Supplementary Material (ESI) for Chemical Communications

Selenate and tellurate complexes of pentavalent uranium

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Electronic Supplementary Information:

General Synthetic Considerations

Reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train, or using standard Schlenk techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained in C_6D_6 using a Bruker Avance 300 MHz spectrometer at ambient temperature. Chemical shifts for ^{1}H NMR spectra were referenced to solvent impurities. Melting points were determined with a Met-Temp II capillary melting point apparatus equipped with a Fluke 50S K/J thermocouple using capillary tubes flame-sealed under nitrogen; values are uncorrected. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility, using a VG ProSpec (EI) mass spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer. X-ray data were collected using a Bruker APEX2 diffractometer. Structural solution and refinement was achieved using the SHELXL program suite.[1] Details regarding data collection are provided in the CIF files.

Benzene-d_6 was obtained from Aldrich (Sure/Seal) and was purified by passage through activated alumina and stored over activated 4 Å molecular sieves prior to use. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried under reduced pressure at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich), hexanes (Aldrich), tetrahydrofuran (Aldrich), and pentanes (Aldrich) were dried over KH for 24 h, passed through a column of activated alumina, and stored over activated 4 Å molecular sieves prior to use. The PhE-EPh reagents were purchased from Aldrich and used as received. $(C_5Me_5)_2U(=N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(THF)$ (**1**) was prepared according to literature procedure.[2] $(C_5Me_5)_2U(=N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(OPh)$ (**5**) is a known compound and has been reported previously.[3]

Caution: Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47 x 10^9 years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

References:

(1) (a) Bruker AXS, *SAINT 7.06*, Integration Software; Bruker Analytical X-ray Systems: Madison, WI, 2003; (b) Sheldrick, G. M. *SADABS 2.03*, Program for Adsorption Correction; University of Göttingen: Göttingen, Germany, 2001; (c) Sheldrick, G. M. *SHELXTL 5.10*, Structure Solution and Refinement Package; Universitiy of Göttingen: Göttingen, Germany, 1997. (2) Arney, D. S. J.; Burns, C. J. *J. Am Chem. Soc.* 1993, **115**, 9840-9841. (3) Graves, C. R.; Vaughn, A. E.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.*, 2008, In Press.

Instrumentation and Sample Protocols

Electronic absorption spectral data were obtained for toluene or toluene-d_8 solutions of complexes over the wavelength range 300–2500 nm on a Perkin-Elmer Model Lambda 950 UV-visible-NIR spectrophotometer. Data were collected in 1 cm and 1 mm path length cuvettes loaded in the Vacuum Atmospheres drybox system described above and run versus the appropriate toluene solvent reference. Samples were typically run at multiple dilutions to optimize absorbance in the UV-visible and near-infrared, respectively. Spectral resolution was typically 2 nm in the visible region and 4–6 nm in the near-infrared.

Voltammetric data were also obtained in the Vacuum Atmospheres drybox system described above. All data were collected using a Perkin-Elmer Princeton Applied Research Corporation (PARC) Model 263 potentiostat under computer control with PARC Model 270 software. Sample solutions were ~1-2 mM in complex with 0.1 M $[Bu_4N][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ or $[Bu_4N][B(C_6F_5)_4]$ supporting electrolyte in THF solvent. All data were collected with the positive-feedback IR compensation feature of the software/potentiostat activated to ensure minimal contribution to the voltammetric waves from uncompensated solution resistance (typically ~1 kΩ under the conditions employed). Solutions were contained in PARC Model K0264 microcells consisting of a ~3 mm diameter Pt disk working electrode, a Pt wire counter electrode, and a Ag wire quasi-reference electrode. Scan rates from 20–5000 mV/s were employed in the cyclic voltammetry scans to assess the chemical and electrochemical reversibility of the observed redox transformations. Half-wave potentials were determined from the peak values in the square-wave voltammograms or from the average of the cathodic and anodic peak potentials in the reversible cyclic voltammograms. Potential calibrations were performed at the end of each data collection cycle using the ferrocenium/ferrocene couple as an internal standard. Electronic absorption and cyclic voltammetric data were analyzed using Wavemetrics IGOR Pro (Version 4.0) software on a Macintosh platform.

