Chemical Communications

Supporting Information for:

Structure and bonding in three-coordinate N-heterocyclic carbene adducts of iron(II) bis(trimethylsilyl)amide

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General experimental considerations

All synthetic manipulations were performed using standard Schlenk techniques. Toluene was degassed and dried by refluxing over sodium-potassium alloy under nitrogen. IMes and IPr were synthesized according to a recent literature report,[1] and [Fe{N(SiMe$_3$)$_2$}$_2$] was synthesized according to Lappert's original method.[2]

^{1}H NMR spectra were acquired using a Bruker Avance 600 MHz NMR spectrometer equipped with a CryoProbe, operating at the ^{1}H frequency of 600.25 MHz and a temperature of 298.1 K. Solvents for NMR spectroscopy were distilled under nitrogen off sodium-potassium alloy or molten potassium, and were stored over activated 4 Å molecular sieves for 24 hours before use.

X-ray diffraction data on **2** and **3** were collected on an OXFORD Diffraction Gemini R Ultra CCD diffractometer using $Cu_{K\alpha}$ radiation (λ = 1.54178 Å). Structure solution and refinement was performed using SIR97,[4] SHELXL97[5] and WinGX.[6]

SQUID measurements were carried out on polycrystalline samples of **2** and **3** by enclosing the sample in O-ring-sealed Kel-F capsules. The capsules were transferred to sample holders in a glovebox, transported to the SQUID magnetometer in a sealed Schlenk tube, and then rapidly transferred to the helium-purged sample space of the magnetometer. Corrections for diamagnetism were made using Pascal's constants, and the magnetic susceptibility data for **2** and **3** were modelled according to the following equation:[3]

$$\chi = \frac{\chi_z + 2\chi_{x,y}}{3}$$

where: $$\chi_z = \frac{2N\beta^2 g^2}{kT} \frac{\exp(D/kT) + 4\exp(-2D/kT)}{\exp(2D/kT) + 2\exp(D/kT) + 2\exp(-2D/kT)}$$

and: $$\chi_{x,y} = \frac{2N\beta^2 g^2}{3D} \frac{9\exp(2D/kT) - 7\exp(D/kT) - 2\exp(-2D/kT)}{\exp(2D/kT) + 2\exp(D/kT) + 2\exp(-2D/kT)}$$

1. X. Bantrelli, S. P. Nolan, *Nature Protocols*, **2011**, *6*, 69.
2. R. A. Anderson, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. –P. Leung, *Inorg. Chem.* **1988**, *27*, 1782.
3. O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.
4. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR 97: A new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **1999**, *32*, 115-119.
5. SHELX97 Programs for crystal structure analysis (Release 97-2). (G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, **1998**).
6. L. J. Farrugia, WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst.* **1999**, *32*, 837-838.

Synthesis of 2. A solution of IPr (0.12 g, 0.33 mmol) in toluene (8 mL) was added to a stirred solution of [Fe{N(SiMe$_3$)$_2$}$_2$] (0.15 g, 0.33 mmol) in toluene (2 mL) at room temperature. The reaction mixture developed a brown colour during the addition, and was stirred overnight. The resulting solution was filtered, concentrated to a volume of 2-3 mL and stored at -28°C overnight, resulting in the formation of large colourless/light-green crystals of **2**·(toluene). Removal of the crystallization solvent followed by washing the crystals with cold pentane and drying in vacuo produced **2** as a light-green polycrystalline material (0.13 g, 53%). Elemental analysis (%) calcd. for $C_{39}H_{72}FeN_4Si_4$ C 61.22, H 9.48, N 7.32; found C 61.34, H 9.58, N 7.39.

Synthesis of 3. Compound **3** was synthesized in an identical manner to **2**·(toluene), using IMes (0.12 g, 0.39 mmol) and 1 (0.12 g, 0.39 mmol). The product **3** was obtained as colourless/light-green crystals. Placing the crystals under a vacuum for ca. 30 minutes resulted in the formation of light-green polycrystalline **3** (0.16 g, 59 %). Elemental analysis (%) calcd. for $C_{33}H_{60}FeN_4Si_4$ C 58.20, H 8.88, N 8.23; found C 58.35, H 8.98, N 8.09.

