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Reductive Cyclotetramerization of CO to Squarate by a U(III) Complex: The X-ray Crystal Structure of $[(U\ (\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}C_5Me_4H)]_2(\mu\text{-}\eta^2\text{: }\eta^2\text{-}C_4O_4)$

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In the early 1970s, the squarate dianion $C_4O_4^{2-}$ was first synthesized directly from CO using electrochemical methods in polar aprotic solvents.[1,2] Now, more than 30 years later, we report that a uranium(III) complex will induce this reductive cyclotetramisation chemically to give the squarate moiety held between two uranium(IV) centers. The electrochemical route requires large overpressures (typically requires 100 bar, with increased efficiency at 350−400 bar), whereas we find that the chemical route described herein proceeds at room temperature and pressure. Reductive cyclooligomerization (or coupling) of CO under mild conditions is a potentially attractive route to more complex organic molecules from a cheap, renewable feedstock.[3] Indeed, simple derivatives of squaric acid and the squarate dianion are currently used extensively in medicinal and biological chemistry,[4,5] bioconjugate chemistry,[6] materials science,[7] dyes,[8] photochemistry,[9] and organic synthesis.[10−13]

We have recently discovered that the U(III) $COT^R/Cp^{R'}$ mixed-sandwich complex $[U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)((\eta\text{-}Cp^*)(THF)]$ induces efficient cyclotrimerisation of CO to give $[(U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)\text{-}(\eta\text{-}Cp^*)]_2(\mu\text{-}\eta^1\text{: }\eta^2\text{-}C_3O_3)$,[14] containing the deltate dianion, the first member of the series of cyclic, aromatic oxocarbons shown in Figure 1.[15]

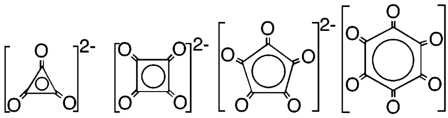
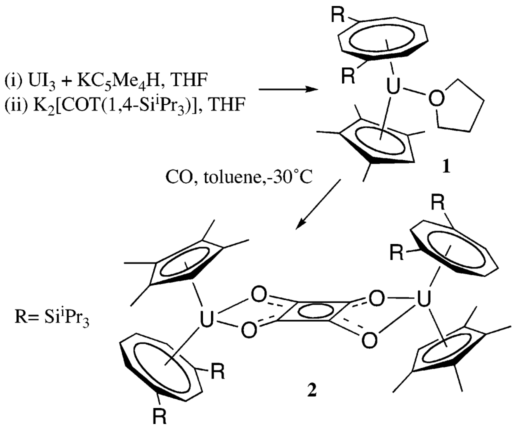


Figure 1. Oxocarbon dianions.

We envisaged that subtle variations in the steric and/or electronic properties of the starting $COT^R/Cp^{R'}$ uranium(III) complex might allow access to other members of this series. Here we present the synthesis of a new complex containing a slight modification of the ligand architecture of $[U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)(THF)]$, via replacement of the Cp* ligand with Cp^{Me_4H}, and its subsequent reaction with CO. The effect of even such a slight change in ligand environment has been previously noted for Cp^{Me_4H} vs Cp*, e.g., strikingly in zirconocene−dinitrogen systems, where the Cp^{Me_4H} ligand allows side-on binding and consequent hydrogenation of N_2 to occur, whereas Cp* prevents side-on binding;[16−19] disparities between Cp^{Me_4H} and Cp* are also evident in N_2 coordination by lanthanide(III) and uranium(III) tris(η-Cp^R) systems.[20−22] Specifically, in uranium chemistry, the bulkier $[U(\eta\text{-}Cp^*)_3]$ demonstrates higher reactivity than $[U(\eta\text{-}Cp^{Me_4H})_3]$, including sterically induced reductions,[23] end-on binding of N_2,[24] and ring opening of THF,[25] none of which have been reported for $[U(\eta\text{-}Cp^{Me_4H})_3]$;[22] however, both species are known to form well-defined carbonyl adducts.[26,27]

The complex $[U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^{Me_4H})(THF)]$ **1** was prepared as a dark-black crystalline material in moderate yield (41%), following a method similar to that used for the synthesis of $[U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)(THF)]$,[14] Scheme 1.[28]

Scheme 1. Synthesis of **1** and **2**



The structure of **1**[28] is found to be almost identical to that of $[U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)(THF)]$, with U-ring U−COT and U−Cp centroid distances of 1.977(5) and 2.506(6) Å, respectively, in **1**, vs 1.975(6) and 2.499(6) Å, respectively, in the latter.[14] The very long U−O(THF) bond of 2.737(4) Å in **1** is also comparable (within esd's) to that found (2.695(4) Å) in $[U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)\text{-}(Cp^*)(THF)]$.[14]

Exposure of a toluene solution of **1** to ambient pressures (1 bar) of CO at −30 °C gives the dimeric uranium(IV) squarate complex **2** (see Scheme 1) as a red crystalline solid, in 66% yield following recrystallization from a mixture of THF and Et_2O.[29] The X-ray structure of **2** has been determined and is shown in Figure 2, together with selected bond lengths and angles.[30]

