Electronic Supplementary Material (ESI) for Dalton Transactions.

Teaching old compounds new tricks: efficient N_2 fixation by simple $Fe(N_2)(diphosphine)_2$ complexes

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Electronic Supplementary Information

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1. Experimental details

General considerations

All chemical manipulations were performed under a N_2 or Ar atmosphere either using standard Schlenk-line techniques or a MBraun Labmaster DP glovebox, unless stated otherwise. Solvents were purchased from VWR: pentane and hexane were dried using an Innovative Technology Pure Solv™ SPS-400; THF and Et_2O were distilled from dark green Na/fluorenone indicator. Solvents were degassed by thorough sparging with N_2 or Ar gas and stored in gas-tight ampoules; pentane, hexane and Et_2O were stored over a K mirror. Deuterated solvents were freeze-pump-thaw degassed, dried, and stored in gas-tight ampoules over 4 Å molecular sieves: THF-d_8 (Sigma-Aldrich, 99.5 atom % D); DMSO-d_6 (VWR, 99.5 atom % D). $^{15}N_2$ (Cambridge Isotope Laboratories, 98% ^{15}N) was transferred from a breakseal flask using a Toepler pump. $FeCp_2$ was purchased from Sigma-Aldrich and purified by sublimation and recrystalisation from cold pentane. *Para*-dimethylaminobenzaldehyde (pdmab) was purchased from Sigma-Aldrich and purified by recrystalisation from cold EtOH. NH_4Cl and $N_2H_4{\cdot}2HCl$ were purchased from Sigma-Aldrich. KC_8,[1] $[^nBu_4N][BArF_{24}]$,[2] *trans*-$Fe(Cl)_2(dmpe)_2$,[3] [*trans*-$Fe(H)(N_2)(dmpe)_2$][BPh_4],[3] *trans*-$Fe(Cl)_2(depe)_2$,[3] [*trans*-$Fe(H)(N_2)(depe)_2$][BPh_4],[3] 2,6,-

dimethylpyridinium (lutidinium) triflate [(LutH)OTf][4] and $H(OEt_2)_2(BArF_{24})$ [$BArF_{24}$ = B(3,5-$(CF_3)_2C_6H_3)_4$][5] were prepared according to literature procedures.

NMR spectra were recorded using Bruker AV-400 (400.4 MHz) spectrometers. Chemical shifts, δ, are reported in parts per million (ppm). ^1H chemical shifts are given relative to Me_4Si and referenced internally to the residual proton shift of the deuterated solvent employed. ^{31}P and ^{15}N chemical shifts were referenced ($\delta = 0$) externally to 85% H_3PO_4 (aq) and neat CH_3NO_2, respectively. ^1H and ^{31}P NMR spectra of solutions prepared in non-deuterated solvents incorporate an internal reference capillary containing a solution of ca. 0.1 M PPh_3 in C_6D_6 and are referenced to residual C_6D_5H and PPh_3 ($\delta = -5.3$) resonances, respectively. Air or moisture sensitive samples were prepared inside the glovebox using NMR tubes fitted with J. Young valves.

Infrared (IR) spectra were recorded using a Perkin Elmer FT-IR Spectrum GX spectrometer. Samples were measured as KBr pellets, which were prepared by grinding the sample with KBr (Sigma, FT-IR grade), and pressing in an air-tight Specac® die using a Specac® manual hydraulic press. Raman spectra were recorded on a LabRAM Infinity instrument (Horiba Jobin-Yvon Ltd., Middlesex, UK) using a He-Ne (red) 633 nm laser, calibrated by reference to the 520.7 nm band of a silicon wafer. Samples were prepared inside an Ar glovebox and deposited as a fine powder on the wall of a sealable quartz cuvette. $^{14}N_2$ stretches were confirmed through comparison with the shifted $^{15}N_2$ stretch of the corresponding ^{15}N isotopically labelled sample.

Electronic spectra were recorded using a Perkin Elmer Lambda 20 UV-visible spectrophotometer. Samples were prepared inside the glovebox using a quartz cuvette with an optical path length of 1 cm and fitted with a J. Young valve.

Electrochemical experiments were carried out using an AutoLab potentiostat controlled by Nova. Measurements were performed inside an Ar or N_2 glovebox on room temperature Et_2O solutions containing the sample (2 mM) and [$^nBu_4N$][$BArF_{24}$] electrolyte (50 mM). A three-electrode configuration was employed: a Pt working electrode (PWE) (BASi, Indiana, USA); a Pt wire counter electrode (99.99 %; GoodFellow, Cambridge, UK); and an Ag wire pseudo-reference electrode (99.99 %; GoodFellow, Cambridge, UK). The PWE and Ag wire were polished using alumina/H_2O, and all electrodes rinsed with Et_2O and dried in a 100 °C oven prior to each measurement. Measurements were calibrated to the ferrocene/ferrocenium couple in Et_2O at the end of each run, and iR-compensated to within 80 ± 5 % of the solution uncompensated resistance.

Single crystal X-ray diffraction data for **3** was collected with an Oxford Diffraction Xcalibur unit; the crystal was mounted on a glass fibre using perfluoropolyether oil and measured in a stream of N_2 at 173 K. The structure was solved by direct methods using SHELX.[6]

Elemental analyses were performed by Mr. S. Boyer of the London Metropolitan University.

Synthesis and characterisation.

$FeN_2(dmpe)_2$ (1).[7, 8] Solutions of **1** can be obtained by dissolving [{Fe(dmpe)$_2$}$_2$(μ-N_2)] (**3**) under N_2. Attempts to grow a single crystal of **1** suitable for X-ray crystallography have yielded only crystals of **3**.

$^{31}P\{^1H\}$ NMR (162 MHz, hexane) δ: 63.3 (s).

$FeN_2(depe)_2$ (2).[9] *(N.B. this reaction requires a N_2 atmosphere.)* To a stirred suspension of Mg powder (564mg, 23.2 mmol) in 15 mL of THF was added 1,2-dibromoethane (0.2 mL, 2.31 mmol). The mixture was heated to 40 °C for 30 min to activate the Mg, evolving C_2H_4 gas. After allowing the mixture to cool to RT, a solution of $FeCl_2depe_2$ (2.5 g, 4.64 mmol) in 30 mL of THF was slowly added and the mixture subsequently sonicated for 20 min. The reaction is typically complete after 2 days of stirring under N_2 with periodic sonication. The resulting orange solution was filtered before addition of 1,4-dioxane (3.95 mL, 46.3 mmol), precipitating a fine white solid. After stirring for 12h, the mixture was filtered through a pad of Celite® on a sintered glass frit and rinsed through with additional THF (3 x 20 mL). THF was subsequently removed *in vacuo* and the remaining solid extracted with pentane (3 x 40 mL). Concentration of the pentane solution and slow cooling to –78 °C yielded orange crystals which were collected by filtration, washed with cold pentane, and then dried in vacuo (2.1 g, 91%).

$^{31}P\{^1H\}$ NMR (162 MHz, hexane) δ: 84.4 (s).

IR (KBr, cm^{-1}): 1956 ($^{14}N_2$), 1889 ($^{15}N_2$).

CV (vs $Cp_2Fe^{+/0}$, Et_2O): –2.03 V (Fe^I/Fe^0).

$Fe^{15}N_2(depe)_2$ (2-$^{15}N_2$). In a Rotaflo® ampoule under an Ar atmosphere, Mg powder (113 mg, 4.65 mmol) was activated with 1,2-dibromoethane in THF as above. THF was then removed by decanting and the mixture submerged in a liquid N_2/pentane bath (–131 °C). A solution of $FeCl_2depe_2$ (500 mg, 0.927 mmol) in 10 mL of THF was added under Ar and the mixture degassed and left under static vacuum. With the mixture still frozen, $^{15}N_2$ (2 eq.) was delivered into the ampoule *via* a Toepler pump. After thawing, the mixture was sonicated for 20 min and subsequently stirred for 2 days with periodic sonication. The reaction was worked up as above, under an Ar atmosphere (350 mg, 76%).

1 and 2 generated *in-situ* by the method of Leigh *et al*.[7, 10] Following the method of Leigh *et al.*, [*trans*-Fe(H)(N_2)(PP)$_2$][BPh_4] (PP = dmpe, depe) and KO^{t}Bu (2 eq.) were combined in THF under a N_2 atmosphere, stirred for 3 h (PP = dmpe) or 24 h (PP = depe), and then filtered through Celite®.

