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Supplementary Information

Activation of Carbon Suboxide (C_3O_2) by U(III) to form a Cyclobutane-1,3-dione Ring.

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General considerations: 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. Filter cannulas were prepared using Whatman 25 mm glass microfiber filters and were pre-dried at 160 °C overnight. Toluene was dried over molten K, distilled under a N_2 atmosphere and kept in a Young's ampules over a potassium mirror under Ar. Hydrocarbons were dried over NaK, distilled under a N_2 atmosphere, and kept in Young's ampules over a potassium mirror under Ar. $SiMe_4$ was purchased from Sigma-Aldrich, freeze-thaw degassed, then stirred over NaK for 3 days before being vac-transferred, freeze-thaw degassed again and kept over activated 4Å molecular sieves in a well-sealed glass bottle in a glovebox (Ar) freezer (-35 ºC). Deuterated toluene and benzene were degassed by three freeze−thaw cycles, dried by refluxing over molten K for 3 days, vacuum distilled, and kept in Young's ampoules in the glovebox under N_2 over activated 4Å molecular sieves. UCp'_3 (**2**) (Cp' = $[C_5H_4SiMe_3]^-$) was prepared according to a published procedure by Evans *et al.*[1] and stored in a glovebox freezer (-35 ºC) under N_2. Carbon suboxide (C_3O_2) was prepared by the de-hydration of malonic acid with P_2O_5 as we have previously described.[2] ^{1}H-NMR and ^{29}Si{^{1}H}-NMR spectra were recorded on a Varian VNMR S400 spectrometer operating at 400 MHz (^{1}H) at 30 °C unless otherwise stated. The spectra were referenced internally to the residual protic solvent (^{1}H) while ^{29}Si{^{1}H} NMR spectra were referenced externally relative to $SiMe_4$. EI-MS mass spectra were recorded on a VG-Autospec Fisons instrument at the University of Sussex unless otherwise stated. IR spectra were recorded on a Perkin Elmer 100 instrument as thin films. Elemental analyses were performed by MicroAnalytisches Labor Pascher.
<u>*NOTE:*</u> C_3O_2 has a strong pungent smell (resembling extremely bad body odour) which can be irritating to the mucus. Furthermore, although when neat it is unstable above -30 ^{0}C, it is more stable when in solution and therefore vacuum traps should be left in a fume-hood for trapped solvents/C_3O_2 to thaw and washed with copious amounts of acetone before using them.

Optimised synthesis of (3): A 250 mL Young's ampule equipped with a right angle sidearm leading to a ball adapter and a stirring bar was charged with 86 mg (0.128 mmol) of (**2**) in a N_2 filled glovebox and *ca* 2 mL of toluene were added to dissolve (**2**). The toluene solution of (**2**) was degassed by cooling at -78 ˚C using solid dry ice and approximately 1 molar equivalent of C_3O_2 was administered at this temperature under static vacuum, in the manner we have previously described. Upon addition of C_3O_2 the colour of the solution turns to an intense wine-red. The ampule was then connected to a Schlenk line and was placed in a -35 ˚C slush bath and let to slowly warm to 10 ˚C. Upon reaching this temperature, volatiles were <u>immediately</u> removed under vacuum and the deep red residue was analysed by NMR in C_6D_6 to show that (**3**) is the major species. The residue was then taken in benzene (*ca* 10 mL) and filtered *via* cannula into a pre-weighed Young's ampule and lyophilised to give 83 mg of a deep red powder. This was taken into an Ar glovebox and extracted with n-heptane, filtered through a glass-microfibre packed Pasteur pipette into a 20 mL scintillation vial and washed until the n-heptane washings were colourless (*ca* 5-7 mL). The insoluble in n-heptane solids were discarded. The volume of the n-heptane solution was reduced (*ca* 1 mL) under a stream of Ar until crystals started forming upon which time it was placed in a -35 ˚C freezer overnight. The solvent was removed carefully using a drown-out pipette and the crystals washed with a small amount of n-heptane three times (total volume used *ca* 1 mL). The crystals of this first recrystallisation (*ca* 5 mg) are quite big but have co-formed on top of an

amorphous matrix of by-product from which they can be separated manually. The mother-liquor of this crystallisation was placed in a -35 ˚C overnight upon which time an amorphous brown-red solid formed that was discarded after it had been washed with 1 mL of n-heptane. The combined n-heptane washings (*ca* 2-3 mL) were let to slowly evaporate in an Ar glovebox over 3 days before being placed in a -35 ˚C freezer to yield a second crop of crystals of the title compound (*ca* 5 mg).
NOTE: It is crucial to remove volatiles the moment (or soon as possible but no more than 5 minutes) the reaction mixture reaches 10 ˚C, otherwise the formation of intractable solids is observed, along with diminishing concentration of (**3**) in the crude reaction mixture (by ^{1}H-NMR). This makes the isolation of (**3**) capricious, albeit possible.
Yield: *ca* 10 mg. Elem. Anal.: Calcd for $C_{106}H_{156}O_6Si_{12}U_4.C_7H_{16}$: C 46.55, H 5.95; Found C 46.40, H 6.14; ^{1}H-NMR (δ C_6D_6): -12.51 (s, 12H, $C_5H_4SiMe_3$), -7.47 (s, 54H, SiMe_3), -7.34 (s, 12H, $C_5H_4SiMe_3$), -6.22 (s, 12H, $C_5H_4SiMe_3$), -5.55 (s, 54H, SiMe_3), 18.63 (s, 12H, $C_5H_4SiMe_3$); ^{29}Si{^{1}H}-NMR (δ C_6D_6): -65.60, -69.57 (*Si*Me_3); IR (thin film): 2178.9 cm^{-1} $\nu_{(CCO)}$, 1832 cm^{-1}, 1732 cm^{-1} $\nu_{(CO)}$ (other resonances were obscured by the vibrations associated with the UCp'$_3$ moieties); EI-MS: No molecular ion observed.