Table S1. Crystal data and structure refinement for [(IPr)Fe{N(SiMe$_3$)$_2$}$_2$] (**2**)

Empirical formula	$C_{39}H_{72}FeN_4Si_4$	
Formula weight	765.22	
Temperature	123(1) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.8510(8) Å	α = 76.430(6)°.
	b = 11.3172(8) Å	β = 80.054(5)°.
	c = 22.8051(13) Å	γ = 66.930(7)°.
Volume	2494.4(3) Å^3	
Z	2	
Density (calculated)	1.019 Mg/m^3	
Absorption coefficient	3.538 mm^{-1}	
F(000)	832	
Crystal size	0.2862 × 0.1423 × 0.0853 mm^3	
Theta range for data collection	4.00 to 63.72°	
Index ranges	-11<=*h*<=12, -11<=*k*<=12, -25<=*l*<=26	
Reflections collected	15902	
Independent reflections	7794 [*R*(int) = 0.0284]	
Completeness to theta = 63.72°	94.7%	
Absorption correction	Analytical	
Max. and min. transmission	0.813 and 0.545	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7794 / 0 / 434	
Goodness-of-fit on F^2	1.065	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0332, *wR*2 = 0.0880	
R indices (all data)	*R*1 = 0.0365, *wR*2 = 0.0913	
Absolute structure parameter	0	
Largest diff. peak and hole	0.321 and -0.220 e.Å^{-3}	

