



ChemComm

---

**Historical account of dinitrogen-bridged diiron complex  
synthesis using a commercial tripodal ligand**

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-04-2025-002058.R1
Article Type:	Communication

SCHOLARONE™  
Manuscripts

## Historical account of dinitrogen-bridged diiron complex synthesis using a commercial tripodal ligand

Received 00th January 20xx,  
Accepted 00th January 20xx

Nathan C. Smythe,<sup>\*a</sup> Joydeb Mondal,<sup>b</sup> Juan G. Duque,<sup>a</sup> Russell K. Feller,<sup>c</sup> Marco Flores,<sup>b</sup> John C. Gordon,<sup>\*d</sup> Neil J. Henson,<sup>e</sup> Moshe Paz-Pasternak,<sup>f</sup> Francisca N. Rein,<sup>a</sup> Brian L. Scott,<sup>c</sup> R. Dean Taylor,<sup>c</sup> Ryan J. Trovitch<sup>\*b</sup>

DOI: 10.1039/x0xx00000x

**The  $KC_8$  reduction of  $(Triphos)FeCl_2$  in toluene under 3.4 atm of  $N_2$  afforded  $[(Triphos)Fe]_2(\mu-N_2)$ , which features a modestly-activated  $N_2$  ligand and antiferromagnetically coupled Fe(0) centres. The addition of  $H_2$  to this compound yielded  $(Triphos)Fe(\mu-H)_3Fe(\mu-H)_3Fe(Triphos)$ .**

Dinitrogen compounds of iron have been studied as molecular mimics for nitrogenase enzymes,<sup>1-4</sup> which employ iron in their active sites.<sup>5</sup> Iron precursors possessing easily displaceable  $N_2$  ligands have also emerged as promising catalysts for reductive transformations over the last two decades.<sup>6-7</sup> A majority of iron dinitrogen compounds possess a weakly-activated  $N_2$  ligand, as judged by infrared spectroscopy ( $\nu_{NN} = 1960-2150\text{ cm}^{-1}$ ) and single crystal X-ray diffraction (N-N dist. = 1.07-1.13 Å).<sup>8</sup> While less common, diiron compounds featuring a bridging  $N_2$  ligand have been described, and increased  $N_2$  ligand reduction has been documented. For example, Holland and co-workers found that  $\beta$ -diketiminate Fe(I) compounds with bridging  $N_2$  ligands exhibit  $\nu_{NN}$  values of 1778-1810  $\text{cm}^{-1}$  and N-N bond distances of 1.18-1.19 Å.<sup>9,10</sup> The two-electron reduction of these compounds results in further  $N_2$  weakening through  $\pi$ -backbonding ( $\nu_{NN} = 1589-1625\text{ cm}^{-1}$ ; N-N dist. = 1.21-1.23 Å),<sup>9,10</sup> and the application of mesityl rather than 2,6-diisopropylphenyl ligand substituents allowed for complete  $N_2$  cleavage (N-N dist. = 2.799(2) Å).<sup>11</sup>

Phosphines have emerged as a privileged ligand class for the synthesis of diiron compounds that feature a bridging  $N_2$  ligand.

