# Precursors to dinitrogen reduction: structures and reactivity of *trans*-[Fe(DMeOPrPE)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)H]<sup>+</sup> and *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup><sup>†</sup>

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trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> and trans-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup> (DMeOPrPE =

1,2-bis(dimethoxypropylphosphino)ethane) were synthesized and their structures determined by X-ray crystallography. These complexes are important species in a dinitrogen reduction scheme involving protonation of an iron(0) dinitrogen complex to produce ammonia. The rates of substitution of the coordinated  $H_2$  and  $N_2$  molecules with acetonitrile were monitored in a variety of organic solvents. The coordinated  $N_2$  substituted ~6 times faster than  $H_2$ , but surprisingly the solvent had little effect on the observed rates. The results suggest that the  $H_2$  molecule in *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> does not participate in hydrogen bonding to the bulk solvent, as was previously observed in the analogous Ru complex. The deprotonation of *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup> to yield Fe(DMeOPrPE)<sub>2</sub>N<sub>2</sub> was investigated in the presence of a variety of anions, and it was found that the anion facilitates the reaction through an ion-pairing interaction in which the anion removes electron density from the hydride ligand.

# Introduction

Since the discovery of the first dinitrogen complex by Allen and Senoff in 1965,<sup>1</sup> extensive research has focused on creating a homogeneous catalyst capable of reducing dinitrogen to ammonia at room temperature and pressure.<sup>2-4</sup> Many remarkable advances have been made toward this goal,<sup>5-7</sup> including the achievement of a catalytic cycle.8 The chemistry of iron dinitrogen complexes represents a growing subset of this field,9,10 largely due to the fact that increasing evidence implicates an iron reaction site in the mechanism of nitrogenase enzymes.<sup>11-13</sup> Several groups, including our own, have found that addition of acid to five-coordinate iron dinitrogen phosphine species yields varying amounts of ammonia and/or hydrazine.14-19 Of particular interest to our group was a cycle pioneered by Leigh (Scheme 1).20 In the Leigh cycle, a trans- $[Fe(P_2)_2(H_2)H]^+$  complex ( $P_2 = a$  bidentate phosphine) is generated from *trans*-[Fe(P<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, a hydride source, and an acid. Following exchange of  $H_2$  for  $N_2$ , the hydride ligand can be "reductively" deprotonated to yield the five-coordinate iron(0) dinitrogen complex  $Fe(P_2)_2N_2$ . Protonation of this complex results in moderate yields of ammonia and/or hydrazine. We were able to modify this cycle by generating the *trans*- $[Fe(P_2)_2(H_2)H]^+$  complex directly from the dichloride starting material and dihydrogen;<sup>21,22</sup> thus, the electrons used for the reduction of dinitrogen to ammonia come directly from  $H_2$  (Scheme 1).

We previously reported that the generation of  $Fe(DMeOPrPE)_2N_2$  (DMeOPrPE = 1,2-bis(dimethoxypropylphosphino)ethane) and the protonation of this complex with 1 M triflic acid resulted in the formation of ammonia (15%) and hydrazine (2%).<sup>16</sup> Here we expand this report by describing further



Scheme 1 Leigh cycle for the reduction of  $N_2$  to  $NH_3$  in  $Fe(P_2)_2N_2$  systems. The direct reaction of the *trans*- $[Fe(P_2)_2Cl_2]^+$  with dihydrogen represents our modification of the Leigh cycle.

details on the synthesis and structural characterization of *trans*- $[Fe(DMeOPrPE)_2(H_2)H]^+$  and *trans*- $[Fe(DMeOPrPE)_2(N_2)H]^+$ , by exploring the substitution kinetics of these complexes with acetonitrile in a variety of organic solvents, and by describing the role of the anion in the deprotonation of *trans*- $[Fe(DMeOPrPE)_2(N_2)H]^+$ .

# Experimental

## Materials and reagents

All manipulations were carried out in a Vacuum Atmospheres Co. glove box (argon- or  $N_2$ -filled) or on a Schlenk line using argon or nitrogen. HPLC grade THF, hexane, and diethyl ether (Burdick and Jackson) were dried and deoxygenated by passing them, under an argon atmosphere, through commercial columns of CuO followed by alumina. Toluene (Aldrich) was distilled under  $N_2$  from CaH<sub>2</sub> and degassed by three freeze–pump–thaw cycles.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: NMR spectra and crystallographic data including the.cif files for I, II, and III. CCDC reference numbers 735060–735062. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b911066f

Commercially available reagents were used as received.  $TlBAr_{F}^{23}$  and  $TlBF_{4}^{24}$  were synthesized by literature procedures. *trans*-Fe(DMeOPrPE)<sub>2</sub>Cl<sub>2</sub><sup>25</sup> and *trans*-[Fe(DMeOPrPE)<sub>2</sub>(CH<sub>3</sub>CN)H]<sup>+22</sup> were synthesized as previously reported. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received.

