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Reductive Coupling of Six Carbon Monoxides by a Ditantalum Hydride Complex

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Sequential coupling of carbon monoxide, which leads to formation of oxocarbons $(CO)_n$, has represented a basic challenge to the development of CO chemistry. A number of metal complexes are known to promote incorporation of CO as carbon units into organic substrates,[1] while the chaining of CO beyond two is rare due to the great tendency of neutral $(CO)_n$ toward dissociation into CO.[2−4]

To overcome this synthetic difficulty, one promising approach is reductive coupling of CO to produce anionic oxocarbons, which are stable relative to the corresponding neutral form.[5] High reduction potentials of low-valent f-elements can be applicable to reductive CO coupling. For instance, lanthanocenes of La(II) and Sm(II) have been reported to reduce CO at 90 psi, yielding a dianionic ketene carboxylate unit.[6] Recently, U(III) complexes have been demonstrated to undergo reductive cyclo-trimerization and -tetramerization of CO under mild conditions.[7] Here we describe reduction of CO with a ditantalum hydride complex, resulting in head-to-head C−C coupling of six CO molecules.

We have previously reported the synthesis of **1** by the reaction of $[(OOO)TaCl_2]_2$ with $KBHEt_3$ ($H_3[OOO]$ = 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-*tert*-butylphenol, the C−H activated ligand is denoted as $[OOCO]^{4-}$), in which a methylene linker of the [OOO] ligand backbone undergoes cyclometalation.[8] This C−H activation is reversible, and **1** can serve as a low-valent tantalum precursor. Thus we examined reduction of CO by **1** (Scheme 1).

Exposure of a THF solution of **1** to an atmosphere of CO under 1 atm at room temperature produced a gradual color change from yellow to deep green over a period of 60 min. After removal of volatiles in vacuo, slow diffusion of hexane into a DME solution of the residue afforded **2** as green crystals in 31% isolated yield. Formally, one can consider the oxidation state of each Ta in **1** and **2** to be Ta(V) and the C_6O_6 unit as an octaanion. The stoichiometry assumes that 2 equiv of **1** furnish eight electrons needed to convert 6 equiv of CO to a $[C_6O_6]^{8-}$ unit. Since **2** contains no C−H activated ligand, two of the three hydrides in each **1** migrate to the [OOCO] ligands. The other hydride remains as a terminal ligand in the product **2**. Overall, the eight-electron reduction can be accounted for by four two-electron C−H reductive eliminations. A single crystal X-ray diffraction study of **2** confirmed its formulation.[9] The presence of hydride ligands in **2** was further established by other means.

The reaction of metal hydrides with proton (H^+) sources is a well-known reaction, and formation of H_2 and a solvated metal complex has been used as a diagnostic test for metal hydrides.[10] Performing protonation of **2** with $[Me_3NH][BPh_4]$ in THF resulted in H_2 gas evolution and the generation of **3** with concomitant precipitation of $K[BPh_4]$ as a white solid.

Slow diffusion of hexane into the THF solution of **3** yielded green crystals that were suitable for X-ray structure analysis (Figure 1). A striking feature of the molecular structure is the encapsulation of a C_6O_6 unit within a shell comprised of four Ta fragments. There is a crystallographic inversion center between C(3) and C(3′) that renders the two halves of the molecule equivalent. The C_6O_6 unit is bound to Ta(1) and Ta(1′) in a $\kappa^2 O,O$ mode, while it is bound to Ta(2) and Ta(2′) in a $\kappa^2 C,O$ mode. Each tantalum atom has an octahedral geometry, with the remainder of the coordination sphere being completed by a tridentate [OOO] ligand and a THF ligand. As a consequence of H_2 release, THF binds to the Ta to offset the loss of the hydride ligands.

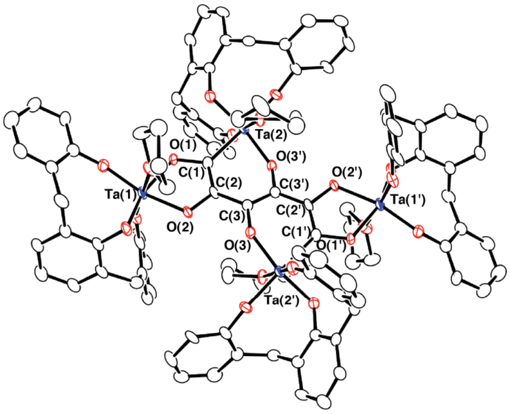

Figure 1. Molecular structure of **3**. All methyl and *tert*-butyl groups attached to the aryloxides have been omitted for clarity.

