Labile Tetranuclear Fe(II) and Co(II) Clusters of a Dipyrrolide Dianion with Two Diamagnetic Ferrous Links

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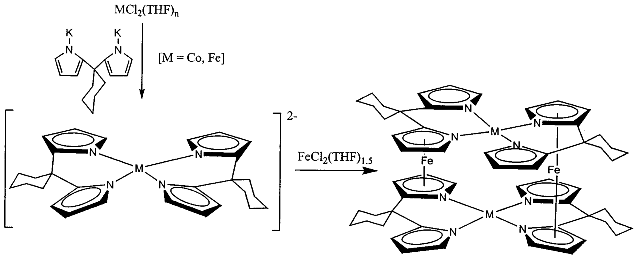
Reaction of the dipotassium salt of the dipyrrolide dianion $[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]^{2-}$ with $FeCl_2(THF)_{1.5}$ afforded the tetranuclear $[\mu,\eta^5\text{-}\{[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Fe\}Fe]_2$ (**1**) cluster containing two diamagnetic ferrous links π-bonded to two pyrrolyl rings of two ligands and closely reminiscent of a ferrocenoid-type arrangement. Reaction of the dianionic metalate $\{[[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Co][K(THF)]_2\}_n$ with $FeCl_2(THF)_{1.5}$ also afforded the corresponding $[\mu,\eta^5\text{-}\{[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Co\}Fe]_2$ nearly isostructural with **1**. This indicates that the two ferrous links provide the driving force for assembling the two clusters, although the two structures are labile and may be disrupted by simple treatment with pyridine.

Introduction

The role played by iron in several metalloenzymes and in hemoglobin as a reversible oxygen carrier continues to provide even today a stimulus for studying the redox chemistry of this metal. Along this line, a plethora of model compounds based on porphyrin ligands have been prepared[1] and their chemistry widely investigated with the aim of designing catalysts for the oxidation of organic substrates.[2]

As part of an ongoing project to study the redox chemistry of mid-valent Fe, we are attempting the preparation of cyclic cluster compounds that might be capable of engaging in multielectron processes via the cooperative interaction of several metals. By holding reactive Fe atoms together in a rigid cluster structure containing both coordinatively unsaturated metal centers and a cavity of adequate size, it is conceivable that the reactivity of divalent Fe in terms of molecular activation might be enhanced. In this paper, we wish to report the preliminary results obtained with the employment of dipyrrolide dianions. Our previous work with low-valent *f*-block elements has shown that primary characteristics of these ligands are the following:[3] (1) an enhanced tendency to increase the reactivity of the metal center,[4] (2) the ability to assemble large cyclic flat cluster structures,[5] (3) the availability of a variety of bonding modes, and (4) the possibility of fine-tuning the metal redox potential in anionic metalate structures.[6]

Scheme 1



Herein, we describe the preparation and characterization of an unusual tetranuclear cluster of divalent iron with dipyrrolide dianion, together with a preliminary assessment of its stability.

Results and Discussion

The reaction of $FeCl_2(THF)_{1.5}$ with either the potassium or sodium salt of the dipyrrolide dianion $[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]^{2-}$ afforded different compounds depending on the stoichiometric ratio of the reaction. The use of one dianion per Fe atom afforded a tetrameric cyclic cluster of formula $[\mu,\eta^5\text{-}\{[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Fe\}Fe]_2$ (**1**), whereas the reaction of two anionic ligands per Fe atom formed the expected -ate complex $(\{[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Fe[K(THF)]_2\}_n$ (**2**) (Scheme 1). The nature of both the ligand substituents and alkali cation did not significantly modify the result of the reaction. Both **1** and **2** are moderately air-sensitive and their structures have been elucidated by X-ray analysis.

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(1) See for example: (a) Riley, D. P. *Chem. Rev.* **1999**, *99*, 2573. (b) Loew, G. H.; Harris, D. L. *Chem. Rev.* **2000**, *100*, 407. (c) Moller, J. K. S.; Skibsted, L. H. *Chem. Rev.* **2002**, *102*, 1167. (d) Louie, A. Y.; Meade, T. J. *Chem. Rev.* **1999**, *99*, 2711.

(2) See for example: (a) Maldotti, A.; Molinari, A.; Amadelli, R. *Chem. Rev.* **2002**, *102*, 3811. (b) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159.

(3) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3657.

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(5) (a) Freckmann, D. M. M.; Dubé, T.; Bérubé, C. D.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 1240. (b) Dubé, T.; Freckmann, D. M. M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 209. (c) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 115.

(6) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 1182.