The molecule has an inversion center at the midpoint of the C_4O_4 ring. The $C_4O_4^{2-}$ moiety is held between two U(IV) centers in a manner similar to that observed in the deltate complex, albeit bound symmetrically in an η^2:η^2 mode in **2**, with similar accompanying U−COT and U−Cp ring centroid distances.[14] The oxocarbon unit is found to be planar, as expected, with the two uranium centers displaced above (U) and below (U′) the plane by 0.429 Å−noticeably further than in the deltate system (which exhibits related displacements of 0.091 and 0.175 Å).[14]

Uranium−oxygen distances in the squarate complex **2** are the same within esd's as the η^2-bound portion of the deltate complex; however, crucially, the uranium−carbon distances are found to be considerably longer (average 3.045 Å in **2** versus 2.662 Å in the deltate analog).[14] The deltate unit in $[(U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]_2(\mu\text{-}\eta^1\text{: }\eta^2\text{-}C_3O_3)$ is stabilized with a C−C agostic interaction with the C_3 core and one U center,[14] with accompanying short U−C distances; thus, the bonding of the squarate unit in **2** appears to be consistent with a more “standard” bonding picture, without agostic

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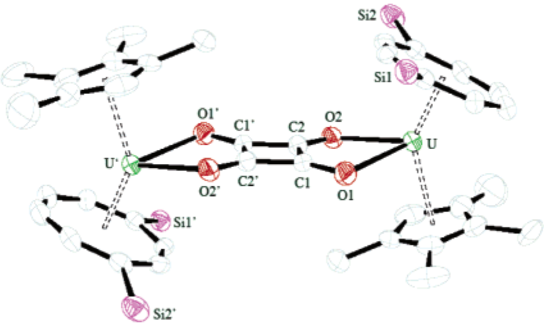

Figure 2. X-ray structure of **2** (isopropyl groups omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (deg): U−O1 2.471(6), U−O2 2.477(5), C1−O1 1.272(9), C2−O2 1.269(10), C1−C2 1.460(11), C1−C2′ 1.449(10), U−COT centroid 1.950(8), U−Cp centroid 2.480(8); O1−U−O2 74.8(2), C1−O1−U 104.4(5), C2−O2−U 103.9(5), O1−C1−C2 127.0(7), O2−C2−C1 128.0(7), C1′−C2−C1 89.6(6), C2′−C1−C2 90.4(6).

interactions. This is also apparent from the regular geometry of the squarate unit in **2**, which has no notable distortions from the structure reported for dipotassium squarate monohydrate.[31] To probe these structural observations, a DFT study was carried out.[28] The unsubstituted compound $[U(\eta\text{-COT})(\eta\text{-Cp})]_2(\mu\text{-}\eta^2\text{:}\ \eta^2\text{-}C_4O_4)]$ (**II**) was used as a model for compound **2** and a geometry optimization performed with the symmetry of the molecule constrained to C_i. In addition, a fragment analysis was conducted in which **II** was separated into two $U(\eta\text{-COT})(\eta\text{-Cp})$ fragments and a C_4O_4 fragment.

There was excellent agreement between the experimental and calculated bond distances and angles in **II**, demonstrating that DFT can predict the molecular structure of **2** accurately and that the level of modeling was appropriate.[28] The calculations indicate that each U is best described as having two electrons localized in 5f orbitals; thus, the U configuration is consistent with U(IV). The COT and Cp ligands bind to the U centers as expected, with the Cp ligands interacting primarily with the metal through a π interaction and the COT ligands with the metal through a δ interaction, and therefore, further discussion focuses on the bonding in the $U(C_4O_4)U$ core.

Fragment analysis indicates that four orbitals of the distorted squarate fragment have the most significant interaction with the two U containing fragments. The interaction between the two U centers and the HOMO, HOMO-3, and HOMO-4 of the $C_4O_4^{2-}$ ligand is straightforward and simply involves donation of electron density from the oxygen atoms of the squarate to the U atoms. All three of these orbitals have substantial O 2p character, with the O 2p orbitals lying in the squarate plane.[28] DFT predicts that the LUMO of the $C_4O_4^{2-}$ fragment, which is π in character, is partially occupied in **II** (0.17 electrons) as it mixes with one of the U 5f-based orbitals.

