Multimetallic Cooperativity in Uranium-Mediated CO$_2$ Activation

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Ⓢ *Supporting Information*

ABSTRACT: The metal-mediated redox transformation of CO$_2$ in mild conditions is an area of great current interest. The role of cooperativity between a reduced metal center and a Lewis acid center in small-molecule activation is increasingly recognized, but has not so far been investigated for f-elements. Here we show that the presence of potassium at a U, K site supported by sterically demanding tris(*tert*-butoxy)siloxide ligands induces a large cooperative effect in the reduction of CO$_2$. Specifically, the ion pair complex [K(18c6)][U(OSi-(O^{t}Bu)$_3$)$_4$], **1**, promotes the selective reductive disproportionation of CO$_2$ to yield CO and the mononuclear uranium(IV) carbonate complex [U(OSi(O^{t}Bu)$_3$)$_4$(μ-κ^2:κ^1-CO$_3$)K$_2$(18c6)], **4**. In contrast, the heterobimetallic complex [U(OSi(O^{t}Bu)$_3$)$_4$K], **2**, promotes the potassium-assisted two-electron reductive cleavage of CO$_2$, yielding CO and the U(V) terminal oxo complex [UO(OSi(O^{t}Bu)$_3$)$_4$K], **3**, thus providing a remarkable example of two-electron transfer in U(III) chemistry. DFT studies support the presence of a cooperative effect of the two metal centers in the transformation of CO$_2$.

heterobimetallic cooperativity
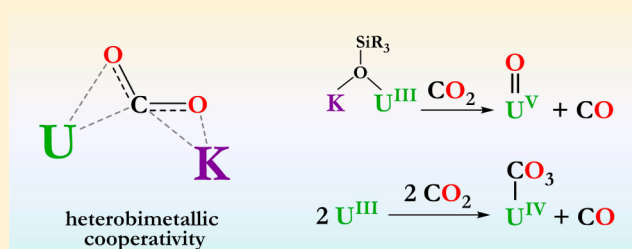
INTRODUCTION

Carbon dioxide is a highly attractive low -cost, abundant, and renewable C1 source for fine chemicals and fuel production.[1−4] A key step in the reduction of CO$_2$ is the cleavage of the C=O bond. The cooperative binding of carbon dioxide at heterobimetallic sites, by pairing an electron-rich metal with a main group Lewis acid, provides an attractive pathway for promoting the activation and reduction of carbon dioxide.[3,5] Notably, the binding of CO$_2$ to heterobimetallic sites has been reported to be a key step in its biological redox transformation.[6]

Although the binding of carbon dioxide at a heterobimetallic Co, K site was first reported in the late 1970s,[7,8] since that pioneering study only one example of C−O bond cleavage at an early/late heterobimetallic complex has so far been reported, by Thomas et al. in 2011.[9]

f-Elements and uranium in particular have emerged as attractive candidates for carbon dioxide reduction,[10−16] yet studies of CO$_2$ activation by f-element complexes remain far less common than those involving d-block transition metals. U(III)-mediated reductive cleavage of carbon dioxide has so far been reported for three different electron-rich ligand systems, bulky carbocyclic ligands, tripodal tris(aryloxide) ligands, and siloxide ligands.[12,17−20] Depending on the ligand, the reduction of CO$_2$ was reported to yield an end-on-bound η^1-OCO$^{\bullet-}$−U(IV) complex,[14] dinuclear uranium(IV) carbonates and CO,[18,20] or μ-oxo−U(IV) complexes and carbon monoxide.[21] In contrast to the reactivity of low-valent early transition metals,[22−24] the formation of terminal uranium monooxoura-

nium complexes from U(III)-mediated reduction of CO$_2$ has not yet been observed. This can be explained by the tendency of the highly nucleophilic oxo ligand to form oxo-bridged complexes[25] and by the rarity of two-electron transfer in U(III) chemistry.[13,26−32]

It is in general recognized that the steric and electronic properties of the ancillary ligand play a very important role in the control of the reactivity of U(III) with small molecules.[13,25,27,31,33−37]

In contrast, the cooperative reactivity at U(III)/Lewis acid sites remains basically unexplored. Here we investigate the reduction of CO$_2$ at a U, K site supported by sterically demanding tris(*tert*-butoxy)siloxide ligands, and we show a large effect of the presence of the potassium site on the reactivity. Bulky siloxide ligands provide attractive ancillary ligands for the study of the reactivity of U(III) with small molecules.[19,30,38−40] In particular, the high reactivity demonstrated by the "ate" complex [K(18c6)][U(OSi(O^{t}Bu)$_3$)$_4$], **1** (Chart 1), toward azides, isoelectronic with CO$_2$, incited us to explore its ability to promote the reduction of CO$_2$. Moreover, the ionic nature of **1** also provides an opportunity to isolate the analogous heterobimetallic U, K complex [U(OSi(O^{t}Bu)$_3$)$_4$K], **2** (Chart 1). The difference in reactivity between complexes **1** and **2** highlights the multimetallic cooperativity that takes place