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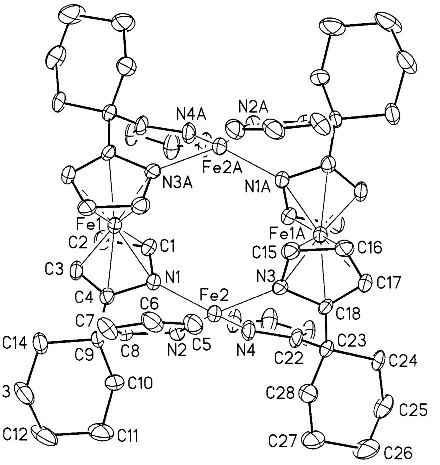

Figure 1. Thermal ellipsoid plot of **1.** Thermal ellipsoids are drawn at the 30% probability level.

Analytical data in agreement with the proposed formulations were also obtained.

The structure of **1** (Figure 1) consists of four Fe atoms forming a planar diamond-shaped core. The four Fe atoms are bridged by four dipyrrolide dianions with the metals present in two different coordination environments. Two of the iron centers, placed on opposite positions of the tetranuclear core, display a severely flattened tetrahedral coordination geometry [N(1)−Fe(2)−N(2) = 90.6(3)°, N(1)−Fe(2)−N(3) = 134.3(3)°, N(1)−Fe(2)−N(4) = 101.6(3)°, N(2)−Fe(2)−N(3) = 99.7(3)°, N(2)−Fe(2)−N(4) = 151.1(3)°, N(3)−Fe(2)−N(4) = 90.5(3)°] defined by the four N atoms of two σ-bonded dipyrrolide dianions [Fe(2)−N(1) = 2.099(8) Å, Fe(2)−N(2) = 1.994(8) Å, Fe(2)−N(3) = 2.126(6) Å, Fe(2)−N(4) = 1.993(8) Å]. The connection between the two identical units is realized by the other two Fe atoms, which adopt a symmetric ferrocenoid-type structure by π-bonding two pyrrole rings from the two separate -ate units [Fe(1)−N(1) = 2.036(8) Å, Fe(1)−C(1) = 2.019(10) Å, Fe(1)−C(2) = 2.083(10) Å, Fe(1)−C(3) = 2.065(8) Å, Fe(1)−C(4) = 2.043(9) Å].

In the -ate complex **2** (Figure 2, parts a and b), the structure consists of one Fe atom surrounded by the four N atoms of two σ-ligated dipyrrolyl dianions [Fe(1)−N(1) = 2.057(2) Å, Fe(1)−N(2) = 2.043(2) Å, Fe(1)−N(3) = 2.051(2) Å, Fe(1)−N(4) = 2.079(2) Å, K (1)−N(4) = 3.234(2) Å], defining a distorted tetrahedral environment [N(1)−Fe−N(2) = 90.20(9)°, N(1)−Fe−N(3) = 125.71(9)°, N(1)−Fe−N(4) = 124.05(9)°, N(2)−Fe−N(3) = 111.88(9)°, N(2)−Fe−N(4) = 118.17(9)°, N(3)−Fe−N(4) = 89.14(8)°]. The distortion is substantially less than in **1** where the interfacing of the two identical -ate units by the two ferrous links is likely to be responsible for the flattening of the tetrahedral coordination geometry. Each of the two potassium atoms is π-bonded to two pyrrole rings of one ligand [K(1)−N(4) = 3.234(2) Å, K(1)−C(19) = 3.079(3) Å, K(1)−C(20) = 3.122(3) Å, K(1)−C(21) = 3.288(3) Å, K(2)−N(3) = 3.095(2) Å, K(2)−C(15) = 3.209(3) Å, K(2)−C(16) = 3.194(3) Å, K(2)−C(17) = 3.038(3) Å, K(2)−C(18) = 2.980(3) Å] and to one molecule of THF. In turn, each potassium atom is π-bonded to the pyrrole ring of a second identical unit, thus assembling an infinite array.

The magnetic moment of **1** shows only a minor variation in the temperature range 55−300 K (μ_{eff} = 7.23−7.47 μ_{B}). At lower temperatures the moment drops rapidly to 3.9 μ_{B} (Figure 3). Although this is a considerably large effect for a simple Zero Field Splitting, the data were nicely fitted by a d^4−d^4 model with a weak antiferromagnetic exchange ($J = -0.84$ cm^{-1}, $g = 2.14$). This is based of course on the assumption that the two metals present in a metallocenic-type arrangement are diamagnetic, which is fairly reasonable given the 18-electron configuration. Complex **2** displays a room temperature magnetic moment ($\mu_{\text{eff}} = 5.67$ μ_{B}) that is substantially higher than expected for the d^6 electronic configuration of a divalent Fe atom in a tetrahedral field [∼5.0−5.2 μ_{B}]. This may be the result of a large orbital contribution, which in turn indicates that dipyrrolide anions provide a weak ligand field.

Anionic -ate types of structures are commonly encountered in the chemistry of dipyrrolide dianions.

