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Redox behaviour of  $([\text{fc}(\text{NP}^i\text{Pr}_2)_2]\text{Fe})_2$ , formation of an iron–iron bond and cleavage of azobenzene†‡Fraser S. Pick,<sup>a</sup> Daniel B. Leznoff<sup>†</sup>  <sup>\*b</sup> and Michael D. Fryzuk  <sup>\*a</sup>

The redox behaviour of the dimeric tetrairon complex,  $([\text{fc}(\text{NP}^i\text{Pr}_2)_2\text{Fe}]_2)$  (where  $\text{fc}(\text{NP}^i\text{Pr}_2)_2 = 1,1'-(\text{C}_5\text{H}_4\text{NP}^i\text{Pr}_2)_2\text{Fe}$ ) has been investigated. Upon reduction with  $\text{K}^+\text{C}_8$  an Fe–Fe bond is formed with the complex maintaining a high spin configuration and having the formula  $[\text{K}(\text{THF})_6][[\text{fc}(\text{NP}^i\text{Pr}_2)_2\text{Fe}]_2]$ . In contrast, oxidation of the complex is ligand based; for example, addition of the 1,2-diiodoethane ( $\text{I}_2$  equivalent) results in the formation of the monomeric iron(II) diiodide  $[\text{fc}(\text{NP}^i\text{Pr}_2)_2\text{Fe}]\text{I}_2$  wherein the phosphine is oxidized. The dimeric tetrairon complex reacts photolytically with azobenzene, cleaving the N=N double bond and forming the new monomeric bis(phosphoramidate) iron complex,  $[\text{fc}(\text{NP}(\text{NPh})^i\text{Pr}_2)_2\text{Fe}]$ . Characterization of these paramagnetic complexes was accomplished by magnetic susceptibility studies and X-ray analyses.

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## Introduction

The impressive transformations facilitated by heterogeneous catalysts<sup>1–6</sup> and multimetallic co-factors in metalloenzymes, such as nitrogenase,<sup>7–10</sup> have led to interest in the study of polynuclear molecular systems.<sup>11–14</sup> The ability of metalloenzymes to perform multielectron reductions<sup>15,16</sup> using iron-based cofactors is particularly noteworthy considering the conditions of the intracellular environment. Despite significant efforts, the binding and activation of substrates by these polynuclear sites remain poorly understood.<sup>16–20</sup> Attempts to create synthetic models of these polyiron sites has been of increasing interest<sup>17,21–26</sup> as such studies may reveal insights into complex redox processes. Of particular note, recent reports of polyiron complexes supported by a biological ligands detail the activation of substrates relevant to nitrogen fixation.<sup>27–31</sup> Such studies are important because these synthetic systems can be more easily studied than the naturally occurring enzymes, which allows for a more detailed description of their electronic structures, factors affecting metal–metal bonding, and substrate binding.<sup>32,33</sup>

Betley and coworkers have contributed to this area with the isolation of the trinuclear, high-spin cluster of Fe(II) centers (**A** in Scheme 1), which is capable of cleaving the N–N bond of azobenzene ( $\text{PhN}=\text{NPh}$ ) with no external reductant.<sup>28</sup> We have previously reported the tetrairon dimer **1** that contains two ferrocenyl diphosphinoamides supporting two high spin Fe(II) ions; this ancillary ligand system also can be used to generate a mixed tetranuclear  $\text{Fe}_2\text{–Co}_2$  system that displays weak Fe–Co interactions.<sup>34</sup> Based on reports from our group and others that show how dinitrogen can be activated and functionalized by dinuclear or trinuclear complexes,<sup>35–41</sup> we investigated the redox reactivity of **1** to examine structural changes, as well as interaction with small molecules related to dinitrogen fixation. In this paper, we report the oxidation and reduction of **1**, and cleavage of azobenzene by **1**.

