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VIP CO Reduction to Methoxide

Facile Conversion of CO/H_2 into Methoxide at a Uranium(III) Center[**]

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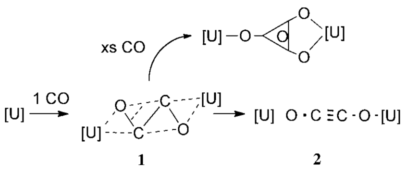
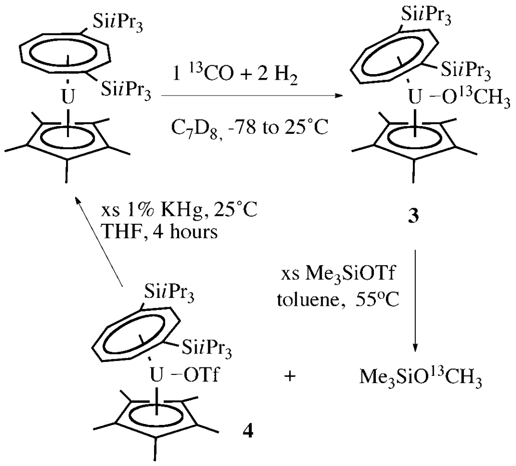
The long-established Fischer–Tropsch process[1] is employed on a very large scale to effect the conversion of synthesis gas (CO/H_2) to hydrocarbons and oxygenates, and continues to attract considerable interest.[2] The C–C coupling reactions implicit in the latter have been extensively modeled using molecular organometallic systems,[3] for example, the formation of enediolate complexes[4] and ethene[5] from reactions of early-transition-metal or f-block hydrides with CO. In 2006, we reported a novel CO-coupling reaction not previously observed in Fischer–Tropsch processes, namely the reductive cyclotrimerization of CO by the U^{III} complex $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ to afford the deltate complex $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_3O_3)$.[6] Subsequent computational studies indicated that this reaction proceeds through a proposed "zig-zag" C_2O_2 intermediate **1**, see Scheme 1: in the presence of excess (xs) CO the latter adds a further molecule of CO to form a deltate structure, whereas in the absence of further CO the zig-zag intermediate slowly ($\Delta G^{\neq}_{\text{calc}} = 60\ \text{kJ mol}^{-1}$) transforms to the (isolated) linear yne diolate complex $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2O_2)$ **2**, see Scheme 1.[7]



Scheme 1. Mechanism of the reductive cyclotrimerization of CO (xs = excess) by $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$.

In the particular context of the Fischer–Tropsch conversion of CO/H_2 to oxygenates, such as ethylene glycol, we were interested to explore the reactivity of the C–C triple bond in **2** towards dihydrogen with a view to synthesizing the derived ethene or ethane diolate complexes. However, exposure of **2** in $[D_8]$toluene to excess dihydrogen (10 bar) did not result in discernible reaction monitored by ^1H and ^{13}C NMR spectroscopy, even after prolonged heating (60 °C, 3 days) and UV irradiation; a similar lack of reactivity towards dihydrogen has been noted for the related yne diolate complex $[U(N\{SiMe_3\}_2)_3]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2O_2)$.[8] Instead, we turned our attention to the potential functionalization of the C_2 unit in **2** through reaction of $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ with ^{13}CO in the presence of H_2. Accordingly, $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ in $[D_8]$toluene at −78 °C was treated with one equivalent of ^{13}CO followed by two equivalents of H_2, with subsequent mixing and warming to room temperature. The ^{13}C NMR spectrum of the resultant solution revealed the formation of an essentially sole ^{13}C-containing product **3**, characterized by a single quartet resonance at $\delta = 319$ ppm, with $J_{CH} = 137$ Hz. Microanalytical, mass spectral and ^1H NMR data were consistent with the formulation of **3** as the U^{IV} methoxide complex $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)OMe]$, that is, the result of hydrogenation of CO at subambient to ambient temperatures and pressures (see Scheme 2).



Scheme 2. Complex **3** as result of hydrogenation of CO. Complex **4** is reduced back to the U^{III} starting complex with potassium amalgam.