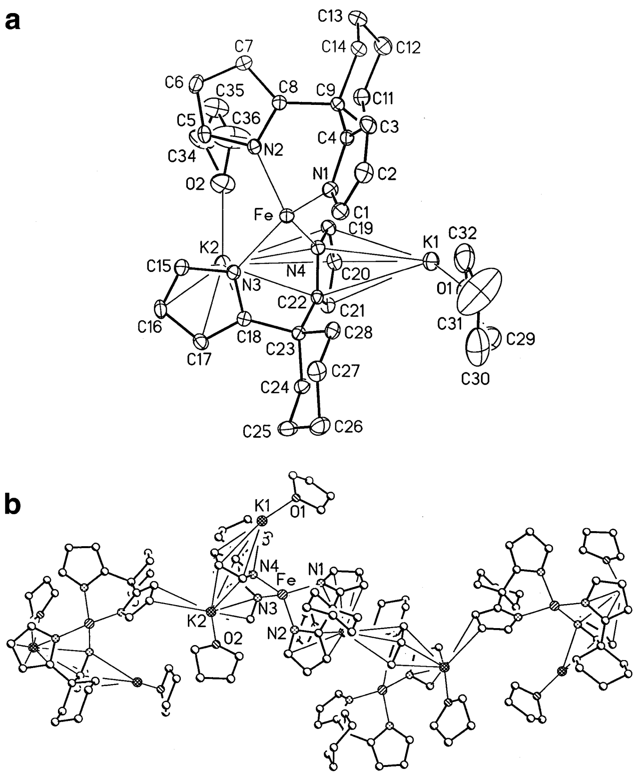

Figure 2. (a) Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at the 30% probability level. (a) PLUTO drawing of **2** showing the polymeric aggregation.

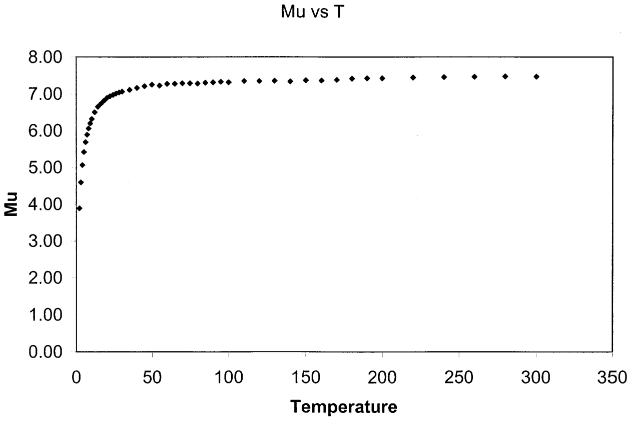

Figure 3. Plot of the magnetic moment of **1** at variable temperatures.

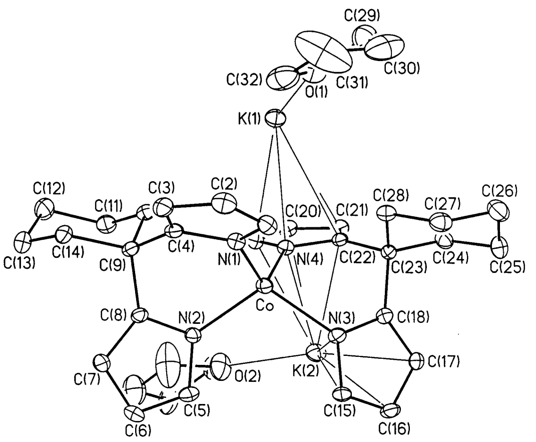

Figure 4. Thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 30% probability level.

Previous work in *f*-block elements,[5a,7] as well as recent results in transition metal chemistry,[4a] has clearly demonstrated an enhanced tendency to form both tetrahedral and octahedral structures, where alkali cations are retained at the exterior of the molecule. This is well reiterated by the reaction of $CoCl_2(THF)_{1.5}$ with either an equivalent amount or an excess of $[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]K_2$ that invariably afforded only $\{[[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Co][K(THF)]_2\}_n$ (**3**). The complex (Figure 4) is basically identical to **2**, and thus the structure does not deserve any special structural consideration. All the bond distances and angles are indeed very similar to those of **2**, including the distortion of the tetrahedral geometry of the metal center, thus indicating that the deviation from the regular tetrahedral geometry is exclusively caused by geometry optimization factors. The room temperature magnetic moment ($\mu_{\text{eff}} = 5.10\ \mu_B$) was as expected for the d^7 electronic configuration of divalent cobalt in a distorted tetrahedral field with a considerable orbital contribution.