## Results and discussion

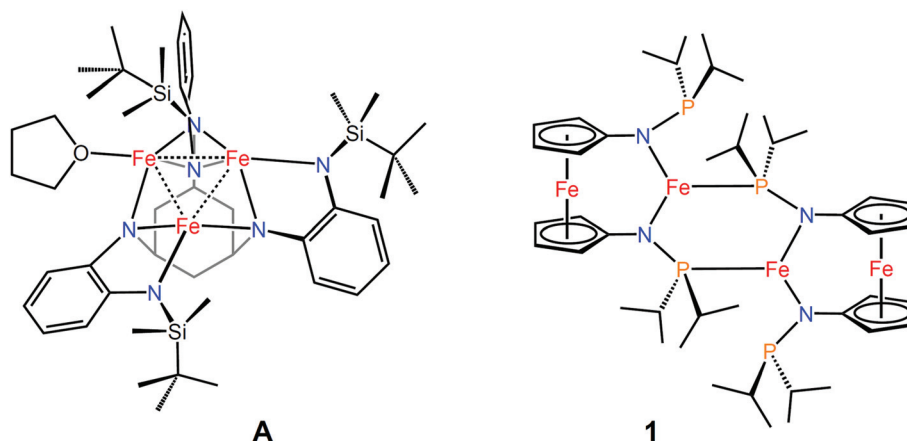
Initially we sought to use cyclic voltammetry to study the redox behaviour of **1** but the results were poor with multiple irreversible waveforms observed in both the reductive and oxidative regimes (see the ESI†). We then examined chemical oxidants and reductants. Although **1** reacts rapidly with numerous oxidants of the type  $\text{Ag}(\text{Y})$  and  $\text{X}_2$  ( $\text{Y} = \text{OTf}^-, \text{Cl}^-, \text{BPh}_4^-, \text{X} = \text{Br}, \text{I}$ ) the cleanest reaction was obtained using the molecular iodine equivalent 1,2-diiodoethane. Treatment of **1** with four equivalents of 1,2-diiodoethane resulted in conversion to a new paramagnetic product. The stoichiometry of the reaction suggested that the oxidation was more than a simple Fe(II)/Fe(III) event. Recrystallization from toluene/hexanes mixture results in the formation of dark red crystals of a new paramagnetic product,

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†Dedicated to Professor Richard A. Andersen on the occasion of his 75th Birthday.

‡Electronic supplementary information (ESI) available. CCDC 1822229–1822231. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt00828k



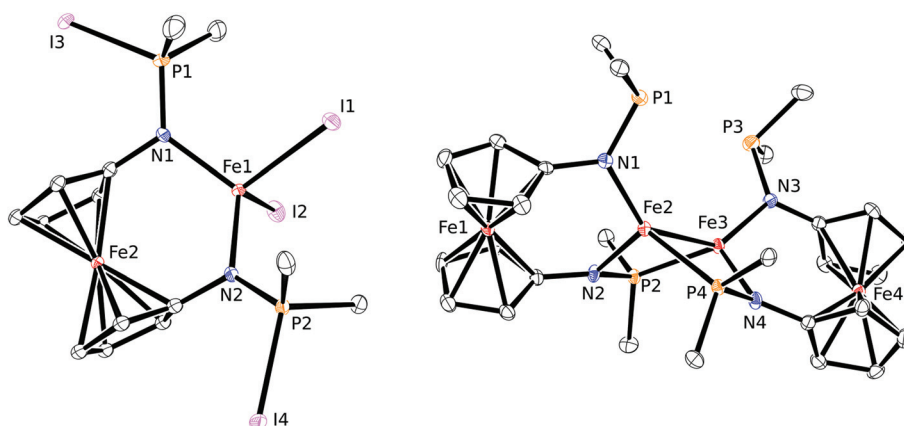
**Scheme 1** The triiron complex **A** from the Betley group (ref. 28) and the dimeric tetrairon complex **1** discussed in this work.

