Supporting Information for

Molecular quadrangle formation from a diuranium μ-η^6,η^6-toluene complex

*Marisa J. Monreal, Jaqueline L. Kiplinger, and Paula L. Diaconescu**

Contents:

General considerations

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[1] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Uranium turnings were purchased from Argonne National Laboratories. $(NN^{fc})UI_2(THF)$ was prepared following a published procedure.[2] KC_8 was prepared using a ball-milling technique[3] by the laboratory of Prof. Richard Kaner (UCLA) and provided as a gift to us. Aromatic N-heterocycles were recrystallized before use; all other materials were used as received. ^1H NMR spectra were recorded on Bruker300 or Bruker500 spectrometers (NSF grant CHE-9974928) at room temperature in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to solvent residual peak, 7.16 ppm (C_6D_6). CHN analyses were performed by UC Berkeley Micro-Mass facility, 8 Lewis Hall, College of Chemistry, University of California, Berkeley, CA 94720.

Synthesis of $(NN^{fc})_2U_2(\mu\text{–}\eta^6,\eta^6\text{-}C_7H_8)$, 1. KC_8 (0.2378 g, 1.759 mmol, 3 equiv) was added to $(NN^{fc})UI_2(THF)$ (0.5902 g, 0.5864 mmol in 40-50 mL toluene) in a 100 mL round bottom flask, and the reaction mixture was stirred for 20 h at room temperature. *Note:* Each time this synthesis is carried out, an aliquot of the reaction mixture is taken at 20 h to check for reaction completion, indicated by complete absence of $(NN^{fc})UI_2(THF)$ signals (^1H NMR (C_6D_6, 298 K): δ 56.6 (s, 12H, $SiCH_3$), 40.5 (s, 18H, $SiC\text{-}CH_3$), -20.3 (m, 4H, C_5H_4), -26.1 (s, 4H, THF-CH_2), -41.0 (m, 4H, C_5H_4), -74.0 (s, 4H, THF-CH_2). Due to the heterogeneous nature of this reaction, reaction times of up to 24 h have sometimes been required). The reaction mixture was then filtered through Celite, and toluene was used to rinse the Celite until the filtrate was clear. The volatiles were removed under reduced pressure, and the resulting product was collected on a medium-porosity frit, washed with hexanes until the filtrate was clear, and dried under reduced pressure. Yield: 0.3451 g, 81%. Anal. calcd. for $C_{51}H_{84}N_4Fe_2Si_4U_2$: C, 42.15%; H, 5.83%; N, 3.86%. Found: C, 42.0%, H, 5.70%, N, 3.97%.

Synthesis of $[(NN^{fc})U(\mu\text{-quinoxaline})]_4$, 2. In a 25 mL Schlenk tube containing a stir bar, quinoxaline (0.0281 g, 0.2159 mmol, 2 equiv, dissolved in and transferred with ~4 mL toluene) was added to **1** (0.1568 g, 0.1079 mmol, in ~6 mL toluene), and toluene was added until the total volume was 12-15 mL. The reaction was stirred vigorously at 85 °C for 1.5 h, during which time a color change from black to brown-black was observed. The reaction was frequently checked to ensure good mixing. The volatiles were removed under reduced pressure. The resulting shiny brown-black solid was dissolved in diethyl ether and filtered through Celite. The diethyl ether filtrate was placed in a -35 °C freezer and crystals formed overnight. Reactions performed with 100-150 mg of **1** routinely gave 20-30 mg crystalline material isolated from diethyl ether after one night at -35 °C. Anal. calcd. for $C_{120}H_{176}N_{16}Fe_4Si_8U_4$: C, 44.44%; H, 5.47%; N, 6.91%. Found: C, 44.71%; H, 5.45%; N, 6.81%.

Dilute reaction of 1 + 2 equiv quinoxaline

In an attempt to encourage sole formation of **2**, the synthesis was carried out in dilute toluene.

In a 350 mL Schlenk tube containing a stir bar, **1** (0.0998 g, 0.0687 mmol) was dissolved in 50 mL toluene. Quinoxaline (0.0179 g, 0.137 mmol, 2 equiv, dissolved and transferred with 10 mL toluene) was added. The reaction mixture was stirred vigorously at 85 ^{o}C for 1.5 h.

^{1}H NMR spectrum of an aliquot of the reaction mixture taken at 1.5 h was identical to reactions not performed in dilute toluene solutions (12-15 mL versus 60 mL total volume), showing a small amount of the secondary product (see p. 7).

Crystalline material isolated from the diethyl ether extract contained the secondary product, which proved to be inseparable from **2**. No further crops could be collected, and the mother liquor eventually underwent decomposition.

Reaction of 1 + slight excess quinoxaline

In order to rule out the chance that the secondary product was forming due to insufficient quinoxaline related to weighing/transferring errors, a reaction was carried out using a slight excess of quinoxaline.

In a 25 mL Schlenk tube containing a stir bar, quinoxaline (2.0 mL of a 0.072 M toluene solution, 2.1 equiv) was added to **1** (0.1000 g in ~6 mL toluene), and toluene was added until the total volume was ~12-15 mL. The reaction mixture was stirred vigorously at 85 ^{o}C for 1.5 h.

^{1}H NMR spectrum of an aliquot of the reaction mixture taken at 1.5 h was similar to reactions done using 2 equiv quinoxaline, showing a small amount of the secondary product (see p. 7).

Crystalline material isolated from the diethyl ether extract also contained the secondary product, which proved to be inseparable from **2**. No further crops could be collected, and the mother liquor eventually underwent decomposition.

