Cyanide Ligand Assembly by Carbon Atom Transfer to an Iron Nitride

Jorge L. Martinez,[†] Hsiu-Jung Lin,[†] Wei-Tsung Lee,[†,‡] Maren Pink,[†] Chun-Hsing Chen,[†] Xinfeng Gao,[†] Diane A. Dickie,[‖,|] and Jeremy M. Smith[†,*]

[†] Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington, IN 47405, USA.

[‖] Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131, USA

Supporting Information Placeholder

ABSTRACT: The new iron(IV) nitride complex PhB(^{i}Pr$_2$Im)$_3$Fe≡N reacts with two equivalents of bis(diisopropylamino)cyclopropenylidene (BAC) to provide PhB(^{i}Pr$_2$Im)$_3$Fe(CN)(N$_2$)(BAC). This unusual example of a four-electron reaction involves carbon atom transfer from BAC to create a cyanide ligand along with the alkyne ^{i}Pr$_2$N-C≡C-N^{i}Pr$_2$. The iron complex is in equilibrium with an N$_2$-free species. Further reaction with CO leads to formation of a CO analogue, which can be independently prepared using NaCN as the cyanide source, while reaction with B(C$_6$F$_5$)$_3$ provides the cyanoborane derivative.

The venerable cyanide ligand occupies a notable spot in the annals of chemistry, starting with the preparation of Prussian blue in 1704.[1,2] Its good σ-donor and π-acceptor properties, combined with its negative charge and ambidentate properties make cyanide a unique and versatile ligand. For example, cyanide is able to stabilize a wide range of coordination numbers and oxidation states, with homoleptic complexes known for coordination numbers 2 to 8 and oxidation numbers 0 to +5.[3] Furthermore, cyanide is commonly used as a bridging group in the rational synthesis of well-defined metal clusters.[4] Cyanide also plays an important role in biology, most notably as a ligand in the active site clusters of [NiFe] and [FeFe] hydrogenases, but also in other contexts, e.g. as defense agent in many plant species.[5]

Cyanide complexes are invariably prepared from alkali metal salts in relatively polar solvents.[3,4] These cyanide salts are in turn manufactured from hydrogen cyanide, which is industrially produced from ammonia and methane, either in the presence (Andrussow process) or absence (BMA process) of air. Hydrogen cyanide is also a byproduct in the manufacture of acrylonitrile by the ammonoxidation of propylene (Sohio process).[6]

While their synthesis from alkali metal salts remains ubiquitous, other methods for the synthesis of transition metal cyanide complexes are known.[7] Most notably, cyanide complexes can be prepared from organonitriles, e.g. by C-C oxidative addition.[8] Cyanide ligands can also be accessed by reaction of carbonyl ligands with hexamethyldisilazide salts,[9] or hexamethyldisilazide complexes with CO.[10] In biology, the carbon and nitrogen atoms of CN⁻ are usually derived from amino acids.[11] For example, *S*-adenosylmethionine lyses free tyrosine to produce the CN⁻ and CO ligands of [FeFe] hydrogenase by a mechanism that involves radical intermediates.[12]

We have shown that iron(IV) nitride complexes supported by tris(carbene)borate ligands show a wide range of nitrogen atom transfer reactivity.[13,14,15] These reactions include two-electron nitrogen atom transfer to a range of phosphines, yielding a family of four-coordinate iron(II) spin crossover complexes.[16] Based on these results, we hypothesized that stronger σ-donor groups would provide additional stabilization of the low spin state. This inspired us to investigate analogous nitrogen atom transfer from these iron nitride complexes to stabilized carbenes, which are generally better σ-donors than phosphines.[17] In this work, we report that the reaction of an iron(IV) nitride with bis(diisopropylamino)cyclopropenylidene does not provide the anticipated ketiminate complex, but instead creates a cyanide ligand by carbon atom transfer from the carbene to the nitride, to the best of our knowledge a unique example of a four-electron carbon atom transfer reaction.

