Supporting Information

Reductive Coupling of Carbon Dioxide to Carbonate and Squarate Products Using A Mixed-Sandwich U(III) Complex

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General Methods

Unless specified otherwise all manipulations were carried out using conventional high vacuum and Schlenk line techniques, under an atmosphere of dry argon, or under a dinitrogen atmosphere in an MBraun glove box. Solvents were refluxed over suitable drying agents under a dinitrogen atmosphere, and distilled and degassed prior to use. Toluene was refluxed over sodium. THF was refluxed over potassium. Diethyl ether and pentane were refluxed over sodium/potassium alloy. NMR solvents were dried by refluxing over potassium (d_6-benzene) or sodium (d_8-toluene) then vacuum transferred into ampules and stored under dinitrogen prior to use. NMR spectra were recorded on Varian VNMRS 400 or Bruker DPX 300 spectrometers at room temperature, unless otherwise stated. Chemical shifts reported in ppm (δ) are relative to the residual proton chemical shift of the deuterated solvent (^{1}H) or the carbon chemical shift of the deuterated solvent (^{13}C). Mass spectra were recorded on a VG autospec Fisons instrument (electron impact ionisation at 70 eV).. Elemental analysis was performed by Micro Analytisches Labor Pascher (Germany). [U(η-C_8H_6{Si^{i}Pr$_3$-1,4}$_2$)(η-C_5Me_5)THF] and [U(η-C_8H_6{Si^{i}Pr$_3$-1,4}$_2$)(η-C_5Me_4H)THF] were prepared as previously described.[i,ii] $^{13}CO_2$ (99% enriched, Cambridge Isotopes) and $^{12}CO_2$ (99.9995%, Linde) were used as supplied. Transfer of $^{13}CO_2$ was via a Toepler pump with calibrated (by transfer of xenon into a receiving vessel of accurately known volume, and differential weighing) delivery pressure. In the case of the stoichiometric reaction of **2** with $^{13}CO_2$, control of stoichiometry was achieved by the use of a standard 5 mm Young's NMR tube of accurately known volume containing a measured volume (microlitre syringe) of solvent (and therefore of known headspace).

Synthesis of [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η- C_5Me_4H)]$_2$(μ-η^1:η^2-CO_3)], ***5b***

A solution of [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η-C_5Me_4H)(THF)] **2** (200 mg, 0.24 mmol) in toluene (20 ml) was free-thaw degassed, cooled to -30ºC and back-filled with 1 bar CO_2. The solution was left to stir and warm up overnight, yielding a ruby red solution. Volatiles were removed *in vacuo* and the resultant red solids were taken up in Et_2O (2 ml). Cooling to -50 ºC for 3 days gave **5b** as a dark red crystalline solid. Yield: 72 mg (0.044 mmol), 37% yield based on 2 equiv. **2**.

^{1}H NMR (C_6D_6, 293 K): δ ppm 30.59 (s, 4H, COT ring-CH), 18.20 (s, 4H, COT ring-CH), 4.66 (s, 12H, Cp^{Me4H}-CH_3), 3.23 (m, 2H, Cp^{Me4H}-CH), 1.10 (d, 36H, ^{i}Pr-CH_3), -2.63 (s, 12H, Cp^{Me4H}-CH_3), -6.77 (d, 36H, ^{i}Pr-CH_3), -8.22 (s, 12H, ^{i}Pr-CH), -60.34 (s, 4H, COT ring-CH).

^{13}C{^{1}H} NMR **5b-$^{13}CO_3$** (C_7D_8, 293 K, selected data): δ ppm 137.6 (s, $^{13}CO_3$).

Anal. Calc. for $C_{71}H_{122}Si_4O_3U_2$: C, 52.93; H, 7.57%; found C, 52.93; H, 7.69%.

MS (EI): *m/z* = 1611 (5%, M^+); 775 (80%, [U(C_8H_6{Si^iPr_3-1,4}$_2$)(C_5Me_4H)]$^+$).

Synthesis of [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η- C_5Me_5)]$_2$(μ-η^1:η^2-CO_3)], ***5a***

5a was prepared in very similar (40%) yield and in an essentially identical fashion to **5b**, except final recrystallisation was from THF/^{t}BuOMe (1:1) at -50˚C .

