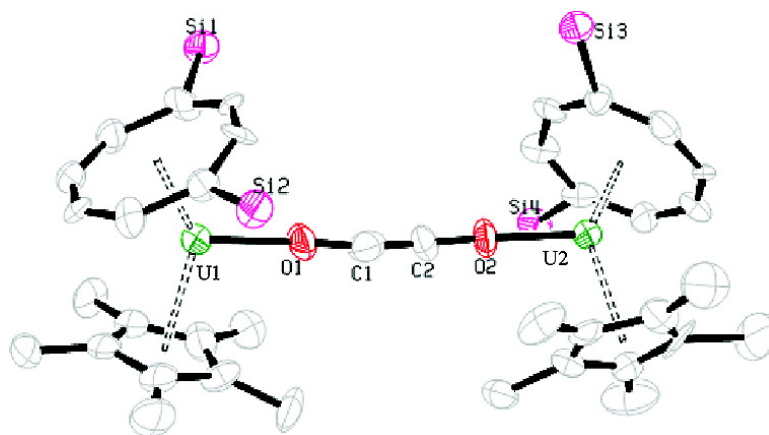


## Mechanistic Studies on the Reductive Cyclooligomerisation of CO by U(III) Mixed Sandwich Complexes; the Molecular Structure of $[(U(\eta\text{-CH}(\text{SiPr-1,4}))(\eta\text{-Cp}^*))(\mu\text{-}\eta\text{-}\eta\text{-CO})]$

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## Mechanistic Studies on the Reductive Cyclooligomerisation of CO by U(III) Mixed Sandwich Complexes; the Molecular Structure of $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2\text{O}_2)]$

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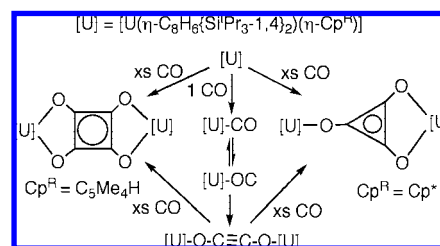
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We have recently reported the reductive cyclooligomerization of CO by the U(III) mixed-sandwich complexes  $[U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^R)(\text{THF})]$  ( $\text{Cp}^R = \text{Cp}^* \text{ or } \text{C}_5\text{Me}_4\text{H}$ ).<sup>1,2</sup> The resultant deltate and squarate complexes,  $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}_3\text{O}_3)]$  and  $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-C}_5\text{Me}_4\text{H}))_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_4\text{O}_4)]$ , are derivatives of the first two cyclic members of the oxocarbon dianions.<sup>3</sup> A potential mechanism for the U(III)-induced formation of the latter is shown in Scheme 1.

Initial formation of a U(III) monocarbonyl complex is followed by the generation of an equilibrium concentration of an isocarbonyl,<sup>4</sup> which then dimerizes to form the linear ynediolate complex (the first member of the oxocarbon series, alkali metal salts of which have been synthesized from CO and alkali metal solutions in liquid ammonia<sup>5</sup>). The electron rich triple bond in the ynediolate complex then adds further CO to form either the deltate or the squarate complex, possibly dictated by the level of steric congestion around the uranium centers, although, given their relative remoteness from the C≡C bond, this explanation seems unlikely and the mechanism in Scheme 1 thus does not obviously account for the high selectivity for deltate vs squarate. In this paper we describe studies on the stoichiometric reaction of CO with  $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2]$ , resulting in the formation of a linear diuranium ynediolate complex which does not react with further CO to give the deltate derivative. Further spectroscopic and computational studies suggest a plausible mechanism for the formation of the deltate complex, in which a “zig-zag” diuranium ynediolate species is the key intermediate.

