis was carried out according to the description of Doonan and Balch[1] with the following change: acidification was accomplished with 3 M H_2SO_4 rather than with HPF_6, and precipitation was effected by adding a small excess of NH_4PF_6, stripping under aspirator vacuum to 5 mL, and adding 20 mL of water. This was done to avoid impurities usually present in HPF_6.

Although crystals suitable for intensity data collection were difficult to grow, a large number of crystals were obtained that sufficed for preliminary photographic studies. The clear, yellow crystals took the form of irregular hexagonal plates. They were found by room-temperature oscillation and Weissenberg photographs to be triclinic.

By chilling a methanolic solution for 2 weeks at −20 °C two single crystals were obtained. The larger of these had the shape of a thick prism and measured 0.10 × 0.15 × 0.17 mm. It was mounted with arbitrary orientation on a Picker four-circle diffractometer under a stream of nitrogen gas at a temperature of about 85 K. An initial unit cell was used to calculate a reduced cell by means of the program TRACER II.[4] Cell dimensions were obtained by a least-squares fit to the 2θ values of ten Mo Kα_1 reflections.[5] They are $a = 10.301$ (8) Å, $b = 15.338$ (9) Å, $c = 8.494$ (7) Å, $\alpha = 105.73$ (5)°, $\beta = 104.65$ (5)°, $\gamma = 96.83$ (8)°, and $V = 1224$ Å^3 at 85 K. The density calculated for two units of $Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$ per unit cell is 1.76 g cm^{-3}, and that observed by flotation at room temperature is 1.65 g cm^{-3}. Intensity data (Mo Kα) were collected at about 85 K with a Picker four-circle automatic diffractometer equipped with an incident-beam monochromator, a pulse-height analyser, and a modified Enraf-Nonius liquid-nitrogen low-temperature apparatus. Coincidence losses were limited by an attenuator mechanism, which was set to keep count rates below 9500 counts/s. A total of 3368 unique reflections below $2\theta = 47°$ were scanned with the θ–2θ method at a scan speed (2θ) of 2° min^{-1} and a range defined by $(2\theta(\alpha_1) - 1°) - (2\theta(\alpha_2) + 1°)$. Stationary background counts were taken for 20 s at each end of the scan. A check reflection measured about every 8 h showed no systematic variation. Lorentz and polarization corrections were applied to the net intensities. Standard deviations for net intensities were estimated from counting statistics. Reflections for which I_{net} was less than $2\sigma(I_{net})$ were considered "unobserved", resulting in 2727 reflections being recorded as "observed". With a linear absorption coefficient of 8.86 cm^{-1} the maximum variation in the transmission coefficient was about 6% and no absorption correction was made. No extinction effects were observed.

Structure Determination and Refinement

The unique part of the Patterson function shows five large peaks of approximately equal height.[6] We note that this is consistent with a centrosymmetric unit cell with the vector from an iron atom to any phosphorus atom different from the vector from that iron to any other phosphorus. One of the peaks, when used as the Fe–Fe vector, gives a consistent and plausible set of phosphorus coordinates. This set of heavy-atom positions was used as input to a Fourier synthesis. The resulting Fourier map clearly showed all atoms heavier than hydrogen.

Space group $P\bar{1}$ was assumed, and the trial structure obtained from the Fourier synthesis was refined by full-matrix least-squares methods. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting factor w was determined by a Hughes weighting scheme with $4F_{min} = 24.5$.[7] Atomic scattering factors for hydrogen were taken from Stewart, Davidson, and Simpson (1965), and those for all other atoms were taken from Doyle and Turner (1968).[8] The initial R index for the trial structure without hydrogen atoms was 0.34, and after three cycles of refinement with isotropic temperature factors R was 0.093, where $R = \sum||F_o| - |F_c||/\sum|F_o|$. At this point the hydrogen atoms were located in a Fourier difference map, in which all peaks over 0.5 e Å^{-3} were attributable to H atoms, and their positions were added to the least-squares input. One more cycle of refinement with isotropic temperature factors for all atoms, in which all 245 parameters were

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Table I. Final Positional and Thermal Parameters

