Supporting Information for

Four-Electron Reduction Chemistry Using an Uranium(III) Phosphido Complex

Pokpong Rungthanaphatsophon, Charles L. Barnes, Steven P. Kelley, and Justin R. Walensky*

Department of Chemistry, University of Missouri, Columbia, MO 65211, USA

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Experimental

General Considerations. All compounds were handled under an inert atmosphere of N_2 inside a glovebox. $HP(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)$,[1] benzyl potassium,[2] $(C_5Me_5)_2UI(THF)$,[3] and $(C_5Me_5)_2UCl_2$[4] were prepared according to the procedure previously reported. Toluene and THF were dried by passing through solvent purification system, MBRAUN, USA. Azidotrimethylsilane, 1-azidoadamantane, and *tert*-butyl isocyanide were purchased from Aldrich and used without further purification. C_6D_6 obtained from Cambridge Isotope Laboratories was subjected to three freeze-pump-thaw cycles and dried over 4 Å molecular sieves prior to use. All ^1H and $^{13}C\{^1H\}$ NMR experiments were performed on 500 or 600 MHz Bruker spectrometers. All $^{31}P\{^1H\}$ and ^{29}Si INEPT experiments were performed on a 300 MHz Bruker spectrometer. All chemical shifts and coupling constant are reported in ppm and Hz, respectively. All ^1H and $^{13}C\{^1H\}$ chemical shifts were reported with respect to residue C_6D_5H at 7.16 ppm and $^{13}C_6D_6$ at 128.06 ppm, respectively. All $^{31}P\{^1H\}$ spectra were calibrated externally to 85% H_3PO_4. All ^{29}Si spectra were calibrated externally to $SiMe_4$. Infrared spectra were recorded as KBr pellets on Perkin-Elmer Spectrum One FT-IR spectrometer.

Synthesis of $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$, 1. To a scintillation vial charged with $(C_5Me_5)_2UI(THF)$ (356 mg, 0.5 mmol), THF (5 mL), and a magnetic stir bar, $KP(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)$ (132 mg, 0.5 mmol) in THF (5 mL) was added at room temperature. The solution was stirred at room temperature overnight. After which, THF was removed *in vacuo*. The solid was then extracted with toluene and filtered through Celite to yield a dark brown solution. After which, toluene was removed *in vacuo* to yield $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$ as a dark brown powder (384 mg, 95%). X-ray quality of $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$ was obtained by concentrated the solution of $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$ in

diethyl ether and placed in the freezer for several days. IR (KBr, cm^{-1}): 2962 (s), 2905 (vs), 2857 (s), 1439 (m), 1377 (w), 1261 (w), 1246 (m), 1095 (br-m), 1021 (m), 906 (w), 838 (vs), 668 (w), 628 (w), 606 (w), 551 (w). Anal. Calcd for $C_{36}H_{58}OPSiU$: C, 53.78; H, 7.27. Found: C, 53.76; H, 7.05.

Synthesis of $(C_5Me_5)_2U[=N(SiMe_3)]_2$, 2. Method A: To a scintillation vial charged with KC_8 (58 mg, 0.42 mmol), THF (2.5 mL), and a magnetic stir bar, $(C_5Me_5)_2UCl_2$ (124 mg, 0.21 mmol) in THF (2.5 mL) was added at room temperature. The solution was stirred for 1 hour at room temperature. Excess amount of azidotrimethylsilane (ca. 0.1 mL, 0.76 mmol) was added via syringe. Gas evolution from the solution was observed immediately follow by a color change from green to brown. The solution was let to stir at room temperature overnight followed by filtration over Celite to yield a dark green solution. THF and excess azidotrimethylsilane were removed in vacuo to yield $(C_5Me_5)_2U[N(TMS)]_2$ as a dark green powder (100mg, 68%). Method B: To a scintillation vial charged with $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$ (206 mg, 0.26 mmol), toluene (3 mL), and a magnetic stir bar, an excess amount of azidotrimethylsilane (ca. 0.1 mL, 0.76 mmol) was added via syringe. Gas evolution from the solution was observed immediately. The solution was left to stir at room temperature overnight. X-ray quality of $(C_5Me_5)_2U[N(SiMe_3)]_2$ was obtained by concentrated this solution to ca. 1 ml and placed in the freezer for several days (48 mg, 27%).^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 4.40 (s, 30H, $C_5(CH_3)_5$), 0.34 (s, 18H, $=N(Si(CH_3)_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 138.9 ($C_5(CH_3)_5$), 16.9 ($=N(Si(CH_3)_3)$), 9.4 ($C_5(CH_3)_5$). ^{29}Si INEPT NMR (C_6D_6, 60 MHz): δ -52.9 ($=N(Si(CH_3)_3)$). IR (KBr, cm^{-1}): 2952 (m), 2904 (m), 2858 (m), 1437 (w), 1377 (w), 1258 (w), 1240 (m), 1084 (w), 1065 (w), 1020 (w), 977 (s), 929 (s), 889 (m), 832 (m), 749 (w). Anal. Calcd for $C_{26}H_{48}N_2Si_2U$: C, 45.73; H, 7.08; N, 4.10. Found: C, 45.93; H, 7.11; N, 3.92.