$[U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*)]$  in *d*<sub>8</sub>-toluene was treated with 0.9 equiv of <sup>13</sup>CO in an NMR tube at −78 °C, followed by thorough mixing and warm-up to room temperature.<sup>6</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the resultant solution revealed the formation of a new <sup>13</sup>C-containing product **1-<sup>13</sup>C**, characterized by a single resonance at δ 313 ppm, together with small amounts (ca. 20%) of the deltate complex  $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}^{13}\text{C}_3\text{O}_3)]$ . Pure **1-<sup>13</sup>C** could be separated from the deltate impurity by fractional crystallization from diethyl ether, although X-ray quality crystals of **1-<sup>13</sup>C** could not be obtained from this or indeed other common solvents. **1-<sup>13</sup>C** displays a strong molecular ion peak at 1637 amu in the mass spectrum, with the correct isotopic distribution, for  $[U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2(^{13}\text{CO})_2$ .<sup>7</sup> The presence of a C–C bond in the (<sup>13</sup>CO)<sub>2</sub> unit in the latter was confirmed by treating  $[U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*)]$  with a 50/50 mixture of <sup>13</sup>CO/<sup>12</sup>CO; the latter resulted in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shown in Figure 1, in which a secondary isotopic shift of 0.18 ppm for the <sup>13</sup>CO/<sup>12</sup>CO isotopomers is clearly evident.

**Scheme 1.** Discounted Mechanism for Oxocarbon Formation



Eventually, crystals of **1-<sup>13</sup>C** suitable for X-ray studies were grown from *tert*-butylmethyl ether at −50 °C, and the structure is shown in Figure 2, together with selected bond lengths and angles.<sup>8</sup> The structure reveals an essentially linear ynediolate ligand bridging two  $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2]$  units. The extremely short C–C distance of 1.177(12) Å in the C<sub>2</sub>O<sub>2</sub> moiety is consistent with a triple bond and comparable to that found in NaOCCONa (1.19 ± 0.3 Å), as determined by powder X-ray diffraction.<sup>9</sup> Reductive coupling of CO to form  $\eta^2$ -coordinated ethyne diol has been reported by Lippard,<sup>10</sup> and Wayland has described CO coupling at rhodium to form a 1,2-ethanedionyl complex,<sup>11</sup> but **1** represents the first organometallic example of CO reductive coupling to form ethyne diolate.

<sup>13</sup>C{<sup>1</sup>H} NMR studies in *d*<sub>8</sub>-toluene showed that **1-<sup>13</sup>C** does not react with excess <sup>13</sup>CO to give  $[(U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*))_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}^{13}\text{C}_3\text{O}_3)]$ , even after heating at 60 °C for 3 days, implying a different mechanism to that suggested in Scheme 1.  $[U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*)]$  in *d*<sub>8</sub>-toluene was treated with 1 equiv of <sup>12</sup>CO at −78 °C in NMR tube, the solution was rapidly transferred to a high-integrity solution IR cell in the glovebox, and an IR spectrum was recorded immediately at room temperature. The latter exhibited a strong absorption at 1920 cm<sup>−1</sup>, in the range 1880–1976 cm<sup>−1</sup> associated with previously reported U(III) monocarbonyls;<sup>12</sup> this band shifts to 1882 cm<sup>−1</sup> for the <sup>13</sup>CO analogue, within 4 cm<sup>−1</sup> of the theoretical value (1878 cm<sup>−1</sup>),<sup>13</sup> so we conclude that the initial step in the formation of **1** is the generation of  $[U(\eta\text{-C}_8\text{H}_6\{\text{Si}^i\text{Pr}_3\text{-1,4}\}_2)(\eta\text{-Cp}^*)(\text{CO})]$ . The CO absorption associated with the latter decayed quite rapidly (ca. 15 min) at room temperature, although examination of the IR spectra revealed no obvious, assignable product(s). This is a significantly shorter time scale than that associated with the appearance of **1** (hours by NMR) under the same conditions, suggesting the existence of a relatively long-lived intermediate. To gain further insight into the mechanism of formation of **1**, a DFT computational study was carried out.

