

SUPPORTING INFORMATION FOR

Selective Conversion of CO₂ to Isocyanate by Low-Coordinate Iron

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*This is the pre-peer reviewed version of the following article: D.L.J. Broere; B.Q. Mercado; P.L. Holland. Angew. Chem. Int. Ed. **2018**, DOI: anie.201802357, which has been published in final form at <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.201802357>. This article may be used for non-commercial purposes in accordance with Wiley-VCH Terms and Conditions for Self-Archiving.*

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Experimental

General considerations. All reactions were performed under an N₂ atmosphere in an M. Braun glovebox maintained at or below 1 ppm of O₂ and H₂O. Glassware was dried at 160 °C under vacuum. Solvents were dried by passage through Q5 columns from Glass Contour Co., with the exception of THF, which was distilled under Ar from a potassium benzophenone ketyl solution. THF-*d*₈ was dried in a potassium benzophenone ketyl solution and distilled before use. Complex **1** and **1**•THF were prepared as reported previously.¹ Research grade CO₂ (99.999%) was obtained from Airgas and used without further purification. ¹H NMR data were recorded on a Bruker Avance 400 or 500 spectrometer (400 or 500 MHz). The temperature of the measurements was determined by the frequency difference between the two observed peaks for a neat methanol sample². All resonances in the ¹H NMR spectra are referenced to the residual solvent peaks (δ 7.16 ppm for benzene, δ 3.58 ppm for THF). Resonances were singlets unless otherwise noted. Line fitting of the resonances in the ¹H NMR spectra was performed using MestReNova 10.0.1. Mössbauer data were recorded on a SEECo spectrometer with alternating constant acceleration; isomer shifts are relative to iron metal at 298 K. The sample temperature was maintained at 80 K in a Janis Research Company Inc. cryostat. The zero-field spectra were simulated using Lorentzian doublets using WMoss (SeeCo). Elemental analyses were obtained from the CENTC Elemental Analysis Facility at the University of Rochester. Microanalysis samples were weighed on a PerkinElmer Model AD-6 Autobalance, analyzed on a PerkinElmer 2400 Series II Analyzer and handled in a VAC Atmospheres glovebox under argon.

Complex 2

A solution of **1** (104.8 mg, 0.20 mmol) in C₆H₆ (9 mL) was placed in a 100 mL resealable Schlenk flask, and was frozen in a dry ice/acetone bath. The headspace was evacuated and filled with CO₂ (0.9 atm, 3.7 mmol). After thawing, the solution was stirred for 15 h at ambient temperature. Volatile materials were removed under vacuum, the residue was washed with pentane (4 mL) and dried in vacuum to give a purple residue (91 mg) consisting of a 95 : 5 mixture of **2** : (formazanate)₂Fe.³ Washing the purple solid with cold toluene (2 mL) and drying in vacuum affords pure **2** (55 mg, 61%) ¹H NMR (400 MHz, 298 K, C₆D₆): δ 29.6 (3H, CH₃), 23.7 (2H, *p*-tol *m*-CH), 15.7 (4H, Ph *m*-CH) 2.39 (2H, *p*-tol *o*-CH), -4.9 (9H, SiMe₃), -16.5 (2H, Ph *p*-CH), -31.5 (4H, Ph *o*-CH)*. ¹H NMR (400 MHz, 298 K, THF-*d*₈): δ 25.4 (3H, CH₃), 20.7 (2H, *p*-tol *m*-CH), 20.53 (4H, Ph, *m*-CH), 17.7 (9H, SiMe₃), -2.1 (2H, Ph *p*-CH), -2.8 (2H, *p*-tol, *o*-CH). Tentative peak assignments were based on relative integration, broadness of the

resonance (*o*-Ph CH protons broaden due to close proximity to the metal center), chemical shift, and similarity to complexes **1**, **1•THF** and (formazanate)₂Fe.³ *integral deviates from the expected value, presumably due to the broadness of the resonance. Magnetic moments using Evans method in C₆D₆ (dimer): $\mu_{\text{eff}} = 6.1 \pm 0.3 \mu_{\text{B}}$. Magnetic moment using Evans method in THF-*d*₈ (monomer): $\mu_{\text{eff}} = 4.9 \pm 0.2 \mu_{\text{B}}$. Anal. Calcd for C₅₂H₅₈Fe₂N₈O₂Si₂ (**2**•C₆H₆): C, 62.77; H, 5.88; N, 11.26; Found: C, 62.99; H, 5.91; N, 11.33. (one equivalent of benzene was confirmed through integration in the ¹H NMR spectrum, and is also found in the asymmetric unit of **3**). Zero-field Mössbauer (80 K): $\delta = 0.80 \text{ mm/s}$ and $|\Delta E_{\text{Q}}| = 1.51 \text{ mm/s}$. FTIR (solid, cm⁻¹): 3085 (w), 3062 (w), 3028 (w), 2949 (w), 1587 (w), 1580 (w), 1509 (m), 1478 (m), 1454 (m), 1407 (w), 1364 (m), 1268 (m), 1250 (m), 1215 (m), 1189 (m), 1178 (m), 1158 (m), 1076 (m), 1044 (w), 1017 (w), 982 (w), 899 (w), 858 (m), 838 (m), 822 (m), 785 (w), 754 (m), 675 (m), 642 (m), 626 (m), 606 (m), 553 (w), 528 (w), 504 (m), 483 (m).