Monodentate phosphines  $P(OMe)_3$ <sup>12</sup> and  $PEt_3$ <sup>13</sup> have long been known to encourage  $N_2$  bridging between the Fe(0) centres of  $[Fe(CO)_2(PR_3)_2]_2(\mu-N_2)$ .<sup>14</sup> Diphosphine ligands have been used to support  $N_2$  bridging between Fe(0),<sup>15,16</sup> Fe(0)/Fe(II),<sup>17</sup> and Fe(II) centres.<sup>18,19</sup> Recent studies have focused on the utilization of polydentate ligands that possess two phosphine moieties,<sup>20-24</sup> and several have relied solely on tridentate and tetradentate phosphine coordination. Using a flexible tridentate scaffold,  $[(P_2P^{Ph})FeH]_2(\mu-N_2)$ <sup>25</sup> and  $[(P_2P^{Ph})Fe]_2(\mu-N_2)$ <sup>26</sup> were found to possess singlet ground states due to antiferromagnetic coupling between the iron centres. This feature was also noted for  $[(P_6ArCH_3)FeH]_2(\mu-N_2)$ , which has a dinucleating hexaphosphine ligand that places the irons in close proximity.<sup>27</sup> In seminal work, Betley and Peters employed the anionic tripodal ligand  $PhBP^{iPr_3}$  to synthesize  $[(PhBP^{iPr_3})Fe]_2(\mu-N_2)$  and  $\{[(PhBP^{iPr_3})Fe]_2(\mu-N_2)\}[Na(THF)_6]$  via Na/Hg reduction of  $(PhBP^{iPr_3})FeCl$ .<sup>28</sup> The former compound was subsequently prepared by  $(PhBP^{iPr_3})FeN$  coupling under vacuum or argon,<sup>29</sup> and found to possess an N-N distance of 1.138(6) Å relative to 1.171(4) Å for  $\{[(PhBP^{iPr_3})Fe]_2(\mu-N_2)\}[Na(THF)_6]$ .<sup>28</sup> At Fe(0), Field and co-workers used a tetradentate tripodal ligand to observe  $[(PP_3)Fe]_2(\mu-N_2)$  by NMR spectroscopy,<sup>30</sup> while the Lu Group used the aluminum-based AltraPhos ligand to prepare an  $N_2$ -bridged compound with an N-N distance of 1.146(7) Å.<sup>31</sup>

In 2011, our team was inspired by the observation of Betley and Peters that reductive coupling of Fe(IV) nitride  $(PhBP^{iPr_3})FeN$  resulted in bimetallic Fe(I) compound,  $[(PhBP^{iPr_3})Fe]_2(\mu-N_2)$ .<sup>29</sup> It was noted that the microscopic reverse (dinitrogen cleavage) “may not be thermally accessible in the present system.” Therefore, we reasoned that a neutral chelate without a donor or acceptor group *trans* to the site of  $N_2$ -binding may allow such reactivity, and we were fortunate to explore this concept with Laboratory Directed Research and Development support.<sup>32</sup> Herein, we describe efforts from over a decade ago that led to the discovery of a Triphos  $[MeC(CH_2PPh)_3]$  iron compound that possesses a bridging dinitrogen ligand. This work was presented at ACS National Meetings;<sup>33-36</sup> but is detailed in this contribution

<sup>a</sup> Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: nsmythe@lanl.gov

<sup>b</sup> School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA. E-mail: ryan.trovitch@asu.edu

<sup>c</sup> Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

<sup>d</sup> Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA. E-mail: jgordon1@bnl.gov

<sup>e</sup> Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

<sup>f</sup> School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, Israel

† Electronic supplementary information (ESI) available: General considerations, procedures, and characterization data. See DOI: 10.1039/x0xx00000x

for members of the community who may benefit from an N<sub>2</sub>-bridged iron compound that features a commercial ligand. We were inspired to share this account due to recent advances by the Tilley Group, who have been exploring the reactivity of related analogs.<sup>37</sup>

Upon commencing this project in 2011, Triphos-ligated iron halide starting materials were not well-characterized, with the exception of chloride-bridged tetraphenylborate salts featuring alkyl substitution on phosphorus.<sup>38,39</sup> We found that heating a simple mixture of FeCl<sub>2</sub> and Triphos in toluene to 100 °C for 72 h resulted in a very light green solution with a small amount of precipitate ascribable to impurities in commercial FeCl<sub>2</sub>. Nearly colorless crystalline material was subsequently obtained by initial concentration of the filtrate and then cooling to -35 °C. Single crystal X-ray diffraction analysis revealed this product to be 4-coordinate (Triphos)FeCl<sub>2</sub> (**1**, Fig. 1). Ultimately, Merten and Apfel described the synthesis of **1** in 2016 upon stirring Triphos and FeCl<sub>2</sub> in THF/acetonitrile (1:1) solution for 24 h,<sup>40</sup> and this compound has been used for subsequent reactivity<sup>41-42</sup> and structural comparison studies.<sup>43</sup>

