

Synthesis and Structure of a Trigonal Monopyramidal Fe(II) Complex and Its Paramagnetic Carbon Monoxide Derivative

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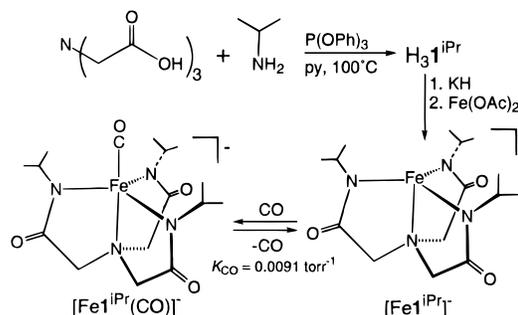
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We report the isolation and structural characterization of an Fe(II) complex containing a trigonal monopyramidal coordination geometry. Trigonal monopyramidal coordination to a metal ion is rare¹ and, to our knowledge, has not been observed previously for Fe(II) ions.² To stabilize this coordination geometry, the tripodal ligand, tris-(*N*-isopropylcarbamoyl-methyl)amine (H_31^{iPr}), was synthesized consisting of a tertiary amine and three deprotonated amides with appended isopropyl groups.³ These isopropyl groups are designed to limit access of exogenous ligands to the Fe(II) center.⁴ This constrained microenvironment can lead to iron adducts with new structural and physical properties, as is illustrated by the formation of a paramagnetic Fe(II)–carbon monoxide complex.

H_31^{iPr} was obtained in a one-step synthesis by treating nitrilotriacetic acid with isopropyl amine and triphenyl phosphite in pyridine (Scheme 1).^{5,6} Isolation of $K[Fe1^{iPr}]$ was accomplished by the following procedure: a solution of H_31^{iPr} (0.200 g, 0.636 mmol) in 10 mL of dry DMF was treated with solid KH (0.077 g, 1.9 mmol) under an Ar atmosphere. After gas evolution ceased, solid $Fe(OAc)_2$ (0.110 g, 0.632 mmol) was added in one portion. The mixture was stirred (1 h) and filtered, and the resulting light yellow solution was concentrated to dryness under reduced pressure to yield a pale yellow powder

Scheme 1



(0.24 g, 78%). Pale yellow crystals were obtained by diffusing diethyl ether into a DMF solution of $K[Fe1^{iPr}]$.⁷

Trigonal monopyramidal coordination in $[Fe1^{iPr}]^-$ is confirmed by an X-ray diffraction study (Figure 1A).⁸ Trigonal ligation to Fe(II) is provided by the three amidate nitrogen donors of $[1^{iPr}]^{3-}$ with an average Fe– N_{amid} distance and N_{amid} –Fe– N_{amid} angle of 2.020(3) Å and 118.7(1)°. The Fe(II) ion lies 0.23 Å out of the trigonal plane formed by N(2)–N(3)–N(4), displaced toward the vacant coordination site. The apical N(1) is positioned perpendicular to the trigonal plane with an average N(1)–Fe– N_{amid} angle of 83.4(1)°. This positioning of N(1) results in $[Fe1^{iPr}]^-$ having near C_3 symmetry where the axis coincided with the Fe–N(1) bond. The Fe–N(1) bond length is 2.098(3) Å, which is similar to those found in other high-spin Fe(II) complexes.^{9,10}

The molecular structure of $[Fe1^{iPr}]^-$ also reveals that the appended isopropyl groups form a cavity about the Fe(II) that encompasses the vacant axial coordination site. The isopropyl groups have adopted bisected conformations in which one methyl moiety of one group is oriented into the cleft formed by the two methyl groups of a neighboring isopropyl group. These conformations position the methyl substituents of each isopropyl group inside the cavity with the methine hydrogens disposed outside the cavity toward the amide carbonyl groups. This arrangement of appended groups occurs, in part, to minimize the steric interactions between the isopropyl and carbonyl groups of each amide moiety.^{11,12}