Synthesis of $(C_5Me_5)_2U[=N(Ad)]_2$, 3. To a a scintillation vial charged with $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$ (49 mg, 0.06 mmol), toluene (3 mL) and a magnetic stir bar, 1-azidoadamantane (22 mg, 0.12 mmol) was added at room temperature. The resulting dark brown solution was let to stir at room temperature overnight. After which, it was concentrated to ca. 1 mL and placed in freezer for several days to yield $(C_5Me_5)_2U[N(Ad)]_2$ as dark brown powder (10 mg, 20%). ^{1}H NMR matches with data previously reported.[5]

Synthesis of $[(C_5Me_5)_2U(CNC(CH_3)_3)(\mu\text{-}CN)]_3$, 4. A scintillation vial charged with $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$ (127 mg, 0.16 mmol), pentane (5 mL), and a magnetic stir bar was chilled in -45 °C freezer for 30 min prior to use. The vial was removed from the freezer and an excess amount of *tert*-butyl isocyanide (ca. 0.1 mL, 0.88 mmol) was added via syringe. The solution was let to stir at room temperature overnight and the excess tert-butyl isocyanide and solvent were removed. The residue was then dissolved in pentane and place in the freezer for several days to yield $[(C_5Me_5)_2U(CNC(CH_3)_3)(\mu\text{-}CN)]_3$ black crystalline powder (56 mg, 57%). Signals correspond to C_5Me_5 and $CNC(CH_3)_3$ were not observed in ^{1}H NMR. IR (KBr, cm^{-1}): 2963 (m), 2909 (s), 2855 (m), 2142 (m), 2087 (w), 1442 (m), 1374 (m), 1260 (m), 1244 (m), 1199 (m), 1084 (vs), 1022 (s), 935 (m), 908 (m), 885 (m), 837 (m), 801 (m). Anal. Calcd for $C_{78}H_{117}N_6U_3$: C, 50.56; H, 6.36; N, 4.54. Found: C, 51.14; H, 6.73; N, 4.29.

Crystallographic data collection and structure determination

Compound **1**, **2**, and **3** were solved by iterative dual space phasing as implemented in SHELXT[6] and refined by full matrix least squares refinement against F^2 using SHELXL.[7] The models were modified with the aid of the visualization/interface program Olex2.[8] Full-occupancy non-hydrogen atoms were located from the difference map and refined anisotropically For compound **3,** after

locating all non-hydrogen atoms associated with the main moiety, significant difference map peaks indicated the presence of disorder affecting one of the Cp* ligands bonded to U2 and the presence of a disordered solvent molecule occupying void space in the lattice. A second conformation of the disordered Cp* ring, related to the first by an approximate 36° rotation about the center of the ring, was located from difference map peaks. The relative occupancies of the two conformations were manually adjusted to minimize the least squares goodness-of-fit and R factors, with relative occupancies of 67% to 33% ultimately producing the most satisfactory fit. Five of the largest difference map peaks located in lattice void space were modeled as carbon atoms belonging to a pentane molecule of crystallization. Based on the comparatively low value of the difference map peak heights and the large isotropic thermal ellipsoids observed when refining these as carbon atoms, it was apparent that the total occupancy of the solvent molecule would be less than 1. Fixing the occupancies at 50% and refining anisotropically produced a model which accounted for the electron density in a satisfactory way and can be interpreted as a pentane molecule for which the terminal carbon atoms are relatively well ordered while the propylene group is highly disordered about a cylinder containing all reasonable conformations. Hydrogen atoms for all full occupancy carbon atoms were placed in calculated positions. Their thermal parameters were constrained to ride on the carrier atom, while their coordinates were allowed to rotate about the C-C bond axis of rotation. Hydrogen atoms bonded to disordered methyl groups were placed in idealized staggered geometries. A rigid group restraint was applied to the anisotropic thermal parameters of all atoms.[9]

