Electronic Supplementary Material (ESI) for Chemical Science.

Controlling Selectivity in the Reductive Activation of CO_2 by Mixed Sandwich Uranium(III) Complexes†

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Electronic Supplementary Information

General Procedures

All manipulations were carried out in a MBraun glovebox under N_2 or Ar (O_2 and H_2O <1 ppm) or by using standard Schlenk techniques under Ar (BOC Pureshield) passed through a column containing BASF R3-11(G) catalyst and activated molecular sieves (4 Å). All glassware was dried at 160 °C overnight prior to use. Celite was predried in a 200 °C oven and then flame-dried under dynamic vacuum ($<2 \times 10^{-2}$ mbar) prior to use. Filter cannulas were prepared using Whatman 25 mm glass microfiber filters and were pre-dried at 160 °C overnight. THF and toluene were dried over molten K and distilled under a N_2 atmosphere and were kept in Young ampules over activated molecular sieves (4 Å) or a potassium mirror, respectively, under Ar. Hydrocarbons were dried over NaK, distilled under a N_2 atmosphere, and kept in Young ampoules over a potassium mirror under Ar. Deuterated toluene, benzene, and THF were degassed by three freeze−thaw cycles, dried by refluxing over K for 3 days, vacuum distilled, and kept in Young ampoules in the glovebox under N_2. The following materials were prepared according to literature methods: $\{U[\eta^8\text{-}C_8H_6(1,4\text{-}SiMe_3)_2](\eta^5\text{-}Cp^{Me5})\ (THF)\}$ (**1a**),[1] KCp^{Me4iPr},[1] $K_2[C_8H_6\{SiMe_3\text{-}1,4\}_2]$[2] (referred to as K_2COT^{tms2}) and $[^nBu_4N][B(C_6F_5)_4]$.[3] KCp^{Me4tBu}[4] was prepared in a manner similar to KCp^{Me4iPr} from $Cp^{Me4tBuH}$ (mixture of isomers) and KBz. $[^nBu_4N][PF_6]$ was purchased from Aldrich and dried *in vacuo* at 100 °C prior to use. $KN(SiMe_3)_2$ was purchased from Aldrich and recrystallised from toluene prior to use and kept under N_2 in a glovebox. Cp^{Me4EtH} (mixture of isomers) was purchased from Aldrich and used as received. KCp^{Me4Et} was accessed by deprotonation of Cp^{Me4EtH} with $KN(SiMe_3)_2$ in toluene over two days at RT followed by filtration and washing with n-pentane in almost quantitative yield. $^{13}CO_2$ was purchased from Cambridge Isotopes and used as received. The U(III) mixed sandwich complexes (**1a**)-(**4**) are somewhat thermally unstable even in the solid state, thus inhibiting accurate elemental analyses and were therefore stored in a glovebox freezer at -35 °C.

^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR data were recorded on a Varian VNMR S400 spectrometer operating at 400 MHz (^1H). The spectra were referenced internally to the residual protic solvent (^1H) or the signals of the solvent (^{13}C). $^{29}Si\{^1H\}$ NMR spectra were referenced externally relative to $SiMe_4$. All spectra were recorded at 30 °C unless otherwise stated. EI-MS mass spectra were recorded on a VG-Autospec Fisons instrument at the University of Sussex unless otherwise stated. Elemental analyses were performed by Mikroanalytisches Labor Pascher or at the Microanalysis Service of the School of Chemistry at University of Bristol.

Gas transfer was via a Toepler pump with calibrated (by transfer of xenon into a receiving vessel of accurately known volume, and differential weighing) delivery pressure. Control of stoichimetry of the gas reactions was achieved by the use of standard 5 mm (for the NMR and IR studies) or shortened 10mm (for preparative scale) Young's NMR tubes of accurately known volume containing measured volumes (microlitre syringe) of solvent (and therefore of known headspace).

Reactions with supercritical CO_2 (99.999% BOC) were performed in a 10 mm sapphire NMR tube equipped with a titanium valve, connected to a high pressure stainless steel line equipped with a high pressure piston pump (High Pressure Equipment Company). In a typical run 30-100 mg of the compound were loaded in the sapphire tube in the glovebox. This was then attached to the high pressure line and evacuated for approximately 30 minutes. It was then chilled to about 15 ºC (water bath with ice) and CO_2 was administered in the vessel by means of the HP pump until liquid CO_2 started condensing (50-55 bar). The reaction vessel was then isolated from the CO_2 supply and was heated at 40 ºC by means of a thermostatted water bath for at least 2 hours. Heating was then ceased and the reaction was left overnight. Excess CO_2 was vented carefully and the reaction vessel was evacuated before being transferred to the glovebox where it was extracted in the appropriate solvent (see below) and purified.

***Synthesis of $\{U[\eta^8\text{-}C_8H_6(1,4\text{-}SiMe_3)_2](\eta^5\text{-}Cp^{Me4tEt})\ (THF)\}$ (2)*:** This was prepared in a manner similar to $\{U[\eta^8\text{-}C8H6(1,4\text{-}SiMe_3)_2](\eta^5\text{-}Cp^{Me5})\ (THF)\}$ (**1a**) starting from 1.23 g of UI_3 (1.98 mmol), 374 mg KCp^{Me4Et} (1 mol eq) and 520 mg K_2COT^{tms2} (0.8 mol eq). It was recrystallised from n-hexane in two crops (5-10 mL) or by slow evaporation at RT of a saturated methylcyclohexane solution (*ca* 5mL) as the (**2**).0.5 C_6H_{14} solvate. Yield 450 mg (40.2%). ^1H-NMR $\delta(C_7D_8)$: -96.31 (br s, 2H, *COT*), -73.92 (br s, 2H, COT), -18.23 and -17.62 (two overlapping br s, 10H, Cp*Me*$_4$Et and THF), -14.19 (br s, 6H, Cp*Me*$_4$Et), -10.32 (br s, 2H, CpMe4(C*H*$_2$CH$_3$)), -7.53 (s, 18H, C_8H_6\{(Si*Me*$_3$)$_2$\}), -5.91 (br s, 3H, CpMe4(CH$_2$C*H*$_3$)), -3.59 (s, 4H, THF), 21.61 (br s, 2H, *COT*); ^{29}Si\{^{1}H\}-NMR $\delta(C_7D_8)$: -168.29 (s, *Si*Me$_3$); EI-MS: 654 (M-THF+F), 635 (M-THF), 248 (COT^{tms2}),135 (CpMe4Et-Me), 73 (SiMe$_3$).

