Fe-catalyzed conversion of N_2 to $N(SiMe_3)_3$ via an Fe-hydrazido resting state

Supplementary Information

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1. Experimental details

All chemical manipulations were performed under an N_2 or Ar atmosphere using standard Schlenk-line techniques or a MBraun Labmaster DP glovebox, unless stated otherwise. Solvents were purchased from VWR: pentane was dried using an Innovative Technology Pure Solv™ SPS-400; Et_2O and THF were distilled from dark green Na/fluorenone indicator. Solvents were degassed by thorough sparging with N_2/Ar gas and stored in gas-tight ampoules; pentane and Et_2O were stored over a K mirror; THF was stored over 4 Å molecular sieves. Deuterated solvents were freeze-pump-thaw degassed, dried, and stored in gas-tight ampoules over 4 Å molecular sieves: 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. All glassware was dried in an oven at 160 °C overnight before use.

NMR spectroscopy

NMR spectra were recorded using Bruker AV-400 (400.4 MHz) spectrometers. Chemical shifts, δ, are reported in parts per million (ppm). ^{1}H and ^{29}Si chemical shifts are given relative to Me_4Si and referenced internally to the residual proton shift of the deuterated solvent employed. ^{19}F, ^{31}P and ^{15}N chemical shifts were referenced ($\delta = 0$) externally to $CFCl_3$, 85% H_3PO_4 (aq) and neat CH_3NO_2, respectively. ^{1}H and ^{31}P NMR spectra of solutions prepared in non-deuterated solvents incorporate an internal reference capillary containing a solution of 0.1 M PPh_3 in C_6D_6 and are referenced to residual C_6D_5H ($\delta = 7.15$ ppm) and PPh_3 ($\delta = -5.4$ ppm) resonances, respectively. Air or moisture sensitive samples were prepared inside a glovebox using NMR tubes fitted with J. Young valves.

Electrochemistry

Electrochemical experiments were carried out using an AutoLab potentiostat controlled by Nova. Measurements were performed inside an Ar glovebox on room temperature Et_2O solutions containing the sample (2 mM) and [$^{n}Bu_4N$][BAr^{F}_4] 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 a Ag wire pseudo-reference electrode (99.99 %; GoodFellow, Cambridge, UK). All electrodes were polished using alumina/H_2O, followed by rinsing with acetone and then Et_2O, and drying in a 100 °C oven prior to each measurement. Measurements were calibrated to the ferrocenium/ferrocene couple at the end of each run, and iR compensated to within 80 ± 5 % of the solution uncompensated resistance.

UV-Visible spectroscopy

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.

X-ray crystallography

Single crystal X-ray diffraction data was collected with an Oxford Diffraction Xcalibur unit; crystals were mounted on a nylon MicroLoop™ using perfluoropolyether oil and measured in a stream of N_2 at 173 K. All structures were solved using the Superflip charge flipping package.[1] All data were subsequently refined with the ShelXL refinement package.[2]

Mass spectrometry

High resolution mass spectra (HRMS) were recorded using a Micromass Autospec Premier (ES+ or EI mode) by Dr Lisa Haigh at Imperial College London.

Gas chromatography

Gas chromatographic measurements were conducted using an Agilent 6890 G1530A GC System and the data processed by GC ChemStation Rev. B. 04. 02. Catalytic N_2 silylation reactions were conducted as detailed below, in either the presence or absence of $\mathbf{1}^{\mathbf{Me/Et}}$. A 1.2 mL aliquot of the relevant reaction mixture was taken after 72 hours, mixed with heptane (22 μL) (as an internal standard) and analysed.

Synthetic details

All chemicals were purchased from Sigma-Aldrich unless stated otherwise. Me_3SiCl and Me_3SiOTf were purified by distillation and stored on 4 Å molecular sieves.

The following chemicals were prepared according to modified literature procedures: KC_8,[3] $KBAr^F_4$,[4] $[^nBu_4N][BAr^F_4]$,[5] $Hg(SiMe_3)_2$,[6] $Fe(depe)_2(^{14/15}N_2)$,[7] $Fe(dmpe)_2(^{14/15}N_2)$,[8] $[Fe(depe)_2(^{14/15}N_2SiMe_3)][BAr^F_4]$, and $[Fe(dmpe)_2(^{14/15}N_2SiMe_3)][BAr^F_4]$.[9]

$Fe(dmpe)_2(NN(SiMe_3)_2)$ ($\mathbf{3}^{\mathbf{Me}}$): To a solution of $Fe(dmpe)_2(N_2)$ (250 mg, 0.65 mmol) in Et_2O (20 mL) under an N_2 atmosphere was added Me_3SiCl (0.83 mL, 6.51 mmol) and KC_8 (879 mg, 6.51 mmol). The resulting suspension was stirred at RT for 30 min before being filtered. Volatiles were then removed *in vacuo*, leaving a dark red oil (220 mg, 83%). The ^{15}N labelled analogue was similarly prepared from $Fe(dmpe)_2(^{15}N_2)$ under a $^{15}N_2$ atmosphere.

^1H NMR (400.4 MHz, C_6D_6) δ: 1.72 (m), 1.67(m), 1.31 (m), 1.21 (m) 1.18 (m), 1.12 (m), 0.30 (s, N-SiCH_3).
$^{13}C\{^1H\}$ NMR (100.0 MHz, C_6D_6) δ: 33.5 (s), 25.0 (s), 23.5 (s), 22.8 (s), 22.4 (s), 14.0 (s), 0.36 (s).

$^{15}N\{^1H\}$ NMR (40.55 MHz, Et_2O) δ: -22 (m, N_α), -248 (m, 16 Hz, N_β).
$^{31}P\{^1H\}$ NMR (162.0 MHz, Et_2O) δ: 77.0 (2 P, d, $^2J_{PP}$ = 8 Hz), 46.8 (1 P, dt, $^2J_{PP}$ = 8 Hz $^3J_{PP}$ = 28 Hz), -48.0 (1 P, d, $^3J_{PP}$ = 28 Hz).
^{29}Si NMR (99.4 MHz, Et_2O, HMBC) δ: -0.1 (s, N-*Si*CH_3).
HRMS (EI): *m/z* found (calculated) for $C_{18}H_{50}FeN_2P_4Si_2$: 530.1829 (530.1812)
UV-Vis (pentane, nm $\{M^{-1}\ cm^{-1}\}$): 488 {1130}

Fe(depe)$_2$[NN(SiMe$_3$)$_2$] (3^{Et}): To a solution of $Fe(depe)_2(N_2)$ (1.00 g, 2.02 mmol) in Et_2O (20 mL) under an Ar atmosphere was added Me_3SiCl (2.56 mL, 20.2 mmol) and KC_8 (2.73 g, 20.2 mmol). The resulting suspension was stirred at RT for 2 hours before being filtered. Volatiles were then removed *in vacuo*, leaving a dark purple oil (1.20 g, 92%). The ^{15}N labelled analogue was similarly prepared from $Fe(depe)_2(^{15}N_2)$ under a $^{15}N_2$ atmosphere.

^1H NMR (400.4 MHz, C_6D_6) δ: 2.03-1.81 (m, overlapping), 1.74-1.47 (m, overlapping), 1.46-1.35 (m), 1.27-1.03 (m, overlapping), 0.33 (s, N-SiCH_3).
$^{13}C\{^1H\}$ NMR (100.0 MHz, C_6D_6) δ: 26.6 (s), 26.4 (d, overlapping), 26.0 (d, $^1J_{PP}$ = 10 Hz), 21.1 (d, $^1J_{PP}$ = 16 Hz), 19.1 (d, $^1J_{PP}$ = 15 Hz), 9.7 (d, $^1J_{PP}$ = 14 Hz), 9.4 (s), 9.1 (s), 8.9 (s), 0.72 (s).
$^{15}N\{^1H\}$ NMR (40.55 MHz, Et_2O) δ: -33 (dq, $^1J_{NN}$ = 16 Hz, $^2J_{NP}$ = 5 Hz, N_α), -260 (d, $^1J_{NN}$ = 16 Hz, N_β).
$^{31}P\{^1H\}$ NMR (162.0 MHz, Et_2O) δ: 102.1 (2 P, d, $^2J_{PP}$ = 13 Hz), 64.6 (1 P, dt, $^2J_{PP}$ = 13 Hz $^3J_{PP}$ = 22 Hz), -17.6 (1 P, d, $^3J_{PP}$ = 22 Hz).
$^{29}Si\{^1H\}$ NMR (99.4 MHz, Et_2O) δ: -0.5 (s, N-*Si*CH_3).
HRMS (EI): *m/z* found (calculated) for $C_{26}H_{66}FeN_2P_4Si_2$: 642.3077 (642.3065)
UV-Vis (pentane, nm $\{M^{-1}\ cm^{-1}\}$): 510 {1760}

[Fe(dmpe)$_2$(NN(SiMe$_3$)$_2$)·SiMe$_3$][BAr^F$_4$] [3^{Me}·SiMe$_3$][BAr^F$_4$]: To a solution of $\mathbf{3^{Me}}$ (11 mg, 0.02 mmol) in Et_2O (1 mL) under an Ar atmosphere was added Me_3SiOTf (3.6 µL, 0.02 mmol) and $KBAr^F_4$ (18 mg, 0.02 mmol). The reaction was stirred for 5 min, before being filtered and the volatiles removed *in vacuo*. The residue was redissolved in Et_2O (1.5 mL) and pentane (5 mL) added, precipitating a dark red solid which was isolated and dried *in vacuo* (22 mg, 77%). The ^{15}N labelled analogue was similarly prepared from $\mathbf{3^{Me}\text{-}^{15}N_2}$.

^{1}H NMR (400.4 MHz, Et_2O, silyl region) δ: 0.50 (br s, P-SiCH_3), 0.16 (s, N-SiCH_3).
^{11}B NMR (128.4 MHz, Et_2O) δ: –6.1 (s).
$^{13}C\{^{1}H\}$ NMR (100.0 MHz, Et_2O) δ: 35.0 (s), 26.2 (s), 25.3 (s), 22.9 (s), 22.4 (s), 14.0 (s), 7.5 (s), 0.36 (s).
^{19}F NMR (376.4 MHz, Et_2O) δ: –79.3 (s).
$^{15}N\{^{1}H\}$ NMR (40.55 MHz, Et_2O) δ: -31 (m, N_α), -258 (d, $^{1}J_{NN}$ = 16 Hz, N_β).
$^{31}P\{^{1}H\}$ NMR (162.0 MHz, Et_2O) δ: 102.1 (2 P, d, $^{2}J_{PP}$ = 13 Hz), 58.0 (1 P, dt, $^{2}J_{PP}$ = 8 Hz $^{3}J_{PP}$ = 44 Hz), -17.2 (1 P, d, $^{3}J_{PP}$ = 44 Hz).
^{29}Si NMR (99.4 MHz, Et_2O, HMBC) δ: -0.1 (s, N-*Si*CH_3).
HRMS (ES): *m/z* found (calculated) for $C_{21}H_{59}FeN_2P_4Si_3$: 603.2304 (603.2286)
UV-Vis (Et_2O, nm {M^{-1} cm^{-1}}): 501 {1160}

[Fe(depe)$_2$(NN(SiMe$_3$)$_2$)·SiMe$_3$][BAr$^F_4$] [3^{Et}·SiMe$_3$][BAr$^F_4$]: To a solution of **3^{Et}** (13 mg, 0.02 mmol) in Et_2O (1 mL) under an Ar atmosphere was added Me_3SiOTf (3.6 μL, 0.02 mmol) and KBAr$^F_4$ (18 mg, 0.02 mmol). The reaction was stirred for 5 min, before being filtered and the volatiles removed *in vacuo*. The residue was redissolved in Et_2O (1.5 mL) and pentane (5 mL) added, precipitating a dark purple solid which was isolated by filtration and dried *in vacuo* (11.9 g, 83%). Crystals suitable for X-ray diffraction were grown by layering of an Et_2O solution of **[3^{Et}·SiMe$_3$][BAr$^F_4$]** with pentane. The ^{15}N labelled analogue was similarly prepared from **3^{Et}-$^{15}N_2$**.

^{1}H NMR (400.4 MHz, Et_2O, silyl region) δ: 0.55 (br s, P-SiCH_3), 0.18 (s, N-SiCH_3).
^{11}B NMR (128.4 MHz, Et_2O) δ: –6.1 (s).
$^{13}C\{^{1}H\}$ NMR (101.0 MHz, Et_2O) δ: 29.1 (s), 26.8 (s), 26.2 (s), 21.2 (s), 19.1 (s), 9.7 (s), 9.4 (s), 9.1 (s), 8.9 (s), 7.3 (s), 0.72 (s).
$^{15}N\{^{1}H\}$ NMR (40.55 MHz, Et_2O) δ: -33 (dq, $^{1}J_{NN}$ = 16 Hz, $^{2}J_{NP}$ = 5 Hz, N_α), -260 (d, $^{1}J_{NN}$ = 16 Hz, N_β).
^{19}F NMR (376.4 MHz, Et_2O) δ: –79.3 (s).
$^{15}N\{^{1}H\}$ NMR (40.55 MHz, Et_2O) δ: -32 (m, N_α), -258 (d, $^{1}J_{NN}$ = 16 Hz, N_β).
$^{31}P\{^{1}H\}$ NMR (162.0 MHz, Et_2O) δ: 99.6 (2 P, m), 70.7 (1 P, m), -5.4 (1 P, br s).
^{29}Si NMR (99.4 MHz, Et_2O, HMBC) δ: 1.6 (s, N-*Si*CH_3).
HRMS (ES): *m/z* found (calculated) for $C_{29}H_{75}FeN_2P_4Si_3$: 715.9270 (715.9281)
UV-Vis (Et_2O, nm {M^{-1} cm^{-1}}): 509 {1040}

Reduction reactions of [$2^{Me/Et}$]][BAr^F_4]: N.B. These reactions were performed under an Ar atmosphere. To a solution of either **[2^{Me}]][BAr^F_4] or [2^{Et}]][BAr^F_4]** (13.2 mg or 14.3 mg, 0.01 mmol) in Et_2O (0.5 mL) inside a J. Young's NMR tube was added KC_8 (1.5 mg, 0.011 mmol), and the resulting suspension shaken briefly. The solids were allowed to settle, and the reaction mixture analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, revealing the presence of **$1^{Me/Et}$** and **$3^{Me/Et}$** in a 1:1 ratio.