Gas-phase SCF energies indicate that **II** is approximately 127 kJ mol^{-1} more stable than the model compound $[U(\eta\text{-COT})(\eta\text{-Cp})]_2(\mu\text{-}\eta^1\text{:}\ \eta^1\text{-}C_4O_4)$ in which the squarate ligand is bound to each U center through only one oxygen atom, and given the preference for U to have high coordination numbers, this is not surprising. Overall, the bonding of the $C_4O_4^{2-}$ ligand to the two U centers in **II** is different from the bonding of the $C_3O_3^{2-}$ ligand in $[(U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-Cp*})]_2(\mu\text{-}\eta^1\text{:}\ \eta^2\text{-}C_3O_3)$. Presumably, the tighter O−C−C bond angles in the squarate ligand (average O−C−C in **2** is 127°) compared with the deltate ligand (average O−C−C is 159°) prevent a metal C−C agostic interaction from occurring in **2**, and bonding only occurs through the oxygen atoms of the ligand. Comparison of the gas-phase SCF energies of $[U(\eta\text{-COT})(\eta\text{-Cp})]_2\text{-}(\mu\text{-}\eta^1\text{:}\ \eta^2\text{-}C_3O_3)] + CO$ and **II** indicates that it is favorable by 136 kJ mol^{-1} for the fourth molecule of CO to bind to the deltate complex to form the squarate complex.

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Note Added after ASAP Publication. The incorrect ^1H NMR data were reported for $K_2COT^{1,4-Si^iPr_3}$ in the Supporting Information published with this paper ASAP on July 8, 2006. The Supporting Information PDF file was corrected on July 21, 2006.

Supporting Information Available: Experimental procedures, computational details, and X-ray data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Silvestri, G.; Gambino, S.; Filardo, G.; Guainazzi, M.; Ercoli, R. *Gazz. Chim. Ital.* **1972**, *102*, 818.
(2) Silvestri, G.; Gambino, S.; Filardo, G.; Spadaro, G.; Palmisano, L. *Electrochim. Acta* **1978**, *23*, 413.
(3) Wayland, B.; Fu, X. *Science* **2006**, *311*, 790.
(4) Xie, J.; Comeau, A. B.; Seto, C. T. *Org. Lett.* **2004**, *6*, 83.
(5) Terao, H.; Sugawara, T.; Kita, Y.; Sata, N.; Kaho, E.; Takeda, S. *J. Am. Chem. Soc.* **2001**, *123*, 10468.
(6) Aime, S.; Botta, M.; Crich, S. G.; Giovenzana, G.; Palnisana, G.; Sisti, M. *Bioconjugate Chem.* **1999**, *10*, 192.
(7) Ajayaghosch, A.; Eldo, J. *Org. Lett.* **2001**, *3*, 2595.
(8) Detty, M. R.; Henne, B. *Heterocycles* **1993**, *35* (2), 1149.
(9) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449.
(10) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053.
(11) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 4895.
(12) Paquette, L. A.; Sturino, C. F.; Doussot, P. *J. Am. Chem. Soc.* **1996**, *118*, 9456.
(13) Tomooka, C. S.; Liu, H.; Moore, H. W. *J. Org. Chem.* **1996**, *61*, 6009.
(14) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *Science* **2006**, *311*, 829.
(15) West, R. *Oxocarbons*, Academic Press New York 1980.
(16) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427* (6974), 527.
(17) Pool, J. A.; Bernskoetter, W. H.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14326.
(18) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229.
(19) Manriquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 3042.
(20) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 5517.
(21) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 6393.
(22) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Fagin, A. A.; Bochkarev, M. N. *Inorg. Chem.* **2005**, *44* (11), 3993.
(23) Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 240.
(24) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 14264.
(25) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 14264.
(26) Parry, J.; Carmona, E.; Coles, S.; Hursthouse, M. *J. Am. Chem. Soc.* **1995**, *117*, 2649.
(27) Evans, W. J.; Kozimor, S. A.; Nyce, W. J.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 13831.
(28) See Supporting Information
(29) Characterising data for **2**: Anal. Calcd. (found) for $C_{74}H_{122}O_4Si_4U_2$: C 53.44 (53.33), H 7.34 (7.40); ^1H NMR (d_8-THF, 293 K): δ ppm 6.21 (s, 12H, $CpMe_4H-CH_3$), 3.12 (s, 2H, $CpMe_4H-CH$), 1.16 (s, 12H, $CpMe_4H-CH_3$), −4.56 (d, 36H, $^iPr-CH_3$), 5.31 (m, 12H, ^iPr-CH), 6.63 (d, 36H, $^iPr-CH_3$), −14.62 (s, 4H, COT ring-CH), −81.02 (s, 4H, COT ring-CH), −85.90 (s, 4H, COT ring-CH);^{13}C NMR for **2**-^{13}CO (d_8-THF, 300 K, selected data): δ ppm −111.4 (s, $^{13}C_4O_4$); MS (EI): $m/z = 1663$ (20%, M+).
(30) Crystal data for **2.Et$_2$O**: Triclinic, FW 1738.26, in the space group P1 bar (No.2); $a = 10.9003(5)$ Å, $b = 13.6373(7)$ Å, $c = 15.7777(6)$ Å; $\alpha = 68.152(3)°$, $\beta = 74.018(3)°$, $\gamma = 73.408(2)°$; Z = 1. Final residual wR2(all data) = 0.142 (R = 0.073, with goodness of fit 1.042 on F2).
(31) Macintyre, W. M.; Werkema, M. S. *J. Chem. Phys.* **1964**, *40* (12), 3563.

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