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Investigation of formally zerovalent Triphos iron complexes[†]

Tufan K. Mukhopadhyay,^a Russell K. Feller,^b Francisca N. Rein,^c Neil J. Henson,^d Nathan C. Smythe,^c Ryan J. Trovitch^{*ac} and John C. Gordon^{*c}

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The reduction of Triphos [PhP(CH₂CH₂PPh₂)₂] iron halide complexes has been explored, yielding formally zerovalent $(\kappa^3$ -Triphos)Fe $(\kappa^2$ -Triphos) and $(\kappa^3$ -Triphos)Fe $(\kappa^2$ -Bpy). Electrochemical analysis, coupled with the metrical parameters of $(\kappa^3$ -Triphos)Fe $(\kappa^2$ -Bpy), reveal an electronic structure consistent with a π -radical monoanion bipyridine chelate that is antiferromagnetically coupled to a low spin, Fe(1) metal center.

Due to the perceived importance of iron in biological nitrogen fixation¹ and its utilization in the Haber–Bosch process,² the study of dinitrogen coordination to well-defined iron complexes remains critical for guiding the development of inexpensive N₂ reduction catalysts.³ In theory, the multi-electron reduction of N₂ between two iron centers, or its direct cleavage to form two equivalents of $L_n Fe \equiv N$,⁴ could facilitate the formation of N-H bonds from H₂ and lead to a simplified, low-energy input NH₃ production cycle.

One approach to this challenge has involved the study of reducing Fe(0) complexes that are supported solely by electrondonating phosphine ligands. Iron dinitrogen complexes featuring two bidentate phosphine ligands have been studied,⁵ although they have yet to afford significant reduction of the N \equiv N bond. This has led researchers towards phosphine-based ligand scaffolds that could occupy four sites (3 basal and 1 apical) of a trigonal bipyramidal coordination environment, leaving one apical site for N₂ coordination. This methodology has allowed the characterization of $[\kappa^4-N(CH_2CH_2PPh_2)_3]Fe(N_2),^6$ $[\kappa^4$ -P(CH₂CH₂PMe₂)₃]Fe(N₂) and its related bridging complex $([\kappa^4-P(CH_2CH_2PMe_2)_3]Fe)_2(\mu^2,\eta^1,\eta^1-N_2)$.⁷ Because the transinfluence imparted by the apical chelate substituent in these complexes acts to deter strong nitrogen coordination (the greater trans-effect of the central phosphine in $[P(CH_2CH_2PMe_2)_3]Fe(N_2)$

leads to facile decomposition), we turned our attention towards iron halide complexes bearing the highly flexible Triphos ligand, PhP(CH₂CH₂PPh₂)₂, and the study of their reduction under N₂. As Triphos is known to coordinate in either a fac- or merfashion within an octahedral metal environment,8 we hypothesized that its coordinative flexibility may allow for the preparation of an iron(0) dinitrogen complex featuring a near tetrahedral geometry. Although such a compound could not be prepared, this contribution offers a detailed investigation of the formally zerovalent (Triphos)Fe complexes that have been synthesized under reducing conditions.

This study commenced with the preparation of a series of iron halide complexes of the general formula (Triphos) FeX_n (X = Cl, Br; n = 2, 3) (1-Cl₂, 1-Br₂, 1-Cl₃, 1-Br₃) via the stoichiometric addition of Triphos to a THF solution of the respective iron halide starting material. Although 1-Cl₂ has been previously reported,9 the structure of this complex in both solution and as a solid remains unknown. Attempts to crystallize 1-Cl₂ resulted in the isolation of slightly opaque colorless crystals, which have been identified as $(\kappa^2$ -Triphos)₂FeCl₂ by single crystal X-ray diffraction (Fig. S1of the ESI[†]).¹⁰

