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U^{III}-Induced Reductive Co-Coupling of NO and CO to Form U^{IV} Cyanate and Oxo Derivates

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There is considerable current interest in the ability of U^{III} centres to bind a variety of small molecules, for example, CO, CO_2 and N_2.[1] We have recently reported the reductive cyclooligomerisation of CO by the U^{III} mixed sandwich complexes $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^R)(thf)]$ ($Cp^R = Cp^*$ or C_5Me_4H) to form the deltate and squarate complexes, $[\{(U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_3O_3)]$[2] and $[\{(U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}C_5Me_4H)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4O_4)]$,[3] and the stoichiometric dimerisation of CO to afford the linear yne diolate complex $[\{(U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}C_5Me_4H)\}_2(\mu\text{-}C_2O_2)]$.[4] To the best of our knowledge there are no fully substantiated f-element nitrosyl complexes, so we were interested to explore the reactivity of $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ towards NO, and the U^{IV} species $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)NO]$ seemed to us to be a very real possibility.

Treatment of a toluene solution of $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ with 1 equivalent of high-purity NO (prepared from $NOHSO_4$ and Hg[5]) at −80°C and slow warming to room temperature resulted in a colour change of the original green-black solution to red-brown, characteristic of U^{IV} in these mixed sandwich complexes.[2–4] To date, however, we have been unable to isolate any tractable product from this reaction. Because we have already established that the "zig-zag" form (Figure 1 a) of the linear yne diolate is the key intermediate in the cyclooligomerisation of CO by $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^R)(thf)]$,[4] the somewhat related derivative of hyponitrous acid (Figure 1 b) may be a possible intermediate/unstable product in the NO reaction.

We reasoned that addition of NO to the zig-zag complex (Figure 1 a) or addition of CO to the putative hyponitrite complex (Figure 1 b) might afford a nitrogen-containing oxocarbon (Figure 1 c). The latter have been the subject of theoretical studies, but not yet isolated.[6] Accordingly, we sought to prepare the $N_2CO_3^{2-}$ uranium complex (Figure 1 c) as an analogue of the deltate complex.[2] A solution of $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ in $[D_8]$toluene was treated with 1 equivalent of NO at −80°C, followed by the addition of 0.5 equivalent of ^{13}CO, and the solution was then allowed to warm to room temperature. ^1H NMR analysis of the reaction mixture showed the presence of two new major products, and ^{13}C NMR studies showed the presence of a new quaternary carbon resonance at $\delta = 249$ ppm. Two new compounds were isolated from the reaction mixture, which the data (see below) show to be the bridging cyanate complex **1** and the bridging oxo complex **2** (see Scheme 1).

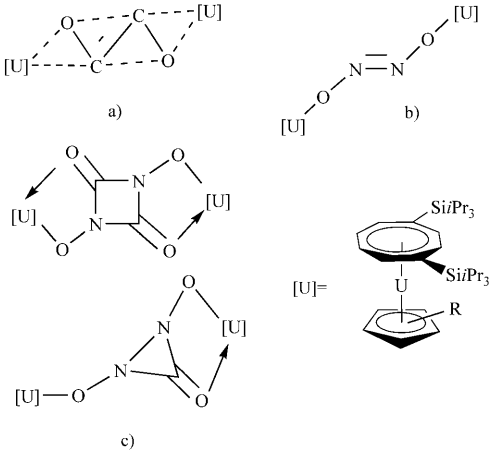

Figure 1. a) The zig-zag intermediate, b) a possible NO intermediate, c) potential nitrogen-containing oxocarbons.