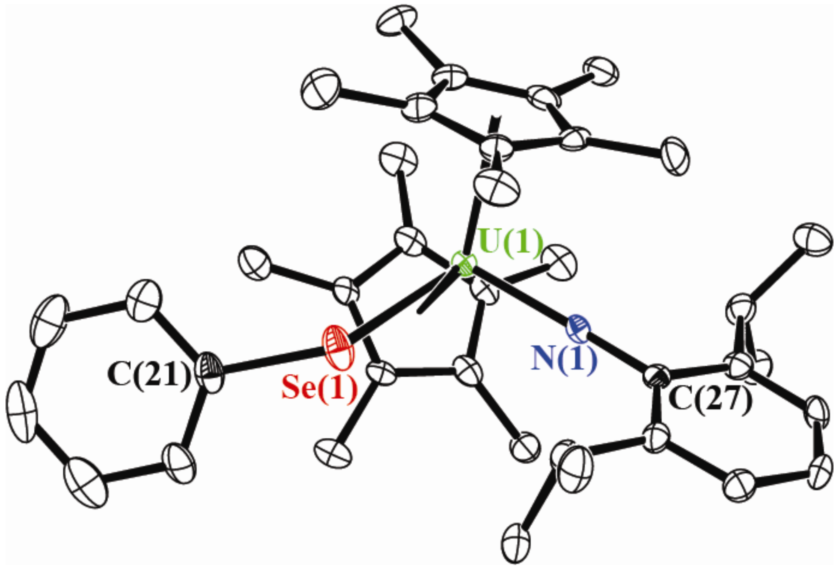

Figure S1. Molecular structure of complex **3** with thermal ellipsoids at the 50% probability level.

Table S1. Bond Lengths [Å] and Angles [°] for $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(SePh)$ (**3**).

U(1)-N(1)	1.984(4)	C(21)-C(22)	1.392(7)
U(1)-C(5)	2.723(5)	C(22)-C(23)	1.393(8)
U(1)-C(15)	2.723(5)	C(23)-C(24)	1.368(9)
U(1)-C(13)	2.725(5)	C(24)-C(25)	1.369(9)
U(1)-C(2)	2.731(5)	C(25)-C(26)	1.386(8)
U(1)-C(14)	2.731(5)	C(27)-C(28)	1.419(7)
U(1)-C(3)	2.735(5)	C(27)-C(32)	1.421(7)
U(1)-C(4)	2.737(5)	C(28)-C(29)	1.397(7)
U(1)-C(1)	2.738(5)	C(28)-C(33)	1.513(7)
U(1)-C(11)	2.756(5)	C(29)-C(30)	1.360(7)
U(1)-C(12)	2.768(5)	C(30)-C(31)	1.379(7)
U(1)-Se(1)	2.8639(6)	C(31)-C(32)	1.390(7)
Se(1)-C(21)	1.918(5)	C(32)-C(36)	1.505(7)
N(1)-C(27)	1.403(6)	C(33)-C(34)	1.535(7)
C(1)-C(5)	1.413(7)	C(33)-C(35)	1.550(7)
C(1)-C(2)	1.416(7)	C(36)-C(38)	1.525(7)
C(1)-C(6)	1.504(7)	C(36)-C(37)	1.547(7)
C(2)-C(3)	1.415(7)		
C(2)-C(7)	1.516(7)	N(1)-U(1)-C(5)	79.50(16)
C(3)-C(4)	1.414(7)	N(1)-U(1)-C(15)	90.44(16)
C(3)-C(8)	1.494(7)	C(5)-U(1)-C(15)	169.11(16)
C(4)-C(5)	1.413(7)	N(1)-U(1)-C(13)	93.70(17)
C(4)-C(9)	1.498(6)	C(5)-U(1)-C(13)	126.03(15)
C(5)-C(10)	1.509(7)	C(15)-U(1)-C(13)	49.89(15)
C(11)-C(12)	1.400(7)	N(1)-U(1)-C(2)	119.95(16)
C(11)-C(15)	1.425(7)	C(5)-U(1)-C(2)	49.48(16)
C(11)-C(16)	1.509(7)	C(15)-U(1)-C(2)	135.74(15)
C(12)-C(13)	1.429(7)	C(13)-U(1)-C(2)	93.65(16)
C(12)-C(17)	1.510(7)	N(1)-U(1)-C(14)	74.88(15)
C(13)-C(14)	1.417(7)	C(5)-U(1)-C(14)	140.55(15)
C(13)-C(18)	1.502(7)	C(15)-U(1)-C(14)	30.12(15)
C(14)-C(15)	1.417(7)	C(13)-U(1)-C(14)	30.12(15)
C(14)-C(19)	1.502(7)	C(2)-U(1)-C(14)	123.36(15)
C(15)-C(20)	1.493(7)	N(1)-U(1)-C(3)	128.99(16)
C(21)-C(26)	1.383(7)	C(5)-U(1)-C(3)	49.75(16)