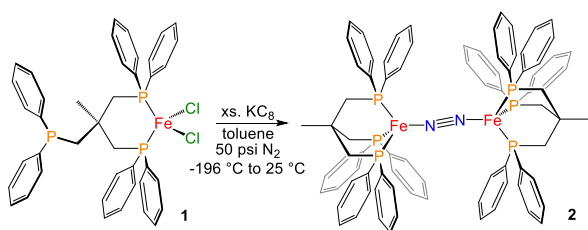


Fig. 1 Preferred synthesis of dinitrogen-bridged **2** from **1**.

With **1** in hand, reductants and conditions were screened to prepare the desired Triphos Fe(0)-N<sub>2</sub> compound. The use of solid potassium to reduce a toluene solution of **1** did not result in a reaction after 1 month (the solution remained colorless). Replacing toluene with Et<sub>2</sub>O allowed for reduction over hours, but an N<sub>2</sub>-bound compound was not observed. Magnesium is a milder reducing agent that has been used to generate N<sub>2</sub> complexes; however, the use of excess Mg activated with I<sub>2</sub> appeared to produce a mixture of halide compounds. Fortunately, a toluene solution of **1** subjected to KC<sub>8</sub> in a nitrogen-filled glovebox for 12 h resulted in a red solution that was filtered through Celite and dried to afford a crude product. Analysis of this mixture by <sup>31</sup>P NMR spectroscopy revealed predominantly free ligand (-25.60 ppm); however, a minor product featuring coordinated phosphines (71.34 ppm) made up approximately 5% of the mixture. Conveniently, this product proved to be essentially insoluble in Et<sub>2</sub>O, allowing for its crystallization and identification as [(Triphos)Fe]<sub>2</sub>(μ-N<sub>2</sub>) (**2**, Fig. 2) by single-crystal X-ray diffraction.

The solid-state structure of **2** (Fig. 2) was found to feature two independent molecules, each with an inversion center along the N-N bond. They feature N-N bond distances that are equivalent within experimental error (1.208(3) Å vs. 1.207(3) Å) and consistent with a modest degree of N<sub>2</sub> activation. The Fe-N (1.7361(16) Å and 1.7251(15) Å) and Fe-P bond lengths (ranging from 2.1186(6) Å to 2.1546(6) Å) are also similar. However, the molecules feature different degrees of N<sub>2</sub> ligand canting;

molecule **1** (illustrated in Fig. 2) features Fe-N-N bond angles of 166.0(2)° while molecule **2** features angles of 172.32(19)°.

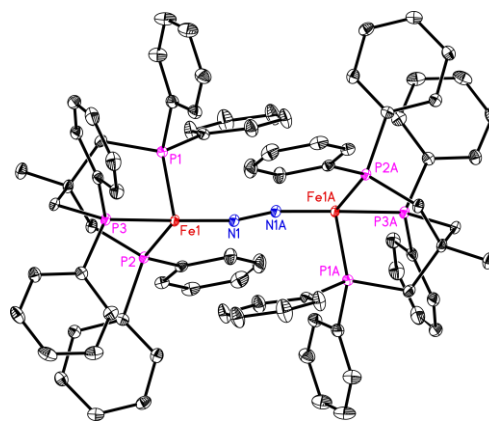


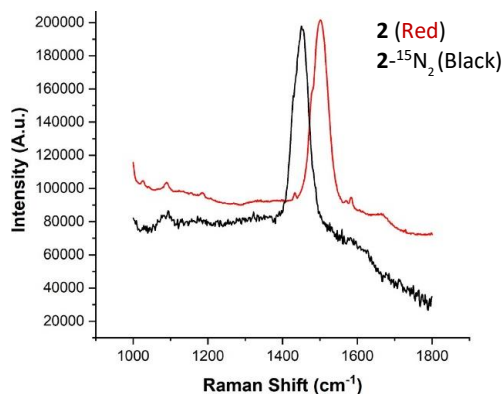
Fig. 2 Structure of **2** at 30% probability ellipsoids.