[{Fe(dmpe)$_2$}$_2$(μ-N_2)] (3). $FeCl_2dmpe_2$ (4 g, 9.37 mmol) and KC_8 (5.065 g, 37.5 mmol) were transferred into a Rotaflo® ampoule and sealed. With the ampoule submerged in a liquid N_2 bath, 40 mL of hexane was slowly added under a 1 bar N_2 pressure and the ampoule resealed. After removal of the liquid N_2 bath and allowing the ampoule to thaw behind a blast shield, a N_2 pressure of ca. 4 bar was obtained. The mixture was subsequently sonicated for 20 min and left to stir for 3 days with periodic sonication. After carefully releasing the pressure, the mixture was filtered through a pad of Celite® on a sintered glass frit and the remaining solids extracted with additional hexane (4 x 40 mL).

The filtrate and extracts were combined and the hexane removed *in vacuo* to yield a red solid consisting of mainly **1** with some **3**. Suspending this solid in 1-2 mL of hexane under an Ar atmosphere with minimal stirring for 5 days results in almost complete conversion to **3**. Minor impurities consisting of **1**, [$\{Fe(dmpe)_2\}_2$(μ-dmpe)], and *cis*-$Fe(H)_2(dmpe)_2$ can be removed by recrystalisation from hexane under Ar to yield red crystals of **3** in >98% purity by ^{31}P NMR (3.21 g, 93%).

Anal. Calcd. for $C_{24}H_{64}N_2Fe_2P_8$: C, 38.94; H, 8.71; N, 3.78. Found: C, 38.93; H, 8.85; N, 3.89.

$^{31}P\{^1H\}$ NMR (162 MHz, hexane) δ: 66.0 (s).

$^{15}N\{^1H\}$ NMR (40.55 MHz, hexane) δ: –55.05 (s).

^1H NMR (40.55 MHz, THF-d_8, 253 K) δ: 1.44–1.30 (overlapped, 40H, 'CH_2CH_2' and Me); 1.20–1.14 (br s, 24H, Me'). *[N.B. the proton resonances of the dmpe ligands could not be resolved in other common solvents; assignment of these resonances was confirmed by ^1H–^{31}P HSQC NMR.]*

Raman (solid, cm^{-1}): 1933 ($^{14}N_2$), 1870 ($^{15}N_2$).

UV-vis (pentane, nm {M cm^{-1}}: 275 {29,974}; 365 {42,312}.

CV (vs $Cp_2Fe^{+/0}$, Et_2O): –2.23 V (Fe^I/Fe^0).

[$\{Fe(dmpe)_2\}_2(\mu$-$^{15}N_2)$] (3-$^{15}N_2$**).** $FeCl_2dmpe_2$ (400 mg, 0.937 mmol) and KC_8 (633 mg, 4.68 mmol) were transferred into a Rotaflo® ampoule and sealed. With the ampoule submerged in a liquid N_2/pentane (–131 °C) bath, 10 mL of hexane was added under an Ar atmosphere and the mixture degassed and left under static vacuum. With the mixture still frozen, $^{15}N_2$ (1.5 eq.) was delivered into the ampoule *via* a Toepler pump. After thawing, the mixture was sonicated for 20 min and subsequently stirred for 5 days with periodic sonication. The reaction was worked up as above, under an Ar atmosphere (240 mg, 69%).

Acidification experiments

General procedure. Inside a glovebox under either an Ar (for compound **3**) or N_2 (for all other compounds) atmosphere, the chosen compound was carefully weighed (0.016 mmol Fe), dissolved in a minimum of solvent, and then filtered through a Celite® frit into bulb A of the distillation apparatus (Figure S1). Additional solvent was used to rinse through any remaining residue on the Celite® frit, up to a total volume of 0.5 mL. The apparatus was then sealed under an Ar or N_2 atmosphere before being transferred to a dual vacuum/gas (Ar or N_2) manifold. With the solution stirring at the desired temperature, precooled acid was added either *via* a syringe (HCl, 1 M in Et_2O; TfOH, neat; 10 eq. per Fe) or cannula (TfOH, 0.32 M in pentane or Et_2O; 10 eq. per Fe). The mixture was stirred at the desired temperature for 30 min, then allowed to warm to room temperature for a further 30 min. During this time, additional HCl (1 M in Et_2O; 20 eq. per Fe) was added to the second empty flask (bulb B). The volatiles in bulb A were subsequently removed *in vacuo*, and both bulbs were submerged in liquid N_2 baths. To the frozen acidified mixture in bulb A, aqueous KOH (40%, 1.5 mL) was added *via* a syringe (*caution: this should be performed under a N_2 flow rather than Ar, which freezes at the temperature of liquid N_2*). With the contents of both bulbs frozen, the entire apparatus was evacuated to ca. 10^{-2} mbar and sealed under a static vacuum by closing all three J. Young valves. Bulb A was removed from the liquid N_2 bath and its contents allowed to thaw, then left to stir at room temperature for 30 min. With bulb B still submerged in liquid N_2, the J. Young valves to both bulbs A and B were carefully opened to allow volatiles from bulb A to distil into bulb B until approximately 50% of the initial volume remained. Bulb B was then sealed, thawed to room temperature, and stirred for a further 5 min. All volatiles in bulb B were subsequently removed *in vacuo* and the remaining residue was dissolved in aqueous HCl (1 M, 0.5 mL) from which a 50 μL aliquot was removed for hydrazine analysis (*vide infra*). The remaining 0.9 fraction was once more dried *in vacuo* and subsequently redissolved in DMSO-d_6 (0.45 mL) for ammonia analysis (*vide infra*).

In control experiments it was found that N_2H_4 (b.p. 114 °C; $N_2H_4{\cdot}H_2O$, b.p. 120 °C) does not entirely transfer across during the base distillation, which must be carried out at room temperature due to the known decomposition of N_2H_4 to NH_3, N_2, and H_2.[11] In order to quantify any N_2H_4 in the remaining residue, aq. HCl (12 M, 1.26 mL; 1 M, 1 mL) was added at 0 °C (*caution: exothermic*), and the mixture subsequently filtered through a Celite® frit, and rinsed with additional aq. HCl (1 M) up to a total volume of 5 mL. In a 5 mL volumetric flask, this solution was rinsed with BuOH (3 X 1 mL) to extract residual Fe-species/contaminants, yielding a clear solution, which was remade up to 5 mL with further aq. HCl (1 M). A fraction of this 5 mL solution was subsequently analysed for hydrazine (*vide infra*).

Quantification of NH_3

After treatment with base (*vide supra*), NH_3 was distilled from the reaction mixture onto HCl, thus chemically trapping it as NH_4Cl, which could then be quantified by ^1H NMR spectroscopy, as reported by others.[12] NH_4^+ ($\delta \approx 7.3$, 1:1:1 triplet, $^1J_{NH} = 51$ Hz, DMSO-d_6; Figure S2) was integrated relative to the vinylic protons of 2,5-dimethylfuran,[13] contained within a DMSO-d_6 capillary insert ($\delta = 5.83$, s, 2H, $T_1 \approx 20.5$ s), which was calibrated using a standard 0.032 M solution of NH_4Cl in DMSO-d_6. To establish whether the N in NH_4^+ produced in the acidification experiments is sourced from the N_2 ligand in the Fe complex, a THF solution of $^{15}N_2$ isotopically labelled **2** (**2**-$^{15}N_2$) was acidified with TfOH inside an Ar glovebox (in the absence of N_2); subsequent analysis by ^1H NMR spectroscopy (as above), resolved a characteristic 1:1 double corresponding to $^{15}NH_4^+$ ($\delta \approx 7.4$, d, $^1J_{NH} = 71$ Hz, DMSO-d_6; Figure S2).

Quantification of N_2H_4

Both the volatile (distilled) and the BuOH washed, non-volatile fractions were analysed separately for N_2H_4 by a standard spectrophotometric method, which employs an acidic pdmab indicator solution to generate a yellow azine dye with a characteristic electronic absorption feature at 458 nm.[14] Accordingly, aliquots taken from these two fractions were diluted to a suitable concentration and the N_2H_4 was quantified by comparison to the calibration curve in Figure S1. Importantly, it was determined through control experiments (Table S1, entries 20-30) that the presence of NH_3 and/or dmpe and depe does not interfere with this method. Likewise, the BuOH washed, non-volatile fraction does not absorb within the range of the UV-vis spectrum measured and thus interference from any residual Fe-species/contaminants may also be ruled out (Figure S3).