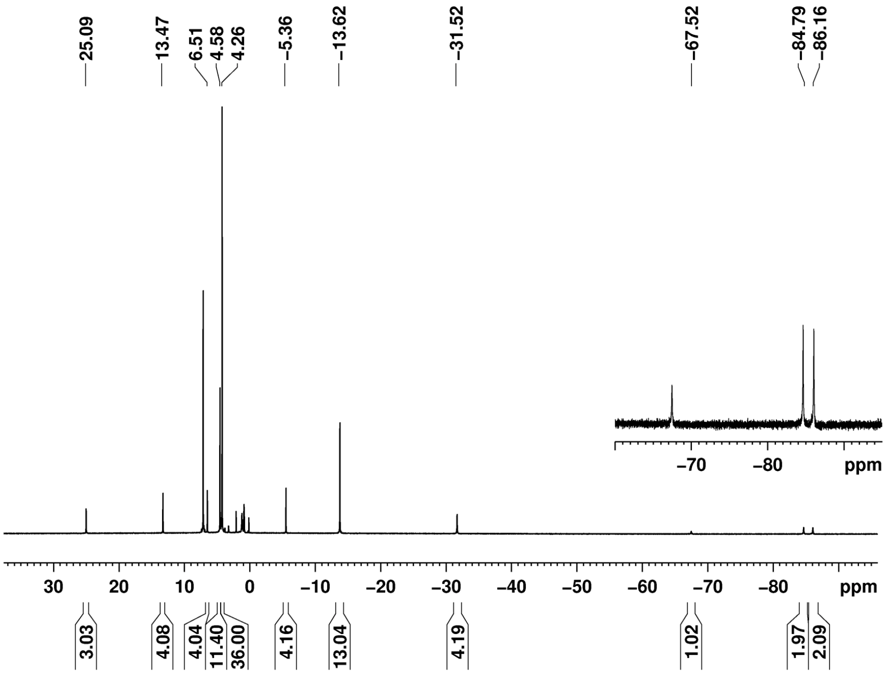
Reaction of 1 + 2 equiv pyrazine

Pyrazine (0.0143 g, 0.179 mmol, 2 equiv) and **1** (0.1285 g, 0.0884 mmol) were combined in a scintillation vial with a total of 15 mL toluene and immediately upon mixing, black solids formed. A ^{1}H NMR spectrum of an aliquot of the reaction was attempted in C_6D_6 at 1 h reaction time: no starting material remained, but the black solids were insoluble in C_6D_6 and no signals were visible in the spectrum. The reaction was allowed to stir at room temperature for a total of 2.5 h. The reaction mixture was dried under reduced pressure and the resulting black powder was collected on a medium-porosity frit and washed with toluene and hexanes. Yield: 0.1136 g. Anal. calc. for $C_{104}H_{168}Fe_4N_{16}Si_8U_4$: C, 41.05%; H, 5.56%; N, 7.36%. Found: C, 40.96%; H, 5.22%; N, 7.06%.

Synthesis of $(NN^{fc})U(NMe_2)_2$

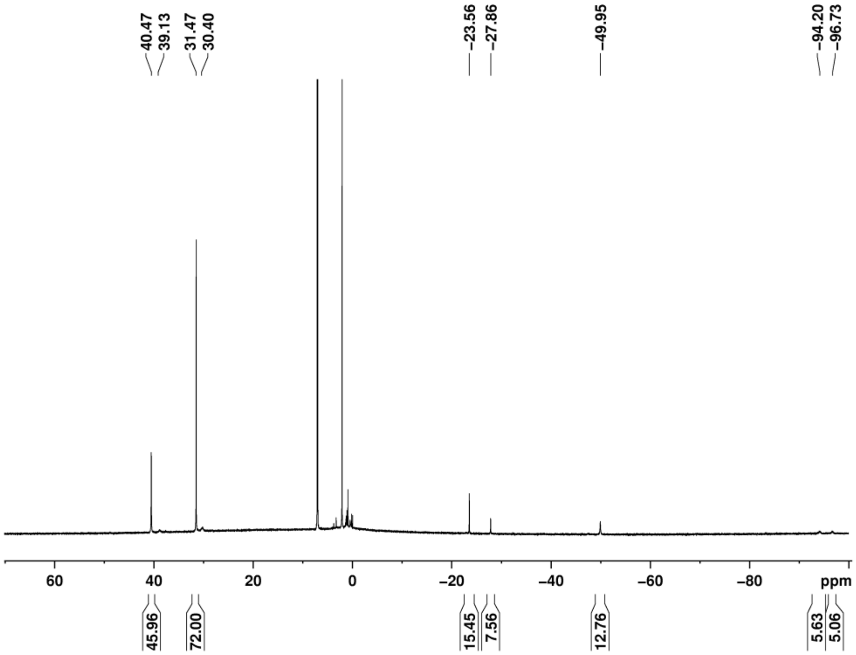
A suspension of $(NN^{fc})UI_2(THF)$[2] (0.2083 g, 0.207 mmol, in 5 mL diethyl ether) was cooled for 30 minutes at -35 °C. Solid $LiNMe_2$ (0.0211 g, 0.414 mmol, 2 equiv) was added, and the reaction mixture was stirred for 30 minutes while warming to room temperature. Diethyl ether was then removed under reduced pressure. The dried product was extracted into toluene, filtered through Celite, and the toluene was removed under reduced pressure. This extraction procedure was repeated two more times using hexanes. After the last filtration, the hexanes filtrate was concentrated to 1-2 mL and placed in a -35 °C freezer. Crystals formed after several hours. Yield (over two crops of crystals): 0.0965 g, 61%. Anal. calc. for $C_{26}H_{50}FeN_4Si_2U$: C, 40.62%; H, 6.56%; N, 7.29%. Found: C, 40.84%; H, 6.53%; N, 7.34%.

