# UC Riverside
## UC Riverside Previously Published Works

**Title**

A Terminal N2 Complex of High-Spin Iron(I) in a Weak, Trigonal Ligand Field

**Permalink**

https://escholarship.org/uc/item/78q5x52n

**Journal**

Journal of the American Chemical Society, 137(28)

**ISSN**

0002-7863

**Authors**

McSkimming, Alex
Harman, W Hill

**Publication Date**

2015-07-22

**DOI**

10.1021/jacs.5b06337

Peer reviewed

# A Terminal N$_2$ Complex of High-Spin Iron(I) in a Weak, Trigonal Ligand Field
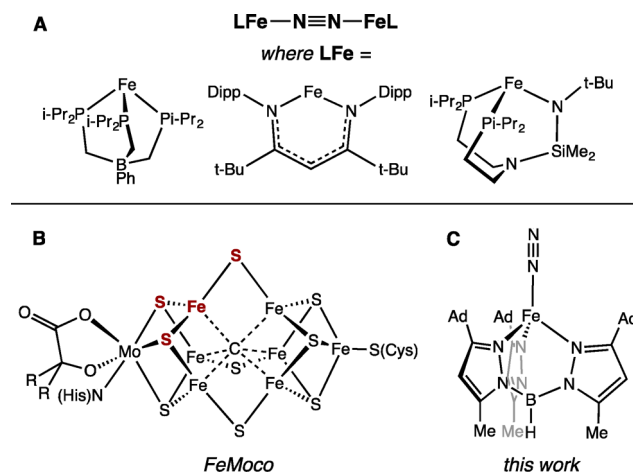
Alex McSkimming and W. Hill Harman*

Department of Chemistry, University of California, Riverside, California 92521, United States

**S** Supporting Information

**ABSTRACT:** The role of Fe in biological and industrial N$_2$ fixation has inspired the intense study of small molecule analogues of Fe−(N$_x$H$_y$) intermediates of potential relevance to these processes. Although a number of low-coordinate Fe−(N$_2$) featuring varying degrees of fidelity to the nitrogenase active site are now known, these complexes frequently feature strongly donating ligands that either enforce low- or intermediate-spin states or result in linear Fe−(N$_2$)−Fe bridging motifs. Given that the nitrogenase active site uses weak-field sulfide ligands to stabilize its reactive Fe center(s), N$_2$ binding to high-spin Fe is of great interest. Herein, we report the synthesis and characterization of the first terminal N$_2$ complex of high-spin ($S = 3/2$) Fe(I) as well as a bridging Fe−(N$_2$)−Fe analogue. Electron paramagnetic resonance and solution magnetic moment determination confirm the high-spin state, and vibrational experiments indicate a substantial degree of activation of the N≡N bond in these complexes. Density functional theory calculations reveal an electronic structure for the terminal adduct featuring substantial delocalization of unpaired spin onto the N$_2$ ligand.

**Figure 1.** (A) Examples of previously reported Fe−($\mu$-N$_2$)−Fe complexes that possess local spin states of $S > 1$. (B) The FeMoco active site of nitrogenase with a potential N$_2$ binding site highlighted. (C) A terminal N$_2$ complex of $S = 3/2$ Fe(I) (this work).

The fixation of atmospheric N$_2$ is an essential process in both the natural world and modern human society.[1] Given the kinetic challenges of activating the N−N triple bond and the inherent chemical complexity of such a process, the systems responsible for biological[2] and industrial[3] N$_2$ fixation have been subjected to intense scrutiny. Despite recent advances in the field, the detailed mechanism of N$_2$ fixation by nitrogenase has yet to be fully elucidated.[4] Indeed, some of the proposed elementary steps of this mechanism are without synthetic precedent. Inspired by the FeMoco active site of nitrogenase (Figure 1B) (and its non-Mo congeners),[5] the synthetic inorganic community has targeted model complexes to reveal the fundamental chemistry of N$_2$ activation at transition-metal centers,[6] culminating in the discovery of synthetic molecular systems based on Mo[7] and Fe[8] for the catalytic reduction of N$_2$ to NH$_3$.

