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CO₂ and CO/H₂ Conversion to Methoxide by a Uranium(IV) Hydride

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ABSTRACT: Here we show that a scaffold combining siloxide ligands and a bridging oxide allows the synthesis and characterization of the stable dinuclear uranium(IV) hydride complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)(\mu-H)_2\}]$, **2** which display high reductive reactivity. The dinuclear bis-hydride **2** effects the reductive coupling of acetonitrile by hydride transfer to yield $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)(\mu-\kappa^2-NC(CH_3)NCH_2CH_3)\}]$, **3**. Under ambient conditions, the reaction of **2** with CO affords the oxomethylene (2-) reduction product $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-CH_2O)(\mu-O)\}]$, **4** that can further add H₂ to afford the methoxide hydride complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-OCH_3)(\mu-O)(\mu-H)\}]$, **5** from which methanol is released in water. Complex **2** also effects the direct reduction of CO₂ to the methoxide complex **5** which is unprecedented in f element chemistry. From the reaction of **2** with excess CO₂, crystals of the bis-formate carbonate complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-CO_3)(\mu-HCOO)_2\}]$, **6** could also be isolated. All the reaction products were characterized by X-ray crystallography and NMR spectroscopy.

INTRODUCTION

The search for more sustainable and selective catalysts for the production of oxygenates from CO or CO₂ hydrogenation continues to drive interest in the homogeneous reduction of CO and CO₂ by molecular hydride complexes.¹ Most studies have focused on d block transition metals, but f block hydrides, because of their different reactivity, may open up new routes for the transformation and reduction of CO and CO₂ to valuable products.^{1f, 1j}

The reduction of CO₂ to methanol by molecular hydride complexes was previously reported for early transition metals^{1f} in high oxidation states but never for f elements. In particular, the two examples of CO₂ functionalization by uranium hydrides reported so far have both resulted in formate formation.² The reaction of early d block^{1c} and 4f block^{1j, 3} metal hydrides with CO has also received less attention than for mid- late-transition metals. However, early d block and f metal hydrides provide pertinent mechanistic and functional models of the surface mediated hydride transfer to CO in the heterogeneously catalysed Fischer-

Tropsch process used on the industrial scale for the conversion of a CO/H₂ mixture to higher hydrocarbons and oxygenate products.^{1c, 4}

CO addition to mononuclear (Sm,^{3a} Ce^{3b}) and polynuclear hydrides (Yb^{3c}, Lu^{3e}) of the 4f block led to the isolation of ethenediolate, etheneolate, propeneolate or oxomethylene ($[OCH_2]^{2-}$) complexes. Further reactivity of such complexes with H₂ was only reported for the dinuclear cerium product $\{[(1,2,4-(Me_3C)_3C_5H_2)_2Ce]_2(\eta^2-OCH_2)\}$ that reacts with H₂ to yield cerium methoxide and cerium hydride complexes.^{3b} Conversion of CO to methoxide was also reported for a mononuclear thorium(IV) hydride complex in the presence of H₂ (6 atm) but the products were not crystallographically characterized.⁵ Spectroscopic evidence of the formation of Th-formyl and Th-oxomethylene intermediates was reported but these intermediates were not isolated.^{6, 5}

In contrast, the only reported example of CO/H₂ conversion to methoxide mediated by a uranium(III) complex reported by Cloke and coworkers was not found to involve a hydride or formyl intermediate, and a mechanism involving hydrogenation of a C₂O₂ intermediate was suggested.⁷ Notably, several U(III) complexes were found to promote the

reductive coupling of CO to yield enediolate, deltate, or squarate products.⁸

The functionalization of CO or CO₂ by uranium hydrides remains poorly studied probably due to the scarce number of uranium hydrides reported so far. In spite of the tremendous advances made in the field of organo-actinide chemistry in the past three decades,⁹ since the seminal work from the early 1980s¹⁰ only a few additional examples of uranium hydrides have been reported.^{2, 9g, 10c, 11}

Here we have used a scaffold combining siloxide ligands and a bridging oxide to synthesize a stable dinuclear diuranium(IV) bis-hydride. The addition of H₂ to the U(III)-O-U(III) core of the previously reported¹² complex [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)}], **1** affords [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-H)₂}], **2**, that is stable with respect to H₂ loss. The bis-hydride complex **2** effects the reduction of CO in ambient conditions to the oxomethylene dianion that reacts further with hydrogen to afford a methoxide complex. Moreover, we show that complex **2** acts as a powerful hydride donor that can reduce CO₂ beyond formate to afford methanol.

EXPERIMENTAL DETAILS

General Methods. All manipulations were carried out under a dry and oxygen free argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 0.1 ppm. Glassware was dried overnight at 140 °C before use. Compounds were characterized by elemental analysis, ¹H and ¹³C NMR spectroscopies, IR spectroscopy and single-crystal X-ray diffraction. **¹H NMR experiments** were carried out using NMR tubes adapted with J. Young valves. ¹H and ¹³C NMR spectra were recorded on Bruker 400 MHz and 600 MHz spectrometers. NMR chemical shifts are reported in ppm with solvent as internal reference. **Elemental analyses** were performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. **IR analyses** were performed with a FT-IR Spectrometer Perkin-Elmer. The measurements were performed using nujol mulls between KBr plates. **Starting materials.** Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Tris(*tert*-butoxy)silanol was purified by sublimation. Depleted uranium was purchased from IBILABS (USA). The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (toluene, toluene-*d*₈ (tol-*d*₈), tetrahydrofuran (THF), THF-*d*₈ and acetonitrile (MeCN)). DMSO-*d*₆ was degassed by three freeze-pump-thaw cycles and stored over activated 3 Å molecular sieves. The complexes {[U(OSi(O^tBu)₃)₃]₂(μ-O)}, and [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)}], **1** were prepared according to their published procedures.¹² Carbon monoxide (N47 Bt-S 10/200) was purchased from Carbogas. ¹³CO (93.13% ¹³C), ¹³CO₂ (93.13% ¹³C) and D₂ (99.8% D) were purchased from Cortecnet and stored over activated 3 Å molecular sieves. **Caution:** Depleted uranium (primary isotope ²³⁸U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10⁹ years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α- and β-counting equipment.