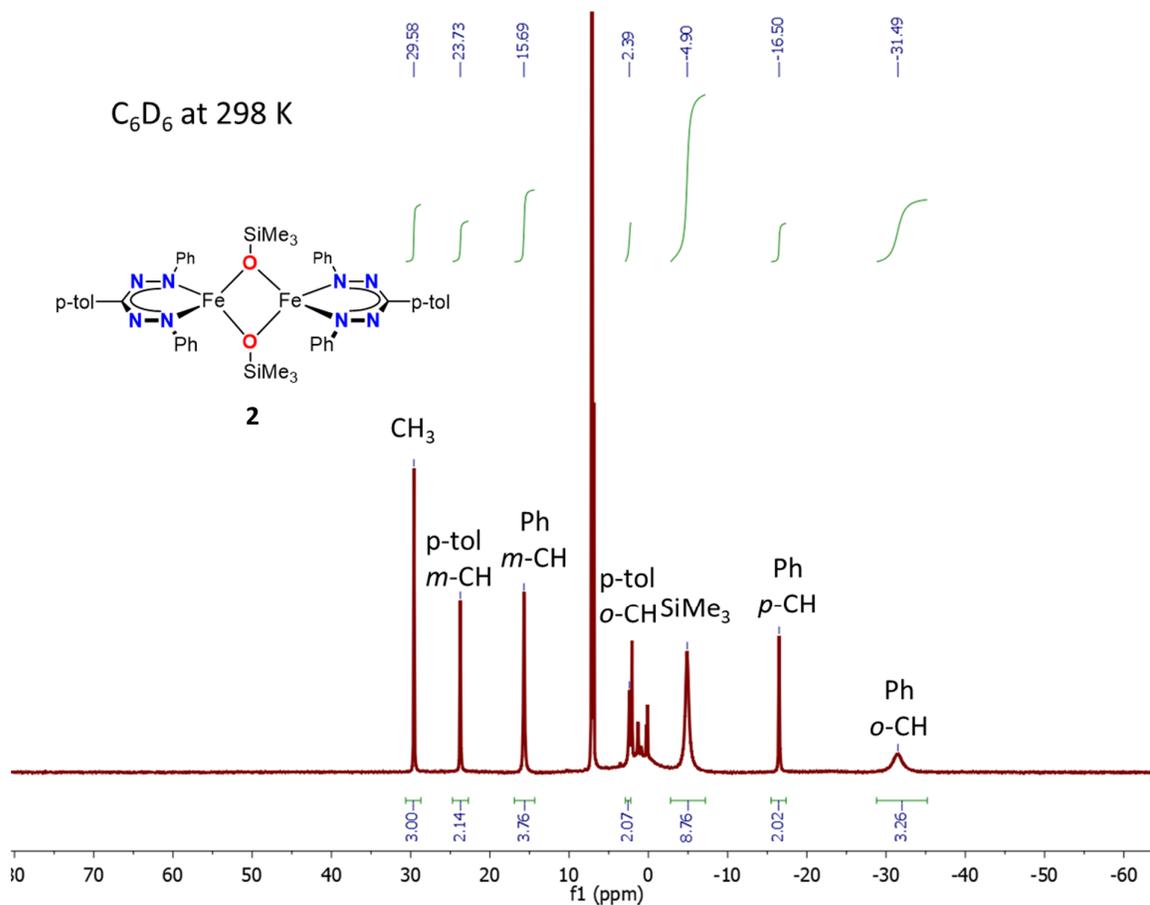


Figure S1. ¹H NMR spectrum of complex **2** in C₆D₆ at 298 K.

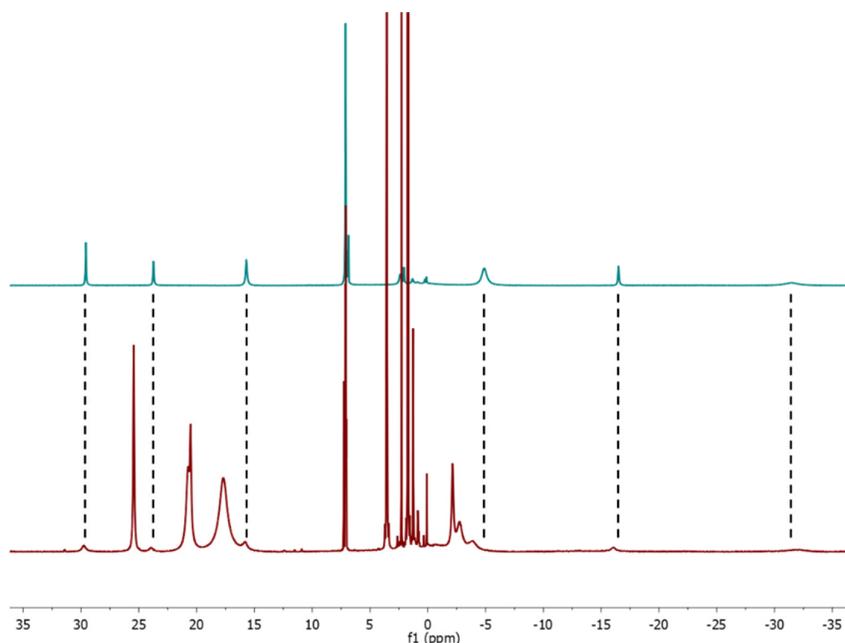
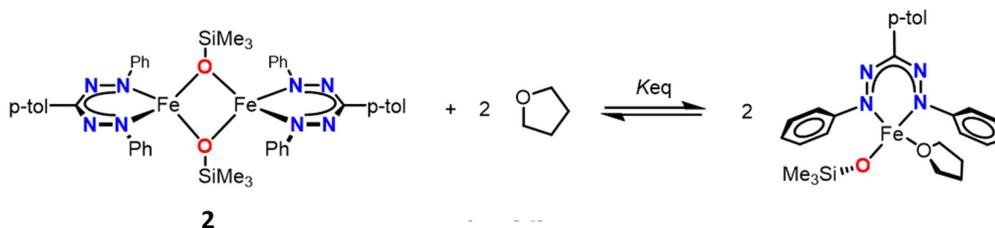


Figure S2. Stacked ^1H NMR spectra of **2** in C_6D_6 (top) and in $\text{THF-}d_8$ (bottom) at 298 K.

VT-NMR of complex **3** in THF

A solution of **2** (5.3 mg, 4.9 μmol) in $\text{THF-}d_8$ (0.5 mL) was placed in a J. Young NMR tube, and analyzed by ^1H NMR spectroscopy at various temperatures (Figure S3). The concentrations of monomer and dimer were determined by integration relative to a C_6H_6 standard. K_{eq} (M) was calculated according to Eq. 1. $[\text{THF}]$ was omitted because it is the solvent and does not change significantly under these conditions. The reaction enthalpy (ΔH°) and entropy (ΔS°) were obtained from the slope and y intercept of the van't Hoff plot (Figure S4) according to Eq. 2 and Eq. 3, respectively (R is the ideal gas constant). When $[\text{THF}]$ (12.33 M at all temperatures) was taken into account for the determination of K_{eq} ΔH° was unaffected and a ΔS° of $-26.9 \pm 0.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ was found. Uncertainties were obtained by least squares curve fitting using the LINEST function in Excel 2013.