The new iron(IV) nitride complex PhB(^{i}Pr$_2$Im)$_3$Fe≡N **1** is prepared analogously to previously reported tris(carbene)borate iron(IV) nitrides.[13] Specifically, irradiation of a mixture of PhB(^{i}Pr$_2$Im)$_3$FeCl and NaN$_3$ leads to formation of **1** in good yield. The red diamagnetic complex shows similar features to previously reported iron(IV) nitrides,[13,18] most notably a resonance at δ = 1003 ppm in the ^{15}N NMR spectrum that is characteristic of the nitride ligand.

Complex **1** reacts with two equivalents of the isolable carbene bis(diisopropylamino)cyclopropenylidene (BAC)[19] to yield diamagnetic PhB(^{i}Pr$_2$Im)$_3$Fe(N$_2$)(CN)(BAC) **2**, which has been structurally characterized by single crystal X-ray diffraction (Figure 1). Reaction with one equivalent of BAC results in only 50 % conversion to the product, with half of the iron starting material unreacted. The molecular structure of **2** reveals the complex to have a six-coordinate iron center that is bound to the tripodal tris(carbene)borate, a BAC ligand and N$_2$. The most remarkable feature of the structure is the identity of the remaining ligand, which has been formulated as cyanide on the basis of crystallographic and spectroscopic data, as well as reactivity studies and independent synthesis, as discussed in more detail below.
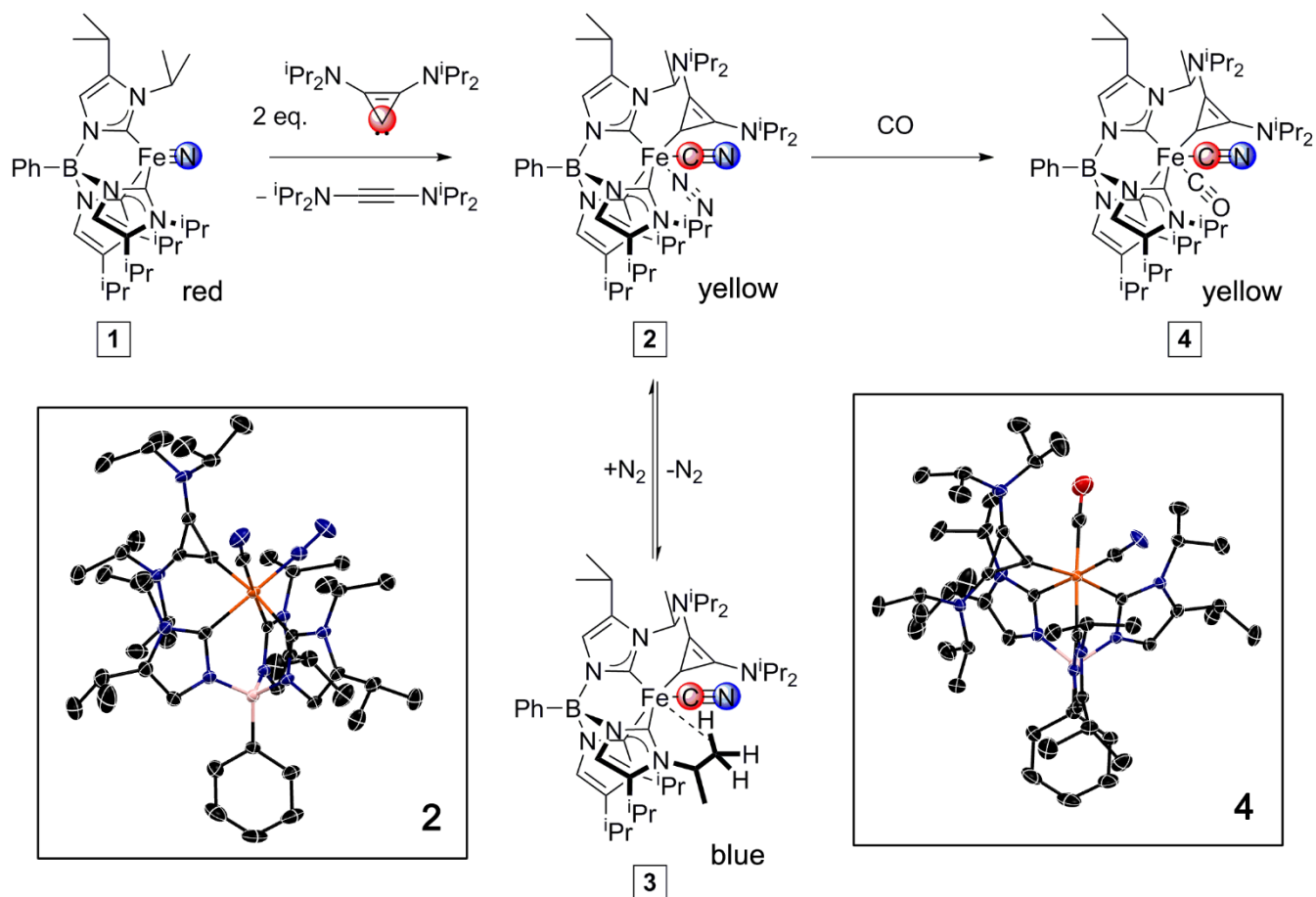
Figure 1. Synthesis of complexes. Insets show the structures of complexes **2** and **4** as determined by single crystal X-ray diffraction. Thermal ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity. Black, blue, pink and orange ellipsoids represent C, N, B and Fe atoms, respectively.