Synthesis of complex [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-H)₂}], **2.** Excess K₂C₈ (32.0 mg, 0.240 mmol, 5 equiv.) was added to a cold solution (−80 °C) of {[U(OSi(O^tBu)₃)₃]₂(μ-O)} (97.2 mg, 0.05 mmol, 1 equiv.) in THF (3 mL). The suspension was stirred at −80 °C for 15 minutes. The reaction mixture was then filtered on cooled glassware. All the volatiles were removed under vacuum at −80 °C and cold toluene (2 mL) added to afford a solution of [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)}], **1**. The ¹H NMR spectrum of the solution in toluene-*d*₈ confirmed the presence of **1** as a pure species and the complex was reacted without further purification to increase the overall yield and purity of the final product (complex **1** decomposes readily at room temperature and is highly soluble). The reaction tube was transferred to a Schlenk line and degassed by freeze-pump-thaw cycles. Hydrogen gas (1 atm) was added into the tube and the reaction mixture was left stirring at room temperature. The reaction mixture turned from dark red to yellow within 15 min. The toluene solution was left standing at −40 °C for 24 h, yielding X-ray suitable crystals of complex [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-H)₂}], **2** (72.0 mg, 70% yield).

¹H NMR of crystals of **2** (400 MHz, tol-*d*₈, 298 K): δ (ppm) = 12.0 (s, 2H), −1.42 (s, CH₃ terminal siloxide). ¹³C NMR of crystals of **2** (101 MHz, tol-*d*₈, 298 K): δ (ppm) = 71.11 (s, C(CH₃)₃), 25.81 (s, C(CH₃)₃). Anal. Calcd for C₇₂H₁₆₄O₂₅K₂Si₆U₂(C₇H₈)_{1.5}: C, 43.25; H, 7.74; N, 0.00. Found: C, 43.25; H, 7.64; N, 0.00. Magnetic moment calculated by Evans method: 2.78 μ_B.

When D₂ was added to a solution of **1**, the complex [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-D)₂}], **D-2** was isolated with similar yield and the proton NMR spectrum showed disappearance of the peak at 12 ppm.

Synthesis of [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-κ²-NC(CH₃)NCH₂CH₃)}], **3.**

MeCN (9 μL of a 3M solution in tol-*d*₈, 0.027 mmol, 2.25 equiv.) was added to a yellow solution of [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-H)₂}], **2** (25.6 mg, 0.012 mmol) in toluene-*d*₈ (0.6 mL). The colour of the solution did not change upon addition, but the ¹H NMR spectrum of the reaction mixture after addition showed the complete disappearance of **2** and the appearance of new signals assigned to [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-κ²-NC(CH₃)NCH₂CH₃)}], **3**. The solution was left standing at −40 °C and X-ray suitable yellow crystals of [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-κ²-NC(CH₃)NCH₂CH₃)}], **3** were collected (16.2 mg, 60% yield). ¹H NMR of crystals of **3** (400 MHz, tol-*d*₈, 298 K): δ (ppm) = 1.55 (s, CH₃ terminal siloxide), −51 (s, 3H, C(CH₃)), −73 (s, 3H, CH₂CH₃), −85 (s, 2H, CH₂CH₃). ¹³C NMR of crystals of **3** (101 MHz, tol-*d*₈, 298 K): δ (ppm) = 73.3 (s, C(CH₃)₃), 30.8 (s, C(CH₃)₃), 22.7 (s, C(CH₃)). Anal. Calcd for C₇₆H₁₇₀N₂O₂₅K₂Si₆U₂(C₇H₈): C, 42.84; H, 7.71; N, 1.20. Found: C, 42.86; H, 7.22; N, 1.52.

The ¹H NMR spectrum of the reaction mixture after addition of 1 equivalent of MeCN to **2** showed the presence of complex **3** and unreacted complex **2**. Single crystals isolated from this reaction confirmed the presence of **3**. When 2 equivalents of MeCN were added to a solution of **D-2**, the species [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-O)(μ-κ²-NC(CH₃)NCD₂CH₃)}], **D-3** was formed as confirmed by ¹H NMR spectroscopy.