^{1}H NMR spectrum: $(NN^{fc})_2U_2(\mu\text{-}\eta^6,\eta^6\text{-}C_7H_8)$, 1



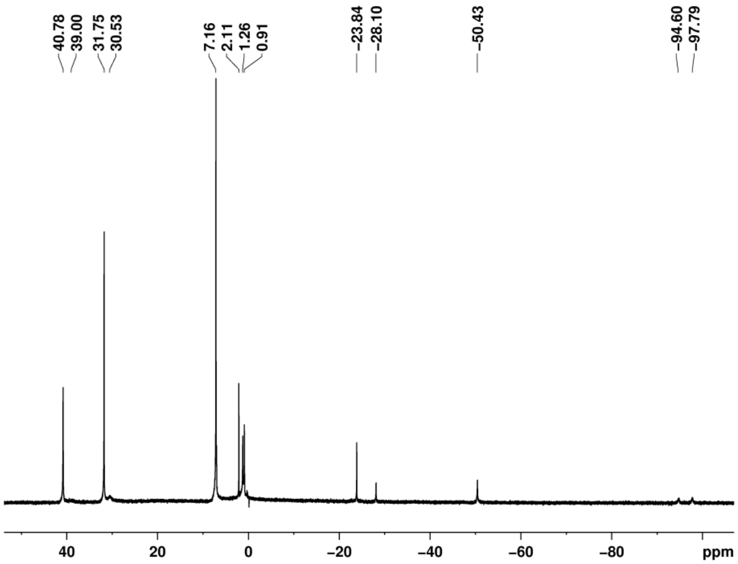
^{1}H NMR (C_6D_6, 300 MHz, 25°C), δ, ppm: 25.10 (s, 3H, μ-toluene-CH_3), 13.47, 6.51, -5.36, and -31.52 (s, 4H, Cp-C*H*), 4.58 and -13.62 (s, 12H, SiCH_3), 4.26 (s, 36H, SiC(CH_3)$_3$), -67.52 (s, 1H, μ-toluene-C*H*), -84.79 and -86.16 (s, 2H, μ-toluene-C*H*) (inset shows magnified aromatic μ-toluene signals).

^{1}H NMR spectrum: [(NN^{fc})U(μ-quinoxaline)]$_4$, 2

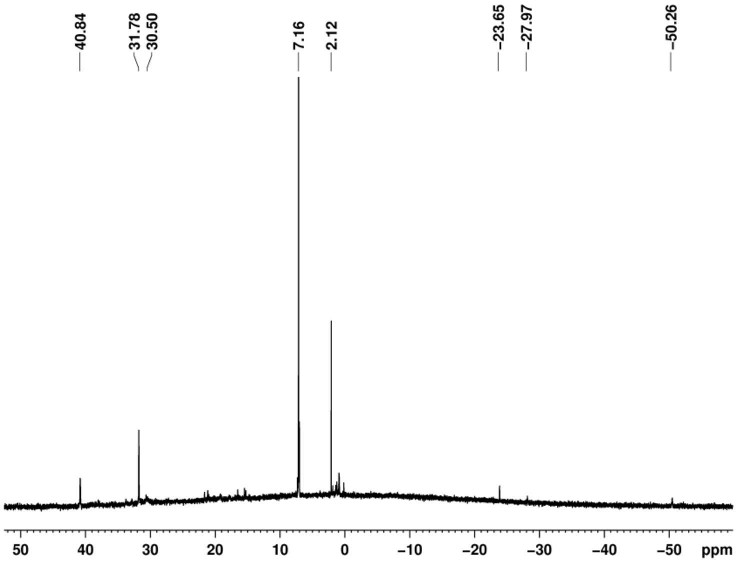


^{1}H NMR (C_7D_8, 500 MHz, 25°C), δ, ppm: 40.47 (s, 48H, SiCH_3), 31.47 (s, 72H, SiC(CH_3)$_3$), -23.56 and -49.95 (s, 16H, Cp-C*H*), -27.86, -94.20, and -96.73 (s, 8H, quinoxaline-C*H*). Small, broad peaks for secondary product can be observed at 39.13 and 30.40 ppm.

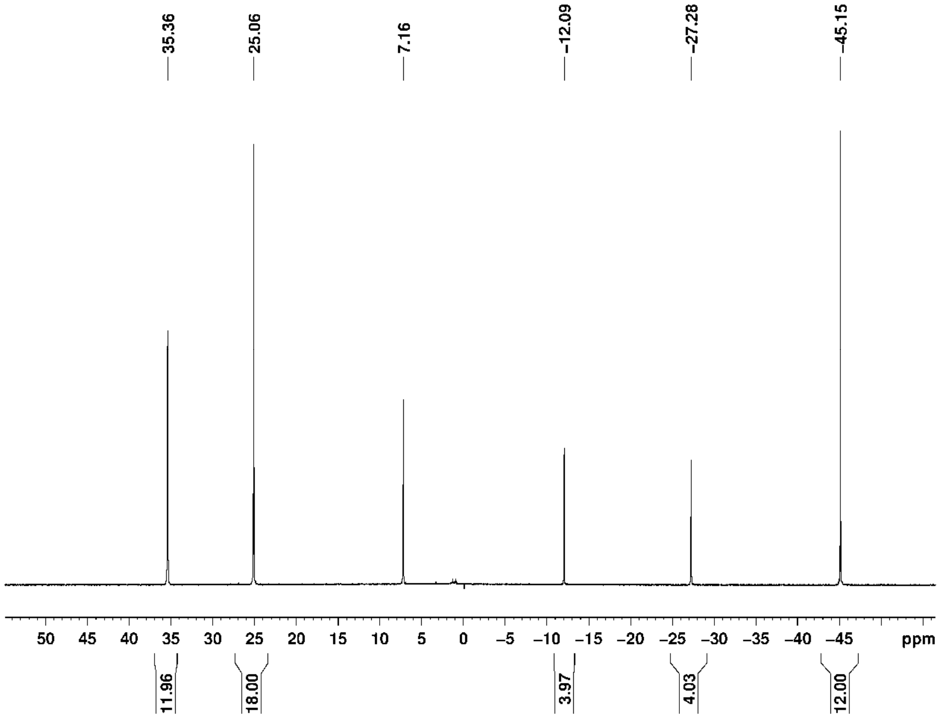
^{1}H NMR spectrum: dilute reaction of 1 + 2 equiv quinoxaline