Crystals of **1** suitable for X-ray diffraction were obtained from a concentrated toluene solution at 4°C, and the structure is shown in Figure 2. The structure shows a binuclear complex located on an inversion centre, in which two $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ units are bridged by two three-atom ligands. The latter three atoms were initially assigned to the nitrogen, oxygen and carbon (the central atom) of a

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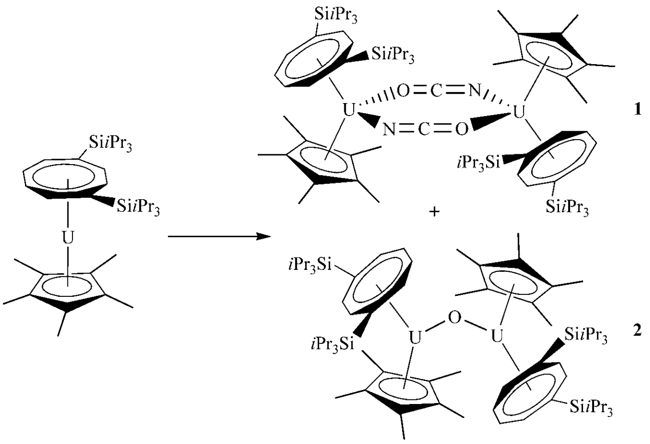

Scheme 1. Reaction of [U(η-C_8H_6{Si*i*Pr_3-1,4}$_2$)(η-Cp*)] with NO and CO in toluene.

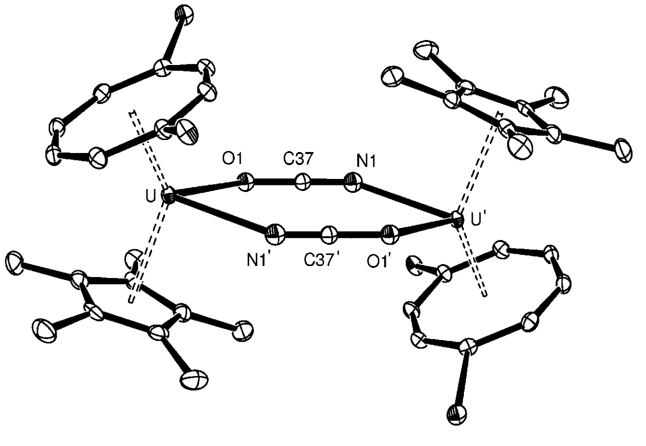

Figure 2. The X-ray structure of **1** (thermal ellipsoids at 30 %, hydrogen atoms and isopropyl groups have been removed for clarity).

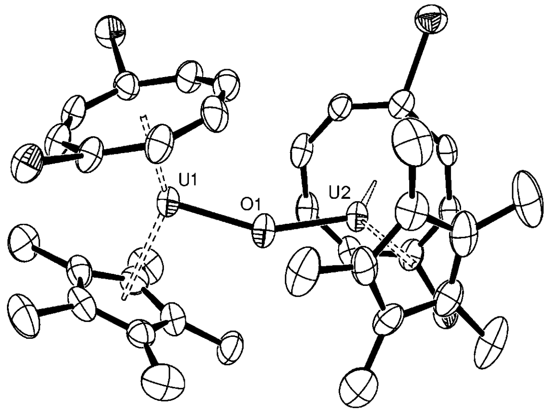

Figure 3. The X-ray structure of **2** (thermal ellipsoids at 50 %, hydrogen atoms and isopropyl groups have been removed for clarity). Selected bond lengths and angles: U1–O1 2.113(5), U2–O1 2.105(6), U1–M3 1.993(9), U1–M4 2.501(9), U2–M1 2.003(9), U2–M2 2.520(9) Å; U1-O1-U2 154.5(3), M3-U1-M4 140.7(3), M1-U2-M2 139.6(3)°. M1, M2, M3 and M4 are the centroids of the U2–COT ring, the U2–Cp ring, the U1–COT ring and the U1–Cp ring, respectively.

linear NCO unit, based on their relative electron densities. However, the data indicated disorder in the nitrogen and oxygen positions, precluding meaningful analysis of bond lengths and angles in the bridging cyanate units. Similar disorder issues were found for the bridging cyanate ligands in [$(Me_2Al(\mu\text{-}OSiMe_3)_2Mg(thf)_2(\mu\text{-}OCN)]_3$.[7] Other data (see the Experimental Section) support the assignment of the three atom bridges in **1** as NCO ligands: a new quaternary carbon (derived from ^{13}CO) resonance at $\delta = 249$ ppm in the ^{13}C NMR, the microanalytical data, and a parent ion in the mass spectrum for the monomer [U(η-C_8H_6{Si*i*Pr_3-1,4}$_2$)(η-Cp*)(NCO)]. The alternative CNO, fulminate linkage seems unlikely on the basis that it would involve cleavage of the CO bond in preference to the (weaker) NO bond.