Synthesis of [K₂{[U(OSi(O^tBu)₃)₃]₂(μ-CH₂O)(μ-O)}], **4.**

¹³CO (0.012 mmol, 1 equiv.) was added to a solution of **2** (26.5 mg, 0.012 mmol), which had been degassed by freeze-

pump-thaw cycles. The colour of the solution changed from yellow-greenish to pale yellow immediately and the ^1H NMR spectrum showed the disappearance of the resonances of the starting material and the appearance of those of a new species. The solution was left standing at -40°C for 24 h. X-ray suitable crystals of complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-}^{13}\text{CH}_2\text{O})(\mu\text{-O})]$, **13C-4**, were recovered (18.6 mg, 70% yield). The quantitative ^{13}C NMR spectrum of **13C-4** in D_2O showed the presence of one equivalent of methanol which was referenced to ^{13}C labelled potassium acetate, $\text{CH}_3^{13}\text{COOK}$ used as internal standard, confirming the presence of the bound oxomethylene dianion in **13C-4**. Methanol formation was also identified by GC-MS analysis on the non-labelled analogue **4** in H_2O : M^+ : 31 m/z . ^1H NMR (400 MHz, tol-d_8 , 298 K): δ (ppm) = -1.13 (s, CH_3 terminal siloxide), -130 (d, 2H, $^{13}\text{CH}_2\text{O}^{2-}$). ^{13}C NMR (101 MHz, tol-d_8 , 298 K): δ (ppm) = 71.06 (s, $\text{C}(\text{CH}_3)_3$), 26.06 (s, $\text{C}(\text{CH}_3)_3$), 22.72 (s, CH_2O^{2-}). ^{13}C NMR (400 MHz, D_2O , 298 K): δ (ppm) = 49 (triplet, $^{13}\text{CH}_2\text{DOD}$). Anal Calcd for $\text{C}_{73}\text{H}_{164}\text{O}_{26}\text{K}_2\text{Si}_6\text{U}_2(\text{C}_7\text{H}_8)_{0.2}$ **4**: C, 40.63; H, 7.59; N, 0.00. Found: C, 40.55; H, 7.25; N, 0.00. Magnetic moment calculated by Evans method: 2.75 μ_B . When excess ^{13}CO is used, complex **13C-4** is formed and was found to slowly react with additional ^{13}CO . The ^1H NMR spectrum shows disappearance of the resonances for **13C-4** and the appearance of those of a new species that remains unidentified. The reaction of **13C-4** with ^{13}CO is complete after 1 week. The ^{13}C NMR in D_2O of the final reaction mixture does not show the presence of methanol, suggesting that an attack of the nucleophilic carbon of the oxomethylene dianion of **13C-4** on ^{13}CO has occurred. When ^{13}CO was added to a solution of **D-2**, the species $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-}^{13}\text{CD}_2\text{O})(\mu\text{-O})]$, **D-4** was formed as confirmed by ^1H NMR spectroscopy, which showed the disappearance of the CH_2 signal.

Synthesis of $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-OCH}_3)(\mu\text{-O})(\mu\text{-H})]$, **5**.

A yellow solution of complex **2** (27.1 mg, 0.013 mmol) in toluene- d_8 (0.6 mL), was degassed by freeze-pump-thawing and ^{13}CO (0.013 mmol, 1 equiv.) was added. When the reaction with ^{13}CO was complete and all **2** had been converted into **4**, H_2 (1 atm) was added to the resulting solution. The mixture turned from yellow to light brown. The ^1H NMR spectrum shows that a new species is formed and does not evolve with time. The excess H_2 was removed under vacuum and the solution was left standing for 24 h, yielding X-ray suitable crystals of complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-OCH}_3)(\mu\text{-O})(\mu\text{-H})]$, **5** (20.8 mg, 75 %). ^1H NMR (400 MHz, tol-d_8 , 298 K): δ (ppm) = -0.05 (s, CH_3 terminal siloxide), -104 (d, 3H, CH_3O), 41 (s, 1H, H-). ^{13}C NMR (^1H coupled) (101 MHz, tol-d_8 , 298 K): δ (ppm) = 71.54 (s, $\text{C}(\text{CH}_3)_3$), 28.5 (q, $\text{C}(\text{CH}_3)_3$), -348 (q, CH_3O). Anal Calcd for mixture of $\text{C}_{73}\text{H}_{166}\text{O}_{26}\text{K}_2\text{Si}_6\text{U}_2$, **5**: C, 40.17; H, 7.67; N, 0.00. Found: C, 40.30; H, 7.34; N, 0.00. ESI-MS: M^+ 2184 m/z , MK^+ 2222 m/z . Magnetic moment calculated by Evans method: 2.37 μ_B . The protonation of the hydroxo group was ruled out because of the absence of bands that could be assigned to a hydroxo ligand in the IR spectrum of **5** (see Supporting info). When D_2 is added to a toluene solution of complex **4**, the species $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-CH}_2\text{DO})(\mu\text{-O})(\mu\text{-D})]$, **D-5** is formed. In the ^1H NMR spectrum of this reaction, the signal at 41 ppm disappears and the doublet at -104 ppm integrates for 2H. When CO (1 atm) and H_2 (1 atm) were added

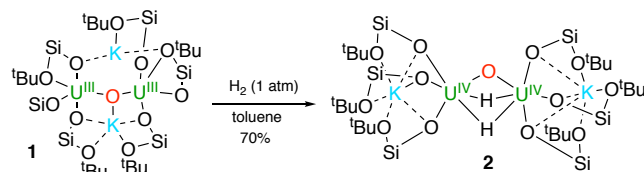
to **1** simultaneously in a pressurized vessel, complex **5** was formed as the only product. When 3 equivalents of $^{13}\text{CO}_2$ were added to a toluene solution of **5**, immediate reaction was observed to afford a new species. The ^{13}C NMR spectrum of this species in D_2O showed the presence of formate, confirming the presence of the hydride ligand in complex **5** that undergoes facile insertion of CO_2 in the U–H bond. ^{13}C NMR of the crude mixture after addition of 3 equivalents of $^{13}\text{CO}_2$ to **5** (101 MHz, D_2O , 298 K): δ (ppm) = 172.4 (HCOO^-), 161.6 (DCO_3^-), 50.4 (CH_3OD).

