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Electronic Structure and Magnetic Anisotropy of an Unsaturred Cyclopentadienyl Iron(I) Complex with 15 Valence Electrons

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Dedicated to Professor Evamarie Hey-Hawkins on the occasion of her 60th birthday

Abstract: The 15 valence-electron iron(I) complex [Cp⁺Fe(iPr₂Me₂)] (1, Cp⁺= C₅(C₅H₄-iPr)); iPr₂Me₂ = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene) was synthesized in high yield from the FeII precursor [Cp⁺Fe(u-Br)]. [⁵⁷]Fe Mössbauer and EPR spectroscopic data, magnetic measurements, and ab initio ligand-field calculations indicate an S = 3/2 ground state with a large negative zero-field splitting. As a consequence, 1 features magnetic anisotropy with an effective spin-reversal barrier of Ueff = 64 cm⁻¹. Moreover, 1 catalyzes the dehydrogenation of N,N-dimethylamine–borane, affording tetramethyl-1,3-diaza-2,4-diboratane under mild conditions.

Decades after cyclopentadienyl iron compounds entered the spotlight,[¹,²] this extensive class of compounds continues to fascinate owing to new fundamental insights[³,⁴] and wide-ranging applications in catalysis and materials science.[⁵,⁶] Countless examples make use of ferrocene derivatives.[⁷]

Mononuclear cyclopentadienyl iron(I) compounds [CpFe-(L)] (L being a two-electron donor) are scarce.[⁸] One example is the [Cp⁺Fe(dppe)] radical (A, Cp⁺ = η⁵-C₅Me₅, dppe = 1,2-bis(diphenylphosphino)ethane; Figure 1). While this complex is stable at room temperature as a monomer, related carbonyl complexes [Cp³Fe(CO)₂] (B, Cp³ = η⁵-C₅H₅, and η⁵-C₅Me₅) usually dimerize very rapidly to carbonyl-bridged complexes C.¹⁰ Monomer–dimer equilibria were observed even with rather bulky pentaaryl-substituted cyclopentadienyl ligands [Cp⁴ = η⁵-C₅Ph₅, η⁵-C₅Ph₅(p-tolyl), and η⁵-C₅(C₅H₄-nBu)₅].¹¹ The penta-isopropyl-substituted complex [η⁵-iPr₂Fe(CO)₅] is a monomer in solution, but forms a carbonyl-bridged dimer in the solid state.¹²

Stable 15 valence electron (VE) iron(I) species of the type [Cp⁺Fe(L)] appear to be unknown.¹³⁻¹⁴ IR spectroscopic studies suggested the formation of a triply bonded species [CpFe(CO)Fe(CO)Fe(CO)] by stepwise decarbonylation of [CpFe(CO)₃] in a 3-methylpentane matrix at 98 K,¹⁵ while prolonged heating of [CpFe(CO)₅] in xylene led to the tetrahedral cluster [Cp₃Fe₂(CO)₄].¹⁶ Herein, we report the synthesis of a 15 VE cyclopentadienyl iron(I) complex [Cp⁺Fe(iPr₂Me₂)] (1, iPr₂Me₂ = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene). Spectroscopic studies, magnetic measurements, and quantum-chemical calculations revealed...
a pronounced magnetic anisotropy for 1, a property required for single-molecule magnets (SMMs).\(^{17-19}\)