Chart 1. Uranium(III) Siloxide Complexes [K(18c6)][U(OSi(O^{t}Bu)$_3$)$_4$], 1, and [U(OSi(O^{t}Bu)$_3$)$_4$K], 2
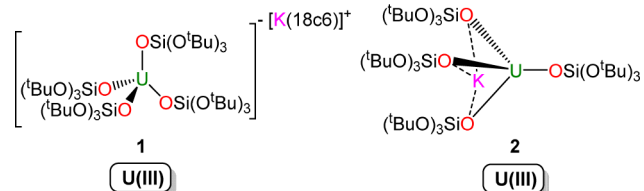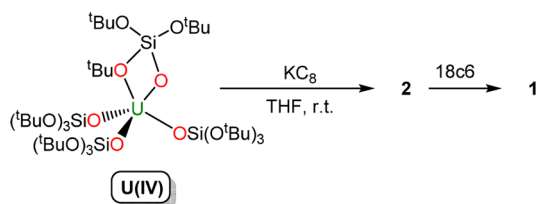

in the reduction of CO_2 by complex **2**, which is further supported by DFT studies.

■ RESULTS AND DISCUSSION

Uranium(III) Potassium Tetrasiloxide Complex. The reduction of the uranium(IV) homoleptic complex [U(OSi-(O^{t}Bu)$_3$)$_4$][30] in THF at room temperature affords [U(OSi-(O^{t}Bu)$_3$)$_4$K], **2**, in 83% yield (Scheme 1).

Scheme 1. Synthesis of [U(OSi(O^{t}Bu)$_3$)$_4$K], 2

X-ray diffraction analysis of single crystals of **2** shows the presence of a neutral heterobimetallic U(III), K complex. In the crystal structure of **2**, shown in Figure 1, the uranium center is
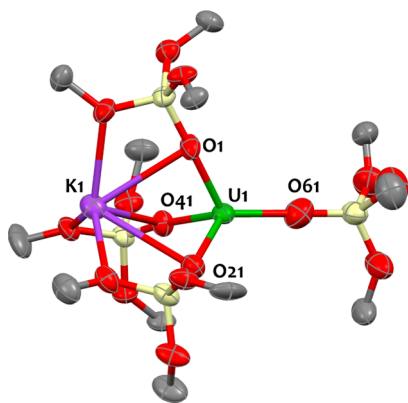

Figure 1. Ellipsoid plot for [U(OSi(O^{t}Bu)$_3$)$_4$K], **2**, crystallized from toluene, probability 50%. Hydrogen atoms and methyl groups are omitted for clarity.

tetracoordinated by four OSi(O^{t}Bu)$_3$ ligands with a C_{3v} local geometry. Three siloxide ligands act as bridging ligands and provide an O$_6$ coordination pocket which accommodates K$^+$, holding the alkali-metal cation in proximity to the uranium center (U1··K1 = 3.576(3) Å). The U−O$^−$ bond distances for the siloxide ligands (U1−O$^-_{av}$ = 2.214(5) Å) lie in the usual range of what is observed in other uranium(III) alkoxide and siloxide compounds.[19,30,38]

The ^{1}H NMR spectrum of **2** in toluene (Figure S1, Supporting Information) shows the presence of only one resonance at −0.24 ppm for the four siloxide ligands. The

resonance is shifted upfield with respect to the [U(OSi-(O^{t}Bu)$_3$)$_4$] precursor (1.06 ppm).[30] The ^{1}H NMR spectrum of **2** at 243 K (Figure S2, Supporting Information) shows an important broadening of the siloxide resonance (shifted further upfield to −1.09 ppm), suggesting the presence of exchange between different solution species. This behavior probably arises from the fluxional coordination of the potassium cation between the four siloxide ligands. To confirm that the potassium cation remains bound in toluene solution, complex **2** was reacted with 18c6. The later addition to a toluene solution of **2** leads to the formation of an insoluble compound which was identified as the previously reported[30] ionic complex **1** (identified by ^{1}H NMR in toluene and THF). This dramatic change in solubility upon addition of 18c6 confirms that complex **2** retains its neutral heterobimetallic structure in toluene solution.

A comparison between the ^{1}H NMR spectra of **1** and **2** in THF reveals an upfield shift of the resonance, from 1.24 to 0.06 ppm, respectively, suggesting that the potassium remains coordinated in THF.

The magnetic moment of **2** (2.38 μ_B) measured in toluene using the Evans method[41] at 298 K is similar to the value previously reported for **1** (a value of 2.63 μ_β was measured in THF)[30] and falls in the range of the values reported for other U(III) coordination compounds.[42−45] As often observed in trivalent uranium complexes, this value is lower than the theoretical value (3.62 μ_B) calculated for a 5f^3 ion with a full spin−orbit coupling.[46]

The neutral complex **2** and the previously reported "ate"-salt analogue [K(18c6)][U(OSi(O^{t}Bu)$_3$)$_4$], **1**, provide very interesting precursors for investigating the effect of the presence of a bimetallic U, K site in the U(III)-mediated reduction of CO_2. Moreover, it is interesting to compare the reactivity with CO_2 of these two mononuclear complexes with that previously reported for the dinuclear trisiloxide complex [U(OSi-(O^{t}Bu)$_3$)$_2$(μ-OSi(O^{t}Bu)$_3$)]$_2$. Notably, we have recently shown that the difference in charge and steric demand of this trisiloxide species compared to the tetrasiloxide complex **1** results in a different reactivity toward azides.[30]

Reactivity with CO_2. The reaction of [U(OSi(O^{t}Bu)$_3$)$_4$K], **2**, with 1 atm of CO_2 in toluene at room temperature affords cleanly the terminal oxo pentavalent uranium complex [UO(OSi(O^{t}Bu)$_3$)$_4$K], **3**, which is isolated analytically pure in 77% yield (Scheme 2). The ^{13}C NMR spectrum of the reaction mixture after reaction of **2** with $^{13}CO_2$ in toluene (Figure S7, Supporting Information) shows the presence of the signal assigned to ^{13}CO at 184.6 ppm.[47]

Proton NMR studies indicate that complex **3** can also be obtained from the reaction of **2** with pyridine N-oxide (Figure S8, Supporting Information).