^{1}H NMR spectrum: reaction of 1 + slight excess quinoxaline



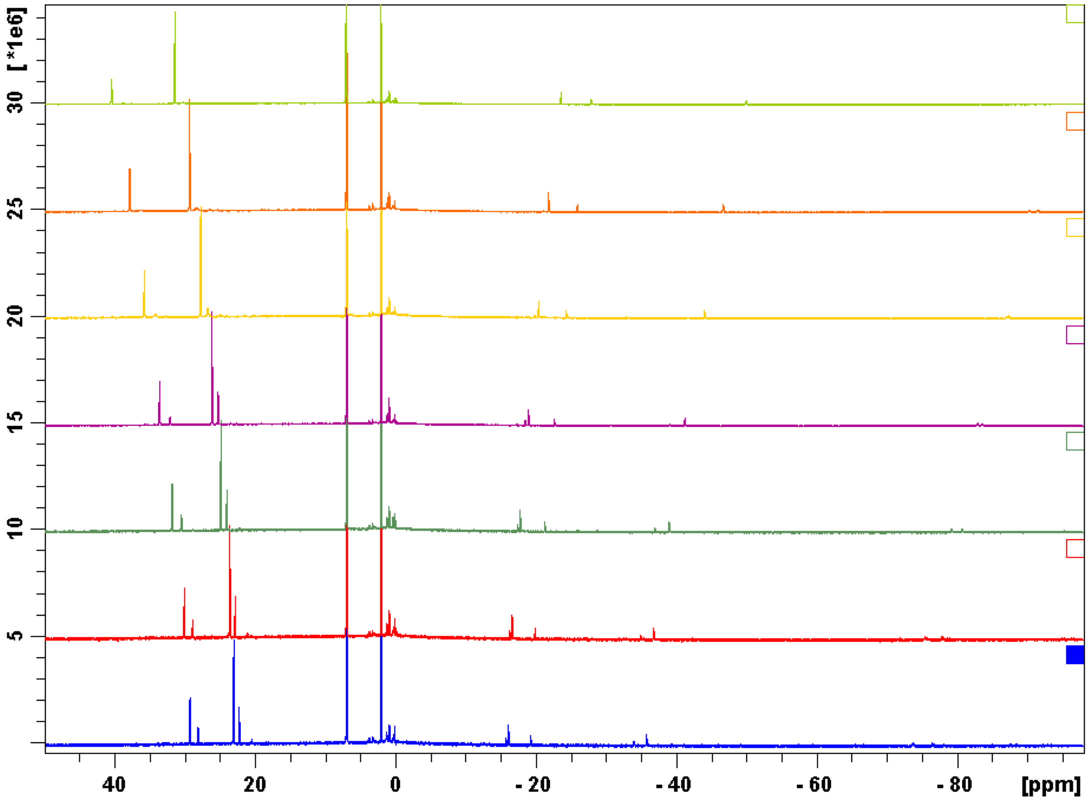
^{1}H NMR spectrum: $(NN^{fc})U(NMe_2)_2$



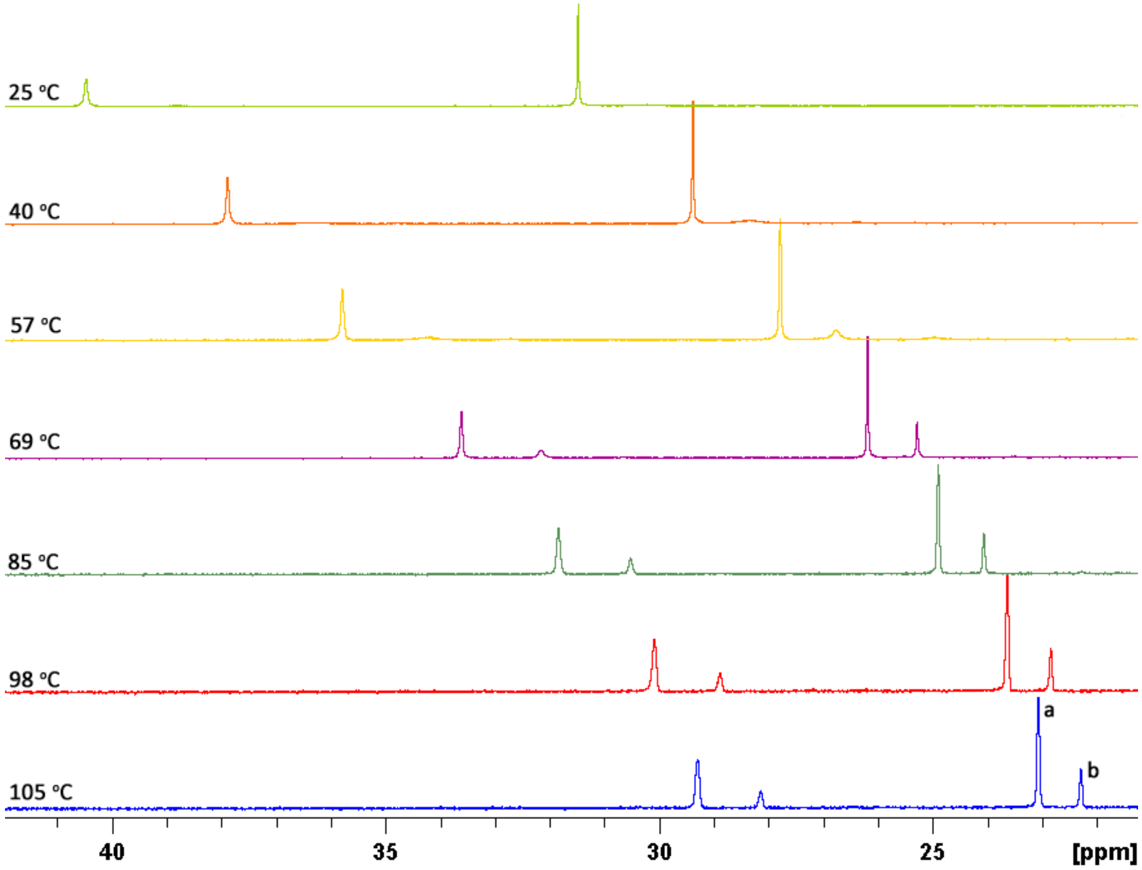
^{1}H NMR (C_6D_6, 300 MHz, 25°C), δ, ppm: 35.36 (s, 12H, $SiCH_3$), 25.06 (s, 18H, $SiC(CH_3)_3$), -12.09 and -27.28 (s, 4H, Cp-C*H*), -45.15 (s, 12H, $N(CH_3)_2$).