Complex 1 was isolated in 78% yield by reducing \([\text{Cp}^\text{Ar}^{\text{FeBr}}(\text{IPr})_2]\) \(2\), which had been prepared in situ from \([\text{Cp}^\text{Ar}^{\text{Fe}}(\mu-\text{Br})_2]\). \(3\), \(\text{Cp}^\text{Ar}^{\text{Fe}} = \text{Cp}(\text{C}_5\text{H}_5,4-\text{Et})_2\) and \(\text{IPr}_2\text{Me}_2\) (Scheme 1), with potassium graphite in benzene over two days.\(^{20}\) Broad \(^1\text{H}\) NMR resonances were observed in \(\text{C}_2\text{D}_6\) solution between \(-36\) and \(61 \text{ ppm}\) (Figure S1 in the Supporting Information). Single-crystal X-ray diffraction revealed the slightly bent “pogo-stick” structure of 1 (Figure 1) with an \(\eta^1\)-coordinated \(\text{Cp}^\text{Ar}^{\text{Fe}}\) ligand and \(\text{Cp}^\text{Ar}^{\text{ centroid}}\)-Fe-Carbone angles of \(162.11(8)^\circ\) and \(171.19(8)^\circ\) for two crystallographically independent molecules in the unit cell. The Fe–Cp\(^\text{Ar}^{\text{ centroid}}\) (centroid) distance \(1.851(1)\) and \(1.847(1) \text{ Å}\) is shorter than in \(2\) \(2.038(1)\) and \(2.020(1) \text{ Å}\) for two crystallographically independent molecules. The Fe–C\(_{\text{carbon}}\) bonds (1.992(2) and 1.996(2) Å) are similar in length to the Fe–C\(_{\text{carbon}}\) bond of \(2.014(2)\) Å for two-coordinate \([\text{IPr}]\text{Fe}^\text{III}[\text{N}\{\text{SiMe}_3\}_2\text{Dipp}]\) (Dipp = \(\text{C}_6\text{H}_{11}-2,6\)-iPr\)\(^{21}\)) and the Fe–C\(_{\text{carbon}}\) bonds of \(2.110(3)\) and \(2.128(3)\) Å observed for Fe\(^{d^3}\) complex 2. Dark-yellow 1 is paramagnetic, thermally stable, and air-sensitive as a solid. A magnetic moment of \(\mu_{\text{eff}} = 5.4(1)\) \(\mu_\text{B}\) was determined in \(\text{C}_2\text{D}_6\) solution using the Evans method.

Linear two-coordinate Fe\(^{d^3}\) \((d^2)\) and Fe\(^{d^1}\) \((d^1)\) complexes possess \(\text{E}^\text{2}\) and \(\text{E}^\text{1}\) electronic ground states and therefore have unquenched orbital momenta.\(^{22-27}\) Spin–orbit coupling leads to orbital moment contributions to the \(S = 2\) and \(S = 3/2\) spins. Therefore, some orientations of the magnetic moment will be strongly preferred (magnetic anisotropy). We were keen to study how the unsymmetric structure that arises from the \(S\) bond of \(2\) \(\text{Fe}^\text{ Ar}^{\text{ centroid}}\)-Fe-Carbone angles \(162.11(8)^\circ\) and \(171.19(8)^\circ\) affects the electronic structure and the magnetic behavior.

Temperature-dependent magnetic susceptibility and variable-temperature/variable-field (VTWH) magnetization measurements (Figure S12) support an \(S = 3/2\) spin ground state, with best fit values of \(g_x = g_y = 2.18, g_z = 2.52, D = -33.4 \text{ cm}^{-1}\), and \(E(D) = 0\). The large negative zero-field splitting parameter \(D\) indicates that at low temperatures, only the Kramers doublet with \(m_s = \pm 3/2\) is populated, which is a prerequisite for Fe\(^{d^1}\)-based SMMs.

A first indication for the SMM-type behavior of 1 came from Mössbauer spectra (Figure S16), which are in line with a large unquenched orbital magnetic moment at low temperature. The spectrum at 80 K is unsymmetrically broadened, indicating the onset of slow paramagnetic relaxation on the Mössbauer time scale (ca. \(10^{-5} \text{ s}\)).\(^{30}\) At 7 K, this leads to a sharp octet, which could be simulated with a spin Hamiltonian calculation for an effective spin of \(S = 3/2\) and a uniaxial internal magnetic field on the iron nucleus of \(H_{\text{int}} = 16.1 \text{ T}\).