The solid-state structure of **3**, shown in Figure 2, was determined by single-crystal X-ray diffraction. In complex **3** the uranium center adopts a distorted octahedral geometry and is coordinated by two oxygen atoms from an κ^2-bound siloxide ligand, three oxygen atoms from three κ^1-bound siloxide ligands, and one terminal oxo ligand. The three κ^1-bound siloxide ligands bridge the uranium center, binding the potassium cation. Each siloxide binds the potassium cation in an κ^2-fashion. The uranium terminal oxo bond distance (U═O = 1.825(2) Å) is in agreement with a multiply bonded ligand and is comparable to the distances (1.817−1.859 Å) found in the few examples of crystallographically characterized mononuclear uranium(V) monooxo compounds.[48−51] Among the

Scheme 2. Reaction of $[U(OSi(O^tBu)_3)_4K]$, 2 (Top), and $[K(18c6)][U(OSi(O^tBu)_3)_4]$, 1 (Bottom), with CO_2
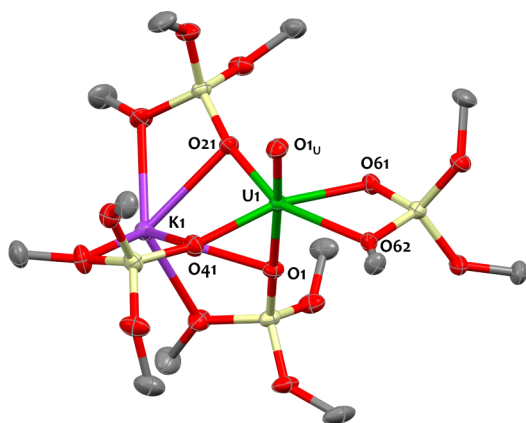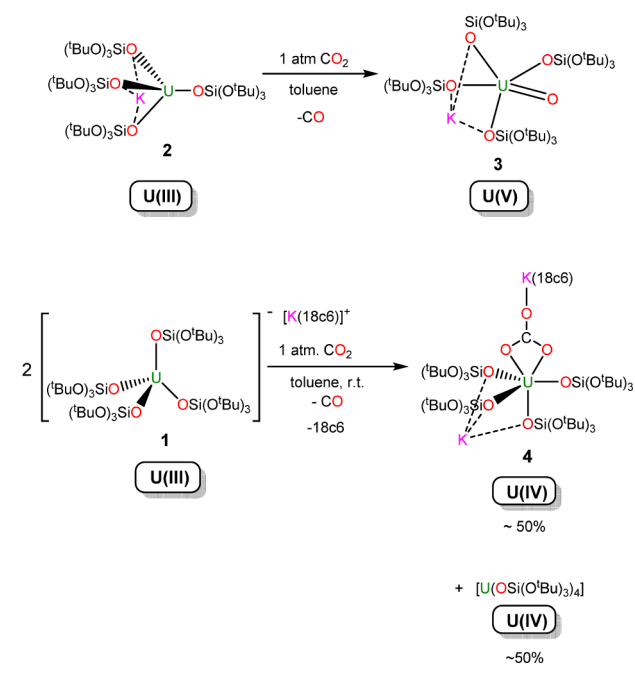

Figure 2. Ellipsoid plot for $[UO(OSi(O^tBu)_3)_4K]$, 3, crystallized from toluene, probability 50%. Hydrogen atoms, methyl groups, and solvent molecules are omitted for clarity.

values of the uranium–siloxide bond lengths, U1–O1 (2.142(2) Å), which is *trans* to the U═O bond, is the shortest one (U1–O2 = 2.183(2) Å; U1–O41 = 2.240(2) Å; U1–O61 = 2.257(2) Å) and might be indicative of an inverse *trans* influence.[52]

The proton NMR spectrum of complex 3 in toluene shows the presence of only one peak at 1.34 ppm, suggesting the presence of a C_{3v} symmetric solution species with four equivalent siloxide groups. This contrasts with the solid-state structure where the coordination of potassium by three out of four siloxides renders the siloxide ligands nonequivalent. Addition of crown ether to a toluene solution of 3 leads to a significant shift of the peak assigned to the siloxides in the proton NMR spectrum. This suggests that potassium remains bound in toluene solution as observed for the U(III) complex 2 but adopts a fluxional coordination.