The “gearing” of isopropyl groups¹³ observed in $[Fe1^{iPr}]^-$ provides a flexible cavity that can accommodate exogenous ligand binding to the Fe(II) center to form five-coordinate complexes. This is demonstrated by the formation of $[Fe1^{iPr}(CO)]^-$ whose molecular structure is shown in Figure 1B.¹⁴ Note that in $[Fe1^{iPr}(CO)]^-$ the isopropyl groups have rotated, enlarging the size of the cavity, as can be seen by the 17.4° reduction in the average angle between the planes formed by O_{amid} – C_{amid} – N_{amid} : N_{amid} – $C_{methine}$ – $H_{methine}$. The binding of an exogenous ligand to $[Fe1^{iPr}]^-$ contrasts with the results found for TMP complexes of $[1^{t-Bu}]^{3-}$, a ligand similar to $[1^{iPr}]^{3-}$ except for the appended *tert*-butyl groups.¹⁵ In these complexes the conformations of *t*-Bu groups prevent binding of exogenous ligands to the metal.

(8) $K[Fe1^{iPr}]$ crystallized with one DMF solvate per molecule in the triclinic space group $P\bar{1}$ with the following cell constants: $a = 8.6150(7)$ Å, $b = 10.3589(8)$ Å, and $c = 14.2889(11)$ Å; $\alpha = 69.800(1)^\circ$, $\beta = 83.897(1)^\circ$, and $\gamma = 84.599(1)^\circ$; $V = 1187.7(2)$ Å³, $Z = 2$. Of 4918 reflections collected ($1.52 \leq \theta \leq 24.12^\circ$, 173(2) K), 3499 were unique data ($F^2 > 2.0\sigma(F^2)$); $R1 = 0.0574$ and $wR2 = 0.1462$ with a GOF(F^2) = 1.101.

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(6) Yield: 60%; FTIR (Nujol, cm^{-1}), $\nu(NH)$ 3316 (s); $\nu(CO)$ 1676 (sh), 1658 (s), 1631 (s); 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.04 (d, 3 H, NH), 4.08 (m, 3 H, $(CH_3)_2CH$), 3.24 (s, 6 H, $-CH_2$), 1.18 (d, 18 H, $(CH_3)_2CH$); mp 146–147 °C (uncorrected); MH^+ *m/e* 315 (CI, isobutane).

(7) Anal. Calcd (Found) for $K[Fe1^{iPr}]\cdot DMF$, $C_{18}H_{34}FeKN_5O_7$: C, 45.09 (45.42); H, 7.15 (7.00); N, 14.61 (14.53). IR (Nujol, cm^{-1}), $\nu(CO)$ 1679 (DMF, s), 1593 (amide, s); λ_{max} (DMF) 343 (2500 $M^{-1} cm^{-1}$); $\mu_{eff} = 5.38\mu_B$ (solid, 298 K), $\mu_{eff} = 4.98\mu_B$ [$(CD_3)_2SO$, 298 K].

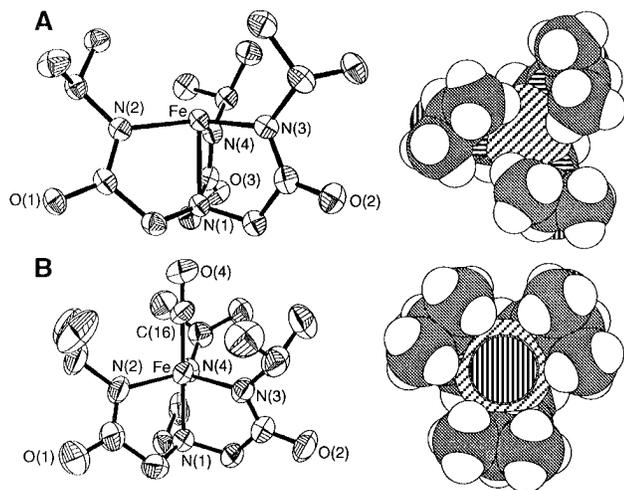


Figure 1. Thermal ellipsoid diagrams of [Fe^{1IPr}]⁻ (A, left) and [Fe^{1IPr}(CO)]⁻ (B, left) and space-filling representations of each complex viewed down their respective pseudo 3-fold axis. The ellipsoids are drawn at the 50% probability level, and hydrogens are removed for clarity.