The tetranuclear structure of **1** containing two Fe atoms in different coordination environments and magnetic states is rather unique among the large collection of cluster structures provided by this ligand system.[3-6] It is conceivable that the driving force for assembling the tetrametallic structure is provided in this case by the two diamagnetic ferrous links linking the two anionic metalate units with 18-electron ferrocenoid structures. In principle, this possibility might be used for assembling heteropolymetallic cluster structures. To test this possibility we have reacted the anionic Co metalate **3** (for which we found no evidence for the formation of cluster structures) with $FeCl_2(THF)_{1.5}$. The reaction afforded dark-orange crystals of the heterometallic $[\mu,\eta^5\text{-}\{[1,1\text{-}(2\text{-}C_4H_3N)_2C_6H_{10}]_2Co\}Fe]_2$ (**4**) (Scheme 1). Not surprisingly, the complex displays crystallographic cell parameters identical with those for **1**. The structure (Figure 5) showed an arrangement identical with that of **1** with comparable bond distances and angles but a less severe flattening of the tetrahedral coordination of the metal. The presence of the two different metals in the ratio 1:1 was conclusively confirmed by analytical determination via X-ray fluorescence. In addition, the room temperature magnetic moment ($\mu_{\text{eff}} = 6.63\ \mu_B$) was substantially lower than in the case of **1** but as expected for two divalent Co in a distorted tetrahedral environment with minimal magnetic exchange. This reiterates the idea that the two atoms present in the metallocenic type of environment are indeed two Fe atoms. This proposal is strongly supported by room temperature ^{57}Fe Mössbauer spectroscopy. The spectrum of **1** gave two sharp symmetric doublets of equal spectral area (within experimental error of 0.6% of total spectral area) and having center shift (CS, with respect to metallic Fe at room temperature), quadrupole splitting (QS), and Lorentzian half width at half-maximum (G) values of CS/QS/G = 0.52/2.51/0.126 and 0.68/1.30/0.139 mm/s (Figure 6). The doublet with broader lines is ascribed to the distorted tetrahedrally N-coordinated site because it is expected to experience larger local strain distortions than the

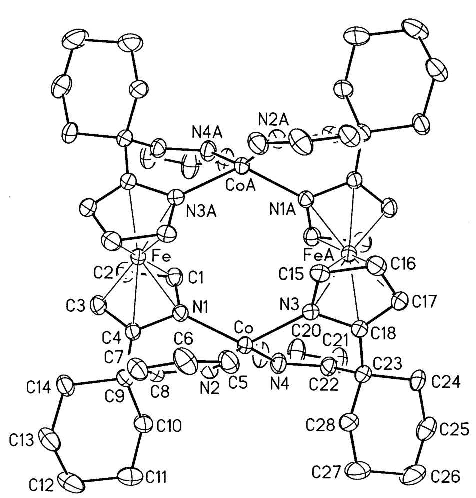

Figure 5. Thermal ellipsoid plot of **4**. Thermal ellipsoids are drawn at the 30% probability level.

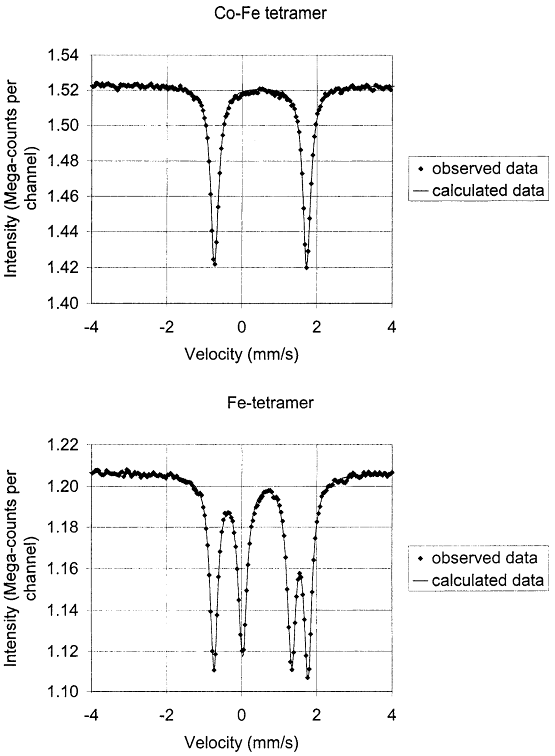

Figure 6. Mossbauer spectra of **1** and **4**.

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[7] Ganesan, M.; Lalonde, M. P.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2443.

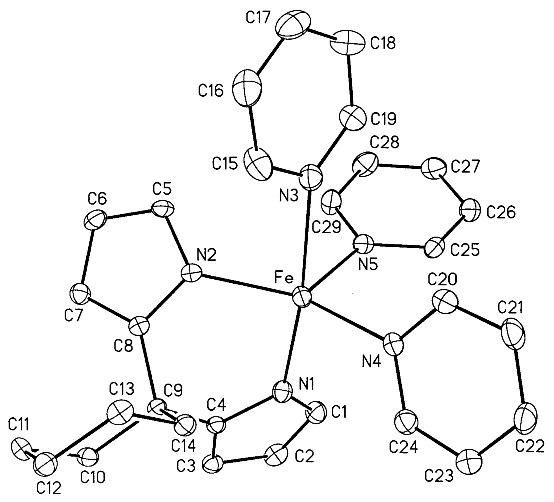

Figure 7. Thermal ellipsoid plot of **5**. Thermal ellipsoids are drawn at the 30% probability level.

more symmetric ferrocenoid irons. Indeed the spectrum of **4** shows only the doublet of the diamagnetic ferrous links with CS/QS/G = 0.50/2.46/0.129 mm/s, showing near perfect occupation of the Co in the tetrahedrally N-coordinated sites (with maximum Fe occupancy of the latter site of 2(1)%).