The disordered pentane molecule was able to be refined anisotropically but reached a point where they oscillated indefinitely from cycle to cycle rather than converged. These values were then fixed for the rest of the refinement. An unsuccessful attempt was made to remove the contribution of the disordered pentane from the structure using PLATON SQUEEZE,[10] which estimated a solvent

contribution of 265 electrons per cell, compared to an expected 168 electrons for a full occupancy pentane molecule. Refinement against modified data caused the disordered Cp* ligands to refine to unrealistic bond distances. Together these indicated that the reflections being modified by SQUEEZE were impacting refinement of the main moiety in an unrealistic way. The half-occupancy pentane molecule does not correspond to any realistic geometry for any single conformation of that molecule but is an acceptable approximation for the space and electron density occupied by a number of randomly disordered conformations. Hydrogen atoms positions were not calculated for this reason.

The final model has prolate thermal ellipsoids for the other Cp* ligand bonded to U2, and for one of the *tert*-butyl isonitrile ligands. For the Cp* ligand this most likely indicates unresolved disorder, however there was insufficient information from the difference map to locate a second conformation and refine it. The structure contains unusually short methyl-to-methyl intramolecular contacts for the two ligands bonded to U2, which is likely a consequence of both the unresolved disorder in the second Cp* ligand and the constraint of hydrogen atoms to idealized geometries.

Table S1. X-ray crystallography data for complexes **1**, **2**, and **4**.

	1	**2**	**4**
CCDC deposit number	1828732	1828736	1829165
Empirical formula	$C_{36}H_{58}OPSiU$	$C_{26}H_{48}N_2Si_2U$	$C_{80.5}H_{117}N_6U_3$
Formula weight (g/mol)	803.91	682.87	1882.88
Crystal habit, color	Needle, Red	Prism, Green	Plate, Brown
Temperature (K)	150(2)	100(2)	100(2)
Space group	$P2_1/n$	$P2_12_12_1$	$Pca2_1$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Volume (Å^3)	3566.8(4)	3038.3(6)	8241.7(7)
a (Å)	9.6794(5)	13.2573(14)	18.8226(9)
b (Å)	20.3019(12)	14.8359(16)	23.0418(10)
c (Å)	18.3009(11)	15.4478(17)	19.0030(9)
α (˚)	90	90	90
β (˚)	97.346(2)	90	90
γ (˚)	90	90	90
Z	4	4	4
Calculated density (Mg/m^3)	1.497	1.493	1.517
Absorption coefficient (mm^{-1})	4.654	5.436	5.922
Final R indices [I > 2σ(I)]	R1 = 0.0282, wR2 = 0.0465	R1 = 0.0250, wR2 = 0.0628	R1 = 0.0388, wR2 = 0.0714

