Cationic silyldiazenido complexes of the Fe(diphosphine)$_2$(N_2) platform: structural and electronic models for an elusive first intermediate in N_2 fixation

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Electronic Supplementary Information

Contents:

1. Experimental details

General considerations

All chemical manipulations were performed under a N_2 or Ar atmosphere either using standard Schlenk-line techniques or an 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. 1,2 difluorobenzene (1,2 DFB) was purchased from Fluorochem and purified by stirring with basic alumina, distillation onto CaH_2, then distillation onto 4Å molecular sieves. 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, THF and 1,2 DFB were 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: 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 recrystallisation from cold pentane. Me_3SiCl was purchased from Sigma and stored over 4 Å molecular sieves. $KBAr^F{}_4$, Fe(depe)$_2$(N_2) (**1**), Fe(dmpe)$_2$(N_2) (**2**) were prepared according to literature procedures.[1, 2, 3] Partial isotopic enrichment of these $^{14}N_2$-isotopomers was achieved *via* N_2 exchange under a $^{15}N_2$ atmosphere, affording samples of Fe(depe)$_2$($^{15}N_2$) (**1-$^{15}N_2$**) and Fe(dmpe)$_2$($^{15}N_2$) (**2-$^{15}N_2$**) .

NMR spectra were recorded using Bruker AV-400 (400 MHz) and Varian Unity-plus (500 MHz) spectrometers. Chemical shifts, δ, are reported in parts per million (ppm). ^{1}H, ^{13}C and ^{29}Si chemical shifts are given relative to Me_4Si and referenced internally to the appropriate residual solvent peak. ^{11}B, ^{15}N, ^{19}F and ^{31}P chemical shifts were referenced externally to $BF_3{\cdot}OEt_2$, $MeNO_2$, $CFCl_3$ and 85% aqueous H_3PO_4 (δ = 0 ppm) respectively. ^{1}H 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 (δ = –5.3 ppm) resonances, respectively. Air or moisture sensitive samples were prepared inside a glovebox using NMR tubes fitted with J. Young valves.

Solution IR spectra were recorded aon Perkin-Elmer GX spectrometer. Solutions were recorded in an air-tight Specac® Omni Cell™ filled with 0.01-0.015 M solutions *via* syringe in a glovebox. $^{15}N_2$ stretches of isotopically labelled samples were established by comparison with the unshifted $^{14}N_2$ stretch in unlabelled samples.

Single crystal X-ray diffraction data for **3** and **4** were collected with an Oxford Diffraction Xcalibur unit; the crystal was mounted on a nylon MicroLoop™ using perfluoropolyether oil and recorded in a stream of N_2 at 173 K. The structure was solved in Olex2[3] by direct methods using the SHELXS[4] solution program and all data were subsequently refined with the ShelXL[5] refinement package.

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

Synthesis and characterisation

$[Fe(depe)_2(N_2SiMe_3)][BAr^F{}_4]$ (3): Inside an N_2 glovebox, a solution of $KBAr^F{}_4$ (180 mg, 0.20 mmol) and Me_3SiCl (25.3 µL, 0.20 mmol) in a 5:1 DFB/Et_2O mixture (3 mL) was added dropwise to a stirring solution of $FeN_2(depe)_2$ (100 mg, 0.20 mmol) in DFB (2 mL), forming a dark purple solution. The reaction was stirred for 5 minutes before being filtered through Celite® and layered with pentane at -30°C, producing dark red crystals of the product, which were washed with pentane then dried *in vacuo* (180 mg, 66%). The ^{15}N labelled analogue **3-$^{15}N_2$** was prepared similarly, in an Ar box, using **1-$^{15}N_2$**.

^{1}H NMR (400.4 MHz, 1,2 DFB) δ: 8.24 (s, 8H, *o*-H), 7.60 (s, 4H, *p*-H), 1.72 (br, t, 8H, PCH_2CH_2P), 1.60 (m, 16H, PCH_2), 1.05 (m, 24H, CH_2CH_3), 0.20 (s, 9H, SiCH_3).

^{11}B NMR (128.4 MHz, 1,2 DFB) δ: –6.1 (s).

$^{13}C\{^{1}H\}$ NMR (100.0 MHz, 1,2 DFB) δ: 162.6 (q, C_{ipso}), 150.7 (d, C_{para}), 135.1 (s, $C_{ortho,\ meta}$), 129.9 (q, CF_3), 23.9 & 20.1 (dquin, PCH_2CH_3), 23.4 (quin, PCH_2CH_2P), 7.7 (d, CH_2CH_3), 2.3 (s, SiCH_3).

$^{15}N\{^{1}H\}$ NMR (40.55 MHz, 1,2 DFB) δ: –9.4 (d, $^{1}J_{NN}$ = 15 Hz, N_α), –139.1 (d, $^{1}J_{NN}$ = 15 Hz, N_β).

^{19}F NMR (376.4 MHz, 1,2 DFB) δ: –63.1 (s).

^{29}Si NMR (99.4 MHz, 1,2 DFB) δ: 6.4 (s).

$^{31}P\{^{1}H\}$ NMR (162.0 MHz, 1,2 DFB) δ: 77.0 (s).

Anal. Calcd. for $C_{55}H_{69}BF_{24}FeN_2P_4Si$: C 46.11, H 4.85, N 1.96. Found: C 45.92, H 4.65, N 2.03.

IR (1,2 DFB, under N_2, cm–1): 1732 ($^{14}N_2$), 1669 ($^{15}N_2$).

[Fe(dmpe)$_2$(N$_2$SiMe$_3$)][BAr$^F_4$] (4): In an N_2 glovebox, a solution of $KBAr^F_4$ (117 mg, 0.13 mmol) and Me_3SiCl (25.3 µL, 0.2 mmol) in DFB (2 mL) was added dropwise to a stirring solution of $FeN_2(dmpe)_2$ (50 mg, 0.13 mmol) in DFB (4 mL), forming a dark red solution. The reaction was stirred for 10 minutes before being filtered through Celite®, layered with pentane and cooled to –30 °C for 48 hours, producing dark red crystals of the product, which were washed with cold Et_2O and pentane then dried *in vacuo* (150 mg, 70%).The ^{15}N labelled analogue **4-$^{15}N_2$** was prepared similarly, using **2-$^{15}N_2$**.

^1H NMR (400.4 MHz, 1,2 DFB) *δ*: 8.24 (s, 8H, *o*-H), 7.60 (s, 4H, *p*-H), 1.67 (dm, 8H, $^2J_{PH}$ = 55 Hz, PC*H$_2$*C*H$_2$*P), 1.32 (d, 24H, $^2J_{PH}$ = 49 Hz, PC*H$_3$*), 0.16 (s, 9H, SiC*H$_3$*).

^{11}B NMR (128.4 MHz, 1,2 DFB) *δ*: –6.1 (s).

$^{13}C\{^1H\}$ NMR (100.0 MHz, 1,2 DFB) *δ*: 162.0 (q, C$_{ipso}$), 150.1 (d, C$_{para}$), 134.5 (s, C$_{ortho, meta}$), 129.2 (q, CF_3), 30.6 (quin, P*C*H$_2$*C*H$_2$P), 17.8 (dquin, P*C*H$_3$), 3.7 (s, Si*C*H$_3$).

$^{15}N\{^1H\}$ NMR (40.55 MHz, 1,2 DFB) *δ*: –0.6 (d,$^1J_{NN}$ = 16 Hz, N_α), –130.3 (d, $^1J_{NN}$ = 16 Hz, N_β).

^{19}F NMR (376.4 MHz, 1,2 DFB) *δ*: –63.1 (s).

^{29}Si NMR (99.4 MHz, 1,2 DFB) *δ*: 9.3 (s).

$^{31}P\{^1H\}$ NMR (162.0 MHz, 1,2 DFB) *δ*: 58.6 (s).

Anal. Calcd. for $C_{47}H_{53}BF_{24}FeN_2P_4Si$: C 42.75, H 4.05, N 2.12. Found: C 42.84, H 4.15, N 2.20.

IR (1,2 DFB, under N_2, cm–1): 1727 ($^{14}N_2$), 1668 ($^{15}N_2$).