For computational expediency, all ring substituents were replaced by hydrogen atoms. Geometry optimizations, transition state

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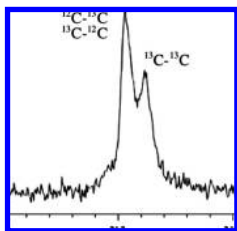


Figure 1. Secondary isotopic shift;  $\Delta\delta = 0.18$  ppm, 18 Hz.

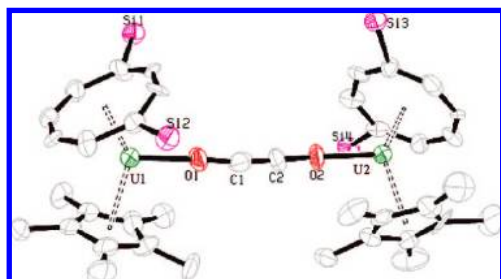


Figure 2. X-ray structure of **I** (isopropyl groups and hydrogens omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.177(12), U(1)–O(1) 2.124(6), U(2)–O(2) 2.141(6), O(1)–C(1) 1.302(10), O(2)–C(2) 1.291(10); C(1)–O(1)–U(1) 178.3(7), C(2)–O(2)–U(2) 175.9(6), C(2)–C(1)–O(1) 176.3(10), C(1)–C(2)–O(2) 179.0(11).

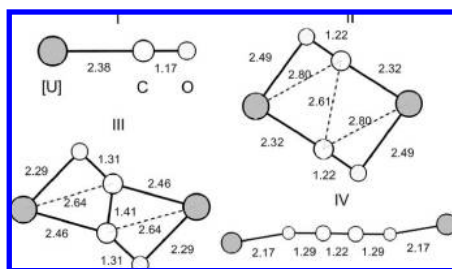


Figure 3. Calculated dimensions (Å) for the UCO units in **I–IV**.

Table 1. Spin States, Relative Energies, and CO Vibrations for **I–IV**, Calculated for CO 2108  $\text{cm}^{-1}$ <sup>a</sup>

	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>
<i>S</i>	3/2	2	2	2
<i>E</i> /kJ mol <sup>-1</sup>	0	-30	-47	-5
<i>v</i> /cm <sup>-1</sup>	1865	1544	1292	1381

<sup>a</sup> Energies from spin-orbit calculations are given in the ESI.

optimizations and frequency calculations were carried out using the ADF program suite ADF2007.01.<sup>6</sup> Four minima were identified on a possible reaction pathway forming a ynediolate, **IV**, from a monomeric carbonyl [U( $\eta$ -Cot)( $\eta$ -Cp)CO], **I**. The structures of the (UCO)<sub>n</sub> units are shown in Figure 3.

The carbonyl **I** forms a dimer, **II**, in which the CO oxygens coordinate to opposing U atoms, and the C–C distance is 2.61 Å. Carbon–carbon bond formation then occurs to form a C<sub>2</sub>O<sub>2</sub> unit with a zig-zag structure, **III**, in which the C–C distance shortens to 1.41 Å and C–U bonding is retained. The transition state connecting **II** to **III** lies 9 kJ mol<sup>-1</sup> above **II** suggesting rapid

formation from the dimer **II**. The ynediolate, **I**, is modeled by **IV**, which has dimensions of the central UOCCOU unit close to those found by X-ray diffraction. The transition state between **III** and **IV** lies 59 kJ mol<sup>-1</sup> above **III** consistent with its formation at a slower rate than the disappearance of **I** (imaginary modes for the transition states are given in the ESI). The calculated frequencies for **I–IV** (Table 1) indicate that only the monomer would show an identifiable CO IR band in the region >1800  $\text{cm}^{-1}$ .

