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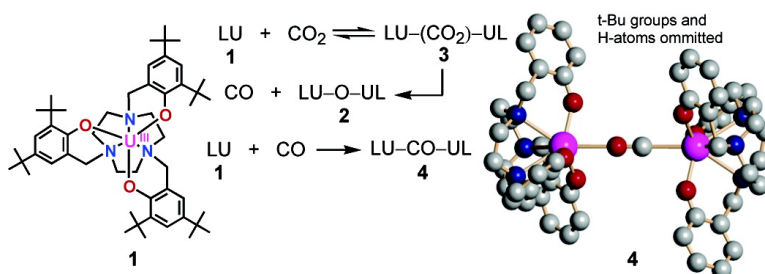
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Carbon Dioxide Reduction and Carbon Monoxide Activation Employing a Reactive Uranium(III) Complex

Ingrid Castro-Rodriguez and Karsten Meyer*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358 La Jolla, California 92093-0358

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In view of the vastness of its supply, carbon dioxide represents a potential source of C1 feedstock for the production of chemicals and fuels. Therefore, interest in the development of metal catalysts that achieve multielectron reduction of carbon dioxide remains high. Our group has previously demonstrated the potential of low-valent uranium complexes for small molecule activation.[1] Encouraged by the remarkable reactivity of our complexes, we set out to exploit this reactivity for CO_2 and CO activation and reduction. Actinide metal carbonyl complexes are scarce but due to potential 6d/5f metal−carbonyl orbital interactions of fundamental importance.[2−5] The continued interest in uranium carbonyl coordination is documented by the [(Cp)$_3$U(CO)] success story: First synthesized in 1986 by Andersen et al.,[2] derivatives of the parent system were crystallographically characterized in 1995[3] and 2003.[5] Cyclopentadienyl derivatives still represent the only uranium complexes known to form carbonyl species; an iso-carbonyl complex of uranium remained elusive. It was reported, however, that lanthanide complexes reduce metal−carbonyl clusters, such as $Mn_2(CO)_{10}$, $Fe_3(CO)_9$, or $Co_2(CO)_8$, to form complexes in which the anionic carbonyl fragment coordinates to the trivalent lanthanide complex via one or more bridging CO ligands. The μ-CO ligand in these M−CO−Ln complexes often is significantly activated.[6,7]

We report here the reaction of the coordinatively unsaturated tris-aryloxide uranium(III) complex [(L)U] (**1**)[8−10] with CO_2 and CO (L = 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclononane, Scheme 1.

Addition of CO_2-saturated pentane (or trace amounts of CO_2 gas) to the deeply colored solution of red-brown **1** in pentane affords a colorless solution. Within minutes of continued stirring, the color changes to pale blue with accompanying CO gas evolution. From the pale-blue solution, the stable μ-oxo bridged U(IV/IV) complex [{(L)U}$_2$(μ-O)] (**2**) was isolated in quantitative yield and characterized by ^{1}H NMR, UV/vis, and X-ray crystallography.[11] The driving force for this remarkable 2e$^−$ cleavage reaction of the thermodynamically stable CO_2 molecule likely is the concerted two ion U(III) to U(IV) oxidation state change, sterically facilitated by the ligand environment. The evolution of CO was qualitatively detected by IR spectroscopy (ν_{CO} = 2145 cm^{-1}). When the reaction is carried out with isotopically labeled $C^{18}O_2$ gas, the reaction results in incorporation of ^{18}O into complex **2**, [{(L)U}$_2$(μ-^{18}O)]. The isotopomers of **2** were characterized by vibrational spectroscopy ($\nu_{as}U^{16/18}OU$).[11] Formation of the intermediate colorless species (**3**) can be monitored by electronic absorption spectroscopy.[11] Attempts to rapidly isolate this intermediate via solvent evaporation in a vacuum resulted in recovery of **1** (Scheme 1). We suggest a dinuclear CO_2-bridged diuranium species as a possible intermediate **3**. This reaction of **1** with CO_2 would be reminiscent of the reductive cleavage of COS by [(Cp′)$_3$U] (Cp′ = MeC$_5$H$_4$), proceeding via a COS-bridged intermediate.[12] Accordingly, complete 2e$^−$ reduction of CO_2 to yield CO and **2** likely proceeds stepwise via a fleeting

Scheme 1
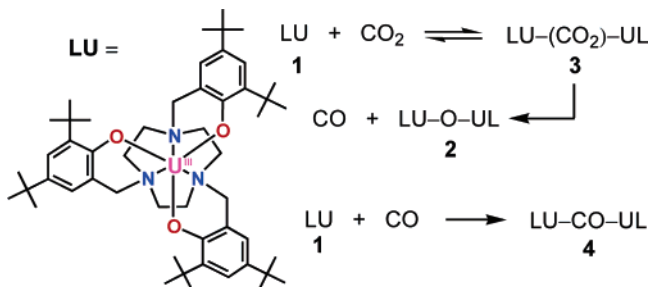
CO_2-bridged intermediate, colorless **3**, that is in equilibrium with **1** and CO_2.