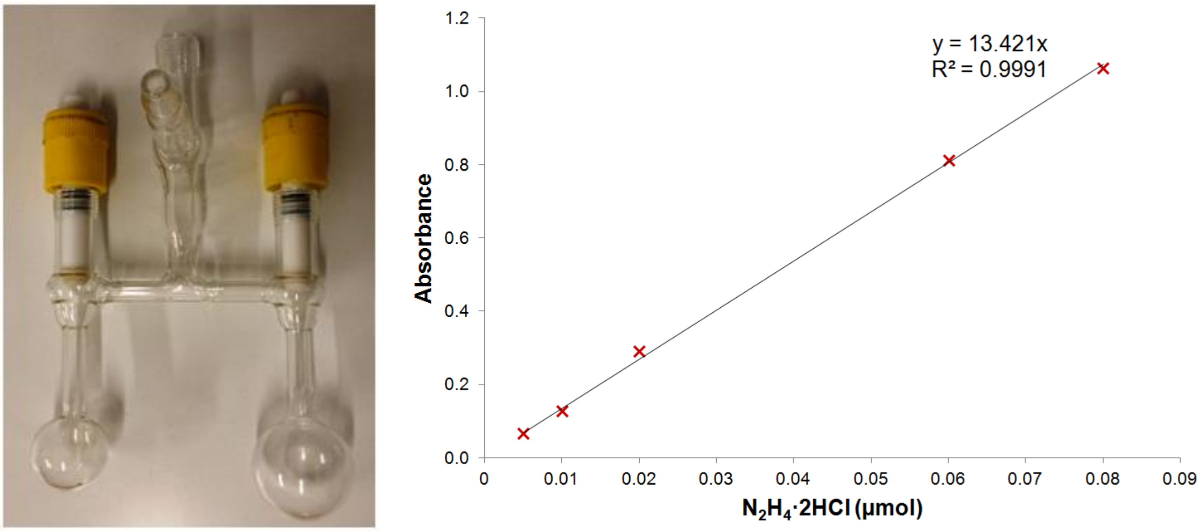

Figure S1. Left: distillation apparatus for the acidification reactions; compounds were acidified in the smaller bulb (A), and base-distilled onto additional acid within the larger bulb (B). Right: UV-vis calibration curve (λ_{max} = 458 nm) for the pdmab hydrazine test.

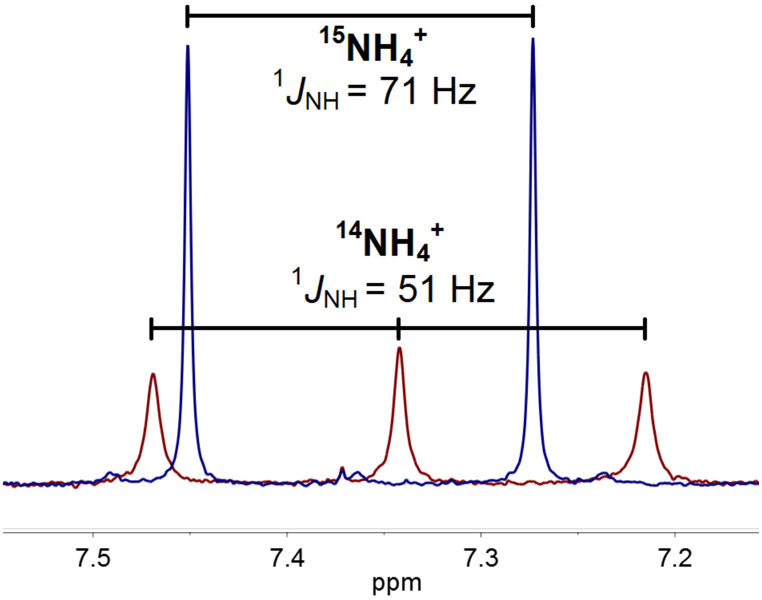

Figure S2. ^{1}H NMR spectra (DMSO-d_6) of $^{14}NH_4^+$ and $^{15}NH_4^+$ generated from the addition of TfOH, inside an Ar glovebox, to THF solutions of **2** and **2**-$^{15}N_2$, respectively, and subsequent base distillation onto HCl.

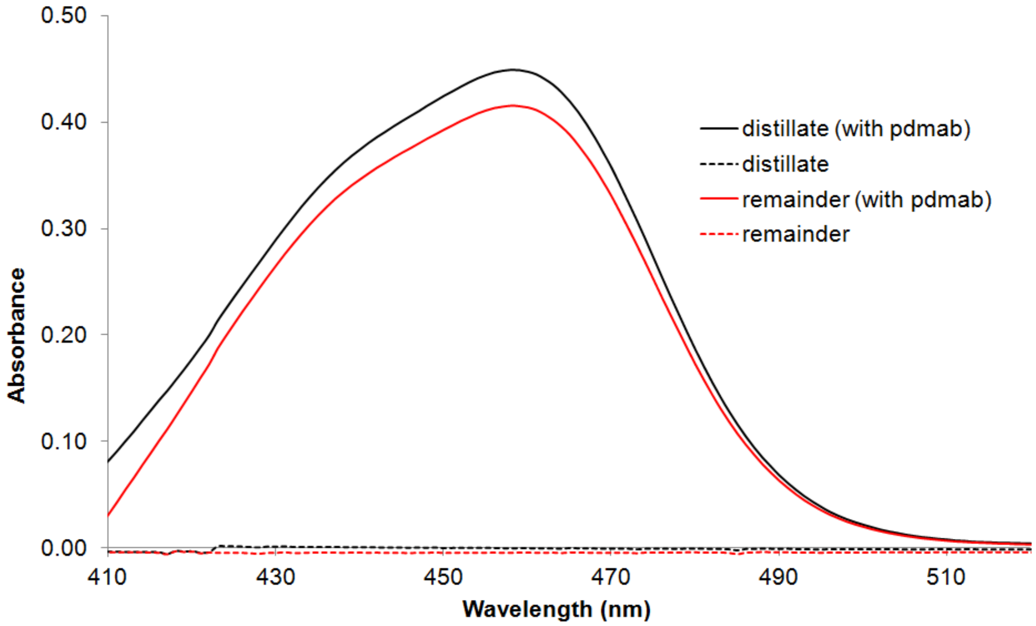

Figure S3. Exemplar UV-vis spectra used for the spectrophotometric determination of N_2H_4 produced in an acidification reaction (**2**, TfOH, Et_2O, rt). Aliquots taken from the distillate and the BuOH washed, non-volatile remainder were analysed both with and without pdmab indicator.

Table S1. Reduced N_2 yields for the acidification of **1-3**.