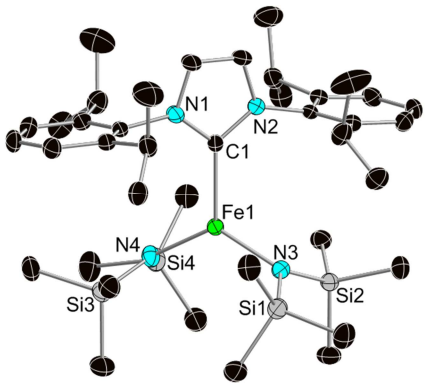


Figure S1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

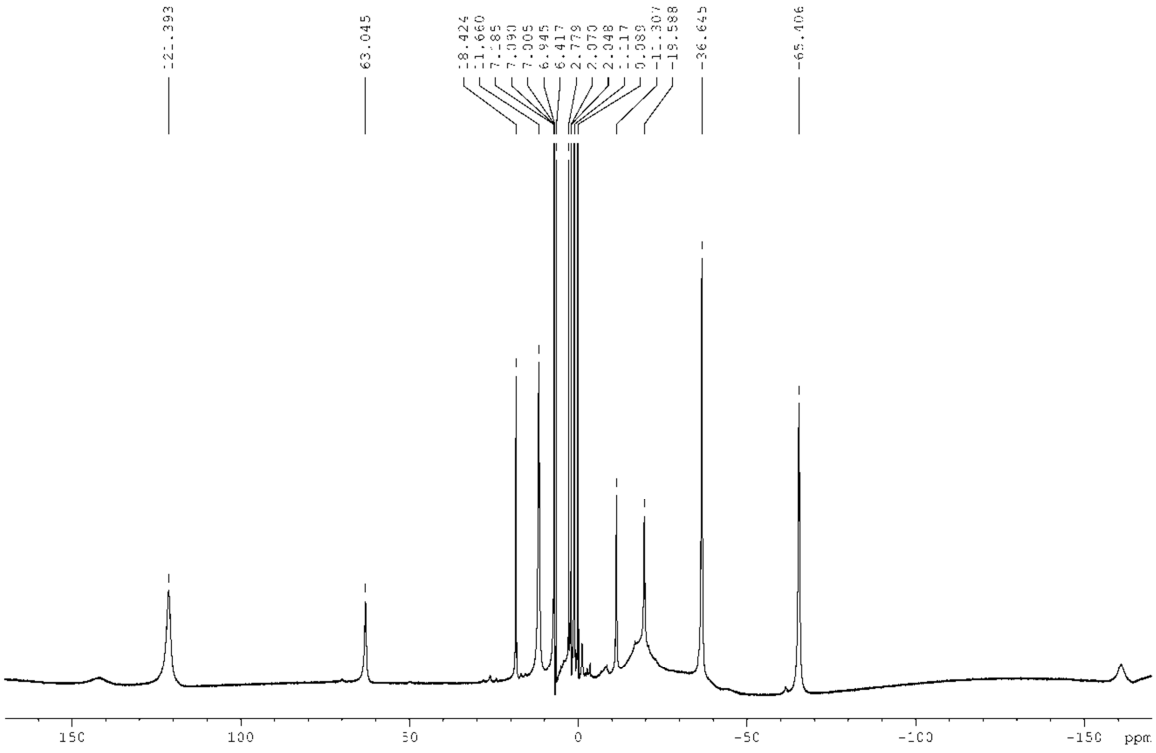


Figure S2. ^{1}H NMR spectrum of **2** (toluene-d_8, 228 K, 400.13 MHz). Assignments made where possible. δ(^{1}H)/ppm: 121.39 (SiMe$_3$ in **2**), 63.05 (SiMe$_3$ in **1**), 18.42 and 11.686 (aromatic CH in **2**), 7.19 (aromatic CH in IPr), 6.42 (imidazole CH in IPr), 2.78 (Me$_2$C<u>H</u>), 1.12 (<u>Me</u>$_2$CH), 0.09 (silicone grease), –11.31 (imidazole CH in **2**), –19.59 (IPr <u>Me</u>$_2$CH in **2**), –36.65 (IPr <u>Me</u>$_2$CH in **2**), –65.41 (IPr <u>Me</u>$_2$CH in **2**).

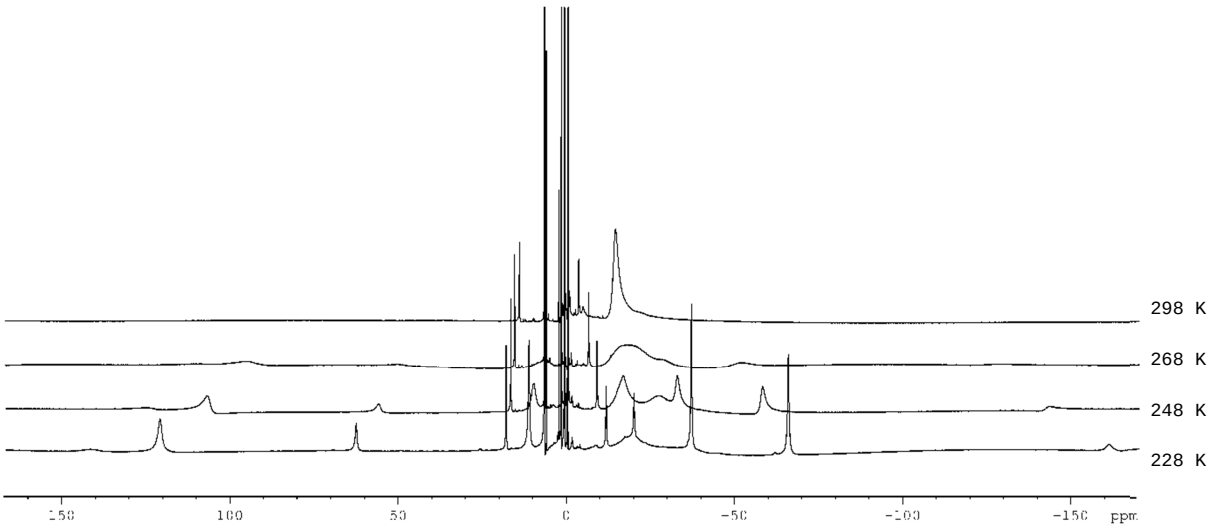


Figure S3. Variable temperature ^{1}H NMR spectrum of **2** in toluene.