A recent study from our laboratory reported the reaction of CO_2 with the electronically related U(III) complex [(L*)U] with L* = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclononane.[1] It was shown that CO_2 coordination to [(L*)U] with the sterically encumbering adamantane derivatized tacn ligand L* results in 1e$^−$ reduction of CO_2 and formation of a charge-separated complex [(L*)U^{IV}(η^1-OCO$^{\bullet-}$)] featuring an η^1-bound CO_2 radical anion.[1] It therefore seems likely that the *tert*-butyl derivatized ligand of complex **1** does not exhibit sufficient steric bulk to prevent dimerization, thereby permitting complete reduction of CO_2 to CO.

In a separate experiment, the reactivity of **1** toward CO was tested. Exposure of a degassed pentane solution of **1** to CO (1 atm) results in a gradual color change from red-brown to light brown. Solvent evaporation to dryness and recrystallization from benzene yields brown hexagonal crystals of the diuranium species [{(L)U}$_2$(μ-CO)]·3C$_6$H$_6$ (**4**).[11] Dinuclear **4** is only slightly soluble in benzene and crystallizes within weeks. Infrared vibrational spectra of crystalline samples exhibit a distinct band at 2092 cm^{-1} (Nujol), suggestive of a coordinated CO. To confirm this assignment, the synthesis of the isotopically labeled CO complex was attempted. Despite numerous tries, however, CO isotopomers of **4** could not be synthesized. This is most likely due to impurities in commercially available sources of CO isotopes that, among other impurities, contain up to 20 ppm CO_2 and 20 ppm O_2.[11] Both impurities lead to rapid formation of **2**, the only isolable product of all labeling experiments. Hexagonal-shaped single crystals obtained from different preparations were studied by X-ray diffraction analyses.[11] A representative resulting structure [{(L)U}$_2$(μ-CO)] in crystals of **4**·3C$_6$H$_6$ (ORTEP plot, Figure 1) was modeled by employing an unsymmetrical U−CO−U entity, with one short U−C bond and a longer U−O isocarbonyl interaction, disordered on two positions at the inversion center.[11] This structure reveals two staggered [(L)U] fragments linked via a linearly bridged CO ligand in a μ:η^1,η^1 fashion. The diatomic CO bridge is centered on a crystallographic inversion center and is fully disordered. The structure is of limited resolution, and thus, no reliable bond distance data are available for the bridging CO ligand.
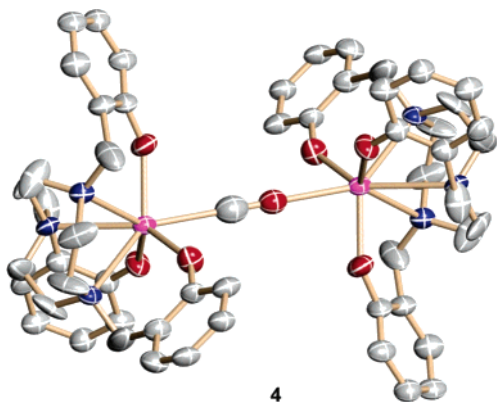
Figure 1. Idealized molecular structure of $[\{(L)U\}_2(\mu: \eta^1,\eta^1\text{-CO})]$ (**4**) in crystals of **4**·$3C_6H_6$. Hydrogen atoms, *tert*-butyl groups, and cocrystallized solvent molecules are omitted for clarity, and thermal ellipsoids are shown at 50% probability.
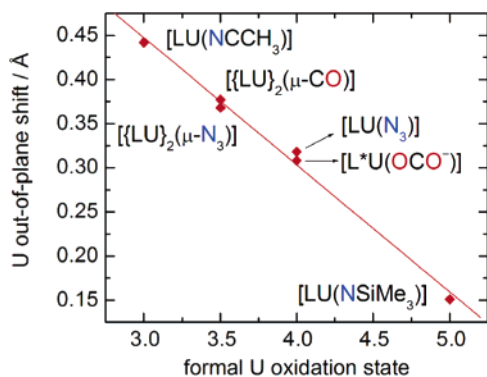

Figure 2. Plot of the uranium out-of-plane shift (as found in the solid-state molecular structure) vs the formal U ions' oxidation state (values for $[(L)U(X)]$, $X = CH_3CN$, N_3^-, Me_3SiN^{2-}, and $CO_2^{\bullet-}$ taken from refs 1 and 9).