The robustness of **1** was probed by attempting reduction with 2 equiv of Na-naphthalene. The idea was of course to leave the two ferrous links intact while reducing the other two metal centers to the highly reactive monovalent state. In line with the behavior of related tetranuclear clusters of low-valent samarium,[3] the cyclic structure was disrupted affording, however, elemental iron and [1,1-(2-$C_4H_3N)_2C_6H_{10}]_2Fe[Na(THF)]_2$ (**6**). This implies that the two ferrous links, which that provide the stability necessary to assemble both **1** and **4**, are in reality the primary target of the reductant. Furthermore, the cluster structure could be cleaved by simple attack by coordinating solvents such as pyridine. For example, simple treatment of **1** with pyridine afforded a high yield of [1,1-(2-$C_4H_3N)_2C_6H_{10}]$-Fe(pyridine)$_3$ (**5**). The structure shows a monomeric complex with the pentacoordinated Fe in a severely distorted trigonal bipyramidal arrangement [N(1)−Fe−N(2) = 89.89(8)°, N(1)−Fe−N(3) = 173.61(8)°, N(2)−Fe−N(3) = 83.73(8)°, N(2)−Fe−N(4) = 142.39(9)°, N(3)−Fe−N(4) = 88.66(8)°, N(3)−Fe−N(5) = 85.03(8)°] defined by the N atoms of three coordinated molecules of pyridine and the two N atoms [Fe−N(3) = 2.411(2) Å, Fe−N(4) = 2.192(2) Å, Fe−N(5) = 2.140(2) Å] of one σ-bonded ligand respectively occupying one axial and one equatorial positions [Fe−N(1) = 2.101(2) Å, Fe−N(2) = 2.040(2) Å] (Figure 7).

In conclusion, a dipyrrolide dianion formed with divalent Fe an unusual tetranuclear cluster with two magnetically nonequivalent Fe atoms. The tendency of Fe to form ferrocenoid-type structures by π-coordinating two pyrrolyl rings may be used for the preparation of heterometallic clusters. However, the mild formation conditions of **5** implies that the ferrocenoid Fe atoms, despite providing the driving force for assembling the clusters, may switch from π- to σ-coordination mode and cleave the cluster structure. This lability, which likely implies the presence of equilibria, is rather intriguing and may be important for reactivity purposes. Further work on this line is in progress.

Experimental Section

All operations were performed under inert atmosphere by using standard Schlenk-type techniques and in the drybox. THF complexes of Fe and Co salts were prepared according to standard procedures, and 1,1-dipyrrolylcyclohexane was prepared by the published procedure.[5a] Methyllithium (1.4 M solution in ether) and NaH and KH (suspension in mineral oil) were obtained from Aldrich, washed with hexane, and dried. Infrared spectra were recorded on Mattson 9000 and Nicolet 750-Magna FTIR instruments from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Room-temperature magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. Samples for magnetic susceptibility measurements at variable temperatures were preweighed inside a drybox equipped with an analytical balance and flame sealed into calibrated 5 mm o.d. quartz tubes. Magnetic measurements were carried out on a Quantum Design MPMS5S SQUID magnetometer at 1.0 T, in the temperature range 2−300 K. Accurate sample mass was determined by difference by breaking the tube after data collection. Background data on the cleaned, empty tube were obtained under identical experimental conditions. Standard corrections for underlying diamagnetism were applied to the data.[8] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector. The ^{57}Fe Mössbauer spectra were collected at room temperature in constant acceleration mode on a velocity range of ±11 mm/s, to identify the possible presence of impurities. The raw spectra were folded to produce a flat background and a zero velocity corresponding to the CS of metallic iron at room temperature. The folded spectra were fitted with use of symmetric (equal areas and equal widths) quadrupole doublets of Lorentzian lines. The absorbers were loaded anoxically in gastight holders and had 235 mg of sample per half inch diameter windows.[9]