Entry	Compound	Acid	Solvent	T (°C)	No. of runs	N_2H_4 (% per Fe)[a]	NH_3 (% per Fe)[a]	Electrons transferred (per Fe)[b]	Yield (%)[c]
1	**1**	TfOH	THF	rt	2	0, 0	0, 0	0.00	0
2	**1**	TfOH	Et_2O	rt	1	9	0	0.36	18
3	**1**	TfOH	pentane	rt	2	10, 8	0, 0	0.36	18
4	**1**	TfOH	pentane	-78	3	4, 3, 4	0, 0, 0	0.15	8
5	**2**	TfOH	THF	rt	1	4	3	0.22	11
6	**2**	TfOH	Et_2O	rt	2	9, 13	6, 6	0.63	32
7	**2**	TfOH	Et_2O	-78	2	7, 5	11, 10	0.57	28
8	**2**	TfOH	pentane	rt	2	22, 20	8, 8	1.07	54
9	**2**	TfOH	pentane	-78	1	24	5	1.10	55
10	**3**	TfOH	pentane	rt	2	4, 4	2, 1	0.22	11
11	**3**	TfOH	pentane	-78	3	2, 2, 2	0, 0, 0	0.08	4
12	**1**	HCl	THF	20	1	0	0	0.00	0
13	**1**	HCl	THF	-40	1	0	0	0.00	0
14	**1** (Leigh method)	HCl	THF	20	1	0	0	0.00	0
17	**2**	HCl	THF	20	2	0, 0	0, 0	0.00	0
18	**2**	HCl	THF	-78	1	0	0	0.00	0
19	**2** (Leigh method)	HCl	THF	20	1	0	0	0.00	0
15	**3**	HCl	THF	20	3	0, 0, 0	0, 0, 0	0.00	0
16	**3**	HCl	THF	-40	1	0	0	0.00	0
20	$FeCl_2(dmpe)_2$	TfOH	pentane	20	1	0	0	0.00	0
21	$FeCl_2(dmpe)_2$	TfOH	pentane	-78	2	0, 0	0, 0	0.00	0
22	$FeCl_2(dmpe)_2$	HCl	THF	20	1	0	0	0.00	0
23	$FeCl_2(depe)_2$	TfOH	pentane	20	1	0	0	0.00	0
24	$FeCl_2(depe)_2$	HCl	THF	20	1	0	0	0.00	0
25	dmpe	HCl	Et_2O	20	1	0	0	0.00	0
26	depe	HCl	Et_2O	20	1	0	0	0.00	0
27	$FeCl_2(dmpe)_2$, NH_4Cl, $N_2H_4 \cdot 2HCl$	HCl	THF	20	1	102	97	-	-
28	$FeCl_2(depe)_2$, NH_4Cl, $N_2H_4 \cdot 2HCl$	HCl	THF	20	1	103	101	-	-
29	$FeCl_2(dmpe)_2$, NH_4Cl	HCl	THF	20	1	0	92	-	-
30	$FeCl_2(depe)_2$, NH_4Cl	HCl	THF	20	1	0	98	-	-

[a] Yield per Fe; [b] averaged over all runs; [c] yield assuming each Fe supplies a max. of two electrons, averaged over all runs.

2. NMR spectra

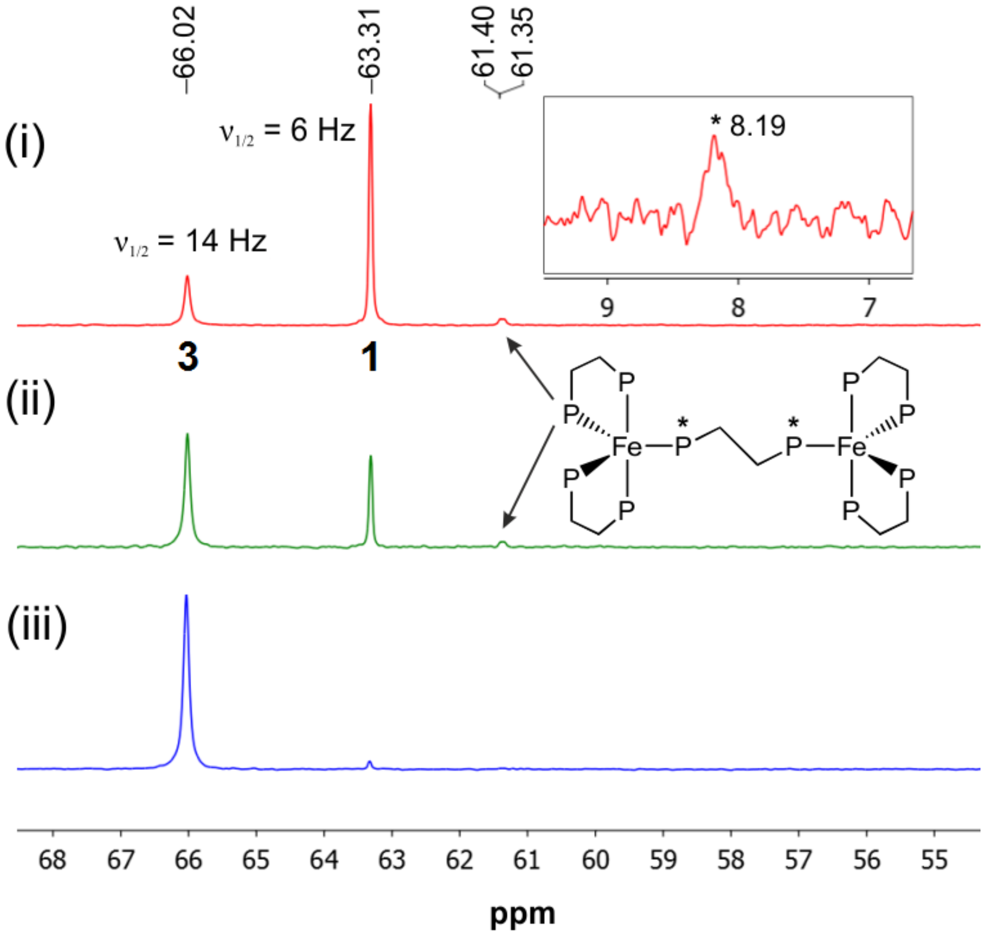

Figure S4. ^{31}P NMR spectra of Fe($^{15}N_2$)(dmpe)$_2$ (**1**-$^{15}N_2$) and [{Fe(dmpe)$_2$}$_2$(μ-$^{15}N_2$)] (**3**-$^{15}N_2$) generated from the reduction of *trans*-Fe(Cl)$_2$(dmpe)$_2$ under $^{15}N_2$ with KC$_8$ (4 eq.) in hexane: (i) reaction mixture after 3 days; (ii) redissolved in hexane after removal of volatiles and drying *in vacuo*; (iii) recrystalised from hexane under argon; P = PMe$_2$.

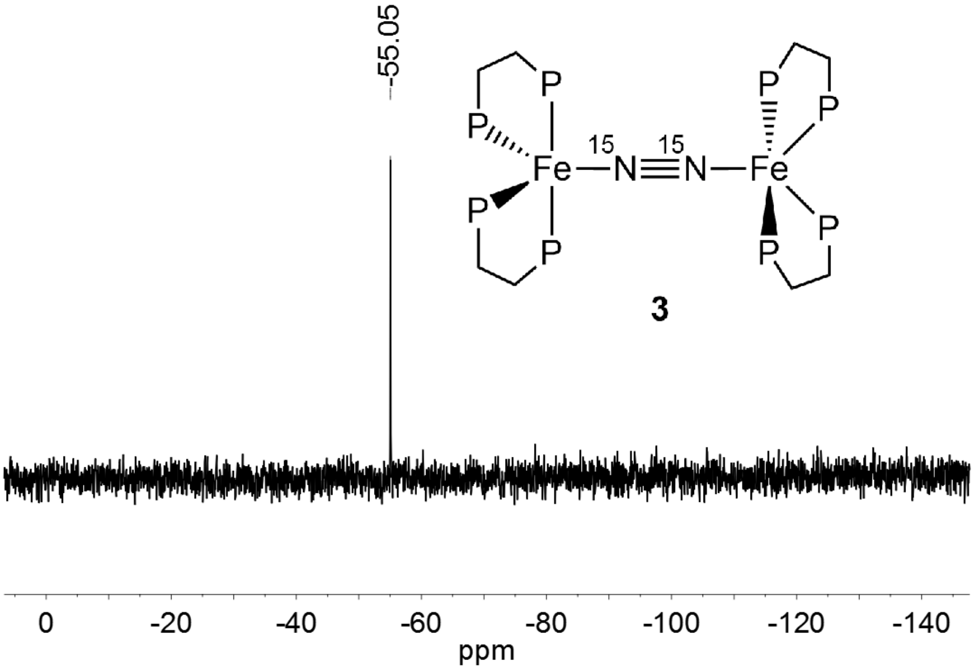

Figure S5. $^{15}N\{^{1}H\}$ NMR spectrum of $[\{Fe(dmpe)_2\}_2(\mu\text{-}^{15}N_2)]$ (**3**-$^{15}N_2$) in hexane under an Ar atmosphere.