Reaction of **2** with CO_2 : isolation of $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-CO}_3)(\mu\text{-HCOO})_2]$, **6**.

CO_2 (0.03 mmol, 3 equiv.) was introduced into a yellow solution of $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-O})(\mu\text{-H})_2]$, **2** (23.3 mg, 0.01 mmol), which was previously degassed by freeze-pump-thaw cycles. The colour of the solution turned light blue immediately. After 24 h at -40°C light blue crystals were formed (20.6 mg). The ^1H NMR spectrum of the light blue crystals showed a mixture of products. Complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-CO}_3)(\mu\text{-HCOO})_2]$, **6** could be identified among the products by X-ray diffraction. The ^{13}C NMR spectra both in toluene- d_8 and in deuterated water indicated the formation of two different products that co-precipitate. The ^{13}C NMR spectra of the light blue crystals in D_2O showed the presence of HCOO^- , CO_3^{2-} and CH_3OD in a ratio 1:0.5:0.25 respectively. The presence of methanol was confirmed by GC-MS analysis. ^1H NMR of the light blue crystals (400 MHz, tol-d_8 , 298 K): δ (ppm) = 12 (s, broad), 1.37 (s), 1.22 (s), -4.30 (s, broad). ^{13}C NMR of the light blue crystals (101 MHz, tol-d_8 , 298 K): δ (ppm) = 73.25 (s, $\text{C}(\text{CH}_3)_3$), 30.75 (s, $\text{C}(\text{CH}_3)_3$), 130, 105, -216 (three ^{13}C for CH_3O^- , HCOO^- and CO_3^{2-}). ^{13}C NMR of the light blue crystals (101 MHz, D_2O , pD 12, 298 K): δ (ppm) = 172 (HCOO^-), 168 (CO_3^{2-}), 50 (CH_3OD). GC-MS anal. for $^{13}\text{CH}_3\text{OH}$ M^+ : 32 m/z . When 0.5 or 1 equivalents of $^{13}\text{CO}_2$ were added to a solution of **2**, the ^1H NMR spectrum showed the presence of complex **5**, the bis(oxo) complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-O})_2]$,¹² and starting material **2**. The ^{13}C NMR spectrum in D_2O after addition of 1 equiv. $^{13}\text{CO}_2$, showed the presence of HCOO^- , CO_3^{2-} and CH_3OD in a ratio 1:0.8:1.75 respectively. ^{13}C NMR after addition of 1 equiv. of $^{13}\text{CO}_2$ (101 MHz, D_2O , pD 12, 298 K): δ (ppm) = 172 (HCOO^-), 169 (CO_3^{2-}), 49.7 (CH_3OD).

RESULTS AND DISCUSSION

When a cold solution (-80°C) of $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-O})]$, **1** in toluene is exposed to 1 atm of H_2 the reaction mixture changes color from dark red to yellow within 15 minutes. The proton NMR spectrum shows the disappearance of the signals of **1** and the appearance of a new species assigned as the bis-hydride-bridging diuranium(IV) complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-O})(\mu\text{-H})_2]$, **2** (Scheme 1).



Scheme 1. Synthesis of the bis-hydride diuranium(IV) complex **2**. Only the $-\text{O}^t\text{Bu}$ groups bound to the metals are shown.

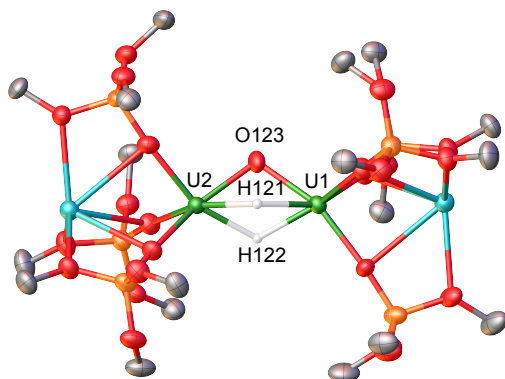
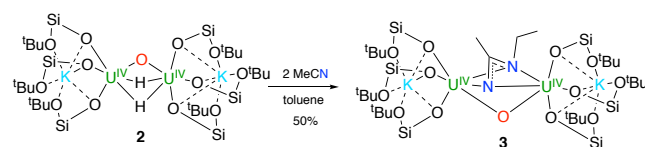


Figure 1. Thermal ellipsoid plots of **2** shown at the 50% probability level. Hydrogen atoms and methyl groups were omitted for clarity.

The ^1H NMR spectrum of **2** shows a signal at 12 ppm integrating for two protons that is absent in the spectrum of the deuterated analogue of **2** (**D-2**), and was assigned to the two bridging hydride ligands. The solid-state structure of compound **2** was determined by X-ray crystallography which supports the presence of two hydrides. The structure of **2** (Figure 1) shows two six-coordinate U(IV) ions, bridged by an oxo ligand (O^{2-}) which is disordered over three positions, with an overall occupancy of one oxygen and an average U-O distance of 2.154(24) Å. The remaining electron density found in the core is modeled to bridging hydrides, disordered over the same three positions.