Preparation of [μ,η^5-{[1,1-(2-$C_4H_3N)_2C_6H_{10}]_2$Fe}Fe]$_2$ (1). A solution of 1,1′-dipyrrolylcyclohexane (0.91 g, 4.2 mmol) in THF was added to a stirred suspension of either KH or NaH (0.21 g, 8.7 mmol) in THF. After the mixture was stirred for 24 h, the addition of a suspension of $FeCl_2(THF)_{1.5}$ (1.0 g, 4.2 mmol) in THF turned the color dark orange. The reaction mixture was stirred for 30 min, filtered, slowly evaporated, and allowed to stand at room temperature to yield bright-orange pyramidal crystals of **1** (0.78 g, 6.4 mmol, 60%). Anal. Calcd (found) for $C_{64}H_{80}N_8O_2Fe_4$: C, 63.17 (63.03); H, 6.62 (6.57); N, 9.21 (9.18). IR (Nujol mull, cm^{-1}): ν 3091 (w), 3042 (s), 1462 (vs), 1377 (s), 1302 (w), 1282 (w), 1264 (w), 1245 (w), 1226 (w), 1213 (w), 1187 (w), 1169 (m), 1129 (s), 1143 (w), 1048 (m), 1035 (m), 1017 (m), 976 (w), 938 (w), 906 (w), 828 (s), 772 (m), 721 (vs).

Preparation of {([1,1-(2-$C_4H_3N)_2C_6H_{10}]_2$Fe[K(THF)]$_2$}$_n$ (2). A solution of 1,1′-dipyrrolylcyclohexane (1.8 g, 8.5 mmol) in THF was added dropwise to a stirred suspension of KH (0.72 g, 17.9 mmol) in THF. A vigorous reaction took place resulting in a cloudy solution. After 1 h of stirring, a suspension of $FeCl_2(THF)_{1.5}$ (1.0 g, 4.2 mmol) was added and the color became slightly yellow. The reaction was allowed to stir overnight and then filtered. The clear yellow solution was concentrated and layered with hexanes. Large, clear crystals of **2** were formed

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(8) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnes, Diamagnetisme, Paramagnetisme, Relaxation Paramagnetique*; Masson: Paris, France, 1957.

(9) Rancourt, D. G. *Hyperfine Interact.* **1998**, *117*, 3.

Table 1. Crystal Data and Structure Analysis Results

	1	2	3	4	5
formula	$C_{64}H_{80}N_8O_2Fe_4$	$C_{36}H_{48}N_4O_2K_2Fe$	$C_{36}H_{48}N_4O_2K_2Co$	$C_{64}H_{80}N_8O_2Co_2Fe_2$	$C_{31.5}H_{33.5}N_{5.5}Fe$
fw	1216.76	702.83	705.91	1222.92	544.99
space group	orthorhombic, *Aba*2	monoclinic, *P*2(1)/*c*	monoclinic, *P*2(1)/*c*	orthorhombic, *Aba*2	monoclinic, *P*2(1)/*n*
a (Å)	20.552(3)	10.9890(8)	11.0006(13)	20.7800(14)	8.6212(15)
b (Å)	19.537(2)	20.4952(14)	20.395(3)	19.5453(13)	17.778(3)
c (Å)	14.2842(16)	16.1207(11)	16.051(2)	14.2942(10)	18.306(3)
β (deg)		101.3950(10)	101.811(3)		100.949(2)
V (Å^3)	5735.4(13)	3559.2(4)	3525.0(8)	5805.6(7)	2754.6(8)
Z	4	4	4	4	4
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	203(2)	203(2)	203(2)	223.(2)	203(2)
D_{calcd} (g cm^{-3})	1.409	1.312	1.330	1.399	1.314
μ_{calcd} (mm^{-1})	1.044	0.694	0.760	1.103	0.578
F_{000}	2560	1488	1492	2568	1148
R, $R_w{}^{2\ a}$	0.0505, 0.0922	0.0554, 0.0868	0.0549, 0.0767	0.0444, 0.0883	0.0549, 0.0932
GoF	1.066	1.059	1.029	1.026	1.027

[a] $R = \sum|F_o| - |F_c|/\sum|F|$. $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