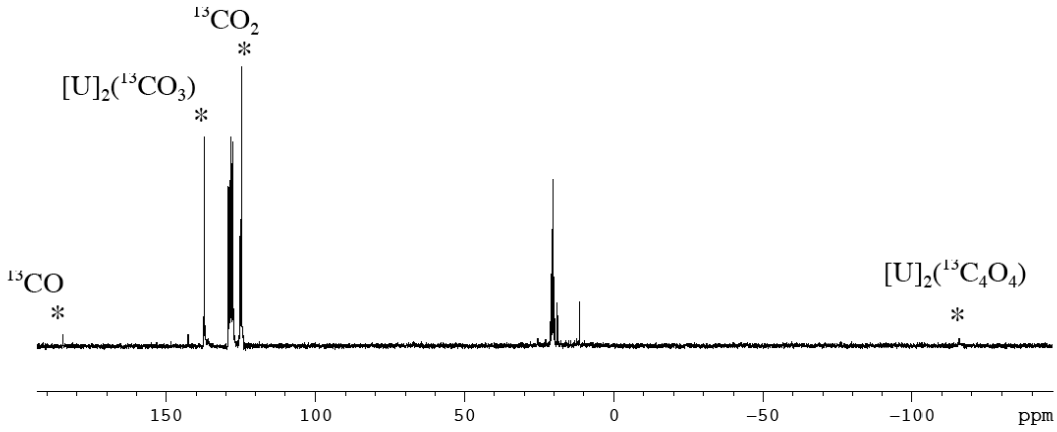
^{1}H NMR (C_7D_8, 293 K): δ ppm 4.89 (s, 30H, C_5Me_5), -5.14 (s, 36H, tips CH_3), -7.51 (br m, 12H, tips CH), -8.03 (br s, 36H, tips CH_3); the ring Hs of the COT ligand could not be unambiguously assigned. ^{13}C{^{1}H} NMR **5a-$^{13}CO_3$** (C_7D_8, 293 K, selected data): δ ppm 113.2 (s, $^{13}CO_3$).

Anal. Calc. for $C_{73}H_{126}O_3Si_4U_2$: C, 53.46; H, 7.74%; found C, 53.40; H, 7.78%.

MS (EI): *m/z* = 1637 (2%, M^+).

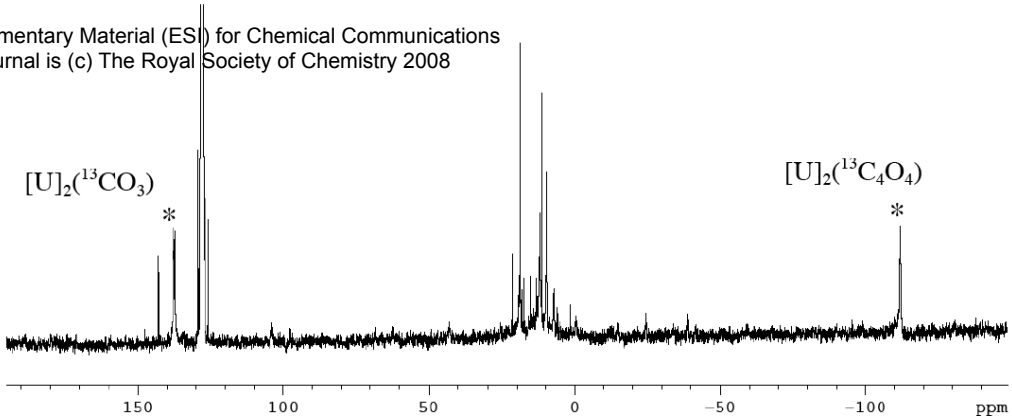
*Reaction of [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η-C_5Me_4H)(THF)] **2** with excess $^{13}CO_2$*

A sample of black, crystalline [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η-C_5Me_4H)(THF)] (40 mg, 5 x 10^{-5} mol) was dissolved in d_8-toluene (0.5 mL) in a 5mm Youngs NMR tube with high-vacuum PTFE stopcock (2.50 mL total volume). The solution was cooled to -78 °C, the headspace evacuated and $^{13}CO_2$ (at 0.85 bar pressure, ca. 8 x 10^{-5} mol, 1.6 equivalents wrt **2**) admitted. The solution was allowed to warm up to room temperature overnight and the $^{13}C\{^1H\}$ spectrum recorded, shown below:



*Stoichiometric reaction of [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η-C_5Me_4H)(THF)] **2** with $^{13}CO_2$*

A sample of black, crystalline [U(η-C_8H_6{Si^iPr_3-1,4}$_2$)(η-C_5Me_4H)(THF)] (60 mg, 7.5 x 10^{-5} mol) was dissolved in d_8-toluene (1.00 mL) in a 5mm Youngs NMR tube with high-vacuum PTFE stopcock (2.50 mL total volume). The solution was cooled to -78 °C, the headspace evacuated and $^{13}CO_2$ (at 0.85 bar pressure, ca. 6 x 10^{-5} mol, 0.8 equivalents wrt **2**) admitted. The solution was allowed to warm up to room temperature overnight and the $^{13}C\{^1H\}$ spectrum recorded, shown overleaf:



[i] O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, and N. Hazari, *Science*, 2006, **311**, 829.

