CO Hydrogenation

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Hydrogenation of CO at a Uranium(III) Center**

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carbon monoxide · coupling · reduction · Fischer–Tropsch synthesis · uranium

Historically, the production of liquid hydrocarbons through the hydrogenation of CO has been explored in times of fossil fuel shortages.[1] This area is currently gaining industrial importance because of rising demands for clean and renewable energy sources. One of the fundamental carbon-fixation reactions in nature is believed to follow the Wood–Ljungdahl pathway, a process where acetyl-CoA is generated from CO, which is either recruited environmentally or enzymatically by reduction of CO_2.[2] However, owing to the stability of inert CO, copying this archetypal reaction poses a major challenge for chemists. An appropriate reducing metal complex is needed to activate and functionalize this and other inert small molecules, such as CO_2 and N_2 which are building blocks of life. In the last decades, low-valent uranium complexes have emerged as excellent candidates for the activation of small molecules. Indeed, Fritz Haber reported that "*uranium as a catalyst exceeds all literature-reported systems in efficiency*" with regards to the conversion of N_2 to NH_3.[3] Recent accounts also suggest that uranium is a suitable additive in the Fischer–Tropsch process, which converts CO and H_2 to liquid fuels.[1,4–7]

Despite uranium's demonstrated potential, the reactions of the f elements with CO are relatively unexplored, especially when compared to the analogous reactions involving transition metals. This observation can perhaps be attributed to the poor π backbonding properties of f element complexes. Synthesized in 1986 by Andersen et al., the first CO complex of uranium, $[(C_5H_4SiMe_3)_3U(CO)]$, displays a certain degree of π backdonation; this was deduced based on the significantly weakened CO stretch of 1976 cm^{-1} in the IR spectrum compared to the analogous band at 2145 cm^{-1} for gaseous CO.[8] Similarly, the crystallographically characterized uranium carbonyl complex $[(C_5Me_4H)_3U(CO)]$, which features the C–O stretch at 1922 cm^{-1} (KBr), was thought to also possess U–CO π backbonding.[9] However, recent density functional theory (DFT) calculations concluded that in $[Cp'_3U]$ ($Cp' = C_5H_4SiMe_3$, C_5HMe_4), the weakening of the C–O bond is due to backbonding from filled ligand-based π orbitals rather than nonbonding metal-based f orbitals.[10]

Employing the sterically more crowded pentamethylcyclopentadienyl ligand, instead of C_5Me_4H, Evans et al. were able to crystallographically characterize the uranium carbonyl complex $[(C_5Me_5)_3U(CO)]$.[11] An inorganic dinuclear mixed-valent uranium carbonyl complex with a Werner-type chelator, namely $[\{((t\mathrm{BuArO})_3\mathrm{tacn})U\}_2(\mu\text{-}CO)]$ ($((t\mathrm{BuArO})_3\mathrm{tacn}$ = trianion of 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane), has also been obtained, purportedly through the nucleophilic attack of $[LU^{IV}–CO^{\bullet-}]$ on $[LU^{III}]$.[12] These few examples up until 2006 helped to advance the field of uranium chemistry and stoked the ongoing discussion on the participation of f orbitals in uranium–ligand bonding. However, in all of these cases the CO ligand was not sufficiently activated or sterically too shielded to engage in further chemical transformations; this would be particularly useful, since the reductive homologation of CO has garnered much interest in the context of C–C bond formation and the Fischer–Tropsch process. The cyclomerization of five and six units of CO has been demonstrated with molten alkali metals, forming croconate and rhodizonate dianions, respectively (Figure 1, **D** and **E**).[13] The squarate dianion (Figure 1, **C**) can be generated by electrochemical methods at very high CO pressures.[14] The formation of the trigonal deltate anion (Figure 1, **B**) from CO eluded researchers until 2006, when Cloke et al. reported the facile cyclotrimerization of CO via a mixed-sandwich U^{III} complex $[U(\eta^5\text{-}Cp^*)\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si\mathit{i}Pr_3)_2\}]$.[4]

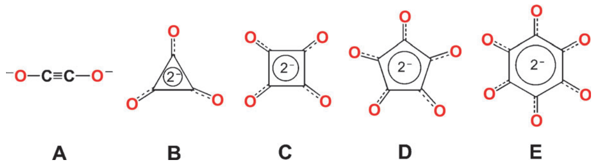

Figure 1. Structures of dianionic $C_nO_n^{2-}$ species ($n = 2–6$).

Subtle steric alterations in the ligand environment also allowed for the isolation of a cyclotetramerized product, the uranium squarate complex.[5] This reaction was suggested to proceed through a relatively long-lived "zigzag" $U–C_2O_2–U$ intermediate, which reacts further with CO (Scheme 1).[6] Thus, under stoichiometric conditions, the uranium ethyne-

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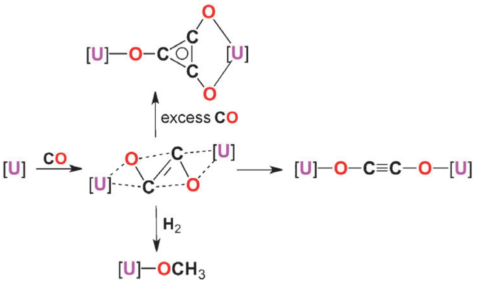
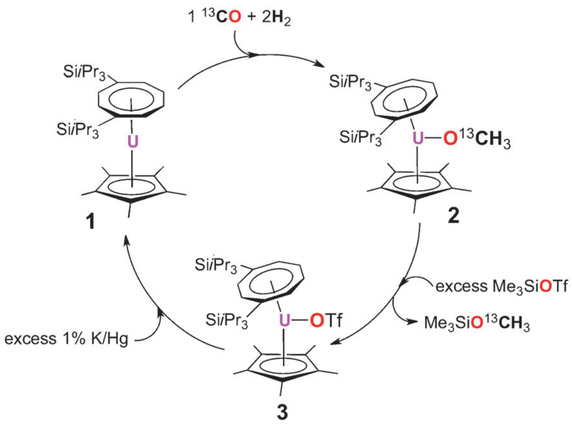