X-ray quality crystals of the second major product of the reaction, the bridging oxo complex **2** formally arising from oxygen abstraction from NO (see above), were obtained from *tert*-butyl methyl ether and the structure is shown in Figure 3, together with selected bond lengths and angles. The single-atom, μ-oxo bridge between the two uranium centres leads to a high degree of steric congestion in **2**, resulting in some unusual structural features compared with other dimeric complexes that incorporate the [U(η-C_8H_6{Si*i*Pr_3-1,4}$_2$)(η-Cp*)] unit: the planes defined by the M1-U2-M2 and M3-U1-M4 vectors in **2** are essentially orthogonal (89.07(2)°) as opposed to **1** and the oxocarbon derivatives in which they are co-planar;[2–4] similarly, the silyl substituents on the C_8 rings point away from the bridging atom in **2**. Nonetheless, the structural parameters of the individual bent [U(η-C_8H_6{Si*i*Pr_3-1,4}$_2$)(η-Cp*)] units in **2** are essentially unperturbed: the ring centroid-U-ring centroid angles M1-U2-M2 139.6(3)° and M3-U1-M4 140.7(3)°, as well as the U-ring centroid distances U1–M3 1.993(9) Å, U1–M4 2.501(9) Å, U2–M1 2.003(9) Å and U2–M2 2.520(9) Å, are all comparable within the esds (esd = estimated standard deviation) to those found in the oxo–carbon derivatives.[2–4]

However, the μ-oxo bridge in **2** is significantly bent (U1-O1-U2 154.5(3)°), in marked contrast to the less sterically congested tris-cyclopentadienyl derivatives [{U(η-$C_5H_5)_3\}_2$(μ-O)][8] and [{U(η-$C_5H_4SiMe_3)_3\}_2$(μ-O)],[9] which display the expected linear U-O-U geometry. Nonetheless, the U–O distances in **2** (U1–O1 2.113(5), U2–O1 2.105(6) Å) are only marginally longer than that in [{U(η-$C_5H_5)_3\}_2$(μ-O)][8] (2.0881(4) Å) and essentially identical within the esds to that in [{U(η-$C_5H_4SiMe_3)_3\}_2$(μ-O)][9] (2.1052(2) Å).

The structural complexity of **2** also persists in solution: the twelve COT (COT = cyclooctatetraene) ring protons typically appear as three sets of four proton signals in the ^{1}H NMR solution spectra of **1** and the oxocarbon derivatives,[2–4] whereas in **2** six sets of two proton signals are evident, consistent with the lack of an inversion centre in the latter.

The catalytic conversion of CO and NO to N_2 and CO_2 is of course well established, for example, in automobile catalytic converters, although the formation of surface-bound NCO species from CO and NO has been observed to occur in reduced Ir/Al_2O_3 systems at temperatures below 200°C.[10] The high oxophilicity of uranium and the reducing power of U^{III} (organometallic U^{IV}/U^{III} redox couples typically lie in the range lie in the range −1.826 to −2.41 V vs. $Fc^{0/+1}$)[11] are likely to be responsible for the proposed de-oxygenation of NO to form the oxo complex **2**. This also suggests the possible intermediacy of a terminal uranium nitride species, which then reacts with CO to form **1**, and further studies on the mechanism of formation of **1** and **2** are in progress.