The FTIR spectrum of 3 shows an absorption at 925 cm^{-1} assigned to the U═O stretch (the U═O stretch was found at

910 cm^{-1} in a recently reported terminal uranium(V) oxo complex).[51] The solid-state magnetic moment of 3 at 300 K measured by superconducting quantum interference device (SQUID) magnetometry (μ_{eff} = 2.03 μB) is significantly lower than the theoretical U(V) free ion value (μ_{eff} = 2.54 μB) but is in the range of magnetic moments previously reported for uranium(V) monooxo complexes (μ_{eff} range = 1.47–1.98 μB).[48–51,53] The magnetic moment undergoes a gradual decrease with decreasing temperature from the value of 2.03 μB at 300 K to the value of 0.75 μB at 2 K. This temperature response of the magnetic moment is characteristic of U(V) complexes.[48,54]

The electronic absorption spectrum (Figure S16, Supporting Information) of the uranium(V) terminal oxo complex shows a set of sharp, low-intensity absorption bands at λ_{max} = 1700 nm (ε = 7.3 M^{-1}·cm^{-1}), λ_{max} = 1590 nm (ε = 20.8 M^{-1}·cm^{-1}), λ_{max} = 1430 nm (ε = 15.1 M^{-1}·cm^{-1}), λ_{max} = 1406 nm (ε = 12.4 M^{-1}·cm^{-1}), λ_{max} = 1073 nm (ε = 12.8 M^{-1}·cm^{-1}), and λ_{max} = 823 nm (ε = 9.6 M^{-1}·cm^{-1}). These distinct absorption bands arise from f–f transitions and are similar to those reported for the uranium(V) terminal oxo complexes $[U(O)\{tacn-(OArR)_3\}]$ (R = ^{t}Bu, Ad)[48] and for octahedral U(V)–alkoxo complexes.[55]

The X-band EPR spectrum of 3 measured at 10 K in a toluene/acetonitrile glass is shown in Figure 3. The EPR signal
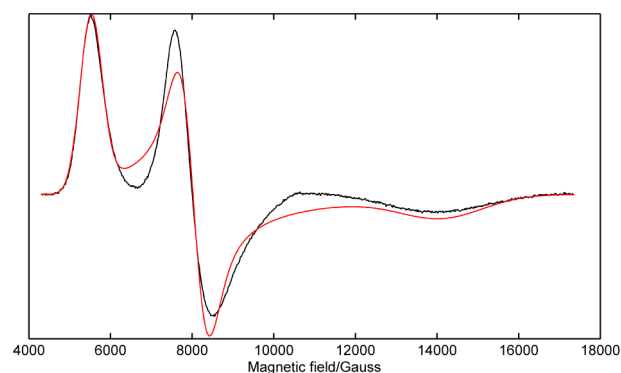

Figure 3. (a) Baseline-corrected X-band EPR spectrum of 3 recorded in toluene/acetonitrile glass at 10 K (ν = 9.65373 GHz, P = 3.17 μW, amplitude modulation 9 G, frequency modulation 100 kHz) (black line). (b) Simulated EPR spectrum of 3 (red line).

was fitted with a rhombic set of g values (g_1 = 1.248; g_2 = 0.856; g_3 = 0.485). While a few uranium(V) imido and uranium(V) monooxo complexes were reported to be EPR silent,[48,51,56] EPR signals were observed for two C_{3v} symmetric U(V)–oxo complexes, the trigonal bipyramidal $[U(O)(NR_2)_3]_2$ (R = SiMe$_3$) ($g_∥$ = 2.17 and $g_⊥$ < 0.7)[49] and the heptacoordinated $[U(O)\{tacn(OArR)_3\}]$[48] ($g_∥$ = 2.15 and $g_⊥$ = 1.14). However, the g values of 3 compare better with those reported for octahedral U(V)–alkoxo complexes[55] with g values of 0.85, 0.80, and 0.47 for the octahedral $[U(V)(O^tBut)_6]$[55a] or 0.91, 0.91, and 0.74 for $[(\eta^8$-$C_8H_8)U(O^iPr)_3]$.[55b] These values are in agreement with the presence of a uranium(V) species in an intermediate ligand field in a distorted octahedral symmetry.[55]

An effective magnetic moment of 0.79 μB at 10 K can be calculated from the measured EPR g values and is in agreement with that obtained from the experimental solid-state susceptibility data at 10 K.

Complex 3 is the first example of a uranium(V) terminal oxo complex obtained from the two-electron reductive cleavage of

CO_2 mediated by a U(III) complex. Two-electron redox transfer is generally rare in uranium chemistry,[13,26−32] and as such, the ability of complex **3** to perform a two-electron reduction of carbon dioxide is quite remarkable.