Although an N$_2$ adduct of the FeMoco has not yet been characterized, biochemical studies have provided compelling evidence for Fe as the likely site(s) of N$_2$ binding.[4] Concurrently, a wealth of model chemistries for N$_2$ and related nitrogenous substrates have been discovered with Fe-based molecular systems,[9] including systems capable of facile, reversible N≡N cleavage.[10] Although the coordination chemistry of N$_2$ with Fe has been studied since the 1970s,[11]

most Fe−(N$_2$) complexes are diamagnetic, 18-electron species,[9] and only recently have paramagnetic Fe−(N$_2$) complexes been fully characterized.[12] Many of these complexes are supported by sterically demanding, strong-field ligands such as phosphines or redox-active pyridine-diimine (PDI) ligands resulting in spin states of $S = 1/2$ or 1 at Fe. These species stand in contrast to a hypothetical N$_2$ adduct of a belt Fe of FeMoco. Given the weak-field nature of sulfide ligands, such a complex would likely feature a locally high-spin Fe (Figure 1B). Targeting synthetic models of N$_2$ coordination to high-spin Fe in weak ligand fields is therefore an important area of study. The only Fe−(N$_2$) complexes thought to have local spin states greater than $S = 1$ are linear Fe−($\mu$-N$_2$)−Fe bimetallic complexes supported by $\beta$-diketiminate (NacNac),[12a] tris(phosphinomethyl)borate (PhBP$^{iPr}_3$),[12b] or hybrid phosphine/amide[12c] ligands (Figure 1A). The bimetallic nature of these complexes complicates the analysis of the local ligand field and spin state at Fe, and while these complexes are capable of substantial N$_2$ activation, the bridging N$_2$ ligand does not experience the polarization of both spin and electron density expected for a terminal N$_2$ adduct. Prior to this work, terminal high-spin Fe(I)−(N$_2$) complexes had not been isolated. Herein, we report the synthesis and characterization of such a complex along with its bridging analogue.

With sufficiently bulky substituents at the 3-position of the pyrazole rings, four-coordinate TpFe complexes can be isolated.[13] Of these complexes, $(PhTp^{tBu})Fe(CO)$ prepared by Parkin et al. is the lone example of a monovalent TpFe complex.[14] We were curious to ascertain if an analogous $N_2$ complex could be prepared and if such a complex might adopt a high-spin state. To wit, reduction of the known complex $Tp^{Ph,Me}FeCl^{15}$ (1) with potassium naphthalenide in toluene gave the deep burgundy $N_2$-bridged dimer $(Tp^{Ph,Me}Fe)_2(N_2)$ (2, Scheme 1). Single-crystal X-ray diffraction (XRD)

**Scheme 1**
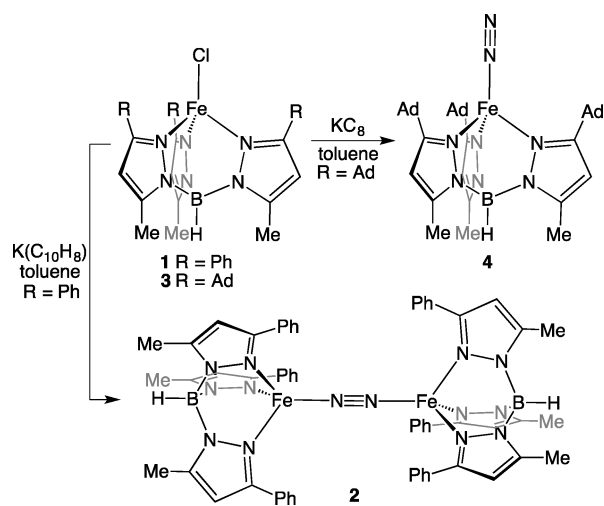


performed on 2 reveals a staggered orientation of the two Tp ligands with an essentially linear $Fe-(N_2)-Fe$ linkage ($\angle Fe-N-N = 177.7°$) which sits on a crystallographically imposed inversion center (Figure 2). The N−N bond length of 1.1804(19) Å for 2 is similar to that found in $[(NacNac)-Fe]_2(N_2)$ complexes and indicative of substantial backbonding from the Fe centers.

The IR spectrum of 2 is featureless in the region containing N−N stretching bands; however, Raman spectroscopy reveals
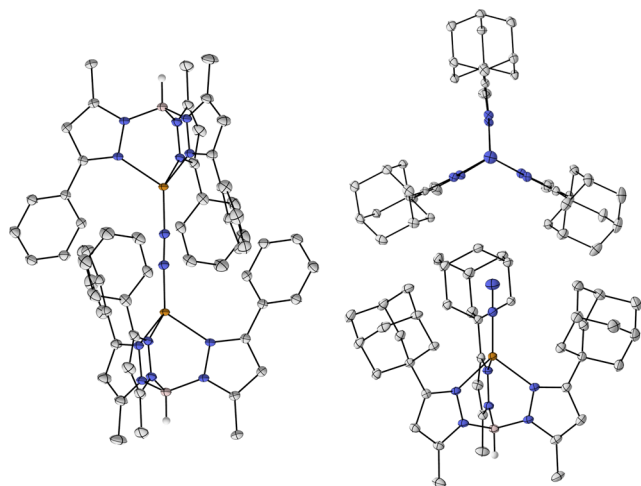