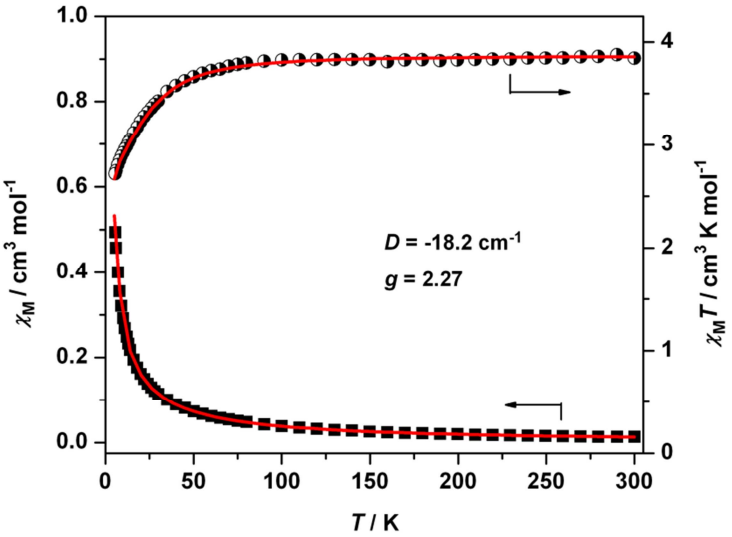


Figure S4. Plots of χ_M *vs*. *T* and $\chi_M T$ *vs*. *T* for **2**.

Table S2. Crystal data and structure refinement for [(IMes)Fe{N(SiMe$_3$)$_2$}$_2$] (**3**)

Empirical formula	$C_{33}H_{60}FeN_4Si_4$	
Formula weight	681.06	
Temperature	123 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 16.6461(3) Å	α = 90°.
	b = 14.2890(3) Å	β = 99.705(2)°.
	c = 16.7741(3) Å	γ = 90°.
Volume	3932.72(13) Å^3	
Z	4	
Density (calculated)	1.150 Mg/m^3	
Absorption coefficient	4.432 mm^{-1}	
F(000)	1472	
Crystal size	0.4431 × 0.3543 × 0.2560 mm^3	
Theta range for data collection	4.10 to 70.66°.	
Index ranges	-20<=*h*<=13, -16<=*k*<=11, -16<=*l*<=20	
Reflections collected	7577	
Independent reflections	3675 [*R*(int) = 0.0285]	
Completeness to theta = 68.00°	99.3 %	
Absorption correction	Analytical	
Max. and min. transmission	0.438 and 0.281	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3675 / 0 / 200	
Goodness-of-fit on *F*^{2}	1.046	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0408, *wR*2 = 0.1068	
R indices (all data)	*R*1 = 0.0419, *wR*2 = 0.1079	
Absolute structure parameter	0	
Largest diff. peak and hole	0.736 and -0.316 e.Å^{-3}	