***Synthesis of {U[η^8-C$_8$H$_6$(1,4-SiMe$_3$)$_2$](η^5-Cp^{Me4iPr}) (THF)} (3)*:** This was prepared in a manner similar to (**2**) starting from 1.23 g of UI$_3$ (1.98 mmol), 401 mg KCp^{Me4iPr} (1 mol eq) and 520 mg K$_2$COT^{tms2} (0.8 mol eq). It can be recrystallised from n-pentane or n-hexane (*ca* 5-10 mL) at -35 °C. Yield: 480 mg (41.9%). ^{1}H-NMR $\delta(C_7D_8)$: -92.93 (br s, 2H, *COT*), -68.09 (br s, 2H, *COT*), -27.69 (br s, 6H, Cp*Me*$_4$iPr), -20.79 (br s, 6H, Cp*Me*$_4$iPr), -10.25 (br s, 6H, CpMe$_4$\{CH(*Me*$_3$)$_2$\}), -7.40 (s, 18H, C_8H_6\{(Si*Me*$_3$)$_2$\}), -4.78 (br s, 1H, CpMe$_4$\{C*H*(Me$_3$)$_2$\}), 16.45 (br s, 2H, *COT*); ^{29}Si\{^{1}H\}-NMR $\delta(C_7D_8)$: -168.94 (s, *Si*Me$_3$); EI-MS: 668 (M-THF+F), 649 (M-THF), 505 (UC8H6tms2+F), 420 (UCpMe4iPr+F), 248 (COTtms2), 164 (CpMe4iPr), 149 (CpMe4iPr-Me), 73 (SiMe$_3$).

***Synthesis of {U[η^8-C$_8$H$_6$(1,4-SiMe$_3$)$_2$](η^5-Cp^{Me4tBu}) (THF)} (4)*:** This was prepared in a manner similar to (**2**) starting from 1.23 g of UI$_3$ (1.98 mmol), 428 mg KCp^{Me4tBu} (1 mol eq) and 520 mg K$_2$COT^{tms2} (0.8 mol eq). It was recrystallised from the minimum amount of n-pentane (*ca* 5 mL) at -80 °C over 2 hours. Yield: 290 mg (24.8%). ^{1}H-NMR $\delta(C_7D_8)$: -94.16 (br s, 2H, *COT*), -68.68 (br s, 2H, *COT*), -24.23 (br s, 9H, CpMe$_4$\{C(*Me*$_3$)$_3$\}), -19.28 (br s, 6H, Cp*Me*$_4$tBu), -10.15 (br s, 4H, *THF*), -9.57 (br s, 6H, Cp*Me*$_4$tBu), -6.56 (s, 18H, C8H6\{(Si*Me*$_3$)$_2$\}), -1.67 (s, 4H, *THF*), 17.67 (br s, 2H, *C8H6*); ^{29}Si\{^{1}H\}-NMR $\delta(C_7D_8)$: -163.60 (s, *Si*Me$_3$); EI-MS: 683 (M-THF+F), 664 (M-THF), 505 (UC8H6tms2+F), 434 (UCpMe4tBu+F), 415 (UCpMe4tBu), 248 (C8H6tms2), 122 (CpMe4tBu-tBu), 73 (SiMe3)

***Synthesis of {U[η^8-C$_8$H$_6$(1,4-SiMe$_3$)$_2$](η^5-Cp^{Me5})}$_2$(μ-O) (6) and {U[η^8-C$_8$H$_6$(1,4-SiMe$_3$)$_2$](η^5-Cp^{Me5})}$_2$(μ-η^2:η^2-C$_2$O$_4$) (7)*:** A 50 mL Young's ampoule with a capillary sidearm was charged in the glovebox with 100 mg (0.144 mmol) of (**1a**) which were dissolved in approximately 0.8 mL of *d^8*-toluene and attached to a Toepler line. The solution was cooled at -78 ºC and degassed and the appropriate amount of $^{13}CO_2$ gas added. Upon addition the solution turns from dark-brown to red accompanied with the formation of a brick-red precipitate. The reaction mixture was left to equilibrate to room temperature overnight and filtered in an Ar filled glovebox through a filter pipette. *Isolation of* (**6**)**:** Solvent was removed from the mother-liquor and the residue extracted in n-pentane (0.5-1.0 mL) in an Ar filled glovebox and the solvent left to slowly evaporate at room temperature before it was placed in a -35 ºC freezer to yield overnight crystals of the title compound as the (**6**).0.5C_5H_{12} solvate. Yield: 45 mg (50%) ^{1}H-NMR $\delta(C_7D_8)$: -114.58 (s, 2H, *COT*), -111.45 (s, 2H, *COT*), -85.93 (s, 2H, *COT*), -82.03 (s, 2H, *COT*), -6.92 (s, 18, C_8H_6\{(Si*Me*$_3$)$_2$\}), 0.51 (s, 18H, C_8H_6\{(Si*Me*$_3$)$_2$\}), 1.70 (s, 30H, Cp*Me*$_5$), 110.37 (s, 2H, *COT*), 111.35 (s, 2H, *COT*); ^{29}Si\{^{1}H\}-NMR $\delta(C_7D_8)$: -108.65 and -103.76 (s, *Si*Me$_3$); No molecular ion observed in the mass spectrum; El. Anal.: Required for $C_{48}H_{78}O_1Si_4U_2$**.**0.5C_5H_{12} C 46.78, H 6.61; The compound readily decomposes and despite repeated attempts an acceptable elemental analysis could not be obtained.