1	2	3	4	5
Fe(1)-N(1) = 2.036(8)	Fe(1)-N(1) = 2,057(2)	Co-N(1) = 2.014(3)	Co-N(1) = 2.079(2)	Fe-N(1) = 2.101(2)
Fe(1)-C(1) = 2.019(10)	Fe(1)-N(2) = 2.043(2)	Co-N(2) = 2.003(3)	Co-N(2) = 1.961(3))	Fe-N(2) = 2.040(2)
Fe(1)-C(2) = 2.083(10)	Fe(1)-N(3) =0.2.051(2)	Co-N(3) = 2.013(3)	Co-N(3) = 2.077(2)	Fe-N(3) = 2.411(2)
Fe(1)-C(3) = 2.065(8)	Fe(1)-N(4) = 2.079(2)	Co-N(4) = 2.031(3)	Co-N(4) = 1.958(3)	Fe-N(4) = 2.192(2)
Fe(1)-C(4) = 2.043(9)	K(1)-N(4) = 3.234(2)	K(1)-N(4) = 3.106(3)	Fe-N(1) = 2.016(2)	Fe-N(5) = 2.140(2)
Fe(2)-N(1) = 2.099(8)	K(1)-C(19) = 3.079(3)	K(1)-C(19) = 3.086(3)	Fe-C(1) = 2.027(3)	N(1)-Fe-N(2) = 89.89(8)
Fe(2)-N(2) = 1.994(8)	K(1)-C(20) = 3.122(3)	K(1)-C(20) =3.120(3)	Fe-C(2) = 2.076(3)	N(1)-Fe-N(3) = 173.61(8)
Fe(2)-N(3) = 2.126(6)	K(1)-C(21) = 3.288(3)	K(1)-C(21) =3.301(3)	Fe-C(3) = 2.073(3)	N(1)-Fe-N(4) = 96.25(9)
Fe(2)-N(4) = 1.993(8)	K(2)-N(4) = 3.034(2)	K(2)-N(4) = 3.016(4)	Fe-C(4) = 2.041(3)	N(1)-Fe-N(5) = 97,97(8)
N(1)-Fe(2)-N(2) = 90.6(3)	K(2)-C(19) = 3.176(3)	K(2)-C(19) = 3.161(3)	N(1)-Co-N(2) = 92.13(9)	N(2)-Fe-N(3) = 83.73(8)
N(1)-Fe(2)-N(3) = 134.3(3)	K(2)-C(20) = 3.292(3)	K(2)-C(20) = 3.300(4)	N(1)-Co-N(3) =130.70(9)	N(2)-Fe-N(4) = 142.39(9)
N(1)-Fe(2)-N(4) = 101.6(3)	K(2)-C(21) = 3.206(3)	K(2)-C(21) =3.208(3)	N(1)-Co-N(4) = 101.71(10)	N(2)-Fe-N(5) = 114.56(9)
N(2)-Fe(2)-N(3) = 99.7(3)	K(2)-C(22) = 3.028(3)	K(2)-C(22) =3.026(3)	N(2)-Co-N(3) = 100.65(10)	N(3)-Fe-N(4) = 88.66(8)
N(2)-Fe(2)-N(4) = 151.1(3)	K(2)-N(3) = 3.095(2)	K(2)-N(3) = 3.090(3)	N(2)-Co-N(4) = 147.06(11)	N(3)-Fe-N(5) = 85.03(8)
N(3)-Fe(2)-N(4) = 90.5(3)	K(2)-C(15) = 3.209(3)	K(2)-C(15) = 3.220(4)	N(3)-Co-N(4) = 92.74(10)	N(4)-Fe-N(5) = 101.31(8)
	K(2)-C(16) = 3.194(3)	K(2)-C(16) = 3.211(4)		
	K(2)-C(17) = 3.038(3)	K(2)-C(17) = 3.046(3)		
	K(2)-C(18) = 2.980(3)	K(2)-C(18) = 2.976(3)		
	N(1)-Fe-N(2) = 90.20(9)	N(1)-Co-N(2) = 91.04(10)		
	N(1)-Fe-N(3) = 125.71(9)	N(1)-Co-N(3) =123.45(11)		
	N(1)-Fe-N(4) = 124.05(9)	N(1)-Co-N(4) = 124.92(10)		
	N(2)-Fe-N(3) = 111.88(9)	N(2)-Co-N(3) = 111.06(11)		
	N(2)-Fe-N(4) = 118.17(9)	N(2)-Co-N(4) = 117.55(11)		
	N(3)-Fe-N(4) = 89.14(8)	N(3)-Co-N(4) = 90.61(1)		

upon standing at room temperature for a few days (1.87 g, 3.0 mmol, 63%). Anal. Calcd (found) for $C_{36}H_{48}N_4O_2FeK_2$: C, 61.52 (61.48); H, 6.88 (6.80); N, 7.97 (7.91). IR (Nujol mull, cm^{-1}): ν 3091 (w), 2917 (s), 1461 (vs), 1435 (s), 1401 (w), 1377 (s), 1297 (w), 1278 (w), 1263 (w), 1228 (w), 1213 (w), 1157 (m), 1127 (w), 1104 (w), 1038 (s), 959 (m), 906 (m), 872 (w), 829 (w), 769 (m), 734 (vs), 724 (s).