Experimental Section

Synthesis of [{U(η-C_8H_6\{Si*i*Pr_3-1,4\}$_2$)(η-Cp*)}$_2$(μ-OCN)$_2$] (1): A sample of black, crystalline [U(η-C_8H_6\{Si*i*Pr_3-1,4\}$_2$)(η-Cp*)(thf)] (100 mg, 1.16×10^{-4} mol) was placed in an ampoule (high-vacuum PTFE stopcock, 45 mL volume) and heated under vacuum (110°C, 1×10^{-5} mbar) for 1 h. The desolvated material was dissolved in [D_8]toluene (1.0 mL). The solution was cooled to −78°C, the headspace evacuated and NO (0.058 bar, 1.16×10^{-4} mol) was admitted, followed by ^{13}CO (0.03 bar, 0.58×10^{-4} mol). The flask was warmed to ambient temperature resulting in a change in colour to red-brown. Cooling to 4°C for 1 week gave the product as black crystals (the supernatant was kept aside for isolation of the second reaction product.) The product was rinsed with pentane (2 mL) at −78°C and dried in vacuo to afford the title compound as black prisms suitable for single-crystal X-ray diffraction. Yield: ≈25 mg; ^1H NMR ($C_6D_5CD_3$, 303 K): $\delta=52.3$ (s, 4H; COT ring-C*H*), 6.84 (brs, 30H; Cp*-C*H*$_3$), −7.45 (brs, 36H; *i*Pr-C*H*$_3$), −8.75 (brs, 12H; *i*Pr-C*H*), −9.26 (brs, 36H; *i*Pr-C*H*$_3$), −54.3 (s, 4H; COT ring-C*H*), −91.6 ppm (s, 4H; COT ring-C*H*); ^{13}C NMR ($C_6D_5CD_3$, 303 K, selected data): $\delta=249.3$ ppm; IR (Nujol): $\tilde{\nu}=2157$ s, 2197 cm^{-1} m ($O^{13}CN$); EIMS: *m*/*z* (%): 833 (100) [(η-C_8H_6\{Si*i*Pr_3-1,4\}$_2$)(η-Cp*)U($O^{13}CN$)]$^+$; elemental analysis calcd (%) for $^{13}C_2C_{72}H_{126}N_2O_2Si_4U_2$: ^{13}C and C 53.46, H 7.62, N 1.68; found: ^{13}C and C 53.27, H 7.57, N 1.83.

Synthesis of [{U(η-C_8H_6\{Si*i*Pr_3-1,4\}$_2$)(η-Cp*)}$_2$(μ-O)] (2): The supernatant from the crystallisation of complex **1** was reduced to dryness in vacuo. The solid mass was taken up in *t*BuOMe (1 mL) and kept at 4°C overnight. A small crop of red-brown crystals suitable for single-crystal X-ray diffraction were separated from the mother liquor and washed with *t*BuOMe (2 mL) at −78°C. Drying in vacuo gave the title compound. Yield: ≈15 mg; ^1H NMR ($C_6D_5CD_3$, 303 K): $\delta=119$ (s, 2H; COT ring-C*H*), 113 (s, 2H; COT ring-C*H*), 6.94 (d, 18H; *i*Pr-C*H*$_3$), 6.45–6.62 (brm, 6H; *i*Pr-C*H*), 3.30 (brs, 30H; Cp*-C*H*$_3$), 0.74 (d, 18H; *i*Pr-C*H*$_3$), −0.59 (d, 18H; *i*Pr-C*H*$_3$), −2.32–−2.48 (brm,6H; *i*Pr-C*H*), −7.37 (d, 18H; *i*Pr-C*H*$_3$), −81.4 (s, 2H; COT ring-C*H*), −85.9 (s, 2H; COT ring-C*H*), −111 (s, 2H; COT ring-C*H*), −116 ppm (s, 2H; COT ring-C*H*); EIMS: *m*/*z* (%): 808 (10) [(η-C_8H_6\{Si*i*Pr_3-1,4\}$_2$)(η-Cp*)U(O)]$^+$.

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