Terminal monooxo complexes are usually obtained from the reaction of U(III) or U(IV) precursors with highly reactive oxygen atom transfer agents.[49,57−60] Uranium(V) monooxo complexes have also been obtained by the reductive cleavage of nitrite by a U(IV) complex[61] and from the metathesis of a U(V)−imido complex with CO_2.[48]

The formation of terminal uranium(V) oxo complexes from the reaction of U(III) with oxo-transfer reagents requires the use of bulky ligands, preventing the formation of more stable dinuclear oxo-bridged U(IV) complexes. Hayton and co-workers have also demonstrated that even in the presence of bulky supporting ligands the nature of the oxo-transfer reactant plays a very important role in the stabilization of terminal vs bridging oxo complexes.[49] Notably, while the stable uranium-(V) oxo complex $[U(O)\{tacn(OArR)_3\}]$ (R = ^tBu) reported by Meyer et al.[21] is obtained from the reaction of the analogous uranium(V) imido complex with CO_2, the reaction of the U(III) complex $[U(tacn(OAr^tBu)_3\}]$ with CO_2 affords the uranium(IV) oxo-bridged complex $\{[U(tacn(OAr^tBu)_3)]_2(\mu\text{-}O)\}$.[21]

The reactivity of **2** with CO_2 is very different from that of the less sterically demanding homoleptic trisiloxide complex of trivalent uranium, $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$, which leads to the reductive disproportionation of CO_2, affording CO and a dimeric uranium(IV)−uranium(IV) carbonate-bridged complex through the concerted one-electron reduction of two molecules of CO_2.[19]

To investigate if the presence of potassium in the structure of **2** plays an important role in such different behavior, we have studied the reactivity of the analogous ion-paired system $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **1** with 1 atm of gaseous CO_2 (Scheme 2). The reaction proceeds instantly at room temperature and is accompanied by evolution of CO. The latter is confirmed by monitoring the reaction of **1** with $^{13}CO_2$ by ^{13}C NMR spectroscopy. The ^1H NMR of the crude mixture shows the characteristic resonance of the tetravalent uranium complex $[U(OSi(O^tBu)_3)_4]$[30] at 1.06 ppm, together with a broad resonance centered at 2.97 ppm for the 18c6 ligand and two resonances at 5.92 and 0.11 ppm assigned to the formation of a new compound which was identified as a U(IV)−carbonate species. Recrystallization of the reaction mixture in toluene produced pale pink single crystals of $[K(18c6)][KU(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3)(OSi(O^tBu)_3)_4]$, **4**, suitable for X-ray diffraction studies. The ^1H NMR spectrum of the reaction mixture shows that **4** and $[U(OSi(O^tBu)_3)_4]$ form in a 1:1 ratio, with a yield of 45(3)% and 44(3)% for **4** and $[U(OSi(O^tBu)_3)_4]$, respectively (determined after addition of naphthalene as an internal standard to the reaction mixture). The separation of **4** from $[U(OSi(O^tBu)_3)_4]$ by recrystallization proved difficult, with analytically pure **4** only isolated in 41% yield after addition of KC_8 to the reaction mixture in toluene, resulting in $[U(OSi(O^tBu)_3)_4]$ converted into **1** and precipitating out of toluene.

The solid-state structure of **4**, set out in Figure 4, shows the presence of a uranium(IV) tetrasiloxide complex with a terminally bound carbonate ligand. The carbonate anion acts as a tridentate bridging ligand between a K(18c6) unit and the U(IV) cation. The uranium in **4** is hexacoordinated with distorted octahedral geometry. A second potassium counter-cation is encapsulated in an O6-core pocket created by three of
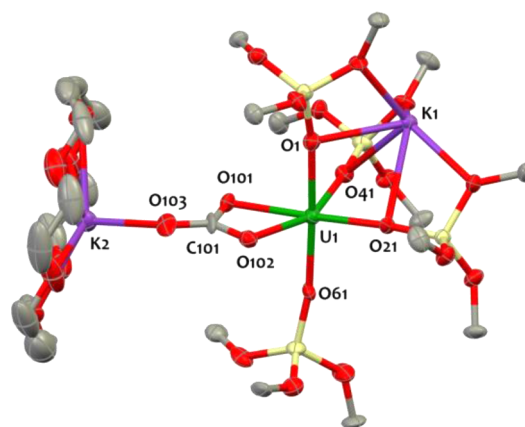

Figure 4. Ellipsoid plot for $[U(OSi(O^tBu)_3)_4(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3)K_2(18c6)]$, **4**, crystallized from toluene, probability 50%. All hydrogen atoms, methyl groups of siloxides, and solvent molecules are omitted for clarity.

the four siloxide ligands. As expected, the U−$O_{siloxide}$ bond distances of the bridging ligands (average value 2.23(1) Å) are slightly longer than those found for the nonbridging ligand (2.205(5) Å), all being in the range of the U−O bond distances found in the other uranium(IV) siloxide complexes.[19,30,38]

The evolution of ^{13}CO and the isolation of a carbonate complex confirms that $[K(18c6)][U(OSi(O^tBu)_3)_4]$ promotes the disproportionation of CO_2, similarly to what was previously observed for the trisiloxide complex $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$.[22] However, in this case the presence of an additional siloxide ligand prevents the formation of the dinuclear carbonate species $[\{U(OSi(O^tBu)_3)_3\}_2\{\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3\}]$. The presence of a coordinating $[K(18c6)]^+$ cation may also play a role in the stabilization of the mononuclear product. Notably, all the previously reported examples of U(III)-promoted disproportionation of CO_2 have led to diuranium carbonate species even in the presence of bulky ligands.[12,18] Moreover, while the dinuclear carbonate $[\{U(OSi(O^tBu)_3)_3\}_2\{\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3\}]$[22] is unstable and undergoes ligand scrambling, complex **4** is stable over a 7 day period with respect to ligand scrambling.