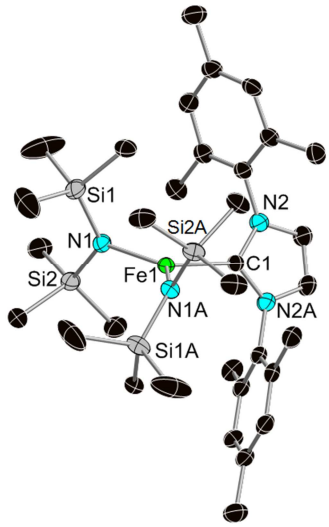


Figure S5. Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

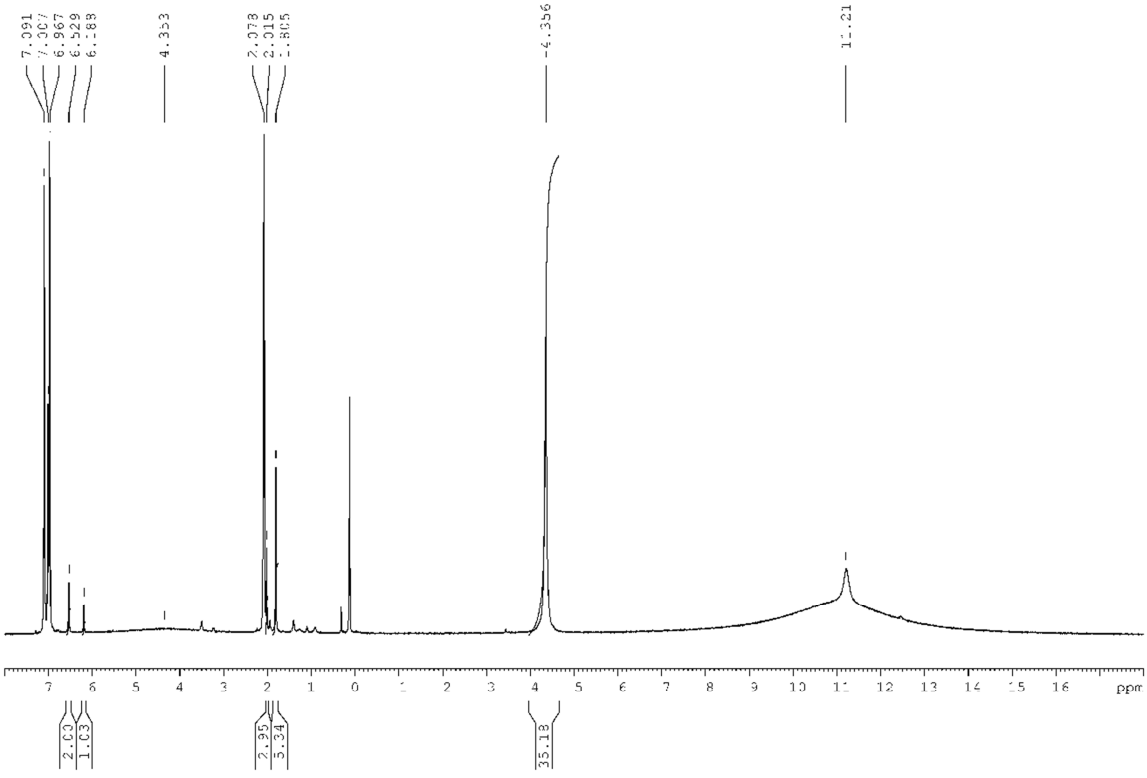


Figure S6. ^{1}H NMR spectrum of **3** (toluene-d_8, 273 K, 400.13 Hz) in the region 8 to –18 ppm. δ(^{1}H)/ppm: 33.16, 6.53 (IMes aromatic CH), 6.19 (IMes imidazolylidene CH), 4.35 (imidazolylidene CH in **3**), 2.02 (IMes *para*-CH_3), 1.81 (IMes *ortho*-CH_3), 0.12 (silicone grease), –4.36 ($SiMe_3$ in **3**), –11.21 (CH_3 in **3**). At higher temperatures, the IMes methyl groups overlap with the toluene methyl solvent resonance.