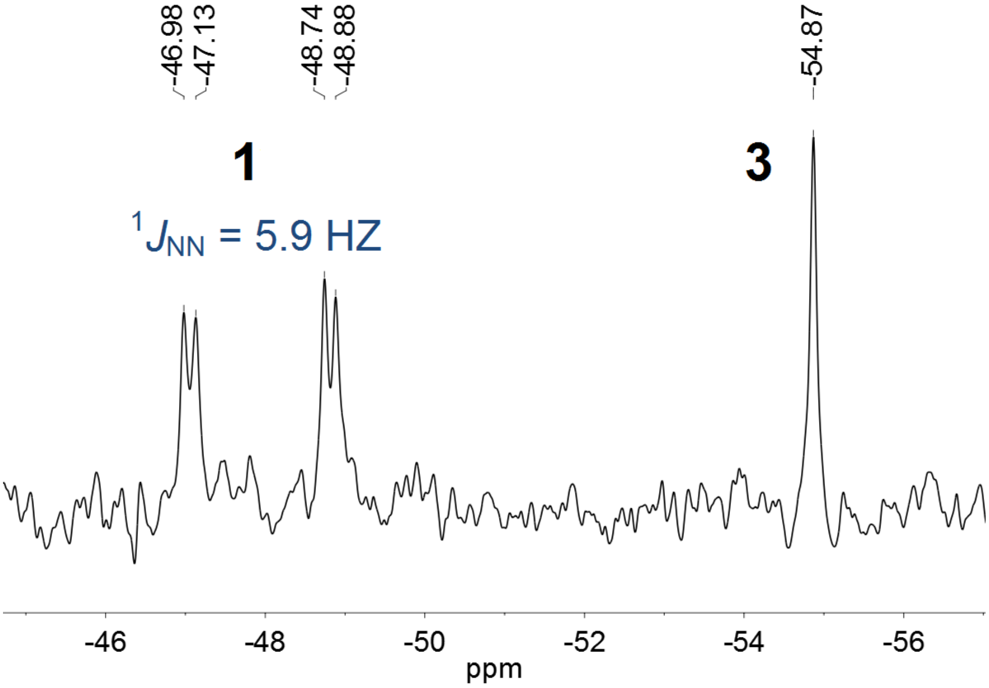

Figure S6. $^{15}N\{^{1}H\}$ NMR spectrum of $Fe(^{15}N_2)(dmpe)_2$ (**1**-$^{15}N_2$) and $[\{Fe(dmpe)_2\}_2(\mu\text{-}^{15}N_2)]$ (**3**-$^{15}N_2$) generated *in situ* from the reduction of *trans*-$Fe(Cl)_2(dmpe)_2$ under $^{15}N_2$ with KC_8 (4 eq.) in hexane.

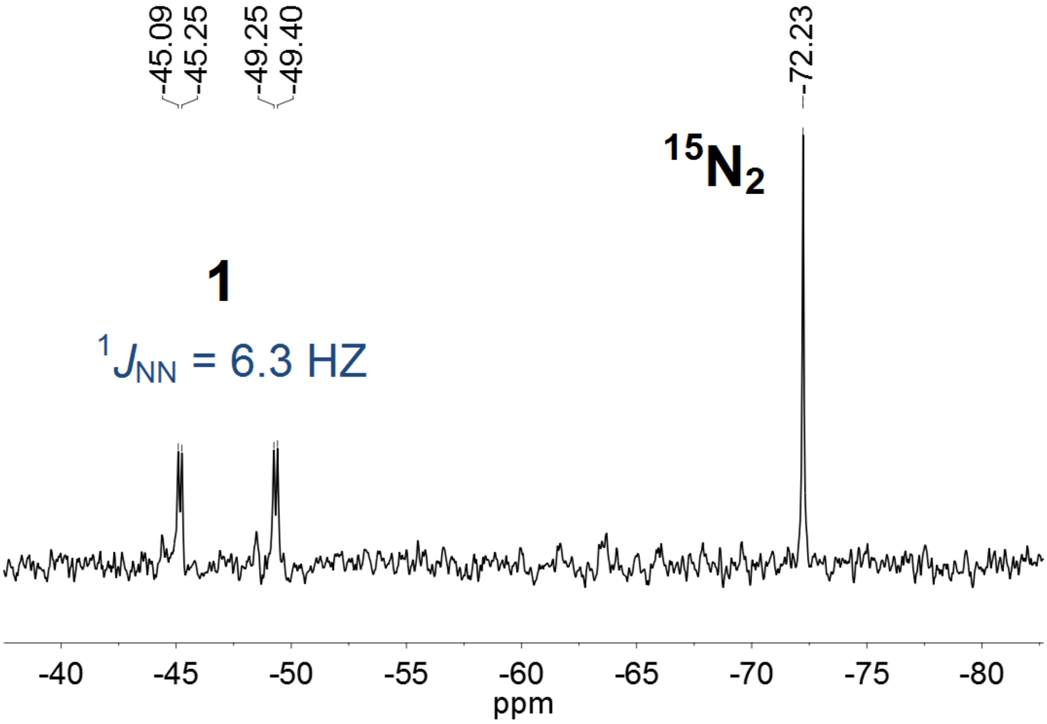

Figure S7. $^{15}N\{^1H\}$ NMR spectrum of Fe($^{15}N_2$)(dmpe)$_2$ (**1**-$^{15}N_2$) generated *in situ* from the deprotonation of *trans*-Fe(H)($^{15}N_2$)(dmpe)$_2$][BPh$_4$] in THF under a $^{15}N_2$ atmosphere.

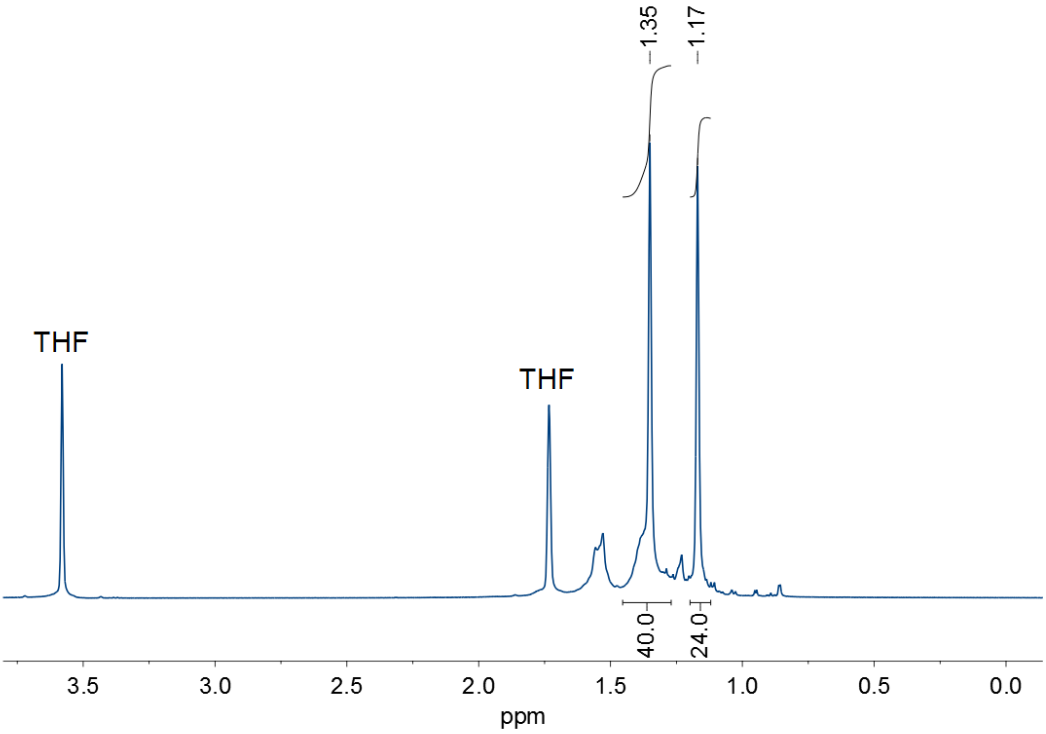

Figure S8. ^1H NMR spectrum of [{Fe(dmpe)$_2$}$_2$(μ-N$_2$)] (**3**) recorded in THF-d$_8$ at 253 K.