$$\text{Eq. 1} \quad K_{\text{eq}} = \frac{[\text{monomer}]^2}{[\text{dimer}]}$$

$$\text{Eq. 2} \quad \text{Slope} = -\Delta H^\circ / R$$

$$\text{Eq. 3} \quad \text{Y-intercept} = \Delta S^\circ / R$$

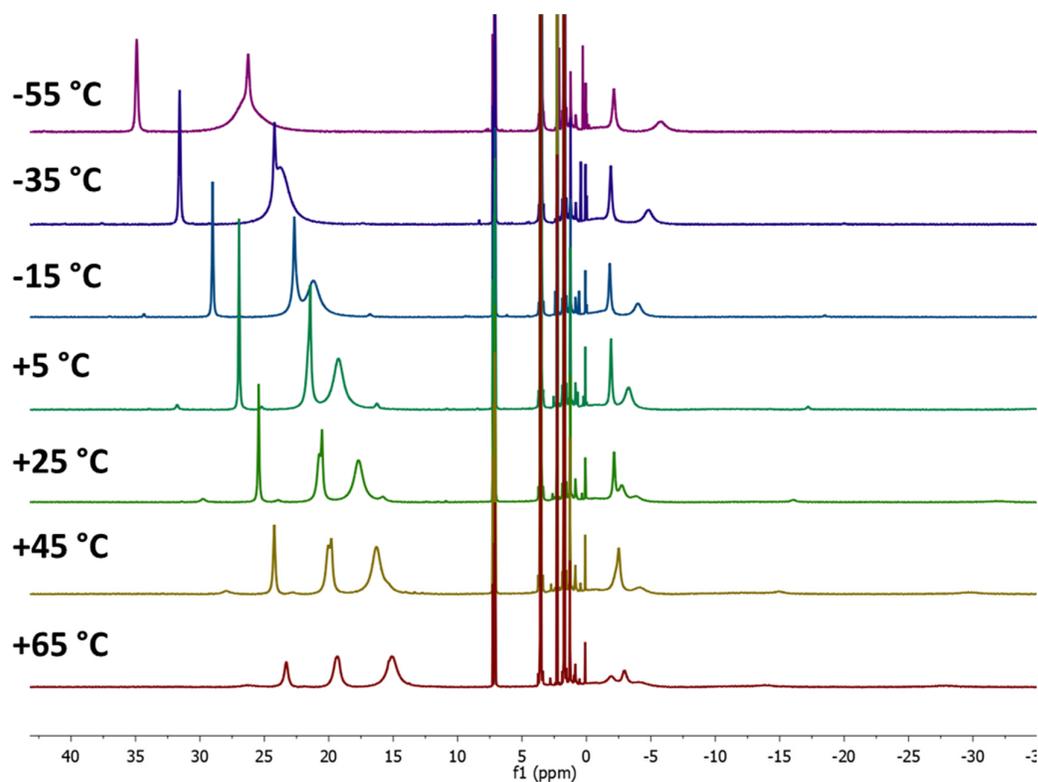


Figure S3. Stacked ^1H NMR spectra of complex **2** in in $\text{THF-}d_8$ at various temperatures showing the increase in dimer concentration with rising temperature

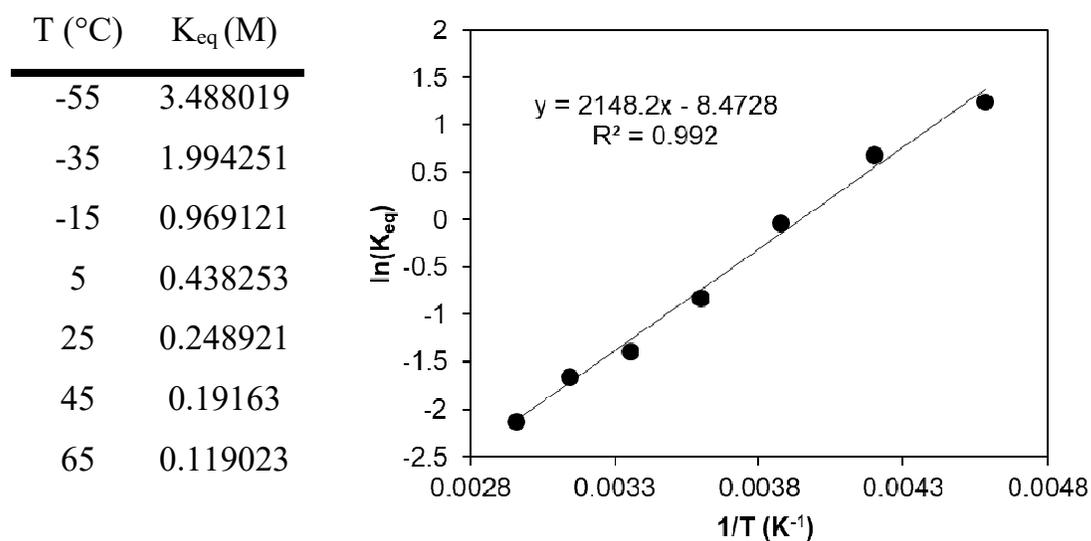


Figure S4. K_{eq} values (M) at various temperatures (left) and the van't Hoff plot based on the equilibrium mixture of dimeric **2** and a mononuclear THF solvate in $\text{THF-}d_8$ solution.

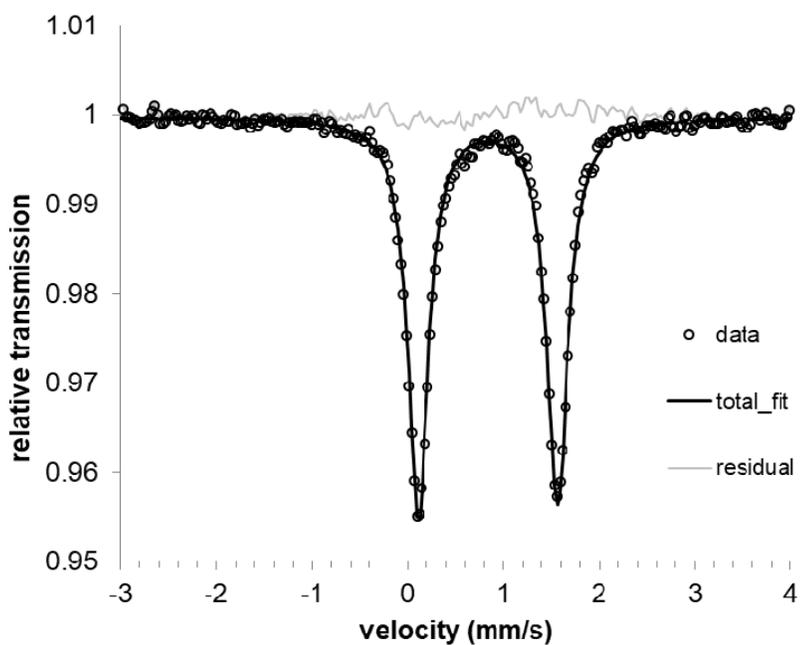


Figure S5. Zero-field Mössbauer spectrum of a solid sample of **2** at 80 K. $\delta = 0.84$ mm/s and $|\Delta E_Q| = 1.45$ mm/s.