For electronic purposes, it is helpful to compare the metrical parameters of **2** to those determined for closely related compounds. Betley and Peters found that [(PhBPiPr<sub>3</sub>)Fe]<sub>2</sub>(μ-N<sub>2</sub>), which possesses Fe(I) centres, features an N-N bond length of 1.138(6) Å.<sup>29</sup> Upon 1-electron reduction to form the mixed-valence Fe(I)/Fe(0) compound [(PhBPiPr<sub>3</sub>)Fe]<sub>2</sub>(μ-N<sub>2</sub>)[Na(THF)<sub>6</sub>], the N-N distance lengthens to 1.171(4) Å, consistent with a greater degree of backbonding into the N<sub>2</sub> ligand π-system.<sup>28</sup> In the case of **2**, which possesses Fe(0) centres, the observed bond distances of 1.208(3) Å vs. 1.207(3) Å are consistent with even greater backbonding. Although **2** and [(P<sub>2</sub>P<sup>Ph</sup>)Fe]<sub>2</sub>(μ-N<sub>2</sub>)<sup>26</sup> are structurally similar, the latter has only been observed by NMR spectroscopy, preventing a comparison of N<sub>2</sub> ligand reduction. An N-N distance of 1.146(7) Å was found for [(AltraPhos)Fe](μ-N<sub>2</sub>), which is shorter than the N-N bond lengths of **2**, due to competitive electron density transfer from Fe to Al.<sup>31</sup> The Co(0) analog of **2** was characterized in 1985 and was found to feature an N-N distance of 1.18(2) Å and Co-N distances of 1.76(1) Å.<sup>44</sup> In comparison, **2** possesses a more reduced N<sub>2</sub> ligand and more M-N double bond character, as Fe is easier to oxidize than Co.

To collect supporting spectroscopic data for **2**, an improved, higher yielding synthesis was required. By vacuum transferring toluene onto a solid mixture of **1** and KC<sub>8</sub> in a Fischer-Porter bottle, we were able to pressurize the reaction vessel to 3.4 atm (50 psi) N<sub>2</sub> before allowing the reaction to thaw and reduction to occur. When the solution was quickly brought into the glovebox and filtered through Celite after warming to ambient temperature (using a copious quantity of toluene as its solubility is poor), moderate to good yields (40-60%) of crude **2** were isolated. Recent experiments have revealed that charging a Parr reactor with **1** and either toluene or benzene, allowing it sit in a liquid N<sub>2</sub>-cooled glove box cold well, adding KC<sub>8</sub>, and quickly pressuring the mixture with 3.4 atm of N<sub>2</sub> outside of the glovebox affords recrystallized yields of around 20%.

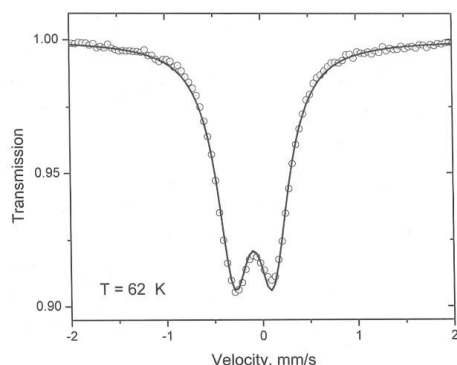
Due to its molecular inversion center, the N-N stretch of **2** could not be observed via IR spectroscopy. The resonance Raman spectrum of **2** in a boron nitride matrix (used to prevent thermal degradation) was found to exhibit an N-N stretching frequency of 1501 cm<sup>-1</sup> (Fig. 3). To confirm the assignment of