Atoms	x	y	z	B, Å²
Fe(1)	0.3780 (1)	0.2108 (1)	0.2271 (2)	0.80 (4)
C(2)	0.5250 (9)	0.3068 (6)	0.3999 (12)	1.31 (16)
N(3)	0.6595 (8)	0.3082 (6)	0.4045 (10)	1.65 (14)
C(4)	0.7072 (10)	0.2357 (7)	0.3116 (12)	1.81 (17)
N(5)	0.6414 (8)	0.1520 (5)	0.2455 (10)	1.38 (14)
C(6)	0.5061 (9)	0.1283 (6)	0.2463 (11)	1.14 (15)
N(7)	0.4753 (9)	0.0438 (5)	0.2451 (9)	1.05 (13)
C(8)	0.5634 (11)	−0.0224 (7)	0.2531 (16)	1.70 (18)
N(9)	0.5092 (9)	0.3789 (6)	0.5144 (10)	1.81 (15)
C(10)	0.6176 (12)	0.4525 (8)	0.6401 (14)	2.14 (19)
C(11)	0.8490 (11)	0.2630 (8)	0.3093 (15)	1.80 (18)
C(12)	0.1841 (12)	0.1615 (8)	0.6174 (15)	1.96 (18)
N(13)	0.2546 (8)	0.1703 (5)	0.4961 (9)	1.18 (13)
C(14)	0.3066 (9)	0.1839 (6)	0.3965 (12)	1.39 (16)
C(15)	0.4476 (9)	0.2465 (6)	0.0642 (11)	1.27 (16)
N(16)	0.4880 (8)	0.2720 (5)	−0.0326 (10)	1.66 (14)
C(17)	0.5401 (13)	0.3104 (9)	−0.1448 (16)	2.27 (20)
C(18)	0.0800 (11)	−0.0317 (8)	−0.1731 (14)	1.73 (18)
N(19)	0.1721 (8)	0.0476 (5)	−0.0455 (10)	1.30 (13)
C(20)	0.2487 (9)	0.1120 (6)	0.0560 (11)	1.18 (15)
C(21)	0.2555 (9)	0.2928 (6)	0.2005 (11)	1.22 (16)
N(22)	0.1751 (8)	0.3371 (5)	0.1708 (10)	1.37 (14)
C(23)	0.0725 (12)	0.3907 (8)	0.1293 (14)	1.84 (18)
P(24)	0.2119 (3)	0.4585 (2)	0.7298 (3)	1.74 (5)
F(25)	0.1911 (7)	0.5396 (5)	0.8769 (8)	3.20 (13)
F(26)	0.1561 (7)	0.5081 (5)	0.5912 (8)	3.20 (13)
F(27)	0.3639 (7)	0.5148 (5)	0.7620 (9)	3.47 (14)
F(28)	0.2723 (8)	0.4100 (5)	0.8663 (10)	4.01 (15)
F(29)	0.0608 (7)	0.4050 (4)	0.6930 (8)	3.01 (12)
F(30)	0.2337 (7)	0.3774 (5)	0.5794 (9)	3.29 (13)
P(31)	0.1813 (3)	0.8500 (2)	0.2646 (3)	1.43 (5)
F(32)	0.1376 (9)	0.8898 (6)	0.4325 (11)	4.74 (17)
F(33)	0.0253 (6)	0.8331 (4)	0.1503 (7)	2.30 (11)
F(34)	0.2076 (8)	0.9528 (5)	0.2522 (10)	4.31 (16)
F(35)	0.3370 (6)	0.8686 (4)	0.3791 (7)	2.03 (10)
F(36)	0.1572 (8)	0.7500 (6)	0.2809 (10)	4.66 (17)
F(37)	0.2271 (8)	0.8140 (6)	0.0978 (10)	4.63 (16)
H(31)	0.743 (17)	0.363 (11)	0.509 (21)	7.0 (40)
H(71)	0.4038 (64)	0.0347 (36)	0.2295 (66)	−0.63 (92)
H(81)	0.645 (21)	0.003 (13)	0.238 (23)	7.5 (48)
H(82)	0.520 (19)	−0.082 (13)	0.153 (24)	8.1 (47)
H(83)	0.586 (13)	−0.0187 (90)	0.335 (19)	2.5 (30)
H(91)	0.4214 (92)	0.3751 (56)	0.517 (10)	0.9 (16)
H(101)	0.573 (11)	0.4911 (74)	0.721 (14)	1.7 (22)
H(102)	0.661 (14)	0.5003 (92)	0.582 (17)	4.4 (20)
H(103)	0.6795 (78)	0.4313 (49)	0.6950 (93)	−1.1 (13)
H(111)	0.902 (17)	0.271 (11)	0.404 (22)	5.4 (37)
H(112)	0.857 (25)	0.304 (19)	0.266 (33)	10.9 (74)
H(113)	0.864 (13)	0.2149 (95)	0.213 (17)	4.0 (29)
H(121)	0.124 (25)	0.196 (16)	0.620 (28)	9.7 (60)
H(122)	0.229 (21)	0.189 (14)	0.732 (28)	8.2 (40)
H(123)	0.153 (19)	0.097 (15)	0.582 (24)	8.0 (48)
H(171)	0.533 (17)	0.272 (12)	−0.240 (23)	6.5 (40)
H(172)	0.631 (15)	0.3201 (89)	−0.089 (17)	4.4 (29)
H(173)	0.487 (17)	0.338 (11)	−0.155 (20)	4.3 (39)
H(181)	0.132 (12)	−0.0589 (82)	−0.247 (15)	2.5 (25)
H(182)	0.008 (18)	−0.013 (11)	−0.219 (21)	6.5 (30)
H(183)	0.0699 (92)	−0.0632 (66)	−0.119 (12)	0.5 (18)
H(231)	−0.006 (11)	0.3474 (74)	0.052 (14)	1.9 (21)
H(232)	0.1089 (98)	0.4303 (68)	0.103 (12)	0.4 (18)
H(233)	0.072 (11)	0.4243 (74)	0.240 (14)	1.8 (22)