**2**, with an empirical formula of  $[\text{fc}(\text{NP}^{\text{I}}\text{Pr}_2)_2]\text{FeI}_4$  (56%). X-ray analysis of **2** revealed the solid-state molecular structure, shown in Fig. 1. The P–N bond shortens from **1** (1.6993(12) Å) to **2** (1.603(7) Å) demonstrating that the electron-rich phosphinoamide arms of the ligand have been oxidized to generate iodophosphinimide units while both iron atoms remain in the formal Fe(II) oxidation state. We suggest that irreversible oxidation of the P–N bond is contributing to the poor quality of the aforementioned CV data in the oxidative regime.

Attempts to generate a dinitrogen complex by reduction of **1** under mild conditions (4 atm  $\text{N}_2$ ) were unsuccessful. Upon reduction with  $\text{KC}_8$ , **1** does not coordinate  $\text{N}_2$  but rather undergoes a rearrangement to form an iron–iron bond between the two internal iron centers (Fig. 1). The Fe1–Fe2 distance decreases from 3.9241(5) Å in **1** to 2.4760(6) Å in **3**, similar to the diiron ( $\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}$ ) tris(phosphinoamide) reported by the Thomas group (2.4645 Å).<sup>29</sup> In order for the iron centers in **3** to get close enough to form a bond the ferrocene backbones of

the ligand must twist to become perpendicular to each other (cp plane to cp plane angle =  $84.75^\circ$ – $86.05^\circ$ ). In addition, the iron–nitrogen bonds elongate slightly in the reduced derivative **3** to 1.975(3) and 1.983(3) Å from 1.9217(12) and 1.9459(12) Å as found in starting **1**. Interestingly, the iron–phosphine bond distances decrease when **1** is reduced; in **1**, the Fe–P bonds are 2.4443(4) Å whereas in the reduced species **3**, they are shorter, *i.e.*, Fe2–P4 is 2.3612(10) and Fe3–P2 is 2.3606(11) Å. This is likely due to increased back bonding to the phosphines in the reduced form **3** whereas the iron–amido (Fe–N) bonds increase slightly due to the increased negative charge shared between the two iron centers.

The Mössbauer spectrum of **3** and the fits are shown in Fig. 2. Formally, complex **3** is a mixed-valent species with the core iron centers with the Fe–Fe bond being Fe(I)/Fe(II) surrounded by two Fe(II) ferrocene units in the ligand framework. We observe two doublets, one with an isomer shift of  $+0.45 \text{ mm s}^{-1}$  and  $\Delta E_{\text{q}}$  of  $2.23 \text{ mm s}^{-1}$  (doublet 1, blue fit in



**Fig. 1** ORTEP diagram of **2** (left) and anionic portion of **3** (right) with ellipsoids drawn at 50% probability. All H atoms and  $^i\text{Pr}$  methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) of **2**: Fe1–Fe2 3.4836(17); N1–P1 1.607(7); N2–P2 1.603(7); Fe1–I1 2.6889(13); Fe1–I2 2.6428(13); P1–I3 2.408(3); P2–I4 2.409(3); I1–Fe–I2 104.97(4); N1–Fe–N2 115.7(3); cp tilt<sup>42,43</sup> 2.78; and **3**: Fe1–Fe2 3.7016(10); Fe2–Fe3 2.4755(7); Fe3–Fe4 3.6954(10); N1–P1 1.690(3); N2–P2 1.651(3); Fe2–N2 1.975(3); Fe2–N1 1.983(3); Fe2–P4 2.3612(10); Fe3–P2 2.3607(10); N1–Fe2–N2 11.49(11); N2–Fe2–P4 110.22(8); N1–Fe2–Fe3 136.97(8); cp tilt<sup>42,43</sup> for Fe1 1.18 and Fe4 0.88.