Variable temperature (VT) ^{1}H NMR spectroscopy experiment

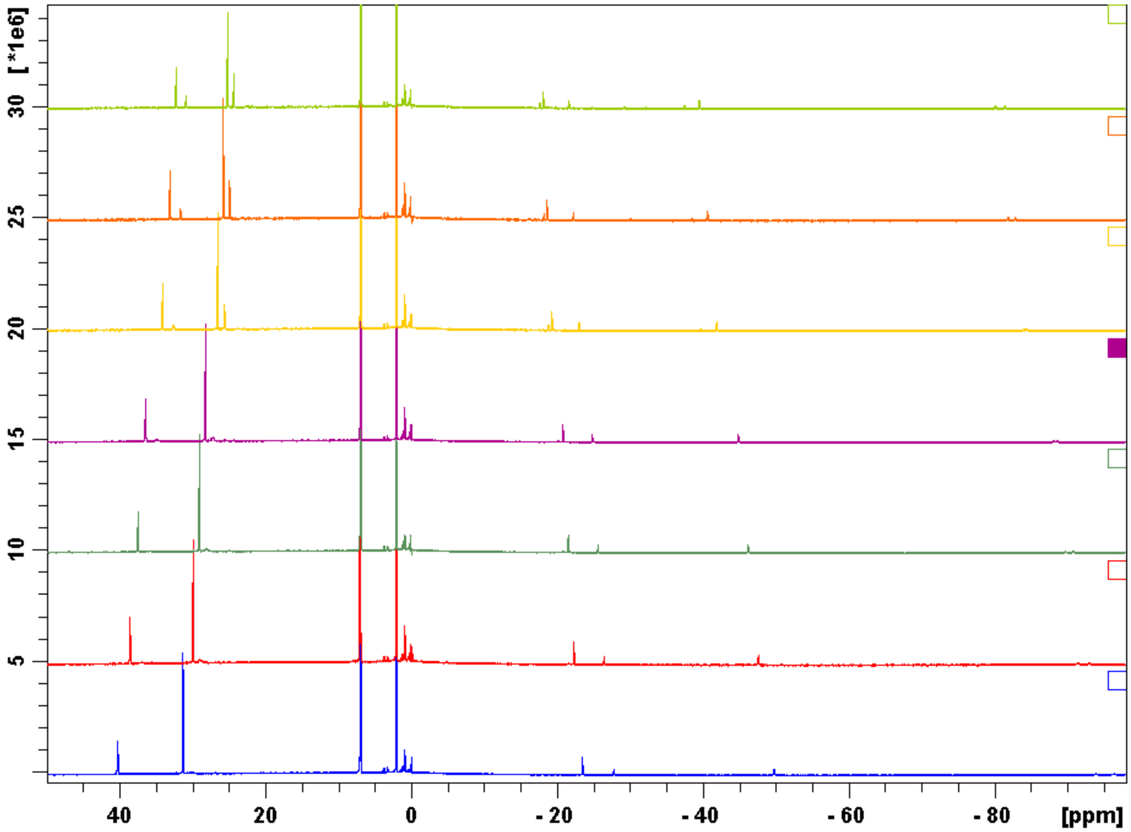
A toluene-*d*$_8$ sample of **2** was heated from room temperature to 105 ^{o}C. Full spectra for each temperature are shown stacked below. Temperatures from top to bottom (^{o}C) are: 25, 40, 57, 69, 85, 98, 105.



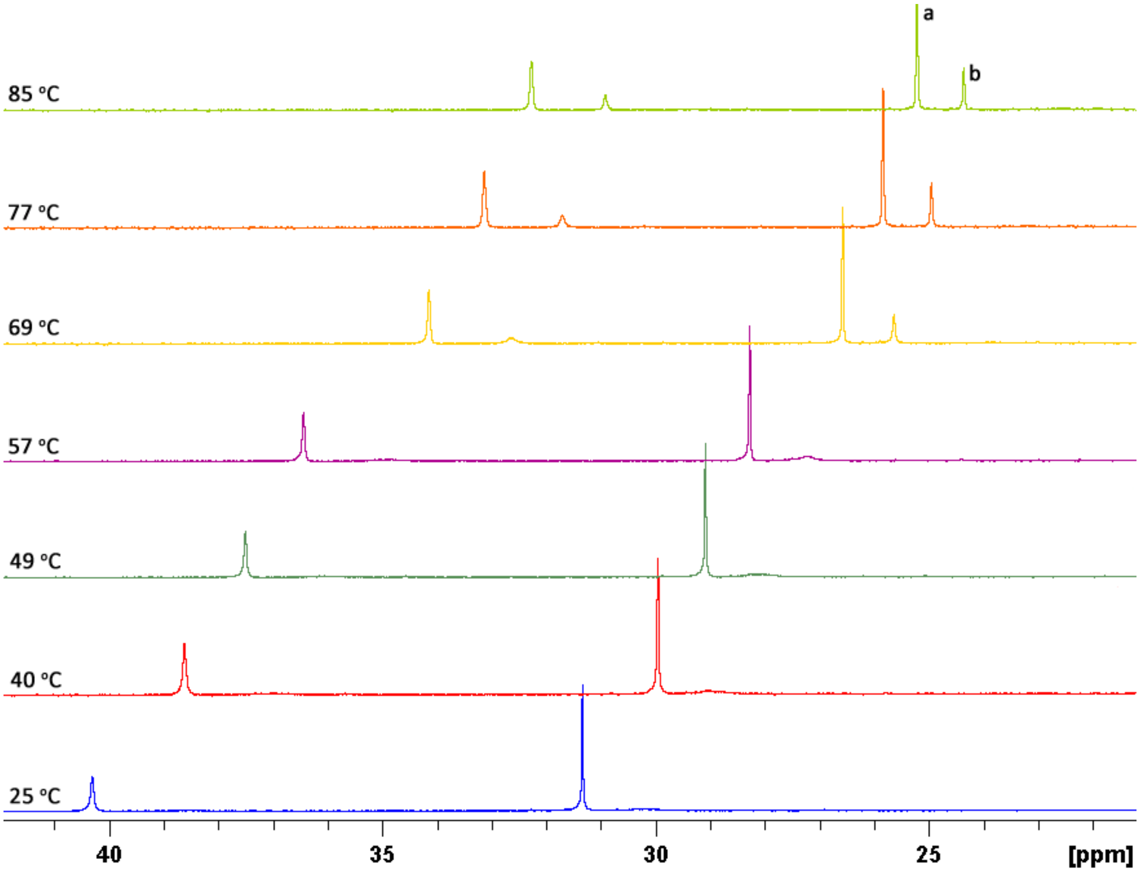
Ratios of major product to minor product (a:b, calculated using integrations of labeled peaks): 25 °C, 9.8; 40 °C, 5.2; 57 °C, 3.2; 69 °C, 2.8; 85 °C, 2.9; 98 °C, 2.9; 105 °C, 2.9.
Stacked spectra of region showing signals used for ratio calculation are shown below.