Thus, the highly reactive U(III)-O-U(III) complex **1**, cleaves molecular hydrogen in ambient conditions acting as a two-electron reducing agent to yield two U(IV) ions and two bridging hydrides. The uranium(IV) bis-hydride **2** shows a remarkable stability with respect to H_2 elimination both in solution and solid state. This contrasts with the tendency of the $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{H})(\mu\text{-H})]_2$ complex^{10c} to readily lose H_2 at room temperature in solution and incited us to investigate the reactivity of **2** towards electrophilic small molecules. We found that **2** reacts readily with two equivalents of MeCN in toluene solution, to yield $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-O})(\mu\text{-}\kappa^2\text{-NC}(\text{CH}_3)\text{NCH}_2\text{CH}_3)\}]_2$, **3** (Scheme 2), where two U(IV) centers are bridged by a dianionic ligand produced from the reductive coupling of two acetonitrile molecules. The reaction is likely to proceed at first with the attack of the acetonitrile triple bond by the two hydride ligands to afford a metal imido species ($\text{M-NCH}_2\text{CH}_3$) that rapidly reacts with a second acetonitrile molecule to afford the dianionic bidentate fragment $\text{-NC}(\text{CH}_3)\text{NCH}_2\text{CH}_3$.



Scheme 2. Reactivity of complex **2** with acetonitrile, to give complex **3**. Only the $\text{-O}^t\text{Bu}$ groups bound to the metals are shown.

The solid-state structure of compound **3**, determined by X-ray crystallography (Figure 2) shows two six-coordinate U(IV) ions, bridged by an oxo ligand (U1-O121 2.124(11) Å, U2-O121 2.106(11) Å) and by the two nitrogen atoms of the

dianionic ligand. The $\text{-NC}(\text{CH}_3)\text{N}$ fragment lies in a plane perpendicular to the U1-U2 axis. The two equal N-C distances (N121-C121 1.34(2) Å, N122-C121 1.33(2) Å) and the geometry of C121 imply an sp^2 hybridization of the carbon and the delocalization of the double bond between the three atoms N121-C121-N122.

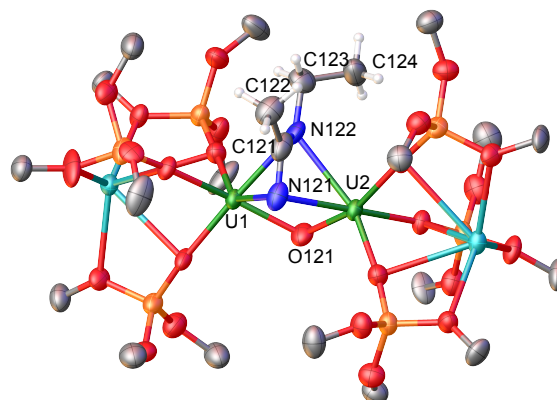


Figure 2. Thermal ellipsoid plots of **3** shown at the 50% probability level. Hydrogen atoms and methyl groups were omitted for clarity. Selected distances (Å): U1-O121 2.124(11), U1-N121 2.360(12), U1-N122 2.650(13), U2-O121 2.106(11), U2-N121 2.458(13), U2-N122 2.555(13).

Further confirmations of the nature of the bridging dianionic ligand was given by ^1H NMR spectroscopy (see Supporting Info). The ^1H NMR spectrum confirmed the presence of a CH_2CH_3 fragment. Moreover, when acetonitrile was reacted with the deuterated analogue **D-2**, the ^1H NMR resonances assigned to the CH_2 group were not observed, demonstrating that the two hydrides are transferred to the nitrile carbon. Previously, reductive coupling of acetonitrile by the U(III) hydride $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{H})]_2$ was reported to yield a diaminocyanopentadienyl dianion and H_2 but none of the hydrogen atoms in the $(\text{C}_6\text{N}_3\text{H}_7)^{2-}$ dianion were found to arise from the U-bound hydrides.¹³

The facile reduction of acetonitrile by complex **2** incited us to explore its reactivity with CO and CO_2 and the possibility of converting them into methoxide.

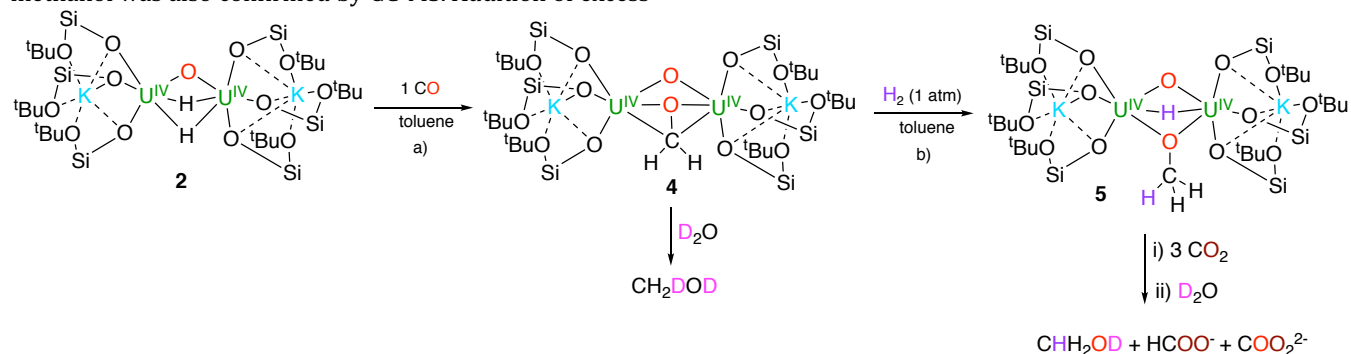
Upon addition of 1 equivalent of CO to a toluene solution of complex **2**, an immediate reaction occurs and the ^1H spectrum indicates full conversion of the diuranium(IV) bis-hydride complex into a new species, identified as complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-CH}_2\text{O})(\mu\text{-O})\}]_2$, **4** (Scheme 3 a). The ^1H NMR spectrum of **4** shows a signal at -130 ppm, which integrates for 2 protons and splits into a doublet in the ^1H NMR spectrum of the ^{13}C labeled analogue $^{13}\text{C-4}$, in agreement with the formation of the CH_2O fragment from ^{13}CO addition to **2**. The molecular structure of complex **4** (Figure 3a) shows two six-coordinate U(IV) atoms bridged by an oxo ligand and an oxomethylene dianion, in a side-on $\mu\text{-}\kappa^2(\text{O})\text{:}\kappa^2(\text{C})$ coordination mode, perpendicular to the U1-U2 axis. The two ligands are disordered over two positions in the core of the molecule with an overall occupancy of 1 for each atom. The C53-O45 bond distance of 1.31(3) Å, is comparable to those found in the complexes $[(1,2,4\text{-}(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2)_2\text{Ce}](\mu\text{-OCH}_2)$ (1.39(1) Å)^{3b} and $[\text{Zr}(\eta^8\text{-C}_8\text{H}_8(\text{OAr}))_2(\mu\text{-CH}_2\text{O})]$ (1.313(14) Å),¹⁴ consistent with the presence of a C-O single bond and a sp^3 carbon atom. The presence of a hypervalent carbon is probably an artefact due to the superposition of two symmetry related