this peak, the synthesis of **2** via vacuum transfer was repeated under  $^{15}\text{N}_2$ . The corresponding  $^{15}\text{N}$  isotopomer was found to feature a resonance Raman shift at  $1450\text{ cm}^{-1}$ , matching the frequency expected for a diatomic oscillator ( $1450\text{ cm}^{-1}$ ). These values suggest that the bridging  $\text{N}_2$  ligand of **2** is more reduced than the same ligand in Holland's  $\beta$ -diketiminato  $\text{Fe(0)}$  compound,  $\text{K}_2\text{BDI}^{\text{Me}}\text{FeNNFeBDI}^{\text{Me}}$ , which was reported to have a  $^{14}\text{N}_2$  stretch at  $1625\text{ cm}^{-1}$  and a  $^{15}\text{N}_2$  stretch at  $1569\text{ cm}^{-1}$ .<sup>10</sup>



**Fig. 3** Resonance Raman spectra for **2** and  $2\text{-}^{15}\text{N}_2$ .

Mössbauer spectroscopic analysis of **2** at 62 K (Fig. 4) revealed a single iron-containing compound with an isomer shift ( $\text{IS}$  or  $\delta$ ) of  $-0.09\text{ mm/s}$  and a quadrupole splitting parameter ( $\Delta E_{\text{Q}}$ ) of  $0.41\text{ mm/s}$ . The observation of a slightly negative isomer shift is reminiscent of data collected for  $\text{Fe(CO)}_5$  ( $\delta = -0.08$ ),<sup>45</sup> and is consistent with formulation of **2** as a low-spin, diamagnetic compound. Moreover, this shift suggests that **2** possesses highly covalent bonds,<sup>46</sup> specifically  $\text{Fe-N}$  and  $\text{Fe-P}$  backbonding [which manifest as short  $\text{Fe-N}$  and  $\text{Fe-P}$  bond lengths of  $1.7251(15)\text{-}1.7361(16)$  and  $2.1186(6)\text{-}2.1546(6)\text{ \AA}$ , respectively]. Compound **2** is diamagnetic ( $S_{\text{T}} = 0$ ), but is believed to feature two high-spin  $\text{Fe(0)}$  atoms ( $S = 1$ ) that are antiferromagnetically coupled through the  $\pi$ -system of the bridging  $\text{N}_2$  ligand. A similar conclusion has been reported for the related compound,  $[(\text{P}_2\text{P}^{\text{Ph}})\text{Fe}]_2(\mu\text{-N}_2)$ .<sup>26</sup>

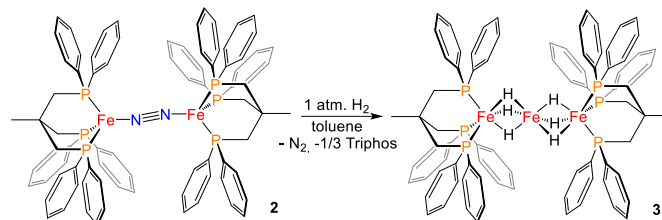


**Fig. 4** Zero-field Mössbauer spectrum of **2** at 62 K.

The analysis of **2** by cyclic voltammetry revealed two reversible oxidations as potentials were scanned upwardly from  $-2.7\text{ V}$  (Fig. S5). The first, with a mid-potential at  $-2.37\text{ V}$ , is assigned to the  $\text{Fe(0)Fe(0)}/\text{Fe(0)Fe(I)}$  couple, while the second

process, having a mid-potential at  $-1.88\text{ V}$ , corresponds to the  $\text{Fe(0)Fe(I)}/\text{Fe(I)Fe(I)}$  couple. Redox potentials of around  $-2\text{ V}$  are common for  $\text{Fe(0)}/\text{Fe(I)}$  couples in mononuclear complexes, but the separation of almost  $0.5\text{ V}$  for the individual oxidations of **2** is consistent with strong electronic communication between the metal centres.