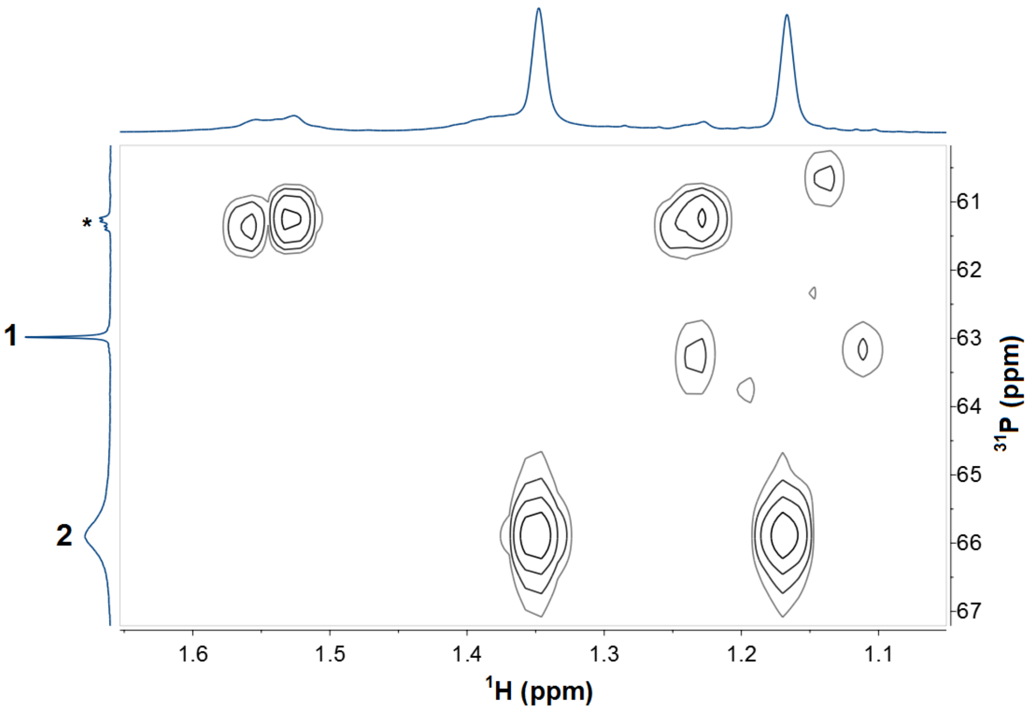

Figure S9. ^{1}H–^{31}P HSQC NMR spectrum of [{Fe(dmpe)$_2$}$_2$(μ-N$_2$)] (**3**) recorded in THF-d$_8$ at 253 K; [{Fe(dmpe)$_2$}$_2$(μ-dmpe)] (**4**) denoted by *****.

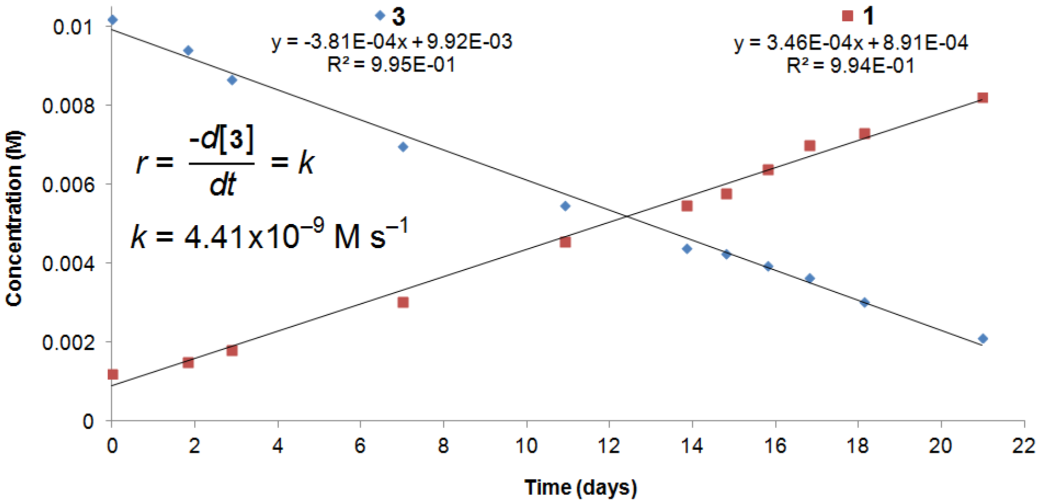

Figure S10. ^{31}P NMR determined concentrations of **3** (◆) and **1** (■) from the *in-situ* decomposition of **3** in pentane (10 mM) under an Ar atmosphere; t½ (**3**) = 13 days.

3. IR spectra

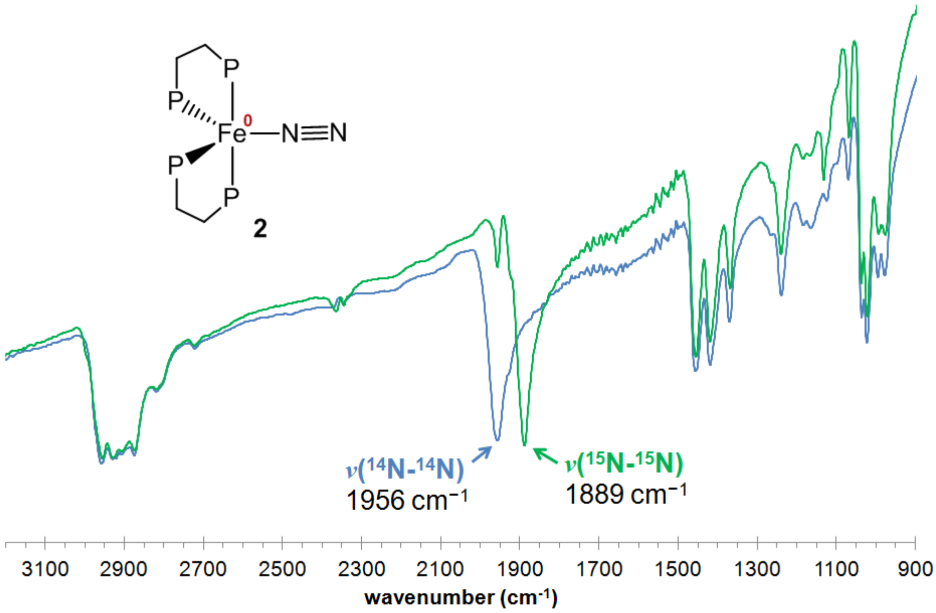

Figure S11. IR spectra of Fe($^{14}N_2$)(depe)$_2$ (**2**) and Fe($^{15}N_2$)(depe)$_2$ (**2**-$^{15}N_2$) recorded as KBr pellets; P = PEt$_2$.

4. Raman spectra

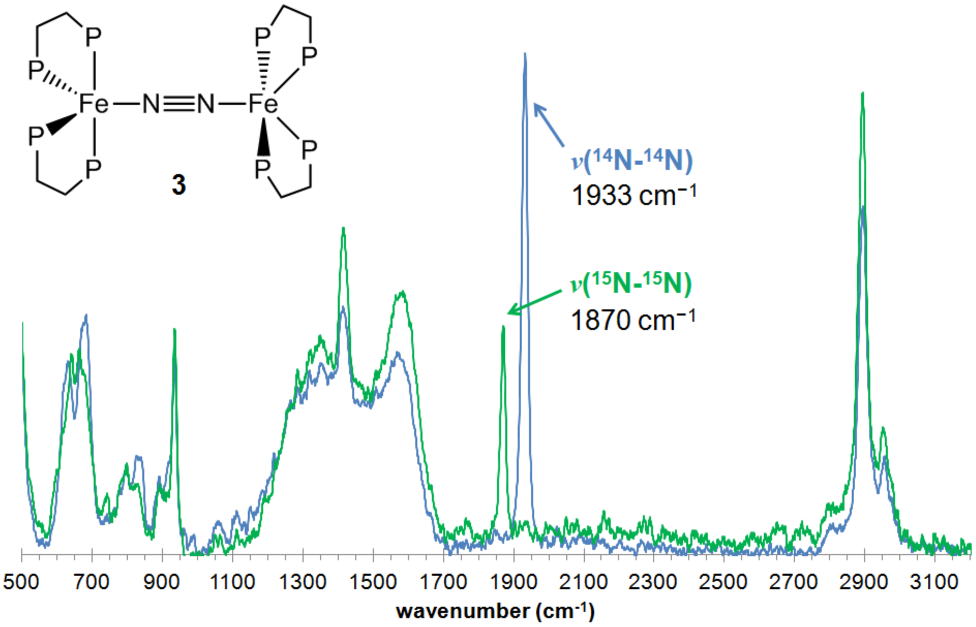

Figure S12. Raman spectra of [{Fe(dmpe)$_2$}$_2$(μ-$^{14}N_2$)] (**3**, blue) and [{Fe(dmpe)$_2$}$_2$(μ-$^{15}N_2$)] (**3**-$^{15}N_2$, green) recorded on powdered samples using a He-Ne (red) 633nm laser; P = PMe$_2$.