C(15)-U(1)-C(3)	140.55(15)	C(1)-U(1)-C(12)	104.74(16)
C(13)-U(1)-C(3)	118.15(16)	C(11)-U(1)-C(12)	29.36(15)
C(2)-U(1)-C(3)	30.01(14)	N(1)-U(1)-Se(1)	102.17(11)
C(14)-U(1)-C(3)	147.63(15)	C(5)-U(1)-Se(1)	105.33(11)
N(1)-U(1)-C(4)	102.00(16)	C(15)-U(1)-Se(1)	80.72(10)
C(5)-U(1)-C(4)	30.00(14)	C(13)-U(1)-Se(1)	128.24(11)
C(15)-U(1)-C(4)	159.99(15)	C(2)-U(1)-Se(1)	118.33(11)
C(13)-U(1)-C(4)	142.69(15)	C(14)-U(1)-Se(1)	109.03(11)
C(2)-U(1)-C(4)	49.21(15)	C(3)-U(1)-Se(1)	88.63(10)
C(14)-U(1)-C(4)	169.51(15)	C(4)-U(1)-Se(1)	81.37(10)
C(3)-U(1)-C(4)	29.95(14)	C(1)-U(1)-Se(1)	130.73(11)
N(1)-U(1)-C(1)	89.95(16)	C(11)-U(1)-Se(1)	80.73(11)
C(5)-U(1)-C(1)	29.99(14)	C(12)-U(1)-Se(1)	107.91(11)
C(15)-U(1)-C(1)	147.54(15)	C(21)-Se(1)-U(1)	126.41(15)
C(13)-U(1)-C(1)	97.70(15)	C(27)-N(1)-U(1)	171.4(3)
C(2)-U(1)-C(1)	30.02(15)	C(5)-C(1)-C(2)	107.5(4)
C(14)-U(1)-C(1)	120.23(15)	C(5)-C(1)-C(6)	127.8(5)
C(3)-U(1)-C(1)	49.72(15)	C(2)-C(1)-C(6)	124.2(5)
C(4)-U(1)-C(1)	49.36(15)	C(5)-C(1)-U(1)	74.4(3)
N(1)-U(1)-C(11)	120.11(16)	C(2)-C(1)-U(1)	74.7(3)
C(5)-U(1)-C(11)	158.35(16)	C(6)-C(1)-U(1)	123.2(3)
C(15)-U(1)-C(11)	30.15(15)	C(3)-C(2)-C(1)	108.7(5)
C(13)-U(1)-C(11)	49.35(16)	C(3)-C(2)-C(7)	126.3(5)
C(2)-U(1)-C(11)	109.17(16)	C(1)-C(2)-C(7)	123.6(5)
C(14)-U(1)-C(11)	49.33(16)	C(3)-C(2)-U(1)	75.2(3)
C(3)-U(1)-C(11)	110.77(16)	C(1)-C(2)-U(1)	75.3(3)
C(4)-U(1)-C(11)	136.77(16)	C(7)-C(2)-U(1)	126.9(3)
C(1)-U(1)-C(11)	132.93(16)	C(4)-C(3)-C(2)	107.2(5)
N(1)-U(1)-C(12)	122.41(16)	C(4)-C(3)-C(8)	127.9(5)
C(5)-U(1)-C(12)	133.83(16)	C(2)-C(3)-C(8)	124.8(5)
C(15)-U(1)-C(12)	49.42(16)	C(4)-C(3)-U(1)	75.1(3)
C(13)-U(1)-C(12)	30.14(15)	C(2)-C(3)-U(1)	74.8(3)
C(2)-U(1)-C(12)	86.34(16)	C(8)-C(3)-U(1)	118.9(3)
C(14)-U(1)-C(12)	49.36(16)	C(5)-C(4)-C(3)	108.6(4)
C(3)-U(1)-C(12)	100.01(16)	C(5)-C(4)-C(9)	124.6(5)
C(4)-U(1)-C(12)	129.91(15)	C(3)-C(4)-C(9)	126.3(5)