2. NMR spectra

NMR spectra for 3 - $[Fe(depe)_2(N_2SiMe_3)][BAr^F_4]$

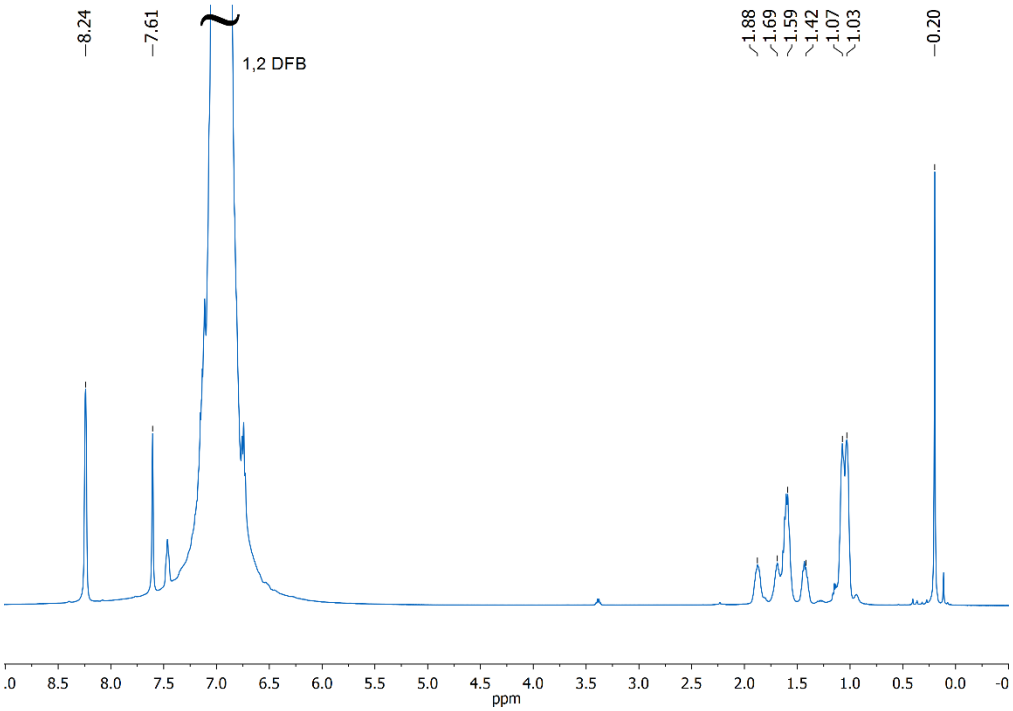


Fig. S1 ^{1}H NMR spectrum of **3** in 1,2 DFB under an Ar atmosphere.

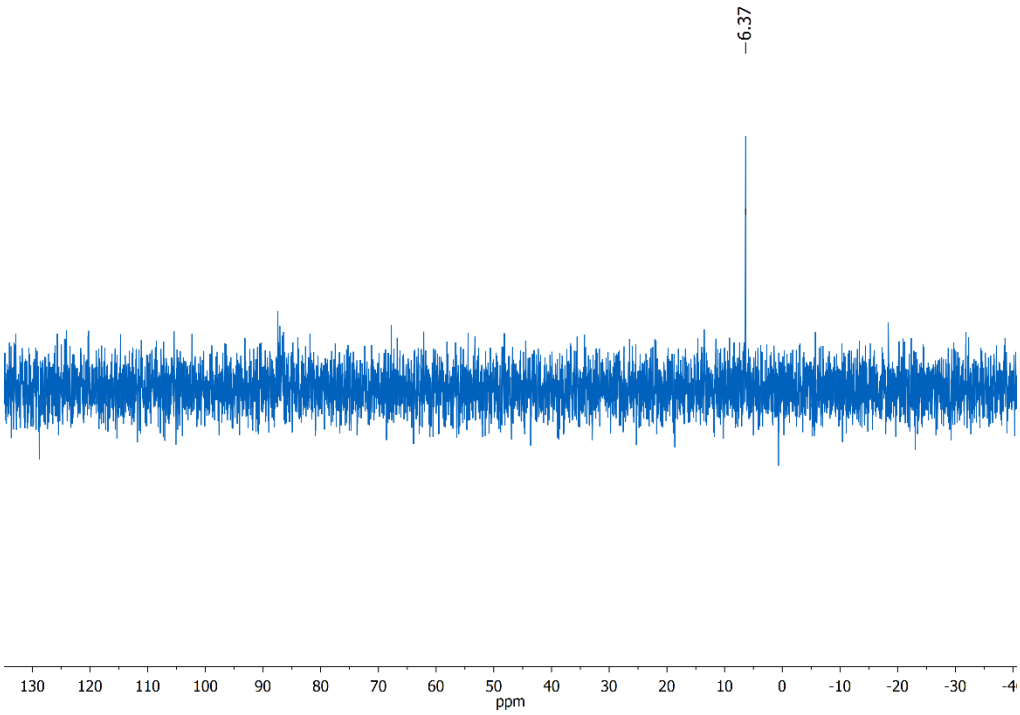


Fig. S2 ^{29}Si{^{1}H} NMR spectrum **3** in 1,2 DFB under an Ar atmosphere.

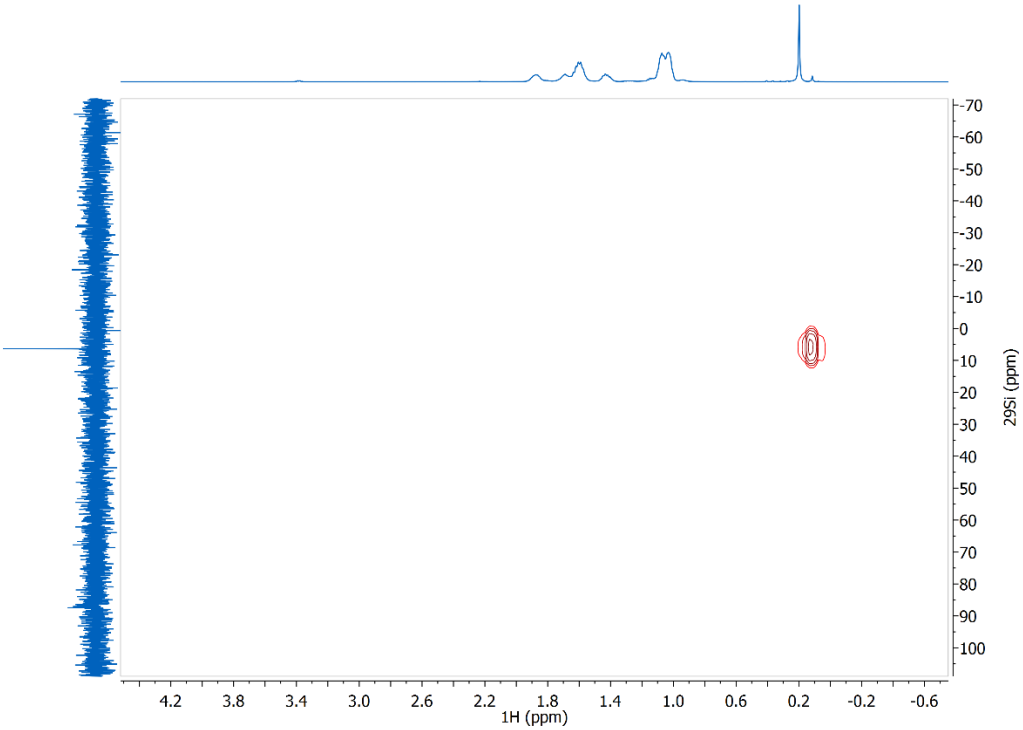


Fig. S3 ^{1}H-^{29}Si HMBC NMR spectrum **3** in 1,2 DFB under an Ar atmosphere.

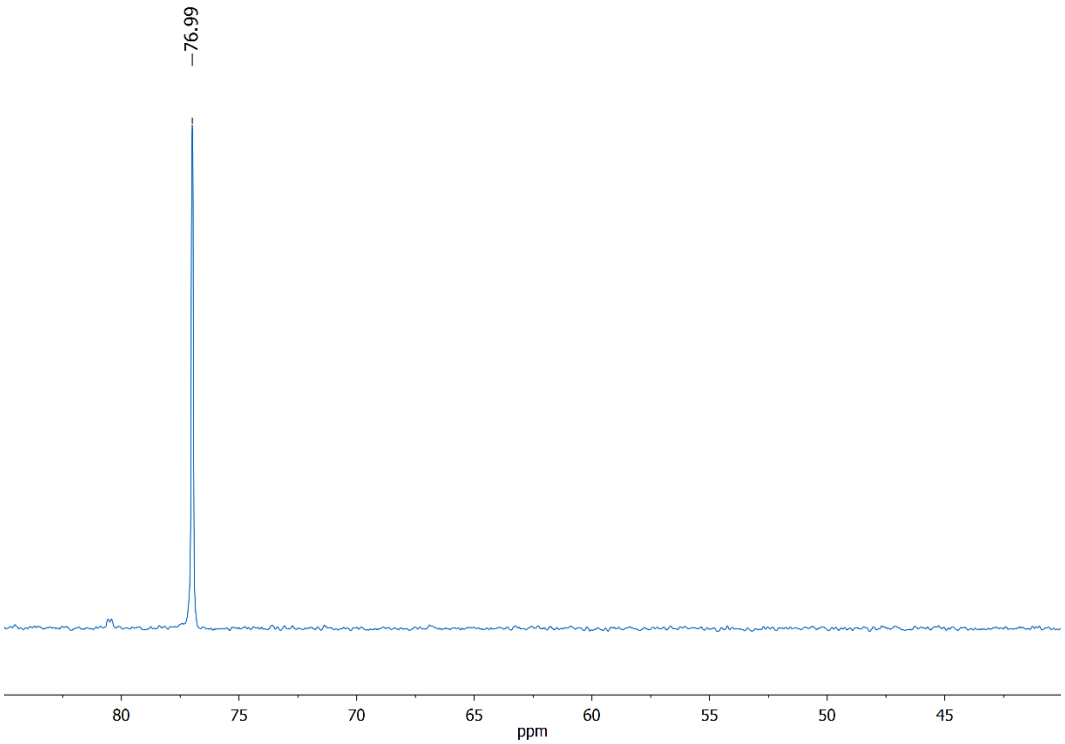


Fig. S4 $^{31}P\{^{1}H\}$ NMR spectrum of **3** in 1,2 DFB under an Ar atmosphere.