#### Instrumentation

<sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra were recorded on either a Varian Unity/Inova 300 spectrometer at an operating frequency of 299.94 (<sup>1</sup>H) and 121.42 (<sup>31</sup>P) MHz or a Varian Unity/Inova 500 spectrometer at an operating frequency of 500.62 (<sup>1</sup>H) and 202.45 (<sup>31</sup>P) MHz. The <sup>1</sup>H and <sup>31</sup>P chemical shifts were referenced to the solvent peak and to an external standard of 1% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O, respectively. NMR samples were sealed under argon or nitrogen in 7 mm J. Young tubes. Note that the <sup>1</sup>H NMR data for the methyl and methylene regions in complexes containing the DMeOPrPE ligand were generally broad and uninformative and therefore are not reported in the synthetic descriptions below. Elemental analyses were performed by Robertson Microlit Laboratories. Mass spectrometer. The samples were dissolved in Et<sub>2</sub>O and introduced into the ionization head (ESI) using the infusion method.

### X-Ray crystallography

X-Ray diffraction data were collected at 100 K (trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H][BPh<sub>4</sub>]) or 173 K ([Fe(DMeOPrPE)<sub>2</sub>Cl]-[BPh<sub>4</sub>] and *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][BPh<sub>4</sub>]) on a Bruker Apex CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$ Å). Absorption corrections were applied by SADABS.<sup>26</sup> The structures were found by direct methods and calculations of difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. The C and O atoms in two of the -(CH<sub>2</sub>)<sub>3</sub>OMe groups of [Fe(DMeOPrPE)<sub>2</sub>Cl][BPh<sub>4</sub>] are disordered over two positions (in 71/29 and 74/26 ratios) and were refined with restrictions; the standard C-C and C-O distances were used in the refinements as targets for corresponding bond distances. H atoms in such groups were treated in calculated positions and refined in a rigid group model. All H atoms in trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H][BPh<sub>4</sub>] were found on the difference F-map and refined with isotropic thermal parameters. It was found that the Fe atom in *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H][BPh<sub>4</sub>] was disordered over two positions (in a 88:12 ratio) related to two opposite orientations of the  $HFe(H_2)$  fragment. The Fe1 and Fe1a positions are out from the average plane of the four P atoms bonded to the Fe atom on 0.14 and 0.22 Å, respectively. The  $H_2$ and H atoms corresponding to one of two possible orientations of the Fe atom were found on the residual density and refined without restrictions with occupation factor  $\mu = 0.88$  similar to that for the Fe1 atom. The second orientation of this fragment, corresponding to an occupation factor of  $\mu = 0.12$ , was not found and these H atoms were not taken into consideration. All calculations were performed by the Bruker SHELXTL 6.10 package.

Crystal data for *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H][BPh<sub>4</sub>] (I).  $C_{60}H_{103}BFeO_8P_4$ , M = 1142.96, triclinic, space group  $P\overline{1}$ , a = 10.8357(10), b = 16.9005(16), c = 18.2311(17) Å,  $\alpha = 90.013(2)$ ,  $\beta = 105.896(1)$ ,  $\gamma = 103.852(2)^\circ$ , V = 3109.8(5) Å<sup>3</sup>,  $D_c = 100.0126$  1.221 g cm<sup>-3</sup>,  $\mu = 0.396$  mm<sup>-1</sup>, Z = 2,  $\lambda = 0.71073$  Å, T = 100 K, 24706 reflections collected, 13266 independent ( $R_{int} = 0.0130$ ),  $R_1$ [ $I > 2\sigma(I)$ ] = 0.0311, w $R_2$  [ $I > 2\sigma(I)$ ] = 0.0811,  $R_1$  (all data) = 0.0346, w $R_2$  (all data) = 0.0842.