Reductive cleavage reactions of $3^{Me/Et}$: Inside a glovebox, **$3^{Me/Et}$** (0.1 mL of a 0.1 M solution in Et_2O, 0.01 mmol), Et_2O (0.4 mL) and either KC_8 or $K_{(s)}$ (6.8 mg, 0.05 mmol; 50 mg, 1.28 mmol) were combined in a vial charged with a glass-coated stirrer bar. The reaction mixture was allowed to stir for 3 days, before being filtered into a J.Young's NMR tube and analysed by ^1H and ^{29}Si-^1H HMBC NMR, which revealed the presence of $KN(SiMe_3)_2$ (verified by comparison with the spectra of a commercial sample). The reactions, based on the intensity of the starting ^1H NMR resonance for the Me_3Si groups in **$3^{Me/Et}$**, provide a yield of $KN(SiMe_3)_2$ of 70-80% via ^1H NMR integration. Me_3SiCl (5.1 μL, 0.04 mmol) was then added, and the solutions re-analyzed by ^1H and ^{29}Si-^1H HMBC NMR spectroscopy, which revealed the presence of $N(SiMe_3)_3$ (verified by comparison with the spectra of a commercial sample).

Reactions of Fe species with $Hg(SiMe_3)_2$: To a solution of either **$1^{Me/Et}$** (3.2 mg or 5.0 mg, 0.01 mmol), **[$2^{Me/Et}$]][BAr^F_4]** (13.2 mg or 14.3 mg, 0.01 mmol), or **$3^{Me/Et}$** (0.1 mL of a 0.1 M solution in Et_2O, 0.01 mmol) in Et_2O (0.5 mL) inside a J. Young's NMR tube was added $Hg(SiMe_3)_2$ (7.6 mg, 0.022 mmol). The resulting solutions were either heated to 50 °C, or allowed to stand under ambient light for 12 hours, before being analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. In all cases no change in the resonances of the Fe-containing starting material was observed, but Me_3Si-$SiMe_3$ was visible in the ^1H NMR spectrum (as compared with an authentic sample, $\delta = 0.06$ ppm) and a dark suspension of Hg^0 could be seen inside the NMR tube.

Representative Procedure for $Fe(PP)_2(N_2)$-catalyzed (PP = dmpe, depe) conversion of N_2 to $N(SiMe_3)_3$

Inside an N_2 glovebox, a 250 ml Rotaflo® ampoule was charged with $Fe(depe)_2(N_2)$ (2.5 mg, 0.005 mmol, 1.0 eq.), KC_8 (680 mg, 5 mmol, 1000 eq.), Me_3SiCl (0.64 mL, 5 mmol, 1000 eq.), Et_2O (20 mL) and a stirrer bar. The ampoule was sealed and the mixture stirred for 72 h, after which a 5 mL portion of the reaction mixture was removed and filtered through Celite®. Any $N(SiMe_3)_3$ present was then converted to NH_4Cl by addition of 2 M HCl in Et_2O (2 mL, 4 mmol, 800 eq.)[10] followed by stirring for 5 min. NH_4Cl was then converted to NH_3 by addition of excess KOH and quantified by our previously published method.[7] Reaction times of greater than 72 h gave no improvement in yield of $N(SiMe_3)_3$, whilst reaction times of 24 or 48 h gave diminished yields (see Table S1.)

The electron yield of these reactions was calculated using the following formula:

$$e^- \; yield = \frac{e^- \; used \; in \; N(SiMe_3)_3 \; formation}{e^- \; available}$$

$$e^- \; used \; in \; N(SiMe_3)_3 \; formation = 6 \times equivalents \; of \; N(SiMe_3)_3 \; formed$$

$$e^- \; available = Equivalents \; of \; KC_8 \; used + e^- \; available \; from \; starting \; complex$$

The final term was set at +2 for $\mathbf{1}^{\mathbf{Me/Et}}$ and −4 for $\mathbf{3}^{\mathbf{Me/Et}}$. For $\mathbf{1}^{\mathbf{Me/Et}}$, this reflects the fact that the starting Fe(0) center in $Fe(PP)_2(N_2)$ is assumed to supply $2e^-$ to a N_2 molecule for N_2 fixation and thus being oxidized to Fe(II) (as documented previously).[7,8] For $\mathbf{3}^{\mathbf{Me/Et}}$, which formally contain Fe(II) and a $[NN(SiMe_3)_2]^{2-}$ ligand, these are treated as $[N_2]^{4-}$ and hence treated as if $4e^-$ reduction of a starting N_2 molecule has already taken place.[11]

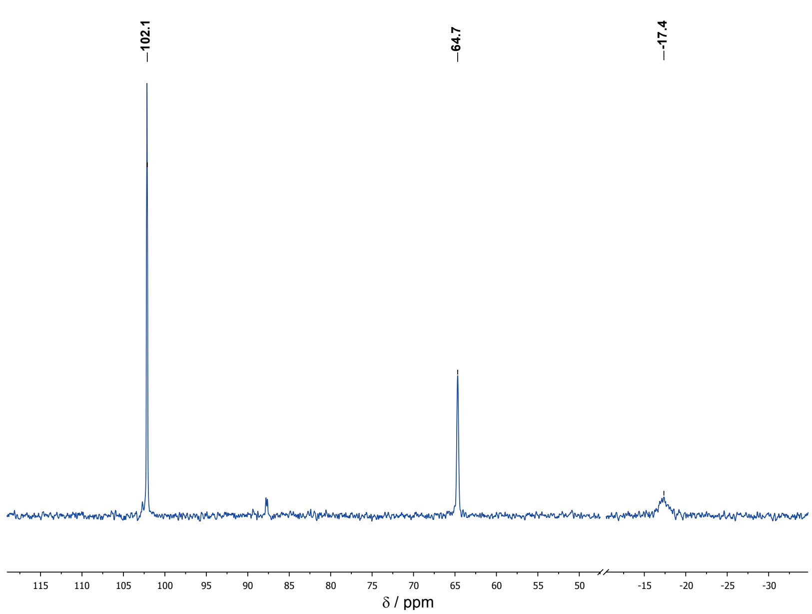

Figure S1. ^{31}P NMR spectrum of an aliquot taken during a catalytic N_2 silylation experiment employing $\mathbf{1}^{\mathbf{Et}}$ showing the presence of $\mathbf{3}^{\mathbf{Et}}$.

Complete results of catalysis reactions

Table 1 in the main text details the results of catalytic N_2 silylation experiments employing $Fe(PP)_2(N_2)$, with yields reported as the average of two runs. For completeness we report in the below table the results of each catalytic reaction.

Table S1. Complete results of catalytic N_2 silylation reactions with $Fe(pp)_2$-based catalysts.[a]

Entry	Catalyst	Me_3SiCl, KC_8 (eq.)	$N(SiMe_3)_3$ (eq.)[b]	e^- yield (%)[c]
1	1^{Me}	1000	45.3	13.8
2	1^{Me}	1000	49.3	14.8
3	1^{Et}	1000	41.7	12.2
4	1^{Et}	1000	42.1	12.7
5[d]	1^{Me}	1000	82.5	24.6
6[d]	1^{Me}	1000	89.1	26.6
7[d]	1^{Et}	1000	67.2	20.0
8[d]	1^{Et}	1000	73.4	21.8
9[d]	1^{Me}	1500	129.2	25.8
10[d]	1^{Me}	1500	113.2	22.6
11[d]	1^{Et}	1500	105.3	19.9
12[d]	1^{Et}	1500	100.1	21.0
13	3^{Me}	1000	58.7	17.6
14	3^{Me}	1000	54.0	16.2
15	3^{Et}	1000	40.9	12.2
16	3^{Et}	1000	40.6	12.2
17	$[3^{Me}\cdot SiMe_3][BAr^F_4]$	1000	52.6	16.4
18	$[3^{Et}\cdot SiMe_3][BAr^F_4]$	1000	40.3	12.1
19[e]	-	1000	0.0	0.0
20[f]	1^{Et}	1000	27.4	8.3
21[g]	1^{Et}	1000	37.1	11.2
22[h]	1^{Et}	1000	46.1	6.9

[a]Experiments performed over 72 h using 0.005 mmol catalyst at 25 °C under 1 atm, unless otherwise stated. N_2, unless otherwise stated; eq. = equivalents. [b]Determined by acid hydrolysis to NH_4^+ and quantified using ^1H NMR (see SI); yield per mol Fe. [c]Yield calculated as the proportion of available e^- used in productive formation of $N(SiMe_3)_3$ (see SI for details). [d]Performed under 4 atm. N_2. [e]Control experiment with no catalyst added. [f]Performed over 24 h. [g]Performed over 48 h. [h]A further 1000 eq. of KC_8 and Me_3SiCl were added after 72 h, and the reaction stirred for a further 72 h.

2. NMR spectra

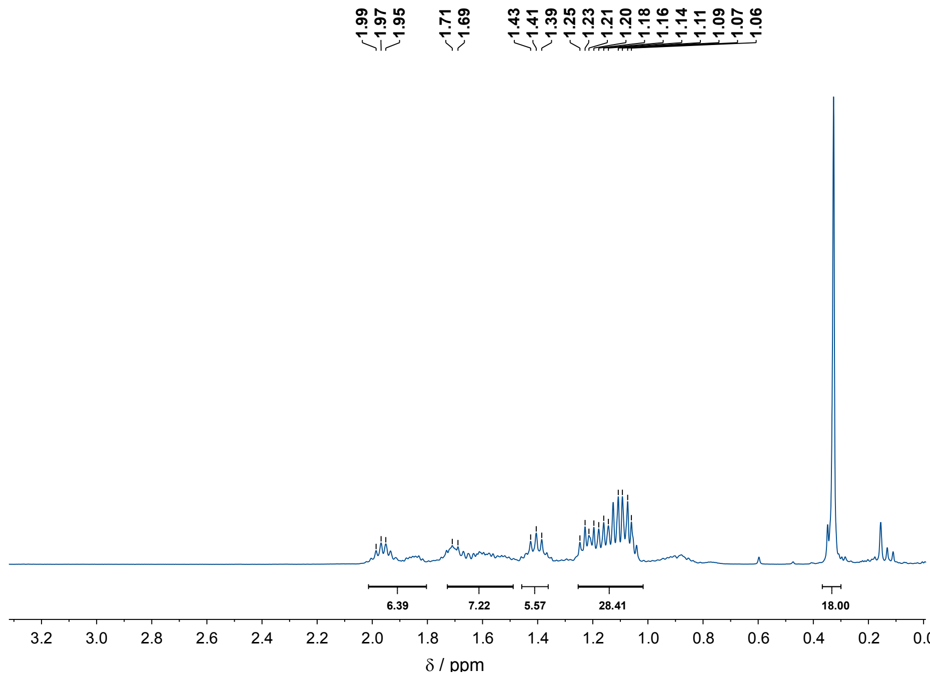

Figure S2. ^{1}H NMR spectrum of Fe(depe)$_2$(NN(SiMe$_3$)$_2$) (**3^{Et}**) recorded as a C_6D_6 solution.

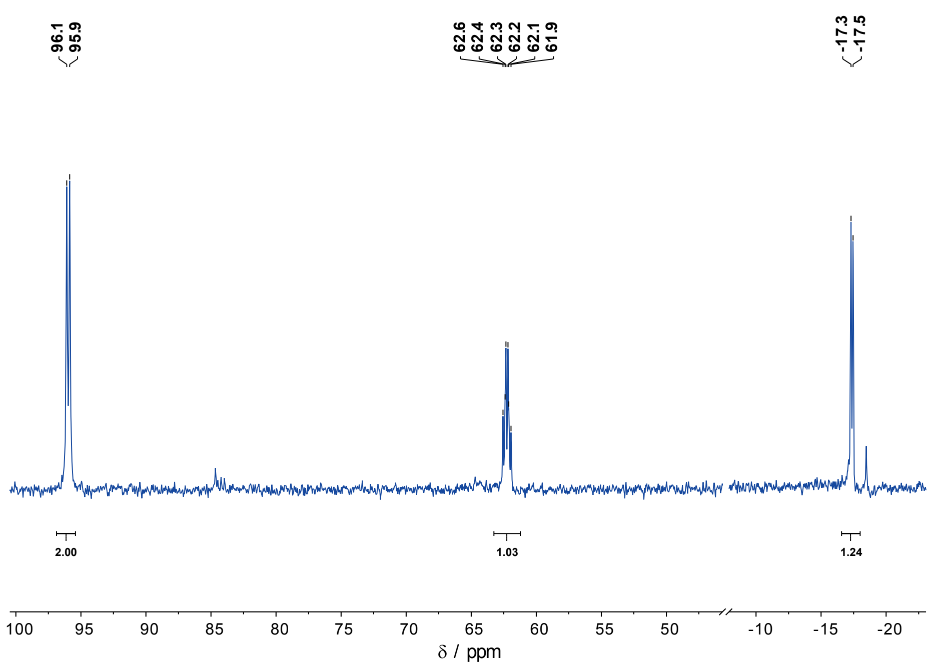

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of Fe(depe)$_2$(NN(SiMe$_3$)$_2$) (**3^{Et}**) recorded as an Et$_2$O solution.

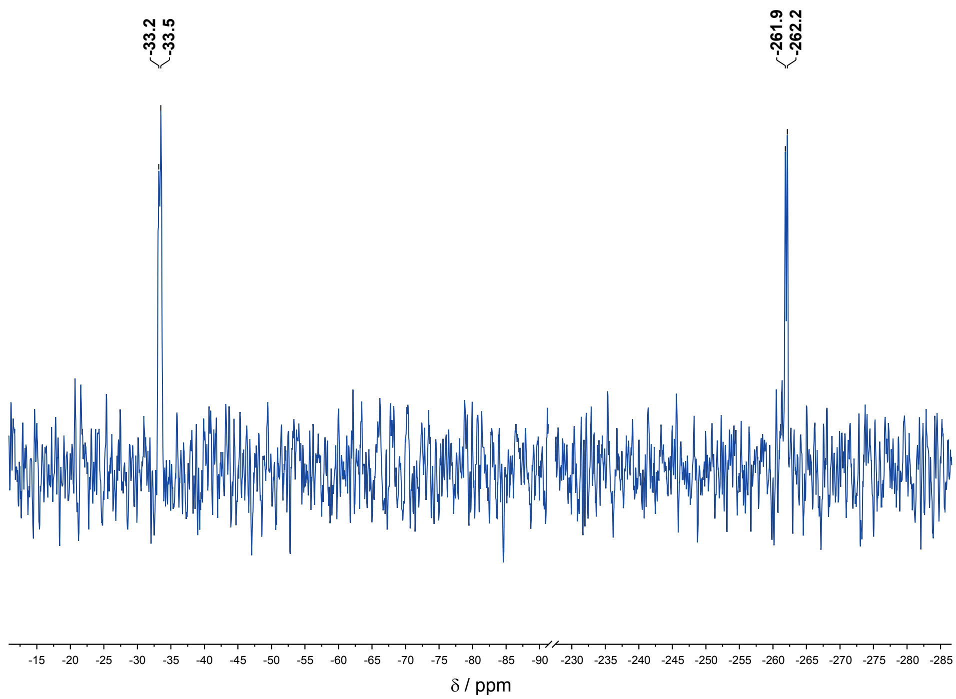

Figure S4. $^{15}N\{^{1}H\}$ NMR spectrum of Fe(depe)$_2$(NN(SiMe$_3$)$_2$) (**3^{Et}**) recorded as an Et$_2$O solution.