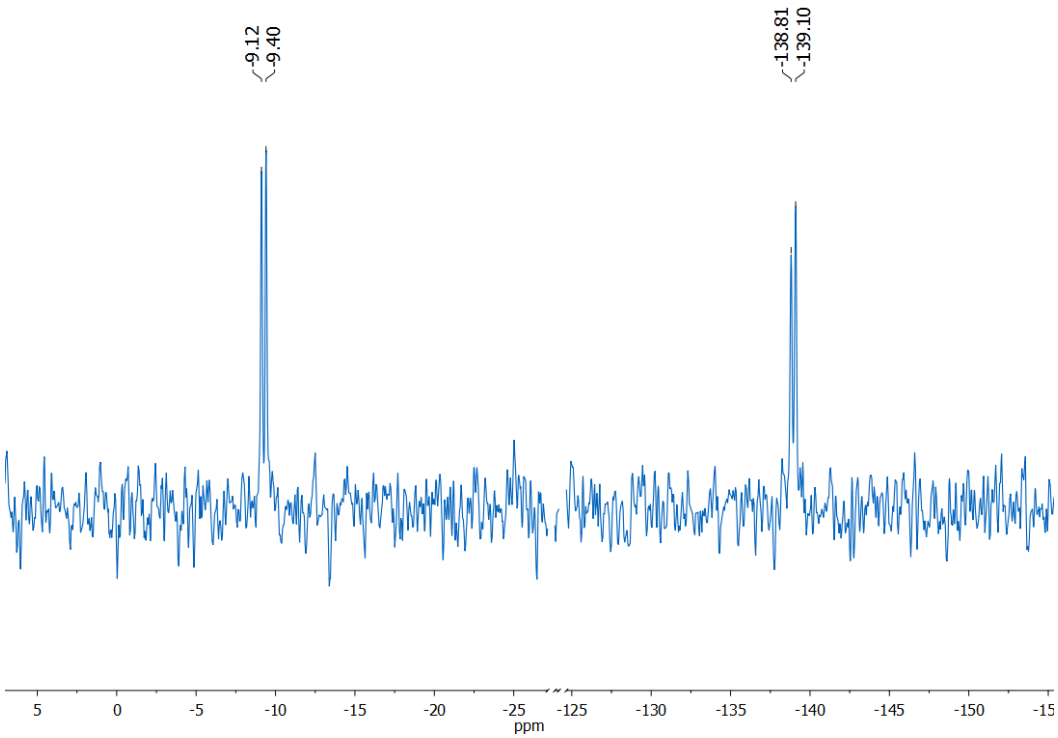


Fig. S5 $^{15}N\{^{1}H\}$ NMR spectrum of **3-$^{15}N_2$** in 1,2 DFB under an Ar atmosphere.

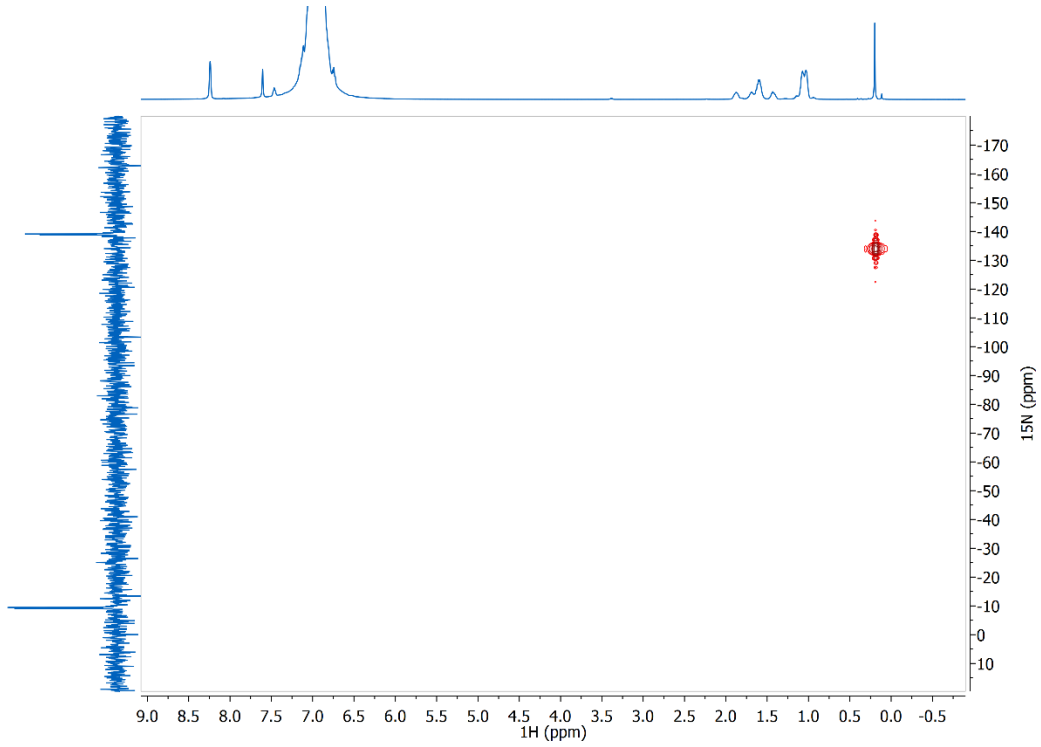


Fig. S6 ^{1}H-^{15}N HMBC NMR spectrum **3-$^{15}N_2$** in 1,2 DFB under an Ar atmosphere.

NMR spectra for 4 - $[Fe(dmpe)_2(N_2SiMe_3)][BAr^F{}_4]$

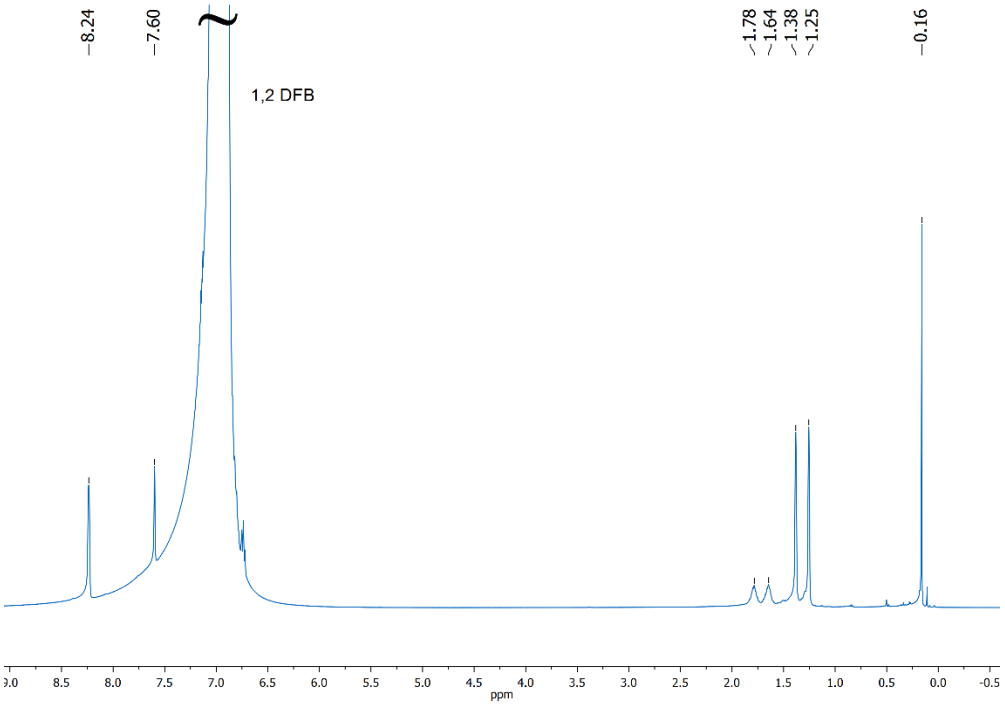


Fig. S7 ^{1}H NMR spectrum of **4** in 1,2 DFB under an Ar atmosphere.