5. UV-vis spectra

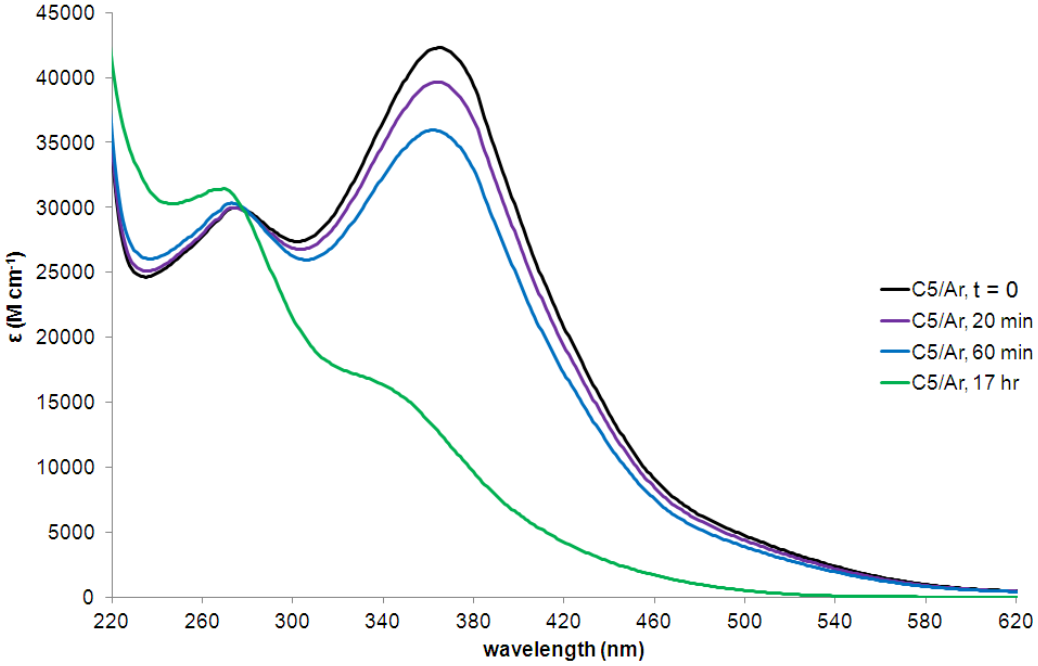

Figure S13. UV-vis spectra of [{Fe(dmpe)$_2$}$_2$(μ-N_2)] (**3**) recorded in pentane under an Ar atmosphere.

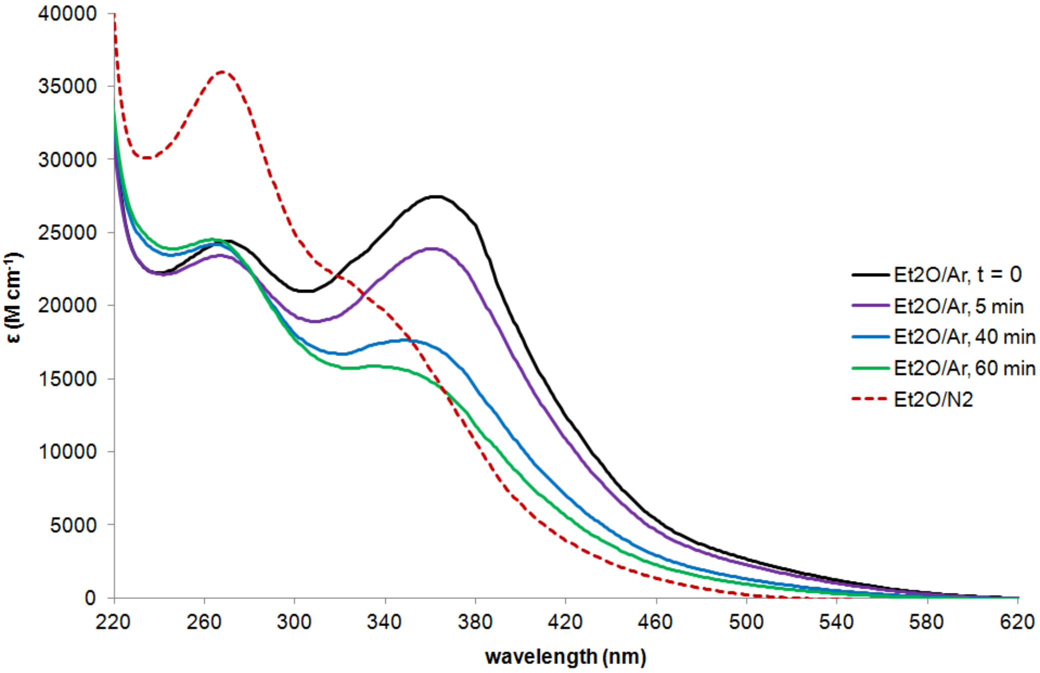

Figure S14. UV-vis spectra of [{Fe(dmpe)$_2$}$_2$(μ-N_2)] (**3**) recorded in Et_2O under either an Ar or N_2 atmosphere.

6. Cyclic voltammograms

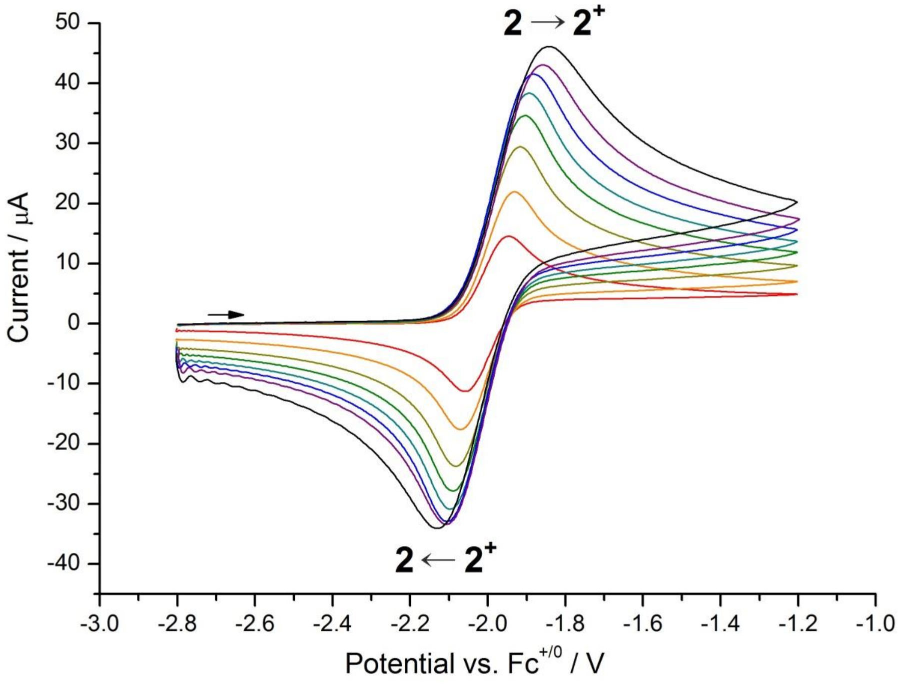

Figure S15. Cyclic voltammetry measurements of $Fe(N_2)(depe)_2$ (**2**); recorded in Et_2O under a N_2 atmosphere; [$^nBu_4N$][$BArF_{24}$] electrolyte; potential plotted relative to the $Cp_2Fe^{+/0}$ couple; arrow indicates direction of scan.