Table III. Anion Bond Distances (Å) with Esd's

P(24)–F(25)	1.584 (7)	P(31)–F(32)	1.590 (9)
P(24)–F(26)	1.595 (7)	P(31)–F(33)	1.602 (7)
P(24)–F(27)	1.615 (8)	P(31)–F(34)	1.605 (9)
P(24)–F(28)	1.579 (8)	P(31)–F(35)	1.597 (6)
P(24)–F(29)	1.582 (8)	P(31)–F(36)	1.573 (9)
P(24)–F(30)	1.606 (8)	P(31)–F(37)	1.584 (9)

Table IV. Distances from Least-Squares Planes (Å)

Atom	I	II	III	IV
Fe(1)	−1.049	0.070	−0.083	−0.849
C(2)	−0.252	−0.009[a]	1.268	−0.062[a]
N(3)	0.012[a]	0.004[a]	1.281	0.094[a]
C(4)	−0.022[a]	−0.165	0.524	−0.053[a]
N(5)	0.030[a]	−0.678	−0.007[a]	−0.015[a]
C(6)	−0.016[a]	−0.989	0.016[a]	0.036[a]
N(7)	0.595	−1.963	−0.016[a]	0.623
C(8)	1.342	−2.764	0.008[a]	1.261
N(9)	0.006	0.010[a]	2.186	0.288
C(10)	0.558	−0.005[a]	3.171	0.834
C(11)	−0.004[a]	0.199	0.490	−0.136
H(31)	0.514	−0.087	2.102	0.592
H(71)	0.422	−1.973	−0.128	0.499
H(91)	−0.101	−0.072	2.222	0.252

[a] Atoms used to determine the plane.

refined, reduced *R* to 0.092. Final positional and thermal parameters are listed with their estimated standard deviations in Table I, and Table II[9] lists calculated and observed structure factors.