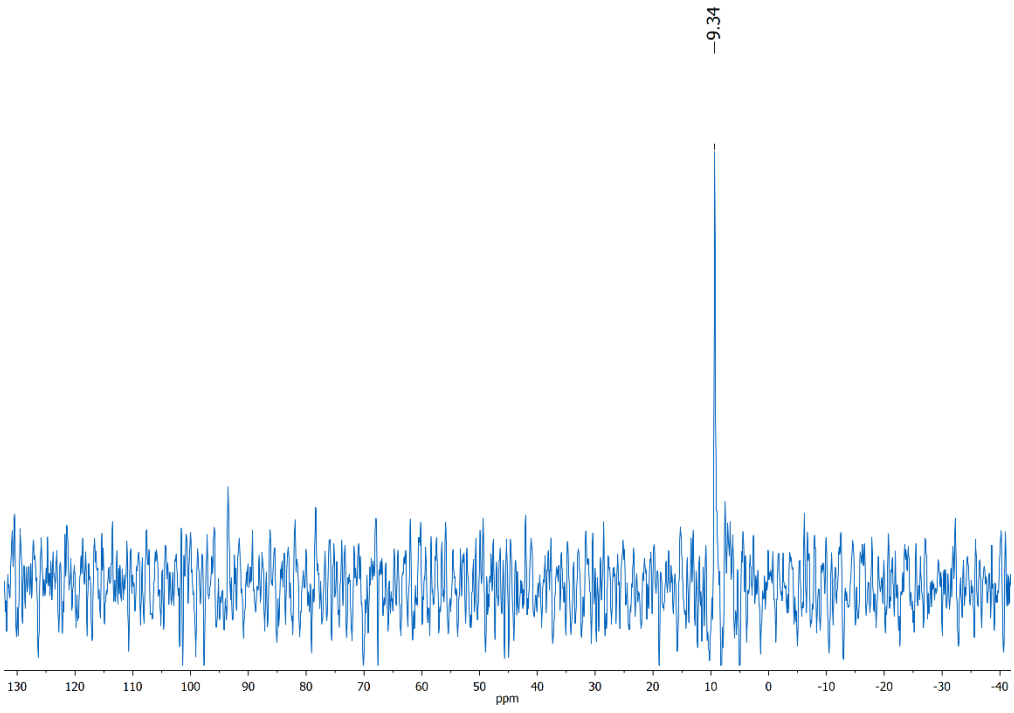


Fig. S8 ^{29}Si{^{1}H} NMR spectrum **4** in 1,2 DFB under an Ar atmosphere.

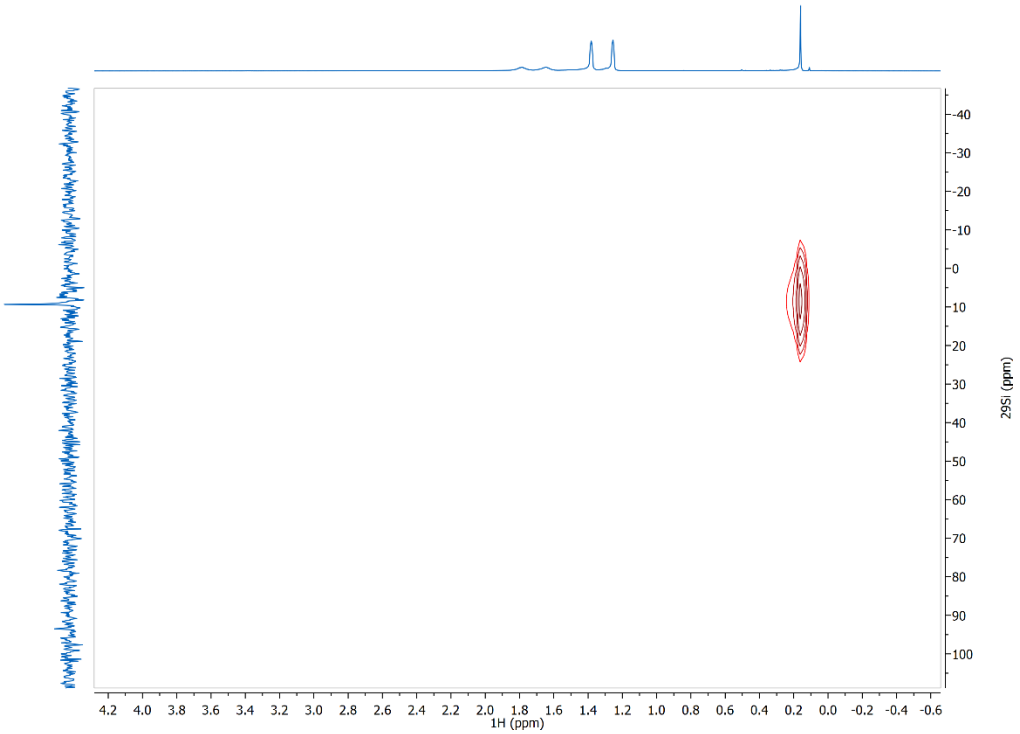


Fig. S9 ^{1}H-^{29}Si HMBC NMR spectrum **4** in 1,2 DFB under an Ar atmosphere.

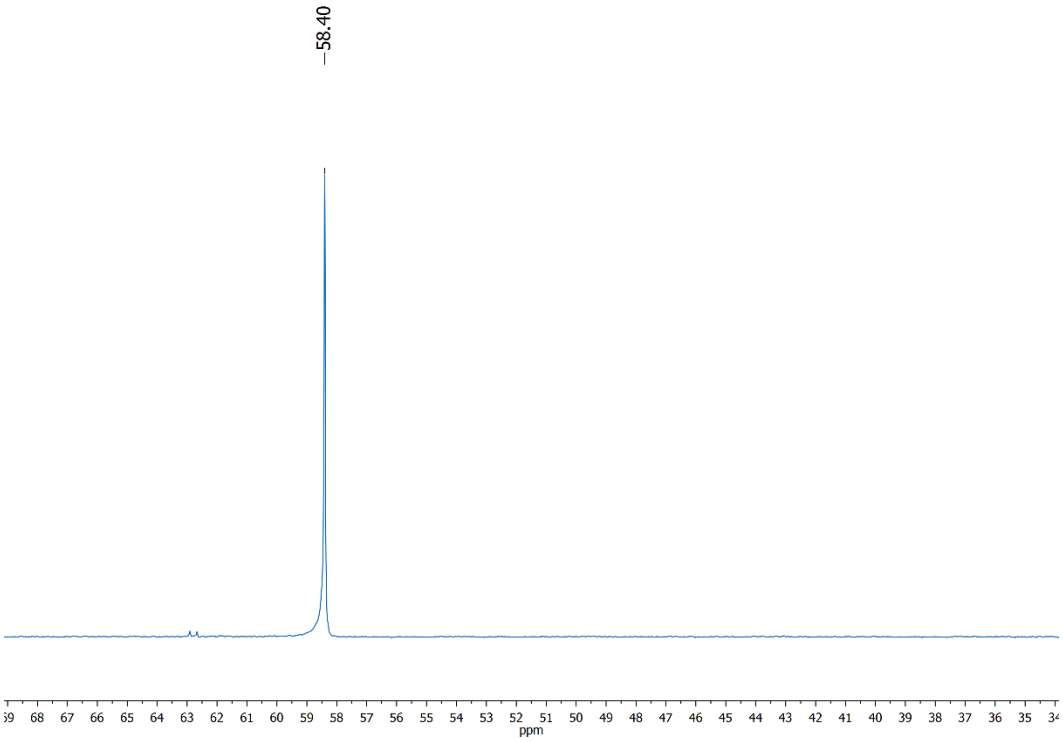


Fig. S10 $^{31}P\{^{1}H\}$ NMR spectrum of **4** in 1,2 DFB under an Ar atmosphere.

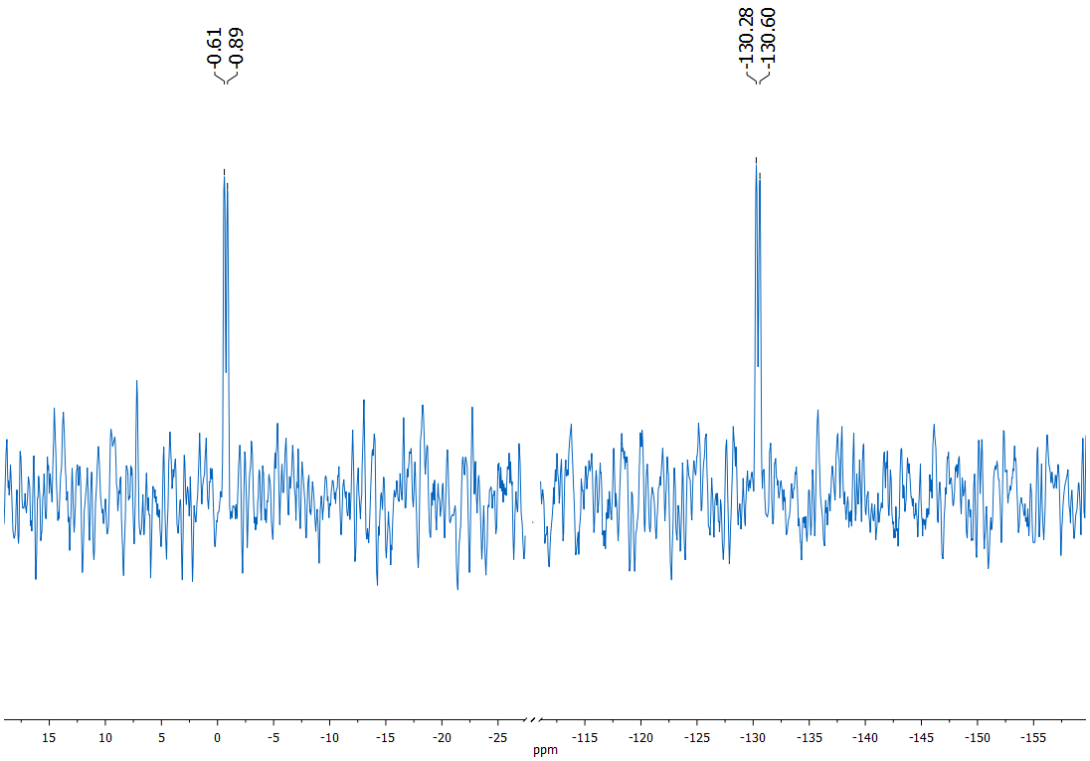


Fig. S11 $^{15}N\{^{1}H\}$ NMR spectrum of **4-$^{15}N_2$** in 1,2 DFB under an Ar atmosphere.