Alternating current (AC) magnetic susceptibility measurements in the absence of a direct current (DC) magnetic field (Figure S13) revealed a characteristic out-of-phase signal even though the characteristic maxima in the imaginary part \(\chi''\) were not observed, which is presumably due to barrierless quantum tunneling of magnetization enabled by the bent structure of 1. The application of DC fields of \(\geq 1000 \text{ Oe}\) (Figure S14), which suppress quantum tunneling, led to the clear observation of frequency-dependent maxima of \(\chi''\) (Figure 2). Analysis of the temperature-dependent \(\chi''\) data (Figure S15) taking into account Raman and Orbach relaxation mechanisms\(^{42}\) revealed an energy barrier of \(U_{\text{eff}} = 63.6 \text{ cm}^{-1}\) and a characteristic relaxation time of \(\tau_0 = 6.8 \times 10^{-8} \text{ s}\). The calculated \(U_{\text{eff}}\) parameter \((63.6 \text{ cm}^{-1})\) is in good agreement with the value estimated from DC susceptibility measurements \((12D = 67 \text{ cm}^{-1})\).

To probe the electronic structure and the magnetic properties of 1, we carried out complete active space self-consistent field (CASSCF) and \(n\) electron valence state perturbation theory to second order (NEVPT2) calculations on the crystallographically determined molecular structure (see the Supporting Information). By using the recently developed ab initio ligand field theory (AILFT),\(^{39}\) the Racah parameters \(B\) and \(C\) and the spin–orbit coupling parameter \(\zeta\) were calculated. The Cp\(^\text{Ar}^{\text{ centroid}}\) and N-heterocyclic carbene (NHC) donors and the considerable tilting of the cyclopentadienyl ligand (Cp–Fe–C angle 166.6\(^\circ\)) lead to a modification of the electronic structure (Figure 3a) compared with an ideal linear MX\(_3\) complex:

i) The NHC ligand features out-of-plane electrons that are available for \(\pi\)-bonding but no such electrons in the ligand plane. This \(\pi\)-anisotropy leads to a splitting of the \(d_{\alpha\alpha}d_{\alpha\beta}\) orbital pair, which would otherwise be degenerate.

ii) Bending of the Cp–Fe–C vector from linearity induces a splitting of the \(3d_{\alpha\alpha}3d_{\alpha\beta}\) orbital pair owing to indirect (via their mixing with \(3d_{\alpha\alpha}n\) \(\alpha\)- and \(\pi\)-overlap with ligand orbitals, which becomes non-zero for C-Fc–C deviating from linearity.

\[\text{Scheme 1. Synthesis of 1; } \text{Ar} = \text{C}_6\text{H}_{14}-4\text{-Et}. \text{ Reagents and conditions: } i) \text{addition of IPr}_2\text{Me}_2, \text{ benzene, RT; } ii) \text{addition of KBr and benzene, loss of KBr and graphite.}\]
Figure 3. a) ALLFT (NEVPT2) ligand-field diagram for 1 with leading 3d MO contributions for Fe. b) Orbitals splitting and electronic configurations for the ground state (σg, energy at 0) and the Σ* excited state (energy at 12 B−Δs) of 1 following holohedrization of the ligand field matrix from the reported C4v to Cσv point symmetry; the diagram has been plotted using parameter values of B = 722 cm−1 and Δs = 751 cm−1 as derived using the procedure elaborated in the Supporting Information. The orbitals d⊥ and d∥, which are singly occupied in both states, were computed at 1979 cm−1 and are not shown.

iii) Large 3d–4s mixing is evident from the very low energy of the MO of d⊥ character. This is due to metal–ligand interactions, which place this MO just above the 3d⊥ MO.

iv) The low symmetry induces extensive 3d MO mixing.

Taken together, these effects (i–iv) lead to an unusual configuration of the 3d orbitals in the (nonrelativistic, spin-free) ground state. In addition, interelectronic repulsion energetically favors a non-aufbau electron distribution in the ground state as shown in Figure 3b for complex 1 following the holohedral symmetry Cσv (see the Supporting Information for details regarding the procedure). The aufbau occupation d⊥,d∥,d⊥,d∥,d⊥,d∥ corresponds to an excited state that is disfavored in energy by 12 B = 8664 cm−1 (B = 722 cm−1) with respect to the 4Δ ground state. This large energy by far exceeds the d⊥–d∥,d⊥–d∥,d⊥–d∥ orbital energy difference of Δs = 751 cm−1.