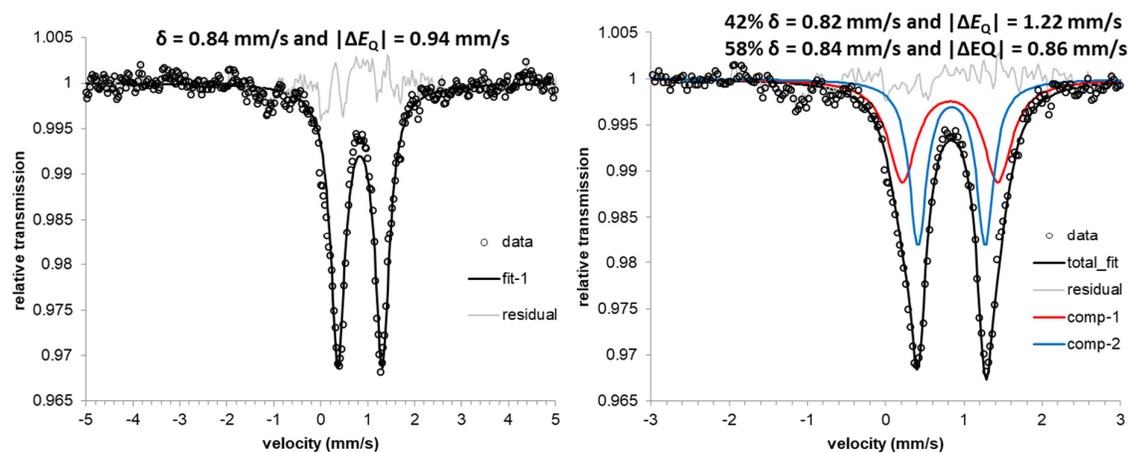


Figure S6. Zero-field Mössbauer spectrum of a frozen THF solution of **2** at 80 K with a one-component fit (left, $\gamma_L = 0.37$ and $\gamma_R = 0.37$) or a two-component fit (right, comp-1: 42% $\gamma_L = 0.43$ and $\gamma_R = 0.43$; comp-2: 58% $\gamma_L = 0.26$ and $\gamma_R = 0.26$).

Complex 3

A solution of **1** (100.1 mg, 0.19 mmol) in pentane (5 mL) was placed in a 50 mL resealable Schlenk flask, and was frozen in a liquid N₂ bath. The head space was evacuated, the mixture was thawed, and the flask was filled with CO₂ (0.9 atm, 1.87 mmol). After stirring for 1 h at ambient temperature the mixture was placed at -40 °C for 4 h. The flask was placed under a dynamic vacuum for 5 seconds, and was filled with N₂. The solution was filtered through Celite (thereby removing crystallized **2**) into a cold vial and placed at -40 °C for 16 h. The mother liquor was decanted off and the crystalline residue was dried in vacuum to give a dark purple solid (40 mg). The mother liquor was kept cold, concentrated to approx. 2 mL and placed at -40 °C for 16 h to give a second crop of dark crystals (15 mg). Combined yield: 55 mg, 54%. ¹H NMR (400 MHz, 298 K, C₆D₆): δ 25.5 (3H, CH₃), 25.1 (3H, CH₃') 21.0 (2H, p-tol *m*-CH), 20.4 (2H, p-tol *m*-CH'), 18.5 (4H, Ph *m*-CH), 16.7 (4H, Ph *m*-CH') 2.6 (9H, SiMe₃), 2.1–0.5 (17H, SiMe₃ + p-tol *o*-CH), -3.8 (9H, SiMe₃), -9.0 (2H, Ph *p*-CH), -12.3 (2H, Ph *p*-CH'), -14.3 (4H, Ph *o*-CH), *-25.3 (4H, Ph *o*-CH')*. Tentative peak assignments were based on relative integration, broadness of the resonance (*o*-Ph CH protons broaden due to close proximity to the metal center), chemical shift, and similarity to complexes **1-2** and (formazanate)₂Fe.³ *integral deviates from the expected value, presumably due to the broadness of the resonance. Anal. Calcd for C₅₀H₆₁Fe₂N₉O₃Si₃: C, 58.19; H, 5.96; N, 12.21 Found C, 58.59; H, 6.12; N, 12.06. Zero-field Mössbauer (80 K): δ = 0.80 mm/s and |ΔE_Q| = 1.51 mm/s. FTIR (solid, cm⁻¹): 3064 (w), 3021 (w), 3003 (w), 2953 (w), 2918 (w), 2895 (w), 2854 (w), 1590 (m), 1514 (m), 1508 (w), 1480 (m), 1453 (m), 1409 (m), 1352 (m), 1305 (w), 1290 (w), 1270 (m), 1252 (m), 1219 (m), 1191 (m), 1158 (m), 1103 (m), 1077 (m), 1042 (w), 1015 (w), 985 (w), 965 (w), 946 (w), 909 (m), 840 (m), 820 (m), 789 (m), 756 (m), 740 (m), 689 (m), 673 (m), 653 (m), 628 (m), 606 (m), 591 (m), 552 (w), 508 (m), 492 (m), 453 (m).