C(5)-C(4)-U(1)	74.4(3)	C(14)-C(15)-C(11)	107.3(4)
C(3)-C(4)-U(1)	74.9(3)	C(14)-C(15)-C(20)	126.5(5)
C(9)-C(4)-U(1)	123.5(3)	C(11)-C(15)-C(20)	125.9(5)
C(4)-C(5)-C(1)	108.0(5)	C(14)-C(15)-U(1)	75.2(3)
C(4)-C(5)-C(10)	124.6(5)	C(11)-C(15)-U(1)	76.2(3)
C(1)-C(5)-C(10)	127.0(5)	C(20)-C(15)-U(1)	119.0(3)
C(4)-C(5)-U(1)	75.6(3)	C(26)-C(21)-C(22)	118.8(5)
C(1)-C(5)-U(1)	75.6(3)	C(26)-C(21)-Se(1)	120.3(4)
C(10)-C(5)-U(1)	120.8(3)	C(22)-C(21)-Se(1)	120.7(4)
C(12)-C(11)-C(15)	108.7(5)	C(21)-C(22)-C(23)	119.7(6)
C(12)-C(11)-C(16)	124.0(5)	C(24)-C(23)-C(22)	120.4(6)
C(15)-C(11)-C(16)	126.8(5)	C(23)-C(24)-C(25)	120.5(6)
C(12)-C(11)-U(1)	75.8(3)	C(24)-C(25)-C(26)	119.6(6)
C(15)-C(11)-U(1)	73.7(3)	C(21)-C(26)-C(25)	121.0(6)
C(16)-C(11)-U(1)	122.7(4)	N(1)-C(27)-C(28)	121.6(4)
C(11)-C(12)-C(13)	108.0(5)	N(1)-C(27)-C(32)	119.0(4)
C(11)-C(12)-C(17)	124.7(5)	C(28)-C(27)-C(32)	119.4(5)
C(13)-C(12)-C(17)	126.5(5)	C(29)-C(28)-C(27)	118.5(5)
C(11)-C(12)-U(1)	74.8(3)	C(29)-C(28)-C(33)	119.0(5)
C(13)-C(12)-U(1)	73.2(3)	C(27)-C(28)-C(33)	122.5(5)
C(17)-C(12)-U(1)	126.2(4)	C(30)-C(29)-C(28)	122.0(5)
C(14)-C(13)-C(12)	107.6(5)	C(29)-C(30)-C(31)	119.8(5)
C(14)-C(13)-C(18)	125.4(5)	C(30)-C(31)-C(32)	121.7(5)
C(12)-C(13)-C(18)	126.5(5)	C(31)-C(32)-C(27)	118.6(5)
C(14)-C(13)-U(1)	75.2(3)	C(31)-C(32)-C(36)	120.1(5)
C(12)-C(13)-U(1)	76.6(3)	C(27)-C(32)-C(36)	121.3(4)
C(18)-C(13)-U(1)	120.9(3)	C(28)-C(33)-C(34)	113.4(5)
C(15)-C(14)-C(13)	108.3(5)	C(28)-C(33)-C(35)	110.1(4)
C(15)-C(14)-C(19)	125.4(5)	C(34)-C(33)-C(35)	108.0(4)
C(13)-C(14)-C(19)	125.5(5)	C(32)-C(36)-C(38)	114.6(4)
C(15)-C(14)-U(1)	74.6(3)	C(32)-C(36)-C(37)	109.5(4)
C(13)-C(14)-U(1)	74.7(3)	C(38)-C(36)-C(37)	110.8(4)
C(19)-C(14)-U(1)	124.3(3)		