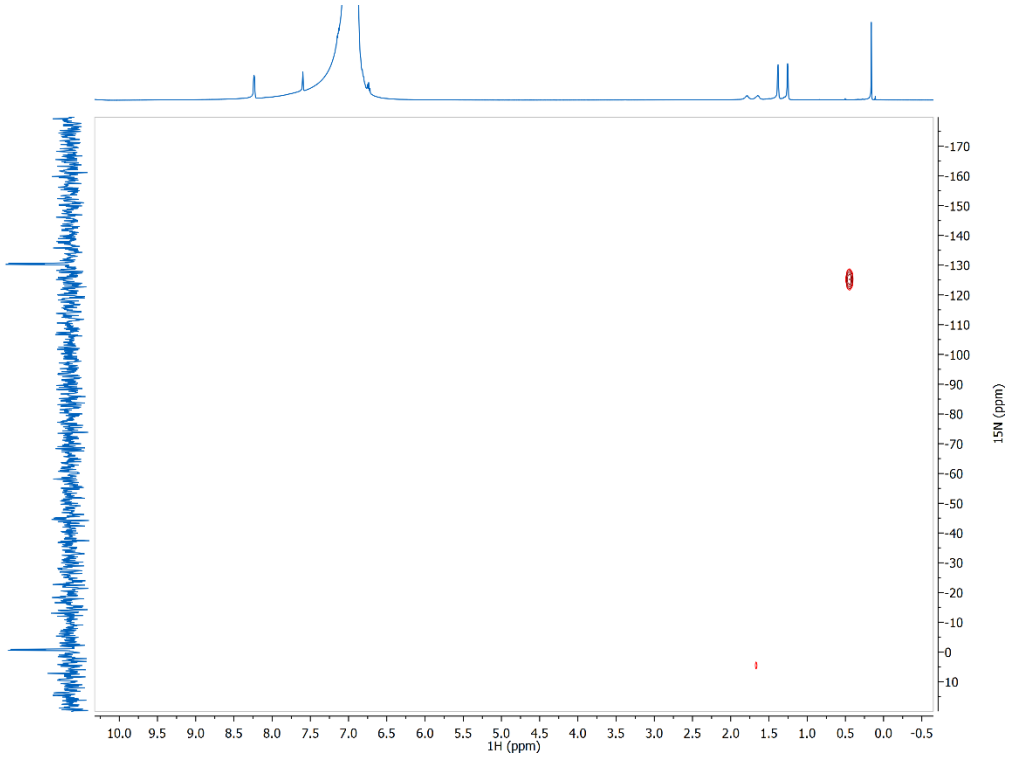


Fig. S12 ^{1}H-^{15}N HMBC NMR spectrum **4-$^{15}N_2$** in 1,2 DFB under an Ar atmosphere.

3. IR spectra

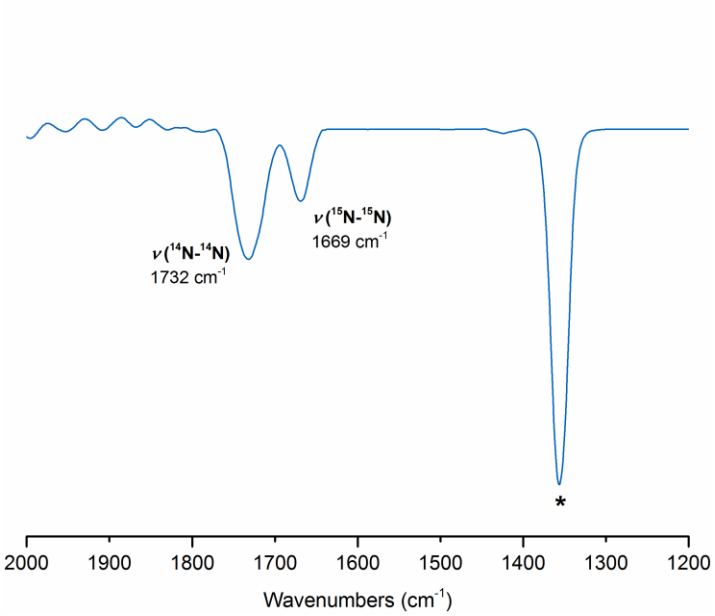


Fig. S13 IR spectrum of ^{15}N isotopically enriched sample of **3** (**3-$^{15}N_2$**) recorded as a 0.015 M solution in 1,2 DFB under an Ar atmosphere, showing both ^{14}N-^{14}N and ^{15}N-^{15}N stretches. The absorption denoted ***** is due to the $[BAr^F{}_4]^-$ anion.

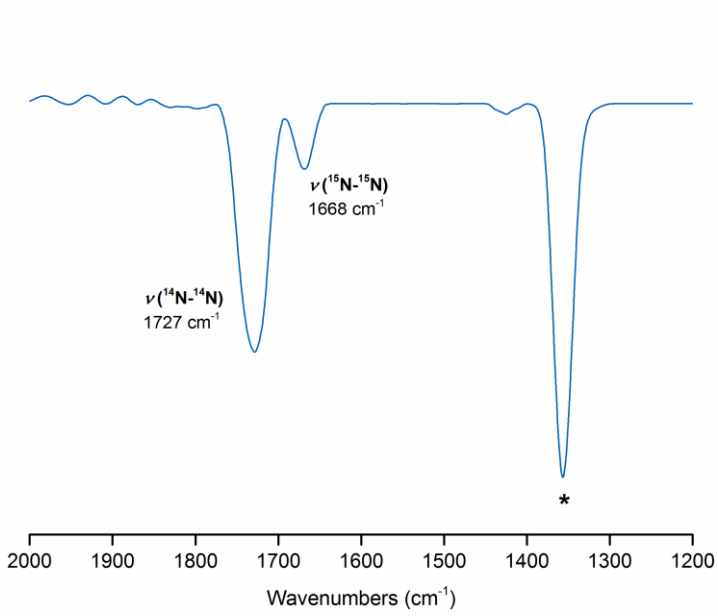


Fig. S14 IR spectrum of ^{15}N isotopically enriched sample of **4** (**4-$^{15}N_2$**) recorded as a 0.015 M solution in 1,2 DFB under an Ar atmosphere, showing both ^{14}N-^{14}N and ^{15}N-^{15}N stretches. The absorption denoted ***** is due to the $[BAr^F{}_4]^-$ anion.

4. X-ray diffraction data

X-ray diffraction data for 3 - $[Fe(depe)_2(N_2SiMe_3)][BAr^F_4]$

3 was refined as a two-component inversion twin. Carbon atom C11 was disordered over two positions, which were allowed to freely refine, converging at a final ratio of 0.70: 0.30. The C11-C12/C11A-C12 and C11-P3/C11A-P3 distances were restrained to be approximately equal. Seven out of the eight CF_3 groups were disordered over two positions, which were allowed to freely refine. Within each CF_3 group, all C-F bond distances were restrained to be approximately equal, and enhanced rigid bond, and similarity thermal restraints were applied to aid refinement.