[ii] O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, and N. Hazari, *J. Am. Chem. Soc.,* 2006, **128**, 9602.

X-Ray Data for 5b

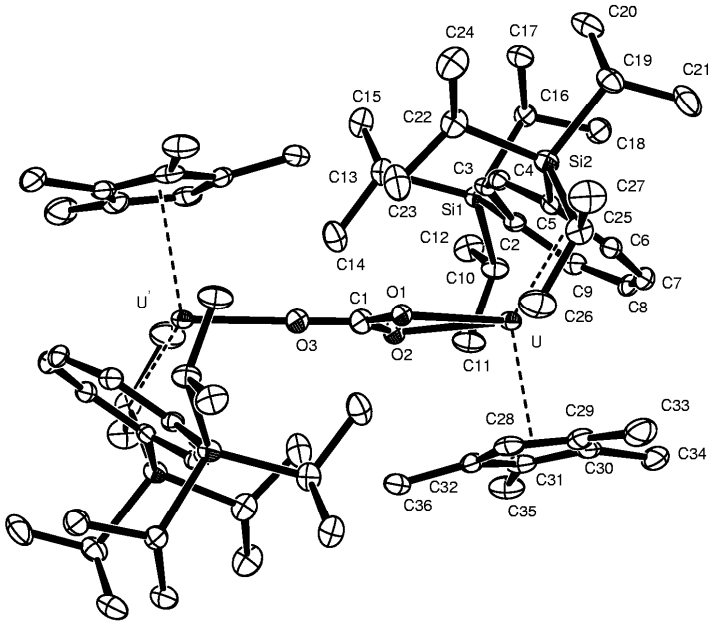


Table 1. Crystal data and structure refinement for [(CO_3){U(cot(tips)2)(C5HMe4)}2] . Et2O

Identification code	apr1906	
Empirical formula	C71 H122 O3 Si4 U2 . C4 H10 O	
Formula weight	1686.23	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No.2)	
Unit cell dimensions	a = 10.5128(6) Å	α= 66.040(3)°.
	b = 13.7949(6) Å	β= 76.536(3)°.
	c = 15.4698(7) Å	γ = 73.608(3)°.
Volume	1948.86(17) $Å^3$	
Z	1	
Density (calculated)	1.44 Mg/m^3	
Absorption coefficient	4.26 mm^{-1}	
F(000)	854	
Crystal size	0.10 x 0.10 x 0.08 mm^3	
Theta range for data collection	3.48 to 26.13°.	

Index ranges	-12<=h<=12, -17<=k<=17, -18<=l<=19
Reflections collected	29815
Independent reflections	7612 [R(int) = 0.062]
Reflections with I>2sigma(I)	6388
Completeness to theta = 26.13°	98.1 %
Tmax. and Tmin.	0.727 and 0.676
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7612 / 0 / 375
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.053, wR2 = 0.108
R indices (all data)	R1 = 0.069, wR2 = 0.115
Largest diff. peak and hole	5.34 and -1.25 e.$Å^{-3}$ (near U atom)

The bridging carbonate group is disordered about the inversion centre and had to be left isotropic. Because of the disorder the dimensions of the carbonate are less reliable.

The disordered Et2O solvate was left isotropic with H atoms omitted.