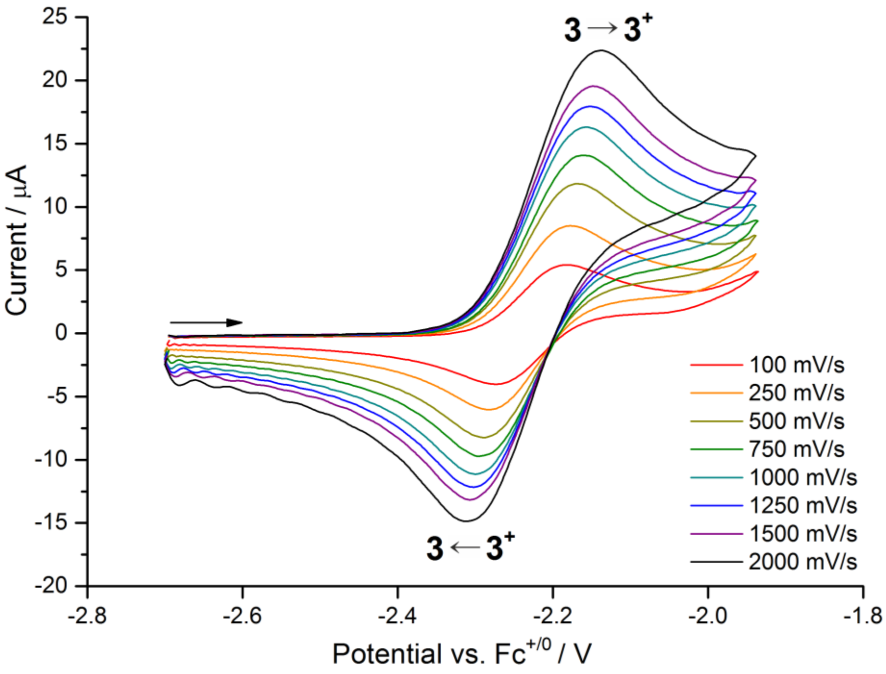

Figure S16. Cyclic voltammetry measurements of [{$Fe(dmpe)_2$}$_2$(µ-N_2)] (**3**); recorded in Et_2O under an Ar atmosphere; [$^nBu_4N$][$BArF_{24}$] electrolyte; potential plotted relative to the $Cp_2Fe^{+/0}$ couple; arrow indicates direction of scan.

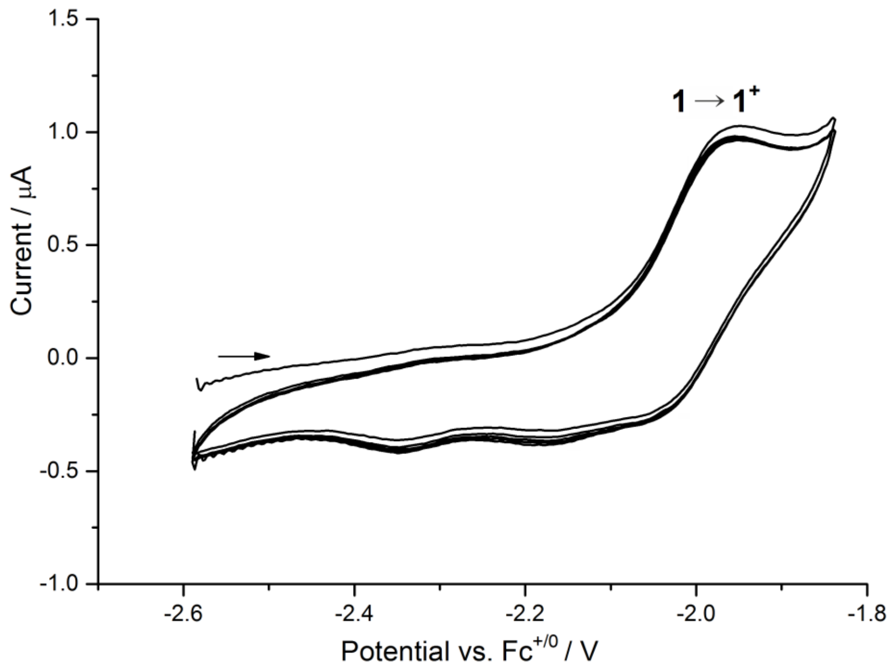

Figure S17. Cyclic voltammetry measurements of $Fe(N_2)(dmpe)_2$ (**1**); recorded in Et_2O under a N_2 atmosphere; 250 mV s^{-1} scan rate; $[^nBu_4N][BArF_{24}]$ electrolyte; potential plotted relative to the $Cp_2Fe^{+/0}$ couple; arrow indicates direction of scan.

7. X-ray diffraction data for 3

The P(1), P(4) dmpe ligand coordinated to Fe(1) was found to be disordered; two orientations of ca. 61 and 39% occupancy were identified. Similarly, the P(21), P(24) and P(31), P(34) dmpe ligands coordinated to Fe(2) were found to be disordered; two orientations of ca. 64 and 36% occupancy were identified. Only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically.

Formula	$C_{24}H_{64}Fe_2N_2P_8$	
Formula weight	740.23	
Temperature	173 K	
Diffractometer, wavelength	OD Xcalibur 3, 0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 9.3450(4) Å	α = 90.674(3)°
	b = 9.6733(3) Å	β = 90.671(4)°
	c = 23.4652(10) Å	γ = 115.639(3)°
Volume, Z	1911.86(14) Å^3, 2	
Density (calculated)	1.286 mg/m^3	
Absorption coefficient	1.110 mm^{-1}	
F(000)	788	
Crystal colour / morphology	Red tabular needles	
Crystal size	0.41 x 0.35 x 0.06 mm^3	
θ range for data collection	2.94 to 29.32°	
Index ranges	-11<=h<=12, -13<=k<=13, -15<=l<=31	
Reflections collected / unique	15856 / 8760 [R(int) = 0.0202]	
Reflections observed [F>4σ(F)]	7245	
Absorption correction	Analytical	
Max. and min. transmission	0.937 and 0.728	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8760 / 452 / 407	
Goodness-of-fit on F^2	1.024	
Final R indices [F>4σ(F)]	R1 = 0.0431, wR2 = 0.0900	
R indices (all data)	R1 = 0.0556, wR2 = 0.0984	
Largest diff. peak, hole	0.774, -0.637 eÅ^{-3}	
Mean and maximum shift/error	0.000 and 0.001	

8. References

1. Weitz, I. S.; Rabinovitz, M., *J. Chem. Soc., Perkin Trans. 1*, **1993**, (1), 117-120.
2. LeSuer, R. J.; Buttolph, C.; Geiger, W. E., *Anal. Chem.*, **2004**, *76* (21), 6395-6401.
3. Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T., *J. Chem. Soc., Dalton Trans.* **1993**, (20), 3041-3049.
4. Arashiba, K.; Miyake, Y.; Nishibayashi, Y., *Nat. Chem.*, 2011, **3**, 120.
5. Brookhart, M.; Grant, B.; Volpe, A. F., *Organometallics* **1992**, *11* (11), 3920.

6. Sheldrick, G., *Acta Crystallogr., Sect. A*, **2008**, *64* (1), 112-122.
7. Leigh, G. J.; Jimenez-Tenorio, M., *J. Am. Chem. Soc.*, **1991**, *113* (15), 5862-5863.
8. Field, L. D.; Li, H. L.; Magill, A. M., *Inorg. Chem.*, **2009**, *48* (1), 5-7.
9. Komiya, S.; Akita, M.; Yoza, A.; Kasuga, N.; Fukuoka, A.; Kai, Y., *J. Chem. Soc., Chem. Commun.*, **1993**, (9), 787-788.
10. Hall, D. A.; Leigh, G. J., *J. Chem. Soc., Dalton Trans.* **1996**, (17), 3539-3541.
11. Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta, J., *J. Am. Chem. Soc.* **1992**, *114* (2), 758-759; Takei, I.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M., *Inorg. Chem.* **2005**, *44* (11), 3768-3770; B. Hitchcock, P.; L. Hughes, D.; J. Maguire, M.; Marjani, K.; L. Richards, R., *J. Chem. Soc., Dalton Trans.* **1997**, (24), 4747-4752; Crossland, J. L.; Zakharov, L. N.; Tyler, D. R., *Inorg. Chem.* **2007**, *46* (25), 10476-10478.
12. Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R., *J. Am. Chem. Soc.* **2005**, *127* (29), 10184-10185; Field, L. D.; Hazari, N.; Li, H. L., *Inorg. Chem.* **2015**, *54* (10), 4768-4776.
13. Gerritz, S. W.; Sefler, A. M., *J. Comb. Chem.*, **2000**, *2* (1), 39-41.
14. Watt, G. W.; Chrisp, J. D., *Anal. Chem.*, **1952**, *24* (12), 2006-2008.