The dramatic difference in the reactivity of complexes **1** and **2** with carbon dioxide highlights the importance of the presence of a coordinated potassium cation in proximity to the uranium center in complex **2**. The heterobimetallic nature of complex **2** associating a highly reducing U(III) ion and an electropositive potassium cation is likely to result in a coordination of the carbon dioxide molecule by the two metal centers as depicted in Scheme 3. A similar coordination mode has been characterized at a Co^I−M (M = Li, Na) site.[8]

Such binding would result in a significant weakening of the C=O bond, which would favor the C=O cleavage pathway

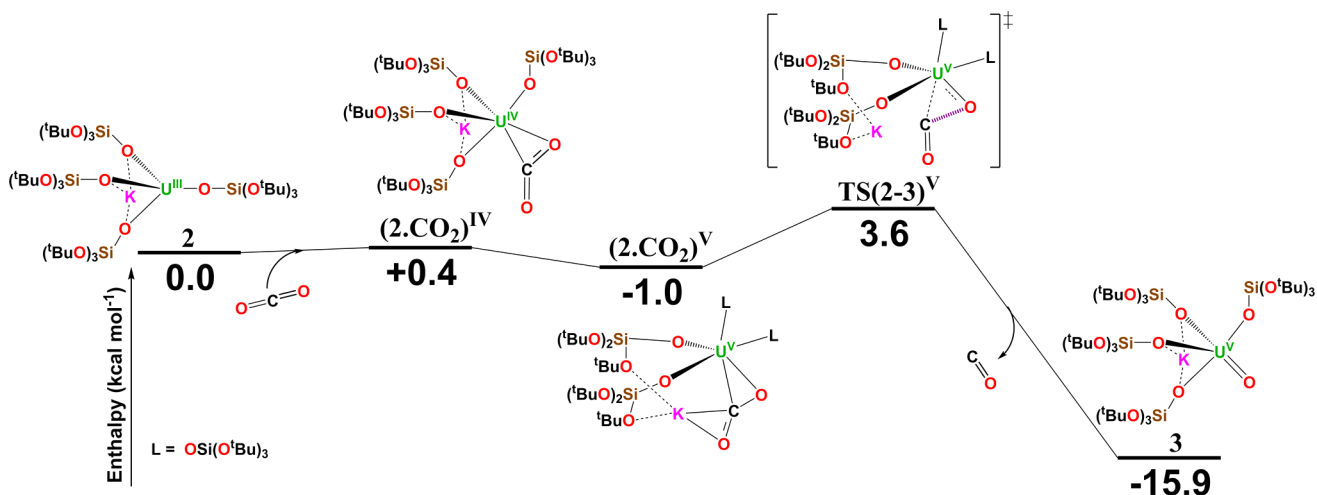**Scheme 3. Possible CO_2 Binding at the U, K Site**
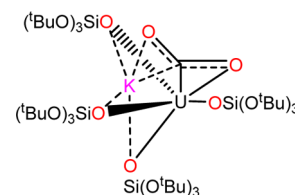
Figure 5. Enthalpy profile at 298 K for the reaction of complex **2** with CO_2, yielding complex **3**.

leading to the terminal uranium(V) oxo complex compared to the disproportionation pathway.

DFT (B3PW91) calculations were carried out to investigate the reaction of **2** with CO_2 displayed in Scheme 2 to shed light on the cooperative effect of the metal centers (U and K) in this transformation of CO_2. This reaction can be viewed as a formal two-electron reduction of CO_2 and a two-electron oxidation of the uranium center. The reaction mechanism (Figure 5) begins with two successive one-electron transfers from the uranium-(III) center of complex **2** to the CO_2-coordinated substrate.

The change of the geometry of CO_2 (from linear to bent due to a first-order Jahn–Teller effect) is diagnostic of the reduction of this moiety. Interestingly, the two successive single-electron reductions are found to be almost athermic at +0.4 kcal·mol^{-1} (from U(III) to U(IV)) and −1.4 kcal·mol^{-1} (from U(IV) to U(V)), leading to an overall merely exothermic process (−1.0 kcal·mol^{-1}). From a geometrical point of view, the negative charge on the reduced CO_2 moiety, which is mainly located on the two oxygen atoms, is stabilized by the coordination to both the uranium and the potassium centers (Figure 6). The coordination of the CO_2 moiety is (η^2-CO:η^2-
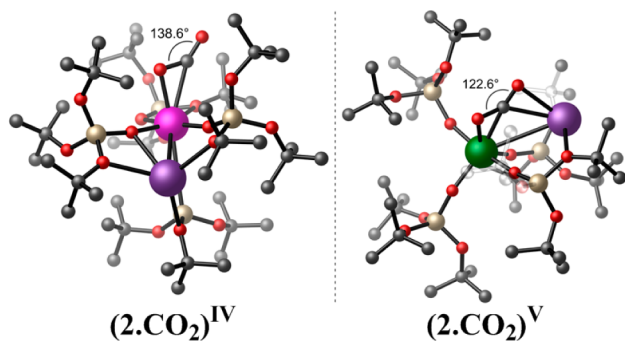
In complex $(\mathbf{2 \cdot CO_2})^V$, one C–O bond is highly elongated and consequently activated. This facilitates the cleavage of the C–O bond, which occurs with an activation barrier of only 4.6 kcal·mol^{-1} and results in the formation of complex **4**. This reaction is exothermic by 15.9 kcal·mol^{-1} and is indeed a formal two-electron oxidation of the uranium center. The C–O bond breaking was also computed without the assistance of the potassium atom and found to occur at a U(IV) intermediate with a much higher enthalpy energy (47 kcal·mol^{-1}; see the Supporting Information). It should be noted that all attempts to locate a reaction pathway involving a U(V) intermediate where the potassium is not present or is in a distant position compared to the coordinated CO_2 molecule were unsuccessful. This supports the significant influence of the potassium atom as well as the cooperative effect between the metal centers in this CO_2 transformation.