The crystallization of 1-Br₂, 1-Cl₃, and 1-Br₃ was also unsuccessful; however, each of these complexes could be effectively characterized by NMR spectroscopy. The ambient temperature ¹H NMR spectra of 1-Br₂ and 1-Cl₃ feature paramagnetically broadened resonances over a 110 or 70 ppm range, respectively, with the Triphos methylene resonances appearing the most shifted from their diamagnetic reference values. In contrast, evidence for Triphos lability was found when investigating 1-Br₃ by ¹H and ³¹P NMR spectroscopy. This complex displays a relatively featureless ¹H NMR spectrum in THF-d₈ at 23 °C with only one significant paramagnetically shifted resonance at 27.51 ppm. Surprisingly, ³¹P NMR spectroscopy revealed the presence of a paramagnetically broadened free Triphos phosphine arm at -22.10 ppm (Fig. S2 of the ESI[†]). This resonance is comparable in shift to those observed for uncoordinated Triphos (-16.87 and -20.43 ppm, THF- d_8); however, it has a peak width at half-height of 449.5 Hz. Although ³¹P resonances are typically not observed for paramagnetic complexes, the weaker ligand field strength of 1-Br₃ when compared to 1-Cl₃,¹¹ permits an arm of the Triphos chelate to dissociate upon dissolution into THF.

The reduction chemistry of each halide starting material was explored with the hope of isolating a Triphos iron complex featuring N₂ coordination. Adding an excess (5 eq.) of freshly

^a Department of Chemistry & Biochemistry, Arizona State University, Tempe, AZ 85287, USA. E-mail: ryan.trovitch@asu.edu;

Fax: +1 480 965 2747; Tel: +1 480 727 8930 ^b Materials Physics and Applications Division, Los Alamos National

Laboratory, Los Alamos, NM 87545, USA

^c Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: jgordon@lanl.gov; Fax: +1 505 667 9905; Tel: +1 505 665 6962

^d Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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cut Na metal to **1-Br**₂ in THF solution under 1 atm. of N₂ afforded the bis(chelate) complex, (κ^3 -Triphos)Fe(κ^2 -Triphos) [**1-**(κ^2 -**Triphos**)], as judged by multinuclear NMR spectroscopy (eqn (1)). The ¹H NMR spectrum of this complex features CH₂- and aryl-resonances that are near their diamagnetic reference values. Additionally, the ³¹P NMR spectrum of **1-**(κ^2 -**Triphos**) revealed five Fe-coordinated phosphorous environments (resonances at 119.23, 99.11, 82.74, 76.95, and 68.24 ppm) and a free phosphine arm at –12.08 ppm (Fig. S3 of the ESI†). This NMR data, coupled with the lack of a magnetic moment for **1-**(κ^2 -**Triphos**) at ambient temperature, is consistent with the formulation of this complex as a low spin Fe(0) complex. The connectivity of **1-**(κ^2 -**Triphos**) was confirmed by single crystal X-ray diffraction; however, data worthy of publication could not be obtained.



Alternatively, $1-(\kappa^2-\text{Triphos})$ was prepared from $1-\text{Br}_3$ and $1-\text{Cl}_3$. Although the reduction of $1-\text{Br}_3$ with Na metal in THF solution proceeded in a similar fashion, the reduction of $1-\text{Cl}_3$ in THF did not proceed readily when Na was used as the reductant. Replacing Na with 5 eq. of K allowed the formation of $1-(\kappa^2-\text{Triphos})$ from $1-\text{Cl}_3$ within 6 hours at 23 °C. The reduction of $1-\text{Br}_2$ to $1-(\kappa^2-\text{Triphos})$ was also successful when as little as 2.5 eq. of K was added to a diethyl ether slurry of $1-\text{Br}_2$. Adding an extra equivalent of Triphos ligand to the Na reduction of $1-\text{gr}_2$ still afforded $1-(\kappa^2-\text{Triphos})$; however, excess free ligand remained in the product mixture, complicating product purification.