Aside from the unexpected coordination sphere, the metrical parameters of **2** are typical for a low spin iron(II) complex. Thus, the bond lengths between iron and the cyanide (1.933(2) Å), tris(carbene)borate (1.975(2) – 2.011(2) Å) ligands are typical for low spin iron iron(II),[3,4,16] while the Fe-BAC bond length (1.974(2) Å) is slightly shorter than observed in iron(0) BAC complexes.[20] Similarly, the C≡N bond length (1.155(2) Å) and Fe-C≡N bond angle (174.9(2) °) are within the expected range for a low spin iron(II) cyanide complex.

It is notable that while the crystals of **2** are yellow, room temperature solutions of the complex are blue. The blue color reversibly changes to yellow when **2** is cooled, which in turn becomes blue under vacuum, suggesting that the N₂ ligand is labile. This hypothesis is confirmed through the structural characterization of blue crystals grown at room temperature, with the crystallographic data also collected at room temperature so as to avoid N₂ binding. The molecular structure reveals that **3** is a five-coordinate iron complex formed by N₂ loss from **2**. While detailed structural insight is limited by the quality of the data, the short distance between iron and one of the tris(carbene)borate isopropyl methyl groups (2.81(1) Å) suggests that loss of the N₂ ligand is accompanied by the formation of an interaction between iron and the isopropyl group.

The solution behavior of **2** is complex, as revealed by variable temperature ¹H NMR spectroscopy. At -50 °C, 10 resonances for the methine protons of the 10 inequivalent isopropyl groups are observed in the ¹H NMR spectrum, consistent with the low symmetry structure observed for **2** in the solid state. Increasing the temperature leads to broadening and coalescence of the resonances, suggesting reversible N₂ binding that is rapid on the NMR timescale. Consistent with this hypothesis, a single broadened resonance (δ = 342.3 ppm) is observed in the room temperature ¹⁵N NMR spectrum of a sample of **2** prepared under an atmosphere of ¹⁵N₂.[21]

The cyanide ligand has been additionally characterized by spectroscopic methods. The ¹⁵N NMR spectrum of ¹⁵N-enriched **2/3** (prepared from a sample of **1** containing 50 % ¹⁵N-enriched nitride) shows a single resonance whose chemical shift (δ = 318 ppm) compares well with that observed for the cyanide ligand in $[Fe(C^{15}N)_6]^{4-}$ (δ = 284 ppm).[22] The solution IR spectrum of **2** shows two strong bands that are assigned to the N₂ (ν_{NN} = 2070 cm⁻¹) and CN⁻ (ν_{CN} = 2094 cm⁻¹) ligands, respectively. Consistent with loss of the N₂ ligand, only the latter band is observed in the solid state IR spectrum of blue **3**. The frequency of this band is typical for that of a terminal cyanide ligand.[4]