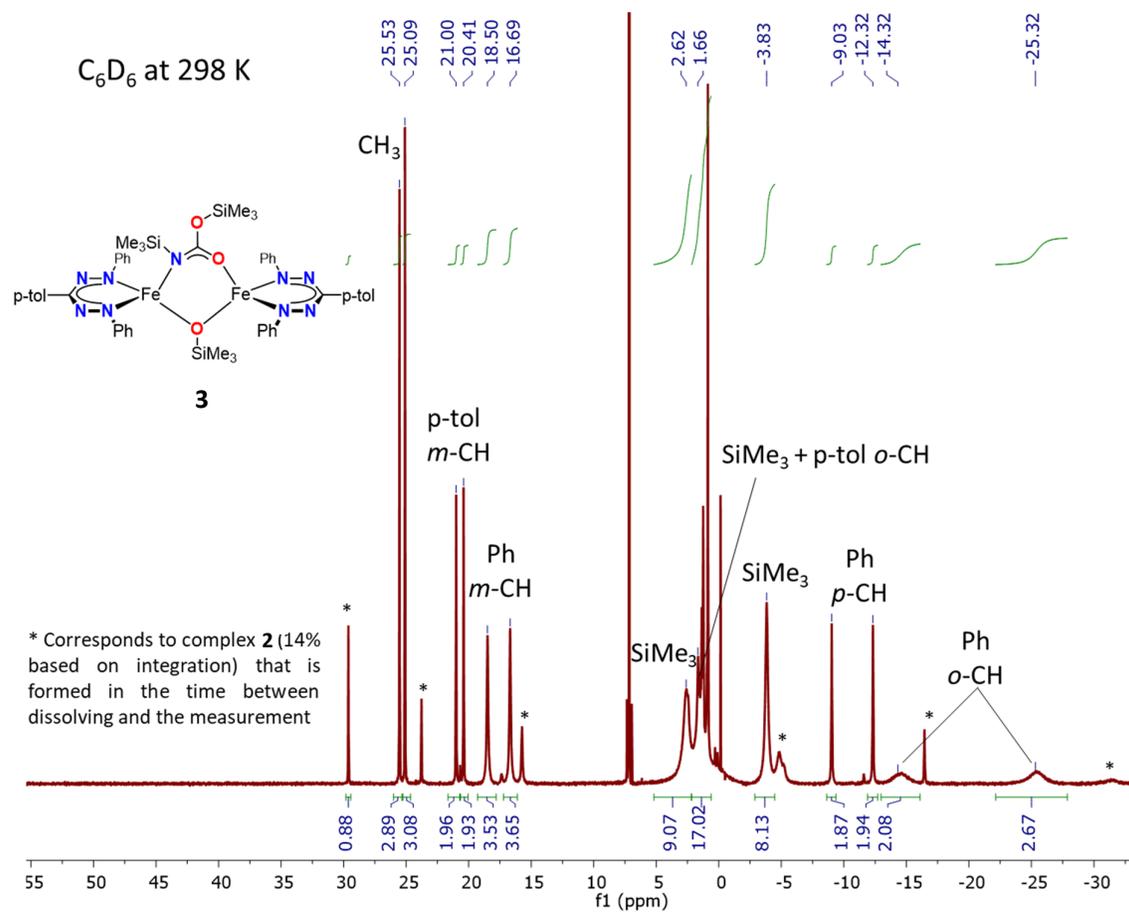


Figure S7. 1H NMR spectrum of complex **3** in C_6D_6 at 298 K. Peaks denoted with * correspond to **2**.

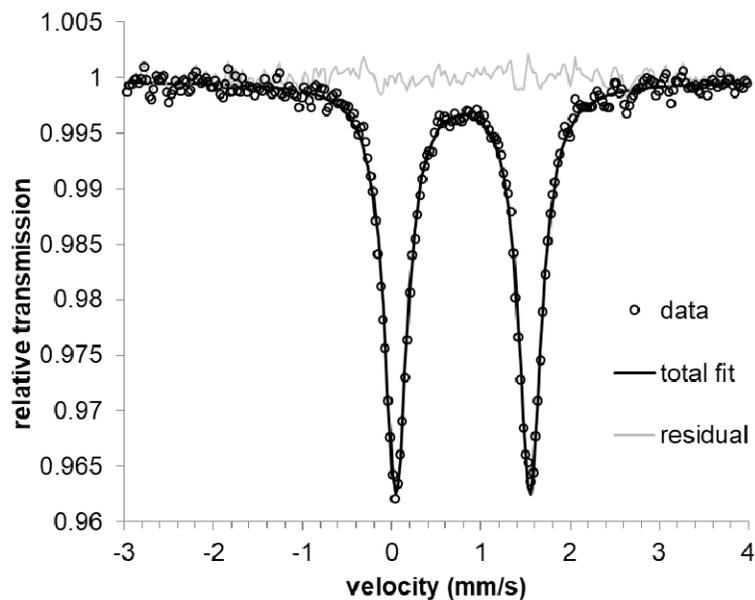


Figure S8. Zero-field Mössbauer spectrum of a solid sample of complex **3** at 80 K. $\delta = 0.81$ mm/s and $|\Delta E_Q| = 1.51$ mm/s.

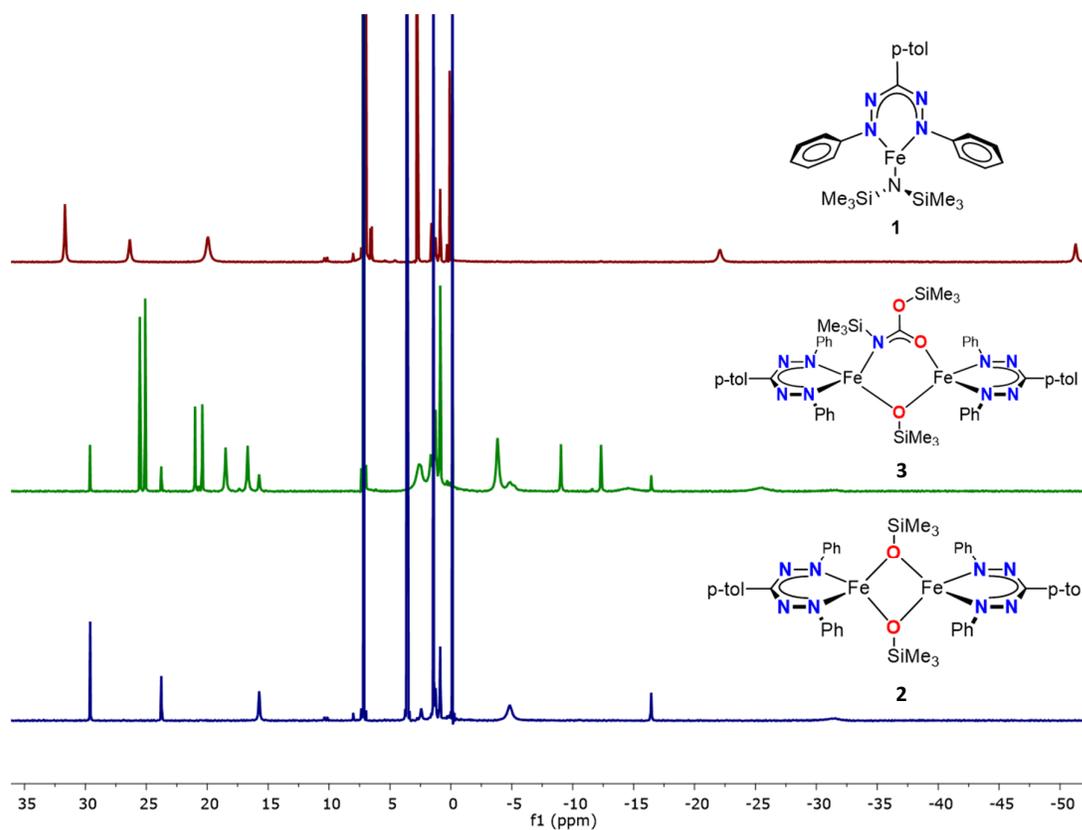


Figure S8. Stacked ^1H NMR spectra of complex **1**, intermediate **3**, and complex **2** in C_6D_6 at 298 K.