Based on literature precedent, the failure of these reactions to yield an isolable Fe–N₂ complex was disappointing, but perhaps not overly surprising. Even though Field and co-workers⁷ were able to spectroscopically identify $[\kappa^4-P(CH_2CH_2PMe_2)_3]Fe(N_2)$ and $([\kappa^4-P(CH_2CH_2PMe_2)_3]Fe)_2(\mu^2-N_2)$, attempts to isolate these complexes were unsuccessful. Upon slow solvent evaporation, loss of the dinitrogen ligand occurred, resulting in the formation of an iron(0) tetramer that is held together by the free arms of a central bis(chelate) moiety closely related to $1-(\kappa^2-Triphos)$.⁷

Because N₂ coordination was not achieved in the experiments described above, the reduction of **1-Br₂** in the presence of more efficient trapping ligands was investigated. Although we were unable to obtain a single, well-defined iron complex when **1-Br₂** was reduced with excess Na metal in the presence of 1 atm. of carbon monoxide or 10 eq. of diphenylacetylene,¹² adding only one eq. of 2,2'-bipyridine (bpy) to the reaction mixture afforded a mixture of **1-**(κ^2 -**Triphos**) and the newly identified complex (κ^3 -Triphos)Fe(κ^2 -2,2'-bipyridine) (**1-Bpy**).

Conducting the same reaction with 5 eq. of bpy allowed the isolation of pure **1-Bpy** following recrystallization from a concentrated ether solution at -35 °C (eqn (2)). Analysis of this complex by ¹H, ¹³C, and ³¹P NMR spectroscopy revealed that **1-Bpy** displays peaks characteristic of a diamagnetic complex. As expected, the ¹H and ¹³C NMR spectra of **1-Bpy** suggest inequivalence between the two bpy ring environments. The ³¹P NMR spectrum of **1-Bpy** displayed only 2 resonances at 112.93 and 91.59 ppm, revealing that the two arms of the Triphos chelate remain equivalent.

2,2'-Bipyridine has thus far enjoyed a rich history in the field of coordination chemistry¹³ and its ability to act as a weak π -acceptor has been well documented in the literature.¹⁴ Although **1-Bpy** can *formally* be described as a diamagnetic, zerovalent iron complex, it was decided that a more detailed electronic structure investigation of **1-Bpy** was warranted. A single crystal obtained from the recrystallization of **1-Bpy** from Et₂O at -35 °C was analyzed by X-ray diffraction and the molecular structure determined for this complex is displayed in Fig. 1.



The metrical parameters of **1-Bpy** are consistent with an approximate square pyramidal coordination geometry about the iron with P(1)–Fe(1)–P/N angles of 116.38(3), 104.83(7), 95.43(7), and 85.02(3) for P(3), N(2), N(1), and P(2), respectively. More importantly, bpy chelate reduction is also evident with bond distances of 1.383(3) and 1.399(3) Å for N(1)–C(5)



Fig. 1 The solid state structure of **1-Bpy** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Relevant bond distances and angles are mentioned where appropriate within the text.



Fig. 2 Cyclic voltammogram of **1-Bpy** in THF (electrolyte = 0.1 M NBu₄PF₆; scan rate = 100 mV s⁻¹). The mid-potentials for bpy $(E_{1/2}^{(L)})$ and Fe $(E_{1/2}^{(M)})$ redox processes are -1.61 V and -0.82 V, respectively.