Isolation of (**7**)**:** The brick red precipitate was placed in a Young's ampoule and 5 mL of diglyme were added. The suspension was heated at almost reflux and filtered while hot to remove an unidentified impurity. The residue was then suspended in dry mesitylene (~3 mL) and gently brought to reflux with a heat-gun to produce a deep-red solution that was immediately filtered hot into a Young's ampoule kept above room temperature (ca 80 ºC) via gentle warming with a heatgun. The filtrate was let to settle to produce within minutes crystals of the title compound, that were isolated by decantation of the supernatant followed by washing with 1.0 mL THF and 3x1.0 mL n-pentane and finally drying in vacuum. Yield: 19 mg (20 %). Due to the insolubility in common organic solvents no spectroscopic data were obtained. EI-MS: 1332 (M), 1197 (M-CpMe5), 621 (UCOT^{tms2}CpMe5), 248 (COT^{tms2}), 121 (CpMe5-Me), 73 (SiMe3); El. Anal.: Required for $C_{50}H_{78}O_4Si_4U_2$ C 45.10 H 5.90; Found: C 44.81 H 6.12.

***Synthesis of {U[η^8-C$_8$H$_6$(1,4-SiMe$_3$)$_2$](η^5-Cp^{Me4Et})}$_2$(μ-η^2:η^2-C$_2$O$_4$) (8) and {U[η^8-C$_8$H$_6$(1,4-SiMe$_3$)$_2$](η^5-Cp^{Me4Et})}$_2$(μ-η^2:η^1-CO$_3$) (11)*:** In a similar manner as above from 150 mg (0.212 mmol) of (**2**).

Isolation of (**8**)**:** In a similar manner to (**7**) the precipitate was taken in refluxing toluene (*ca* 5 mL) before filtered hot. The crystalline material was isolated by filtration in the glovebox using a small porosity 3 ftitted glass filter followed by washing with 0.5 mL of THF and 1 mL toluene and finally 1 mL n-pentane and drying in vacuum. This material was contaminated by approximately 20% (**8**) and was isolated pure by a second crystallisation from toluene. Yield: 29 mg (20%) ^{1}H-NMR δ(C_4D_8O): -67.55 (s, 4H, *C8H6*), -52.16 (s, 4H, *COT*), -12.00 (s, 36H, $C_8H_6\{(SiMe_3)_2\}$), 0.69 (s, 4H, $CpMe_4(CH_2CH_3)$), 3.15 (s, 12H, $CpMe_4(CH_2CH_3)$), 4.41 (s, 12H, $CpMe_4(CH_2CH_3)$), 13.05 (s, 6H, $CpMe_4(CH_2CH_3)$), 31.73 (s, 4H, *COT*); $^{13}C\{^1H\}$-NMR δ(C_4D_8O): -43.74 (s, [U]-C_2O_4-[U]); $^{29}Si\{^1H\}$-NMR δ(C_4D_8O): -115.8; EI-MS: 1361 (M), 1212 (M-CpMe4Et), 635 (UCOT^{tms2}CpMe4Et), 248 (COT^{tms2}), 135 (CpMe4Et-Me), 73 ($SiMe_3$); El. Anal.: Required for $C_{52}H_{82}O_4Si_4U_2$ C 45.94 H 6.08; Found: C 45.99 H 5.98.

***Isolation of* (11):** After filtration and evaporation of the mother-liquor of the precipitate the residue was extracted in THF (1-2 mL) which was let to evaporate at room temperature until crystals started forming at the edge of the solvent. It was cooled at -35 ºC overnight before the crystals were separated by careful decantation and washed with n-pentane. The supernatant and washing were worked up the same way to give two more crops. Yield: 43 mg (30 %) ^{1}H-NMR δ(C_7D_8): -13.76 (s, 36H, $C_8H_6\{(SiMe_3)_2\}$), -0.74 69 (s, 4H, $CpMe_4(CH_2CH_3)$), 1.01 (s, 12H, $CpMe_4(CH_2CH_3)$), 3.72 (s, 12H, $CpMe_4(CH_2CH_3)$), 7.85 (s, 6H, $CpMe_4(CH_2CH_3)$), the COT protons could not be located; $^{13}C\{^1H\}$-NMR δ(C_7D_8): 44.09 (s, [U]-CO_3-[U]); $^{29}Si\{^1H\}$-NMR δ(C_7D_8): -115.5; EI-MS: 1331 (M), 1181 (M-CpMe4Et), 654 (UCOT^{tms2}CpMe4Et + F), 635 (UCOT^{tms2}CpMe4Et), 505 (UCOT^{tms2}+F), 248 (COT^{tms2}), 135 (CpMe4Et-Me), 73 ($SiMe_3$); El. Anal.: Required for $C_{51}H_{82}O_3Si_4U_2$ C 46.00 H 6.21; Found: C 45.99 H 6.60

***Synthesis of {U[η^8-$C_8H_6(1,4\text{-}SiMe_3)_2$]($\eta^5$-$Cp^{Me4iPr}$)}$_2$($\mu$-$\eta^2$:$\eta^2$-$C_2O_4$) (9) and {U[$\eta^8$-$C_8H_6(1,4\text{-}SiMe_3)_2$]($\eta^5$-$Cp^{Me4iPr}$)}$_2$($\mu$-$\eta^2$:$\eta^1$-$CO_3$) (12)*:** In a similar manner as for (**8**), (**11**) starting from 150 mg (0.207 mmol) of (**3**).