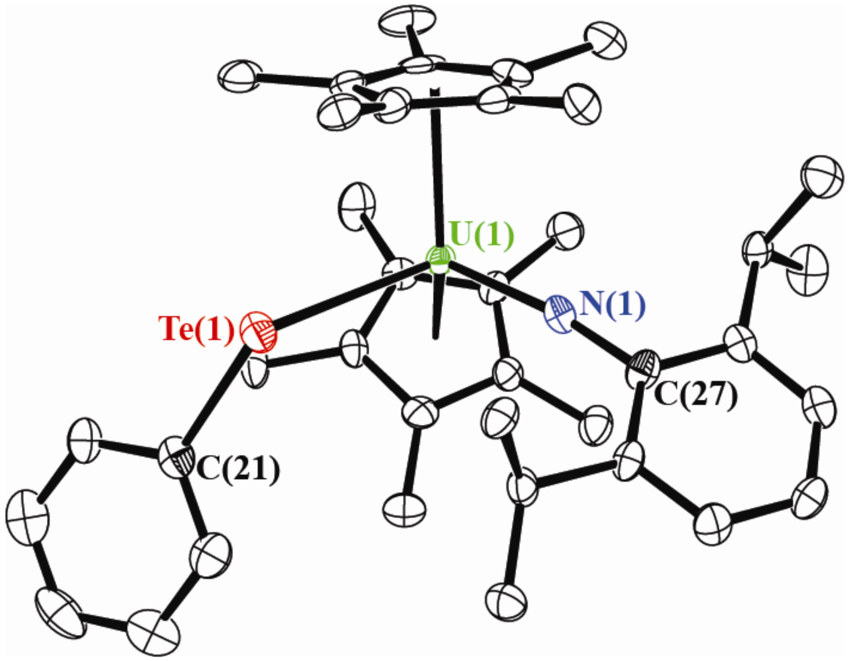

Figure S2. Molecular structure of complex **4** with thermal ellipsoids at the 50% probability level.

Table S2. Bond Lengths [Å] and Angles [°] for $(C_5Me_5)_2U(=N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(TePh)$ (**4**).

U(1)-N(1)	1.960(6)
U(1)-C(11)	2.707(8)
U(1)-C(15)	2.711(8)
U(1)-C(14)	2.745(8)
U(1)-C(1)	2.750(8)
U(1)-C(3)	2.750(8)
U(1)-C(4)	2.751(8)
U(1)-C(5)	2.757(8)
U(1)-C(2)	2.763(8)
U(1)-C(12)	2.765(7)
U(1)-C(13)	2.768(8)
U(1)-Te(1)	3.0845(9)
Te(1)-C(21)	2.127(8)
N(1)-C(27)	1.407(10)
C(1)-C(5)	1.392(11)
C(1)-C(2)	1.416(13)
C(1)-C(6)	1.511(12)
C(2)-C(3)	1.408(12)
C(2)-C(7)	1.495(12)
C(3)-C(4)	1.431(13)
C(3)-C(8)	1.517(13)
C(4)-C(5)	1.416(12)
C(4)-C(9)	1.502(11)
C(5)-C(10)	1.505(12)
C(11)-C(15)	1.414(11)
C(11)-C(12)	1.422(11)
C(11)-C(16)	1.491(12)
C(12)-C(13)	1.418(11)
C(12)-C(17)	1.492(11)
C(13)-C(14)	1.418(11)
C(13)-C(18)	1.484(11)
C(14)-C(15)	1.420(12)
C(14)-C(19)	1.480(11)
C(15)-C(20)	1.488(11)
C(21)-C(22)	1.375(11)
C(21)-C(26)	1.392(12)
C(22)-C(23)	1.383(13)
C(23)-C(24)	1.378(14)
C(24)-C(25)	1.388(14)
C(25)-C(26)	1.372(13)
C(27)-C(28)	1.418(11)
C(27)-C(32)	1.424(11)
C(28)-C(29)	1.377(11)
C(28)-C(33)	1.520(11)
C(29)-C(30)	1.376(12)
C(30)-C(31)	1.376(12)
C(31)-C(32)	1.384(11)
C(32)-C(36)	1.509(11)
C(33)-C(34)	1.522(11)
C(33)-C(35)	1.541(11)
C(36)-C(38)	1.503(11)
C(36)-C(37)	1.520(11)
N(1)-U(1)-C(11)	95.3(2)
N(1)-U(1)-C(15)	76.3(2)
C(11)-U(1)-C(15)	30.3(2)
N(1)-U(1)-C(14)	91.7(3)
C(11)-U(1)-C(14)	49.8(3)
C(15)-U(1)-C(14)	30.2(2)
N(1)-U(1)-C(1)	128.2(3)
C(11)-U(1)-C(1)	117.6(3)
C(15)-U(1)-C(1)	147.3(3)
C(14)-U(1)-C(1)	140.1(2)
N(1)-U(1)-C(3)	91.1(3)
C(11)-U(1)-C(3)	96.9(3)
C(15)-U(1)-C(3)	120.0(3)
C(14)-U(1)-C(3)	146.7(3)
C(1)-U(1)-C(3)	48.9(3)
N(1)-U(1)-C(4)	79.6(3)
C(11)-U(1)-C(4)	125.4(3)