and N(2)–C(6), respectively, along with a significantly shortened C(5)-C(6) bond distance of 1.420(4) Å. A striking, comprehensive electronic structure investigation of eighteen bpy-supported transition metal complexes was recently reported by Scarborough and Wieghardt¹⁵ providing extensive insight for linking the bond distances found for 1-Bpy with an accurate electronic structure description. As described in their report, the bond distances determined for uncoordinated neutral bpy (bpy⁰),¹⁶ the potassium salt of bpy monoanion $(bpy^{\bullet-})$,¹⁷ and the disodium salt of bpy dianion (bpy²⁻),¹⁸ serve as representative examples for each degree of bpy reduction. Upon comparing each set of reference distances to the metrical parameters determined for 1-Bpy, it is clear that this complex features a π -radical monoanionic bpy ligand. As Scarborough and Wieghardt point out,¹⁵ previously reported bpy complexes that truly possess this chelate as a π -radical monoanion feature C(5)–C(6) bonds in the narrow range between 1.41-1.43 Å.¹⁹ Although most of the 1-Bpy bipyridine bond lengths are statistically indistinguishable from the same distances found for K(2,2'-bpy)(en),¹⁷ the C(5)–C(6) distance of 1.420(4) Å determined for 1-Bpy remains the best structural indication that the bpy ligand should be described as a π -radical monoanion.

Remembering that 1-Bpy is diamagnetic, the electronic structure of this complex should be assigned as having a singly reduced π -radical bpy ligand that is antiferromagnetically coupled to a low spin Fe(1) center.²⁰ To further bolster this claim, 1-Bpy was also investigated by electrochemistry. Starting from isolated 1-Bpy, cyclic voltammetry shows two reversible oxidations as the potentials are scanned from -2.4 to 0.0 V (Fig. 2). The first, with mid-potential at -1.61 V, is typical of the bpy^{•-}/bpy⁰ couple $(E_{1/2}^{(L)})^{21}$ while the second process at -0.82 V corresponds to the metal-based Fe^I/Fe^{II} couple $(E_{1/2}^{(M)})$. Compared to **1-Br**₂ $(E_{1/2}^{(M)} = -1.20 \text{ V})$, the positive shift of >0.4 V for the Fe^I/Fe^{II} redox potential of **1-Bpy** is consistent with the replacement of the charge-donating anionic ligands in 1-Br₂ by the charge-accepting bidentate ligand in 1-Bpy. Additionally, since no evidence for reduction of Fe(1) to Fe(0) was found in a range of potentials as low as -2.5 V, the formulation of **1-Bpy** as Fe(I)-(bpy^{•-}) instead of Fe(0)-(bpy⁰) is fully supported.

Importantly, heating a solution of **1-**(κ^2 -**Triphos**) in the presence of 5 eq. of bpy to 80 °C for 23.5 hours resulted in clean conversion to **1-Bpy** and Triphos as judged by multinuclear NMR spectroscopy. Based on the electronic structure description of **1-Bpy**, this chelate substitution therefore leads to a one electron oxidation of the metal center. In addition to challenging traditional coordination complex redox chemistry, this observation highlights the importance of electronic structure determination when studying low-valent metal complexes.

X-ray crystallographic data for complexes **1-Bpy** (CCDC 884463) and (κ^2 -Triphos)₂FeCl₂ (CCDC 884464) in CIF format have been deposited at the Cambridge Crystallographic Data Centre. We would like to thank the LANL LDRD Program for financial support and Dr Brian L. Scott for help with X-ray crystallography.