Synthesis of (4): In a similar manner as above C_3O_2 was added to a toluene solution of (**1**) (86 mg; 0.128 mmol) in a 250 mL Young's tap. The reaction mixture adopts the deep red wine colouration as above and was placed in a -78 ˚C slush bath which was allowed to slowly warm to -60 ˚C upon which time volatiles were removed under vacuum. The residue was taken in benzene (*ca* 8 mL), filtered and lyophilised as above to produce a deep red powder (48 mg). This was extracted in n-pentane (*ca* 2 mL), filtered through a glass-microfibre Pasteur pipette in an Ar glovebox and the volume of the filtrate slowly reduced by evaporation (*ca* 1 mL) at RT before being placed in a -35 ˚C freezer to yield overnight crystals of UCp'$_4$. The supernatant was removed by a drown-out pipette and the procedure described above was repeated another two times until no more UCp'$_4$ crystallised. The solvent was allowed to completely evaporate, and the resulting deep red-brown film was dried for a few minutes under vacuum. It was then dissolved in $SiMe_4$ (*ca* 1 mL), and the solution let to evaporate to *ca* half before being placed in a -35 ˚C freezer, to produce overnight crystals of the title compound. Yield: 16 mg. Elem. Anal.: Calcd for $C_{50}H_{78}OSi_6U_2$: C 44.83, H 5.87; Found: C 44.30, H 5.99. ^{1}H-NMR (δ C_7D_8): -13.30 (s, 6H, $C_5H_4SiMe_3$), -8.26 (s, 27H, SiMe_3), -6.74 (s, 27H, SiMe_3), -6.42 (s, 6H, $C_5H_4SiMe_3$), -2.42 (s, 6H, $C_5H_4SiMe_3$), 0.02 (s, 6H, $C_5H_4SiMe_3$); ^{29}Si{^{1}H}-NMR (δ C_7D_8): -70.70, -76.03 (*Si*Me_3); IR (thin film): 2060 cm^{-1} $\nu_{(CCO)}$; EI-MS: 1340 (M), 1201 (M-Cp'), 1129 (M-Cp'-$SiMe_3$), 668 (UCp'$_3$F), 649 (UCp'$_3$), 531 (UCp'$_2$F) (the source of the fluorine originates from $N(CF_2CF_3)_3$ used in the calibration of the spectrometer).

X-ray Crystallography: Data for all compounds were collected using an Agilent Gemini Ultra diffractometer using with either an Enhance Ultra (Cu *Kα*) source, equipped with an Eos CCD area detector, operating in ω scanning mode to fill the Ewald sphere. All collections were carried out at 173 K. Control, integration and absorption correction were handled by the CrysAlis Pro software. The crystals were mounted on MiTiGen loops, from dried vacuum oil kept over 4Å in an MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX package and all software packages within.[3] All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. In the case of (**3**) a highly disordered molecule of crystallisation solvent (n-heptane) was located but could not be adequately modelled. This disorder was treated using the SQUEEZE routine in PLATON.[4] Crystal structure, data

collection and refinement details are given in the following table of this Supporting Information.

Compound	**3**	**4**
Colour, Habit	Brown-Red, Block	Light Brown, Plate
Size/mm	0.09 x 0.2 x 0.3	0.02 x 0.1 x 0.3
Empirical Formula	$C_{106}H_{156}O_6Si_{12}U_4$	$C_{50}H_{78}Si_6U_2.1/2C_4H_{12}Si$
M	2815.50	1427.94
Crystal System	Triclinic	Triclinic
Space Group	*P -1*	*P -1*
a/Å	12.6651(4)	9.0648(4)
b/Å	15.1115(5)	14.3955(7)
c/Å	19.1954(6)	25.3043(8)
α/°	101.395(3)	87.990(3)
β/°	104.401(3)	89.525(3)
γ /°	111.570(3)	72.969(4)
V/ Å^3	5910.4(8)	3155.3(2)
Z	1	2
μ/mm^{-1}	14.816	15.847
T (K)	173(2)	173(2)
θmin/max	3.85/67.075	3.710/67.078
Completeness	98.7 to 67.075	99.0 to 67.078
Reflections Total/Independent	11780/10282	11156/9792
R_{int}	0.0288	0.0517
Final *R1* and *wR2*	0.0271/0.0734	0.0463/0.1260
Goof	0.829	1.117
Larget peak hole/ e.Å^{-3}	0.8 and -1.2	1.702 and –2.034
ρ_{calc}/g.cm^{-3}	1.399	1.506

[1] M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.,* 2013, **135**, 13310.

[2] N. Tsoureas, J. C. Green, F. G. N. Cloke, H. Puschmann, S. M. Roe and G. Tizzard, *Chem. Sci.*, 2018, DOI: 10.1039/C8SC01127C

[3] L. J. Farrugia, *J. Appl. Cryst.,* 1999, **32**, 837.

[4] A. Spek, *J. Appl. Cryst.,* 2003, **36**, 7; P. van der Sluis and A. L. Spek, *Acta Cryst.,* 1990, **A46**, 194.