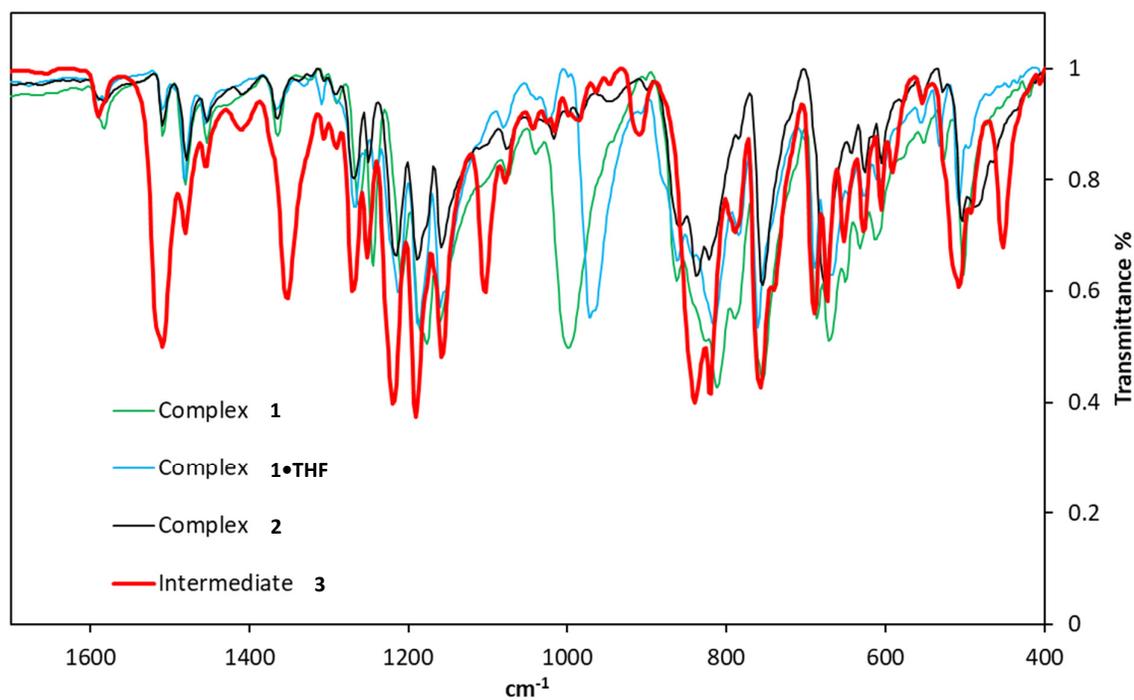


Figure S9. Overlay of the FTIR spectra of complex **1** (green), **1**•THF (blue), **2** (black) and **3** (thick red). Spectra are of solids using ATR, collected with 2 cm^{-1} resolution.

In situ NMR spectroscopy of the reaction of **1** and **2** with CO₂

A solution of **1** (5.3 mg, 10 μmol) or **1**•THF (6.0 mg, 10 μmol) and bisbenzyl (1.9 mg, 10 μmol) in C₆D₆ (0.5 mL) was placed in a J. Young NMR tube containing a CoCp₂ capillary. The solution was frozen in a dry ice/acetone bath, the head space was evacuated and backfilled with CO₂ (0.9 atm), and transported frozen to the NMR spectrometer. The solution was thawed in a water bath ($t = 0$), shaken twice, and placed in the NMR spectrometer at 298 K. Spectra were recorded at regular intervals and the concentration of TMSNCO and Fe complexes were determined based on integration relative to the bisbenzyl standard and CoCp₂ standard, respectively.

Effect of THF on the decay of intermediate **3** in C₆D₆ at 298 K

Two identical solutions of **3** (5.2 mg, 5 μmol) in C₆D₆ (0.5 mL) were prepared. To one of the solutions THF (1 μL, 2 equiv, 10 μmol) was added. Each solution was placed in a J. Young tube, and the ratio of **2** and **3** was analyzed by ¹H NMR spectroscopy at various time points (Figure S9).

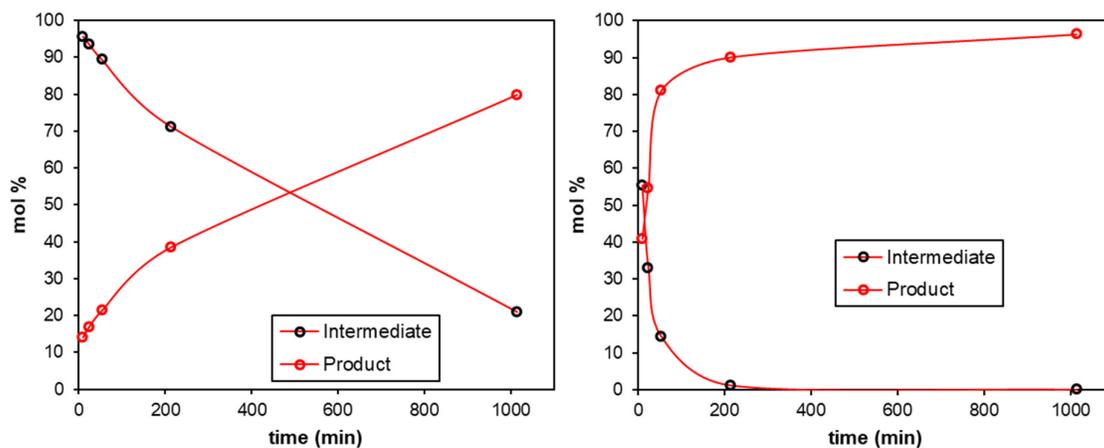


Figure S10. Plot of the mol percentage of intermediate **3** and product **2** as a function of time for a solution in C₆D₆ (left), and an analogous solution containing 2 equiv of THF (right).

Preparation of ^{13}C labeled **3**

A solution of **1** (57 mg, 0.11 mmol) in pentane (3 mL) was placed in a 50 mL resealable Schlenk flask, and was frozen in a liquid N_2 bath. The head space was evacuated, the mixture was thawed, and the flask was backfilled with $^{13}\text{CO}_2$ (0.35 atm, 0.73 mmol). After stirring for 1 h at ambient temperature the mixture was placed at $-40\text{ }^\circ\text{C}$ for 4 h. The flask was placed under a dynamic vacuum for 5 seconds, and was filled with N_2 . The solution was filtered through Celite into a cold vial and placed at $-40\text{ }^\circ\text{C}$ for 16 h. The mother liquor was decanted off and the crystalline residue was dried in vacuum to give a dark purple solid (8 mg). The mother liquor was kept cold, concentrated to *ca.* 1 mL and placed at $-40\text{ }^\circ\text{C}$ for 16 h to give a second crop of dark crystals (22 mg). Combined yield: 30 mg, 54%.