enantiomers with a $\mu-\kappa^1:\kappa^1$ bound CH_2O . A similar artefact was found in the $[(1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2)_2\text{Ce}](\mu-\text{OCH}_2)$ complex.^{3b}

The CO triple bond undergoes a four-electron reduction by the two hydrides in **2** to yield two new C-H bonds. The oxomethylene ligand is likely to form via the insertion of CO into the U-H bond to afford a formyl intermediate that then adds a second hydride ligand. Overall, the diuranium(III) complex **1** mediates the stepwise conversion of H_2 and CO to yield a CH_2O^{2-} dianion which is readily transformed into methanol by addition of D_2O . The detection of a triplet at 50 ppm (^{13}C -deuterium coupling) in the ^{13}C NMR spectrum of **4** in D_2O reveals the presence of CH_2DOD . The formation of methanol was also confirmed by GC-MS. Addition of excess

CO to **4** results in the slow complete conversion into a new species that was not further characterized.

Because of the anticipated nucleophilic character of the CH_2O^{2-} carbon, we also investigated the possibility of direct heterolytic cleavage of H_2 to afford methoxide. The addition of 1 atm H_2 to complex **4**, resulted in the clean formation of a new species, identified as the methoxide complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu-\text{OCH}_3)(\mu-\text{O})(\mu-\text{H})\}]$, **5** (Scheme 3 b)). The proton NMR spectrum of **5** shows the presence of a peak at -104 ppm, which integrates for 3H and splits into a well-resolved doublet in the ^1H NMR spectrum when ^{13}C -**4** is used.



Scheme 3. Reduction of carbon monoxide to oxomethylene(2-) (a) and subsequent reaction with hydrogen to give the methoxide complex, **5** (b).

The proton-coupled ^{13}C NMR spectrum of **5** shows a quartet at -348 ppm, in agreement with the presence of the methoxide group. The singlet found in the spectrum at 41 ppm, which integrates for one proton, was assigned to a bridging hydride. When D_2 is added to ^{13}C -**4** the hydride signal disappears and the doublet at -104 ppm integrates for two protons, in agreement with the formation of $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu-\text{OCH}_2\text{D})(\mu-\text{O})(\mu-\text{D})\}]$, **D-5**.

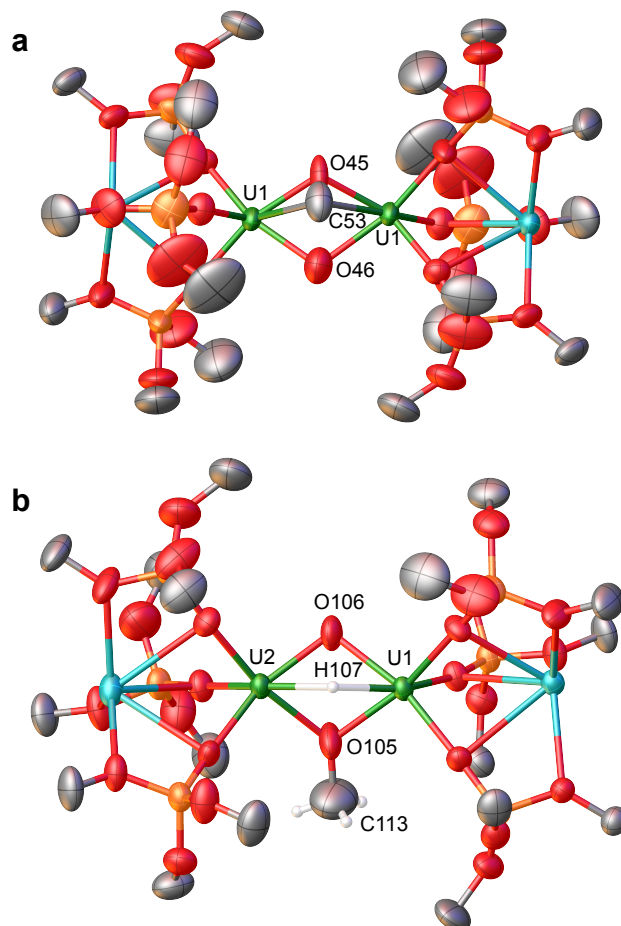


Figure 3. Thermal ellipsoid plots of **4** (a) and **5** (b) shown at the 50% probability level. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances (Å) for: **4**: U1-O46 2.115(13), U1-O45 2.198(10), U1-C53 2.617(18), C53-O45 1.31(3); for **5**: U1-O106 2.204(18), U1-O105 2.295(12), U2-O106 2.182(19), U2-O105 2.309(12), O105-C113 1.44(3).