Furthermore, the calculations indicate that there is no clear thermodynamic preference for the formation of a U(V)–carbonate complex from the U(V)–oxo complex (only 1.1 kcal/mol, which is far below the precision of the method). The formation of a U(IV)–carbonate complex may involve the concerted one-electron reduction of two molecules of CO_2 as previously reported for the neutral trisiloxide system.[19] The potassium could also play a role in such a concerted pathway.

■ CONCLUDING REMARKS

In conclusion, the tetrasiloxide complexes [K(18c6)][U(OSi-(O^{t}Bu)$_3$)$_4$], **1**, and [U(OSi(O^{t}Bu)$_3$)$_4$K], **2**, have proven an interesting platform for the study of the parameters ruling the U(III)-mediated CO_2 activation. The presented reactivity provides a new example of how sterical demand and charge can be used to tune the reactivity of uranium(III) with CO_2. Notably, the more sterically demanding environment of **1** and **2** promotes a different reactivity with CO_2 of these tetrasiloxide complexes compared to the previously reported trisiloxide analogue [U(OSi(O^{t}Bu)$_3$)$_3$]$_2$,[21] affording mononuclear carbonate and oxo species.

More importantly, we show for the first time that such reactivity can be controlled by the presence of a coordinated alkali-metal ion bound in close proximity to the U(III) center. The ionic pair structure of complex **1** promotes the reductive disproportionation of CO_2, affording a mononuclear uranium-(IV) carbonate complex. In contrast, the heterobimetallic

Figure 6. Structures of the optimized complexes $(\mathbf{2 \cdot CO_2})^{IV}$ and $(\mathbf{2 \cdot CO_2})^V$.

CO). In complex $(\mathbf{2 \cdot CO_2})^{IV}$, the two C–O bond distances are 1.207 and 1.258 Å compared with 1.168 Å in the free CO_2. In the same way, the distances are even more elongated in complex $(\mathbf{2 \cdot CO_2})^V$, in line with a second reduction of the CO_2 (1.229 and 1.375 Å).

structure of **2** promotes the C=O bond cleavage of the coordinated CO_2, affording a terminal uranium(V) oxo complex and CO. The outcome of this reaction is even more remarkable considering the difficulty in obtaining terminal uranium (V) oxo complexes in uranium chemistry. The DFT studies support the presence of a cooperative effect of the two metal centers in the transformation of CO_2. This provides a rare example of C–O bond cleavage at a molecular heterobimetallic site and the first one at an f-element/Lewis acid pair.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert 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 1 ppm. Glassware was dried overnight at 130 °C before use. Elemental analyses were performed under argon by Analytische Laboratorien GmbH in Lindlar, Germany.

Starting Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Eurisotop (deuterated solvents) in their anhydrous form, conditioned under argon, and vacuum distilled from K/benzophenone (toluene and THF). All reagents were dried under high vacuum for 7 days prior to use. Syntheses were performed using glass-covered stirring bars. Depleted uranium turnings were purchased from the Société Industrielle du Combustible Nucléaire of Annecy France. [U{OSi-($O^tBu)_3$}$_4$][30] and **1**[30] were prepared according to the published procedures.

Caution: Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10^9 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 [U{OSi($O^tBu)_3$}$_4$K] (2). KC_8 (37.1 mg, 0.274 mmol, 1.5 equiv) was added at room temperature to a solution of [U{OSi($O^tBu)_3$}$_4$] (236 mg, 0.182 mmol, 1 equiv) in THF (3 mL). The reaction mixture turned dark brown and was stirred for 1 h. The suspension was centrifuged with the supernatant collected. All volatiles were then removed in vacuo, and the resulting brown solid was dissolved in a minimum amount of toluene (∼0.5 mL) and stored at −40 °C overnight to afford **2** as dark brown crystals in 83% yield (201 mg, 0.151 mmol). Anal. Calcd for **2**, $C_{48}H_{108}KO_{16}Si_4U$: C, 43.32; H, 8.18; N, 0.00. Found: C, 42.23; H, 7.88; N, 0.00. This analysis was repeated twice, and each time it presented a low carbon probably due to carbide formation. A perfect elemental analysis was obtained for complex **3** when prepared from the same batch of **2**. ^{1}H NMR (200 MHz, toluene-d_8, 298 K): δ −0.24 (s, 108H, OC(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (200 MHz, toluene-d_8, 298 K): δ 28.06 (s, OC(CH$_3$)$_3$), 67.05 (s, OC(CH$_3$)$_3$).