Slow cooling of a toluene solution from 3 to −50 °C gave red-brown crystals suitable for single-crystal X-ray diffraction studies, and the structure is shown in Figure 1, together with selected bond lengths and angles.[9]

The structure shows the anticipated bent sandwich unit, with a terminal methoxide group. The distances between the metal and the ring centroids in the $U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)$ fragment (U–M1 2.4887(2) and U–M2 1.95590(2) Å) are identical within the estimated standard deviations (esds) to those for other U^{IV} complexes incorporating this fragment, for example, $[U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_3O_3)$ (U–M1 2.480(8) and U–M2 1.950(8) Å), although the M1–U–

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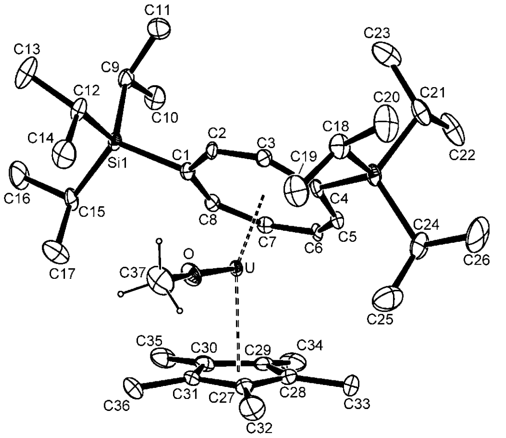

Figure 1. X-ray structure of **3** (thermal ellipsoids at 30%, hydrogens of the OMe group shown, all others removed for clarity). Selected bond lengths and angles: U–M1 2.4887(2), U–M2 1.95590(2), U–O 2.058(4) Å; C37–O–U 178.3(5), M1–U–M2 135.809(9)°. M1 and M2 are the centroids of the five- and eight-membered rings, respectively.

M2 angle in **3** (135.809(9)°) is slightly more acute than that in the latter (141.8(2)°).[6] The U–OMe linkage in **3** is essentially linear (178.3(5)°) with a U–O distance of 2.058(4) Å, and the structural features are comparable to those found in other (rare) examples of U^{IV} terminal methoxide complexes.[10]

To gain insight into the bonding situation in **3**, computational studies were carried out at the DFT (B3PW91/SDD-(U,Si)-6-31G(d,p)(C,O,H)) level. The optimized structure is in excellent agreement with the experimental one (see the Supporting Information) indicating that the method is suitable for the description of **3**. In particular, the metal–centroid distances are nicely reproduced (U–M1 2.486 and U–M2 1.958 Å) as well as the M1–U–M2 angle (136.3°). The U–OMe distance is also perfectly reproduced (2.055 Å) as well as the linearity (U–O–C angle of 178.9°). The bonding in complex **3** has been studied using MO and NBO analyses. Both methods indicate a double bond between U and O (see Figure 2 for the occupied MOs), strongly polarized towards oxygen. At the NBO level, the polarization is highlighted since the two bonds are only defined at the second-order donor–acceptor level (donation from a σ lone-pair orbital of the oxygen into an empty d orbital, 123 kcal mol^{-1}, as well as a donation from a π lone-pair orbital of the oxygen into an empty d orbital, 69 kcal mol^{-1}). The Wiberg bond index of 1.35 is also consistent with some double-bond character. This situation is rather unique since, for example, the U−O bond in Cp''_2UO ($Cp'' = C_5H_2tBu_3$) was reported to only exhibit single-bond character.[11] The Gibbs free-energy of formation of complex **3** is computed to be −76.6 kcal mol^{-1} with respect to the CO adduct (i.e. $2[U]\text{-}CO + 3H_2 \rightarrow 2[U]\text{-}OMe$, where $[U] = [U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$), in excellent agreement with the experimental observation.

Figure 2. Bonding situation in **3**. Occupied molecular orbitals of the U–OMe bond.

Whilst we have been unsuccessful in liberating methanol from **3** (e.g. by treatment with stoichiometric HCl or HOTf), the OMe group may be smoothly converted into Me_3SiOMe by treatment of **3** with Me_3SiOTf with concomitant formation of the U^{IV} triflate complex $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)OTf]$ **4** (see Scheme 2). Complex **4** can be reduced back to the U^{III} starting complex $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ with potassium amalgam in THF at a conversion of >60% as determined by ^{1}H NMR spectroscopy—the final step in a hypothetical U^{III}-mediated cycle which converts $CO + H_2 + Me_3SiOTf$ to Me_3SiOMe (see Scheme 2).