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN

Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for apr1906. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
U	6457(1)	3652(1)	6832(1)	35(1)
Si(1)	3056(2)	5260(2)	8380(1)	38(1)
Si(2)	5521(2)	611(2)	7184(2)	41(1)
O(1)	5738(10)	3953(9)	5349(7)	37(2)
O(2)	5220(10)	5342(8)	5807(7)	42(2)
O(3)	4508(12)	5531(11)	4495(8)	47(3)
C(1)	5080(20)	5002(18)	5226(12)	48(4)
C(2)	4372(7)	4113(6)	8116(5)	36(2)
C(3)	3941(8)	3562(6)	7673(5)	35(2)
C(4)	4438(8)	2631(6)	7425(5)	37(2)
C(5)	5595(8)	1777(6)	7519(5)	36(2)
C(6)	6731(8)	1575(6)	7959(5)	39(2)
C(7)	7144(8)	2048(6)	8470(5)	42(2)
C(8)	6662(8)	2979(6)	8699(5)	41(2)
C(9)	5537(8)	3853(6)	8530(5)	42(2)
C(10)	3883(9)	6238(6)	8523(6)	48(2)
C(11)	4894(10)	6729(8)	7658(7)	66(3)
C(12)	2862(10)	7137(8)	8810(7)	64(3)
C(13)	1801(9)	5956(7)	7487(6)	48(2)
C(14)	2315(11)	6801(8)	6554(6)	67(3)
C(15)	456(9)	6469(8)	7898(7)	62(2)
C(16)	2122(8)	4572(6)	9598(5)	42(2)
C(17)	1536(9)	3680(7)	9588(6)	53(2)
C(18)	2968(9)	4123(8)	10407(6)	60(2)
C(19)	4931(10)	-445(7)	8346(6)	56(2)
C(20)	3555(11)	8(8)	8785(7)	73(3)
C(21)	5885(12)	-927(8)	9080(7)	80(3)
C(22)	4233(9)	1046(7)	6348(6)	53(2)
C(23)	4642(12)	1775(8)	5324(7)	72(3)
C(24)	3741(11)	98(8)	6346(8)	72(3)
C(25)	7247(9)	-7(7)	6697(6)	53(2)
C(26)	7928(11)	780(9)	5813(8)	83(3)
C(27)	7309(11)	-1041(8)	6529(9)	80(3)

C(28)	8756(8)	3581(8)	5599(6)	55(2)
C(29)	9234(8)	3036(8)	6483(7)	58(2)
C(30)	9051(9)	3777(8)	6922(6)	55(2)
C(31)	8456(8)	4819(8)	6285(6)	53(2)
C(32)	8284(8)	4693(7)	5457(6)	44(2)
C(33)	10013(10)	1867(9)	6824(9)	91(4)
C(34)	9615(11)	3580(11)	7791(7)	94(4)
C(35)	8235(10)	5883(8)	6405(8)	72(3)
C(36)	7871(10)	5561(8)	4552(6)	66(3)
O(1S)	58(18)	287(14)	-432(11)	96(5) *
C(1S)	-170(30)	-760(20)	-210(20)	203(10)
C(2S)	-280(20)	-990(20)	-899(18)	191(9)

* occupancy 0.5

Table 3. Bond lengths [Å] and angles [°] for apr1906.

U-M(1)	1.948(7)
U-O(3)'	2.227(12)
U-O(1)	2.422(10)
U-O(2)	2.427(10)
U-M(2)	2.492(8)
U-C(6)	2.653(7)
U-C(4)	2.656(7)
U-C(3)	2.674(7)
U-C(9)	2.677(7)
U-C(7)	2.689(8)
U-C(8)	2.692(7)
U-C(5)	2.698(7)
U-C(2)	2.714(7)
U-C(28)	2.714(8)
U-C(32)	2.731(8)
U-C(31)	2.776(8)
U-C(29)	2.789(8)
U-C(30)	2.820(8)
Si(1)-C(2)	1.899(8)
Si(1)-C(10)	1.903(8)
Si(1)-C(13)	1.904(8)
Si(1)-C(16)	1.905(8)
Si(2)-C(22)	1.896(9)
Si(2)-C(25)	1.897(9)
Si(2)-C(19)	1.898(8)
Si(2)-C(5)	1.904(7)
O(1)-C(1)	1.37(2)
O(2)-C(1)	1.219(17)
O(3)-C(1)	1.26(3)
C(2)-C(9)	1.402(10)
C(2)-C(3)	1.420(9)
C(3)-C(4)	1.412(10)
C(4)-C(5)	1.422(10)
C(5)-C(6)	1.415(10)
C(6)-C(7)	1.406(10)
C(7)-C(8)	1.397(11)