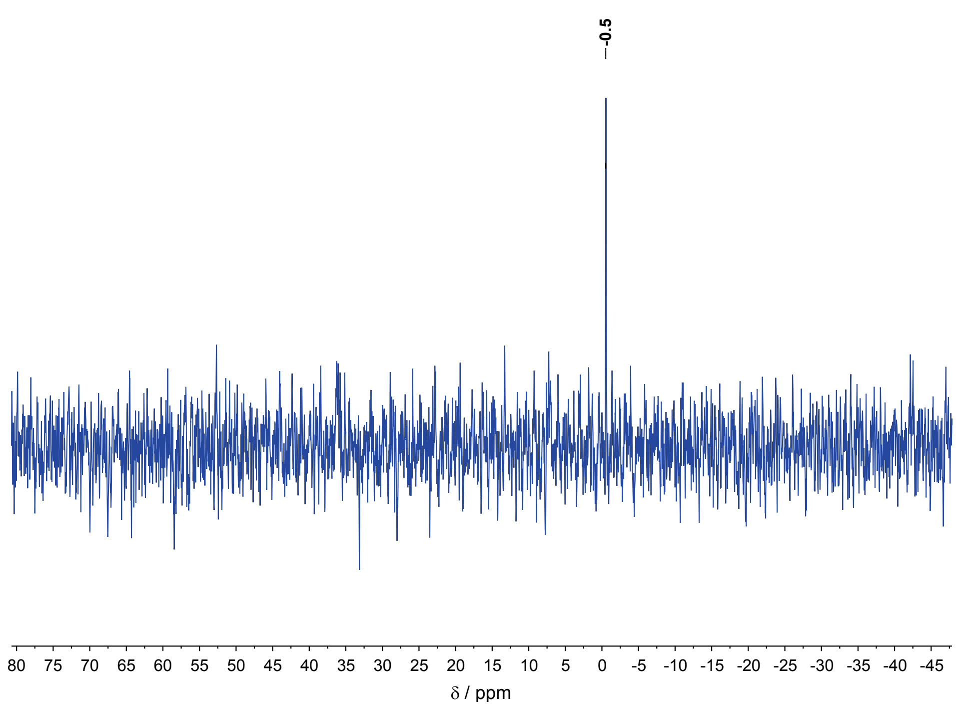

Figure S5. $^{29}Si\{^{1}H\}$ NMR spectrum of Fe(depe)$_2$(NN(SiMe$_3$)$_2$) (**3^{Et}**) recorded as an Et$_2$O solution.

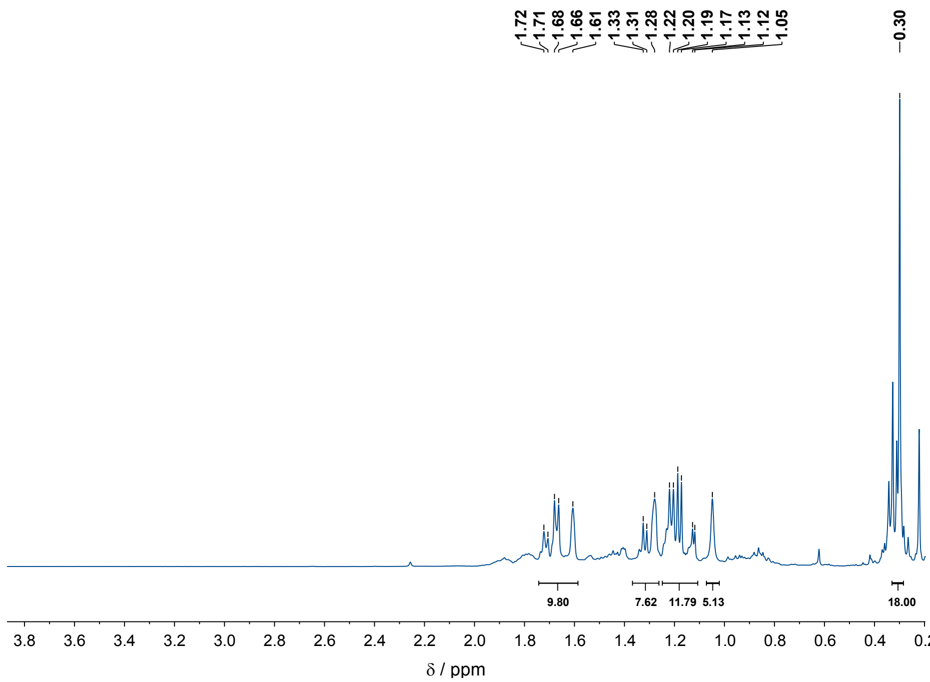

Figure S6. ^{1}H NMR spectrum of $Fe(dmpe)_2(NN(SiMe_3)_2)$ ($\mathbf{3^{Me}}$) recorded as a C_6D_6 solution.

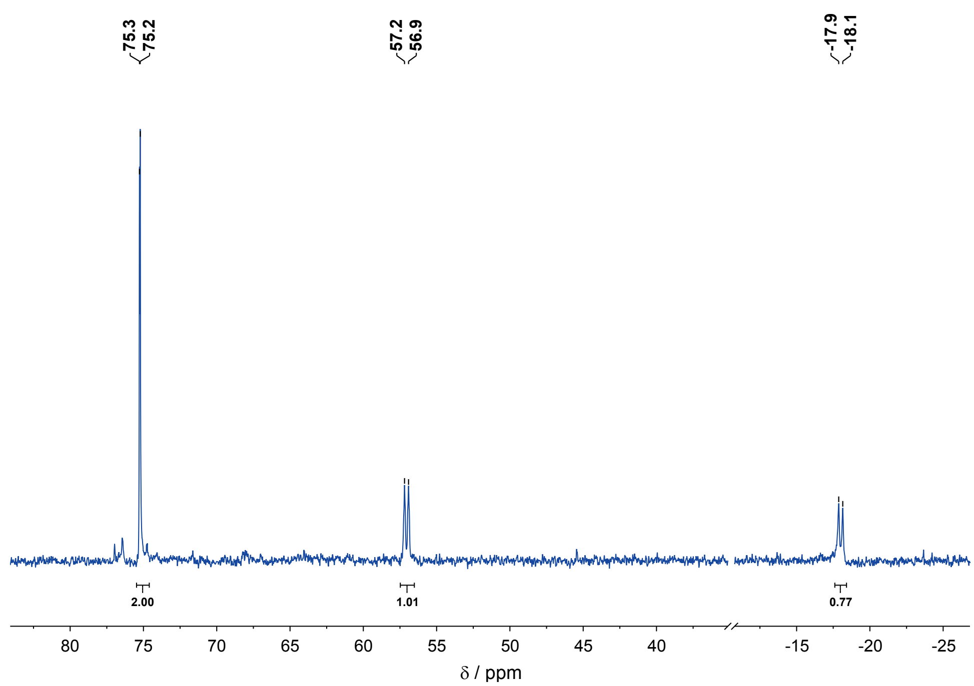

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of $Fe(dmpe)_2(NN(SiMe_3)_2)$ ($\mathbf{3^{Me}}$) recorded as an Et_2O solution.

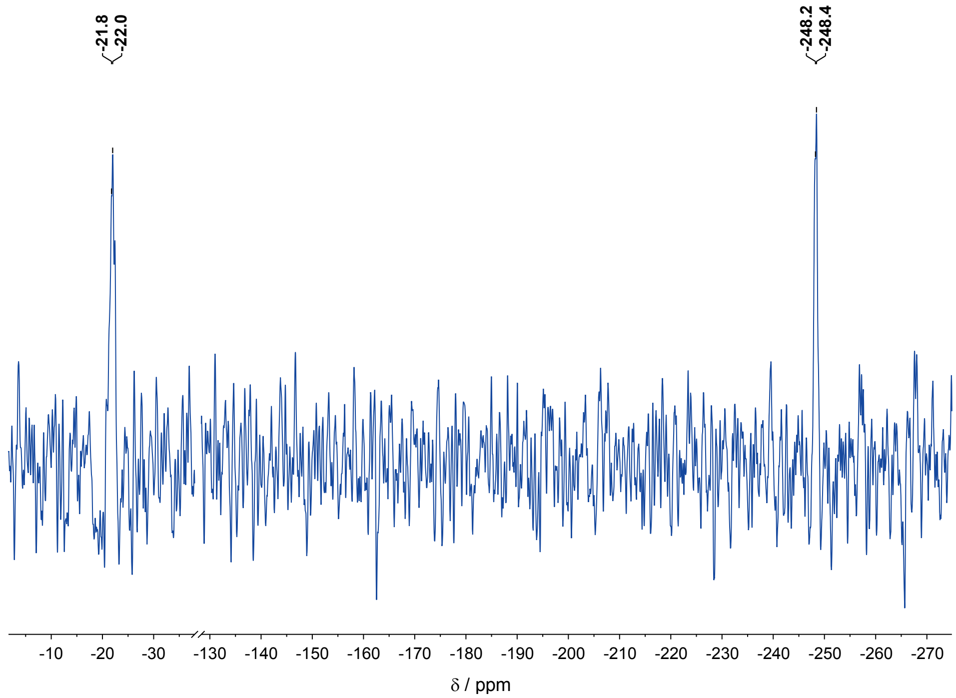

Figure S8. $^{15}N\{^{1}H\}$ NMR spectrum of $Fe(dmpe)_2(NN(SiMe_3)_2)$ (**3^{Me}**) recorded as an Et_2O solution.

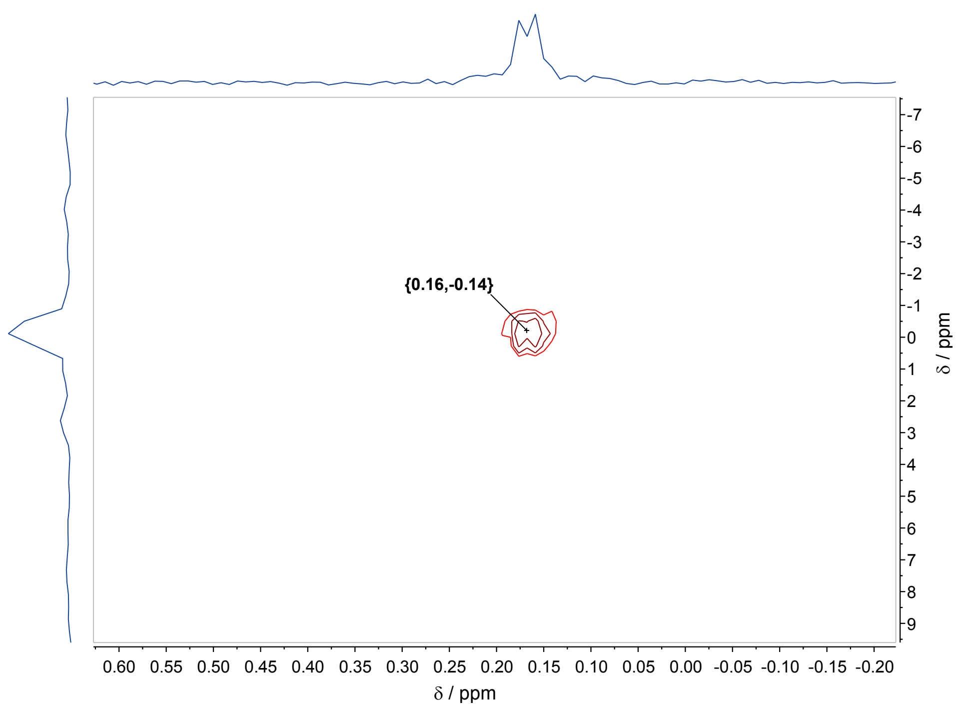

Figure S9. ^{29}Si-^{1}H HMBC NMR spectrum of $Fe(dmpe)_2(NN(SiMe_3)_2)$ (**3^{Me}**) recorded as an Et_2O solution.

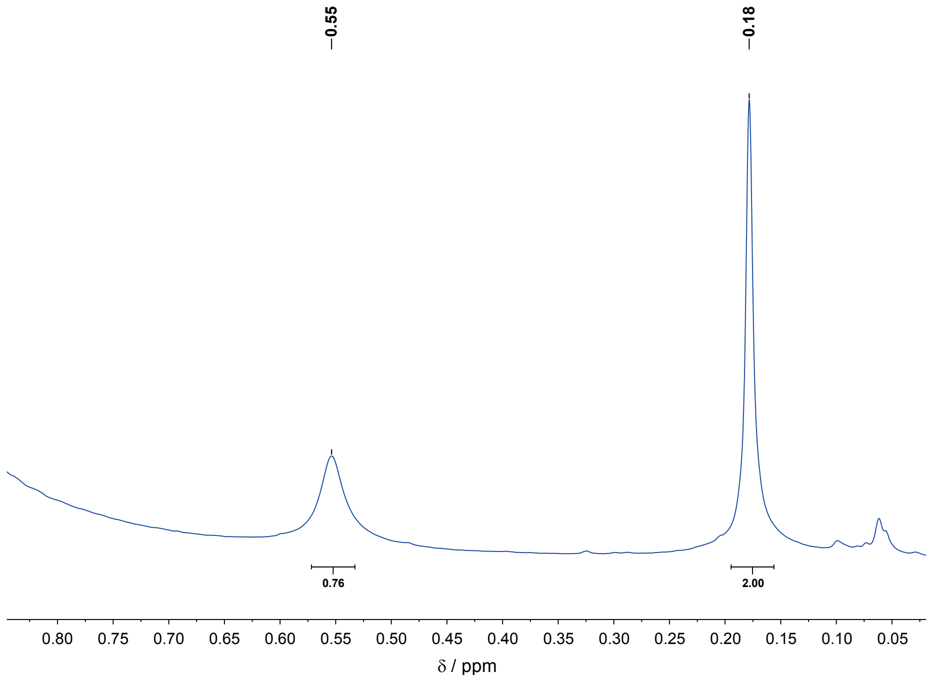

Figure S11. ^{1}H NMR spectrum (silyl region only) of $[Fe(depe)_2(NN(SiMe_3)_2)\cdot SiMe_3][BAr^F_4]$ (**$[3^{Et}\cdot SiMe_3][BAr^F_4]$**) recorded as an Et_2O solution.