Description and Discussion

The cation is found to be somewhat like **2**, with a six-membered chelate ring; however, the bonding is not as extensively delocalized as is implied by **2**. Figure 1 shows the packing arrangement in the unit cell.[10] Figure 2 shows the numbering scheme used for the cation and also selected bond distances and bond angles in the cation. Table III lists bond distances for the anions.[11] Examination of C–N bonds around the ring reveals two short bonds, C(4)–N(5) and C(6)–N(7), with lengths of 1.28 (1) and 1.29 (1) Å, respectively, suggesting a bond order near 2 for these bonds. The N(3)–C(4) bond is 1.40 (1) Å long; this is not surprising, since there is a hydrogen atom on N(3) and none on N(5).[12] Similarly, the N(5)–C(6) distance is 0.11 Å longer than the C(6)–N(7) distance. Therefore C(4)–N(5) and C(6)–N(7) have been represented as double bonds. Calculation of least-squares planes containing atoms in and around the chelate ring yielded results shown in Table IV. The following sets of atoms are found to be coplanar within 0.05 Å: N(3), C(4), N(5), C(6), C(11); C(2), N(3), N(9), C(10); N(5), C(6), N(7), C(8). Fe(1) is close (≤0.08 Å) to the latter two planes. None of the planes is close to coincidence with any of the others. The angles between the normals to these planes are as follows: first and second, 21.8°; second and third, 33.6°; first and third, 50.7°. The C(4)–N(5)–C(6)–N(7) torsional angle is −152°. Thus the π systems of the C(4)–N(5) and C(6)–N(7) bonds are considerably tilted with respect to each other, and an extensively conjugated system is precluded. The long N(5)–C(6) bond bears this out. On the other side of the ring, the C(2)–N(9) and C(2)–N(3) distances differ by only 0.05 Å, and N(9), C(2), and N(3) presumably have a more delocalized π system. The N(9)–C(2)–N(3)–C(4) torsional angle is 172°. However, C(4) is still significantly (0.16 Å) out of the C(2)–N(3)–N(9)–C(10) plane.

A six-membered ring structure reminiscent of the ring described here was found in π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$.[13] There the Fe–C distances are slightly shorter than those determined by us (1.88 vs. 1.95 Å) presumably reflecting the effect of single H atoms compared to the $-NHCH_3$ groups on the cations in the present compound.

The isotropic temperature coefficients for the fluorine atoms are all in the range from 2.0 to 4.7 Å², allowing these atoms to be located. At room temperature one generally expects the temperature coefficients to have increased by a factor of about 3 over their values at 85 K; thus in a room-temperature study the fluorine temperature coefficents may be in the range 12–15 Å², making it very difficult to locate accurately the fluorine atoms in this and other hexafluorophosphates. It seems probable that many structures containing hexafluorophosphate, including those previously found impossible to determine at

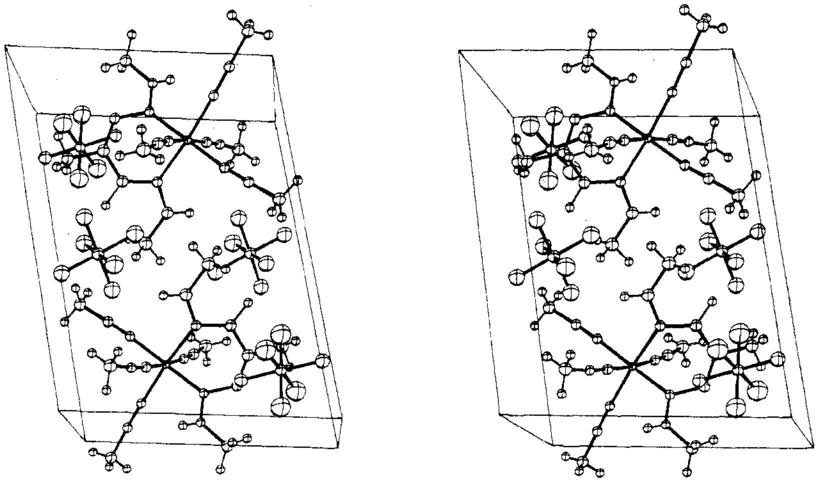


Figure 1. Stereoscopic packing diagram of the unit cell. The *a* axis is across the page, *b* down the page, and *c* out of the page toward the viewer.