Isolation of (**9**)**:** As for (**9**) but the crystalline material was washed with pentane (3x1.0 mL) after canulla filtration and dried in vacuum. Yield: 58 mg (40%) ^{1}H-NMR δ(C_4D_8O): -63.94 (s, 4H, *C8H6*), -46.98 (s, 4H, *C8H6*), -13.17 (s, 12H, $CpMe_4\{CHMe_2\}$), -10.33 (s, 36H, C8H6{(Si*Me₃*)₂}), -0.01 (s, 12H, $CpMe_4\{CHMe_2\}$), 7.47 (s, 2H, $CpMe_4\{CHMe_2\}$), 12.68 (s, 12H, $CpMe_4\{CHMe_2\}$), 27.67 (s, 4H, *C8H6*); $^{29}Si\{^1H\}$-NMR δ(C_4D_8O): -115.31 (s, *Si*Me₃); $^{13}C\{^1H\}$-NMR δ(C_4D_8O): -32.81 ([U]-C_2O_4-[U]); EI-MS: 1388 (M, 4.5%), 1225 (M-CpMe4iPr, 2.0%), 1151 (M-CpMe4iPr-TMS), 737 (U COT^{tms2}CpMe4iPr+C_2O_4), 668 (U COT^{tms2}CpMe4iPr+F), 649 (U COT^{tms2}CpMe4iPr), 505 (UCOT^{tms2}+F), 248 (COT^{tms2}), 164 (CpMe4iPr), 149 (CpMe4iPr-Me), 73 (SiMe3); El. Anal: Required for $C_{54}H_{86}O_4Si_4U_2$ C 46.74, H 6.25; Found: C 46.82, H 6.50

***Isolation of* (12):** Removal of volatiles from the mother-liquor followed by extraction in either n-pentane or a 2:1 mixture ^{t}BuOMe/THF (1-2 mL in total), slow evaporation until crystals appear and overnight refrigeration at -35 ºC gave (11) which was isolated by careful decantation of the solvent and was washed with $SiMe_4$ (2x0.5 mL). Yield: 35 mg (25%) ^{1}H-NMR δ(C_7D_8): -17.55 (s, 12H, $CpMe_4\{CH(Me_3)_2\}$), -11.49 (s, 36H, C8H6{(Si*Me₃*)₂}), -4.54 (s, 12H, $CpMe_4\{CH(Me_3)_2\}$), 16.47 (s, 12H, $CpMe_4\{CH(Me_3)_2\}$); $^{29}Si\{^1H\}$-NMR δ(C_7D_8): -115.31 (s, *Si*Me₃); $^{13}C\{^1H\}$-NMR δ(C_7D_8): 69.49 (s, [U]-CO_3-[U]); EI-MS: 1388 (M+CO, 2.5%), 1359 (M, 5%), 1151 (M-CpMe4iPr-TMS), 668 (U COT^{tms2}CpMe4iPr+F), 649 (U COT^{tms2}CpMe4iPr), 505 (U COT^{tms2}+F), 486 (U COT^{tms2}), 248 (COT^{tms2}), 164 (CpMe4iPr), 149 (CpMe4iPr-Me), 73 (SiMe3); El. Anal: Required for $C_{53}H_{86}O_3Si_4U_2$ C 46.82, H 6.38; Found: C 46.50, H 6.42.

***Isolation of* (12) from reaction of (3) with scCO$_2$:** Extraction of the solids in pentane (ca 5 mL) followed by the minimum amount of toluene to dissolve the rest of the residue, slow evaporation at RT until crystals form and finally overnight refrigeration (-35°C) to complete the crystallisation. The crystals were isolated by careful removal of the mother-liquor *via* a drawn-out Pasteur pipette and washing with cold (-35°C) n-pentane (2x0.5 mL). Further evaporation and refrigeration of the combined mother-liquor and washings produced a second crop.

***Alternative synthesis of (9) from {U[η^8-$C_8H_6(1,4\text{-}SiMe_3)_2$]($\eta^5$-$Cp^{Me4iPr}$)Cl} (10) and $Tl_2C_2O_4$*:** In a Young's ampoule, 150 mg (0.207 mmol) of (**3**) were dissolved in an Ar filled glovebox in *ca* 10 mL of n-pentane with vigorous stirring and treated with 25 μL (1.1 mol eq) of ^{t}BuCl added *via* a microsyringe to give instantly a bright red solution. This was stripped from volatiles under vacuum to give (**10**) spectroscopically pure (see below). The latter was combined with 56 mg (0.5 mol eq) of $Tl_2C_2O_4$, toluene added (5 mL) and stirred vigorously overnight to produce an amorphous white precipitate which was filtered through a short plug of Celite and washed with hot toluene to give a bright red solution from which toluene was removed under vacuum slowly to induce crystallisation of (**9**) in approximately 5% yield. NMR data for {U[η^8-C8H6(1,4-$SiMe_3)_2$](η^5-Cp^{Me4iPr})Cl} (**12**): ^{1}H-NMR δ(C_7D_8): -100.43 (s, 2H, *COT*), -91.96 (s, 2H, *COT*), 11.49 (s, 18H, C8H6{(Si*Me*$_3)_2$}), -9.73 (s, 6H, $CpMe_4\{CH(Me_3)_2\}$), 3.12 (s, 6H, $CpMe_4\{CH(Me_3)_2\}$), 9.51 (s, 1H, $CpMe_4$\{C*H*$(Me_3)_2$\}), 12.91 (s, 6H, $CpMe_4\{CH(Me_3)_2\}$), 81.85 (s, 2H, *COT*); ^{29}Si{^{1}H}-NMR δ(C_7D_8): -100.61 (s, *Si*Me_3).