Structure **I** has three unpaired electrons. One is confined to a localized f orbital while the other two have partial f and partial CO  $\pi^*$  character. Formation of the dimer, **II**, brings the two CO carbons into close proximity, aligning the  $\pi^*$  orbitals poised for C–C bond formation. We propose that **III** is the relatively long-lived intermediate which has the potential to react further with CO to form the delatate and squarate complexes. In the absence of further reagent, the U–C bonds break, the OCCO unit unfolds, and the ynediolate, **IV**, is formed. The gas phase energetics (Table 1) give **IV** a higher energy than **III** suggesting that **III** should be the stable product. However the calculations neglect the bulky substituents present on all rings, which would be expected to destabilize **III** relative to **IV**. In support of this thesis, the substituents are known to affect the course of subsequent reaction. Also the more open coordination sphere of **IV** may lead to additional stabilization by solvation.

In conclusion, the role of the actinide in the initial C–C bond formation is not only to reduce the bound CO but also to act as a Lewis acid binding an additional CO oxygen, and thus aligning the two CO groups in a favorable orientation for the C–C bond forming process.

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

## References

- (1) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *Science* **2006**, *311* (5762), 829.
- (2) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *J. Am. Chem. Soc.* **2006**, *128* (30), 9602.
- (3) West, R. *Oxocarbons*; Academic Press: New York, 1980.
- (4) Maron, L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2002**, *124* (20), 5614.
- (5) Buchner, W.; Weiss, E. *Helv. Chim. Acta* **1964**, *47*, 1415.
- (6) See ESI for full experimental and computational details.
- (7) Characterising data for 1–13C: Anal. Calcd (found) for (<sup>13</sup>C)<sub>2</sub>C<sub>72</sub>-H<sub>126</sub>O<sub>2</sub>Si<sub>4</sub>U<sub>2</sub>: <sup>13</sup>C and C 54.38 (54.10), H 7.75 (8.01); <sup>1</sup>H NMR (*d*<sub>6</sub>-benzene, 303 K):  $\delta$  ppm 55.0 (s, 4H, COT ring-CH), 3.95 (s, 30H, Cp\*-CH<sub>3</sub>), -3.22 (36H, d, *i*Pr-CH<sub>3</sub>), -9.77 (36H, d, *i*Pr-CH<sub>3</sub>), -11.84 (12H, m, br, *i*Pr-CH), -32.8 (s, 4H, COT ring-CH), -54.1 (s, 4H, COT ring-CH); <sup>13</sup>C NMR (*d*<sub>6</sub>-benzene, 303 K, selected data):  $\delta$  ppm 314.2 (s, br, <sup>13</sup>C<sub>2</sub>O<sub>2</sub>); <sup>29</sup>Si NMR (*d*<sub>8</sub>-toluene, 303 K, selected data):  $\delta$  ppm -114.8; MS (EI): *m/z* = 1663 (20%, M<sup>+</sup>).
- (8) Crystal data for 1-<sup>13</sup>C·2(*t*BuOMe): Orthorhombic, FW 1812.46, in the space group *Pbca* (No. 61); *a* = 14.4419(2), *b* = 24.1793(3), *c* = 51.1378(7) Å;  $\alpha = \beta = \gamma = 90^\circ$ ; *Z* = 8. Final residual *wR*<sub>2</sub> (all data) = 0.130 (*R* = 0.078, with goodness of fit 1.306 on *F*<sup>2</sup>).
- (9) Weiss, E.; Buchner, W. *Chem. Ber.* **1965**, *98* (1), 126.
- (10) Vrtil, R. N.; Rao, C. P.; Bott, S. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110* (22), 7564.
- (11) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* **1988**, *110* (18), 6063.
- (12) Conejo, M. d. M.; et al. *Chem. Eur. J.* **1999**, *5* (10), 3000.
- (13) Timney, J. A. Transition Metal Carbonyls: Infrared Spectra. In *Encyclopedia of Inorganic Chemistry*; Crabtree, R. H., Ed.; Wiley: 2008.

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