Formula	$C_{55}H_{69}BF_{24}FeN_2P_4Si$	
Formula weight	1432.75	
Temperature (K)	173.05(10)	
Diffractometer, wavelength	OD Xcalibur 3, 0.71073 Å	
Crystal system, space group	Orthorhombic, $P2_12_12_1$	
Unit cell dimensions	a = 12.9303(4) Å	α = 90°
	b = 19.1287(6) Å	β = 90°
	c = 26.3957(12) Å	γ = 90°
Volume, Z	6528.7(4) $Å^3$, 4	
Density (calculated)	1.458 gcm^{-3}	
Absorption coefficient	0.453 mm^{-1}	
F(000)	2936.0	
Crystal colour / morphology	Red blocks	
Crystal size	0.179 x 0.301 x 0.436 mm^3	
2θ range for data collection	4.898° to 56.484°	
Index ranges	$-13 \leq h \leq 16$, $-24 \leq k \leq 15$, $-31 \leq l \leq 16$	
Reflections collected	16034	
Independent reflections	11810 [R_{int} = 0.0257, R_{sigma} = 0.0675]	
Absorption correction	Analytical	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11810 / 668 / 1007
Goodness-of-fit on F^2	1.049
Final R indices [I>=2σ (I)]	R_1 = 0.0589, wR_2 = 0.1471
R indices [all data]	R_1 = 0.0789, wR_2 = 0.1666
Largest diff. peak, hole	0.47, -0.36 eÅ^{-3}
Flack parameter	0.53(3)

X-ray diffraction data for 4 - [Fe(dmpe)$_2$(N$_2$SiMe$_3$)][BAr$^F_4$]

Enhanced rigid bond restraints were applied to all atoms in the dmpe ligands to aid refinement. 5 out of the 16 CF_3 groups were disordered over two positions, which were allowed to freely refine; in each case, only the major component was refined anisotropically. Within each CF_3 group, all C-F bond distances were restrained to be approximately equal, and enhanced rigid bond and similarity thermal restraints were applied to aid refinement.

Formula	$C_{47}H_{53}BF_{24}FeN_2P_4Si$	
Formula weight	1320.54	
Temperature (K)	173.00(14)	
Diffractometer, wavelength	OD Xcalibur 3, 0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/m$	
Unit cell dimensions	a = 17.0435(3) Å	α = 90°
	b = 7.6295(6) Å	β = 89.9978(15)°
	c = 18.3435(4) Å	γ = 90°
Volume, Z	11764.3(3)Å^3, 8	
Density (calculated)	1.491 gcm^{-3}	
Absorption coefficient	0.496 mm^{-1}	
F(000)	5360.0	
Crystal colour / morphology	Red blocks	

Crystal size	0.331 x 0.483 x 0.622 mm^3
2θ range for data collection	4.572° to 56.594°
Index ranges	$-22 \leq h \leq 18$, $-49 \leq k \leq 42$, $-20 \leq l \leq 23$
Reflections collected	66244
Independent reflections	24747 [R_{int} = 0.0256, R_{sigma} = 0.0400]
Absorption correction	Analytical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11810 / 731 / 1528
Goodness-of-fit on F^2	1.012
Final R indices [I>=2σ (I)]	R_1 = 0.0779, wR_2 = 0.2048
R indices [all data]	R_1 = 0.1067, wR_2 = 0.2281
Largest diff. peak, hole	1.45, -0.61 $eÅ^{-3}$

5. Computational Methods

DFT calculations were carried out using the ADF program suite version 2013.01 and 2014.01.[7-9] Geometry optimisations and fragment calculations employed the BP86 functional[10-14] and TZP basis sets.[15] Local minima were confirmed by frequency calculations.

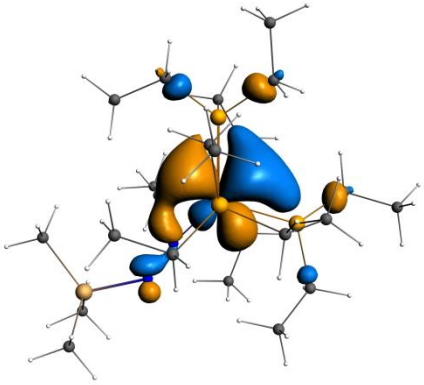
Structural results

Table 1. Key geometric parameters (Å and °) for $[Fe(PP)_2(NN\text{-}R)]^+$ (PP = dmpe/depe; R = $SiMe_3$, H) and $Fe(PP)_2(N_2)$ compounds.

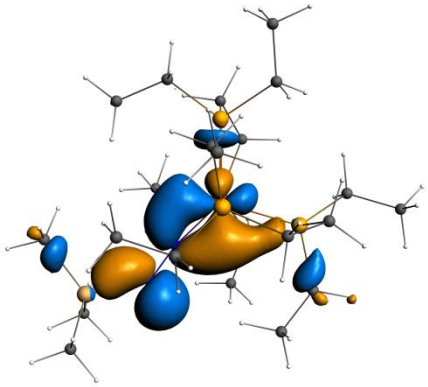
	Fe-N (Å)	**N-N (Å)**	**N-N-R (°)**	**Fe-N-N (°)**
$Fedepe_2N_2SiMe_3^+$	1.69	1.21	138	170
$Fedmpe_2N_2SiMe_3^+$	1.69	1.20	133	173
$Fedepe_2N_2H^+$	1.68	1.22	113	175
$Fedmpe_2N_2H^+$	1.68	1.22	113	172
$Fedepe_2N_2$	1.79	1.15	n/a	180
$Fedmpe_2N_2$	1.80	1.14	n/a	180
$Fedepe_2N_2SiMe_3^+$ (X-ray)	1.69	1.19	133	170
$Fedmpe_2N_2SiMe_3^+$ (X-ray)	1.69	1.20	127	176

Orbitals

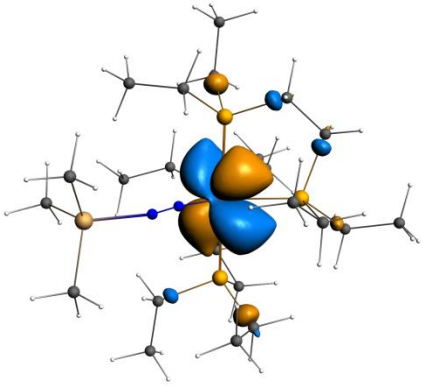
$[Fe(depe)_2(NN\text{-}SiMe_3)]^+$ (3)



HOMO

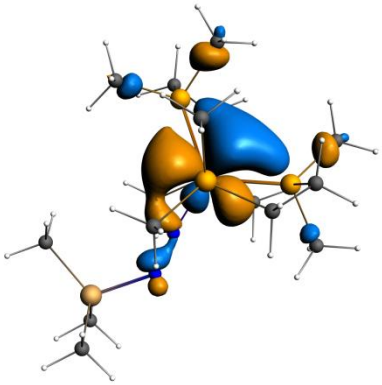


HOMO-1



HOMO-2

$[Fe(depe)_2(NN\text{-}SiMe_3)]^+$ (4)



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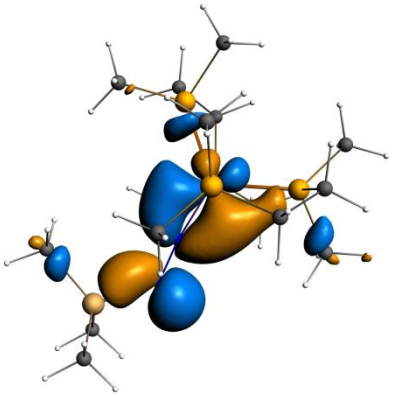

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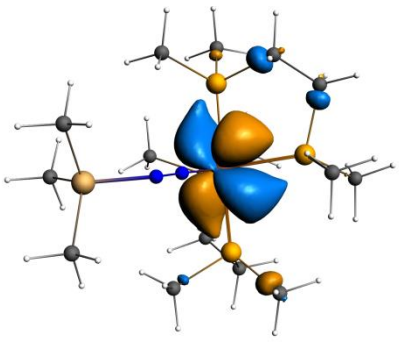

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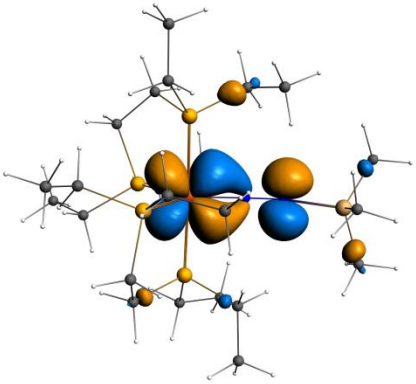

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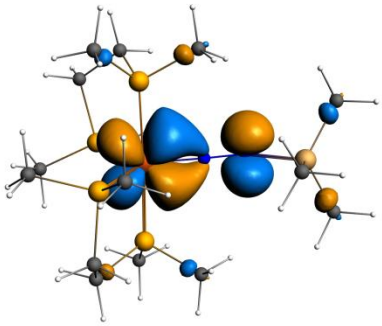
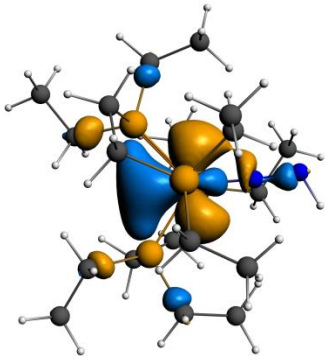


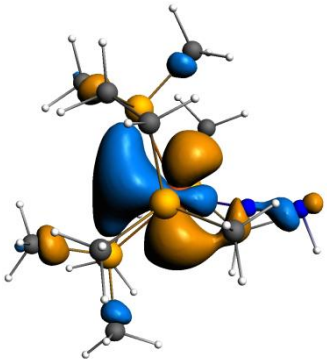
HOMO-3

[Fe(depe)$_2$(NN-H)]$^+$ (5)