Immediately after heating to 105 °C, the toluene-d_8 sample of **2** was cooled to room temperature. Full spectra for each temperature are shown stacked below. Temperatures from top to bottom (°C) are: 85, 77, 69, 57, 49, 40, 25.



Ratios of major product to minor product (a:b, calculated using integrations of labeled peaks): 85 ^{o}C, 3.1; 77 ^{o}C, 3.0; 69 ^{o}C, 3.2; 57 ^{o}C, 4.6; 49 ^{o}C, 5.1; 40 ^{o}C, 4.8; 25 ^{o}C, 10.3.
Stacked spectra of region showing signals used for ratio calculation are shown below.



Absorption spectroscopy experimental details and UV-vis/NIR spectra of 2 and $(NN^{fc})U(NMe_2)_2$

UV-vis (Figure SX1, left) and NIR (Figure SX2, solid trace) spectra of toluene solutions of **2** were recorded on a Shimadzu UV-3101PC UV-vis-NIR scanning spectrophotometer using a 1 cm quartz cell with an air-free Teflon adapter. UV-vis (Figure SX1, right) and NIR (Figure SX2, dotted trace) spectra of toluene solutions of $(NN^{fc})U(NMe_2)_2$ were recorded on a Perkin Elmer Lambda 950 UV-vis-NIR spectrophotometer using a 1 mm quartz cell with an air-free Teflon adapter. Solvent (toluene) data was collected and either manually subtracted out (NIR for both compounds, UV-vis for $(NN^{fc})U(NMe_2)_2$) or used as a blank before sample data was collected (UV-vis of **2**).

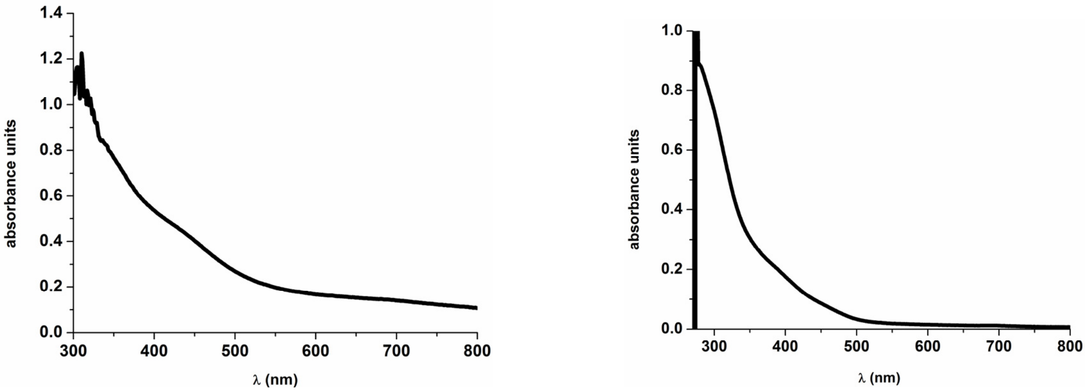


Figure SX1. UV-vis spectra of toluene solutions of **2** (left) and $(NN^{fc})U(NMe_2)_2$ (right)

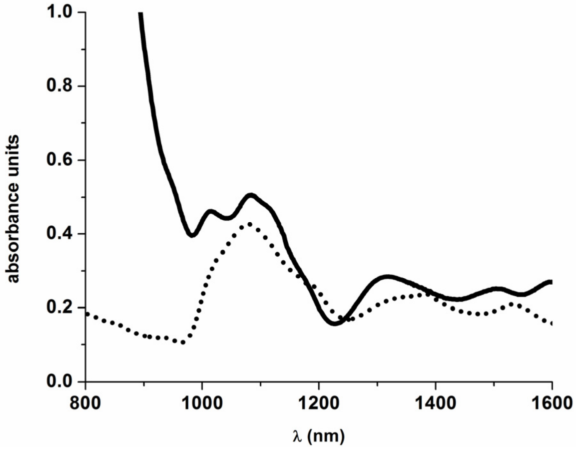


Figure SX2. Near-infrared (NIR) spectra for **2** (solid trace) and $(NN^{fc})U(NMe_2)_2$ (dotted trace).

Magnetic susceptibility data for 1

Measurements for each compound were carried out on batches obtained independently until at least two different experiments gave super-imposable results. The samples used were recrystallized multiple times. Magnetic susceptibility measurements were recorded using a SQUID magnetometer at 5000 G. The samples were prepared in the glove box (ca. 50 mg), loaded in a gelatin capsule that was positioned inside a plastic straw and carried to the magnetometer in a tube under N_2. The sample was quickly inserted into the instrument, centered and data obtained from 5 to 300 K. The contribution from the sample holders was not accounted for. Effective magnetic moments were calculated either by linear regression from plots of $1/\chi_{mol}$ versus T (K) for Curie-Weiss behavior or by using the formula $2.828*\sqrt{(T*\chi_{mol})}$ for non-Curie-Weiss behavior.