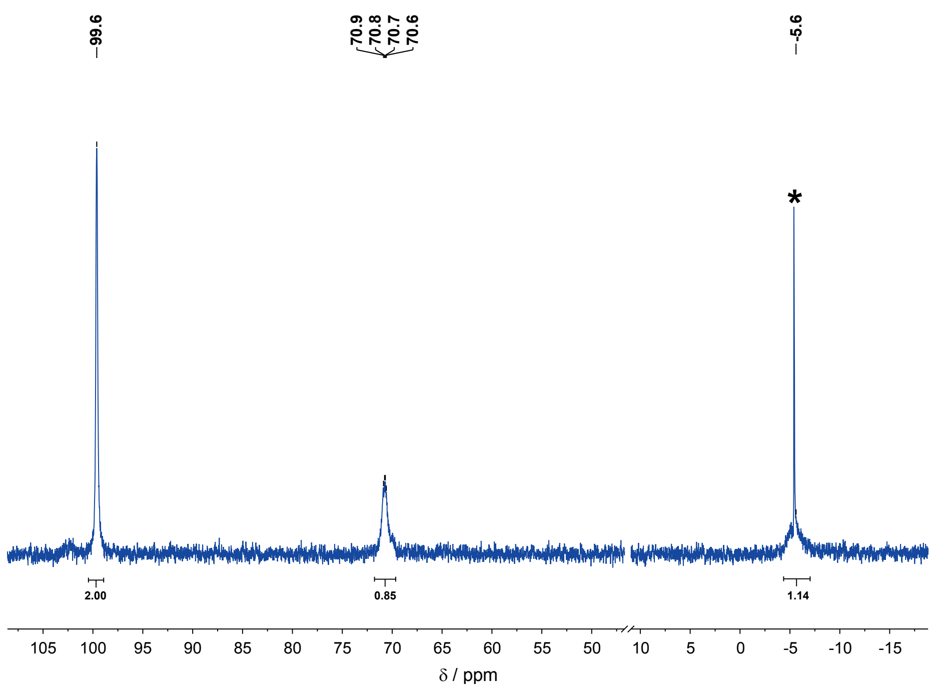

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of $[Fe(depe)_2(NN(SiMe_3)_2)\cdot SiMe_3][BAr^F_4]$ (**$[3^{Et}\cdot SiMe_3][BAr^F_4]$**) recorded as an Et_2O solution. The sharp resonance denoted with a * originates from a PPh_3 internal standard.

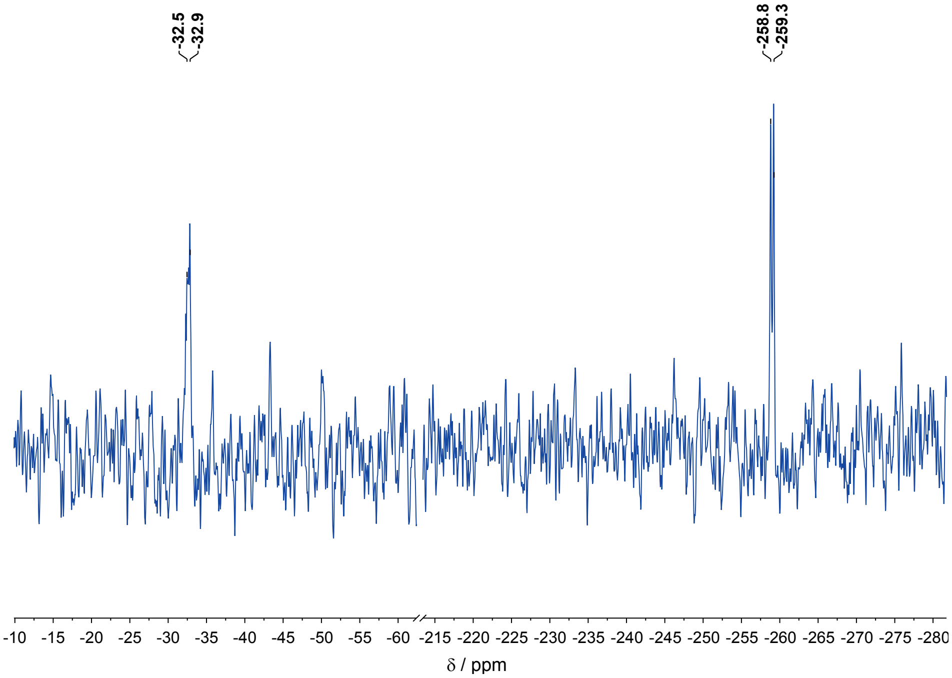

Figure S12. $^{15}N\{^1H\}$ NMR spectrum of [Fe(depe)$_2$(NN(SiMe$_3$)$_2$)·SiMe$_3$][BAr$^F{}_4$] (**[3^{Et}·SiMe$_3$][BAr$^F{}_4$]**) recorded as an Et$_2$O solution.

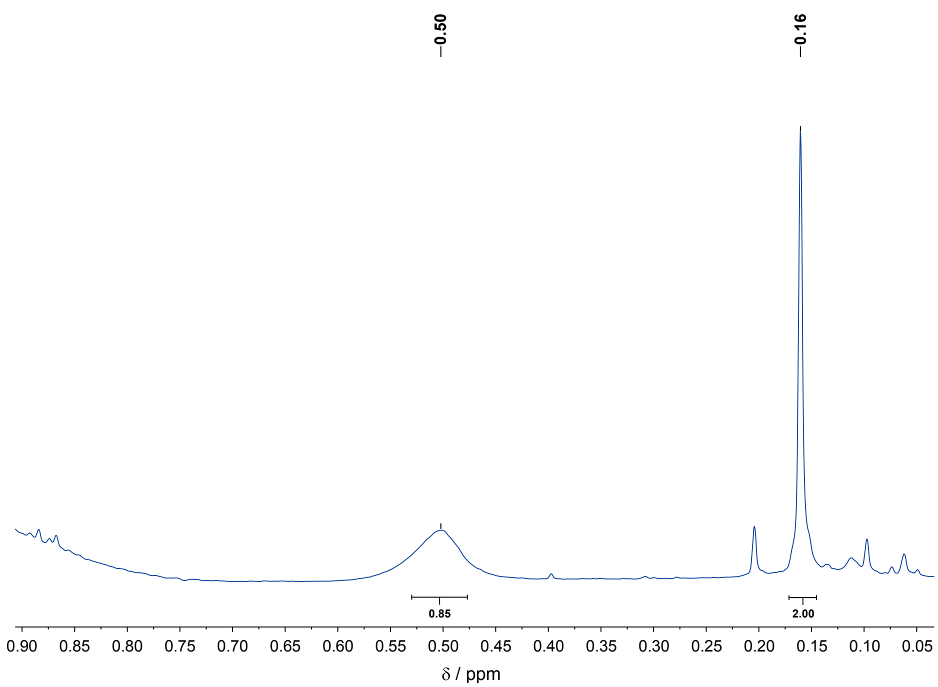

Figure S13. ^1H NMR spectrum (silyl region only) of [Fe(dmpe)$_2$(NN(SiMe$_3$)$_2$)·SiMe$_3$][BAr$^F{}_4$] (**[3^{Me}·SiMe$_3$][BAr$^F{}_4$]**) recorded as an Et$_2$O solution.

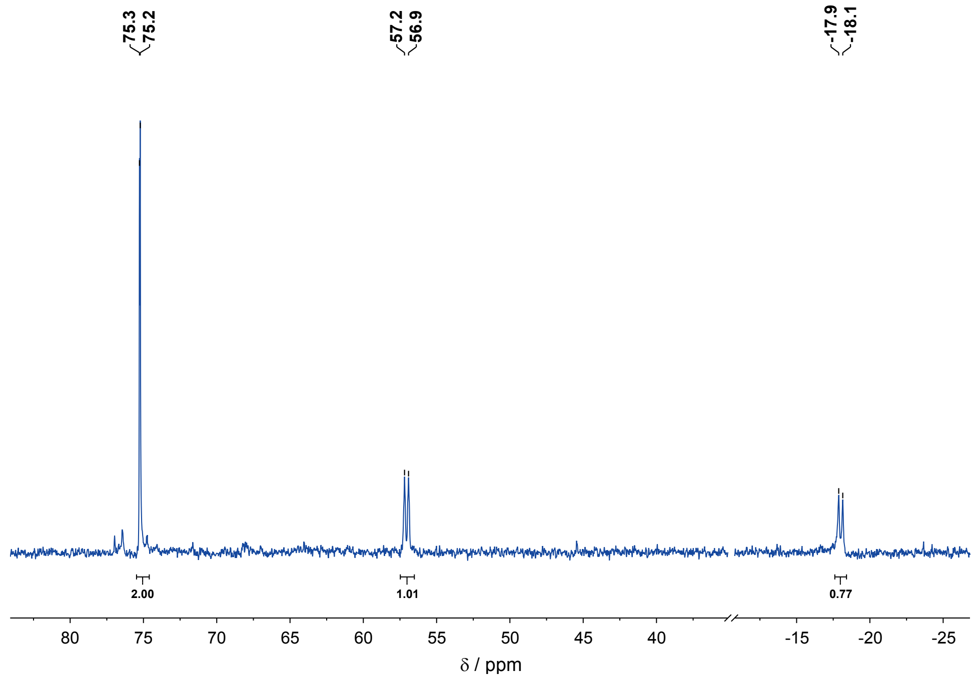

Figure S14. $^{31}P\{^1H\}$ NMR spectrum of $[Fe(dmpe)_2(NN(SiMe_3)_2)\cdot SiMe_3][BAr^F_4]$ (**$[3^{Me}\cdot SiMe_3][BAr^F_4]$**) recorded as an Et_2O solution.

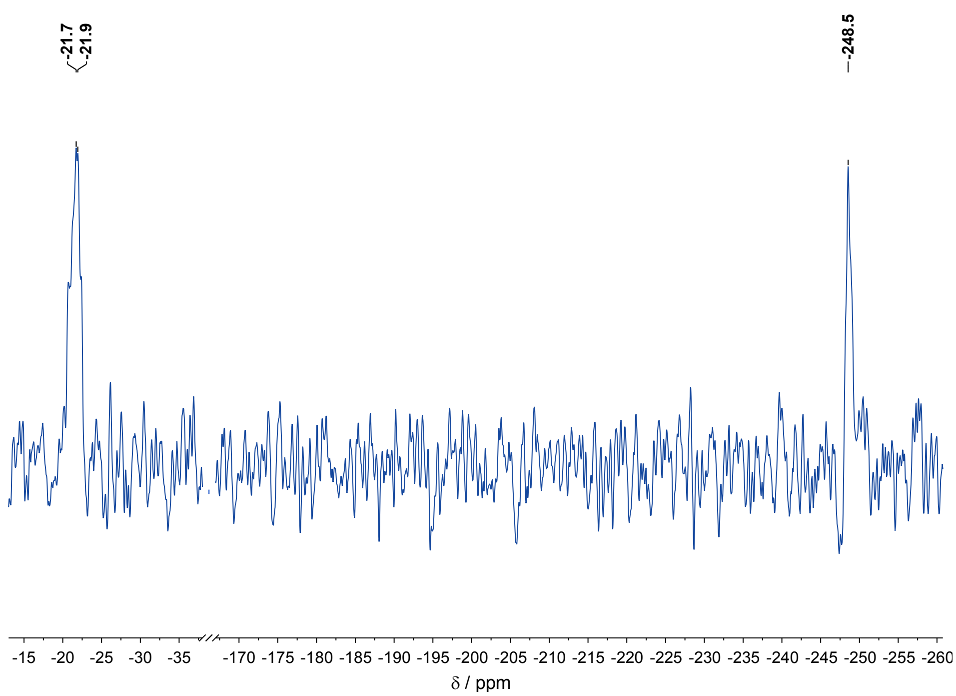

Figure S15. $^{15}N\{^1H\}$ NMR spectrum of $[Fe(dmpe)_2(NN(SiMe_3)_2)\cdot SiMe_3][BAr^F_4]$ (**$[3^{Me}\cdot SiMe_3][BAr^F_4]$**) recorded as an Et_2O solution.

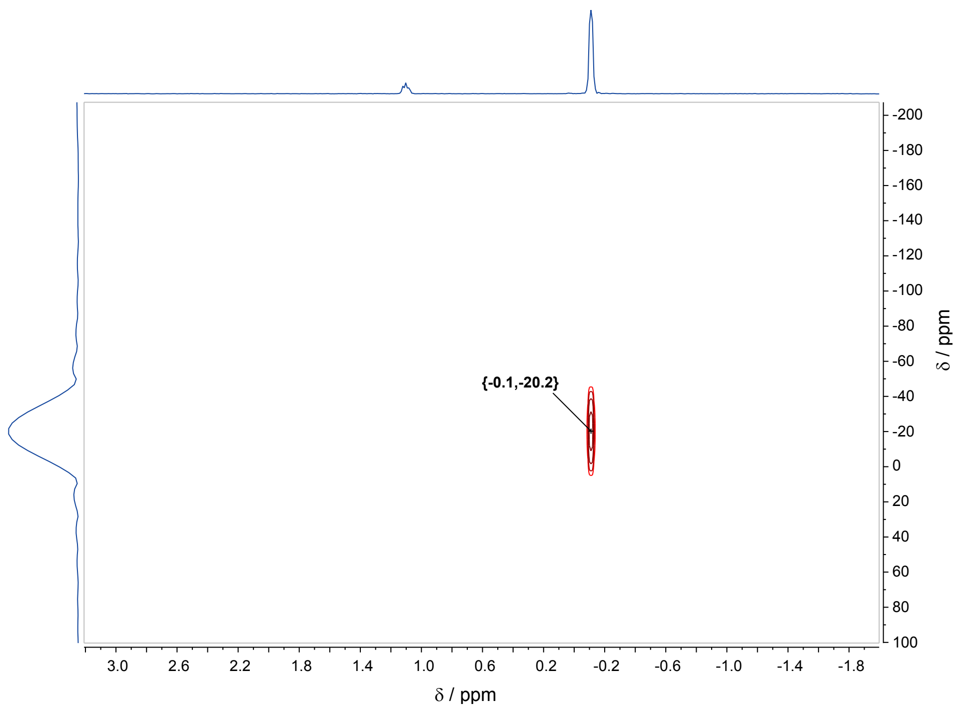

Figure S16. ^{29}Si-^{1}H HMBC NMR spectrum of a commercial sample of $KN(SiMe_3)_2$ recorded as an Et_2O solution at 20 °C.