Notes and references

- 1 B. M. Hoffman, D. R. Dean and L. C. Seefeldt, Acc. Chem. Res., 2009, 42, 609–619.
- 2 A. Hellman, E. J. Baerends, M. Biczysko, T. Bligaard, C. H. Christensen, D. C. Clary, S. Dahl, R. van Harrevelt, K. Honkala, H. Jonsson, G. J. Kroes, M. Luppi, U. Manthe, J. K. Nørskov, R. A. Olsen, J. Rossmeisl, E. Skúlason, C. S. Tautermann, A. J. C. Varandas and J. K. Vincent, *J. Phys. Chem. B*, 2006, **110**, 17719–17735.
- 3 J. L. Crossland and D. R. Tyler, *Coord. Chem. Rev.*, 2010, **254**, 1883–1894.
- 4 J. M. Smith and D. Subedi, Dalton Trans., 2012, 41, 1423-1429.
- 5 (a) R. A. Cable, M. Green, R. E. Mackenzie, P. L. Timms and T. W. Turney, J. Chem. Soc., Chem. Commun., 1976, 270–271; (b) A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, J. Chem. Soc., Dalton Trans., 1993, 3041–3049; (c) S. Komiya, M. Akita, A. Yoza, N. Kasuga, A. Fukuoka and Y. Kai, J. Chem. Soc., Chem. Commun., 1993, 787–788; (d) J. D. Gilbertson, N. K. Szymczak and D. R. Tyler, J. Am. Chem. Soc., 2005, 127, 10184–10185.
- 6 T. A. George, D. J. Rose, Y. Chang, Q. Chen and J. Zubieta, *Inorg. Chem.*, 1995, 34, 1295–1298.
- 7 L. D. Field, R. W. Guest and P. Turner, *Inorg. Chem.*, 2010, **49**, 9086–9093.
- 8 J. M. O'Connor, K. Hiibner, A. Closson and P. Gantzel, Organometallics, 2001, 20, 1482–1485.
- 9 S. G. Davies, H. Felkin and O. Watts, J. Chem. Soc., Chem. Commun., 1980, 4, 159–160.
- The ambient temperature structure of this complex with two co-crystallized acetone molecules has been reported. M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1981, **20**, 3430–3435.
- 11 R. H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley & Sons, Inc., Hoboken, NJ, 4th edn, 2005, p. 12.
- 12 Reduction of 1-Br₂ with Na in the presence of CO resulted in a mixture of complexes believed to be of the type previously described in R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem.*, 1971, 10, 1841–1850. Reduction in the presence of 10 eq. of diphenylacetylene afforded 1-(κ²-Triphos).
- 13 E. C. Constable, Adv. Inorg. Chem., 1989, 34, 1-37.
- 14 H. Tom Dieck, K.-D. Franz and F. Hohmann, *Chem. Ber.*, 1975, **108**, 163–173.
- 15 C. C. Scarborough and K. Wieghardt, *Inorg. Chem.*, 2011, **50**, 9773–9793.
- 16 M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress and W. H. Woodruff, J. Am. Chem. Soc., 1981, 103, 4945–4947.
- 17 E. Gore-Randall, M. Irwin, M. S. Denning and J. M. Goicoechea, *Inorg. Chem.*, 2009, 48, 8304–8316.
- 18 H. Bock, J.-M. Lehn, J. Pauls, S. Holl and V. Krenzel, Angew. Chem., Int. Ed., 1999, 38, 952–955.
- (a) M. Irwin, R. K. Jenkins, M. S. Denning, T. Krämer, F. Grandjean, G. J. Long, R. Herchel, J. E. McGrady and J. M. Goicoechea, *Inorg. Chem.*, 2010, 49, 6160–6171; (b) S. J. Kraft, P. E. Fanwick and S. C. Bart, *Inorg. Chem.*, 2010, 49, 1103–1110; (c) D. Roitershtein, A. Domingos, L. C. J. Pereira, J. R. Ascenso and N. Marques, *Inorg. Chem.*, 2003, 42, 7666–7673; (d) M. Schultz, J. M. Boncella, D. J. Berg, T. D. Tilley and R. A. Anderson, *Organometallics*, 2001, 21, 460–472; (e) W. J. Evans and D. K. Drummond, *J. Am. Chem. Soc.*, 1989, 111, 3329–3335.
- 20 T. Liu, B. Li, C. V. Popescu, A. Bilko, L. M. Pérez, M. B. Hall and M. Y. Darensbourg, *Chem.-Eur. J.*, 2010, **16**, 3083–3089.
- 21 (a) C. Creutz, Comments Inorg. Chem., 1982, 1, 293; (b) A. A. Vlcek, Coord. Chem. Rev., 1982, 43, 39.