Table 1. Selected Bond Distances and Angles for [Fe^{1IPr}]⁻ and [Fe^{1IPr}(CO)]⁻

distance (Å) or angle (deg)	[Fe ^{1IPr}] ⁻	[Fe ^{1IPr} (CO)] ⁻	distance (Å) or angle (deg)	[Fe ^{1IPr}] ⁻	[Fe ^{1IPr} (CO)] ⁻
Fe–N(1)	2.098(3)	1.991(3)	N(2)–Fe–N(3)	116.8(1)	120.0(1)
Fe–N(2)	2.017(3)	1.995(3)	N(2)–Fe–N(4)	121.4(1)	117.3(1)
Fe–N(3)	2.017(3)	2.000(3)	N(3)–Fe–N(4)	117.8(1)	116.4(1)
Fe–N(4)	2.026(3)	2.001(3)	Fe–C(16)–O(4)		179.1(3)
Fe–C(16)		1.749(3)	d[Fe–N _{amid}] ^a	0.232	0.293

^a Displacement of Fe from the plane formed by N(2)–N(3)–N(4).

The binding of CO causes a reduction in the Fe–N bond distances. As shown in Table 1, the average Fe–N_{amid} distance is shortened by 0.023 Å (to 1.997(3) Å) in [Fe^{1IPr}(CO)]⁻, while the Fe–N(1) distance has been reduced to 1.991(3) Å. This shortening of bond lengths is suggestive of a reduction in spin state at the Fe(II) center.¹⁵ Carbon monoxide binding to Fe(II) normally produces complexes that are diamagnetic,^{15,16} yet both [Fe^{1IPr}]⁻ and [Fe^{1IPr}(CO)]⁻ are paramagnetic. At room temperature [Fe^{1IPr}]⁻ is high spin with an $\mu_{\text{eff}} = 5.38 \mu_{\text{B}}$, a magnetic moment that is similar to those reported for other $S = 2$ Fe(II) complexes.¹⁷ In contrast, [Fe^{1IPr}(CO)]⁻ has an $\mu_{\text{eff}} = 3.41(2) \mu_{\text{B}}$, consistent with an $S = 1$ formulation.¹⁸ The Mössbauer spectrum of a powder sample of [Fe^{1IPr}(CO)]⁻ at 4.2 K shows a single quadrupole doublet with parameters relative to iron metal of $\delta = 0.26$ and $\Delta E_{\text{q}} = 1.07$ mm/s. The spectrum is not affected by a weak applied magnetic field of 45 mT, which is consistent with a non-Kramers spin system for the complex. The powder Mössbauer spectrum of [Fe^{1IPr}]⁻ at 4.2 K exhibits

a paramagnetic pattern spanning approximately 9 mm/s in a field of 45 mT; this paramagnetic spectrum collapses to a single quadrupole doublet at 77 K with parameters of $\delta = 1.05$ and $\Delta E_{\text{q}} = 3.31$ mm/s. The Mössbauer parameters observed for [Fe^{1IPr}]⁻ are typical of high-spin Fe(II) centers, while those found for [Fe^{1IPr}(CO)]⁻ are within the range of the few known $S = 1$ Fe(II) complexes for which Mössbauer data are available.^{19,20} Powder and frozen solution EPR spectra of [Fe^{1IPr}]⁻ at 4.2 K exhibit an integer spin resonance near $g = 8$, which is typical of $S = 2$ Fe(II) complexes and consistent with the observation of a paramagnetic Mössbauer spectrum in a weak applied field.²¹ Extended Hückel calculations²² indicate that for [Fe^{1IPr}]⁻ the d_{z^2} (a) and $d_{x^2-y^2}$, d_{xy} (e) orbitals have nearly the same energy and lie higher than the d_{xz} and d_{yz} (e) orbitals; upon CO binding the d_{z^2} orbital is raised significantly leading to an orbital arrangement that gives rise to the paramagnetism found in [Fe^{1IPr}(CO)]⁻.