**Crystal data for** *trans*-**[Fe(DMeOPrPE)<sub>2</sub>Cl][BPh<sub>4</sub>] (II).**   $C_{60}H_{100}$ BClFeO<sub>8</sub>P<sub>4</sub>, M = 1175.39, triclinic, space group  $P\bar{1}$ , a = 13.5949(11), b = 15.4389(13), c = 16.0182(13) Å,  $\alpha = 97.9400(10)$ ,  $\beta = 94.0320(10)$ ,  $\gamma = 103.9340(10)^{\circ}$ , V = 3213.0(5) Å<sup>3</sup>,  $D_c = 1.215$  g cm<sup>-3</sup>,  $\mu = 0.425$  mm<sup>-1</sup>, Z = 2,  $\lambda = 0.71073$  Å, T = 173 K, 30 038 reflections collected, 13 652 independent ( $R_{int} = 0.0450$ ),  $R_1$  $[I > 2\sigma(I)] = 0.0625$ , w $R_2$   $[I > 2\sigma(I)] = 0.1304$ ,  $R_1$  (all data) = 0.0933, w $R_2$  (all data) = 0.1504.

Crystal data for *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][BPh<sub>4</sub>] (III).  $C_{60}H_{101}BFeN_2O_8P_4$ , M = 1168.97, triclinic, space group  $P\overline{1}$ , a = 13.466(2), b = 15.443(3), c = 16.219(3) Å,  $\alpha = 97.2619(3)$ ,  $\beta = 94.169(3)$ ,  $\gamma = 104.408(3)^\circ$ , V = 3221.5(10) Å<sup>3</sup>,  $D_c = 1.205$  g cm<sup>-3</sup>,  $\mu = 0.384$  mm<sup>-1</sup>, Z = 2,  $\lambda = 0.71073$  Å, T = 173 K, 36 541 reflections collected, 14419 independent ( $R_{int} = 0.0194$ ),  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0451, w $R_2$  [ $I > 2\sigma(I)$ ] = 0.1264,  $R_1$  (all data) = 0.0561, w $R_2$  (all data) = 0.1367.

#### Methods

Synthesis of trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H][BPh<sub>4</sub>] (I). trans-Fe(DMeOPrPE)<sub>2</sub>Cl<sub>2</sub> (1.86 g, 2.086 mmol), NaBPh<sub>4</sub> (1.43 g, 4.172 mmol), and Proton Sponge (0.45 g, 2.086 mmol) were combined as solids in a 120 mL Fischer-Porter tube. THF (15 mL) and Et<sub>2</sub>O (15 mL) were then added, and the resulting solution was immediately charged with 1 atm of  $H_2$ . The solution turned from green to orange to a faint yellow with the production of a white precipitate (NaCl) over the course of several hours. The reaction was allowed to stir for 48 h to ensure completion. The solution was then filtered through Celite under an argon atmosphere. The complex was precipitated as an oil by addition of hexane. The oil was redissolved in toluene, filtered through Celite, and again precipitated with hexane. The remaining oil was triturated with hexane to yield 2.32 g (97% yield) of a tan colored powder. X-Ray quality crystals were grown by slow evaporation of a THF solution. Anal. calcd. for C<sub>60</sub>H<sub>103</sub>BFeO<sub>8</sub>P<sub>4</sub>: C, 63.02; H, 9.09%. Found: C, 62.98; H, 9.30%.  ${}^{31}P{}^{1}H{}$  NMR (toluene-d<sub>8</sub>):  $\delta$  85.0 (s). <sup>31</sup>P NMR (toluene-d<sub>8</sub>):  $\delta$  85.0 (d, <sup>2</sup>J<sub>P-H</sub> = 47 Hz). <sup>1</sup>H NMR (toluene-d<sub>8</sub>) of the hydride region:  $\delta$  -11.1 (s, br) and  $\delta$  -15.1 (quintet,  ${}^{2}J_{H-P} = 49$  Hz).