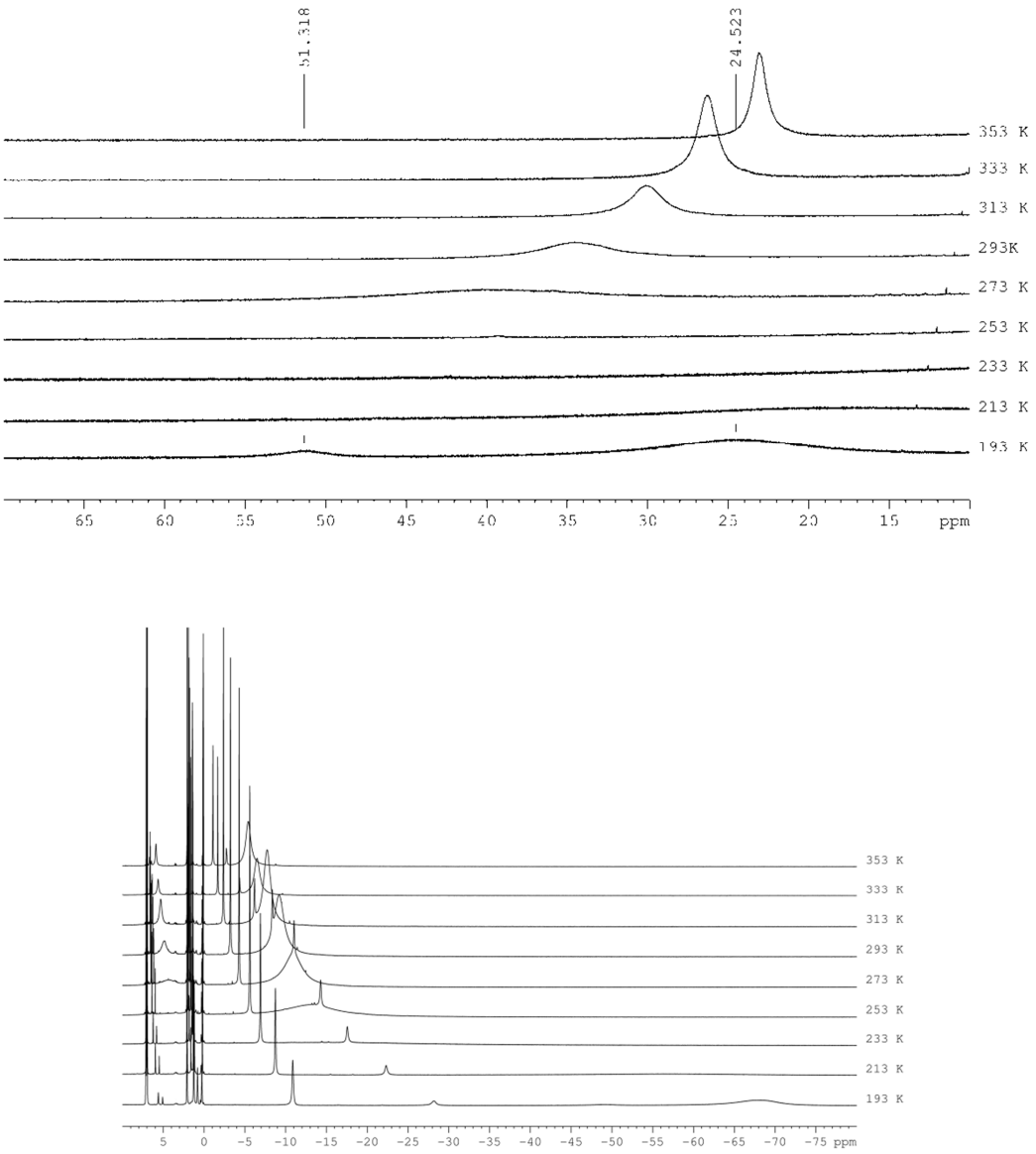


Figure S7. ^{1}H NMR spectrum of **3** in the temperature range 193-353 K (toluene-d_8, 400.13 Hz). Low-field region (upper) and high-field region (lower).

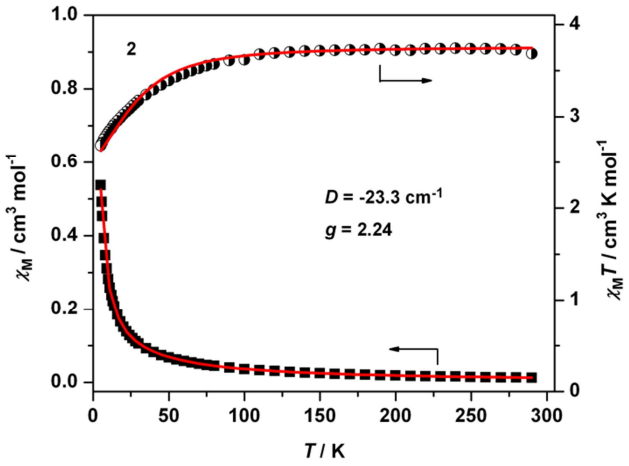


Figure S8. Plots of χ_M *vs*. *T* and $\chi_M T$ *vs*. *T* for **3**.