Synthesis of {U[η⁸-C_8H_6(1,4-$SiMe_3)_2$](η⁵-Cp^{Me4tBu})}$_2$(μ-η²:η¹-CO_3) (13): In a similar manner as above from 160 mg (0.217 mmol) of (**4**). After removal of solvent the residue was extracted with n-pentane (2x2 mL) and the undissolved residue taken in *ca* 0.3 mL of toluene and the two combined. This solution was let to slowly evaporate until crystals were observed and then refrigerated at -35 °C to give the title compound in two crops. Yield: 55 mg (32%). ^{1}H-NMR δ(C_7D_8): -17.89 (s, 18H, $CpMe_4$\{C(*Me*$_3)_3$\}), -11.16 (s, 36H, COT{(Si*Me*$_3)_2$}), -5.28 (s, 12H, Cp*Me*$_4$tBu), 23.46 (s, 12H, Cp*Me*$_4$tBu); ^{29}Si{^{1}H}-NMR δ(C_7D_8): -116.08, (s, *Si*Me_3); ^{13}C{^{1}H}-NMR δ(C_7D_8): 84.46 (s, [U]-*C*O_3-[U]); EI-MS: 1386 (M), 1165 (M-CO3-CpMe4tBu+O), 682 (U COT^{tms2}CpMe4tBu+F), 663 (U COT^{tms2}CpMe4tBu), 486 (U COT^{tms2}), 431 (UCpMe4tBu+F), 415 (UCpMe4tBu), 122 (CpMe4tBu-tBu), 73 (SiMe3); El. Anal.: Required for $C_{55}H_{90}O_3Si_4U_2$ C 47.60, H 6.54; Found: C 47.48, H 6.30

Cyclic Voltametry

Electrochemical studies were performed in an Ar glovebox using a BASi Epsilon-EC potentiostat under computer control. IR drop was compensated by the feedback method. CV experiments were performed using a three-electrode configuration with a Au disc (2.0 mm^2) or glassy carbon disc (7.0 mm^2) as the working electrode, a Pt wire as the counter electrode and a Ag wire as the pseudoreference electrode. Sample solutions were prepared by dissolving the analyte (*ca.* 5 mM) in THF (2.0 cm^3) followed by addition of a supporting electrolyte. For U(III) complexes **1a** - **4**, CV experiments with 0.1 M [^{n}Bu$_4$N][PF$_6$] as the supporting electrolyte showed only an irreversible oxidation process at *ca.* +0.7 V vs $Ag^{+/0}$, indicating sample decomposition to an unidentified U(IV) species, most likely *via* fluoride abstraction from electrolyte anions. Studies in 0.05 M [^{n}Bu$_4$N][B($C_6F_5)_4$] electrolyte showed quasi-reversible processes which were stable over 20 cycles. ^{1}H NMR spectroscopy showed no reaction between U(III) complexes **1a** - **4** and an excess of [^{n}Bu$_4$N][B(C_6F_5)] in THF-d_8 after 24 hours at room temperature.

For bimetallic U(IV) carbonate and oxalate complexes, 0.05 M [^{n}Bu$_4$N][B($C_6F_5)_3$] electrolyte did not provide a sufficiently negative potential window for the study of both U(IV)/U(III) reduction processes. Complexes **9**, **11**, **12** and **13** showed greater stability than **1a** - **4** in 0.1 M [^{n}Bu$_4$N][PF$_6$], owing to the comparative inertness of the U(IV) oxidation state, and the larger electrochemical window of this electrolyte allowed the two quasi-reversible processes to be adequately resolved.

The reported half potentials are referenced to the $FeCp_2^{+/0}$ redox couple, which was measured by adding ferrocene (*ca.* 1 mg) to the sample solution.

	Process 1		**Process 2**	
Compound	**$E_{½}^{(1)}$ /V**	**ΔE_p $^{(1)}$ /mV**	**$E_{½}^{(2)}$ /V**	**ΔE_p $^{(2)}$ /mV**
1a	-2.10	84	-1.57	81
2	-2.11	88	-1.60	77
3	-2.02	119	-1.55	130
4	-2.03	167	-1.53	127

Table S1. Electrode potentials vs $FeCp_2^{+/0}$ in 0.05 M [^{n}Bu$_4$N][B($C_6F_5)_4$] / THF at 25 °C. Scan rate 100 mVs^{-1}.

	Process 1		**Process 2**			
Compound	**$E_{½}^{(1)}$ /V**	**$\Delta E_p^{(1)}$ /mV**	**$E_{½}^{(2)}$ /V**	**$\Delta E_p^{(2)}$ /mV**	**$\Delta E_{½}^{(1)\text{-}(2)}$/V**	***K_c***
[**2**]$_2$(CO$_3$) (**11**)	-2.17	159	-2.85	148	0.68	3.12×10^{11}
[**3**]$_2$(C$_2$O$_4$) (**9**)	-2.15	70	-2.63	76	0.48	1.30×10^{8}
[**3**]$_2$(CO$_3$) (**12**)	-2.11	90	-2.78	89	0.67	2.11×10^{11}
[**4**]$_2$(CO$_3$) (**13**)	-2.12	80	-2.79	82	0.67	2.11×10^{11}

Table S2. Electrode potentials vs $FeCp_2^{+/0}$ in 0.1 M [^{n}Bu$_4$N][PF$_6$] / THF at 25 °C. Scan rate 100 mVs^{-1}. $\Delta E_{½}^{(1)\text{-}(2)} = E_{½}^{(1)} - E_{½}^{(2)}$. $K_c = \exp[\Delta E_{½}^{(1)\text{-}(2)}F/RT]$.