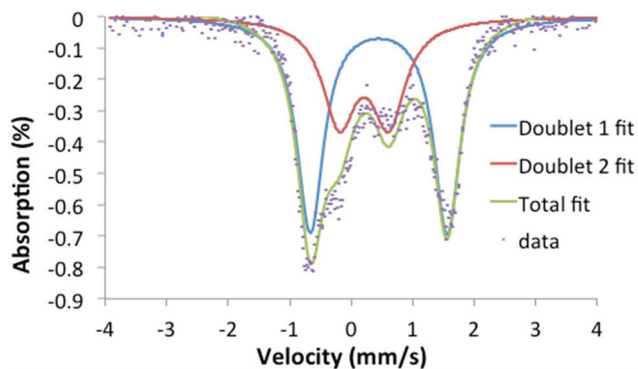


Fig. 2 Zero-field Mössbauer spectrum of **4** fit as a pair of quadrupolar doublets, with  $\delta = +0.45 \text{ mm s}^{-1}$ ,  $\Delta E_Q = 2.23 \text{ mm s}^{-1}$  (blue line, doublet 1 fit) and  $\delta = +0.21 \text{ mm s}^{-1}$ ,  $\Delta E_Q = 0.77 \text{ mm s}^{-1}$  (red line, doublet 2 fit). The total fit is shown as a green line.

Fig. 2); this doublet corresponds to the two ferrocene Fe(II) centers and matches our previous assignment<sup>34</sup> of the ferrocene centers in starting **1**. The remaining doublet (doublet 2, red fit) with an isomer shift of  $+0.23 \text{ mm s}^{-1}$  and  $\Delta E_Q$  of  $0.77 \text{ mm s}^{-1}$  is assigned to the core Fe centers, and because there is only one doublet, this is consistent with a delocalized mixed-valent system. The broadness of the inner doublet compared to the outer doublet is also consistent with a mixed-valent electronic structure for these inner core Fe centers.<sup>44</sup> The isomer shift and  $\Delta E_Q$  values do not match other somewhat related complexes in the literature. For example, a diiron tris(diphenylformamidate) species<sup>45</sup> is formally a mixed-valent Fe(I)/Fe(II) system with an isomer shift of  $+0.65 \text{ mm s}^{-1}$  and  $\Delta E_Q$  of  $+0.32 \text{ mm s}^{-1}$ ; however, the very different ligand environment and high symmetry of this latter tris(formamidate) complex make comparisons difficult. Analogy to other systems has not been helpful either as there is considerable variation of Mössbauer parameters for other Fe derivatives.<sup>46–48</sup>

The iron–iron bond, formed upon reduction of **1**, illustrates the potential for the storage of reducing equivalents in this system; however, we were unable to capitalize on this as compound **3** is unstable in solution: a  $\text{C}_6\text{D}_6$  solution **3** reverts back to over 50% compound **1** in less than 24 hours. In the solid-state, however, **3** is stable in the glovebox freezer ( $-35 \text{ }^\circ\text{C}$ ) for up to a week. The magnetic moment of **3** ( $7.8\mu_{\text{B}}$ ) indicates that the complex maintains a maximally high spin  $S = 7/2$  ground state. We also tried without success to reduce **3** further by addition of more  $\text{KC}_8$ , but this did not result in any change as evidenced by NMR spectroscopy. In fact, a K mirror in the NMR tube extended the lifetime of **3** in  $\text{C}_6\text{D}_6$  solution as evidence by the persistence of the paramagnetically shifted peaks due to **3**.

It has been observed that diiron systems displaying a M–M bond contract upon oxidation<sup>47</sup> with the rationale being a depopulation of the M–M anti-bonding orbitals. However, in a recent contribution, Betley and coworkers report<sup>33</sup> that the same triiron system, which activates  $\text{PhN}=\text{NPh}$  (**A** in Scheme 1) contracts the Fe–Fe distance ( $0.13 \text{ \AA}$ ) upon

reduction. Compound **1** and **A** represent rare examples of iron–iron interactions that increase upon reduction while maintaining a high-spin state, and therefore populating the Fe–Fe anti-bonding orbitals. The reactivity of **3** with nitrogen rich substrates such as  $\text{PhN}=\text{NPh}$  has so far led to complicated mixtures, no doubt due to the high reactivity of this complex.