C(15)-U(1)-C(4)	140.7(3)
C(14)-U(1)-C(4)	169.9(2)
C(1)-U(1)-C(4)	48.9(2)
C(3)-U(1)-C(4)	30.2(3)
N(1)-U(1)-C(5)	101.5(3)
C(11)-U(1)-C(5)	141.6(3)
C(15)-U(1)-C(5)	169.1(2)
C(14)-U(1)-C(5)	159.9(3)
C(1)-U(1)-C(5)	29.3(2)
C(3)-U(1)-C(5)	49.1(3)
C(4)-U(1)-C(5)	29.8(2)
N(1)-U(1)-C(2)	120.7(3)
C(11)-U(1)-C(2)	92.9(3)
C(15)-U(1)-C(2)	122.8(3)
C(14)-U(1)-C(2)	134.5(3)
C(1)-U(1)-C(2)	29.8(3)
C(3)-U(1)-C(2)	29.6(3)
C(4)-U(1)-C(2)	49.3(2)
C(5)-U(1)-C(2)	48.9(3)
N(1)-U(1)-C(12)	124.0(2)
C(11)-U(1)-C(12)	30.1(2)
C(15)-U(1)-C(12)	49.5(2)
C(14)-U(1)-C(12)	49.2(2)
C(1)-U(1)-C(12)	99.6(2)
C(3)-U(1)-C(12)	103.4(3)
C(4)-U(1)-C(12)	132.7(2)
C(5)-U(1)-C(12)	128.8(2)
C(2)-U(1)-C(12)	85.3(2)
N(1)-U(1)-C(13)	121.2(2)
C(11)-U(1)-C(13)	49.6(2)
C(15)-U(1)-C(13)	49.5(2)
C(14)-U(1)-C(13)	29.8(2)
C(1)-U(1)-C(13)	110.6(2)
C(3)-U(1)-C(13)	131.8(3)
C(4)-U(1)-C(13)	157.3(2)
C(5)-U(1)-C(13)	136.1(2)
C(2)-U(1)-C(13)	108.3(2)
C(12)-U(1)-C(13)	29.7(2)
N(1)-U(1)-Te(1)	107.53(18)
C(11)-U(1)-Te(1)	133.82(17)
C(15)-U(1)-Te(1)	118.23(17)
C(14)-U(1)-Te(1)	89.04(18)
C(1)-U(1)-Te(1)	78.42(19)
C(3)-U(1)-Te(1)	121.5(2)
C(4)-U(1)-Te(1)	98.37(19)
C(5)-U(1)-Te(1)	72.69(19)
C(2)-U(1)-Te(1)	107.8(2)
C(12)-U(1)-Te(1)	109.46(17)
C(13)-U(1)-Te(1)	84.40(17)
C(21)-Te(1)-U(1)	121.5(2)
C(27)-N(1)-U(1)	170.6(6)
C(5)-C(1)-C(2)	108.9(8)
C(5)-C(1)-C(6)	127.0(9)
C(2)-C(1)-C(6)	123.9(8)
C(5)-C(1)-U(1)	75.6(5)
C(2)-C(1)-U(1)	75.6(5)
C(6)-C(1)-U(1)	119.2(5)
C(3)-C(2)-C(1)	107.4(8)
C(3)-C(2)-C(7)	124.5(9)
C(1)-C(2)-C(7)	126.7(8)
C(3)-C(2)-U(1)	74.7(5)
C(1)-C(2)-U(1)	74.6(5)
C(7)-C(2)-U(1)	127.3(6)
C(2)-C(3)-C(4)	108.3(8)
C(2)-C(3)-C(8)	124.6(9)
C(4)-C(3)-C(8)	125.9(8)
C(2)-C(3)-U(1)	75.7(5)
C(4)-C(3)-U(1)	75.0(5)
C(8)-C(3)-U(1)	125.5(6)
C(5)-C(4)-C(3)	106.9(8)
C(5)-C(4)-C(9)	126.4(8)
C(3)-C(4)-C(9)	126.0(8)