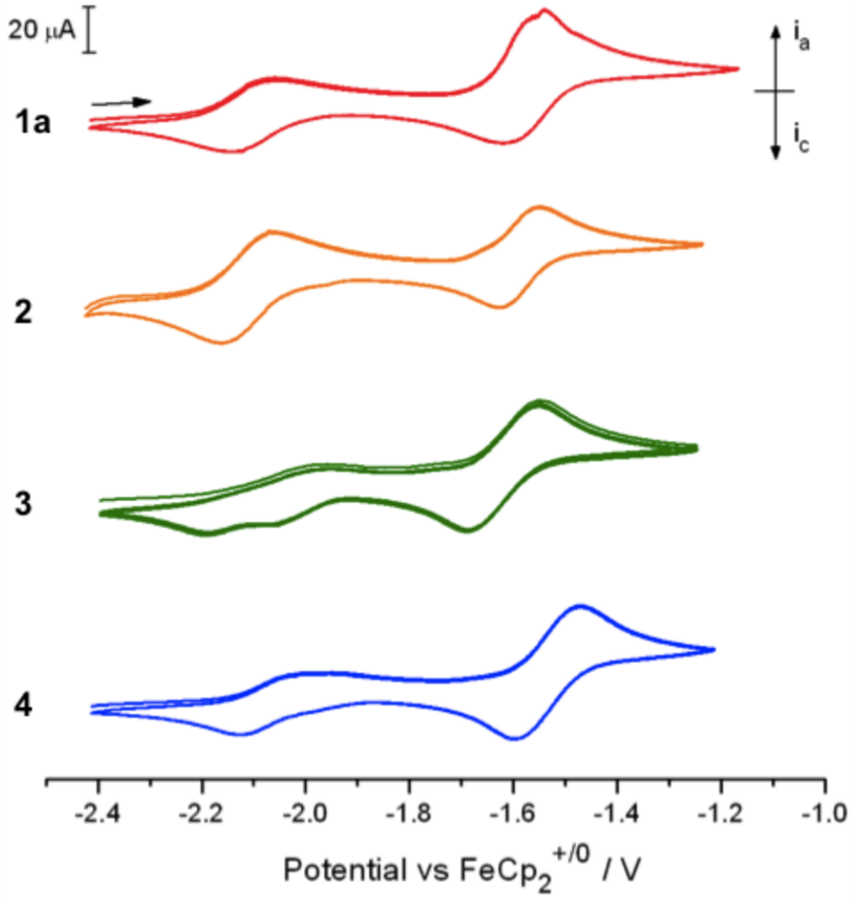

Figure S1: Stacked CV plots for **1a** - **5** in 0.1 M [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] / THF. Scan rate 100 mV s^{-1}.

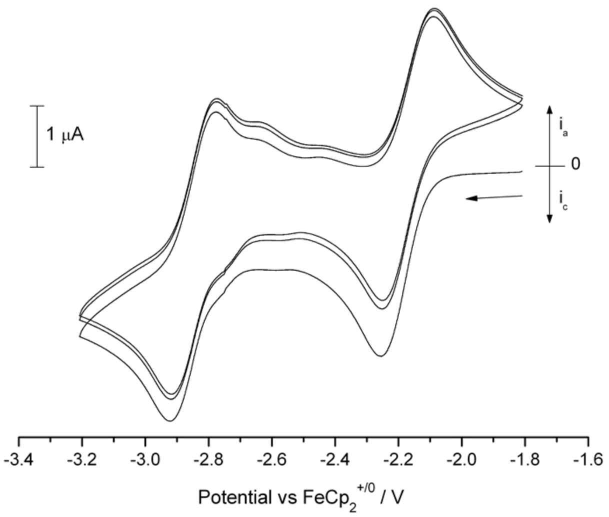

Figure S2: Overlaid CV scans (3 cycles) of {U[η^8-C_8H_6(1,4-$SiMe_3$)$_2$](η^5-Cp^{Me4Et})}$_2$(μ-η^2:η^1-CO_3)} (**11**) in 0.1 M [^{n}Bu$_4$N][PF$_6$] / THF. Scan rate 100 mV s^{-1}.

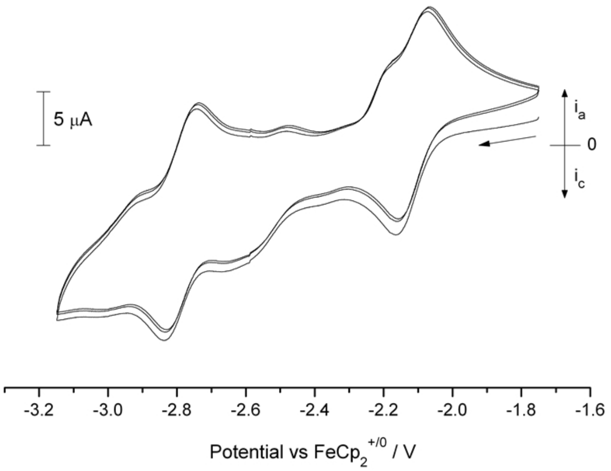

Figure S3: Overlaid CV scans (5 cycles) of {U[η^8-C_8H_6(1,4-$SiMe_3$)$_2$](η^5-Cp^{Me4iPr})}$_2$(μ-η^2:η^1-CO_3)} (**12**) in 0.1 M [^{n}Bu$_4$N][PF$_6$] / THF. Scan rate 100 mV s^{-1}.