The S = 3/2 ground state additionally splits into two separate Kramers doublets, \( |m_s|= \pm 1/2 \) and \( |m_s|= \pm 3/2 \), through spin–orbit coupling. The \( |m_s|= \pm 3/2 \) Kramers doublet is the magnetic ground state owing to the negative zero-field splitting parameters \( D = -42 \) cm−1 and \( E = -0.50 \) cm−1. The experimental value of \( D = -33.4 \) cm−1, see above) is somewhat smaller, presumably owing to vibronic coupling. Large orbital contributions to the effective magnetic moment are apparent from the calculated effective g-tensor values with dominant axial (Ising-type) anisotropy for the ground-state Kramers doublet (\( g_z, g_x = 8.362, 0.075 \), and \( g_y = 2.955, 4.056, 4.182 \)). These can be compared with the computed intrinsic spin Hamiltonian values of \( g_z, g_x = 2.802, 2.080, 2.067 \).

The results of the calculations are consistent with our EPR spectroscopic data for 1. The Δm = 3 transition within the magnetic \( |m_s|= \pm 3/2 \) ground-state doublet is formally forbidden, and hence associated with a very weak EPR signal intensity. Accordingly, X-band EPR measurements at 30 K using a microwave power of about 1 mW merely showed the signals of a minor \( S=1/2 \) impurity (< 0.1 % of the total Fe concentration according to spin integration measurements, see Figure S17). Only in spectra recorded with a higher microwave power (200 mW) and at a lower temperature (8 K), a derivative signal consisting of a relatively sharp low-field peak at \( g_{eff} = 7.76 \) became visible (Figure S18), which corresponds to the main \( S=3/2 \) species. This signal can be assigned to the resonance stemming from the z-component of the very anisotropic \( g_{z,3/2} \) tensor of the \( \pm 3/2 \) Kramers doublet. With a sufficiently large zero-field splitting relative to the microwave energy (\( \hbar \nu \approx 0.3 \) cm−1 for X-band), the effective g-value (\( g_{eff} \)) of the \( g_{z,3/2} \) signal should depend only on the rhombicity parameter E/D and the real g-value of the \( S=3/2 \) species.[40] The deviation of the measured effective g-value from the expected value of six thus shows that the g-tensor of the \( S=3/2 \) system indeed has a z-component that is significantly larger than two. Based on the near-zero rhombicity parameter (E/D ≈ 0) found by the magnetic measurements and the calculations, a reasonable value of \( g_z \approx 2.55 \) can be estimated from spectral simulations, thus reproducing the position of the experimentally observed EPR signal at \( g_{eff} = 7.76 \). This value compares well with the value of \( g_z = 2.6 \) reported for [(nacnac)Fe2(AdNNNADL)] [nacnac = HC(C(Me)N(C6H4-2,6-Pr2))], which also has an S=3/2 ground state with a large negative zero-field splitting, \( D < 0 \).[40]

The SMM-type behavior of 1 is unusual given the unsymmetric, non-linear molecular structure.[17,21–27] Several linear FeI and FeII complexes have been reported to feature large unquenched orbital contributions to the magnetic moment.[21–27,29–31,34–37] A few of these have SMM properties. For example, the FeII complex [{(CyPr3)Fe(C6H4-2,6-Pr2)}], which has a linear structure, does not show slow magnetic relaxation in the absence of an applied field owing to fast quantum tunneling of magnetization,[25] but a spin-reversal barrier of \( U_{eff} = 28.1 \) cm−1 was determined in a DC field of 750 Oe. Similar spin-reversal barriers were determined for linear FeI species, for example, [K(L)][FeI(N(SiMe3)2)2] (L = [18]crown-6 and [2,2,2]crypt, \( U_{eff} = 43 \) and 64 cm−1)[33] trigonal-planar [(CAAC)FeCl] (\( U_{eff} = 22.4 \) cm−1)[34] [FeII(N(SiMe3)2)2(PCy3)2][26,32] and the tetrahedral complex [(PNP)FeCl4] (PNP = N2-P(CHMe2)3-4-methylphenyl), \( U_{eff} = 32–26 \) cm−1.[28] Significantly, the highest spin-reversal barrier reported for any Fe-based SMM was observed for [K(crypt-222)][FeII(C(SiMe3)2)2] (D, \( U_{eff} = 264 \) cm−1), which has axial \( D_{eff} \) symmetry and a “E ground state.[30] As a consequence, D shows magnetic hysteresis and blocking of the magnetization at temperatures below 4.5 K.