Scheme 1.
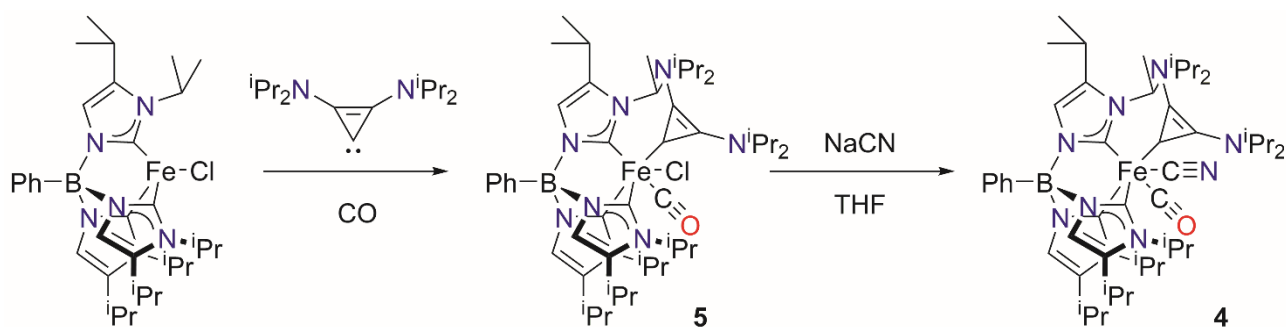
The other product of the reaction between **1** and BAC is the alkyne $^iPr_2N-C\equiv C-N^iPr_2$, which has been characterized by multinuclear NMR spectroscopy and CI-MS. A notable spectroscopic feature of this compound is the dramatically downfield shift (δ = 206 ppm) of the alkyne carbon resonance in the $^{13}C\{^1H\}$ NMR spectrum, likely a consequence of the presence of the electron-withdrawing nitrogen atoms.

The combined structural and spectroscopic data therefore reveals that the reaction between **1** and BAC results in carbon atom transfer to the nitride, leading to the assembly of a new cyanide ligand. To the best of our knowledge, this is a unique example of a four electron atom transfer reaction, with two of the electrons provided by iron and two by the cyclopropenylidene.

Preliminary reactivity studies confirm the structural formulation. Exposing **2/3** to an atmosphere of carbon monoxide results in N_2 ligand substitution and quantitative formation of the CO analogue $PhB(^iPr_2Im)_3Fe(CO)(CN)(BAC)$ **4**, which has been characterized by single crystal X-ray diffraction (Figure 1). The metrical parameters **4** are unexceptional for a low-spin iron(II) complex, with typical Fe-C(imidazolylidene) (1.981(1) – 2.022(2) Å), Fe-BAC (1.970(2) Å), Fe-CO (1.889(2) Å) and Fe-CN (1.806(2) Å) bond lengths. The Fe-C-N bond angle is close to linear (175.9(2) °).

In contrast to **2**, there is no evidence for reversible ligand binding in **4**. Thus, the room temperature ^1H NMR spectrum is consistent with the low-symmetry structure observed in the solid state. For example, six well-resolved septets assigned to the tris(carbene)borate isopropyl methine groups are observed in the room temperature spectrum, as expected for C_1 symmetry. The resonances assigned to the cyclopropenylidene ligand are broadened, suggesting restricted rotation around the Fe-C bond. The infrared spectrum reveals bands at 2078 cm^{-1} and 1900 cm^{-1}, which are assigned as ν_{CN} and ν_{CO}, respectively. When complex **4** is prepared from ^{13}CO, the band at 1900 cm^{-1} is replaced by a new band at 1850 cm^{-1}, while the band at 2078 cm^{-1} remains unchanged. This observation provides further evidence that the latter band is associated with the cyanide ligand. The ^{15}N NMR spectrum of an isotopically-enriched sample shows a single resonance for the cyanide ligand, whose chemical shift is essentially the same as **2/3** (δ = 315 ppm).

Complex **4** can be accessed through an alternate synthetic route (Scheme 1). Specifically, the reaction of $PhB(^iPr_2Im)_3FeCl$ with CO in the presence of 1 equiv. cyclopropenylidene provides the spectroscopically characterized diamagnetic complex $PhB(^iPr_2Im)_3FeCl(CO)(BAC)$ **5** (ν_{CO} = 1900

cm^{-1}), which in turn reacts with excess NaCN to provide **4** in high yield. The spectroscopic signatures of the complex prepared by this route are identical to those observed for the complex whose synthesis originates from **1**.