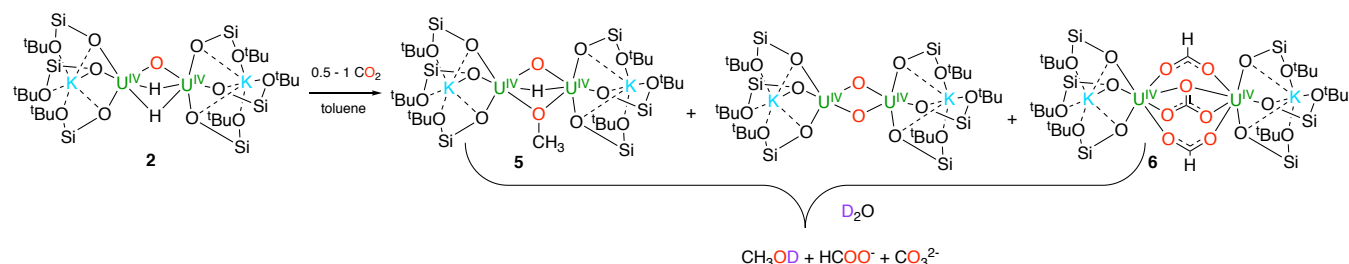
The molecular structure of **5** (Figure 3b) shows two six-coordinate U(IV) atoms bridged by an oxo ligand, an hydride (the oxo and the hydride are disordered over two positions with an occupancy of 1 for each atom) and a methoxide ligand that bridges the metal centers through the oxygen atom. The U-O_{oxo} distances of 2.204(18), 2.182(19) Å and the U-O-U angle 102.1(9)° are similar to those found in **4**.

The solution magnetic moment determined by the Evan's method for complexes **2** (2.78 μ_B), **4** (2.75 μ_B) and **5** (2.37 μ_B), falls for all complexes in the range of those reported for complexes of U(IV) (1.36 μ_B - 3.79 μ_B)¹⁵ and are similar to the magnetic moment measured for the diuranium(IV) complex $[U(OSi(O^tBu)_3)_2(\mu-O)]$ (2.87 μ_B). The similarity of the magnetic moments measured for **2**, **4** and **5** indicates that the oxidation state of the uranium remains unchanged during reactivity.

Finally, upon addition of 3 equivalents of CO₂ to complex **5**, the carbon NMR spectrum in D₂O (see Supporting info) showed the presence of formate, bicarbonate and methanol (Scheme 3). The formation of formate confirms

unambiguously the presence of the hydride ligand in **5**. The facile non-reversible heterolytic cleavage of dihydrogen by **4** is the result of cooperative H₂ activation by the two Lewis acid uranium centers and the nucleophilic oxomethylene ligand. Metal-ligand cooperative reactivity towards small molecules is rare in actinide chemistry¹⁶ but we recently reported the cooperative H₂ cleavage by a bifunctional metal nitride.^{2b}

These results prompted us to explore the reduction of CO₂ by complex **2**. Upon addition of 3 equivalents of CO₂ to **2** at room temperature, a mixture of products formed immediately. Crystals of complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-CO_3)(\mu-HCOO)_2\}]$, **6** were isolated and characterized by X-ray analysis. The solid-state structure of compound **6** (Figure 4) shows two seven-coordinate U(IV) ions, bridged by two formate ligands and a carbonate ligand, indicating that both the U-H and the U-O bonds undergo CO₂ insertion. The U-O bond distances for the formate ligands range between 2.338(11) and 2.403(12) Å and are similar to those found in the only other example of a formate-bridged diuranium(IV) complex (2.409(3) and 2.356(3) Å).^{2b} Both hydrogens of the formate moieties were located in the Fourier difference map. The carbonate ligand bridges the two metal centers in a $\mu-\eta^2(O,O'):\eta^2(O'',O')$ mode with an average U-O bond distance for the carbonate ligand of 2.448(30) Å.



Scheme 4. Reduction of carbon dioxide by complex **2**, to give a mixture of compounds, **5**, **6** and bis-oxo.

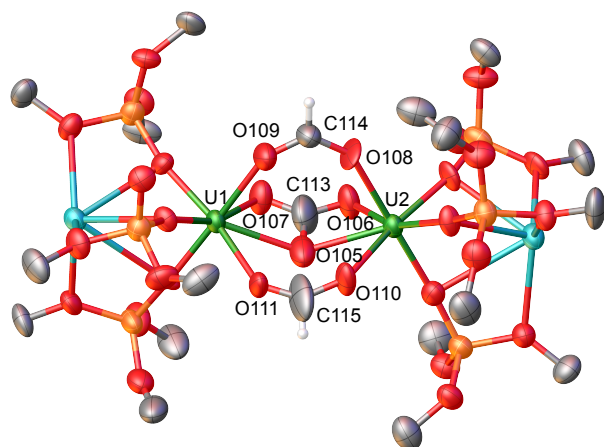


Figure 4. Thermal ellipsoid plots of **6** at shown at the 50% probability level. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances (Å) for **6**: U1-O109 2.361(13), U1-O111 2.403(12), U1-O105 2.409(14), U1-O107

2.448(13), U1-C113 2.835(19), U2-O108 2.338(11), U2-O110 2.400(11), U2-O106 2.455(13), U2-O105 2.482(14).