Synthesis of [Fe(DMeOPrPE)<sub>2</sub>Cl][BPh<sub>4</sub>] (II). NaBPh<sub>4</sub> (0.384 g, 1.12 mmol) was added to a Et<sub>2</sub>O solution of *trans*-Fe(DMeOPrPE)<sub>2</sub>Cl<sub>2</sub> (0.1 g, 0.112 mmol) under argon. After stirring for 1 h the solvent was evaporated. The yellow residue was extracted into toluene and the solution was filtered through Celite. The complex was precipitated as a yellow solid by addition of hexane. The yellow powder was washed with hexane followed by diethyl ether (0.097 g, 74% yield). Crystals suitable for X-ray diffraction were grown from a saturated diethyl ether solution. <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-d<sub>8</sub>) at 193 K:  $\delta$  55.9 (s). <sup>31</sup>P NMR (toluene-d<sub>8</sub>) at 193 K:  $\delta$  55.9 (s). No <sup>31</sup>P resonances were observed at room temperature. Anal. calcd. for C<sub>60</sub>H<sub>100</sub>BClFeO<sub>8</sub>P<sub>4</sub>: C, 61.31; H, 8.58%. Found: C, 60.98; H, 8.39%. ESI (Et<sub>2</sub>O, +ve): 855.4 [Fe(DMeOPrPE)<sub>2</sub>Cl]<sup>+</sup>. Synthesis of *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][BPh<sub>4</sub>] (III). A THF–Et<sub>2</sub>O solution of I prepared by the method above was charged with 2 atm of N<sub>2</sub> in a Fischer-Porter tube and stirred for 48 h. The Fischer-Porter tube was vented and refilled with N<sub>2</sub> several times over the course of the reaction to remove free H<sub>2</sub>. The solution color changed from light yellow to light brown over the course of the reaction. The solvent was evaporated under an N<sub>2</sub> atmosphere and the resulting brown oil was triturated with hexanes to yield 2.28 g of a tan solid (94% yield). X-Ray quality crystals were grown by hexane diffusion into a THF solution. Anal. calcd. for C<sub>60</sub>H<sub>101</sub>BFeN<sub>2</sub>O<sub>8</sub>P<sub>4</sub>: C, 61.62; H, 8.71; N, 2.40%. Found: C, 61.94; H, 8.97; N, 2.25%. IR(KBr): ( $v_{NN}$ ) 2088 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-d<sub>8</sub>):  $\delta$  75.8 (d, <sup>2</sup>J<sub>P-H</sub> = 49 Hz). <sup>1</sup>H NMR (toluene-d<sub>8</sub>) of the hydride region:  $\delta$  –18.6 (quintet, <sup>2</sup>J<sub>H-P</sub> = 49 Hz).

Generation of *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]X (X = BF<sub>4</sub>, OTf, PF<sub>6</sub>, BAr<sub>F</sub>). These compounds were prepared analogously to I using the appropriate counter-ion source: TIBF<sub>4</sub>, TIOTf, TIPF<sub>6</sub>, or TIBAr<sub>F</sub>. The NMR characterization of these complexes matched that reported for the BPh<sub>4</sub> complex. These complexes were not isolated.

Generation of *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]X (X = BF<sub>4</sub>, OTf, PF<sub>6</sub>, BAr<sub>F</sub>). These compounds were prepared analogously to III using the appropriate *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]X starting material. These complexes were not isolated. <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-d<sub>8</sub>):  $\delta$  75.5–76.9 (s). <sup>31</sup>P NMR (toluene-d<sub>8</sub>):  $\delta$  75.5–76.9 (d, <sup>2</sup>J<sub>P-H</sub> = 49 Hz). <sup>1</sup>H NMR (toluene-d<sub>8</sub>) of the hydride region: BF<sub>4</sub>,  $\delta$  –18.35 (quintet, <sup>2</sup>J<sub>P-H</sub> = 49 Hz); OTf,  $\delta$  –18.4 (quintet, <sup>2</sup>J<sub>P-H</sub> = 49 Hz); BPh<sub>4</sub>,  $\delta$  –18.6 (quintet, <sup>2</sup>J<sub>P-H</sub> = 49 Hz); BAr<sub>F</sub>,  $\delta$  –18.8 (quintet, <sup>2</sup>J<sub>P-H</sub> = 49 Hz).

Generation of Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>). trans-[Fe(DMeOPrPE)<sub>2</sub>-(N<sub>2</sub>)H][X] (X = BPh<sub>4</sub>, BF<sub>4</sub>, OTf, PF<sub>6</sub>, BAr<sub>F</sub>) (30 mg) was dissolved in 0.6 mL of toluene-d<sub>8</sub>. 'BuOK (2 equivalents) was added as a solid to the solution under an N<sub>2</sub> atmosphere. The solution color changed from pale brown to bright orange over the course of the reaction. The reaction was agitated for 16 h. These complexes were not isolated. All of these complexes were shown to undergo deprotonation except the BAr<sub>F</sub> containing complex. <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-d<sub>8</sub>):  $\delta$  79.5 (s). <sup>31</sup>P NMR (toluene-d<sub>8</sub>):  $\delta$  79.5 (s).