3. Cyclic voltammetry

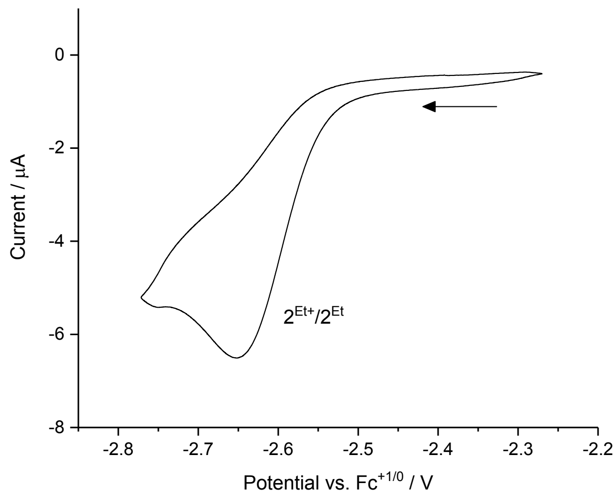

Figure S17. Cyclic voltammogram of $[Fe(depe)_2(NNSiMe_3)][BAr^F_4]$ (**$[2^{Et}][BAr^F_4]$**) (2 mM) recorded as an Et_2O solution under an Ar atmosphere; $[^nBu_4N][BAr^F_4]$ electrolyte (50 mM).

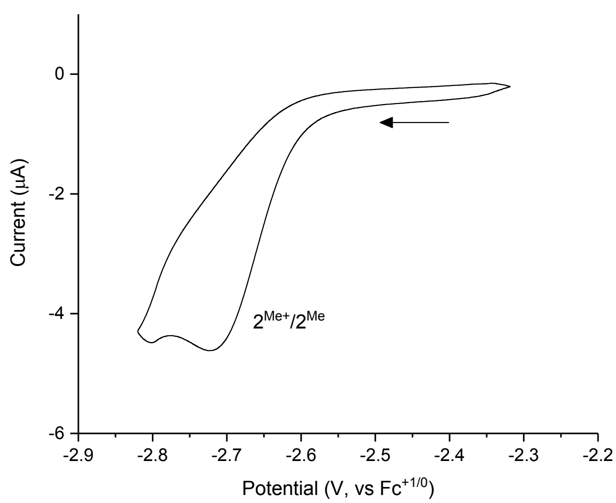

Figure S18. Cyclic voltammogram of $[Fe(dmpe)_2(NNSiMe_3)][BAr^F_4]$ (**$[2^{Me}][BAr^F_4]$**) (2 mM) recorded as an Et_2O solution under an Ar atmosphere; $[^nBu_4N][BAr^F_4]$ electrolyte (50 mM).

4. UV-Vis spectra

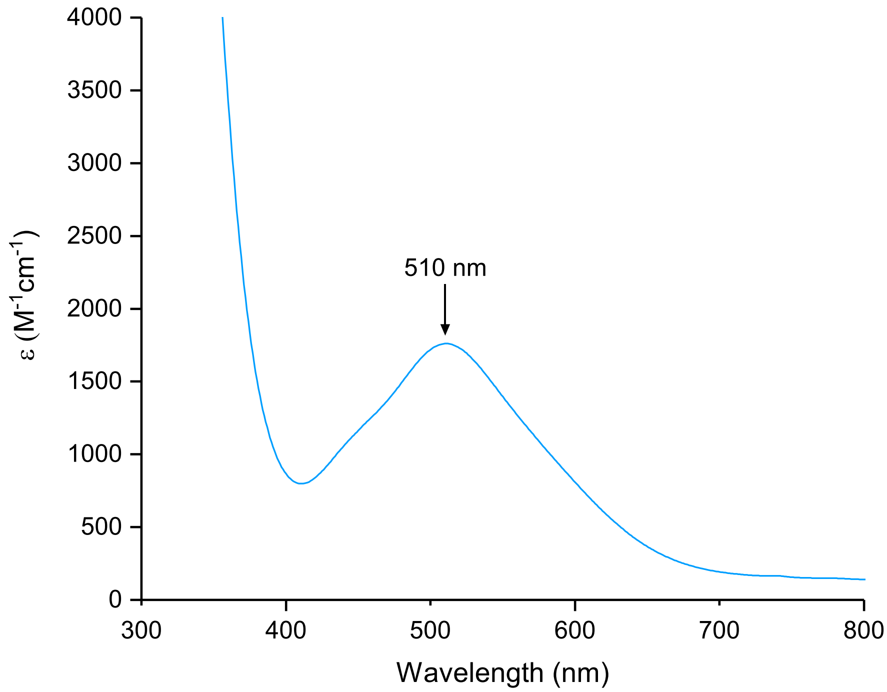

Figure S19. UV spectrum of $Fe(depe)_2(NN(SiMe_3)_2)$ (**3**$^{\mathbf{Et}}$) recorded as a pentane solution under an Ar atmosphere.

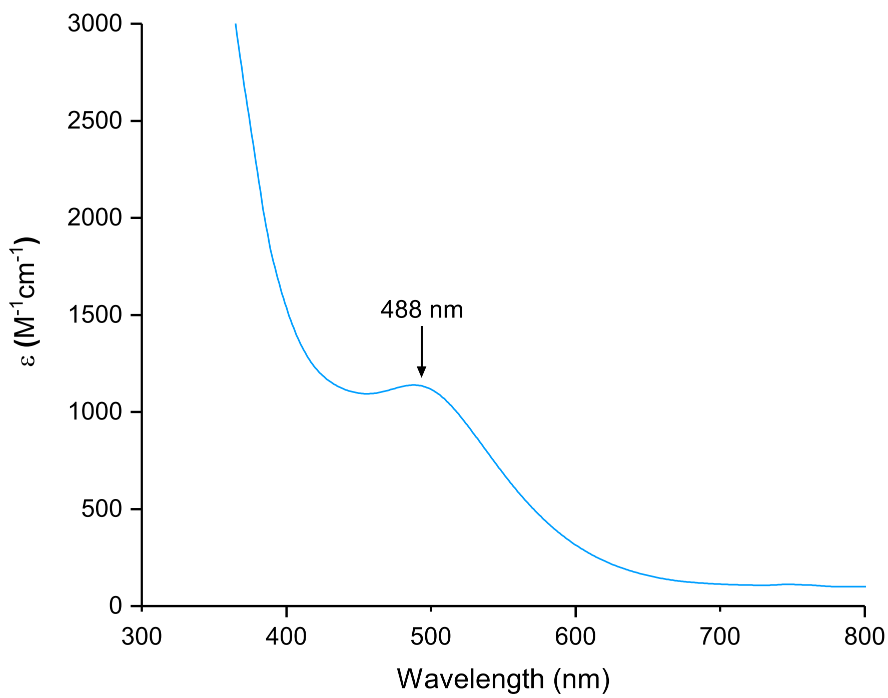

Figure S20. UV spectrum of $Fe(dmpe)_2(NN(SiMe_3)_2)$ (**3**$^{\mathbf{Me}}$) recorded as a pentane solution under an Ar atmosphere.

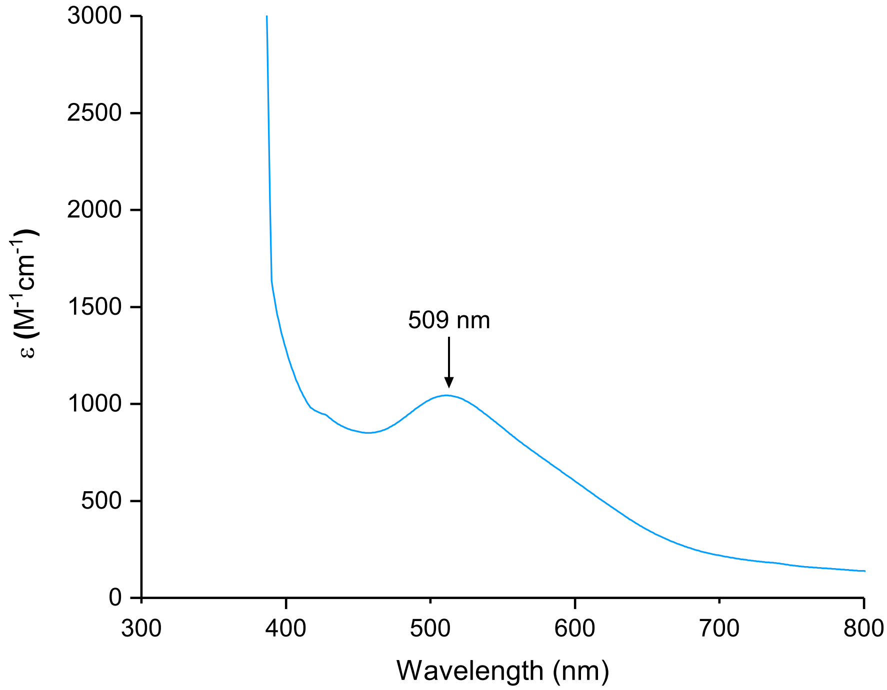

Figure S21. UV spectrum of [Fe(depe)$_2$(NN(SiMe$_3$)$_2$)·SiMe$_3$][BAr$^F_4$] (**[3^{Et}·SiMe$_3$][BAr$^F_4$]**) recorded as an Et_2O solution under an N_2 atmosphere.

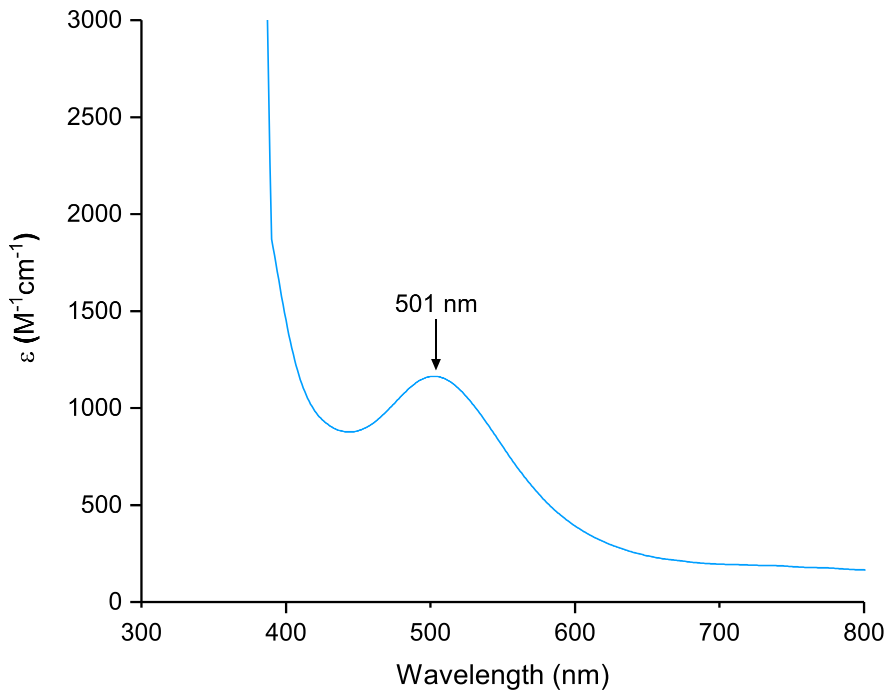

Figure S22. UV spectrum of [Fe(dmpe)$_2$(NN(SiMe$_3$)$_2$)·SiMe$_3$][BAr$^F_4$] (**[3^{Me}·SiMe$_3$][BAr$^F_4$]**) recorded as an Et_2O solution under an N_2 atmosphere.

5. X-Ray diffraction data

[3^{Et}·$SiMe_3$][BAr^F_4] - [Fe(depe)$_2$(NN($SiMe_3$)$_2$)·$SiMe_3$][BAr^F_4]

This data set was modelled as a two-component twin in an approximate 77:23 ratio. Some CF_3 groups of the [BAr^F_4]$^-$ counterion were found to be disordered over two orientations and were modelled as such, with suitable bond length restraints applied. One ethyl group of a depe ligand was found to be disordered over two positions and was modelled as two components in a 50:50 ratio. Cif data may be retrieved from the Cambridge Structural Database (CCDC 1850110).

Formula	$C_{61}H_{87}BF_{24}FeN_2P_4Si_2$	
Formula Weight	1579.10	
Temperature	173.00(14)	
Diffractometer, Wavelength	Agilent Xcalibur 3E, 0.71073Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 11.9577(6) Å	α = 94.728(4)°
	b = 16.1735(5) Å	β =105.621(5)°
	c = 20.8289(13) Å	γ = 95.118(3)°
Volume, Z	3840.1(3), 2	
Density (calculated)	1.366 g/cm^3	
Absorption coefficient	0.422 mm^{-1}	
F(000)	1632	
Crystal color / morphology	Purple plates	
Crystal size	0.438 × 0.377 × 0.094 mm^3	
2θ range for data collection	4.4 to 56.6°	
Index Ranges	$-15\leq h\leq 15$, $-19\leq k\leq 19$, $-23\leq l\leq 27$	
Reflections collected	15949	

Independent Reflections	15949 [R_{int} = N/A]
Absorption correction	Analytical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15949/216/1001
Goodness-of-fit on F^2	1.026
Final R indices [I>=2σ (I)]	R_1 = 0.080, wR_2 = 0.20
R indices (all data)	R_1 = 0.143, wR_2 = 0.222
Largest diff. peak, hole	0.96, -0.56 eÅ^{-3}

6. Computational details

Density functional calculations were carried out using the ADF program suite, version 2014.1.[12] The Slater-type orbital (STO) basis sets were of triple-ζ quality augmented with one polarization function (ADF basis TZP). Core electrons were frozen (C, N 1s; Fe 2p) in our model of the electronic configuration for each atom. The local density approximation (LDA) by Vosko, Wilk and Nusair (VWN)[13] was used together with the exchange correlation corrections of Becke and Perdew (BP86).[14] Optimized geometries were confirmed as local mimima via frequency calculations.