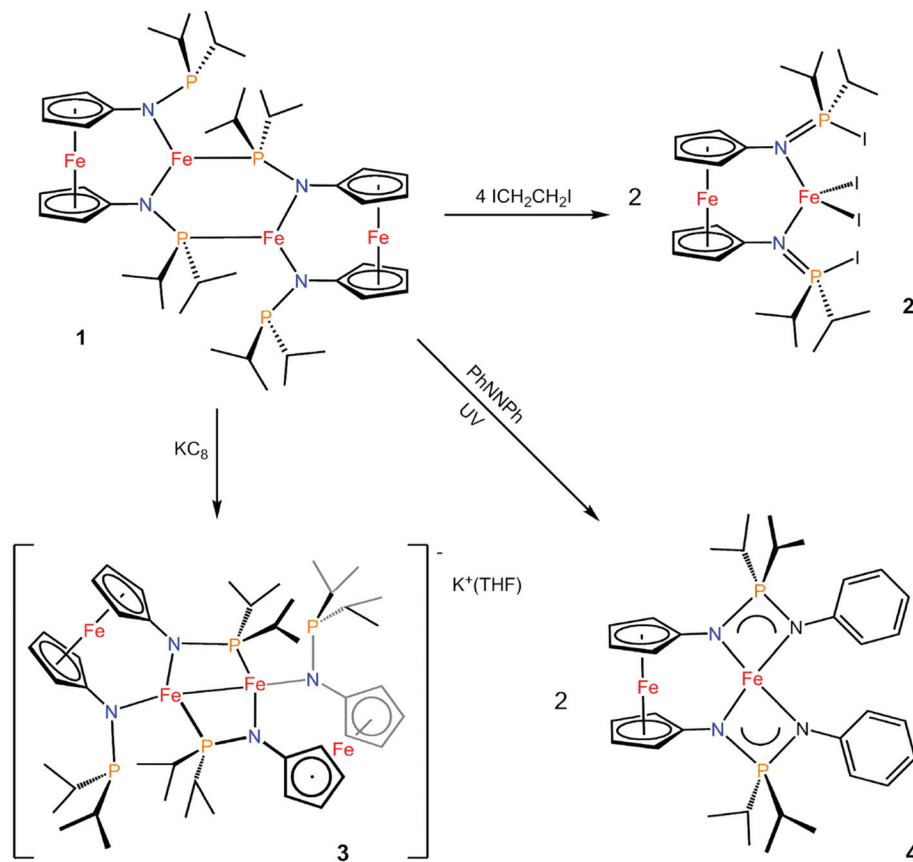
While **1** was unable to coordinate dinitrogen even under reducing conditions, we wondered how **1** would react with the N=N double bond in azobenzene. Cleavage of  $\text{PhN}=\text{NPh}$  is known for iron<sup>49</sup> and ruthenium<sup>50</sup> carbonyl clusters, both of which are proposed to involve transfer of the putative metal imidos to coordinated CO to form isocyanates. More recently a trinuclear ruthenium hydride<sup>51</sup> and a trinuclear iron complex<sup>28</sup> have been shown to cleave  $\text{PhN}=\text{NPh}$  into metal imidos. We envisioned that complex **1**, containing four iron(II) centers, might also have the available reducing equivalents to cleave the  $\text{PhN}=\text{NPh}$  double bond.

Exposing compound **1** to azobenzene does not result in a reaction as evidenced by NMR spectroscopy. Even heating the mixture to  $70 \text{ }^\circ\text{C}$  for 12 hours does not result in any new signals in either the paramagnetic or diamagnetic  $^1\text{H}$  NMR spectra. However, when a solution of **1** and  $\text{PhN}=\text{NPh}$  in  $\text{C}_6\text{D}_6$  was irradiated with UV light ( $350 \text{ nm}$ ) a new paramagnetic product was detected by NMR spectroscopy (compound **4** in Scheme 2). Single crystals were obtained by cooling a solution of **4** in pentane, and the solid-state structure is shown in Fig. 3.