Substitution kinetic experiments. In an NMR tube fitted with a septum, trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]BPh<sub>4</sub> (I) (0.3 mL of a 0.00746 M solution in toluene-d<sub>8</sub>, 0.00224 mmol), a solvent (0.3 mL of either toluene, acetone, tetrahydrofuran, dimethylformamide, dimethylacetamide, hexamethylphosphoramide), and acetonitrile (12 µL, 0.230 mmol) were sequentially added under Ar. Immediately after addition of the acetonitrile, the reaction was monitored by  ${}^{31}P{}^{1}H$  NMR spectroscopy. For the first 25 min, a spectrum was taken every 5 min. In the following 30 min, a spectrum was collected at 10 min intervals. For the remaining 6 h, the interval was increased to 30 min. The concentration of trans-[Fe(DMeOPrPE)2H(H2)]BPh4 was determined by  ${}^{31}P{}^{1}H$  peak integrations. The rate constants were then obtained by fitting the data (concentration versus time) with a single parameter exponential decay function using SigmaPlot software. The kinetic data for the reaction of acetonitrile with trans-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]BPh<sub>4</sub> (III) were acquired in the same manner (identical concentration and solvents), except the following time intervals were used: a spectrum was taken every 30 s for the first 3 min; a spectrum was collected at 1 min intervals in the following 6 min; a spectrum was collected at 2 min intervals in the following 12 min; and the interval was increased to 5 min for the remaining 30 min.

Test for hydrogen bonding in *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]-[BPh<sub>4</sub>]. A solution of I in toluene-d<sub>8</sub> (0.00746 M, 0.3 mL) was placed in an NMR tube fitted with a septum. The tube was then placed into the NMR magnet and allowed to equilibrate at -40 °C for 15 min. After this equilibration period, the <sup>1</sup>H spectrum was acquired and referenced to the toluene resonances. The sample was then ejected, 10  $\mu$ L (60 equivalents) of acetone-d<sub>6</sub> was added, and the sample placed back into the magnet. The procedure was repeated until 1000 equivalents of acetone had been added. The H<sub>2</sub> resonance shifted ~0.04 ppm downfield upon addition of the acetone; however, other resonances of I also underwent shifts of similar magnitudes, both downfield and upfield in direction.

#### **Results and discussion**

#### Synthesis of dihydrogen and dinitrogen complexes

The iron dihydrogen complex *trans*-[Fe(DMeOPrPE)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)H]<sup>+</sup> was previously synthesized as the PF<sub>6</sub><sup>-</sup> salt; however, attempts to isolate this complex as a solid were unsuccessful.<sup>16,22</sup> Following the same synthetic procedure, but using NaBPh<sub>4</sub> instead of TlPF<sub>6</sub>, an isolable solid (**I**) was obtained (eqn (1)).

$$P_{P} = MeO + \frac{3}{3}P + \frac{1}{3}OMe$$

$$H_{2} + \frac{1}{3}P + \frac{1}{3}OMe$$

$$H_{2} + \frac{1}{3}OMe$$

The solution characterization of I by NMR spectroscopy matched the previously reported data for the trans- $[Fe(DMeOPrPE)_2(\eta^2-H_2)H][PF_6]$  complex,<sup>22</sup> with a single resonance observed in the  ${}^{31}P{}^{1}H$  spectrum (85.0 ppm) and a broad singlet (-11.1 ppm) and quintet (-15.1 ppm,  ${}^{2}J_{HP}$  = 49 Hz) observed in the low temperature (-40 °C) <sup>1</sup>H spectrum. X-Ray quality crystals of I were grown by slow evaporation of a THF solution (Fig. 1). All hydrogen atoms were located, allowing visualization of the intact  $\eta^2$  dihydrogen ligand. The structure closely matches the previously published X-ray structures of trans-[Fe(DPPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> and trans-[Fe(DMPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> (DPPE = 1,2-bis(diphenylphosphino)ethane; DMPE = 1,2bis(dimethylphosphino)ethane).<sup>27,28</sup> Although the dihydrogen ligand was clearly found, X-ray methods are unreliable in accurately measuring the H-H bond distance, as evidenced by the fact that the measured H–H bond length (0.69 Å) is shorter than that of free dihydrogen (0.74 Å) and significantly shorter than the bond length determined by NMR methods.29

Previous work showed that the reaction of *trans*- $Fe(DMeOPrPE)_2Cl_2$  with  $H_2$  proceeds through a stepwise mechanism (Scheme 2); displacement of one chloride ligand with  $H_2$  occurs first, followed by heterolysis of the coordinated  $H_2$  to form the hydride ligand, and finally displacement of the second chloride with another equivalent of  $H_2$ .<sup>22</sup>



Scheme 2 Mechanism of the reaction of trans-Fe(DMeOPrPE)<sub>2</sub>Cl<sub>2</sub> with H<sub>2</sub>.



Fig. 1 Molecular structure of *trans*-[Fe(DMeOPrPE)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)H][BPh<sub>4</sub>] (I). Ellipsoids are drawn at 50% probability. The tetraphenylborate anion and hydrogen atoms of the phosphine ligands have been omitted for clarity.