Modelling the disproportionation of 2^{Me} to 1^{Me} and 3^{Me}

Modelling the mechanism of the proposed bimolecular disproportionation of $\mathbf{2^{Me}}$ to $\mathbf{1^{Me}}$ and $\mathbf{3^{Me}}$ was challenging, a result of the change of complex spin during the course of reaction (two S = ½ species forming S = 0 products). Nevertheless, the free energy of the disproportionation reaction was calculated to be highly favorable ($\Delta_rG = -179$ kJ mol^{-1}), and a possible transition state involving an S_N2-type reaction between N_β of one $\mathbf{2^{Me}}$ molecule with the Me_3Si group of another (Si-$N_\beta\cdots$Si distance = 3.20 Å) on the singlet surface was identified, displaying a feasible activation energy (76 kJ mol^{-1}). Confirmation of this transition state as a saddle point on the potential energy surface was obtained by a frequency calculation.

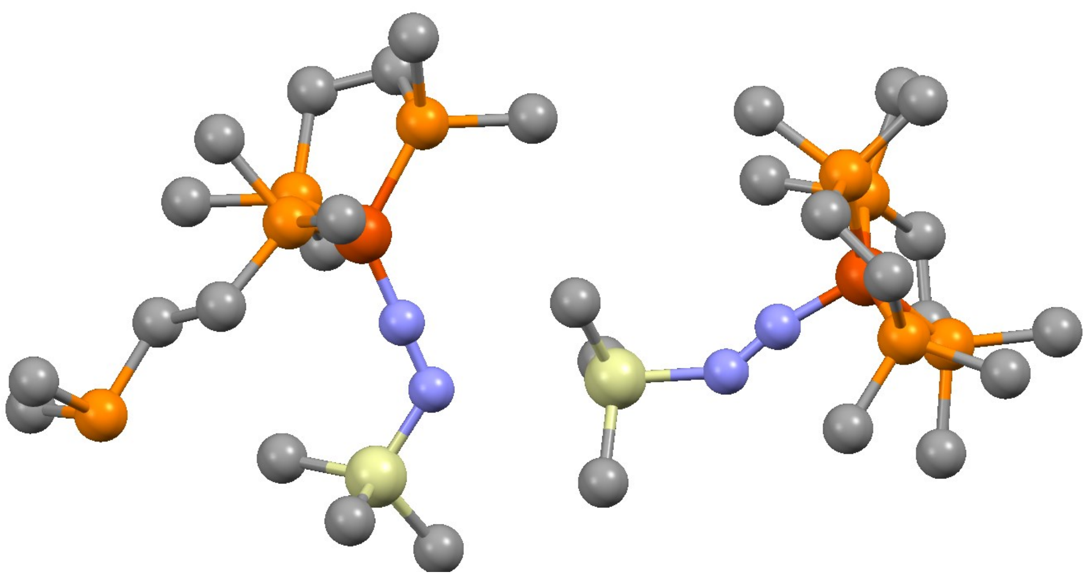

Figure S23. The structure of the transition state for the disproportionation of $Fe(dmpe)_2(N_2SiMe_3)$ ($\mathbf{2^{Me}}$).

Cartesian coordinates of the transition state for the disproportionation of 2^{Me}

Fe	-1.56960519	5.65899492	-0.79454070
P	-2.73564593	7.48888780	-0.76843114
P	-5.39252754	7.35567097	-4.51554996
P	0.07618460	6.04487105	0.54016229
P	-0.14015215	5.75762949	-2.39270299
Si	-2.96522044	1.72771024	1.89690919
N	-2.47193280	4.26512850	-0.86068603
C	-3.66601205	7.88893615	0.81398141
H	-2.94230431	8.04769617	1.62443112
H	-4.30476410	8.78280365	0.71855441
C	-4.52814552	7.36523656	-6.17314095
H	-3.82378129	8.20505268	-6.27578833
H	-3.97966855	6.42153660	-6.29854555
C	0.37253465	4.10839123	-3.11792700
H	-0.50770847	3.63605551	-3.57372652
H	1.16584523	4.20753808	-3.87505440
C	-3.89159115	7.52211076	-3.40298719
H	-3.27331049	6.62510367	-3.57059182
H	-3.29278541	8.39148607	-3.72327125
C	-0.25734682	6.70480315	-4.00687994
H	-1.08389086	6.30526781	-4.60946290
H	-0.46753482	7.76228630	-3.79783128
C	-4.23795911	7.60564313	-1.91703971
H	-4.88972056	6.76370937	-1.63381196
H	-4.78365627	8.53713968	-1.68799813
N	-3.11194415	3.18058577	-0.94814359
C	-2.03349378	9.20127977	-1.07711809
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H	-1.53167090	9.22401115	-2.05340479
H	-4.71679359	0.08725929	1.20214582
H	2.05519423	4.89525585	-0.34025408
H	-0.25220748	5.01679399	2.75739264
H	-5.08842535	1.73679457	0.63050672
C	-6.00667682	9.12175965	-4.50869031
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H	-6.44032653	9.35490604	-3.52687520
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H	0.43306472	8.47841260	0.82470591
H	-0.50032588	7.80740177	2.18192011
C	-1.57166572	1.02766957	0.85530451
H	-1.65803202	1.46728247	-0.14851426
H	-1.64058675	-0.06748717	0.78961983
H	-0.59238023	1.29706434	1.27477120
H	0.67404880	6.62958804	-4.59005440
C	-4.38475198	0.91007217	-2.32757129
H	-4.80758252	0.49488394	-1.40219893
H	-3.40442635	0.44029099	-2.49406541
H	-4.28645852	7.02285268	1.08011917
H	-2.75417432	2.76642556	-4.29998270
C	-4.70061609	1.15207619	1.47294635
H	-5.36747132	1.29646121	2.33569046
H	-5.27779413	7.42798808	-6.97441984
C	1.74812524	5.95308279	-0.36723684
H	2.52069962	6.53737896	0.15844581
Si	-4.22331614	2.79628607	-2.26542964
C	-2.85078494	3.52490224	2.39422381
H	-2.61898894	4.15629128	1.51074757
H	-2.05466969	3.67226841	3.13683089
H	-3.80145026	3.86278001	2.83191520
C	0.48025632	4.87333783	1.95216962
H	0.40390263	3.84007261	1.58940751
H	1.49118919	5.05525860	2.35055316
H	-5.20542036	9.84452911	-4.72797793
H	-5.04524023	0.61510423	-3.15756141
C	-5.94003549	3.54631243	-1.96435274
H	-5.90368547	4.64325962	-2.02881257
C	1.54116304	6.40635137	-1.81025696
H	2.35220008	6.07668590	-2.48012190
H	1.48582860	7.50518322	-1.86795829
H	-2.81329431	9.97961323	-1.05230304
H	-6.33047937	3.27802094	-0.97157910
H	-6.66089053	3.19504593	-2.71951158
C	-3.56373102	3.41145736	-3.92899613
H	1.27641465	7.58733818	2.12679825
H	-4.35717986	3.44415903	-4.69046141
H	-3.15860679	4.42621756	-3.80483888
H	0.71634321	3.45642878	-2.30442141

Fe	-1.49502443	0.48218219	6.10473774
P	0.67100628	0.34323008	5.60017152
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H	1.69349781	-1.75807612	6.31583780
H	1.99093782	-1.49759113	4.58594782
C	-0.00244150	-2.29281862	5.07030081
H	0.18771170	-3.36892629	5.20184777
H	-0.34999067	-2.13259050	4.03873909
P	-1.38112105	-1.71251443	6.19532665
C	1.14316514	1.08964729	3.96708758
H	2.21107024	0.94461800	3.75092334
H	0.91620995	2.16327838	3.96288448
H	-0.31394995	3.62006425	9.13040482
H	0.75882467	2.26800784	8.66479964
H	-3.26329248	3.51730431	6.60526248
P	-1.16042417	2.42375486	7.12273533
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H	2.08009473	2.04621884	6.72162103
C	-4.93299547	0.38349385	6.22115521
C	-0.28620173	2.58322527	8.76296908
N	-2.16604256	0.74691096	4.52880023
N	-2.72230949	0.73015165	3.48307459
C	-2.79409389	-2.70469899	5.50641848
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H	-5.83612334	0.43016092	6.84535633
C	-3.85833224	-0.72107566	8.60335147
H	-3.07021846	-0.74042526	9.36723711
H	-3.98934887	-1.73489564	8.20550420
C	-0.99579114	-2.70134569	7.73006432
H	-0.92990214	-3.77692076	7.50819592
H	-1.76986531	-2.53956410	8.48877364
H	-4.93816659	-0.54843330	5.64239172
C	-0.38408820	3.84097905	6.20730599
H	-0.89743437	3.96931949	5.24594068
H	0.67616710	3.64522082	6.00424809
P	-3.39075612	0.47573415	7.25488002
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H	-4.73437906	2.32785399	8.22023759
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H	-2.69414270	4.05437207	8.20404255
H	0.54361493	0.61771978	3.17879193
H	3.04105770	0.64734985	6.18479654
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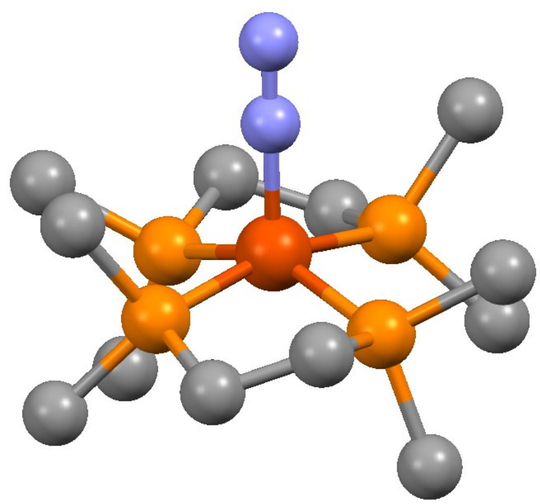
H	-2.50829322	-3.75790669	5.37382530
H	-0.04158704	-2.35473593	8.14766069
H	-0.46160887	4.77186883	6.78699433
H	-4.80393796	-0.40764346	9.06869259

Cartesian coordinates for geometry optimized Fe-containing species



$Fe(N_2)(dmpe)_2$ (1^{Me})

Fe	-0.00000000	0.00000000	0.42376047
P	-1.29295064	1.75897335	0.12391708
C	-3.07669529	1.28772110	-0.26752853
H	-3.18702760	1.33127967	-1.36209810
H	-3.76913448	2.02649705	0.16417452
C	-3.32418830	-0.12839242	0.23786702
H	-4.21820401	-0.58853707	-0.21165203
H	-3.45014003	-0.13985757	1.33119744
P	-1.78587290	-1.13807196	-0.13264146
C	-1.52930040	2.86161811	1.61155387

H	-2.24568133	3.67160699	1.41066971
H	-0.56396156	3.29693077	1.90138740
H	3.14775004	2.20304628	-1.94169130
H	1.39017982	2.35068455	-2.24943766
H	3.45014003	0.13985757	1.33119744
P	1.78587290	1.13807196	-0.13264146
C	-1.07268118	3.08698468	-1.16997354
H	-1.00507696	2.62052179	-2.16144199
H	-0.15519253	3.66227725	-0.99045756
C	1.52930040	-2.86161811	1.61155387
C	2.17859289	1.68402472	-1.88023565
N	-0.00000000	0.00000000	2.22382082
N	-0.00000000	0.00000000	3.36525424
C	-2.23517240	-2.70621371	0.77388547
H	-2.16464458	-2.52158156	1.85412482
H	-1.53914386	-3.51604173	0.51824149
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C	1.07268118	-3.08698468	-1.16997354
H	1.00507696	-2.62052179	-2.16144199
H	0.15519253	-3.66227725	-0.99045756
C	-2.17859289	-1.68402472	-1.88023565
H	-3.14775004	-2.20304628	-1.94169130
H	-1.39017982	-2.35068455	-2.24943766
H	0.56396156	-3.29693077	1.90138740
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H	2.16464458	2.52158156	1.85412482
H	1.53914386	3.51604173	0.51824149
P	1.29295064	-1.75897335	0.12391708
C	3.07669529	-1.28772110	-0.26752853
H	3.18702760	-1.33127967	-1.36209810
H	3.76913448	-2.02649705	0.16417452
C	3.32418830	0.12839242	0.23786702
H	4.21820401	0.58853707	-0.21165203
H	-1.88399777	2.25553230	2.45498344
H	-1.92606712	3.78111162	-1.15352208
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H	2.19361088	0.79854064	-2.52899701
H	-3.25586786	-3.03399712	0.52587505
H	-2.19361088	-0.79854064	-2.52899701
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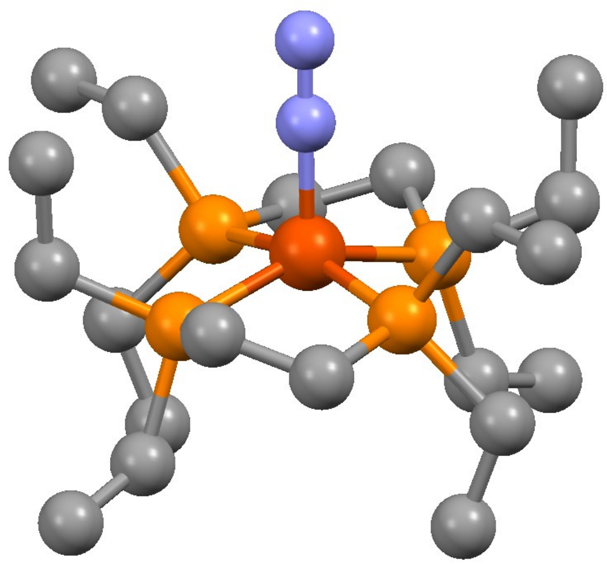
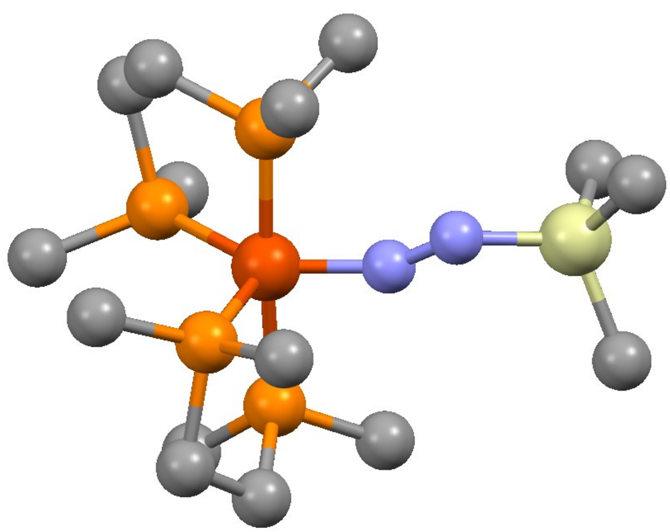