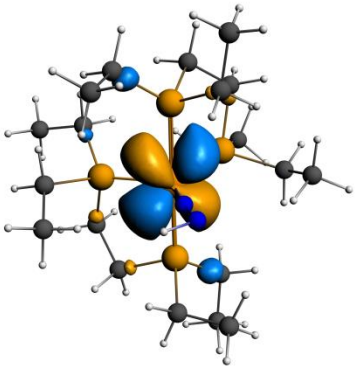
[Fe(dmpe)$_2$(NN-H)]$^+$ (6)



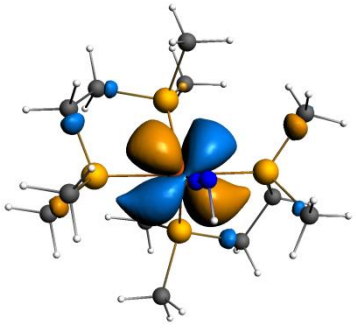
HOMO



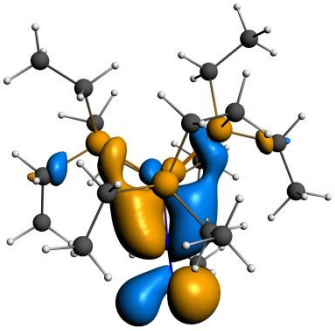
HOMO



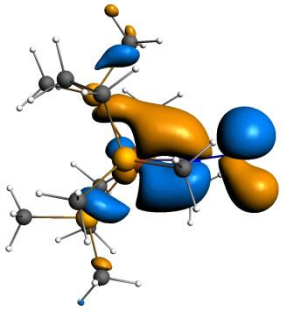
HOMO-1



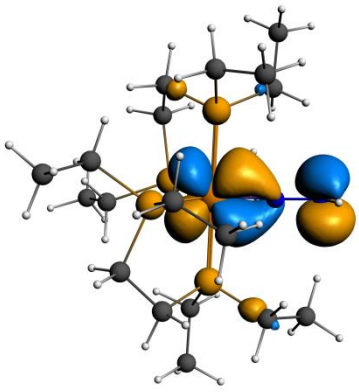
HOMO-1



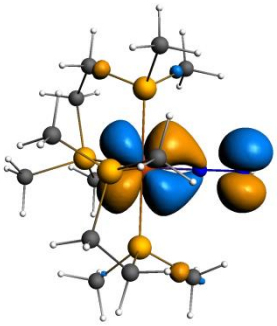
HOMO-2



HOMO-2



HOMO-3



HOMO-3

Fragment analysis

Table 2. Charge on NNR fragment and % occupancy of LUMO and SOMO

	Charge on fragment[a]		**% occ of NNR fragment orbitals**	
	NNR	**FeP_4**	**LUMO**	**SOMO**
$Fedepe_2N_2SiMe_3^+$	-0.16	1.16	0.42	0.93
$Fedmpe_2N_2SiMe_3^+$	-0.14	1.14	0.41	0.91
$Fedepe_2N_2H^+$	-0.29	1.29	0.39	1.14
$Fedmpe_2N_2H^+$	-0.28	1.28	0.38	1.13
$Fedepe_2N_2$	-0.31	0.31	0.29, 0.32	n/a
$Fedmpe_2N_2$	-0.30	0.30	0.29, 0.29	n/a

[a] Hirshfeld charge[16, 17]

Cartesian coordinates

$[Fe(depe)_2(NN\text{-}SiMe_3)]^+$ (3)

Fe	15.85391736	9.37057927	2.88775707
P	15.27733689	11.43987934	3.63279801
P	14.26437065	9.77100444	1.32850779
P	17.47538273	9.03076927	4.46390649
P	17.55339427	9.67696266	1.46609066
Si	13.66143136	5.60881271	3.95106383
N	15.22564697	7.82267021	3.13871740
C	14.52175539	11.69767047	5.33181632
H	15.34395254	11.69285385	6.06208206
H	14.09468054	12.71261343	5.34791239
C	14.34322335	9.21530941	-0.45565914
H	13.52718114	9.73481896	-0.98450236
H	15.28209776	9.61021386	-0.87394119
C	17.93934530	8.27166090	0.28161268
H	17.15194330	8.30731986	-0.48855084
H	18.88632124	8.51462290	-0.22557926
C	13.95870587	11.60053423	1.15929022
H	14.79491753	12.01891875	0.57801032
H	13.03552970	11.78911788	0.59062420
C	17.64470849	11.13167815	0.27742252
H	16.76489059	11.05579983	-0.38077613
H	17.48176080	12.02475910	0.89997935
C	13.91028766	12.19168192	2.56876364
H	12.95014117	11.95085209	3.05077377
H	14.00118306	13.28812304	2.56441598
N	14.89069103	6.66452420	3.13804691
C	16.54539314	12.83522240	3.57060004

H	17.50225183	12.41690626	3.91833975
H	16.68198205	13.03101587	2.49482772
C	18.00333301	6.86836104	0.89572054
H	18.09141686	6.10987481	0.10413166
H	17.10208593	6.64363372	1.48380171
H	18.87807044	6.74846594	1.55110795
C	12.60530694	9.10228095	1.87218478
H	12.74580313	8.01280459	1.93502568
H	12.47549327	9.44425576	2.91095024
C	17.70897636	10.17282134	5.93564541
H	17.79473923	11.19549209	5.53832982
H	16.75351355	10.13594856	6.48245865
C	14.65637842	4.12972661	4.54389846
H	15.39959420	4.41003619	5.30398724
H	15.18588842	3.65604031	3.70411689
H	13.98770561	3.37645811	4.98957374
C	18.91336282	11.31115309	-0.56820651
H	18.83358978	12.22389683	-1.17600440
H	19.07288503	10.47390386	-1.26052243
H	19.81226793	11.41279432	0.05524712
C	13.46323392	10.65957447	5.71268772
H	12.57956357	10.71973604	5.05933050
H	13.11342417	10.82077489	6.74252114
H	13.86404059	9.63806778	5.63864113
C	14.25039862	7.69989307	-0.67443405
H	14.38181512	7.45979252	-1.73893792
H	13.27088951	7.30663568	-0.36971630
H	15.01982797	7.15778742	-0.10718737
C	12.74470376	6.49055779	5.34266172
H	13.38549244	6.67956328	6.21517680

H	11.90809990	5.85672727	5.67980309
H	12.32184147	7.44916513	5.00914198
C	17.48691425	7.36237342	5.30242399
H	17.33099669	6.62057240	4.50412234
H	18.50464719	7.20342091	5.69162762
C	11.37245079	9.43479926	1.02363367
H	11.46321619	9.06101049	-0.00598511
H	11.18003272	10.51624175	0.97448030
H	10.47749459	8.96834767	1.46057085
C	19.17163179	9.88552777	2.39979689
H	20.02645766	9.65891128	1.74494099
H	19.24327927	10.94941012	2.68003454
C	16.24141421	14.14549992	4.30646315
H	17.02610508	14.88689316	4.09795911
H	16.20220077	14.00686396	5.39497290
H	15.28582123	14.58795533	3.98987411
C	18.87265922	9.88036497	6.89175517
H	19.85038943	9.96240504	6.39737778
H	18.80372674	8.87974945	7.33959362
H	18.86668177	10.60742490	7.71671533
C	12.47207416	5.10074675	2.58401801
H	11.82543099	5.93061702	2.26369963
H	11.81500644	4.29798335	2.95606668
H	13.00730871	4.71623075	1.70403366
C	19.16216162	8.99523571	3.64186563
H	19.94045495	9.27753866	4.36564868
H	19.34213981	7.94464700	3.36796936
C	16.45120174	7.18742435	6.41549421
H	15.43996873	7.42793038	6.06194847
H	16.66356611	7.83195079	7.27944369

H	16.44612539	6.15078923	6.78035554

$[Fe(dmpe)_2(NN\text{-}SiMe_3)]^+$ (4)

Fe	4.35504227	19.31745737	13.80184121
P	4.85203421	19.53681372	11.61763083
P	2.40798293	20.27995187	13.20836777
P	5.87359508	20.81483947	14.45284733
P	3.84808183	19.18866571	16.00097302
Si	4.54850483	14.92538566	13.52400333
N	4.79927826	17.69038601	13.78397237
N	5.26309624	16.57961392	13.80053511
C	2.32324557	20.54551710	11.34479029
H	1.88961027	19.63361050	10.90483261
H	1.64027965	21.37640452	11.11426966
C	1.88808349	21.97033718	13.79554391
H	1.79162486	21.99042738	14.88814655
H	0.92219744	22.25301741	13.35149789
H	2.64692406	22.70867580	13.50039152
C	6.04738400	22.55652276	13.82490092
H	6.25629187	22.56440671	12.74641664
H	6.86771294	23.07624612	14.34189968
H	5.11141364	23.10543462	13.99865240
C	2.46206257	20.10184919	16.83542938
H	2.60289176	21.18583717	16.73368738
H	2.45717017	19.84682789	17.90487663
H	1.48903475	19.83035516	16.40633535
C	4.52257926	18.00370051	10.63077378
H	5.22243400	17.21903382	10.94758705
H	4.66161866	18.19380502	9.55682436