Interestingly, the ¹³C NMR spectrum in D₂O of the reaction mixture of **2** with CO₂ (3 equiv.) shows, in addition to formate and bicarbonate, the presence of CH₃OD which was confirmed by GC-MS analysis. This suggests that a methoxide complex is also formed in the reaction of **2** with CO₂. Indeed, when 0.5-1 equivalents of CO₂ were added to a solution of **2** (Scheme 4), the proton NMR spectrum shows the presence of unreacted **2** but also the presence of signals corresponding to complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-OCH_3)(\mu-O)(\mu-H)\}]$, **5** and to the previously reported diuranium(IV) bis-oxo complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)_2\}]$.¹²

The absence of ¹³C-deuterium coupling for the ¹³C NMR signal assigned to CH₃OD confirms that all the protons leading to methanol formation originate from the hydrides ligands in **2**. Stepwise formation of formate, methylene diolate and methoxide complexes has been proposed for the heterogeneously catalyzed hydrogenation of CO₂ in industrial processes. An analogous mechanism was proposed for the

conversion of CO₂ to methoxide by the zirconocene hydrido complex Cp₂Zr(H)Cl (Schwartz's reagent)¹⁷ with carbon dioxide on the basis of spectroscopic studies.¹⁸

A plausible mechanism for methoxide formation from the reaction of **2** with CO₂ involves the transfer of three hydrides from two molecules of **2** to a CO₂ molecule followed by oxide abstraction to afford **5** and the previously reported diuranium(IV) bis-oxo complex (See Scheme S1 in supplementary information). After the insertion of a molecule of CO₂ into a U-H bond has occurred, the resulting formate undergoes the intermolecular reduction of the formate ligand by a second dihydride complex **2** to afford the methoxide complex **5**. No evidence of methylene diolate intermediates could be found. The formate reduction to methoxide is a competitive pathway compared to the insertion of CO₂ into the second U-H bond to yield **6**, even in the presence of excess CO₂. However, the amount of methoxide formed increases at lower CO₂ to **2** ratios and, only in these conditions, the identification of **5** and bis-oxo was possible. Notably, the quantitative evaluation by ¹³C NMR spectroscopy of the reaction products after hydrolysis of the reaction mixture showed formate:methanol ratios of 1:1.75 for the 1:1 (**2**:CO₂) and of 1:0.25 for the 1:3 (**2**:CO₂) reaction.

The insertion of CO₂ into the uranium(IV)-hydride bond has some rare precedents^{2, 19} and in two cases the resulting U(IV) formate was crystallographically characterized.² The insertion of CO₂ into the U(IV)-O bond to afford carbonate was also reported.²⁰ However, the reduction of CO₂ to methoxide by a uranium hydride complex has not yet been reported.

CONCLUSIONS

In conclusion we have shown that the scaffold provided by siloxide ligands and a bridging oxo enables the non-reversible addition of H₂ to the diuranium(III) complex **1** to afford a stable diuranium(IV) bis-hydride complex. The reactivity shown by this oxo- and hydride- bridged complex differs significantly from that of previously reported U(IV) bis-hydride complexes supported by cyclopentadienyl ligands, that are unstable with respect to hydrogen loss.^{2a, 10c} Notably the complex **2** does not undergo elimination of H₂ either spontaneously or promoted by substrates. In contrast the hydrides in the reported oxo- hydride- bridged complex show high reductive activity towards different substrates. The oxide bridge holds the uranium cations together during reactivity and facilitates the isolation of uranium-bound reduction products. Carbon monoxide reduction results in the isolation of a unique diuranium(IV) oxomethylene bridged complex that cleaves H₂ at room temperature, affording a methoxide as the unique product. The oxide-supported diuranium(IV) hydride also effects the reduction of carbon dioxide to afford methoxide which is unprecedented in f element chemistry. Thus, these results provide a novel example of ligand-based reduction of CO and CO₂ at a uranium center. The binding and activation of small molecules such as CO, CO₂ or N₂ at highly reducing uranium(III) centers has witnessed a rapid development in recent years,^{9f, 20a, 21} but examples of ligand based activation of small molecules at less reducing uranium(IV) centers are still rare.^{11a, 22} Moreover, the results presented here show that polynuclear oxide-supported hydrides are excellent candidates for the

conversion of CO and CO₂ to methoxide, furthering the understanding of analogous transformation at metal oxide surfaces.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral data, (PDF file), and crystallographic information (CIF files). The Supporting Information is available free of charge on the ACS Publications website.

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Funding Sources

Swiss National Science Foundation grant number and 200021_ 178793

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We acknowledge support from the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Dr. Euro Solari for carrying out the elemental analyses, Dr. F. Fadaei-Tirani for important contributions to the X-ray single crystal structure analyses and Sylvain Sudan for preliminary experiments.

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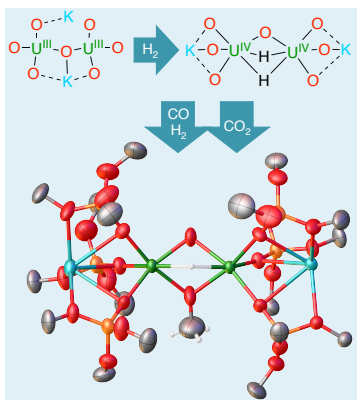
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