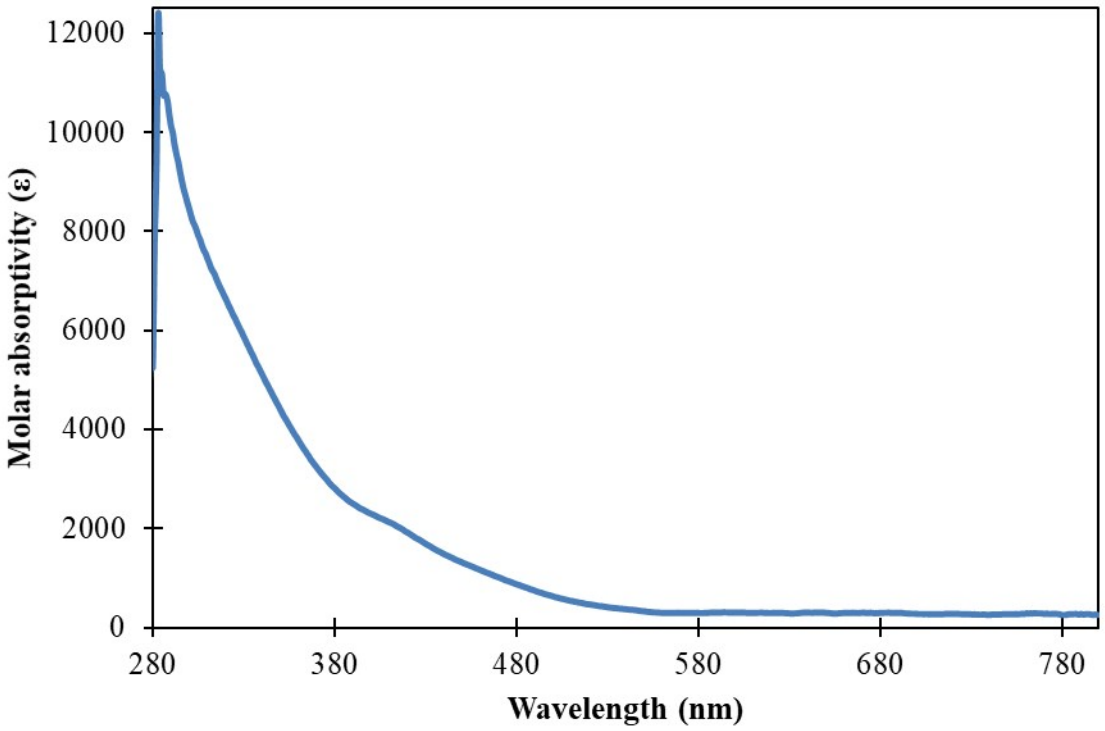

Figure S1. UV-vis spectrum of **1** at 8.55×10^{-5} M in toluene.