H	3.49970269	17.64838735	10.81122072
C	5.42377265	14.26004014	11.99991693
H	5.13459238	14.79816879	11.08536049
H	5.16309227	13.19919918	11.85607634
H	6.51626254	14.32481008	12.11074831
C	7.63427273	20.23072387	14.33751968
H	7.72485409	19.25524560	14.83542132
H	8.31555334	20.95067917	14.81476779
H	7.93126397	20.10298430	13.28924808
C	5.75862545	21.13389758	16.30046730
H	6.72599587	21.49041218	16.68503131
H	5.02281827	21.93908178	16.45764850
C	0.82073997	19.34776575	13.46230300
H	0.92374597	18.33556435	13.04784624
H	-0.01509339	19.86172693	12.96476166
H	0.58736292	19.25890014	14.53152103
C	5.02737030	13.95150187	15.05711774
H	6.11484748	13.98694543	15.21916532
H	4.73866110	12.89534661	14.93618560
H	4.53095812	14.33027338	15.96259544
C	3.73341428	20.78098305	10.80105811
H	4.10170474	21.78422930	11.06926121
H	3.78718795	20.68449438	9.70554499
C	6.51895587	19.96880936	10.93035029
H	6.86686253	20.94054078	11.30394637
H	6.46062324	20.01315117	9.83306226
H	7.24871768	19.19759185	11.21238496
C	2.68391882	15.04748523	13.28847940
H	2.19000794	15.48831610	14.16658261
H	2.26192801	14.04085308	13.13779065

H	2.42593249	15.65205095	12.40674843
C	5.30215947	19.84007556	16.97581113
H	5.02341284	19.98499463	18.03082456
H	6.09419786	19.07509763	16.93811325
C	3.60146280	17.50392282	16.71830409
H	2.66988872	17.06692898	16.33415593
H	3.54273861	17.56185677	17.81412681
H	4.43966548	16.85500825	16.43499843

$[Fe(depe)_2(NN\text{-}H)]^+$ (5)

Fe	15.86470347	9.37623024	2.86789468
P	15.32260679	11.45048559	3.58980426
P	14.24655916	9.74968185	1.32200371
P	17.48195596	9.01005789	4.45084576
P	17.56273014	9.73816796	1.45661382
H	18.76470594	8.75456915	7.33394527
N	15.16233384	7.89304620	3.21302162
C	14.54338825	11.66143867	5.28079130
H	15.35733382	11.64198891	6.01967775
H	14.11645930	12.67628553	5.31168445
C	14.32228750	9.14041139	-0.44236419
H	13.48651774	9.62013726	-0.97770918
H	15.24625542	9.54244686	-0.88685299
C	17.98113553	8.31104010	0.31134022
H	17.21017842	8.33036902	-0.47600931
H	18.93804564	8.54964150	-0.17852957
C	13.98304172	11.58143442	1.11467901
H	14.81554594	11.96530966	0.50546707
H	13.05207617	11.77774575	0.56163958

C	17.61432858	11.15760962	0.22660293
H	16.76375156	11.00714966	-0.45684223
H	17.38117482	12.06292667	0.80769543
C	13.97501552	12.21237269	2.50854519
H	13.01343206	12.02031342	3.00866550
H	14.10327833	13.30423243	2.47002719
N	14.56619302	6.86193447	3.49610518
C	16.60876890	12.82533332	3.58623890
H	17.53203038	12.40127609	4.01058449
H	16.82561162	13.00402566	2.52082455
C	18.03786628	6.91903995	0.94881497
H	18.12517022	6.14462047	0.17343920
H	17.12912553	6.71678806	1.53487292
H	18.90406803	6.80647917	1.61586434
C	12.58563929	9.12557903	1.90108259
H	12.70257225	8.04029269	2.04149635
H	12.45716272	9.53039659	2.91748353
C	17.63284262	10.07486311	5.98689641
H	17.67686167	11.12180933	5.65024299
H	16.67124052	9.95859576	6.51154941
H	18.74012488	10.45886628	7.80973265
C	16.52531929	6.98058510	6.27947946
H	15.49669541	7.10770731	5.91801624
H	16.66046107	7.61397255	7.16700719
C	18.90032622	11.37618550	-0.58331383
H	18.78736911	12.25468069	-1.23443327
H	19.13360125	10.52073782	-1.23104629
H	19.76837448	11.56008447	0.06435911
C	13.47972436	10.61549209	5.62761661
H	12.59931494	10.69565660	4.97261959

H	13.12594340	10.75580016	6.65892176
H	13.87368373	9.59317782	5.53349120
C	14.26240451	7.61662358	-0.60444772
H	14.35113874	7.34164114	-1.66473268
H	13.31104804	7.20662727	-0.23827823
H	15.07713009	7.11863040	-0.05964006
H	16.63540186	5.93699748	6.60680065
C	19.17758283	9.10716181	3.64759142
H	19.92067721	9.43810206	4.38752205
H	19.44138165	8.07546761	3.37030954
C	17.55764299	7.29638681	5.19121519
H	17.46022019	6.59696017	4.34619888
H	18.57991747	7.17195451	5.58282322
C	11.36134155	9.42999669	1.02980116
H	11.44137146	8.98491145	0.02794827
H	11.19014710	10.50937740	0.90803583
H	10.46004345	9.01051234	1.49922527
C	19.15653442	10.00780847	2.41086655
H	20.02774102	9.82390541	1.76397548
H	19.17838542	11.07181632	2.69773535
C	16.26761381	14.14893922	4.28186032
H	17.07462228	14.87774517	4.12026131
H	16.15016523	14.02508553	5.36637580
H	15.34275577	14.59744585	3.89183488
C	18.79462468	9.78131603	6.94561810
H	19.77511362	9.93745062	6.47493662
H	14.89925382	6.03680634	2.95227943

$[Fe(dmpe)_2(NN\text{-}H)]^+$ (6)

Fe	4.35696434	19.30810421	13.79944303
P	4.85800443	19.49291401	11.60986696
P	2.45162237	20.35712276	13.21826040
P	5.81820561	20.86678971	14.43181445
P	3.88591501	19.12886310	16.01908037
H	6.52609781	19.82904065	9.85032690
N	4.75129707	17.67862260	13.76181778
N	5.20440035	16.54271028	13.76992805
C	2.40292889	20.68095455	11.36035612
H	1.90048194	19.81766370	10.89657881
H	1.78501990	21.56673916	11.15202647
C	1.93902557	22.02493062	13.86633233
H	1.84310603	22.00598157	14.95932458
H	0.97230455	22.32188745	13.43417438
H	2.69468309	22.77536650	13.59563639
C	6.00181231	22.57046023	13.71483516
H	6.25394232	22.52021392	12.64689249
H	6.80041030	23.12020699	14.23431076
H	5.06021191	23.12580106	13.82394304
C	2.38275901	19.83653717	16.84745095
H	2.34188366	20.92585068	16.71957953
H	2.42768518	19.60941127	17.92220571
H	1.46569695	19.39497030	16.43628845
C	4.41615896	17.98874557	10.62644299
H	5.06471274	17.15595496	10.93091475
H	4.55621832	18.17506553	9.55196915
H	3.37333467	17.70051939	10.81496450
H	7.23316025	19.00135958	11.26669535

C	3.86989452	17.42760230	16.73355955
H	2.99521038	16.87605697	16.36193242
H	3.81528732	17.48218867	17.82959124
C	7.57920997	20.28191675	14.40189793
H	7.65595877	19.32399492	14.93428875
H	8.24181131	21.02062586	14.87651824
H	7.91099778	20.11877384	13.36892651
C	5.61701830	21.26563266	16.25177563
H	6.53953593	21.71940314	16.64469587
H	4.81277446	22.01325653	16.34559159
C	0.86292860	19.41970652	13.41945293
H	0.97938144	18.40908660	13.00465863
H	0.04458944	19.93533126	12.89560391
H	0.59570787	19.33109117	14.48013577
H	4.77673284	16.88387297	16.43956204
C	5.25069399	19.97159955	16.97959205
H	4.93044498	20.14419310	18.01808192
H	6.10756060	19.27976158	17.00560934
C	3.82617011	20.82235390	10.81644764
H	4.26551505	21.79335793	11.09536997
H	3.86805027	20.73788001	9.71950500
C	6.55827428	19.80806467	10.94928318
H	6.95559867	20.76640870	11.30813658
H	4.48966172	15.82049828	13.53691894

$Fe(depe)_2(N_2)$ (1)

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

$Fe(dmpe)_2(N_2)$ (2)

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
H	2.24568133	-3.67160699	1.41066971
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
C	2.23517240	2.70621371	0.77388547
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	3.78111161	-1.15352208

H	1.88399777	-2.25553230	2.45498344
H	2.19361088	0.79854064	-2.52899701
H	-3.25586786	-3.03399712	0.52587505
H	-2.19361088	-0.79854064	-2.52899701
H	3.25586786	3.03399712	0.52587505
H	1.92606712	-3.78111161	-1.15352208

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