Reactivity studies performed a decade ago revealed that adding  $1\text{ atm H}_2$  to **2** resulted in the formation of  $(\text{Triphos})\text{Fe}(\mu\text{-H})_3\text{Fe}(\mu\text{-H})_3\text{Fe}(\text{Triphos})$  (**3**, Fig. 5), but not ammonia. In 2019, Roemelt and Apfel observed that the slow decomposition of  $(\text{Triphos})\text{Fe}(\text{H})(\text{BH}_4)$  afforded **3**, the structure of which was confirmed by single crystal X-ray diffraction.<sup>42</sup> Multinuclear NMR data for **3** has not been described, but our samples have been found to exhibit paramagnetically shifted and broadened resonances over a  $100\text{ ppm}$  sweep width ( $25\text{ }^\circ\text{C}$ , benzene- $d_6$ ), in addition to peaks that are consistent with a diamagnetic hydride complex. The integration of these compounds varies between samples, and crystalline **3** (composition confirmed by single crystal X-ray diffraction) provides a mixture of both in solution. The diamagnetic compound gives rise to a single  $^{31}\text{P}$  resonance at  $58.38\text{ ppm}$ , along with the expected  $^1\text{H}$  and  $^{13}\text{C}$  peaks for bound  $\text{Triphos}$ . It also features an  $\text{Fe-H}$  resonance at  $-16.54\text{ ppm}$  that integrates to  $2\text{H}$  (rather than  $6\text{H}$ ) relative to two  $\text{Triphos}$  ligands. A  $^1\text{H}$  COSY experiment did not reveal cross-peaks to neighbouring hydrides, and monitoring a benzene- $d_6$  solution over  $24\text{ h}$  did not result in lower  $\text{Fe-H}$  integration values (i.e., the hydrides do not undergo deuterium exchange with the solvent). Our current hypothesis is that **3** exhibits shifted and broadened peaks in benzene- $d_6$  at  $25\text{ }^\circ\text{C}$ , but undergoes partial dissociation to form  $(\text{Triphos})\text{Fe}(\mu\text{-H})_2\text{Fe}(\text{Triphos})$ .



**Fig. 5** Conversion of **2** to **3** under  $\text{H}_2$ .

The Mössbauer spectrum of crystalline **3** at  $75\text{ K}$  is also provided in Fig. S10 of the ESI. Notably, two  $\text{Fe}$  environments were identified; a majority component ( $72\%$ ) attributed to two  $(\text{Triphos})\text{Fe}(\mu\text{-H})_3$  moieties having  $\delta = -0.01\text{ mm/s}$  and  $\Delta E_{\text{Q}} = 0.51\text{ mm/s}$ , and a minority component ( $28\%$ ) attributed to the pseudo-octahedral bridging  $\text{FeH}_6$  environment with  $\delta = -0.10\text{ mm/s}$  and  $\Delta E_{\text{Q}} = 0.18\text{ mm/s}$ . Therefore, the ligated and bridging  $\text{Fe}$  centres of solid **3** are best viewed as low-spin  $\text{Fe(II)}$  hydrides.

In conclusion, the reduction of  $(\text{Triphos})\text{FeCl}_2$  (**1**) in toluene using  $\text{KC}_8$  under  $1\text{ atm}$  of  $\text{N}_2$  allowed for the initial observation of  $[(\text{Triphos})\text{Fe}]_2(\mu\text{-N}_2)$  (**2**). Repeating this reduction under  $3.4\text{ atm}$  of  $\text{N}_2$  increased the quantity of **2** that could be obtained for spectroscopic analysis, a strategy that may more broadly allow for dinitrogen compound isolation. The subsequent addition of  $\text{H}_2$  to **2** allowed for the direct preparation of  $(\text{Triphos})\text{Fe}(\mu\text{-H})_3\text{Fe}(\mu\text{-H})_3\text{Fe}(\text{Triphos})$  (**3**).