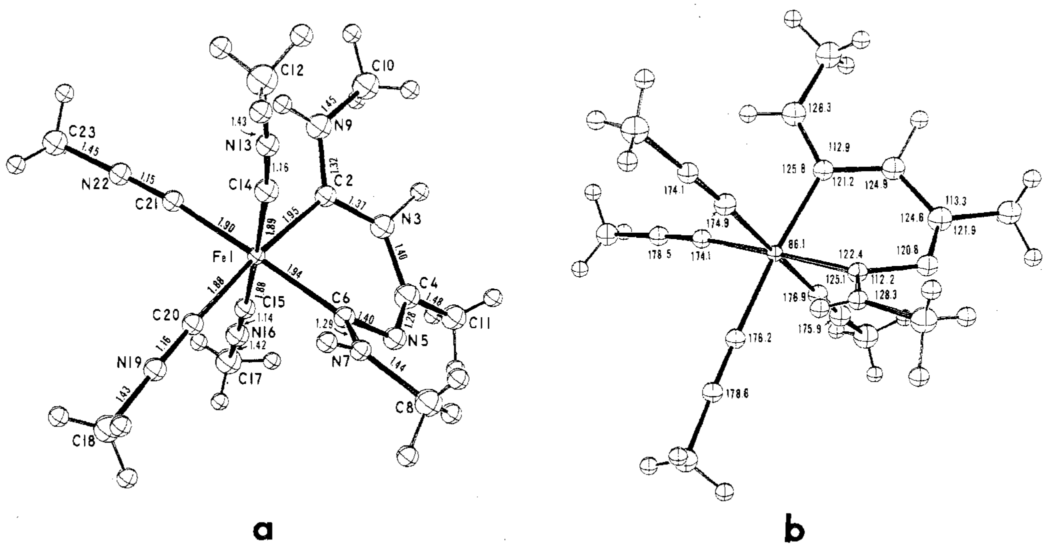


Figure 2. (a) Bond distances and numbering scheme. (b) Bond angles. Estimated standard deviations are between 0.01 and 0.02 Å for the distances and between 0.7 and 1.0° for angles with C or N atoms in the centers. All angles around the Fe atom are within 5° of the ideal octahedral angles with esd of 0.4°, with the following exception: C(2)–Fe(1)–C(20), 174.7 (4)°. Note that the molecule displayed in (b) has been rotated relative to that in (a).

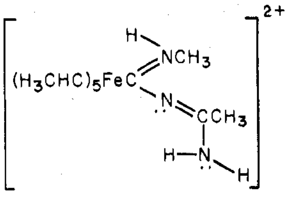
room temperature, can be resolved very well even when refined without the use of anisotropic temperature factors, if data are collected at low temperature.

The hydrogen atoms in the terminal methyl groups generally appear in the difference Fourier map as rings with three maxima marking the most favored positions for the hydrogen atoms. This, along with the very large temperature factors and the high estimated standard deviations on the temperature factors, indicates that the methyl groups are rotating almost freely but that potential-energy minima do exist. The hydrogen atoms on the nitrogens in the side chains of the chelate ring (H(71) and H(91)) are 2.32 (6) and 2.1 (1) Å, respectively, from adjacent fluorine atoms; this is closer than the generally accepted van der Waals distance of 2.6 Å, suggesting the existence of weak hydrogen bonds.

At the time this compound was made, Doonan and Balch[1] also synthesized an analogous addition product of acetamidine and hexakis(methyl isocyanido)ruthenium(II). The infrared spectra of the iron and ruthenium complexes are very similar, with the exception of a weak absorption at 2888 cm^{-1} in the iron complex which is absent in the ruthenium compound. The ^1H NMR spectra (taken at room temperature in acetonitrile-d_3) match line for line, and all lines in one compound are within 0.05 ppm of their counterparts in the other compound, excepting a resonance found in the iron complex at τ 1.40 and in the ruthenium complex at 1.49. It therefore seems likely that the iron and ruthenium complexes have similar structures.

A ^1H NMR study was made of the ruthenium compound in acetone-d_6 at various temperatures from ambient temperature to −90 °C. At room temperature the peak found in the acetonitrile-d_3 spectrum (vide supra) at τ 1.82 occurs at 0.90 in acetone-d_6.[14] As the temperature is lowered, the peak broadens and splits and also moves downfield. At −80 °C two peaks are observed at τ 0.64 and 0.12. The resonance was assigned to hydrogen atoms on the side-chain nitrogens, which at room temperature were presumed to be equivalent, becoming nonequivalent as the temperature was lowered. This was explicable in terms of either **1** or **2**. In **2** the ring hydrogen was thought to move rapidly between the two ring nitrogens at room temperature but to remain on one nitrogen under colder conditions. This hypothesis is consistent with the structure found for the iron complex. If H(31) remains on N(3), then H(71) and H(91) experience different environments. It is also consistent with the fact that, at room temperature, the complex has been found to protonate and deprotonate rapidly and reversibly in solvents such as water and methanol. By acidifying to near pH 2 the color of the solution changes from bright yellow to deep red-orange, and the solubility increases dramatically; both effects are readily reversed when the solution is made more basic. It is reasonable, then, that in solution the ring hydrogen might move from one side of the ring to the other fairly rapidly at room temperature.