Substitution of the first chloride with H<sub>2</sub> likely proceeds through a dissociative mechanism because this reaction does not proceed in organic solvents without the addition of a chloride abstracting reagent. In support of this hypothesis, [Fe(DMeOPrPE)<sub>2</sub>Cl]<sup>+</sup> (II) was synthesized by reacting trans-Fe(DMeOPrPE)<sub>2</sub>Cl<sub>2</sub> with NaBPh<sub>4</sub> in diethyl ether in the absence of  $H_2$ .<sup>30</sup> The product was isolated as a yellow powder and X-ray quality crystals were grown from a saturated diethyl ether solution (Fig. 2). The five-coordinate structure is best described as having a slightly distorted squarepyramidal geometry: using the angular structural parameter  $\tau$ defined by Addison et al., the complex has only 13% trigonal bipyrimidal distortion.32 The chloride ligand of II occupies the apical position and the P-Fe-Cl angles range from 92.69° to 98.93°. The Fe-Cl bond length (2.35 Å) of II is unchanged from that of the dichloride starting material (2.35 Å), while the Fe-P bonds (2.28-2.32 Å) are slightly lengthened.<sup>25</sup> The fivecoordinate complex II readily binds H<sub>2</sub> in solution to form *trans*- $[Fe(DMeOPrPE)_2(H_2)Cl]^+$ , as evidenced by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy, consistent with the mechanism in Scheme 2.33

The dihydrogen complex I is a convenient starting material for the generation of *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup>. Complex III, *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][BPh<sub>4</sub>], was synthesized from



**Fig. 2** Molecular structure of  $[Fe(DMeOPrPE)_2CI]^+$  (II). Ellipsoids are drawn at 50% probability. The tetraphenylborate anion and hydrogen atoms have been omitted for clarity.

I by a ligand substitution reaction with  $N_2$  (eqn (2)) at 1 atm. Because I is slightly more stable than III, the reaction vessel must be purged with  $N_2$  several times to remove any residual  $H_2$  to achieve complete conversion.

As with the *trans*-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> complex, previous attempts to isolate the *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup> complex as the PF<sub>6</sub><sup>-</sup> salt were unsuccessful.<sup>22</sup> Using the BPh<sub>4</sub><sup>-</sup> counterion, complex **III** was isolated as a tan solid. Again, the NMR characterization of **III** matched with the previously reported data,<sup>22</sup> with a singlet at 75.8 ppm in the <sup>31</sup>P{<sup>1</sup>H} spectrum and a hydride resonance at –18.6 ppm (<sup>2</sup>J<sub>HP</sub> = 49 Hz) in the <sup>1</sup>H spectrum. To determine the solid-state structure, light brown crystals of **III** were grown by layering a THF solution with hexanes and allowing the solution to stand under an N<sub>2</sub> atmosphere for ~1 week. The molecular structure of **III** shows the end-on bonded dinitrogen ligand *trans* to the hydride ligand (Fig. 3). The iron–phosphorus bond lengths in **III** range from 2.23–2.24 Å; these bond lengths closely match the DMPE<sup>34</sup> and DEPE<sup>35</sup> analogs. The N–N bond length of 1.11 Å shows slight elongation compared with free

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Fig. 3 ORTEP representation of *trans*- $[Fe(DMeOPrPE)_2(N_2)H]^+$  (III). Ellipsoids are drawn at 50% probability. The tetraphenylborate counter-ion and hydrogen atoms of the phosphine ligands have been omitted for clarity.

dinitrogen (1.10 Å), with the N–N bond length falling in between the DMPE (1.13 Å)<sup>34</sup> and DEPE (1.07 Å)<sup>35</sup> complexes.

#### Effect of solvent on the rate of H<sub>2</sub> and N<sub>2</sub> substitution

The substitution of H<sub>2</sub> and N<sub>2</sub> by various small molecules is a commonly observed reaction because these ligands are typically weakly bonded.<sup>36,37</sup> Both I and III are important species in the Leigh-type dinitrogen reduction cycle and their substitution reactivity was studied to gain insights into how to improve the yields of ammonia. It was previously shown with the trans- $[Ru(DMeOPrPE)_2(H_2)H]^+$  complex that a coordinated dihydrogen molecule can act as a hydrogen bond donor to a neutral acceptor molecule in solution, an interaction termed dihydrogen hydrogen bonding (DHHB).<sup>38</sup> If the coordinated H<sub>2</sub> in I were capable of donating a hydrogen bond to the bulk solvent, we wanted to explore how this would affect the reactivity. The substitution reactions of H<sub>2</sub> and N<sub>2</sub> in I and III, respectively, by acetonitrile were chosen for study because these reactions have been studied in great detail in analogous systems39-41 and the product of the reaction, trans-[Fe(DMeOPrPE)2(MeCN)H]+, has previously been characterized.<sup>22</sup> Complexes I and III are amenable to studies where the solvent needs to be varied because the DMeOPrPE ligand provides solubility in a spectrum of solvents. The BPh<sub>4</sub>anion also provides a weakly interacting counterion, minimizing any potential ion-pairing effects.