We would like to acknowledge LANL for support through the Laboratory Directed Research and Development Program (20110358ER). CRediT: N.C.S. – conceptualization, funding acquisition, investigation, writing of original draft; J.M. – investigation, validation; J.D. – investigation; R.K.F. – investigation; M.F. – investigation; J.C.G – conceptualization, funding acquisition, project administration; N.J.H. – investigation, M.P.-P. – investigation, F.N.R. – investigation, B.L.S. – investigation; R.D.T. – investigation; R.J.T. – conceptualization, funding acquisition, writing of later drafts.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

CCDC 2442949 contains the supplementary crystallographic data for this paper. Additional data that support this article have been included as part of the ESI.†

### Notes and references

- A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 3041-3049.
- J. S. Anderson, J. Rittle and J. C. Peters, *Nature*, 2013, **501**, 84-87.
- T. M. Buscagan, P. H. Oyala and J. C. Peters, *Angew. Chem. Int. Ed.*, 2017, **56**, 6921-6926.
- M. J. Chalkley, M. W. Drover and J. C. Peters, *Chem. Rev.*, 2020, **120**, 5582-5636.
- R. R. Eady, *Chem. Rev.*, 1996, **96**, 3013-3030.
- S. C. Bart, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.* 2004, **126**, 13794-13807.
- A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science*, 2012, **335**, 567-570.
- J. L. Crossland and D. R. Tyler, *Coord. Chem. Rev.*, 2010, **254**, 1883-1894.
- J. M. Smith, R. J. Lachicotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rodgers and P. L. Holland, *J. Am. Chem. Soc.*, 2001, **123**, 9222-9223.
- J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela and P. L. Holland, *J. Am. Chem. Soc.*, 2006, **128**, 756-769.
- M. M. Rodriguez, E. Bill, W. W. Brennessel and P. L. Holland, *Science*, 2011, **334**, 780-783.
- H. Berke, W. Bankhardt, G. Huttner, J. Von Seyerl and L. Zsolnai, *Chem. Ber.* 1981, **114**, 2754-2768.
- H. Berke, R. Reiner, G. Huttner and L. Zsolnai, *Z. Naturforsch. B*, 1984, **39**, 1380-1388.
- H. Kandler, C. Gauss, W. Bidell, S. Rosenberger, T. Bürgi, I. L. Eremenko, D. Veghini, O. Orama, P. Burger and H. Berke, *Chem. Eur. J.*, 1995, **1**, 541-548.
- A. M. Tondreau, B. L. Scott and J. M. Boncella, *Organometallics*, 2016, **35**, 1643-1651.
- L. R. Doyle, P. J. Hill, G. C. Woldgoose and A. E. Ashley, *Dalton Trans.*, 2016, **45**, 7550-7554.
- J. B. Geri, J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 5952-5956.
- W. E. Silverthorn, *J. Chem. Soc. D*, 1971, 1310-1311.
- J. M. Bellerby, M. J. Mays and P. L. Sears, *J. Chem. Soc., Dalton Trans.*, 1976, 1232-1236.
- W. A. Chomitz and J. Arnold, *Chem. Commun.* 2007, 4797-4799.
- D. L. M. Suess and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 4938-4941.
- J. Higuchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Dalton Trans.*, 2018, **47**, 1117-1121.
- Y. Sekiguchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Chem. Commun.* 2017, **53**, 12040-12043.
- J. Petit, A. Cavaillé, N. Saffon-Merceron, M. Fustier-Boutignon and N. Mézailles, *Dalton Trans.* 2021, **50**, 9554-9559.