**Figure 2.** Thermal ellipsoid plots (50% probability) of the solid-state structures of 2 (left) and 4 (top view, top right; side view, bottom right). Orange, blue, pink, and gray ellipsoids represent Fe, N, B, and C atoms, respectively. Hydrogen atoms bonded to carbon and cocrystallized solvent molecules are omitted for clarity.

an absorption at 1779 $cm^{-1}$, consistent with a strongly activated $N_2$ unit. Solution magnetic moment determination by the method of Evans gives a value for $\mu_{eff}$ of $6.9 \pm 0.2\ \mu_B$, consistent with a well-isolated $S = 3$ ground state at ambient temperature (spin-only value for $S = 3$:6.9 $\mu_B$). Either strong ferromagnetic superexchange coupling between two $S = 3/2$ Fe(I) centers or a three-spin ferrimagnetic interaction involving two $S = 2$ Fe(II) centers coupled antiferromagnetically to a triplet $(N_2)^{2-}$ ligand would be consistent with these data. However, ferromagnetic superexchange coupling via $N_2$ is typically weak,[16] at odds with the effective magnetic moment observed for 2 at ambient temperature. The latter three-spin model has been used to explain magnetic Mossbauer data collected on the related $[(NacNac)Fe]_2(\mu-N_2)$.[17] Given its similarity to these complexes, the three-spin model is a compelling description for 2. This analogy is further supported by the presence of an intense near IR band (903 nm, 3300 $M^{-1}cm^{-1}$) observed for 2 (see Supporting Information, SI) similar to that observed in the neutral $[(NacNac)Fe]_2(\mu-N_2)$ complexes.[18] Detailed spectroscopic and magnetic studies are underway to further characterize these interactions.

The successful synthesis of 2 led us to explore the possibility of stabilizing an analogous terminal Fe−($N_2$) complex through the introduction of vertically oriented steric bulk at the 3-position of the pyrazole donors. We therefore prepared the complex $Tp^{Ad,Me}FeCl$ (3) that was then reduced by $KC_8$ in toluene to give pale purple $Tp^{Ad,Me}Fe(N_2)$ (4) (Scheme 1). XRD on single crystals of 4 grown from toluene reveals an approximately three-fold symmetric pseudotetrahedral coordination sphere at Fe,[19] with a N≡N distance of 1.1187(17) Å (Figure 2). In contrast to 2, solid samples of 4 possess an intense IR absorption at 1959 $cm^{-1}$, consistent with a strongly activated, terminally bound $N_2$ ligand. Evans' method data on 4 give a value for $\mu_{eff}$ of $3.8 \pm 0.2\ \mu_B$, consistent with an $S = 3/2$ Fe(I) center. The most compelling evidence for the assignment of a high-spin state for 4 comes from X-band EPR spectroscopy. A frozen toluene solution of 4 at 106 K reveals prominent features at $g_{eff} = 4.0$ and $g_{eff} = 2.0$ consistent with transitions within the $m_S \pm 1/2$ doublet of an axial $S = 3/2$ system (Figure 3).[20] Under the conditions investigated, no hyperfine structure was resolved.

Density functional theory (DFT) calculations (M06L[21] with a custom Alrichs[22] basis set via ORCA,[23] see SI) were carried out on the model complex $TpFe(N_2)$ in order to gain insight into the electronic structure of 4. Geometry optimization on the quartet surface reproduced the experimental geometry well, yielding an essentially $C_{3v}$ structure in the absence of any symmetry constraints. Optimization on the doublet surface resulted in a higher energy structure (by ~0.035 $E_h$) that deviated substantially from three-fold symmetry, lending further support for an $S = 3/2$ assignment for 4 (see SI). Interestingly, Mulliken spin population analysis designates only two atoms in the molecule with significant spin density (>0.05): Fe (3.31) and the distal nitrogen of the $N_2$ ligand ($N_\beta$, −0.24) (Figure 4).