To probe the effect of solvent on the rate of substitution, the following solvents were used: toluene, acetone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMA), and hexamethylphosphoramide (HMPA). These solvents were chosen because both I and III were stable in them and they represent a spectrum of hydrogen-bond accepting strengths without having any hydrogen-bond donating ability. A stock solution

**Table 1** Summary of rate constants for I and III in various solvents, as well as solvent hydrogen-bond accepting strengths ( $\beta$ ) and solvent polarity ( $E_{\rm T}(30)$ ) parameters<sup>42</sup>

Solvent	$I k_{obs} (\times 10^{-4})/s^{-1}$	III $k_{\rm obs} \; (\times 10^{-4}) / {\rm s}^{-1}$	β	$E_{\rm T}(30)$
Toluene	$1.70 \pm 0.03$	$11.22 \pm 0.16$	0.11	33.9
Acetone	$2.16 \pm 0.06$	$13.10 \pm 0.26$	0.43	42.2
THF	$1.71 \pm 0.04$	$11.36 \pm 0.21$	0.55	37.4
DMF	$1.71 \pm 0.02$	$8.40 \pm 0.13$	0.69	43.8
DMA	$1.58 \pm 0.04$	$8.40 \pm 0.14$	0.76	43.7
HMPA	$1.57\pm0.02$	$8.12\pm0.18$	1.05	40.9

(0.00746 M) of I or III in toluene-d<sub>8</sub> (0.3 mL) was mixed with an equal volume of one the solvents listed above and to that solution a 100-fold excess of acetonitrile was added to ensure pseudo first-order kinetics. The rate of substitution was then determined by monitoring the disappearance of I or III in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (Fig. 4). The hydrogen bond accepting strengths of the solvents were quantified using the  $\beta$  parameter. Because these complexes are charged and the substitution is expected to proceed by a dissociative mechanism, solvent polarity could also affect the observed rates. Consequently, the solvent polarity was quantified using the  $E_{\rm T}(30)$  parameter.<sup>42</sup> The data and results are summarized in Table 1.



**Fig. 4** Sample kinetic trace of the concentration of **I** as a function of time in a toluene–DMF (50: 50) solvent mixture.

As can be seen in Table 1, the rate of N<sub>2</sub> substitution with acetonitrile occurs ~6 times faster than H<sub>2</sub> substitution. The solvent has little effect on the rates of substitution. Upon changing from a non-polar solvent like toluene to a polar solvent like HMPA, the rate constants change by less than a factor of 2 for both I and III. Furthermore, the rate constants for both I and III do not trend with hydrogen bond accepting strength ( $\beta$ ) or with solvent polarity ( $E_{\rm T}(30)$ ). This result suggests that either hydrogen bonding to the coordinated dihydrogen in I is very weak and does not affect the lability of the H<sub>2</sub> molecule or that hydrogen bonding to coordinated H<sub>2</sub> is not occurring in this system. Unfortunately, two of the three tests previously used to determine the hydrogen bonding ability of  $H_2$  in the trans-[Ru(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> complex could not be used for I because the pyridine-N-oxide probe molecule used in the prior study of the trans-[Ru(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> complex readily displaced the H<sub>2</sub> molecule in I.43 The third test for hydrogen bonding, titrating I with a hydrogen bond accepting solvent and monitoring the chemical shift of the  $H_2$  resonance, yielded no shift in the  $H_2$  resonance attributable to hydrogen bonding. This result, combined with the kinetic data in Table 1, suggests that the  $H_2$  molecule in I is either unable to donate a hydrogen bond, in contrast to the Ru analog, or that if DHHB is occurring then it is too weak to have any effect on the substitution reactivity.