Reaction of 2 with CO_2. CO_2 (1 atm) was condensed onto a frozen solution of **2** (183 mg, 0.138 mmol, 1 equiv) in toluene (4 mL). The mixture was allowed to warm to room temperature slowly, upon which evolution of CO was observed and the solution turned from a dark brown to a pale pink. The reaction was stirred for 1 h. Then all volatiles were removed in vacuo. The resulting pink solid was recrystallized from a minimum amount of hexanes, affording [UO{OSi($O^tBu)_3$}$_4$K] (**3**) as pink crystals in 75% yield (138 mg, 0.103 mmol). Anal. Calcd for **3**, $C_{48}H_{108}KO_{17}Si_4U$: C, 42.81; H, 8.08; N, 0.00. Found: C, 42.60; H, 8.08; N, 0.00. ^{1}H NMR (200 MHz, toluene-d_8, 298 K): δ 1.34 (s, 108H, OC(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (200 MHz, toluene-d_8, 298 K): δ 32.12 (s, OC(CH$_3$)$_3$), 72.83 (s, OC(CH$_3$)$_3$).

Reactivity of 2 with Pyridine N-Oxide. Pyridine *N*-oxide (1.2 mg, 0.012 mmol, 1 equiv) in toluene-d_8 (0.5 mL) was added to **2** (16.7 mg, 0.012 mmol, 1 equiv) and the resulting mixture stirred for a few minutes. The solution lightened from a dark brown to a pale pink

color. Inspection of the ^{1}H NMR spectrum confirmed the conversion of **2** to **3**.

Reaction of [K(18c6)][U(OSi($O^tBu)_3$)$_4$] (1) with CO_2. CO_2 (0.014 mmol, 1 atm) was added to an NMR tube containing a brown suspension of [K(18c6)][U(OSi($O^tBu)_3$)$_4$] (22.4 mg, 0.014 mmol, 1 equiv) in toluene (0.5 mL). Immediately, the mixture turned pale blue, and CO bubbling was observed. Generation of CO during the reaction was confirmed by ^{13}C NMR. The reaction was stirred at room temperature over 1 h. The ^{1}H NMR (toluene-d_8, 400 MHz, 298 K) spectrum recorded for the crude mixture shows a characteristic resonance at 1.06 ppm corresponding to [U(OSi($O^tBu)_3$)$_4$] together with a broad signal at 2.97 ppm corresponding to the 18c6 protons and two signals at 5.92 and 0.11 ppm that we attribute to the formation of uranium(IV) carbonate species. Pale pink single crystals of [K(18c6)][KU(μ-η^1:η^2CO_3)(OSi($O^tBu)_3$)$_4$] (**4**) suitable for X-ray diffraction were grown upon allowing the crude toluene mixture to stand at −40 °C. The addition of KC_8 to the crude reaction mixture resulted in conversion of [U(OSi($O^tBu)_3$)$_4$] to **1**, which precipitated out, allowing for **4** to be isolated cleanly in 41% yield. Anal. Calcd for **4**, $C_{61}H_{133}K_2O_{25}Si_4U$: C, 43.22; H, 7.91; N, 0.00. Found C, 42.89; H, 8.21; N, 0.00. ^{1}H NMR (200 MHz, toluene-d_8, 298 K): δ 0.11 (s, 81H, OC(CH$_3$)$_3$), 1.56 (s, 24H, CH$_2$-18c6), 5.91 (s, 27H, OC(CH$_3$)$_3$).

Integration of the ^{1}H NMR peaks in the spectrum of the reaction mixture in deuterated toluene with respect to an internal standard (naphthalene) allows for elucidation of the yield of **4** (9.2 mg, 45(3)%) and [U(OSi($O^tBu)_3$)$_4$] (7.6 mg, 44(3)%). Both **4** and [U(OSi($O^tBu)_3$)$_4$] are formed in a 1:1 ratio as expected.

X-ray Crystallography. Diffraction data were taken using an Oxford-Diffraction XCallibur S κ geometry diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). To prevent evaporation of cocrystallized solvent molecules, the crystals were coated with light hydrocarbon oil, and the data were collected at 150 K. The cell parameters were obtained with intensities detected on three batches of five frames. The crystal−detector distance was 4.5 cm. The number of settings and frames was established taking into consideration the Laue symmetry of the cell by CrysAlisPro Oxford-Diffraction software:[62] 523 for **2** and **3**·(hexane)$_{0.5}$ and 377 for **4**·(toluene)$_{1.25}$. Narrow data were collected for 1° increments in ω with a 6 s exposure time for **2** and **3**·(hexane)$_{0.5}$ and 20 s for **4**·(toluene)$_{1.25}$. Unique intensities detected on all frames using the Oxford-Diffraction RED program were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections for **3**, using face indexation analytical correction for **4** with the ABSPACK Oxford-Diffraction program.[62] Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure. The structures were solved by direct methods using the Superflip software,[63] refined with Olex2-1.2, and finalized with the shelxtl package computing_structure_refinement. Olex2 is a complete structure solution, refinement, and analysis program.[64] All non-hydrogen atoms were found by difference Fourier syntheses and refined on F^2. Hydrogen atoms were fixed in ideal positions by Fourier synthesis and refined. Full crystallographic details are given in Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ESI/MS, and UV−vis spectra, magnetic and electrochemistry data, computational data, and X-ray crystallographic data and files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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6723

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