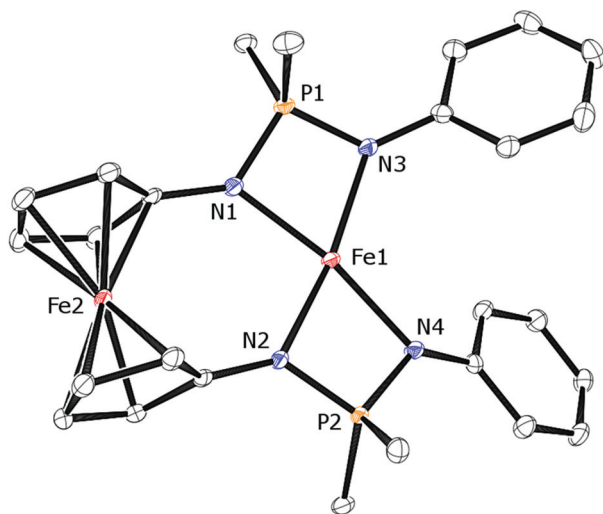
Unexpectedly, two new P–N bonds were formed with similar P1–N1 and P1–N3 bond lengths of  $1.6119(14) \text{ \AA}$  and  $1.6260(14) \text{ \AA}$  respectively, indicate a delocalized phosphoramidate anion. Interestingly the ferrocene linker forces the iron center to adopt a distorted square-planar geometry ( $\tau_4^{52} = 0.19$ ). Compound **4** displays a room temperature magnetic moment of  $2.9\mu_{\text{B}}$ , consistent with the spin only value of two unpaired electrons ( $S = 1$ ) and other square planar Fe(II) complexes.<sup>53</sup> Phosphoramidates have been used to support metal–metal bonds in alkali earth metals,<sup>54–56</sup> rare earth element polymerization catalysts<sup>57–61</sup> and group 10 cross-coupling catalysts.<sup>62–64</sup> To the best of our knowledge this is the first report of a bis(phosphoramidate)iron complex, however, a diiron system with a bridging phosphoramidate backbone has been reported.<sup>65</sup>

Since there was no reaction with the readily available *trans* form of azobenzene, we initially hypothesized that **1** could only react with *cis*- $\text{PhN}=\text{NPh}$  due to steric congestion. To test this we produced a mixture of *cis/trans*- $\text{PhN}=\text{NPh}$  by photolysis and then added compound **1** in the absence of UV light. No reaction was observed, although **1** does seem to catalyze the *cis* to *trans* isomerization of azobenzene (see ESI†). Compound **4** could only be produced when both reactants are exposed to UV light together, indicating that the role of UV radiation is more than just isomerization of azobenzene.

While phosphoramidates are most commonly synthesized from phosphines and organic azides, synthesis from azobenzene is preceded. Recently, a reaction between the Ti/Co



Scheme 2



**Fig. 3** ORTEP diagram of **4** with ellipsoids drawn at 50% probability. All H atoms and <sup>i</sup>Pr methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–Fe2 4.0103(4); N1–P1 1.6142(13); P1–N3 1.6260(14); N1–Fe1 2.0558(13); P1–Fe1 2.7176(5); N3–Fe1 2.0634(14); N1–P1–N3 96.90(7); N1–Fe1–N2 98.04(5); N1–Fe1–N3 72.13(5); N3–Fe1–N4 118.01(5).

phosphinoamide complex, (THF)Ti(μ-ArNPR<sub>2</sub>)<sub>3</sub>Co(N<sub>2</sub>), and azobenzene has been reported, which resulted in cleavage of azobenzene and formation of one phosphoramidate and one bridging metal imido.<sup>66</sup> Given the observations of an imido unit in the Ti–Co system above, it is likely that an iron imido is produced in the reaction between PhN=NPh and compound **1**, but this imido quickly reacts with a phosphinoamide arm of the ligand. The complex most similar to **4** is Fe(ArNPR<sub>2</sub>)<sub>3</sub>Fe (PMe<sub>3</sub>),<sup>29</sup> which reacts with organic azides to produce an iron imido. However, this imido is not reported to react with the bound amidophosphine ligands and we suggest that the geometric differences between the two complexes, namely the presence of η<sup>1</sup>-N-phosphinoamides, are responsible for the divergent reaction profiles of these similar complexes.