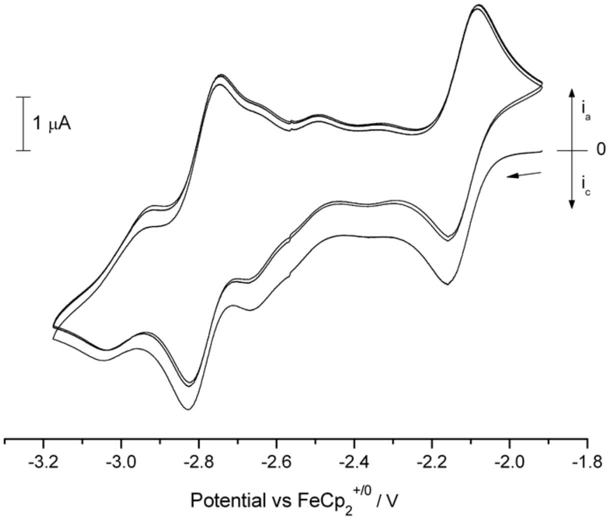

Figure S4: Overlaid CV scans (3 cycles) of $\{U[\eta^8\text{-}C_8H_6(1,4\text{-}SiMe_3)_2](\eta^5\text{-}Cp^{Me4tBu})\}_2(\mu\text{-}\eta^2\text{:}\eta^1\text{-}CO_3)\}$ (**13**) in 0.1 M $[^nBu_4N][PF_6]$ / THF. Scan rate 100 mV s^{-1}.

Computational Details

The uranium atoms were treated with two different effective core potentials (ECPs). The 5f in-core ECP was adapted to the uranium +4 oxidation state in combination with an adapted basis set and additional f-polarization functions to account for the reactions that involved dinuclear uranium(IV) complexes.[5] The very small core Stuttgart–Dresden ECP was also used in combination with its adapted basis set to study the oxidation steps from +3 to +4.[6] Carbon, oxygen, and hydrogen atoms were described with a 6-31G(d,p) double-z basis set.[7] The calculations were carried out at the DFT level of theory with the hybrid functional B3PW91[8] Geometry optimizations were performed without any symmetry restrictions and the nature of the extrema (minima and transition states) was verified with analytical frequency calculations. Gibbs free energies were obtained at T=298.15 K within the harmonic approximation. IRC calculations were performed to confirm the connections of the optimized transition states. DFT calculations were carried out with the Gaussian09 program.[9] Dispersion corrections were treated with the DFTD3 program.[10] The electronic density (at the DFT level) was analyzed by using natural bond orbital (NBO) analysis.[11]

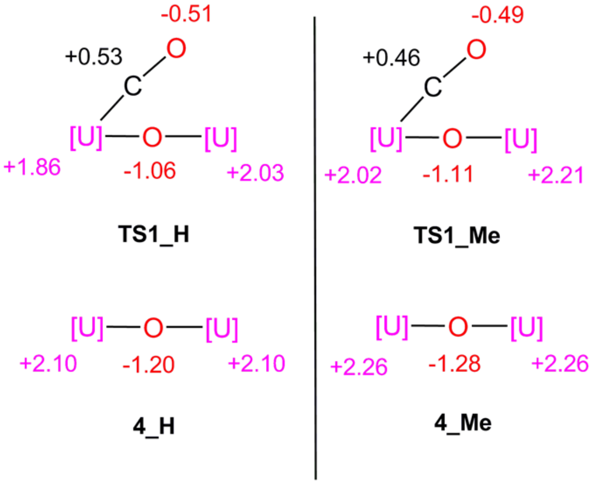

Figure S5: Selected NPA charges of **TS1_H**, **4_H**, **TS1_Me** and **4_Me**. Ligands have been omitted for clarity.

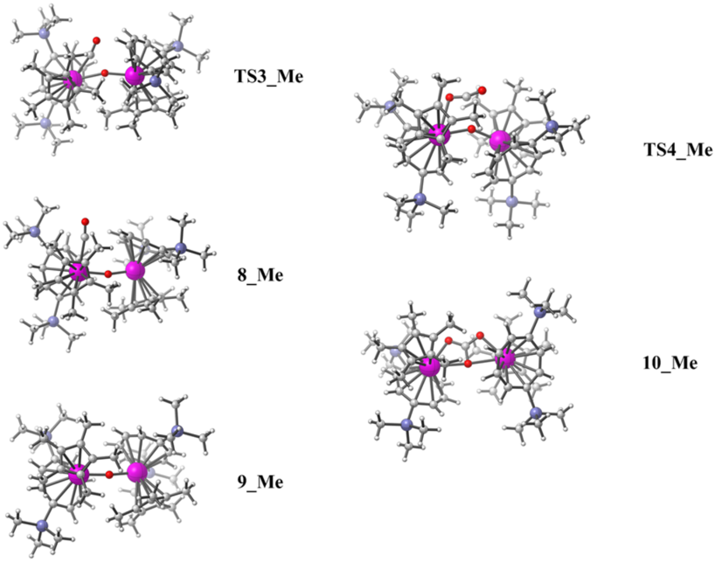

Figure S6: Computed structures linked to the energy profile in Figure 11 of the main text for R=Me. Structures with R = ^{t}Bu are qualitatively similar. (Uranium : pink, carbon : grey, hydrogen = white, oxygen = red, silicon = blue).