C(8)-C(9)	1.416(11)
C(10)-C(12)	1.536(11)
C(10)-C(11)	1.545(12)
C(13)-C(15)	1.512(12)
C(13)-C(14)	1.536(12)
C(16)-C(18)	1.523(11)
C(16)-C(17)	1.530(11)
C(19)-C(21)	1.509(13)
C(19)-C(20)	1.524(13)
C(22)-C(23)	1.529(13)
C(22)-C(24)	1.536(11)
C(25)-C(26)	1.529(13)
C(25)-C(27)	1.531(12)
C(28)-C(29)	1.400(13)
C(28)-C(32)	1.412(12)
C(29)-C(30)	1.391(13)
C(29)-C(33)	1.521(13)
C(30)-C(31)	1.435(13)
C(30)-C(34)	1.489(12)
C(31)-C(32)	1.419(11)
C(31)-C(35)	1.501(12)
C(32)-C(36)	1.487(12)

M(1)-U-O(3)’	122.6(4)
M(1)-U-O(1)	120.3(4)
M(1)-U-O(2)	119.6(4)
M(1)-U-M(2)	137.6(4)
O(3)’-U-M(2)	99.3(4)
O(1)-U-M(2)	97.0(4)
O(2)-U-M(2)	98.1(4)
C(2)-Si(1)-C(10)	110.4(4)
C(2)-Si(1)-C(13)	113.0(3)
C(10)-Si(1)-C(13)	113.4(4)
C(2)-Si(1)-C(16)	104.6(3)
C(10)-Si(1)-C(16)	106.7(3)
C(13)-Si(1)-C(16)	108.1(4)
C(22)-Si(2)-C(25)	113.0(4)
C(22)-Si(2)-C(19)	107.5(4)

C(25)-Si(2)-C(19)	108.5(4)
C(22)-Si(2)-C(5)	111.4(3)
C(25)-Si(2)-C(5)	110.8(4)
C(19)-Si(2)-C(5)	105.2(3)
C(1)-O(1)-U	93.3(9)
C(1)-O(2)-U	97.2(12)
C(1)-O(3)-U'	175.3(14)
O(2)-C(1)-O(3)	127(2)
O(2)-C(1)-O(1)	115.5(17)
O(3)-C(1)-O(1)	117.2(13)
C(9)-C(2)-C(3)	130.7(7)
C(9)-C(2)-Si(1)	113.3(5)
C(3)-C(2)-Si(1)	115.2(6)
C(4)-C(3)-C(2)	137.9(7)
C(3)-C(4)-C(5)	138.1(7)
C(6)-C(5)-C(4)	129.4(7)
C(6)-C(5)-Si(2)	113.5(5)
C(4)-C(5)-Si(2)	116.4(5)
C(7)-C(6)-C(5)	136.3(7)
C(8)-C(7)-C(6)	135.9(8)
C(7)-C(8)-C(9)	136.1(7)
C(2)-C(9)-C(8)	135.3(7)
C(12)-C(10)-C(11)	110.7(7)
C(12)-C(10)-Si(1)	112.6(6)
C(11)-C(10)-Si(1)	114.5(6)
C(15)-C(13)-C(14)	109.4(7)
C(15)-C(13)-Si(1)	113.1(6)
C(14)-C(13)-Si(1)	113.5(6)
C(18)-C(16)-C(17)	110.4(7)
C(18)-C(16)-Si(1)	113.5(6)
C(17)-C(16)-Si(1)	111.0(5)
C(21)-C(19)-C(20)	109.5(8)
C(21)-C(19)-Si(2)	114.6(6)
C(20)-C(19)-Si(2)	111.2(6)
C(23)-C(22)-C(24)	110.1(7)
C(23)-C(22)-Si(2)	114.7(7)
C(24)-C(22)-Si(2)	113.8(6)
C(26)-C(25)-C(27)	110.0(8)

C(26)-C(25)-Si(2)	115.0(6)
C(27)-C(25)-Si(2)	114.2(7)
C(29)-C(28)-C(32)	109.1(8)
C(30)-C(29)-C(28)	108.8(8)
C(30)-C(29)-C(33)	126.0(10)
C(28)-C(29)-C(33)	124.6(10)
C(29)-C(30)-C(31)	107.3(8)
C(29)-C(30)-C(34)	126.3(10)
C(31)-C(30)-C(34)	125.3(9)
C(32)-C(31)-C(30)	108.1(8)
C(32)-C(31)-C(35)	125.3(9)
C(30)-C(31)-C(35)	126.1(8)
C(28)-C(32)-C(31)	106.7(8)
C(28)-C(32)-C(36)	125.2(8)
C(31)-C(32)-C(36)	127.7(8)

Symmetry transformations used to generate equivalent atoms: ‘ -x+1,-y+1,-z+1

M1 and M2 are the centroids for the C(2) to C(9) and C(28) to C(32) rings.