Scheme 1. Reactivity of the "zigzag" U–C_2O_2–U intermediate. [U] = $[U(\eta^5\text{-}Cp^*)\{\eta^8\text{-}1,4\text{-}(SiiPr_3)_2C_8H_6\}]$.

diolate complex $[\{U(\eta^5\text{-}Cp^*)[\eta^8\text{-}1,4\text{-}(SiiPr_3)_2C_8H_6]\}]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2O_2)]$ (Figure 1, **A**) is produced (Scheme 1).[6] Since then, there have been two more reports describing the reductive coupling of CO by uranium to form alkynediolates.[15,16]

Recently, in Fischer–Tropsch-inspired fashion, Cloke et al. reported the remarkable reaction of CO/H_2 with the U^{III} complex **1** to give the uranium methoxide complex $[U(\eta^5\text{-}Cp^*)(OMe)\{\eta^8\text{-}1,4\text{-}(SiiPr_3)_2C_8H_6\}]$ (**2**; Scheme 2).[7] Interestingly, the isolated alkynediolate complex $[\{U(\eta^5\text{-}Cp^*)[\eta^8\text{-}1,4\text{-}(SiiPr_3)_2C_8H_6]\}]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2O_2)]$ does not react further with H_2. Hydrogenation only occurs when the U^{III} starting complex $[U(\eta^5\text{-}Cp^*)\{\eta^8\text{-}1,4\text{-}(SiiPr_3)_2C_8H_6\}]$ (**1**) is exposed to 1 equiv of ^{13}CO followed by 2 equiv of H_2 (Scheme 2). With a slight excess of H_2, the reaction proceeds remarkably selectively with no discernible C-containing by-products. The molecular structure of **2** features the terminal methoxide ligand coordinated to the U^{IV} bent-sandwich unit (Figure 2). The U-O-C bond angle is close to linear (178.3(5))° while the U–O bond length is 2.058(4) Å. Although DFT studies support a certain degree of double-bonding between U and O, the silylated methoxide is liberated, alongside formation of the U^{IV} triflate complex **3** (Scheme 2), when **2** is treated with Me_3SiOTf. Conversion of **3** back to **1** is possible through K/Hg reduction in THF. Complex **1** does not react with H_2; this strongly suggests that formation of **2** does not proceed via a uranium(IV) hydride species. Additionally, a solution of the "zigzag" U–C_2O_2–U intermediate (trapped at −78 °C) was demonstrated to react with H_2 to form **2** (Scheme 1). Mechanistically, involvement of a uranium hydride is not likely and hydrogenation of the "zigzag" intermediate is more probable.



Scheme 2. The synthetic cycle involves U-mediated hydrogenation of ^{13}CO to form the methoxide complex **2**, followed by formation of $Me_3SiO^{13}CH_3$ and uranium triflate **3**, which can be reduced back to **1** by treatment with K/Hg.

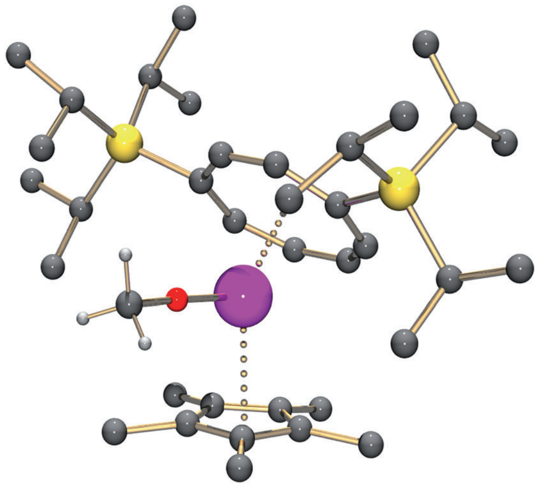


Figure 2. Ball-and-stick representation of **2**. All H atoms, except those of the methoxide, are removed for clarity; U violet, Si yellow, O red, C gray.

This work of Cloke et al. showcases the reducing power of trivalent uranium complexes and demonstrates impressively two U metal centers working cooperatively for the effective and facile functionalization of CO. These finding are all the more noteworthy when one considers that trivalent uranium complexes also mediate the reductive disproportionation of CO_2, yielding dinuclear carbonate-bridged uranium complexes and CO.[17,18] Hence, in a hypothetical catalytic cycle, CO_2 is transformed to CO, which subsequently is converted to methanol or its derivatives.

As building blocks of life and potential chemical feedstocks, CO, CO_2, and N_2 are actively studied in numerous fields, such as biology, inorganic chemistry, and electrochemistry. The approaches may differ but the goals are similar—the synthesis of medicinally, chemically, and industrially relevant materials by nature-inspired processes like nitrogen and carbon fixation.

Although only stoichiometric, the CO_2 reduction and CO hydrogenation reactions presented by Cloke et al. represent significant milestones in the activation and functionalization of carbon oxides. Liberating the functionalized product and achieving a stoichiometric cycle are crucial steps to developing efficient catalytic processes. Further studies on the activation of small molecules with uranium will undoubtedly yield fruitful advances in the field of uranium catalysis. Given the richness of the chemistry of uranium(III) complexes observed thus far, we can anticipate more unusual bonding and reactivity rarely observed with other metals.

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