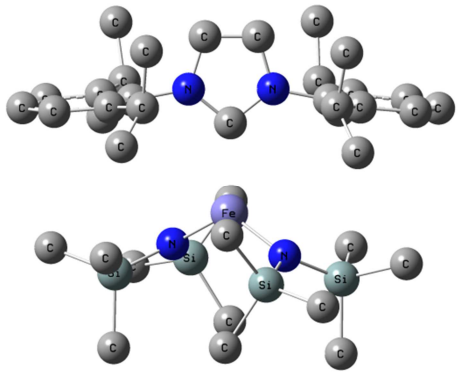


Figure S9. Structure of **2** optimized at the B3LYP/Def2-SVP level of theory with COSMO simulation in toluene. Hydrogen atoms not shown.

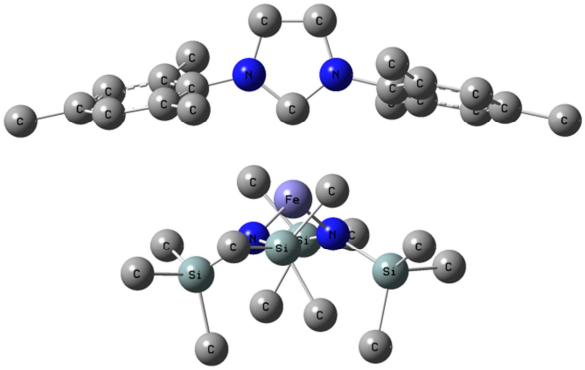


Figure S10. Structure of **3** optimized at the B3LYP/Def2-SVP level of theory with COSMO simulation in toluene. Hydrogen atoms not shown.