## Conclusions

In this report we present a polyiron complex that, under photolytic conditions, cleaves azobenzene through a proposed but undetected iron imido species. We also note that **1** undergoes a ligand rearrangement forming an iron–iron bond upon reduction while maintaining a high-spin *S* = 7/2 state. From a ligand design perspective it appears that amidophosphine



donors are too electron-rich to study oxidation of high-spin iron clusters. Further work will involve determining whether the proposed imido, generated during the reaction of **1** with PhN=NPh, can be trapped before transfer to the phosphine. New ligand designs will focus on scaffolds that can support higher nuclearity iron systems that are more redox-innocent, and stay dimeric throughout redox processes and their reactions with nitrogen-rich small molecules.

## Experimental

### General experimental procedures

All manipulations were performed under an atmosphere of dry and oxygen-free dinitrogen by means of standard Schlenk or Glovebox techniques. Anhydrous diethylether, toluene, hexanes and THF were purchased from Sigma-Aldrich, sparged with dinitrogen and dried further by passage through towers containing activated alumina and molecular sieves. Benzene- $d_6$ , THF- $d_8$  and pentane were refluxed over sodium benzophenone ketyl, vacuum transferred and freeze-pump-thaw degassed. 1,2-Diiodoethane and PhN=NPh were purchased from Sigma-Aldrich and used as received.  $KC_8$ <sup>67</sup> and compound **1**<sup>34</sup> were prepared by literature methods.

<sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra were recorded on a Bruker AV-300 or AV-400 MHz spectrometer at room temperature. <sup>1</sup>H NMR spectra were referenced to residual proton signals in C<sub>6</sub>D<sub>6</sub> (7.16 ppm) and C<sub>4</sub>D<sub>8</sub>O (3.58 ppm); <sup>31</sup>P NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> (0.0 ppm); microanalyses (C, H, N) and mass spectroscopy (low resolution EI) were performed at the Department of Chemistry at the University of British Columbia. Magnetic moments in solution were obtained using Evans NMR method.<sup>68,69</sup> The <sup>57</sup>Fe Mössbauer spectrum of **3** was recorded at Simon Fraser University using a W.E.B. Research Mössbauer spectroscopy system at room temperature under a He atmosphere. A <sup>57</sup>Co (in rhodium matrix) source with a strength of approx. 10 mCi was used. The detector was a Reuters-Stokes Kr/CO<sub>2</sub> proportional counter. The sample powder was loaded in a glovebox into a high-density polyethylene flat washer, wrapped in parafilm, and secured with Kapton tape. The velocity was scanned at a rate between 4 mm s<sup>-1</sup> and -4 mm s<sup>-1</sup>, using a constant acceleration triangle waveform, and calibrated against iron foil, measured at 295 K in zero magnetic field. All isomer shifts ( $\delta$ ) are relative to the iron foil. Fitting of the data was performed using WMOSS software, which is available free of charge at <http://wmoss.org/>.

**[fc(NP<sup>i</sup>Pr<sub>2</sub>I)<sub>2</sub>]FeI<sub>2</sub> (2)**. To an oven-dried Schlenk flask was added ([fc(NP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Fe)<sub>2</sub> (0.100 g, 0.0996 mmol) and toluene (5 mL). A solution of ICH<sub>2</sub>CH<sub>2</sub>I (0.118 g, 0.419 mmol) in toluene (5 mL) was added dropwise and the resulting solution was allowed to stir for 16 h. The volatiles were removed *in vacuo* and the resulting solids were recrystallized from a 50/50 mixture of toluene and hexanes resulting in dark red crystalline solids which were dried *in vacuo*. Yield 0.112 g,