The average U−O(ArO) and U−N(tacn) distances in **4** were determined to be 2.185(5) and 2.676(4) Å. The U−N(tacn) bond distance is very similar to that found in the (L)U fragments of $[(L)U(\text{alkane})]$ ($d(\text{U−N(tacn)}) = 2.676(6)$ Å)[10] and $[(L)U(NCCH_3)]$ ($d(\text{U−N(tacn)}) = 2.699(6)$ Å).[9] In contrast, the average U−O(ArO) bond distance in **4** is significantly shorter than those found in structurally related trivalent (L)U complexes. In fact, $d(\text{U−O(ArO)})$ in **4** is similar to the corresponding U−O(ArO) distances found in tetravalent $[(L)U(OAr)]$ with $d(\text{U−O(ArO)}) = 2.195(4)$ Å.[8] Another noteworthy structural parameter of **4** is the displacement of the U ion out of the idealized trigonal aryloxide plane toward the coordinated tacn polyamine chelator. While the trivalent U ion in seven-coordinate $[(L)U(NCCH_3)]$ is situated -0.442 Å below the ligand plane, the out-of-plane shift in **4** was determined to be only -0.377 Å. A diagram delineating this structural parameter for known complexes of the $[(L)U(L_{ax})]$ type clearly illustrates a linear correlation of higher oxidation states with smaller out-of-plane shifts (Figure 2).[1,9] On the basis of this correlation and in agreement with the crystallographic disorder, **4** can be assigned an average oxidation state of $+3.5$ suggestive of a mixed-valent U(III/IV) species.[11] Hence, we propose formation of dinuclear **4** via the nucleophilic attack of a charge-separated $LU^{IV}-CO^{\bullet-}$ fragment on the coordinatively unsaturated U(III) of $[(L)U]$ (**1**). This mechanism is reminiscent of that suggested by Tilley and Andersen for the charge-separated complex $[(CO)_3Co-CO-Yb(Cp^*)_2(THF)]$.[7] In this context, the μ-azido-bridged U(III/IV) species $[\{(L)U\}_2(\mu\text{-}N_3)]$ (**5**)[11] was synthesized by reacting $[(L)U^{IV}(N_3)]$ with $[LU^{III}]$ to serve as an isostructural analogue of triatomic-bridged intermediate **3** as well as an electronic model for mixed-valent **4**. The out-of-plane shift found in mixed-valent **5** is virtually identical to that of **4** (Figure 2) and thus supports the charge separation proposed for mixed-valent **4**.

In summary, we reported the $2e^-$ reduction of CO_2 by the U(III) species **1** to yield CO and μ-oxo bridged **2**. This reaction proceeds via a colorless intermediate **3**, which was observed spectroscopically. Complex **1** also reacts with CO to yield the first crystallographically characterized CO-bridged diuranium complex **4** with a $\mu:\eta^1,\eta^1$ CO ligand and mixed U(III/IV) valences. The $\mu:\eta^1,\eta^1$ CO binding mode reported here is, to the best of our knowledge, unprecedented in uranium coordination chemistry and thus complements the only other crystallographically characterized uranium carbonyl species, $[(Cp)_3U(CO)]$ ($Cp = C_5Me_4H$, C_5Me_5), both featuring an η^1-coordinated CO ligand.[3,5] The bridging μ-CO binding mode in **4** has previously only been observed for di- and polynuclear TM metal carbonyls and their adducts with oxophilic metals, such as Ti(III), V(III), Al(III), lanthanides, alkaline, and earth-alkaline ions.[6,7,13]

Supporting Information Available: Experimental and spectroscopic details of the new compounds, ORTEP plots, and details for the refinement of **4**, **5**, and $[(L)U(THF)]$ (PDF, CIF).[11] This material is available free of charge via the Internet at http://pubs.acs.org.

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