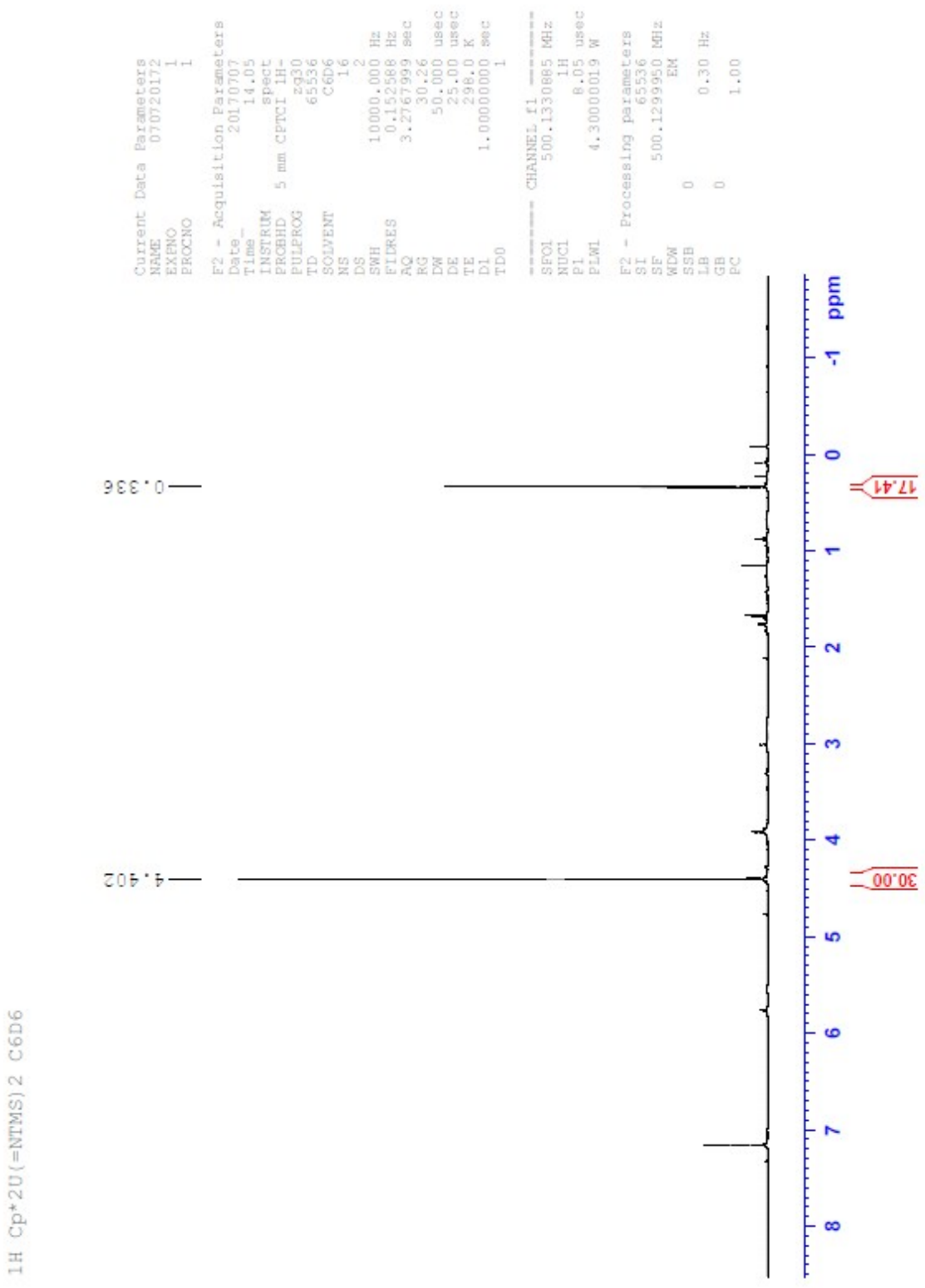

Figure S2. ^{1}H NMR spectrum of **$(C_5Me_5)_2U[=N(SiMe_3)]_2$, 2.**

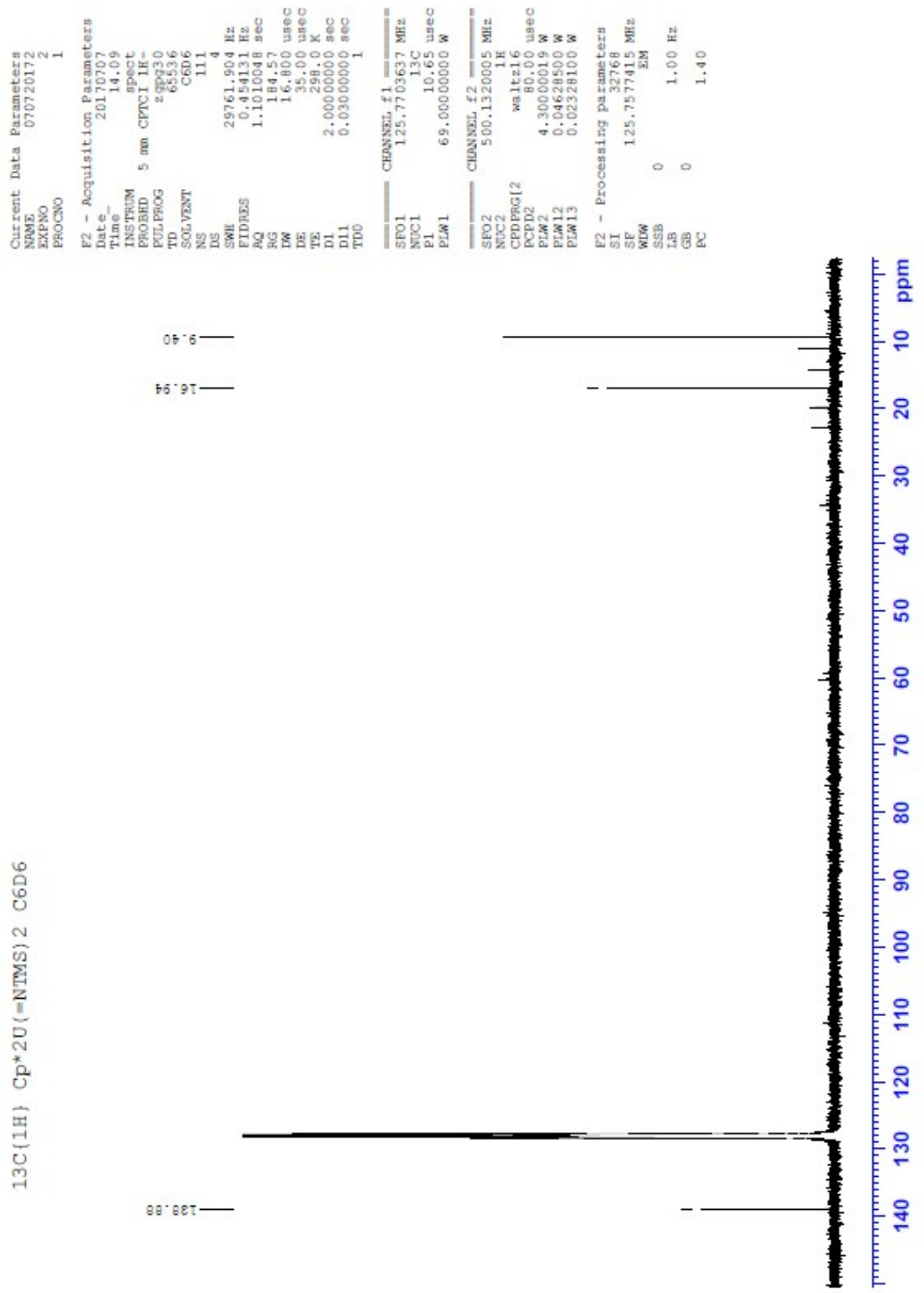

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **$(C_5Me_5)_2U[=N(SiMe_3)]_2$, 2.**