The conversion of CO/H_2 to methanol (and higher alcohols) is an industrially important process carried out on a Cu/ZnO heterogeneous catalyst and has been extensively investigated.[12] The reactions of CO with organometallic hydride complexes have also been studied, as potential models for key steps in the heterogeneous reaction. Early work by Bercaw and co-workers showed that the hydrogenation of a metal-bound CO ligand in $[Zr(\eta\text{-}Cp^*)_2(CO)_2]$ at 110 °C to afford the methoxide complex $[Zr(\eta\text{-}Cp^*)_2(OMe)(H)]$ proceeds through the hydride complex $[Zr(\eta\text{-}Cp^*)_2(H)_2CO]$.[13] More recently, Andersen and co-workers have shown that $[Ce(\eta\text{-}C_5H_2tBu_3)_2H]$ will effect the conversion of CO/H_2 to methoxide, forming $[Ce(\eta\text{-}C_5H_2tBu_3)_2OMe]$, under relatively mild conditions, through a formyl intermediate.[14] This immediately raises the question as to whether the formation of **3** proceeds through a U^{IV} hydride species, that is, $U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)H$. However, exposure of a $[D_8]$toluene solution of $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ to excess dihydrogen at 1 bar did not reveal evidence for formation of a hydride and there was no change in the ^{1}H NMR spectrum of the starting material. Complex $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]$ in $[D_8]$toluene was then reacted with one equivalent of ^{13}CO at −78 °C, allowed to warm briefly (1 min) to 20 °C and then recooled to −78 °C; at this point there is only a trace amount of yne diolate **2** monitored by ^{13}C NMR spectroscopy, and under these conditions the proposed, relatively long-lived zig-zag intermediate **1** (see Scheme 1) is likely to be the dominant species in solution.[7] Exposure of this solution to dihydrogen also results in the formation of the methoxide **3** as essentially the only ^{13}CO-derived product. Thus, we suggest that **3** may arise from hydrogenation of the zig-zag intermediate **1**, as opposed to classical hydride reduction of bound CO. Detailed experimental and computational mechanistic studies on the formation of **3** are underway and will be reported in due course.

Experimental Section

Synthesis of **3**: Complex $[U(\eta\text{-}C_8H_6\{SiiPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)THF]$ (500 mg, 0.574 mmol) was heated under vacuum (45 min, 100 °C, 1×10^{-6} mbar) to remove coordinated tetrahydrofuran (THF). The desolvated solid was dissolved in toluene (1 mL) to give a black solution, and the ampoule was cooled to −78 °C and attached to a Toepler pump equipped with a gas-addition line. To the cold degassed solution was added ^{13}CO (0.574 mmol) followed by H_2 (1.15 mmol, two equivalents per U); the reaction flask was then sealed and allowed to warm to room temperature overnight. The resulting red-brown solution was then stripped of solvent to provide the title compound as a brown powder (405 mg, 86 %). An analytically pure sample, and crystals suitable for X-ray diffraction, were obtained by slow cooling of a pentane or toluene solution of **3** to −50 °C. ^{13}C NMR (100 MHz, $[D_8]$toluene, 303 K, selected data): $\delta = 319$ ppm, $O^{13}CH_3$ (quartet, $J_{C-H} = 137$ Hz). ^{1}H NMR (400 MHz, $[D_8]$toluene, 303 K): $\delta = 142$ (d, 3 H, $O^{13}CH_3$, $J_{H-C} = 137$ Hz), 113 (s, 2 H, COT ring-C*H*), −5.54 (br d, 18 H, *i*Pr-C*H*$_3$, $J_{H-H} = 4.6$ Hz), −6.23 (s, 15 H, Cp*-C*H*$_3$), −14.9 (br d, 18 H, *i*Pr-C*H*$_3$, $J_{H-H} = 4.6$ Hz), −18.0 (br m, 6 H, *i*Pr-C*H*), −40.6 (s, 2 H, COT ring-C*H*), −87.8 ppm (s, 2 H, COT ring-C*H*); elemental analysis calcd (%) for $^{13}CC_{36}H_{66}OSi_2U$: ^{13}C and C 54.18, H 8.09; found: ^{13}C and C 54.32, H 8.18; EIMS: *m*/*z* (%): 821 (25, M^+).

Reaction of **3** with Me_3SiOTf: To **3** (100 mg, 0.122 mmol) dissolved in $[D_8]$toluene (0.5 mL) was added Me_3SiOTf (0.122 mmol, 27 mg, 22 μL) through a microsyringe, and the mixture was heated at 55 °C overnight. The volatile components were transferred under vacuum to afford a red-brown solid residue and a $[D_8]$toluene solution of $Me_3SiO^{13}CH_3$, identified by its NMR spectra. The ^{1}H, ^{19}F NMR and EI mass spectroscopic data for the solid residue showed it to be $U(\eta\text{-}C_8H_6\{Si\mathit{i}Pr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)OTf$, **4**. ^{1}H NMR (400 MHz, $[D_8]$toluene, 303 K): $\delta = 104$ (s, 2 H, COT ring-C*H*), 13.6 (s, 15 H, Cp*-C*H*$_3$), −4.47 (br d, 18 H, *i*Pr-C*H*$_3$), −6.15 (br m, 6 H, *i*Pr-C*H*), −9.25 (br d, 18 H, *i*Pr-C*H*$_3$), −112 (s, 2 H, COT ring-C*H*), −115 ppm (s, 2 H, COT ring-C*H*). ^{19}F NMR (376 MHz, $[D_8]$toluene, 303 K): $\delta = -94.4$ ppm (s); EIMS: *m*/*z* (%): 938 (3 %, M^+).

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