X-Ray Crystallography

Data sets for (**2**), (**3**), (**4**), (**6**), (**7**), (**8**), (**9**), (**11**), and (**13**) were collected collected on a Bruker-Nonius KappaCCD area detector diffractometer with a sealed-tube source (Mo *Kα*) and an Oxford Cryosystems low-temperature device (173 K), operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect,[12] Scalepack, and Denzo.[13] Absorption corrections were based on equivalent reflections using SADABS.[14] In the case of (**12**) data were collected using an Agilent Gemini Ultra diffractometer with an Enhance source (Mo *Kα*) equipped with an Eos CCD area detector and the same temperature device as above. The strategy used for data collection is the same as previously. Control, integration and absorption correction were handled by the CrysAlis Pro software.[15] The crystals were mounted on a glass fiber with silicon grease or MiTiGen loops, from dried vacuum oil kept over 4Å in a MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX package[16] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. In the case of (**6**) a highly disordered molecule of n-pentane was found in the asymmetric unit that could not be successfully modeled and as such this disorder was treated using the SQUEEZE routine in PLATON.[17] In the case of (**11**) the CpMe4Et ligand is disordered over two positions due to the centrosymmetric space group. Although this disorder was modeled successfully it resulted in unstable and/or non-converging refinements. As a result a model without the disorder has been included and therefore the corresponding thermal ellipsoids are big thus yielding level A alerts. The same applies in the case of (**8**). In the case of (**12**) some of the disordered atoms of the CpMe4iPr ligand have abnormal thermal ellipsoids resulting in level B alerts. Attempts to rectify this by restraining the afore mentioned parameters resulted in non-converging refinements (L.S. > 32) Crystal structure and refinement details are given in the following two tables:

Compound	**2**	**3**	**4**	**6**	**7**
Colour, Habit	Brown, Plate	Brown, Plate	Brown, Plate	Red, Block	Red, Plate
Size/mm	0.08x0.06x0.02	0.08x0.08x0.02	0.2x0.06x0.01	0.04x0.04x0.02	0.06x0.03x0.02
Empirical Formula	$C_{29}H_{49}OSi_2U$	$C_{30}H_{51}OSi_2U$	$C_{31}H_{53}OSi_2U$	$C_{96}H_{153}O_2Si_8U_4$	$C_{50}H_{78}O_4Si_4U_2$
M	707.89	721.92	735.94	2516.02	1331.54
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	*Pbca*
a/Å	10.840(2)	11.789(2)	12.092(2)	22.913(5)	10.480(2)
b/Å	14.869(3)	18.961(4)	19.621(4)	13.686(3)	21.616(4)
c/Å	19.149(4)	14.176(3)	13.755(3)	38.185(8)	23.669(5)
α/°	90	90	90	90	90
β/°	91.19(3)	96.89(3)	96.30(3)	107.06(3)	90
γ /°	90	90	90	90	90
V/ Å^3	3085.9(11)	3145.8(11)	3243.8(11)	11448(4)	5361.9(18)
Z	4	4	4	4	4
μ/mm^{-1}	5.356	5.255	5.098	5.764	6.162
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
θmin/max	3.126, 27.459	2.39, 27.47	2.37, 27.41	2.98, 27.46	3.197, 26.371
Completeness	99.4 to θ 27.459	99.7 to θ 27.47	98.8 to θ 27.41	97.4 to θ 27.46	99.8 to 26.371
Reflections Total/Independent	7015/5655	7194/5675	7304/5729	25509/16218	5455/2945
R_{int}	0.0586	0.0799	0.0715	0.0668	0.1878
Final *R1* and *wR2*	0.0284 and 0.0648	0.0363 and 0.0796	0.031 and 0.0823	0.0508 and 0.1285	0.0787 and 0.1221
Larget peak hole/ e.Å^{-3}	1.122 and -0.893	1.217 and -1.826	1.619 and -1.728	2.944 and -1.593	1.420 and -1.259
ρ_{calc}/g.cm^{-3}	1.524	1.524	1.507	1.460	1.649

Compound	**8**	**9**	**11**	**12**	**13**
Colour, Habit	Red, Plate	Red, Plate	Red, Plate	Red, Plate	Red, Plate
Size/mm	0.10x0.08x0.04	0.08x0.04x0.01	0.2x0.06x0.03	0.2x0.1x0.02	0.12x0.08x0.02
Empirical Formula	$C_{52}H_{82}O_4Si_4U_2$	$C_{54}H_{86}O_4Si_4U_2$	$C_{51}H_{82}O_3Si_4U_2$	$C_{106}H_{171}O_6Si_8U_4$	$C_{55}H_{90}O_3Si_4U_2$
M	1359.64	1387.64	1331.64	2719.27	1387.68
Crystal System	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space Group	*Cmca*	$P2_1/n$	*Pnma*	$Pca2_1$	$P2_1/c$
a/Å	21.741(4)	12.917(3)	23.330(5)	43.8503(11)	11.737(2)
b/Å	23.447(5)	13.555(3)	21.460(4)	10.3313(2)	18.983(4)
c/Å	10.829(2)	16.582(3)	10.710(2)	24.2758(6)	25.761(5)
α/°	90	90	90	90	90
β/°	90	100.86(3)	90	90	95.43(3)
γ /°	90	90	90	90	90
V/ Å^3	5520.1(19)	2851.2(10)	5362.1(18)	10997.7(4)	5714(2)
Z	4	4	4	4	4
μ/mm^{-1}	5.989	5.797	6.162	6.009	5.784
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
θmin/max	3.48/27.47	3.26, 27.48	3.425, 27.483	2.94, 26.372	2.922, 27.484
Completeness	99.8 to 27.47	98.6 to 27.48	99.8 to 27.483	99.7 to 27.484	99.4 to 27.484
Reflections Total/Independent	3237/2517	6452/4774	6298/4569	15780/13293	13030/10213
R_{int}	0.1158	0.0520	0.1128	0.0461	0.1207
Final *R1* and *wR2*	0.0437 and 0.0901	0.0452 and 0.1103	0.0524 and 0.1336	0.0449 and 0.0794	0.0443 and 0.1142
Larget peak hole/ e.Å^{-3}	1.077 and -1.564	2.711 and -1.171	3.098 and -2.390	1.637 and -1.462	3.182 and -2.119
ρ_{calc}/g.cm^{-3}	1.670	1.616	1.684	1.642	1.613

CCDC 1000008-1000017 contain the supplementary crystallographic data for this paper.

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