55.7%. <sup>1</sup>H NMR ( $\delta$  in ppm, C<sub>6</sub>D<sub>6</sub>, 293 K, 400 MHz) 18.36 (s), 4.74 (s), 3.19 (s), 0.88 (s), -9.33 (s). Anal. calcd for C<sub>29</sub>H<sub>44</sub>Fe<sub>2</sub>I<sub>4</sub>N<sub>2</sub>P<sub>2</sub>: C, 31.61; H, 4.02; N, 2.54. Found: C, 31.94; H, 4.12; N, 2.50.  $\mu_{\text{eff}}$  (solution 293 K) 5.5 $\mu_B$ .

**(K(THF)<sub>6</sub>)([fc(NP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Fe)<sub>2</sub> (3)**. To an oven-dried Schlenk flask was added ([fc(NP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Fe)<sub>2</sub> (0.100 g, 0.0996 mmol) and toluene (5 mL) and chilled to -30 °C. In a separate Schlenk flask KC<sub>8</sub> (0.054 g, 0.3984 mmol) was suspended in toluene (5 mL) and chilled to -30 °C. The ([fc(NP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Fe)<sub>2</sub> solution was cannula transferred on to the KC<sub>8</sub> slurry and allowed to warm to room temperature with stirring for 6 h. The resulting slurry is filtered through Celite and the volatiles are removed *in vacuo* leaving a black residue. The residue is dissolved in a minimal amount of THF, layered with hexanes and cooled to -35 °C resulting in the formation of black crystals, which were filtered and dried *in vacuo*. Yield: 0.094 g, 0.064 mmol, 64%. <sup>1</sup>H NMR ( $\delta$  in ppm, C<sub>6</sub>D<sub>6</sub>, 293 K, 400 MHz) 188.42 (s), 36.80 (s), 34.10 (s), 25.32 (s), 15.14 (s), 12.08 (s), 11.51 (s), -2.75 (s), -17.86 (s), -29.72 (s). Anal. calcd for C<sub>68</sub>H<sub>120</sub>Fe<sub>4</sub>KN<sub>4</sub>O<sub>6</sub>P<sub>4</sub>: C, 55.33; H, 8.19; N, 3.80. Found: C, 55.11; H, 7.82; N, 3.98.  $\mu_{\text{eff}}$  (solution 293 K) 7.8 $\mu_B$ .

**[fc(NP<sup>i</sup>Pr<sub>2</sub>NPh)<sub>2</sub>]Fe (4)**. An oven dried bomb was loaded with ([fc(NP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Fe)<sub>2</sub> (0.100 g, 0.100 mmol), PhN=NPh (0.020 g, 0.110 mmol) and toluene (10 mL). The bomb was sealed, removed from the glovebox and irradiated with UV-light (350 nm) for 20 hours. The solution was then filtered, removing minimal solids, and reduced *in vacuo* to 1 mL. Pentane (1 mL) was added and the solution was cooled to -40 °C resulting in formation of an orange powder. Yield: 0.057 g, 0.083 mmol, 83%. <sup>1</sup>H NMR ( $\delta$  in ppm, C<sub>6</sub>D<sub>6</sub>, 293 K, 400 MHz) 109.02, 103.18, 98.59, 33.36, 29.81, 28.06, 23.23, 22.36, 19.92, 19.08, 17.06, 14.66, 14.13, 13.24, 12.35, 11.19, 10.91, -2.08, -4.67, -5.73, -14.75, -18.43, -22.89, -23.74. Anal. calcd for C<sub>34</sub>H<sub>46</sub>FeN<sub>4</sub>P<sub>2</sub>: C, 64.97; H, 7.38; N, 8.91. Found: C, 64.55; H, 7.24; N, 8.65.  $\mu_{\text{eff}}$  (solution 293 K) 2.9 $\mu_B$ .

## Author contributions

This manuscript was written through contributions of all authors.

## Conflicts of interest

The authors declare no competing financial interest.

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