C(5)-C(4)-U(1)	75.3(5)	C(11)-C(15)-U(1)	74.7(5)
C(3)-C(4)-U(1)	74.9(5)	C(14)-C(15)-U(1)	76.3(5)
C(9)-C(4)-U(1)	122.5(5)	C(20)-C(15)-U(1)	124.8(5)
C(1)-C(5)-C(4)	108.5(8)	C(11)-C(15)-C(14)	108.3(7)
C(1)-C(5)-C(10)	127.4(8)	C(11)-C(15)-C(20)	126.1(8)
C(4)-C(5)-C(10)	122.9(8)	C(14)-C(15)-C(20)	124.5(7)
C(1)-C(5)-U(1)	75.1(5)	C(22)-C(21)-C(26)	118.9(8)
C(4)-C(5)-U(1)	74.9(5)	C(22)-C(21)-Te(1)	118.6(6)
C(10)-C(5)-U(1)	126.1(5)	C(26)-C(21)-Te(1)	122.4(7)
C(15)-C(11)-C(12)	107.8(7)	C(21)-C(22)-C(23)	120.8(9)
C(15)-C(11)-C(16)	125.5(7)	C(24)-C(23)-C(22)	119.9(9)
C(12)-C(11)-C(16)	126.4(7)	C(23)-C(24)-C(25)	120.0(9)
C(15)-C(11)-U(1)	75.0(5)	C(26)-C(25)-C(24)	119.6(10)
C(12)-C(11)-U(1)	77.2(5)	C(25)-C(26)-C(21)	120.9(9)
C(16)-C(11)-U(1)	119.2(5)	N(1)-C(27)-C(28)	121.6(7)
C(13)-C(12)-C(11)	108.0(7)	N(1)-C(27)-C(32)	118.7(7)
C(13)-C(12)-C(17)	123.8(7)	C(28)-C(27)-C(32)	119.7(7)
C(11)-C(12)-C(17)	127.0(8)	C(29)-C(28)-C(27)	118.1(7)
C(13)-C(12)-U(1)	75.3(4)	C(29)-C(28)-C(33)	120.2(7)
C(11)-C(12)-U(1)	72.7(4)	C(27)-C(28)-C(33)	121.7(7)
C(17)-C(12)-U(1)	127.7(6)	C(30)-C(29)-C(28)	122.9(8)
C(12)-C(13)-C(14)	108.1(7)	C(31)-C(30)-C(29)	118.6(8)
C(12)-C(13)-C(18)	125.4(8)	C(30)-C(31)-C(32)	122.2(8)
C(14)-C(13)-C(18)	125.8(8)	C(31)-C(32)-C(27)	118.4(7)
C(12)-C(13)-U(1)	75.0(4)	C(31)-C(32)-C(36)	120.9(7)
C(14)-C(13)-U(1)	74.2(4)	C(27)-C(32)-C(36)	120.6(7)
C(18)-C(13)-U(1)	124.8(5)	C(28)-C(33)-C(34)	109.6(6)
C(13)-C(14)-C(15)	107.8(7)	C(28)-C(33)-C(35)	112.6(7)
C(13)-C(14)-C(19)	127.3(8)	C(34)-C(33)-C(35)	108.3(7)
C(15)-C(14)-C(19)	124.4(8)	C(38)-C(36)-C(32)	114.6(7)
C(13)-C(14)-U(1)	76.0(4)	C(38)-C(36)-C(37)	111.2(7)
C(15)-C(14)-U(1)	73.6(5)	C(32)-C(36)-C(37)	108.1(6)
C(19)-C(14)-U(1)	122.7(6)		