The one-electron frontier molecular orbitals calculated for $TpFe(N_2)$ provide some insight into the origin of this spin distribution (Figure 5). While care should be taken in the interpretation of canonical orbitals,[24] the orbital structure shown in Figure 5 is not readily described in terms of five, two-electron d-orbitals that are filled according to the Aufbau principle in either a low- or high-spin configuration. The lowest-energy d-orbital has $d_{z^2}$ parentage followed by a
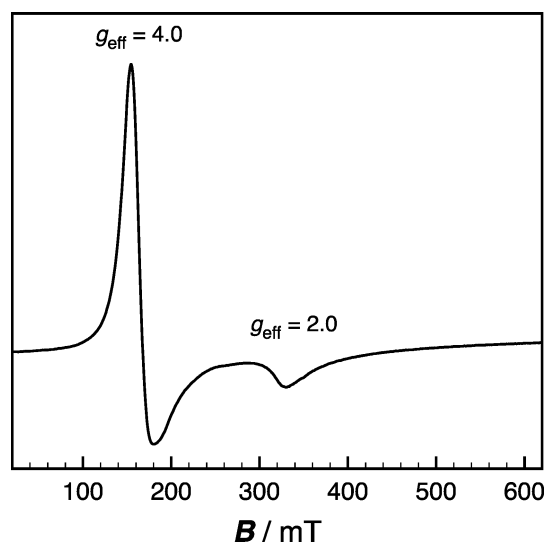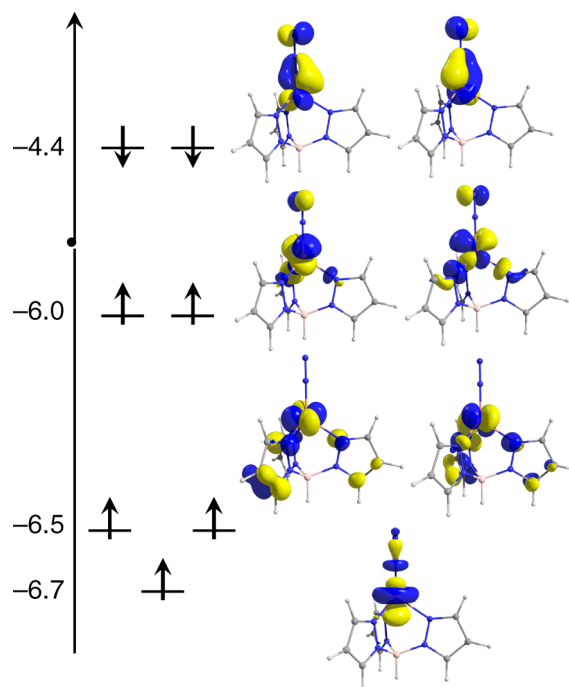
**Figure 3.** X-band EPR spectrum of **4** at 106 K in a toluene glass collected at a microwave frequency of 9.326 GHz.
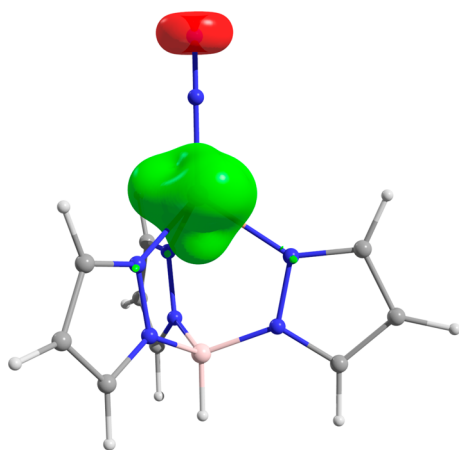


**Figure 4.** Spin-density isosurface calculated for the model complex $TpFe(N_2)$. Green represents positive spin and red represents negative spin. Mulliken spin populations: Fe = 3.31, $N_\beta$ = −0.24.



**Figure 5.** Canonical single-electron Kohn−Sham orbitals calculated for $TpFe(N_2)$ (see text for computational details). Orbital energies are in eV.

polarization of the $N_2$ ligand. This work definitively establishes the viability of terminal $N_2$ coordination to high-spin Fe(I), and the weak-field nature of **4** renders it a compelling model for hypothetical $N_2$ binding in a terminal mode to an unsaturated Fe site in nitrogenase. Future studies are directed toward spectroscopic corroboration of the spin-polarization of the $N_2$ ligand of **4** and the potential ramifications of this electronic structure on subsequent $N_2$ functionalization reactivity.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures and characterization, spectroscopic data, crystallographic analyses, and computational data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06337.