The $S = 1$ spin state observed in [Fe^{1IPr}(CO)]⁻ represents the first example of a paramagnetic Fe(II)–CO complex. The formation of this complex results from the ability of the [1^{IPr}]³⁻ to control the cavity architecture around Fe(II) to restrict the binding of additional ligands and produce a trigonal bipyramidal coordination geometry. The $S = 1$ state is readily achieved in [Fe^{1IPr}(CO)]⁻, but not in six-coordinate Fe(II) carbonyl complexes, owing to the inaccessibility of the $S = 0$ in trigonal symmetry. The binding of CO to [Fe^{1IPr}]⁻ is unusually weak: [Fe^{1IPr}]⁻ reversibly binds CO with a K_{CO} of 0.0091 Torr⁻¹.²³ This binding constant is significantly lower than those reported for most Fe(II) complexes, especially for complexes having linear Fe–C–O motifs as is found in [Fe^{1IPr}(CO)]⁻.^{15a,24} A possible explanation for this lower CO binding constant is that the energy difference between states $S = 2$ and $S = 0$ in distorted-octahedral symmetry is significantly greater than the energy difference between states $S = 2$ and $S = 1$ in trigonal symmetry.²⁵ The constrained microenvironment must also affect exogenous ligand binding, given the large structural reorganization observed upon CO binding (*vide supra*). The relative magnitudes of these electronic and structural effects on exogenous ligand binding can be further examined because the design of [1^{IPr}]³⁻ allows for convenient access to ligands with cavities having different structural and physical properties.²⁶ Studies to address the relative contributions of these effects are in progress.

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Supporting Information Available: Structure determination summaries and tables of X-ray structural data for K[Fe^{1IPr}] and K[Fe^{1IPr}(CO)]; plot of P_{CO} vs % CO uptake and qualitative MO diagrams (Figures S1 and S2) (23 pages). See any current masthead page for ordering and Internet access instructions.

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(14) K[Fe^{1IPr}(CO)] was synthesized by treating a DMF solution of K[Fe^{1IPr}] with excess CO. Diffusion of ether into this solution afforded deep blue crystals in 70% yield. Anal. Calcd (Found) for K[Fe^{1IPr}(CO)]·DMF·H₂O, C₁₉H₃₆FeKN₅O₆: C, 43.43(43.35); H, 6.90(6.49); N, 13.33(13.78); IR (Nujol, cm⁻¹), $\nu(\text{CO})$ 1940 (s), 1678 (DMF, s), 1599 (amide, s); λ_{max} (DMF) 390 (sh), 590 (ϵ , 670 M⁻¹ cm⁻¹), 696 (sh); $\mu_{\text{eff}} = 3.41(2) \mu_{\text{B}}$ (solid, average of three independent measurements at 298 K). K[Fe^{1IPr}(CO)] crystallized with one DMF solvate per molecule in the triclinic space group *P1* with the following cell constants: $a = 9.4318(1)$ Å, $b = 10.9041(3)$ Å, and $c = 12.8403(3)$ Å; $\alpha = 82.938(1)^\circ$, $\beta = 87.196(1)^\circ$, and $\gamma = 83.674(1)^\circ$; $V = 1301.73(5)$ Å³, $Z = 2$. Of 6673 reflections collected ($1.60 \leq \theta \leq 25.10^\circ$, 298(2) K), 4431 were unique data ($F^2 > 2.0\sigma(F^2)$); $R1 = 0.0501$ and $wR2 = 0.1184$ with a GOF(F^2) = 1.084.

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(22) Extended Hückel calculations were done on a CAChe workstation with software provided by CAChe Scientific.

(23) K_{CO} was obtained from the relationship $K_{\text{CO}} = (P_{1/2})^{-1}$. $P_{1/2}$ (110-10) Torr) was measured by volume difference of CO uptake by [Fe^{1IPr}]⁻ in DMF at various partial pressures of CO.

(24) The K_{CO} observed for [Fe^{1IPr}]⁻ is at least 10³ lower than those found for Fe(II) porphyrin complexes (Suslick, K. S.; Reinert, T. J. *J. Chem. Educ.* **1985**, *62*, 974). A similar K_{CO} has been reported for a nonheme Fe(II) complex containing a bent Fe–C–O motif (ca. 170⁰).^{15a}

(25) The release of CO from the trigonal bipyramidal [Fe^{1IPr}(CO)]⁻ complex requires promotion of only one electron to a d_{z^2} orbital to form the uncarbonylated high-spin TMP complex, whereas octahedral Fe(II) complexes require promotion of two electrons to the d_{z^2} , $d_{x^2-y^2}$ orbitals.

(26) For a recent account of the relevance of linear Fe–C–O motifs in biomolecules with constrained microenvironments, see: Lim, M.; Jackson, T. A.; Anfirud, P. A. *Science* **1995**, *269*, 962.

(27) **Note Added in Proof:** Another $S = 1$ Fe–CO complex has been isolated recently by S. A. Koch (submitted for publication).