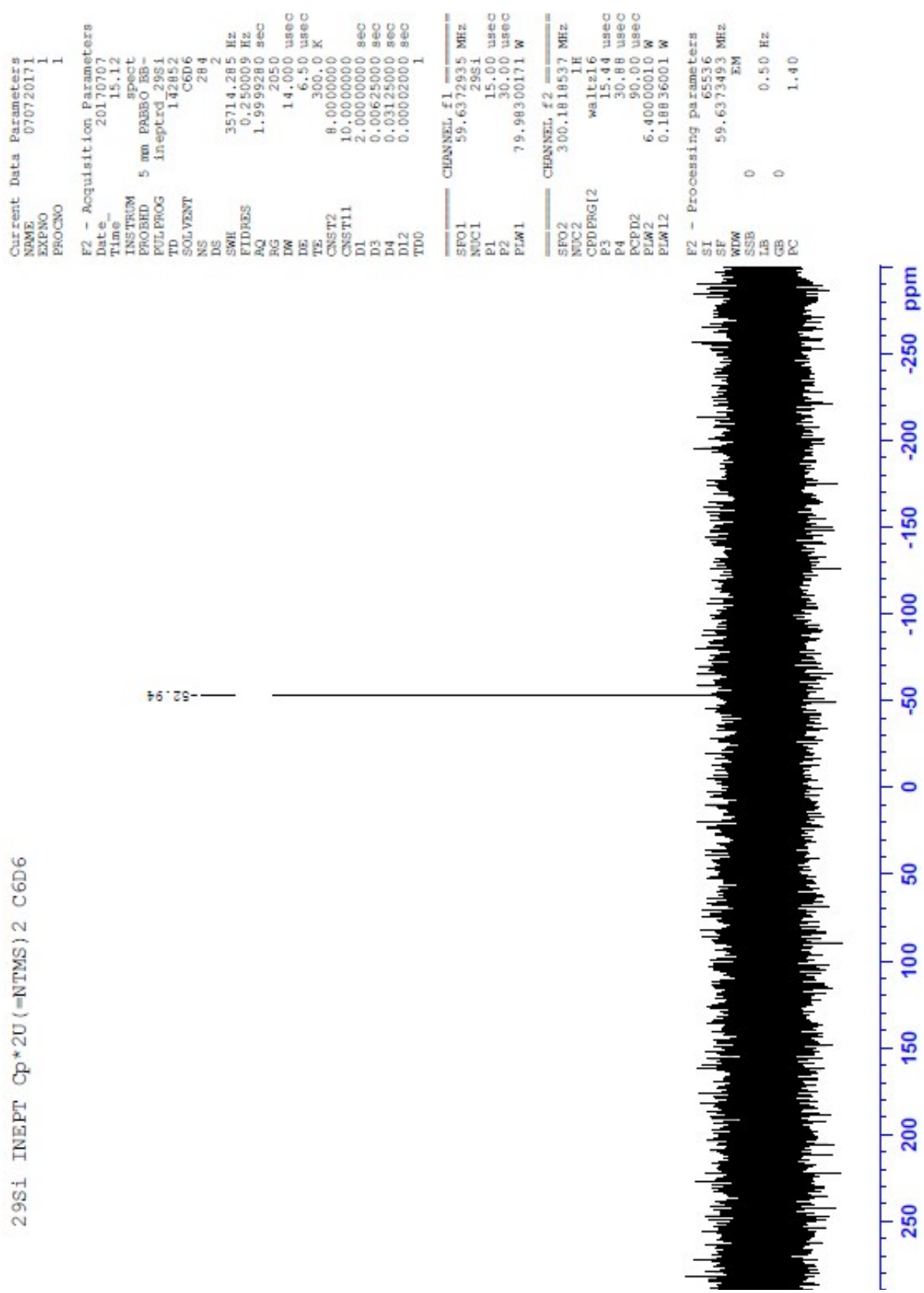

Figure S4. ^{29}Si INEPT NMR spectrum of **$(C_5Me_5)_2U[=N(SiMe_3)]_2$, 2.**

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