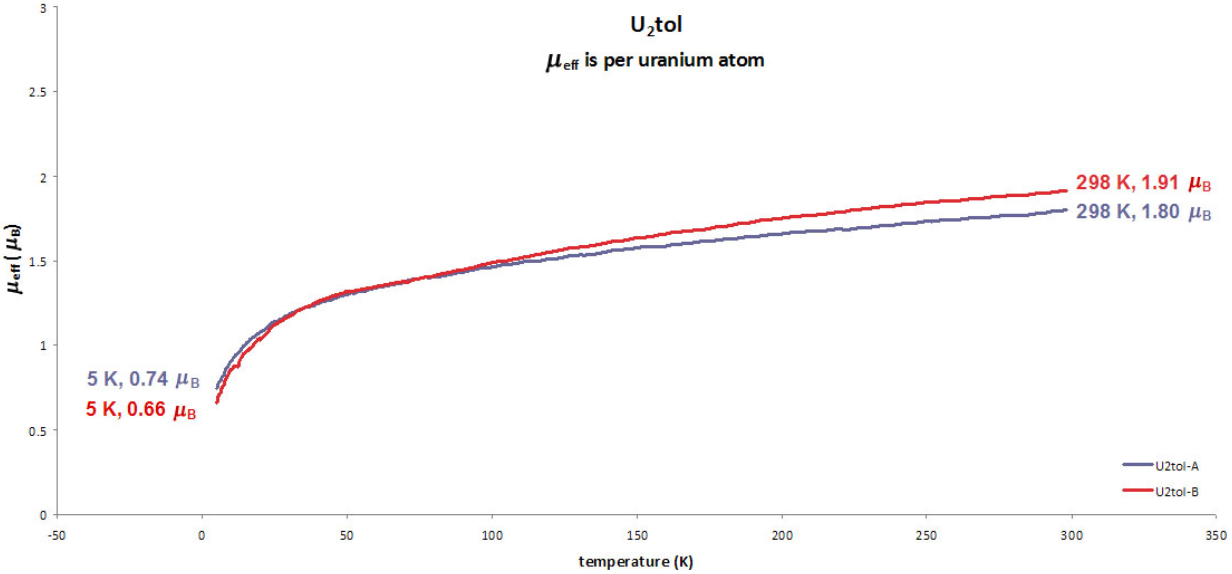


Figure SX3. Magnetic susceptibility data for **1** showing super-imposable results for two samples, independently prepared and purified.

Crystal structure of 1

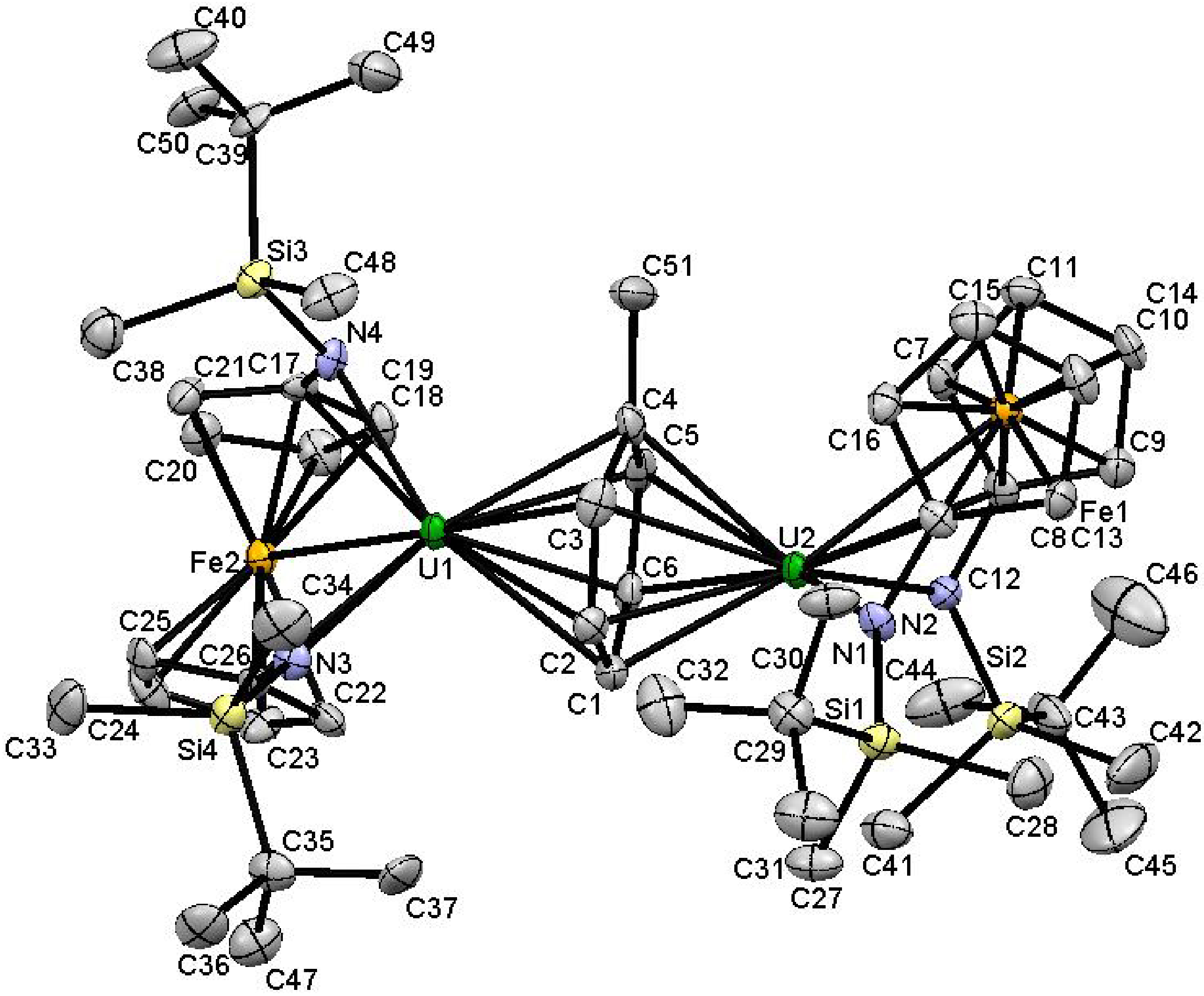


Figure SX4. Thermal-ellipsoid (50% probability) representation of **1**; hydrogen atoms omitted for clarity.

X-ray quality crystals were obtained from a concentrated toluene solution placed in a -35 °C freezer in the glove box. The crystal was two-component non merohedral twin. The second domain was rotated 180 degrees about reciprocal axis -1 1 0. Some of the methyl groups were slightly disordered; the disorder was not modeled. A total of 23597 reflections ($-19 \leq h \leq 16$, $-20 \leq k \leq 20$, $0 \leq l \leq 20$) were collected at T = 100(2) K with $2\theta_{\max} = 56.65°$, of which 15546 were observed reflections. The residual peak and hole electron density were 2.01 and -1.63 eA^{-3}. The least-squares refinement converged normally with residuals of R_1(obs) = 0.0522 and GOF = 1.004. Crystal and refinement data for 1: formula $C_{51}H_{84}N_4Si_4Fe_2U_2$, formula weight = 1453.34, triclinic, space group $P\bar{1}$, a = 14.3594(14), b = 14.9877(14), c = 15.2355(15), α = 91.472(1), β = 118.893(1), γ = 100.730(1)°, V = 2795.0(5) Å^3, Z = 2, μ = 6.407 mm^{-1}, F(000) = 1420, R_1(all) = 0.0984 and wR_2(all) = 0.1098.