As expected, the newly formed cyanide ligand shows Lewis basic properties. Thus, **2/3** react with $B(C_6F_5)_3$ to yield the diamagnetic adduct $PhB(^iPr_2Im)_3Fe(N_2)(CNB(C_6F_5)_3)(BAC)$ **6**. As has been observed for other adducts between cyanide ligands and $B(C_6F_5)_3$, the cyanide stretch moves to a higher frequency in the IR spectrum (ν_{CN} = 2133 cm^{-1}),[23] while the cyanide resonance shifts upfield in the ^{15}N NMR spectrum (δ = 183 ppm).[24,25]

A plausible mechanism for the formation of **2** involves the initial formation of an iron(II) ketiminate complex from **1** and one equivalent of BAC. This complex undergoes a [2+2] cycloreversion reaction that extrudes the alkyne and generates an isocyanide ligand. A related transformation involving pyrolytic alkyne extrusion from a cyclopropenone has been reported.[26] Complex **2** is formed via a sequence of transformations involving isocyanide isomerization and coordination of BAC and N_2 ligands, although the timing of these steps is unclear.

In summary, we have established a new synthetic route to the cyanide ligand, specifically through a four-electron reaction involving carbon atom transfer from bis(diisopropylamino)cyclopropenylidene to a nitride ligand. We anticipate that this elemental synthesis will find application to the synthesis of other cyanide ligands. More generally, this readily accessible and stable carbene may also serve as a carbon atom transfer reagent in other synthetic applications, for example in the preparation of the metal carbide complexes.[27]

ASSOCIATED CONTENT

Supporting Information

Full experimental and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

Jeremy M. Smith: smith962@indiana.edu

Present Addresses

[‡] Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, IL 60660, USA.

[|] Department of Chemistry, MS 015, Brandeis University, 415 South Street, Waltham, MA 02453, USA

Notes
The authors declare no competing financial interests.

ACKNOWLEDGMENT

REFERENCES

[1] History of Prussian Blue: Kraft, A. *Bull. Hist. Chem.* **2008**, *33*, 61-67.

[2] First reports of Prussian Blue synthesis: (a) Woodward, J. *Phil. Trans.* **1724**, *33*, 15-17; (b) Brown, J. *Phil. Trans.* **1724**, *33*, 17-24.

[3] Sharpe, A.G. "The Chemistry of Cyano Complexes of the Transition Metals" Academic Press, London: 1976

[4] (a) Dunbar, K.; Heintz, R.A. *Prog. Inorg. Chem.* **1997**, *45*, 283-391; (b) Shatruk, M.; Avendana, C.; Dunbar, K. *Prog. Inorg. Chem.* **2009**, *56*, 155-334.

[5] Bjarnholt, N.; Møller, B.L. *Phytochemistry* **2008**, *69*, 1947-1961.

[6] Pesce, L.D. "Cyanides" in Kirk-Othmer Encylcopedia of Chemical Technology 5th Ed., John Wiley & Sons, Hoboken: 2004.

[7] Fehlhammer, W.P.; Fritz, M. *Chem. Rev.* **1993**, *93*, 1243-1280.

[8] (a) Garcia, J.J.; Jones, W.D. *Organometallics* **2000**, *19*, 5544-5545; (b) Garcia, J.J.; Brunkan, N.M.; Jones, W.D. *J. Am. Chem. Soc.* **2002**, *124*, 9547-9555; (c) Ateşin, T.A.; Li, T; Lachaize, S.; Brennessel, W.W.; Garcia, J.J.; Jones, W.D. *J. Am. Chem. Soc.* **2008**, *129*, 7562-7569; (d) Acosta-Ramírez, A.; Flores-Álamo, M.; Jones, W.D.; Garcia, J.J. *Organometallics* **2008**, *27*, 1834-1840; (e) Ateşin, T.A.; Li, T; Lachaize, S.; Garcia, J.J.; Jones, W.D. *Organometallics* **2008**, *27*, 3811-3817; (f) Li, T.; Garcia, J.J.; Brennessel, W.W.; Jones, W.D. *Organometallics* **2010**, *29*, 2430-2445; (g) Evans, M.E.; Li, T. Jones, W.D. *J. Am. Chem. Soc.* **2010**, *132*, 16278-16284; (h) Swartz, B.D.; Brennessel, W.W.; Jones, W.D. *Organometallics* **2011**, *30*, 1523-1529; (i) Xu, H.; Williard, P.G.; Bernskoetter, W. *Organometallics* **2012**, *31*, 1588-1590.