The reaction by which the Fe complex is formed probably takes place via nucleophilic attack on a coordinated isocyanide carbon atom and involves an intermediate similar to **3**. If the same nitrogen which attacked the first isocyanide carbon also attacks the second, compound **1** will result; if, on the other hand, the other acetamidine nitrogen attacks the second carbon, a cation like **2** will be formed. Since the structure is now known to be similar to **2**, one may conclude that the second nucleophilic attack involved in forming the chelate ring is carried out by the second nitrogen.



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Application of infrared and Mössbauer spectroscopy resulted in different proposed structures for the Fe complex described. The differences between both of those structures and that found by X-ray methods are significant. This once more illustrates the hazards involved in attempting to determine molecular structures by spectroscopic methods where precedents do not exist.

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Registry No. $Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$ (**1**), 49631-73-4; $Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$ (**2**), 56292-62-7.

Supplementary Material Available: Table II, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(11) All valence angles in the anions are within 2.3° of ideal octahedral angles, with estimated standard deviations between 0.4 and 0.5°.
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Synthesis and Structure of a Cobaltocenium Cobaltacarborane Zwitterion. Cobaltocenium and Tetrahydrofuran Derivatives of *nido,closo*-$[2,3\text{-}(CH_3)_2C_2B_3H_5]CoH[2,3\text{-}(CH_3)_2C_2B_4H_4]$

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The preparation and characterization of the title compounds are described. The species $5\text{-}[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)]\text{-}[2,3\text{-}(CH_3)_2C_2B_4H_3]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]$ and $\sigma\text{-}(CH_2)_4O\text{-}[2,3\text{-}(CH_3)_2C_2B_4H_3]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]$ were obtained from the reaction of $[2,3\text{-}(CH_3)_2C_2B_3H_5]CoH[2,3\text{-}(CH_3)_2C_2B_4H_4]$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in tetrahydrofuran under ultraviolet light, separated via thick-layer chromatography, and characterized from their NMR, infrared, and mass spectra. A single-crystal x-ray diffraction study of the cobaltocenium derivative established its structure. The molecule is a zwitterion composed of a $[(CH_3)_2C_2B_4H_3]Co^{III}[(CH_3)_2C_2B_3H_5]^-$ unit and a $(C_5H_5)Co^{III}(C_5H_4)^+$ group, with the latter substituent attached to the closo portion of the metallocarborane system at B(5). The metallocarborane structure is in agreement with that originally proposed for $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ on the basis of spectroscopic evidence and consists formally of a Co^{3+} ion face-bonded to a pyramidal C_2B_4 and a cyclic C_2B_3 ligand. The latter group has two B–H–B hydrogen bridges which were located and refined. Crystal data: mol wt 438.98; space group *Pbca* (No. 61); $a = 11.339$ (6), $b = 16.703$ (22), $c = 22.332$ (18) Å; $V = 4230$ (7) Å^3; $d_{calcd} = 1.386$ g cm^{-3} for $Z = 8$. The structure was refined by full-matrix least-squares methods to a final R value of 0.063 and R_w of 0.071 for the 1725 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

A series of metallocarboranes containing the cyclic 2,3-$C_2B_3H_7^{2-}$, 2,3-$C_2B_3H_5^{4-}$, and 2,4-$C_2B_3H_5^{4-}$ ligands and the pyramidal 2,3- and 2,4-$C_2B_4H_6^{2-}$ ligands (or their C-substituted derivatives) has been reported from this laboratory.[1] The formal $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$ groups are isoelectronic with $C_5H_5^-$; however, due to the presence of two B–H–B bridges, $C_2B_3H_7^{2-}$ functions only as a capping group, whereas $C_2B_3H_5^{4-}$ face-bonds simultaneously to two metal atoms, as in the triple-decked sandwich species[1a-d,2a-c] $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$. The pyramidal $C_2B_4H_6^{2-}$ ligands are, of course, of the capping type.

Because of their close relationship to the metallocene sandwich compounds, the metal complexes of these ligands are of interest structurally and stereochemically. Several crystallographic studies of metallocarboranes containing substituted derivatives of $C_2B_3H_5^{4-}$ or $C_2B_4H_6^{2-}$ have been conducted,[2-4] but the only prior structural investigation of a $C_2B_3H_7^{2-}$ complex has been that of 1,2,3-$(CO)_3FeC_2B_3H_7$.[5]

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