Crystal structure of 2

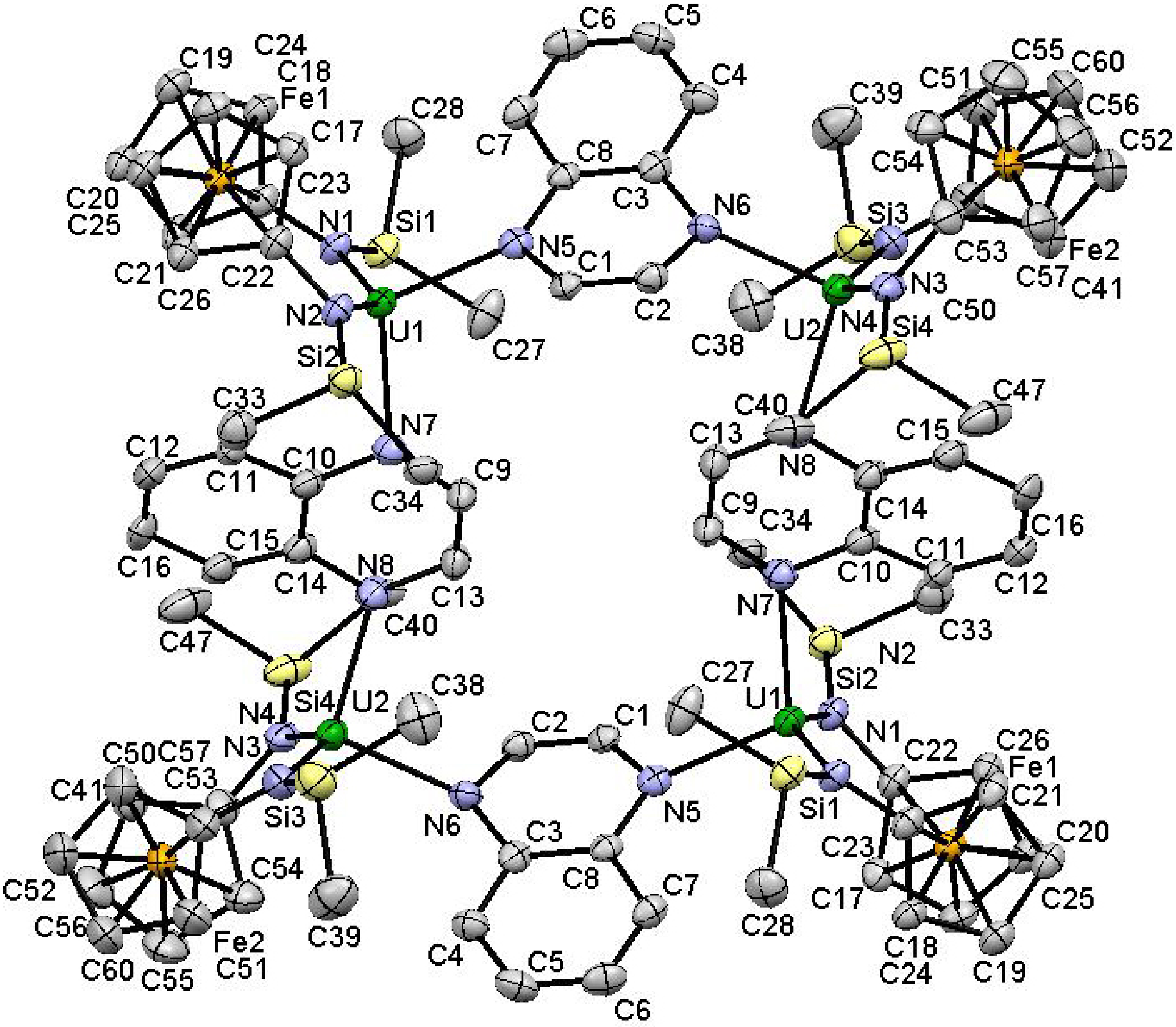


Figure SX5. Thermal-ellipsoid (50% probability) representation of **2**; hydrogen atoms omitted for clarity.

X-ray quality crystals were obtained from a diethyl ether solution placed in a -35 °C freezer in the glove box. The unit cell contains half of a molecule. One of the ferrocene ligands (ferrocene group and one amide substituent) was disordered and the disorder was modeled. The unit cell contains large accessible voids; solvent molecules could not be modeled to fit this space (it is possible that some solvent was lost during crystal handling) and the program SQUEEZE was used. A total of 19281 reflections ($-44 \leq h \leq 44$, $-44 \leq k \leq 44$, $-48 \leq l \leq 47$) were collected at T = 100(2) K with $2\theta_{\max}$ = 53.01°, of which 12328 were unique. The residual peak and hole electron density were 1.77 and -1.75 eA^{-3}. The least-squares refinement converged normally with residuals of R_1(obs) = 0.0580 and GOF = 0.946. Crystal and refinement data for **2**: formula $C_{120}H_{176}N_{16}Si_8Fe_4U_4$, formula weight = 3243.01, space group R-3, a = 35.332(7), b = 35.332(7), c = 38.836(8), α = β = 90, γ = 120°, V = 41986(16) Å^3, Z = 9, μ = 3.847 mm^{-1}, F(000) = 14328.0, R_1 (all)= 0.0911 and wR_2 (all) = 0.1580.

References

1 A. B. G. Pangborn, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics*, 1996, **15**, 1518-1520.
2 M. J. Monreal and P. L. Diaconescu, *Organometallics*, 2008, **27**, 1702-1706.
3 S. M. Hick, C. Griebel and R. G. Blair, *Inorg. Chem.*, 2009, **48**, 2333-2338.