$Fe(N_2)(depe)_2$ (1^{Et})

Fe	3.88294390	5.85956077	8.49846107
P	5.17738460	6.39522501	6.77897024
C	6.94336653	5.89752987	7.17387408
H	6.96407991	4.79675354	7.14575148
H	7.65283853	6.26453186	6.41469410
C	7.26952956	6.40375318	8.57844885
H	7.49942925	7.48040388	8.55369349
H	8.14092543	5.89567906	9.02069429
P	5.74781040	6.16882661	9.67822698
N	3.88294149	4.07061657	8.49846264
N	3.88293994	2.92520176	8.49846365
C	5.38508866	8.20722099	6.27281103
H	4.40270742	8.50724851	5.87539461
H	5.49130182	8.74874782	7.22620032
C	6.49564569	8.61978919	5.29659330
H	6.39769372	8.12851740	4.31782814
H	7.49649730	8.38697594	5.68891822
H	6.46227673	9.70601046	5.11735455
C	4.98163036	5.62648588	5.06698888
H	3.97488310	5.90421519	4.71391739
H	5.69508751	6.11689151	4.38500236
C	5.16085319	4.10312983	5.00576659

H	4.88160659	3.71850100	4.01286514
H	4.54545260	3.58776945	5.75631828
H	6.20671948	3.81394024	5.18370781
C	6.08409417	7.51135841	10.96233170
H	5.34984779	7.36586022	11.77166393
H	7.07444726	7.31592383	11.40293309
C	6.01912610	8.95003338	10.43572823
H	6.87397670	9.17977988	9.78279762
H	6.04180616	9.67450410	11.26418128
H	5.10116642	9.12154817	9.85399470
C	6.23778132	4.64114139	10.67326612
H	5.35084824	4.37707665	11.26950124
H	6.32100684	3.84409898	9.91660888
C	7.48502990	4.66797641	11.56550489
H	8.38614714	4.98249962	11.01680042
H	7.68697136	3.66316710	11.96850996
H	7.36523742	5.34357797	12.42478283
P	2.58850464	6.39523153	10.21795095
C	0.82252137	5.89754046	9.82304798
H	0.80180502	4.79676424	9.85117252
H	0.11305036	6.26454570	10.58222732
C	0.49635970	6.40376217	8.41847232
H	0.26646292	7.48041354	8.44322578
H	-0.37503754	5.89568963	7.97622778
P	2.01807823	6.16882956	7.31869460
C	2.38080547	8.20722897	10.72410696
H	3.36318752	8.50725454	11.12152285
H	2.27459377	8.74875441	9.77071672
C	1.27024956	8.61980189	11.70032397
H	1.36820020	8.12853156	12.67908999
H	0.26939732	8.38699065	11.30799946
H	1.30362145	9.70602338	11.87956080
C	2.78425681	5.62649490	11.92993366
H	3.79100482	5.90422212	12.28300466
H	2.07080099	6.11690366	12.61191932
C	2.60502987	4.10313944	11.99115864
H	2.88427544	3.71851161	12.98406077
H	3.22042907	3.58777607	11.24060786
H	1.55916280	3.81395236	11.81321793
C	1.68179809	7.51136000	6.03458752

H	2.41604407	7.36585840	5.22525554
H	0.69144446	7.31592732	5.59398647
C	1.74677004	8.95003573	6.56118845
H	0.89192005	9.17978568	7.21411865
H	1.72409193	9.67450505	5.73273412
H	2.66473018	9.12154907	7.14292168
C	1.52810319	4.64114391	6.32365816
H	2.41503555	4.37707573	5.72742351
H	1.44487552	3.84410306	7.08031681
C	0.28085468	4.66798072	5.43141935
H	-0.62026171	4.98250733	5.98012326
H	0.07891051	3.66317124	5.02841604
H	0.40064899	5.34358044	4.57214021

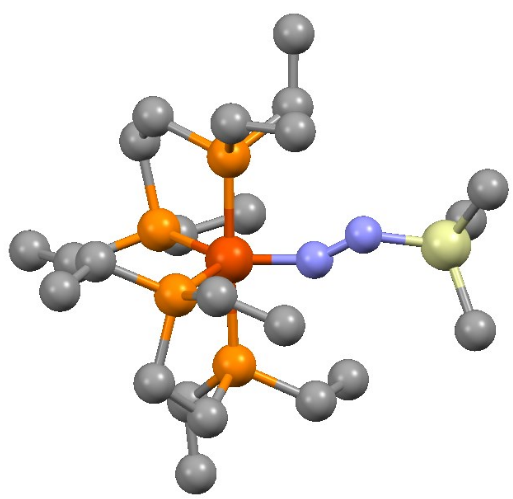


Fe(dmpe)$_2$(N$_2$SiMe$_3$) (2^{Me})

Fe	4.13880939	19.36070235	13.79569006
P	4.52210138	19.35677070	11.64919677
P	2.43199297	20.66152029	13.26164519
P	5.86800612	20.53228522	14.41846234
P	3.62295655	19.22149824	16.00599539
Si	5.11261637	14.98533992	13.46715602
N	4.56632004	17.63509394	13.81477810
N	5.26282563	16.74046284	13.27846762
C	2.38902096	21.04059470	11.40451078
H	1.69833563	20.31913616	10.94253122

H	1.97824576	22.04537043	11.22601782
C	2.20030065	22.40365334	13.92229283
H	2.12367895	22.38689536	15.01621968
H	1.29516272	22.87691926	13.51159441
H	3.07742358	23.00516155	13.64925501
C	6.39991949	22.21223416	13.79604759
H	6.62320153	22.15736374	12.72169321
H	7.29474231	22.57903322	14.32173655
H	5.58066239	22.92974250	13.93707935
C	2.38024588	20.26940972	16.92718141
H	2.62670268	21.33269008	16.81492121
H	2.38682700	20.01961123	17.99776892
H	1.36957119	20.10415586	16.53344177
C	3.73068763	17.99372975	10.66652584
H	4.12219278	17.04121947	11.04533404
H	3.95497124	18.08397849	9.59402125
H	2.64491091	18.00848181	10.82240021
C	6.46610880	14.27035027	12.36441423
H	6.32467363	14.57526652	11.31762008
H	6.46714696	13.17063850	12.40013743
H	7.45766508	14.62223016	12.68494989
C	7.51744303	19.66330113	14.32169016
H	7.42098937	18.66616967	14.77028616
H	8.30633979	20.23080601	14.83763073
H	7.80647056	19.52166045	13.27338649
C	5.82283629	20.88972903	16.27021761
H	6.83285021	21.09918509	16.65640927
H	5.21849642	21.80049363	16.41055165
C	0.67087195	20.06620798	13.47390107
H	0.58213273	19.06667469	13.02875749
H	-0.05242966	20.74781281	13.00054076
H	0.42982902	19.98274223	14.54156271
C	5.37973112	14.39700608	15.25130470
H	6.32437275	14.78083144	15.66294473
H	5.41827289	13.29693167	15.28765360
H	4.56217332	14.72002365	15.91148403
C	3.79424375	20.86652899	10.82685136
H	4.43620009	21.72225191	11.08515212
H	3.79008110	20.76236643	9.73048415
C	6.23235264	19.26445928	10.93909770

H	6.82329685	20.13596889	11.24795470
H	6.20518996	19.21881571	9.84087908
H	6.70588570	18.35227524	11.32794582
C	3.40960510	14.39659234	12.88146015
H	2.61264040	14.88513188	13.46081594
H	3.30162748	13.30799071	13.00335792
H	3.24764596	14.63499472	11.82043118
C	5.17027209	19.69616417	16.96988088
H	4.93255908	19.90214759	18.02556300
H	5.83884964	18.82183685	16.94205331
C	3.22950615	17.56589816	16.74193341
H	2.20999647	17.27465270	16.45594371
H	3.31105740	17.57940337	17.83841006
H	3.92691181	16.83224509	16.32157633



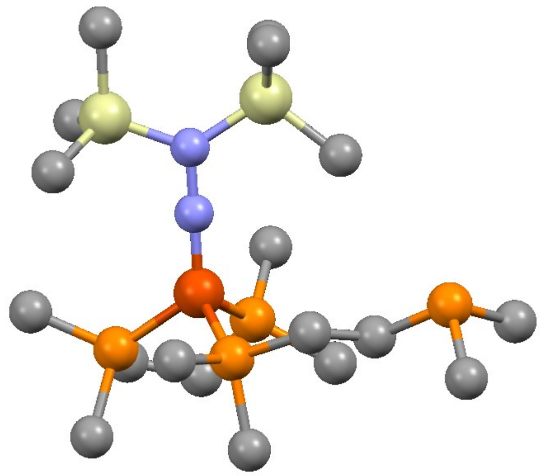
Fe(depe)$_2$(N$_2$SiMe$_3$) (2^{Et})

Fe	15.81579601	9.46841124	2.93227813
P	15.33100602	11.53582546	3.60449244
P	14.19664141	9.80578585	1.45673090
P	17.40809665	9.08325920	4.55716046
P	17.50330913	9.57141943	1.52131881
Si	13.87180698	5.44816132	3.64356116
N	15.16959101	7.84625806	3.24311729
C	14.63137058	11.89872382	5.32115384
H	15.47806211	11.88827824	6.02478913

H	14.23366457	12.92667003	5.32222529
C	14.21809945	9.24087307	-0.33727409
H	13.41060120	9.78338410	-0.85857009
H	15.16536002	9.61269511	-0.76169211
C	17.77355512	8.15053054	0.30916448
H	16.97691030	8.24596394	-0.44669758
H	18.73060549	8.31139253	-0.21394605
C	13.91739182	11.63989597	1.19522660
H	14.73939465	11.99919684	0.55551950
H	12.97481706	11.82176117	0.65504218
C	17.76602520	11.01425695	0.32721662
H	16.84811444	11.07424922	-0.28057323
H	17.75890725	11.90892325	0.96898084
C	13.95175767	12.31610365	2.56526672
H	13.00276043	12.14390048	3.09720603
H	14.09028936	13.40640472	2.49580793
N	14.49732671	6.87488038	2.81934790
C	16.62332703	12.92486795	3.49099828
H	17.56870063	12.49873153	3.86096735
H	16.76555515	13.06720525	2.40711325
C	17.73025211	6.74893715	0.93016539
H	17.74554888	5.97618785	0.14534650
H	16.82131181	6.61177256	1.53297414
H	18.60075555	6.56621755	1.57821406
C	12.50476683	9.22079326	2.01471368
H	12.63574057	8.13912165	2.17747172
H	12.37030574	9.65680181	3.01809845
C	17.93414103	10.31664713	5.89048844
H	18.23404496	11.23365303	5.35832464
H	17.01412708	10.57369647	6.43856724
C	15.23389199	4.34045389	4.37191948
H	15.76081151	4.83680740	5.20023802
H	15.97798682	4.07321905	3.60598394
H	14.80207038	3.40438453	4.76416892
C	18.99967724	11.03789533	-0.58580005
H	19.03786907	11.97718252	-1.15922668
H	18.99106235	10.21395862	-1.31262351
H	19.93465624	10.96797210	-0.01085566
C	13.55899200	10.90118109	5.76869220
H	12.64928048	10.98111240	5.15361737

H	13.26262766	11.07958196	6.81400827
H	13.92568275	9.86787507	5.67708238
C	14.08452042	7.73024631	-0.56658384
H	14.20924260	7.48788850	-1.63333733
H	13.09646372	7.36339423	-0.25554461
H	14.82784387	7.16589569	0.01177205
C	12.64138712	5.91081007	5.01340447
H	13.13102016	6.48716867	5.81280607
H	12.20170180	5.00814814	5.46903659
H	11.81865857	6.52310668	4.61337820
C	17.25815225	7.51233108	5.56149760
H	17.04419745	6.72824210	4.82024293
H	18.23836976	7.28538529	6.01014968
C	11.28533666	9.50172567	1.12954267
H	11.37344385	9.02944762	0.13978851
H	11.11813700	10.57846080	0.97174883
H	10.37379592	9.09926911	1.59929016
C	19.16644627	9.58470680	2.42625381
H	19.97607084	9.22263438	1.77235301
H	19.38753996	10.63719481	2.67319556
C	16.35552235	14.27648866	4.16561680
H	17.15464344	14.99504840	3.92481164
H	16.31387055	14.18689004	5.25985245
H	15.40661948	14.72289793	3.83197185
C	19.02718811	9.90588162	6.88537903
H	19.97198041	9.64892802	6.38479288
H	18.72519625	9.04087060	7.49258474
H	19.24312590	10.73303290	7.57967272
C	12.96559694	4.48893442	2.29087813
H	12.14788965	5.08647525	1.86047759
H	12.53112452	3.55851243	2.68966403
H	13.65137356	4.22079539	1.47289070
C	19.05462741	8.74572847	3.70325162
H	19.90026024	8.91567956	4.38785076
H	19.04846227	7.67246054	3.45694428
C	16.15781385	7.54663531	6.62501086
H	15.18852098	7.78264929	6.16484295
H	16.35722017	8.30227343	7.39934876
H	16.06771174	6.57453741	7.13255064

Fe(dmpe)$_2$(NN(SiMe$_3$)$_2$) (3^{Me})