Why is the spin-reversal barrier in I smaller than that in D? To address this question, we performed calculations on the model complex [Fe(CHO)2]− (see the Supporting Information), which has a D6h symmetric structure. Compared to I, D has higher ground-state anisotropy (\( g_z = 10 \) in [Fe(CHO)2]−, \( g_z = 8.4 \) in I) and a larger energy separation between the ground and the lowest excited Kramers doublet (224 cm−1 in [Fe(CHO)2]−, 84 cm−1 in I). However, the most striking difference is the direct relaxation pathway predicted to be available in I. As shown by Figure 4, the transitions from the ground state to the excited states are accompanied by sizable horizontal pathways (usually referred to as quantum tunnel-
neering of magnetization); these are larger for the excited state (1.62) and smaller, yet non-negligible (0.48), for the ground state. Unlike the vertical transitions, which require an absorption (emission) of vibrational quanta that is hardly accomplished at cryogenic temperatures, horizontal transitions provide a pathway for magnetic relaxation in 1. In particular, direct transitions between the ground-state sublevels are expected to dominate for temperatures of 2 to 10 K. For [Fe(CH$_3$)$_2$]$,^9$ we did not observe horizontal relaxation because with the high $D_{2h}$ symmetry and without vibrations lifting the center of inversion, there is no transversal anisotropy that can assist the reversal of the magnetic moment (Figure S19).

In an initial study of the reactivity and the catalytic properties of 1, we found that this complex does not react with H$_2$ and N$_2$ under ambient conditions, but it is an active (pre)catalyst for the dehydrogenation of $N,N$-dimethylamine–borane (DMAB).[43–48] This reaction came to our attention through a recent report by Manns and co-workers, who used the carbonyl complexes [CpFe(CO)$_3$], [CpFe(CO)$_2$], and [CpFe$_2$(CO)$_3$]([C$_8$H$_8$CN]) as catalyst precursors.[49] In the presence of 1 (5 mol%), DMAB was completely converted within 7 h into tetramethyl-1,3-diaza-2,4-diboratane (4) and bis(dimethylamino)borane (5), which were formed in a 9:1 ratio according to $^1$B NMR spectroscopy (Scheme 2 and Figures S3–S5). Tetramethyl-1,3-diboratane 6 was detected as an intermediate. Catalyst 1 remained active after conversion was complete as shown by the addition of fresh substrate (Figures S9 and S10). Quantitative poisoning studies with P(OMe)$_3$ and dibenzo[a,e]cyclooctatetraene (DCT) point towards a homogeneous mechanism (Scheme 2, see the Supporting Information for details).

In summary, we have synthesized the first 15 VE cyclopentadienyl iron(I) complex 1, which is a rare organometallic iron complex with a heteroleptic structure and the properties of a single-molecule magnet.[17,18] The basis for the SMM behavior is the unusual electronic structure, where extensive metal–ligand interactions and 3d–4s mixing that are due to the bent structure produce a nearly orbitally degenerate ground state. As a consequence, 1 shows slow relaxation of the magnetization in the presence and even in the absence of an external magnetic field. Furthermore, 1 catalyzes dimethylamine–borane dehydrogenation, a reaction for which only a few other iron catalysts are known.[19–28] This initial result bodes well for the future development of further synthetic and catalytic applications of 1 and related cyclopentadienyl iron(I) complexes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbene ligands · cyclopentadienyl ligands · homogeneous catalysis · iron · magnetic properties

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value is somewhat higher than the typical values. However, a value of $\delta$ was determined for this complex based on magnetic measurements and $^{19}$Fe Mössbauer studies. In contrast to $I\text{Fe}^{\text{III}}$ complexes, we determined $^{19}$Fe Mössbauer parameters for a few two-coordinate Fe complexes (ca. 0.4 to 0.5 mm/s), indicating the high sensitivity of the Mössbauer parameter to the electronic and geometric effects of coordinating ligands.