## ■ AUTHOR INFORMATION

### Corresponding Author

*hill.harman@ucr.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

## ■ REFERENCES

(1) Smil, V. *Enriching the Earth*; MIT Press: Cambridge, MA, 2001.
(2) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.
(3) Ertl, G. *J. Vac. Sci. Technol., A* **1983**, *1*, 1247.
(4) Hoffman, B. M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D. R.; Seefeldt, L. C. *Chem. Rev.* **2014**, *114*, 4041.

degenerate set that is essentially nonbonding with respect to the σ-bonding framework of the molecule. A second *e* set higher in energy is antibonding with respect to the Tp−Fe σ-bonds with some delocalization on to the $N_2$ ligand. The remaining two β-spin electrons reside in a pair of approximately degenerate orbitals that exhibit substantial backbonding to the $N_2$ ligand. The spin density found on the distal nitrogen of the bound $N_2$ ligand is presumably a result of this differential backbonding in the α- and β-spin manifolds. One interpretation of these results would place **4** on a continuum in between $Fe(I)−(N_2)$ and $Fe(III)−(N_2)^{2−}$, by analogy to the $N_2$-bridged diiron complex **2** and related complexes,[25] although the latter formulation would admittedly be extreme. More detailed computational study of these complexes will accompany further spectroscopic investigations.

In summary, through the use of a bulky Tp supporting ligand, we have synthesized the first example of a terminal $N_2$ complex of high-spin Fe(I). EPR studies unequivocally indicate an $S = 3/2$ ground state for **4**. This assignment is further substantiated by magnetic moment determination and DFT calculations, the latter of which indicate substantial spin

(5) Eady, R. R. *Chem. Rev.* **1996**, *96*, 3013.

(6) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.

(7) (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76. (b) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120.

(8) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, *501*, 84.

(9) Crossland, J. L.; Tyler, D. R. *Coord. Chem. Rev.* **2010**, *254*, 1883.

(10) MacLeod, K. C.; Vinyard, D. J.; Holland, P. L. *J. Am. Chem. Soc.* **2014**, *136*, 10226.

(11) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (b) Ghilardi, C. A.; Midollini, S.; Sacconi, L.; Stoppioni, P. *J. Organomet. Chem.* **1981**, *205*, 193.

(12) Selected examples: (a) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222. (b) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782. (c) Chomitz, W. A.; Arnold, J. *Chem. Commun.* **2007**, 4797. (d) Mankad, N. P.; Whited, M. T.; Peters, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 5768. (e) Scott, J.; Vidyaratne, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2008**, *47*, 896. (f) Rose, R. P.; Jones, C.; Schulten, C.; Aldridge, S.; Stasch, A. *Chem. - Eur. J.* **2008**, *14*, 8477. (g) Moret, M.-E.; Peters, J. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 2063. (h) Rudd, P. A.; Liu, S.; Gagliardi, L.; Young, V. G., Jr.; Lu, C. C. *J. Am. Chem. Soc.* **2011**, *133*, 20724. (i) Stieber, S. C. E.; Milsmann, C.; Hoyt, J. M.; Turner, Z. R.; Finkelstein, K. D.; Wieghardt, K.; DeBeer, S.; Chirik, P. J. *Inorg. Chem.* **2012**, *51*, 3770. (j) Suess, D. L. M.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 4938. (k) Creutz, S. E.; Peters, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 1105.

(13) Jové, F. A.; Pariya, C.; Scoblete, M.; Yap, G. P. A.; Theopold, K. H. *Chem.—Eur. J.* **2011**, *17*, 1310 and references therein .

(14) Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 10561.

(15) Tietz, T.; Limberg, C.; Stößer, R.; Ziemer, B. *Chem. - Eur. J.* **2011**, *17*, 10010.

(16) Hendrich, M. P.; Gunderson, W.; Behan, R. K.; Green, M. T.; Mehn, M. P.; Betley, T. A.; Lu, C. C.; Peters, J. C. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 17107.

(17) Stoian, S. A.; Vela, J.; Smith, J. M.; Sadique, A. R.; Holland, P. L.; Münck, E.; Bominaar, E. L. *J. Am. Chem. Soc.* **2006**, *128*, 10181.

(18) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756.

(19) Crystallization of **4** from THF/pentane mixtures affords hexagonal crystals in which the complex resides on a crystallographic three-fold axis. These structures are complicated by the presence of badly disordered solvent molecules.

(20) Hagen, W. R. *Adv. Inorg. Chem.* **1992**, *38*, 165.

(21) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101−1.

(22) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(23) Neese, F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73.

(24) Autschbach, J. *J. Chem. Educ.* **2012**, *89*, 1032.

(25) Holland, P. L. *Dalton Trans.* **2010**, *39*, 5415.