- T. M. Buscagan, P. H. Oyala and J. C. Peters, *Angew. Chem. Int. Ed.*, 2017, **56**, 6921-6926.
- D. J. Schild and J. C. Peters, *ACS Catal.*, 2019, **9**, 4286-4295.
- C. H. Arnett and T. Agapie, *J. Am. Chem. Soc.*, 2020, **142**, 10059-10068.
- T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2003, **125**, 10782-10783.
- T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2004, **126**, 6252-6254.
- L. D. Field, R. W. Guest and P. Turner, *Inorg. Chem.*, 2010, **49**, 9086-9093.
- P. A. Rudd, S. Liu, L. Gagliardi, V. G. Young, Jr. and C. C. Lu, *J. Am. Chem. Soc.*, 2011, **133**, 20724-20727.
- J. C. Gordon, "Developing a Mild Catalytic Route for the Reduction of N<sub>2</sub> to NH<sub>3</sub>," FY2013 LDRD Annual Report, Los Alamos National Laboratory, pp. 226-227.
- N. C. Smythe, J. C. Gordon, N. J. Henson, F. N. Rein, B. L. Scott and R. J. Trovitch, 243<sup>rd</sup> ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012, INOR-793.
- J. C. Gordon, N. J. Henson, F. N. Rein, B. L. Scott, N. C. Smythe and R. J. Trovitch, 243<sup>rd</sup> ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012, INOR-1115.
- N. C. Smythe, J. Duque, R. K. Feller, J. C. Gordon, N. J. Henson, M. Paz-Pasternak, F. N. Rein, B. L. Scott, R. D. Taylor and R. J. Trovitch, 245<sup>th</sup> ACS National Meeting & Exposition, New Orleans, LA, United States, April 7-11, 2013, INOR-1080.
- T. K. Mukhopadhyay, T. M. Porter, M. Flores, R. K. Feller, B. L. Scott, R. D. Taylor, M. Paz-Pasternak, N. J. Henson, F. N. Rein, N. C. Smythe, J. C. Gordon and R. J. Trovitch, 246<sup>th</sup> ACS National Meeting & Exposition, Indianapolis, IN, United States, September 8-12, 2013, INOR-614.
- T. D. Tilley, R. C. Handford and R. Bryant, ISOS-20, Hiroshima, Japan, May 12-17, 2024.
- C. Bianchini, P. Dapporto, C. Mealli and A. Meli, *Inorg. Chem.* 1982, **21**, 612-615.
- K. Kashiwabara, Y. Ozeki, M. Kita, J. Fujita and K. Nakajima, *Bull. Chem. Soc. Jpn.* 1995, **68**, 3453-3457.
- A. Petuker, K. Merz, C. Merten and U.-P. Apfel, *Inorg. Chem.* 2016, **55**, 1183-1191.
- A. Petuker, S. Mebs, N. Schuth, P. Gerschel, M. L. Reback, B. Mallick, M. van Gastel, M. Haumann and U.-P. Apfel, *Dalton Trans.* 2017, **46**, 907-917.
- L. Iffland, A. Khedkar, A. Petuker, M. Lieb, F. Wittkamp, M. van Gastel, M. Roemelt and U.-P. Apfel, *Organometallics*, 2019, **38**, 289-299.
- A. Petuker, P. Gerschel, S. Piontek, N. Ritterskamp, F. Wittkamp, L. Iffland, R. Miller, M. van Gastel and U.-P. Apfel, *Dalton Trans.* 2017, **46**, 13251-13262.
- F. Ceconi, C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and M. Bacci, *J. Chem. Soc., Chem. Commun.* 1985, 731-733.
- J. M. Rall, M. Schorpp, M. Keilwerth, M. Mayländer, C. Friedmann, M. Daub, S. Richert, K. Meyer and I. Krossing, *Angew. Chem. Int. Ed.* 2022, **61**, e303304080.
- E. Bill, <sup>57</sup>Fe-Mössbauer Spectroscopy and Basic Interpretation of Mössbauer Parameters, In Practical Approaches to Biological Inorganic Chemistry; R. R. Crichton and R. O. Louro, Eds.; Elsevier: 2020, 201-228.

# Data Availability Statement

CCDC 2442949 contains the supplementary crystallographic data for this paper. Additional data that support this article have been included as part of the ESI.†