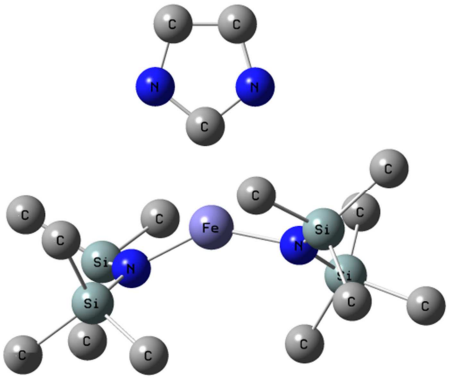
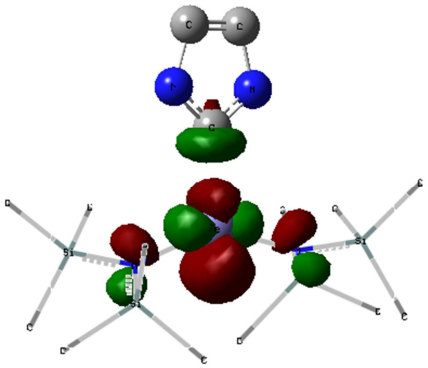
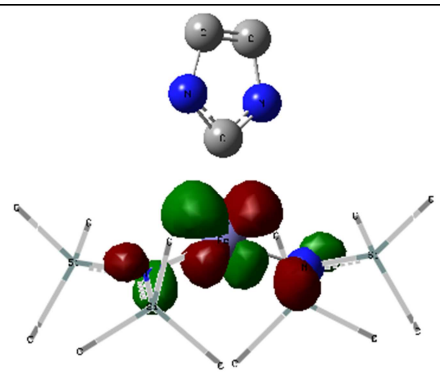
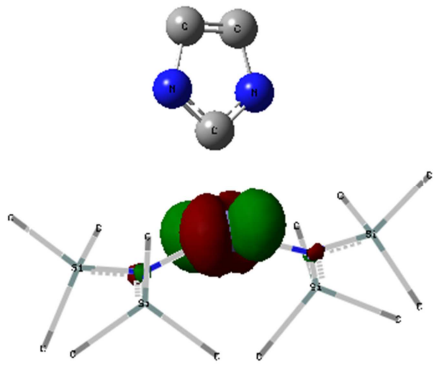
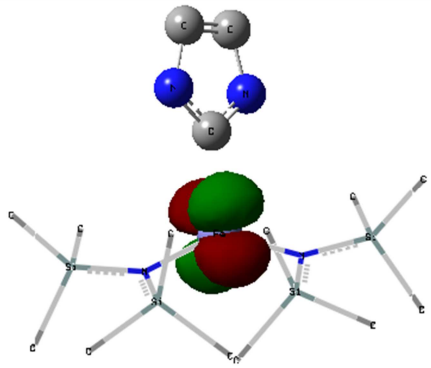
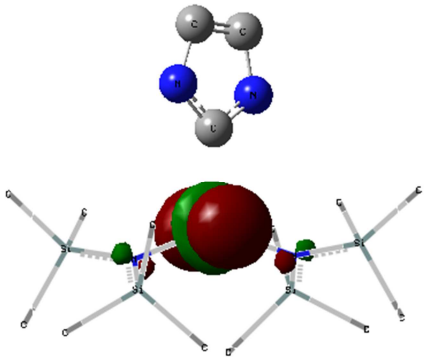
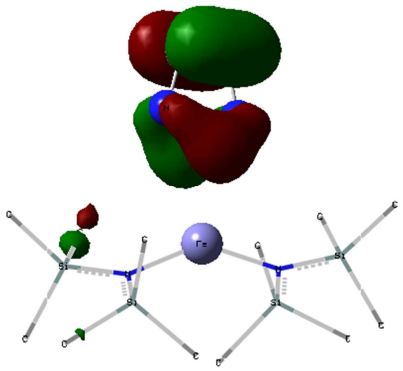
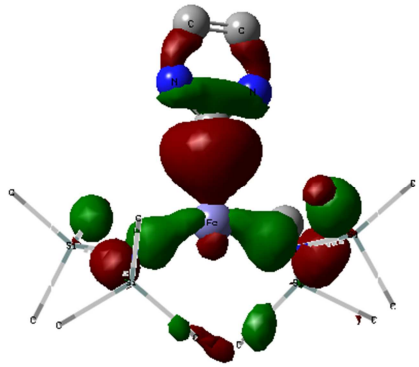
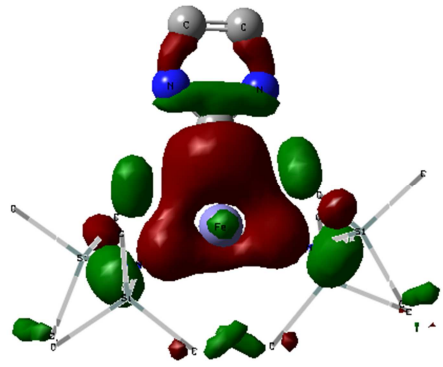
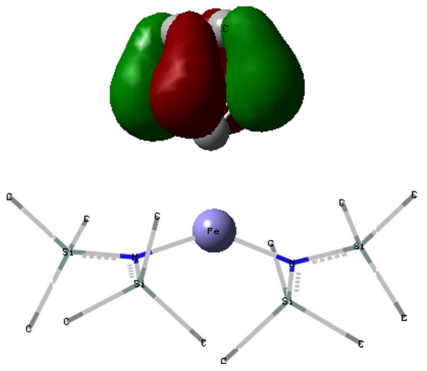
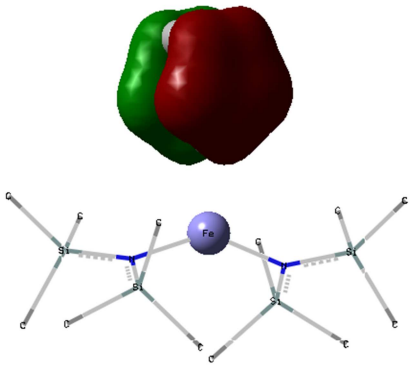


Figure S11. Structure of **5** optimized at the B3LYP/Def2-SVP level of theory with COSMO simulation in toluene. Hydrogen atoms not shown.

Table S12. Selected quasi-restricted orbitals for **5** (B3LYP/Def2-SVP, isosurface value = 0.04 a.u.)

	-3.229 eV (No. 121)
	-3.870 eV (No. 120)
	-4.113eV (No. 119)
	-4.301 eV (No. 118)

	 -5.026 eV (No. 117)
	 -7.367 eV (No. 112)
	 -8.543 eV (No. 102)
	 -9.083 eV (No. 101)
	 -9.326 eV (No. 100)



-12.874 eV (No. 69)