# Anion effects in the deprotonation of *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup>

The deprotonation of the *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup> complex is a key step in the Leigh cycle for producing ammonia (Scheme 1). In order to determine if there was an anion effect on the deprotonation reaction, the *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H]<sup>+</sup> complex was synthesized with various anions. The complexes with various counterions were synthesized analogously to I and III using the appropriate chloride abstractor and anion source (Scheme 3). Spectroscopic characterization by NMR (<sup>31</sup>P and <sup>1</sup>H) showed the resulting metal complexes to be identical to the metal complexes in molecules I and III.



X= BAr<sub>F</sub><sup>-</sup>, OTf<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>

Scheme 3 Synthetic scheme for trans-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][X] complexes.

Deprotonation of the *trans*-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][X] complexes was then performed using 2 equivalents of 'BuOK, and the completion of the reaction was determined by a shift in the <sup>31</sup>P{<sup>1</sup>H} resonance (~3 ppm downfield), the loss of hydride coupling in the <sup>31</sup>P spectrum, and the disappearance of the hydride peak in the <sup>1</sup>H NMR spectrum (Table 2). All of the complexes, with the exception of the BAr<sub>F</sub><sup>-</sup> complex (BAr<sub>F</sub><sup>-</sup> = tetrakis(3,5bis(trifluoromethyl)phenyl)borate), were shown to undergo deprotonation to yield Fe(DMeOPrPE)<sub>2</sub>N<sub>2</sub> within 16 h (Table 2).

Closer inspection of the <sup>1</sup>H NMR spectra (Table 2) reveals that the hydride resonance shifts downfield as the size of the anion decreases, with the largest anion (BAr<sub>F</sub><sup>-</sup>) being the only complex that was not deprotonated. This could be explained by an ion-pairing phenomenon in which the anion is closely associated with the hydride ligand and assists in the deprotonation reaction.<sup>45-47</sup> It is proposed that the interaction of the anion with the hydride ligand decreases the electron density of the hydride and helps facilitate the deprotonation by 'BuOK. As the anions become larger, the approach to the hydride ligand becomes more hindered due to steric interactions with the phosphine ligands, and the ion-pairing interaction is diminished. Thus, the BAr<sub>F</sub><sup>-</sup>

Table 2 NMR data of trans-[Fe(DMeOPrPE)<sub>2</sub>(N<sub>2</sub>)H][X] complexes

Anion	Initial <sup>31</sup> P $\delta$ (ppm)	<sup>31</sup> P $\delta$ w/base (ppm)	Hydride $\delta$ (ppm)
BF <sub>4</sub> -	76.9	79.5	-18.35
$PF_6^-$	75.8	79.8	-18.4
OTf⁻	76.0	79.3	-18.4
$BPh_4^-$	75.7	79.6	-18.6
$BAr_{F}$	75.5	75.5	-18.8

anion is too large to approach the hydride ligand, and the hydride ligand is not activated toward deprotonation. This hypothesis is merely speculative and further studies would be needed to confirm this hypothesis. However, this data does show that ion-pairing interactions can greatly affect the reactivity of metal hydrides, and thus the choice of anion needs to be considered when designing cationic metal hydride systems.

#### Conclusion

The trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> and trans-[Fe(DMeOPrPE)<sub>2</sub>- $(N_2)H^{\dagger}$  complexes were synthesized and characterized both in solution and in the solid-state. Both molecules are important species in a Leigh-type dinitrogen reduction cycle and their substitution reactivity was studied to gain insights into how to improve the yields of ammonia. The coordinated  $H_2$  and  $N_2$ molecules in these complexes are weakly bonded and can be displaced by a wide variety of small molecules. The substitution rates with acetonitrile were monitored to determine the relative substitution rates of H<sub>2</sub> versus N<sub>2</sub>. It was determined that the rate of N<sub>2</sub> substitution occurred ~6 times quicker than H<sub>2</sub> substitution, but neither complex showed any rate dependence on the solvent. The inability of solvent to impact the substitution of the H<sub>2</sub> complex was of particular interest because our recent work showed that coordinated  $H_2$  can participate in hydrogen bonding in the analogous Ru complex.<sup>38</sup> However, <sup>1</sup>H NMR experiments suggest that the H<sub>2</sub> ligand is not involved in hydrogen bonding in the trans-[Fe(DMeOPrPE)<sub>2</sub>(H<sub>2</sub>)H]<sup>+</sup> complex. Consequently, this is one reason why the solvent has no influence on the substitution rate in the Fe complex. In a final set of experiments, the effect of the anion on the deprotonation of III to yield Fe(DMeOPrPE)<sub>2</sub>N<sub>2</sub> was explored. The results suggest that an ion-pairing interaction of the anion with the hydride ligand removes electron density from the hydride ligand and thereby facilitates the deprotonation reaction.

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