[9] (a) Behrens, H.; Ranley, H.-J.; Lindner, E. *Z. Anorg. Allg. Chem.* **1974**, *409*, 299-310; (b) Behrens, H.; Moll, M.; Popp, W.; Würstl, P. *Z. Naturfosch. B* **1977**, *32*, 1227-1229; (c) Moll, M.; Behrens, H.; Merbach, P.; Trummer, K.-H.; Thiele, G.; Wittmann, K. P. *Z. Naturfosch. B* **1986**, *41*, 606-616; (d) Lyon, E.J.; Georgakaki, I.P.; Riebenspies, J.J.; Darensbourg, M.Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 3178-3180.

[10] Sellmann, D.; Geipel, F.; Heinemann, F.W. *Chem. Eur. J.* **2000**, *6*, 4279-4284.

[11] Swanson, K.D.; Duffus, B.R.; Beard, T.E.; Peters, J.W.; Broderick, J.B. *Eur. J. Inorg. Chem.* **2011**, 935-947.

[12] (a) Driesner, R.C.; Challand, M.R.; McGlynn, S.E.; Shepard, E.M.; Boyd, E.S.; Broderick, J.B.; Peters, J.W.; Loach, P.L. *Angew. Chem. Int. Ed.* **2010**, *49*, 1687-1690; (b) Shepard, E.M.; Duffus, B.R.; George, S.J.; McGlynn, S.E.; Challand, M.R.; Swanson, K.D.; Roach, P.L.; Cramer, S.P.; Peters, J.W.; Broderick, J.B. *J. Am. Chem. Soc.* **2010**, *132*, 9247-9249; (c) Kuchenreuther, J.M.; George, S.J.; Grady-Smith, C.S.; Cramer, S.P.; Swartz, J.R. *PLOS ONE*, **2011**, *6*, e20346; (d) Kuchenreuther, J.M.; Myers, W.K.; Stich, T.A.; George, S.J.; NejatyJahromy, Y.; Swartz, J.R.; Britt, R.D. *Science* **2013**, *342*, 472-475; (e) Suess, D.L.M.; Kuchenreuther, J.M.; De La Paz, L.; Swartz, J.R.; Britt, R.D. *Inorg. Chem.* **2015**, *55*, 478-487; (f) Suess, D.L.M.; Pham, C.C.; Bürstel, I.; Swartz, J.R.; Cramer, S.P.; Britt, R.D. *J. Am. Chem. Soc.* **2016**, *138*, 1149-1149.

[13] (a) Scepaniak, J.J.; Fulton, M.D.; Bontchev, R.P.; Duesler, E.N.; Kirk, M.L.; Smith, J.M. *J. Am. Chem. Soc.* **2008**, *130*, 10515 (b) Scepaniak, J.J.; Young, J.A; Bontchev, R.P.; Smith, J.M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3158.

[14] Smith, J.M.; Subedi, D. *Dalton Trans.* **2012**, *41*, 1423.

[15] (a) Scepaniak, J.J.; Bontchev, R.P.; Johnson, D.L.; Smith, J.M. *Angew. Chem. Int. Ed.* **2011**, *50*, 6630; (b) Scepaniak, J.J.; Margarit, C.G.;

Harvey, J.N.; Smith, J.M. *Inorg. Chem.* **2011**, *50*, 9508; (c) Lee, W.-T.; Juarez, R.A.; Scepaniak, J.J.; Muñoz, S.B; Dickie, D.A.; Wang, H.; Smith, J.M. *Inorg. Chem.* **2014**, *53*, 8425; (d) Muñoz, III, S.B.; Lee, W.-T.; Dickie, D.A.; Scepaniak, J.J.; Subedi, D.; Pink, M.; Johnson, M.D.; Smith, J.M. *Angew. Chem. Int. Ed.* **2015**, *54*, 10600; (e) Ding, M.; Rouzières, M.; Losovyj, Y.; Pink, M.; Clérac, R.; Smith, J.M. *Inorg. Chem.* **2015**, *54*, 9075.