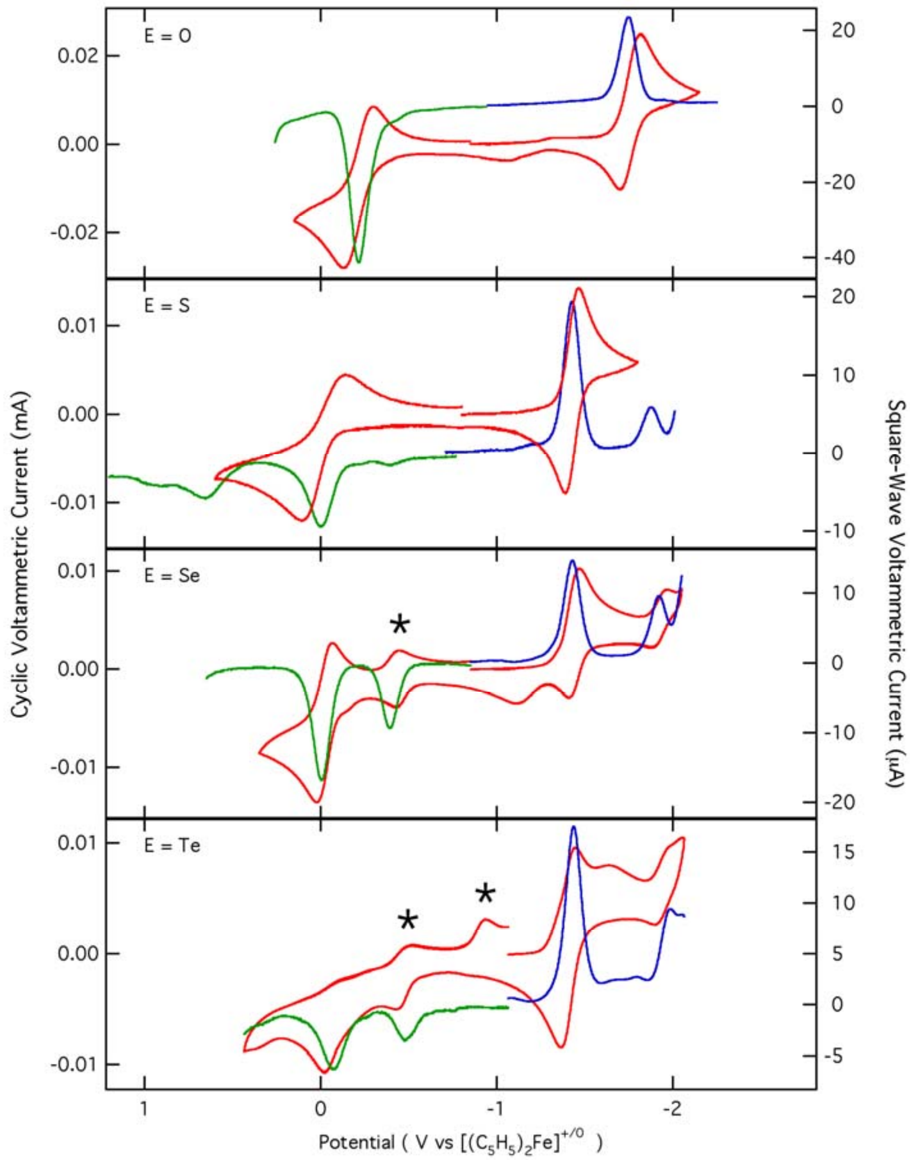

Figure S3. Voltammetric data for $(C_5Me_5)_2U(=N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(E\text{-}Ph)$ complexes. Data collected in ~ 0.1 M $[Bu_4N][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$/THF. Red traces – cyclic voltammograms at 200 mV/s. Green and blue traces – square-wave voltammograms at 25 mV pulse height and 60 Hz. Waves marked with asterisks are attributed to the U^{IV} decomposition products. Data for E = Se and Te were obtained on freshly prepared solutions within 2 minutes of dissolution of complex in the electrolyte solution.

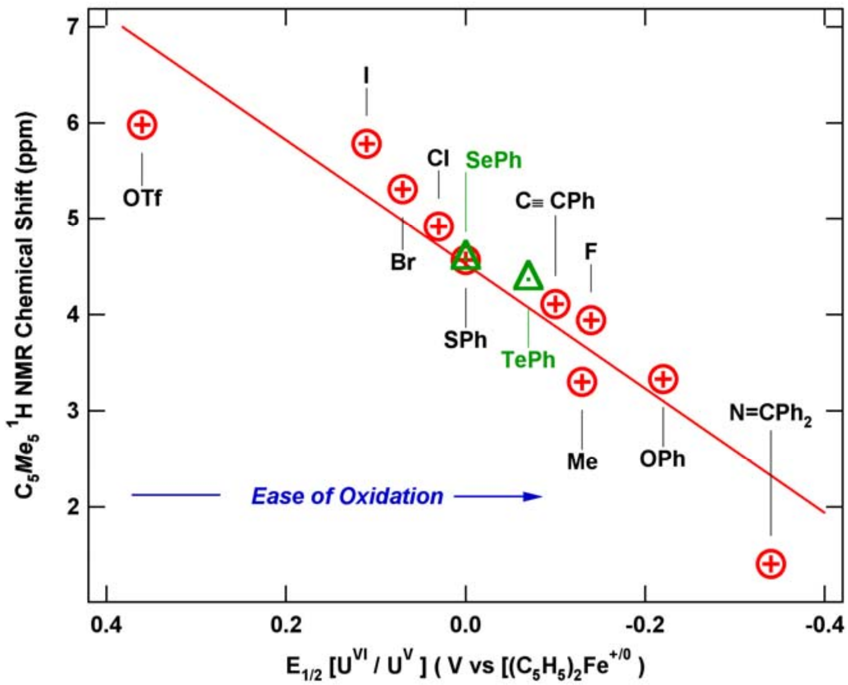

Figure S4. Linear correlation between ^{1}H NMR chemical shift of the $C_5\mathit{Me}_5$ protons and oxidation potential for $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(X/Y)$. The correlation includes all available data points (R^2 = 092).