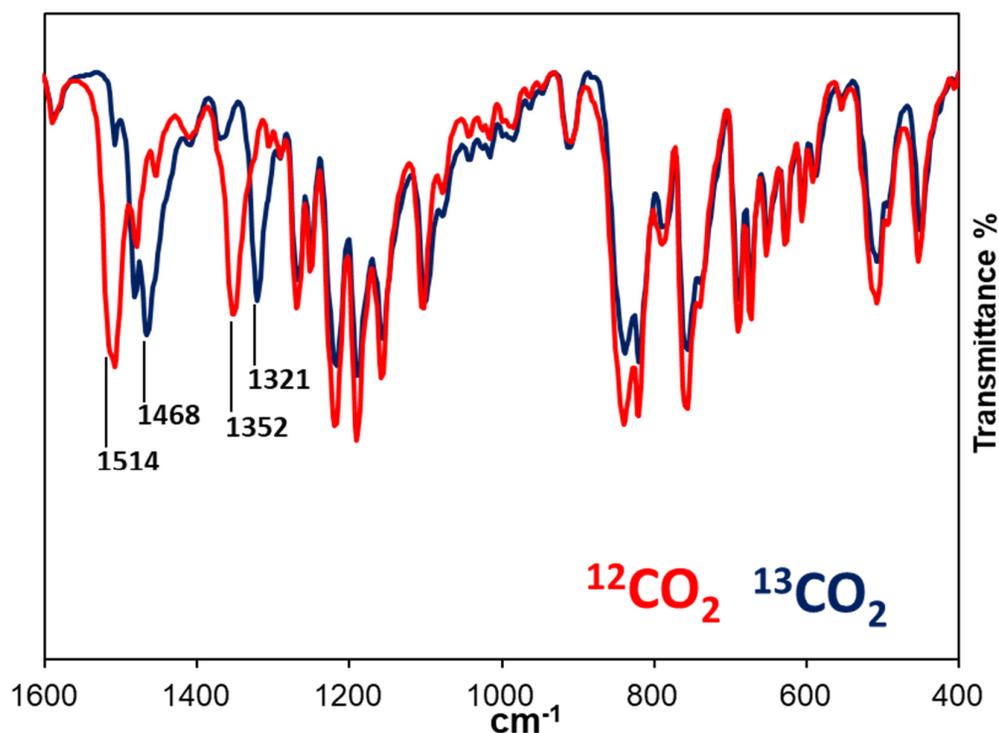


Figure S11. Overlay of the ATR-IR spectra of complex **3** that was synthesized using natural abundance CO_2 (red) and $^{13}\text{CO}_2$ (blue).

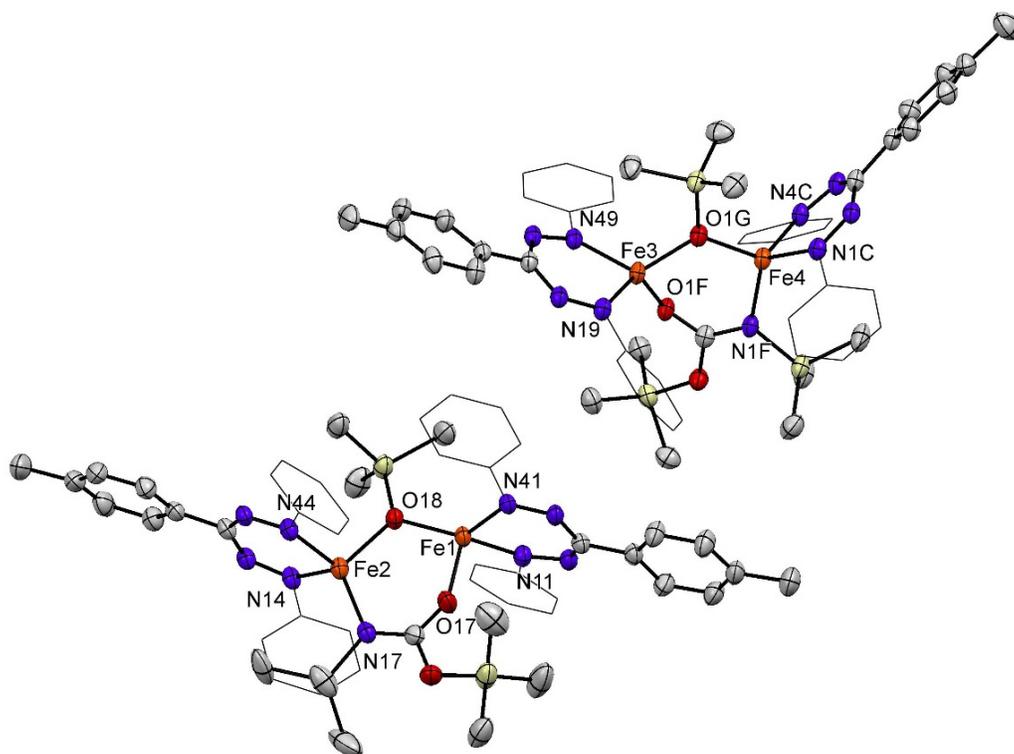


Figure S12. The two crystallographically independent molecules that are found in the asymmetric unit of **3** that differ in the relative orientation of the two formazanate ligands.

X-ray Crystallography

Complex 2

Low-temperature diffraction data (ω -scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu K α ($\lambda = 1.54178 \text{ \AA}$) for the structure of **2**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Several high angle reflections were obscured by the cold stream and subsequently omitted from the refinement. The full numbering scheme of **2** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1815893 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

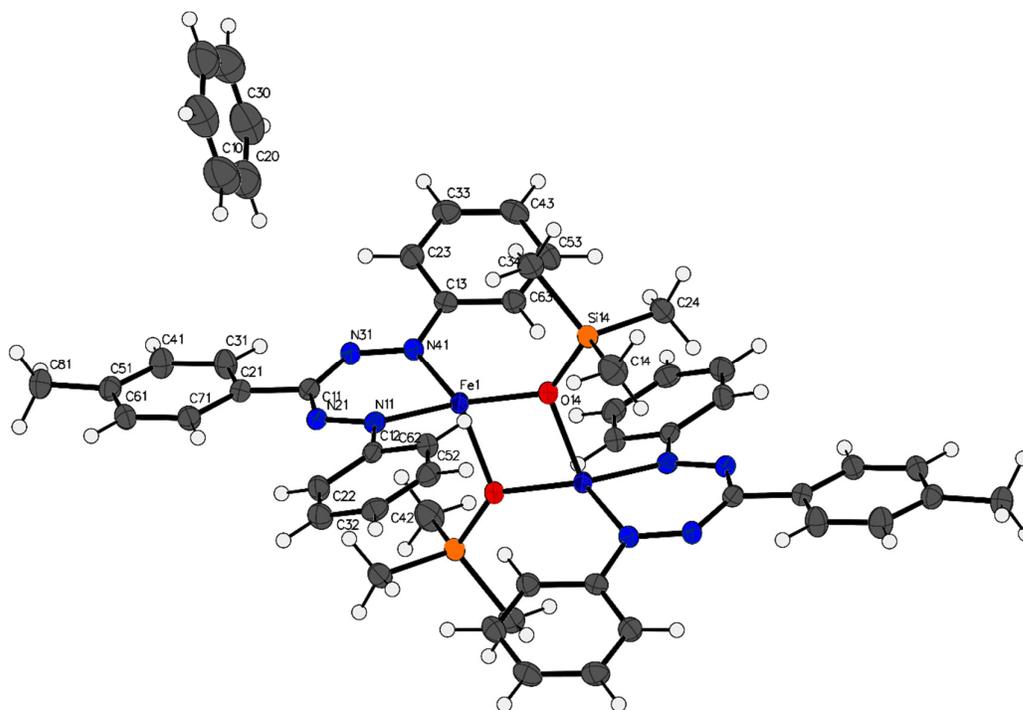


Figure S13. The complete numbering scheme of **2** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity. Only the asymmetric unit is labeled.