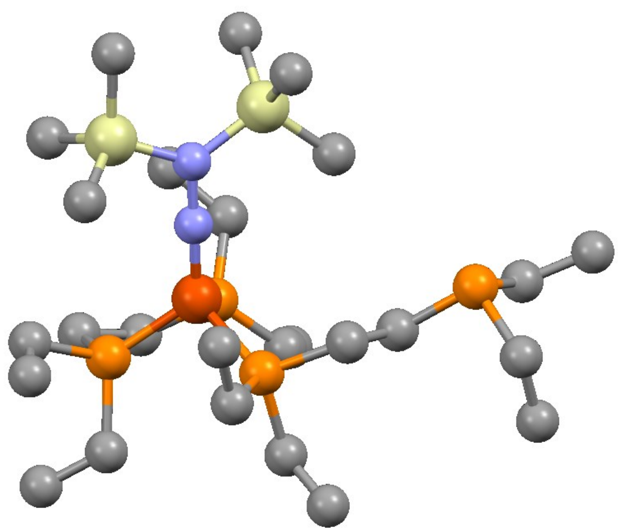


Fe	16.20569684	8.70134644	3.63417717
P	15.04231064	10.53801937	3.64425773
P	12.50029005	10.68188812	-0.18593705
P	17.79212659	9.18643090	5.01248650
P	17.69289230	8.83347823	2.07752847
Si	14.84822088	5.32623144	5.37288428
N	15.30144023	7.33648689	3.74142658
C	14.06506156	10.83936886	5.20913431
H	14.75581478	10.96584574	6.05308648
H	13.41739536	11.72702435	5.13659576
C	13.40991429	10.82376382	-1.81219389
H	14.14184210	11.64601685	-1.81489386
H	13.93091796	9.87894398	-2.01954347
C	18.09073832	7.20205468	1.25863705
H	17.20183996	6.84538579	0.72177729
H	18.92821616	7.28891277	0.55010021
C	13.98080110	10.70422168	0.96996747
H	14.58574165	9.81911739	0.72057830
H	14.59661098	11.59368224	0.75456300
C	17.66722943	9.89762404	0.54089586
H	16.82733379	9.60081038	-0.10054560
H	17.52768816	10.94951586	0.82224456
C	13.58866948	10.64540213	2.44621021
H	12.97117212	9.75423693	2.64059232

H	12.98881432	11.52694483	2.72877960
N	14.54855359	6.20627301	3.82946697
C	15.72743591	12.26143095	3.40664824
H	16.41494071	12.50026205	4.22683005
H	16.28818910	12.31472106	2.46475115
H	13.98615568	3.27392548	6.42643575
H	19.64925285	7.78400024	4.26871051
H	17.14722469	8.45682975	7.26855207
H	13.78634925	3.13291630	4.67388110
C	11.93274396	12.45481354	-0.02112749
H	11.15512484	12.65340651	-0.77168734
H	11.48343962	12.60766884	0.96933727
C	18.12623998	10.87518486	5.75485127
H	18.32907814	11.59878252	4.95502013
H	17.24634478	11.21701825	6.31605347
C	16.63512738	4.71338585	5.35334441
H	17.29442296	5.50299377	4.96726645
H	16.73506343	3.83931375	4.69314467
H	16.98325138	4.42279640	6.35572277
H	18.60294760	9.79790295	-0.03019473
C	14.68463547	4.05646922	1.70397093
H	14.70211003	3.23597211	2.43534419
H	15.72598108	4.31487155	1.46332060
H	13.44879570	9.95291391	5.40924445
H	14.76209695	7.34780710	0.91324408
C	13.70039461	3.82938809	5.51919666
H	12.64654446	4.11880380	5.62754410
H	12.68445831	10.99025096	-2.62032422
C	19.47546394	8.86983852	4.21127153
H	20.28600743	9.36929372	4.76536262
Si	13.74879954	5.57532653	2.34066894
C	14.51041551	6.50007786	6.80562282
H	14.99472065	7.46776860	6.62132490
H	14.89039522	6.08856335	7.75248734
H	13.43009897	6.67271742	6.91652981
C	17.96107547	8.19490928	6.57957903
H	17.88787928	7.12532882	6.35245975
H	18.92350346	8.40004087	7.07181584
H	12.75547453	13.17310167	-0.15877698
H	14.21082097	3.67291010	0.78693928

C	11.95907833	5.10574870	2.72607681
H	11.42161307	5.95279767	3.17605507
C	19.39071519	9.32362775	2.75374134
H	20.20013831	8.91133634	2.13138279
H	19.45039332	10.42177169	2.68753432
H	14.92219765	13.01190372	3.38944559
H	11.87616805	4.24651897	3.40372867
H	11.44350170	4.84185853	1.78960478
C	13.76333626	6.90401049	1.01372218
H	18.99041024	10.84453155	6.43471990
H	13.47187888	6.45664609	0.05150911
H	13.05514876	7.71395630	1.23486538
H	18.33517446	6.46386399	2.03259696

Fe(depe)$_2$(NN(SiMe$_3$)$_2$) (3^{Et})



Fe	16.22909536	8.75488330	3.66534636
P	15.09750956	10.63442084	3.60757006
P	12.39659107	10.49201690	-0.11051848
P	17.80827906	9.21983153	5.07334434
P	17.77203566	8.81292819	2.14524002
Si	14.84470254	5.27198588	5.29654131
N	15.32916693	7.38110510	3.75828566
C	14.19490093	11.08247115	5.20121917
H	14.98141408	11.26572016	5.95004341
H	13.64692027	12.02837230	5.06639659

C	13.19618711	10.63537123	-1.80382696
H	13.81491397	11.54433515	-1.87094638
H	13.88420298	9.77817803	-1.87464072
C	17.93547665	7.28429526	1.06184878
H	17.02197896	7.23891518	0.44877033
H	18.78046694	7.42928357	0.37139418
C	13.92335888	10.73599866	0.96065965
H	14.60468744	9.91074960	0.69968482
H	14.43829363	11.67411497	0.69929347
C	17.93215966	10.14874899	0.82296778
H	16.97500802	10.15098407	0.27888604
H	17.95913763	11.09252665	1.38869788
C	13.59986483	10.67255816	2.45489619
H	13.03927316	9.75157112	2.67607028
H	12.95719615	11.51811622	2.75081952
N	14.62603211	6.21145239	3.77491112
C	15.87640096	12.30234007	3.19387114
H	16.74744991	12.39689846	3.85698568
H	16.28512586	12.17817957	2.18021890
C	18.11107042	5.98690103	1.85238074
H	18.11760597	5.11432614	1.18220051
H	17.30048425	5.86410683	2.58232281
H	19.06249993	5.97976734	2.40397088
C	11.53067995	12.15787662	0.04951313
H	10.61034413	12.06731413	-0.54915894
H	11.18814643	12.20187443	1.09602956
C	18.38294384	10.96778625	5.50405439
H	18.58937906	11.44901525	4.53578736
H	17.49918487	11.48308734	5.91093532
C	16.65136668	4.74122486	5.43600026
H	17.31829374	5.59101174	5.23697688
H	16.88623562	3.95103872	4.70826652
H	16.87310614	4.35331534	6.44151820
C	19.10946827	10.09246371	-0.15841728
H	19.12008707	10.98597843	-0.80079442
H	19.05258968	9.21849562	-0.82066184
H	20.07568169	10.05422681	0.36421270
C	13.24686809	9.98433302	5.69086258
H	12.36437440	9.89742201	5.04160049
H	12.88671342	10.19607408	6.70819446

H	13.75328154	9.00902557	5.69387908
C	12.17693904	10.58152367	-2.94787183
H	12.67889227	10.57370615	-3.92640705
H	11.50340140	11.45027369	-2.93137118
H	11.55353356	9.67829771	-2.88122599
C	14.33816401	6.31628962	6.77884401
H	14.91729292	7.24547655	6.83223702
H	14.50294827	5.75367693	7.71068161
H	13.27231531	6.57985482	6.72552097
C	17.76687792	8.45038121	6.78318355
H	17.46888541	7.40367672	6.62910174
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C	12.28513147	13.43726487	-0.32309870
H	12.56491198	13.44988279	-1.38565683
H	13.20601796	13.55599013	0.26489552
H	11.66213916	14.32561559	-0.13883491
C	19.50955461	8.89700661	2.91844237
H	20.22299691	8.26879469	2.36409884
H	19.85831034	9.93821566	2.82859816
C	15.02227481	13.57391693	3.26500697
H	15.60157730	14.44479816	2.92277463
H	14.68838951	13.78875699	4.28877050
H	14.12793101	13.50816317	2.62975617
C	19.57988384	11.14588844	6.44512286
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H	19.79444637	12.21420150	6.60066622
C	13.75451202	3.72451052	5.29487370
H	12.68648025	3.96933909	5.36793864
H	14.01825359	3.13805372	6.18923803
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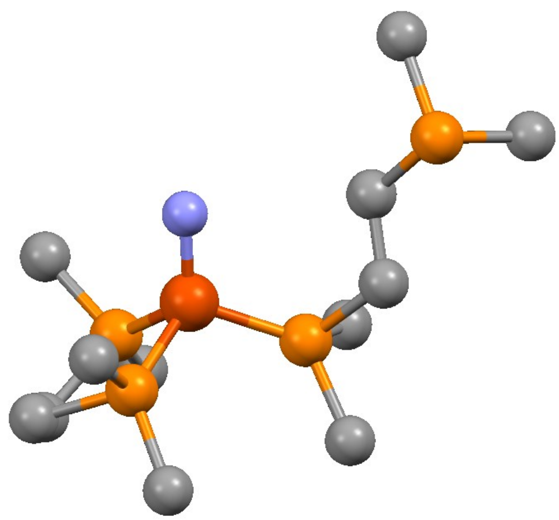
H	20.29435545	8.80875354	4.97161511
H	19.31359258	7.40614395	4.49461421
C	16.80737357	9.13936006	7.75853338
H	15.79826862	9.22346657	7.33167771
H	17.14447881	10.15469747	8.01086333
H	16.72925218	8.57572096	8.69928041
Si	13.76448603	5.66497660	2.28067965
C	14.57046158	4.08844747	1.60638383

H	14.57306009	3.26211076	2.33017236
H	15.61141517	4.27997094	1.31045776
H	14.02345179	3.74475160	0.71460460
C	11.94567702	5.32535975	2.66894031
H	11.47725743	6.20292512	3.13735644
H	11.80005471	4.46134211	3.32996312
H	11.40749240	5.12059621	1.73004049
C	13.87683570	7.00439332	0.97002947
H	13.74365805	6.55189570	-0.02414211
H	13.10017915	7.77146249	1.09419331
H	14.85424843	7.50272109	1.01127198

$[Fe(dmpe)_2N]^-$



Fe	19.14370965	13.69526398	3.61693823
P	18.06590249	15.25289172	2.62317012
P	14.44126098	12.74861193	1.37472232
P	19.44810244	14.23332261	5.65203458
P	21.21578271	14.06933465	3.29763601
H	17.82621173	16.46175738	0.42584233
N	18.55888806	12.22937845	3.34105470
C	17.65186083	16.97140922	3.28566036
H	18.58821258	17.53374683	3.40543187
H	16.97216471	17.52965877	2.61901806
C	14.80723257	11.11164200	0.54528412
H	15.45127776	11.22879585	-0.34054023

H	15.32098901	10.46319421	1.26785200
C	22.21406365	12.53626607	2.83431375
H	21.85690597	12.18125083	1.85762124
H	23.30067208	12.72056022	2.78791167
C	16.18726703	13.38734384	1.54096846
H	16.75542471	12.65964151	2.15583129
H	16.66218685	13.40465742	0.54421562
C	22.07733827	15.23666668	2.09007365
H	21.79926572	14.96117939	1.06291351
H	21.73762442	16.26444215	2.27856151
C	16.27706312	14.75342429	2.21896365
H	15.75360541	14.72235940	3.18817088
H	15.81048441	15.54869628	1.61011544
H	13.86767470	10.62428375	0.24701318
C	18.57549065	15.80198037	0.89411604
H	19.53531085	16.33162662	0.95636731
H	18.72097734	14.90972829	0.27098082
C	21.30248829	14.12375370	6.09467941
H	21.50303731	13.06144349	6.30756637
H	17.68187755	13.12861107	6.96509374
H	21.52424314	14.69622310	7.01149726
C	13.86414710	13.69797704	-0.13696613
H	12.89024170	13.30909684	-0.46908019
H	13.73231213	14.75615658	0.12781063
C	18.96896583	15.81772783	6.57363335
H	19.43942096	16.67880380	6.08023054
H	17.87827147	15.94350725	6.51526248
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C	22.12544378	14.59036484	4.89276516
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H	14.58334906	13.62612187	-0.96873090

7. References

1 Palatinus, L.; Chapuis, G., *J. Appl. Crystallogr.*, **2007**, *40*, 786.
2 Sheldrick, G. M., *Acta Crystallogr. Sect. C*, **2015**, *71*, 3.
3 Weitz, I. S.; Rabinovitz, M., *J. Chem. Soc. Perkin Trans. 1*, **1993**, 117.
4 Yakelis, N. A.; Bergman, R. G., *Organometallics*, **2005**, *24*, 3579.
5 LeSuer, R. J.; Buttolph, C.; Geiger, W. E., *Anal. Chem.*, **2004**, *76*, 6395.
6 Fields, R.; Haszeldine, R. N.; Hutton, R. E., *J. Chem. Soc. C*, **1967**, 2559.
7 Hill, P. J.; Doyle, L. R.; Crawford, A. D.; Myers, W. K.; Ashley, A. E., *J. Am. Chem. Soc.*, **2016**, *138*, 13521.
8 Doyle, L. R.; Hill, P. J.; Wildgoose, G. G.; Ashley, A. E., *Dalton Trans.*, **2016**, *45*, 7550.
9 Piascik, A. D.; Hill, P. J.; Crawford, A. D.; Doyle, L. R.; Green, J. C.; Ashley, A. E., *Chem. Commun.*, **2017**, *53*, 7657.
10 Prokopchuk, D. E.; Wiedner, E. S.; Walter, E. D.; Popescu, C. V.; Piro, N. A.; Kassel, W. S.; Bullock, R. M.; Mock, M. T., *J. Am. Chem. Soc.*, **2017**, *139*, 9291.
11 Dilworth, J. R., *Coord. Chem. Rev.*, **2017**, *330*, 53.
12 ADF2016, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
13 Vosko, S. H.; Wilk, L.; Nusair, M., *Can. J. Phys.*, **1980**, *58*, 1200.
14 Becke, A. D., *Phys. Rev. A*, **1988**, *38*, 3098.