[16] (a) Scepaniak, J.J.; Harris, T.D.; Vogel, C.S.; Sutter, J.; Meyer, K.; Smith, J.M. *J. Am. Chem. Soc.* **2011**, *133*, 3824-3827; (b) Mathonière, C.; Lin, H.-J.; Siretanu, D.; Clérac, R.; Smith, J.M. *J. Am. Chem. Soc.* **2013**, *135*, 19083-19086; (c) Lin, H.-J.; Siretanu, D.; Dickie, D.A.; Subedi, D.; Scepaniak, J.J.; Mitcov, D.; Clérac, R.; Smith, J.M. *J. Am. Chem. Soc.* **2014**, *136*, 13326-13332.

[17] Selected reviews: (a) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407-5413; (b) Díez-González, S.; Nolan, S.P. *Coord. Chem. Rev.* **2007**, *251*, 874-883; (c) Schuster, O.; Yang, L.; Raubenheimer, H.G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445-3478; (d) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 8810-8849.

[18] (a) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252–6254; (b) Vogel, C.; Heinemann, F. W.; Sutter, J.; Anthon, C.; Meyer, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2681– 2684.

[19] (a) Lavallo, V.; Canac, Y. Donnadieu, B.; Schoeller, W.W.; Bertrand, G. *Science* **2006**, *312*, 722-724; (b) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W.W.; Bertrand, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 6652.

[20] Lavallo, V.; El-Batta, A.; Bertrand, G.; Grubbs, R.H. *Angew. Chem. Int. Ed.* **2011**, *50*, 268-271.

[21] This chemical shift is comparable to observations for other iron(II) complexes containing terminal N_2 ligands, see: Hazari, N. *Chem. Soc. Rev.* **2010**, *39*, 4044-4056.

[22] Sano, M.; Yoshikawa, Y.; Yamatera, H. *Inorg. Chem.* **1982**, *21*, 2521-2523.

[23] Manor, B.C.; Ringenberg, M.R.; Rauchfuss, T.B. *Inorg. Chem.* **2014**, *53*, 7241-7247.

[24] Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C.W. *Organometallics* **2006**, *25*, 3070-3075.

[25] No B-N coupling is observed in the ^{15}N NMR spectrum; typical $J_{BN} < 10$ Hz, see Wrackmeyer, B.; Tok, O.L. *Z. Naturfosch.* **2007**, *62b*, 220-224; (b) Nöth, H.; Wrackmeyer, B. "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds" Springer-Verlag, Berlin: 1978.

[26] Wilcox, C.; Breslow, R. *Tetrahedron Lett.* **1980**, *21*, 3241-3242.

[27] (a) Peters, J.C.; Odom, A.L.; Cummins, C.C. *Chem. Commun.* **1997**, 1995-1996; (b) Enriquez, A.E.; White, P.S.; Templeton, J.L. *J. Am. Chem. Soc.* **2001**, *123*, 4992-5002; (c) Greco, J.B.; Peters, J.C.; Baker, T.A.; Davis, W.M.; Cummins, C.C.; Wu, G. *J. Am. Chem. Soc.* **2001**, *123*, 5003-5013; (d) Carlson, R.G.; Gile, M.A.; Heppert, J.A.; Mason, M.H.; Powell, D.R.; Vander Velde, D.; Vilain, J.M. *J. Am. Chem. Soc.* **2002**, *124*, 1580-1581; (e) Caskey, S.R; Stewart, M.H.; Kivela, J.E.; Sootsman, J.R.; Johnson, M.J.A.; Kampf, J.W. *J. Am. Chem. Soc.* **2006**, *127*, 16750-16751; (f) Stewart, M.H.; Johnson, M.J.A.; Kampf, J.W. *Organometallics* **2007**, *26*, 5102-5110; (g) Cordner, R.L.; Hill, A.F.; Wagler, J. *Organometallics* **2008**, *27*, 5177-5179.

SYNOPSIS TOC.