Table S1. Crystal data and structure refinement for **2**.

Identification code	007-17041	
Empirical formula	C ₅₂ H ₅₈ Fe ₂ N ₈ O ₂ Si ₂	
Formula weight	994.94	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7134(6) Å	α = 78.011(4)°.
	b = 10.3996(6) Å	β = 72.009(5)°.
	c = 14.3679(7) Å	γ = 66.091(5)°.
Volume	1256.26(14) Å ³	
Z	1	
Density (calculated)	1.315 g/cm ³	
Absorption coefficient	5.464 mm ⁻¹	
F(000)	522	
Crystal size	0.200 x 0.050 x 0.050 mm ³	
Theta range for data collection	3.249 to 66.788°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17	
Reflections collected	44652	
Independent reflections	4370 [R(int) = 0.0502]	
Completeness to theta = 66.788°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.62776	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4370 / 0 / 302	
Goodness-of-fit on F ²	1.070	
Final R indices [I > 2σ(I)]	R1 = 0.0273, wR2 = 0.0688	
R indices (all data)	R1 = 0.0290, wR2 = 0.0709	
Largest diff. peak and hole	0.233 and -0.311 e.Å ⁻³	

Complex 3

Low-temperature diffraction data (ω -scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu $K\alpha$ ($\lambda = 1.54178 \text{ \AA}$) for the structure of **3**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (134 e/\AA^3), it is likely that ~ 3 hexane molecules are present in the unit cell. See "platon_squeeze_details" in this .cif for more information. The full numbering scheme of **3** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1815894 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

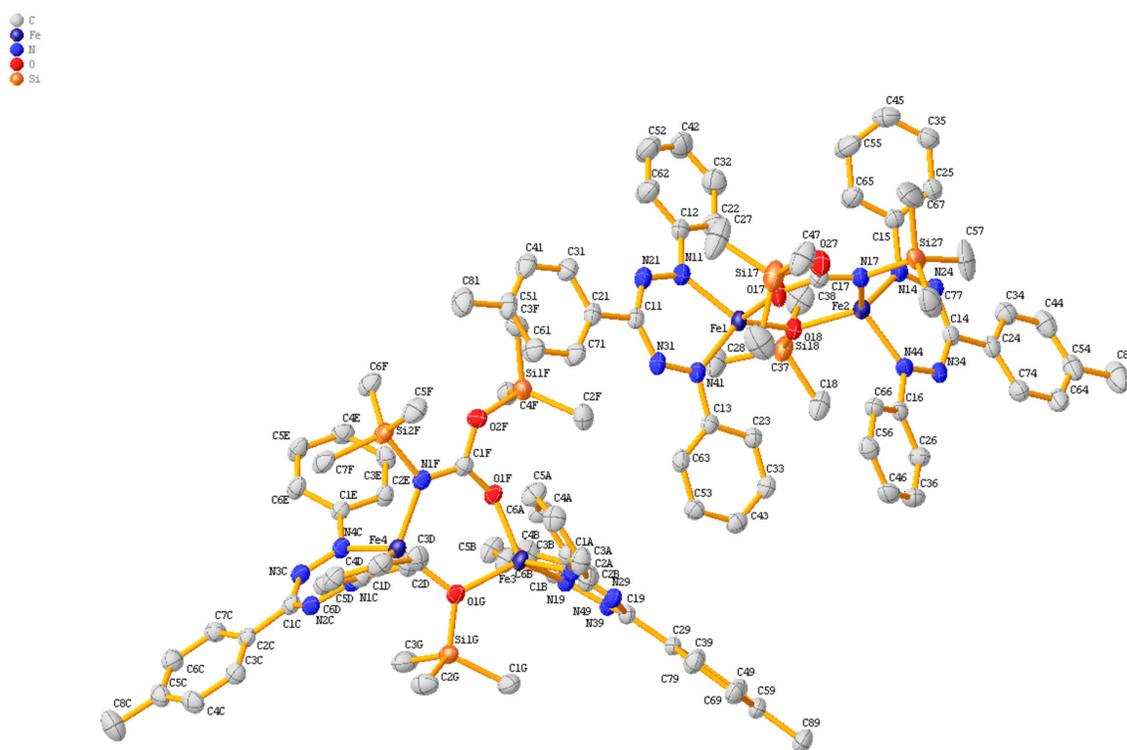


Figure S14. The complete numbering scheme of **3** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S2. Crystal data and structure refinement for **3**.

Identification code	007a-17097	
Empirical formula	C ₅₀ H ₆₁ Fe ₂ N ₉ O ₃ Si ₃	
Formula weight	1032.04	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9146(3) Å	α = 66.499(2)°.
	b = 22.1800(6) Å	β = 87.974(2)°.
	c = 26.3106(6) Å	γ = 79.128(2)°.
Volume	5730.6(3) Å ³	
Z	4	
Density (calculated)	1.196 g/cm ³	
Absorption coefficient	5.020 mm ⁻¹	
F(000)	2168	
Crystal size	0.200 x 0.040 x 0.040 mm ³	
Crystal color and habit	Red Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	1.833 to 67.011°.	
Index ranges	-12 ≤ h ≤ 12, -26 ≤ k ≤ 26, -31 ≤ l ≤ 31	
Reflections collected	210161	
Independent reflections	19999 [R(int) = 0.0867]	
Observed reflections (I > 2σ(I))	14508	
Completeness to theta = 67.011°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.66729	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	19999 / 0 / 1229	
Goodness-of-fit on F ²	0.957	
Final R indices [I > 2σ(I)]	R1 = 0.0354, wR2 = 0.0800	
R indices (all data)	R1 = 0.0552, wR2 = 0.0843	
Largest diff. peak and hole	0.382 and -0.318 e.Å ⁻³	

References

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² Amman, C; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319-321

³ Travieso-Puente, R.; Broekman, J. O. P.; Chang, M.-C.; Demeshko, S.; Meyer, F.; Otten, E. *J. Am. Chem. Soc.* **2016**, *138*, 5503.