Preparation of {[[1,1-(2-$C_4H_3N)_2C_6H_{10}]_2$Co][K(THF)]$_2$}$_n$ (3). A solution of 1,1′-dipyrrolylcyclohexane (1.80 g, 8.4 mmol) in THF was added dropwise to a suspension of KH (0.71 g, 17.7 mmol) in THF. A vigorous reaction took place resulting in a cloudy solution. After 1 h of stirring, the addition of a suspension of $CoCl_2(THF)_{1.5}$ (1.0 g, 4.2 mmol) afforded a deep purple color. The reaction was allowed to stir overnight and then centrifuged. The dark-purple solution was concentrated and layered with hexanes. Large, purple crystals of **3** were formed upon standing at room temperature for 2 days (2.22 g, 3.1 mmol, 75%). Anal. Calcd (found) for $C_{36}H_{48}N_4O_2CoK_2$: C, 61.25 (61.18); H, 6.85 (6.83); N, 7.94 (7.89). IR (Nujol mull, cm^{-1}): ν 3084 (w), 2906 (vs), 1461 (vs), 1440 (s), 1401 (w), 1377 (s), 1341 (w), 1298 (m), 1277 (w), 1265 (w), 1228 (w), 1214 (w), 1198 (w), 1159 (m), 1127 (m), 1106 (m), 1093 (w), 1038 (s), 961 (m), 906 (m), 890 (w), 872 (w), 841 (w), 828 (w), 781 (m), 769 (m), 733 (vs), 724 (s).

Preparation of [μ,η^5-{[1,1-(2-$C_4H_3N)_2C_6H_{10}]_2$Co}Fe]$_2$ (4). A solution of **3** (0.3 g, 0.4 mmol) in THF was added to a stirred suspension of $FeCl_2(THF)_{1.5}$ (1.0 g, 0.4 mmol). The dark burgundy solution was stirred for an additional 2 h and then allowed to stand at room temperature for 2 days. Large dark-orange crystals of **4** were isolated from the white residue by repeated decantation with THF (0.14 g, 0.11 mmol, 53%). Anal. Calcd (found) for $C_{64}H_{80}Co_2Fe_2N_8O_2$: C, 62.85 (62.78); H, 6.59 (6.54); N, 9.16 (9.09). IR (Nujol mull, cm^{-1}): ν 3091 (w), 3042 (s), 1462 (vs), 1377 (s), 1302 (w), 1282 (w), 1264 (w), 1245 (w), 1226 (w), 1213 (w), 1187 (w), 1169 (m), 1129 (s), 1143 (w), 1048 (m), 1035 (m), 1017 (m), 976 (w), 938 (w), 906 (w), 828 (s), 772 (m), 721 (vs).

Preparation of [1,1-(2-$C_4H_3N)_2C_6H_{10}$]Fe(pyridine)$_3$ (5). A solid sample of **1** (0.1 g, 0.082 mmol) was treated with hot pyridine. The resulting bright orange solution was filtered and allowed to stand at −37 °C for 2 days upon which orange-yellow crystals of **5** separated (0.1 g, 0.18 mmol, 55%). Anal. Calcd (found) for $C_{31.5}H_{33.5}FeN_{5.5}$: C, 69.42 (69.38); H, 6.20 (6.17); N, 14.14 (14.09).

Attempted Reduction of 1. A solution of **1** (0.5 g, 0.41 mmol) in THF (30 mL) was treated with 4 equiv of Na(naphthalene). The color became very dark and the colloidal Fe separated by the reaction mixture was eliminated by centrifugation. The brown mother liquor was layered with hexane and allowed to stand at room temperature upon which crystals of [1,1-(2-$C_4H_3N)_2C_6H_{10}]_2$Fe[Na(THF)$_2$]$_2$ (**6**) separated (0.4 g, 0.49 mmol, 31%). Employment of less than 4 equiv of reducing agents only afforded lower yield of **6** and unreacted

1. Anal. Calcd (found) for $C_{44}H_{64}N_4O_4FeNa_2$: C, 64.86 (64.68); H, 7.92 (7.84); N, 6.88 (6.81).

X-ray Crystallography. Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer, using 0.3° ω-scans at 0, 90, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[10]

The systematic absences and unit-cell parameters were uniquely consistent for the reported space group for **2**, **3**, and **5**, $P2_1/c$ ($P2_1/n$) [No.14], and consistent for *Aba*2 [No. 41] and *Acam* (*Cmca*) [No. 64] for **1** and **4**. Only the solution in the noncentrosymmetric space group option, *Aba*2 [No. 41], yielded chemically reasonable and computationally stable results of refinement for **1** and **4**. Refinement of the Flack parameter yielded nil in both cases, indicating that the true hand for each data-set was determined correctly. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. For each of the isomorphous structure pairs, **4** and **1**, and **2** and **3**, the atomic coordinates of the first solved were used as a trial solution for the second. The compound molecule is located on a 2-fold rotation axis for **4** and **1**. The compound exists as an infinite chain for **2** and **3**. A half-molecule of cocrystallized pyridine solvent was located disordered at an inversion center in **5**. A molecule of cocrystallized tetrahydrofuran solvent was located in each asymmetric unit of **4** and **5**. All non-hydrogen atoms, except the disordered pyridine molecule in **5**, which was treated as a rigid hexagon with isotropically refined atoms, were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library.[11] Relevant crystal data and bond distances and angles are given in Tables 1 and 2, respectively.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for structures reported in this work; Ortep plot with full labeling scheme for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] *SADABS*; Bruker AXS: Madison, WI, 2000.

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