A close look at the bond distances within the $Ta_4C_6O_6$ core gives insight into electron localization within the complex. The average Ta−O and Ta−C distances 1.964(5) and 2.198(8) Å are in the ranges for the corresponding single bonds.[11,12] The C−O distances [average 1.379(9) Å] are comparable to enolate C−O bond distances.[12,13] The C(1)−C(2)−C(3)−C(3′)−C(2′)−C(1′) linkage exhibits short−long bond alternation as follows: 1.367(11), 1.455(10), and 1.357(16) Å, respectively. These metric parameters suggest an important contribution from a hexatriene−hexaolate form as shown in Scheme 1.

Complexes **2** and **3** are further characterized by NMR spectroscopy. The ^1H NMR spectrum of **2** at 253 K in THF-d_8 exhibits the number of the peaks expected for a molecule with C_i point group symmetry, as observed in the solid state. A singlet resonance typical of a terminal tantalum hydride is observed at 17.59 ppm integrating to 2H.[11,14] As the temperature is raised, these signals are severely broadened. For **3**, the low-temperature ^1H NMR spectrum indicated the presence of isomers[15] in equilibrium. Warming the sample results in observation of a time-average C_{2h} symmetric molecule. These behaviors are caused by a fluxional process involving dynamic dissociation and recoordination of the THF ligands.

To confirm the origin of the C_6O_6 unit, the isotopically enriched product **2-^{13}C** was analogously prepared by treatment of **1** with ^{13}CO. Subsequent protonation of **2-^{13}C** yielded **3-^{13}C**. The ^{13}C NMR spectrum of **2-^{13}C** exhibits three resonances for the C_6O_6 unit at 143.1, 160.2, and 219.3 ppm, but C−C coupling is not adequately

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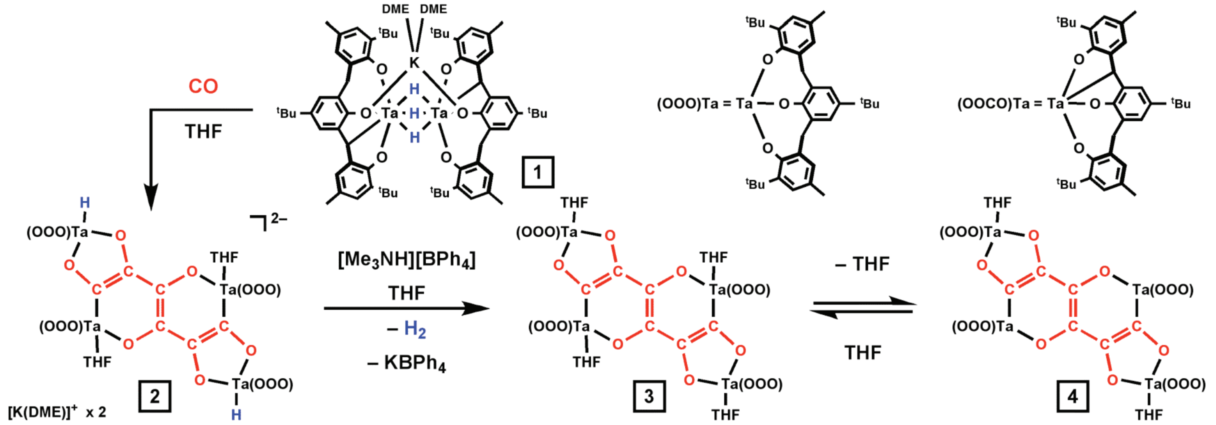
Scheme 1



resolved even at low temperatures owing to a broadening of resonances associated with a reversible THF-dissociation process. In the ^{13}C NMR spectrum of **3-^{13}C** at 323 K, the corresponding resonances appear as multiplets and are downfield shifted at 145.1, 165.5, and 221.3 ppm. These data unambiguously confirm that all carbon atoms in the C_6O_6 unit arise from external CO.

Additional evidence of the lability of the THF ligands is provided by isolation of a desolvated product from **3**. One observation is that loss of THF undergoes a striking color change from green to purple upon exposure of **3** to vacuum in solid or dissolution of **3** in toluene. Addition of THF to the purple product results in regeneration of the diagnostic green color of **3**. Standing a saturated pentane solution of **3** afforded purple crystals identified as **4** by X-ray structure analysis.[9] Dissociation of the two THF ligands creates two trigonal-bipyramidal Ta centers, while the other Ta metals remain octahedral. The $Ta_4C_6O_6$ core is reserved, and its internal C−C bond distances exhibit a pattern similar to that found in **3**.

The UV−visible spectra of the C_6O_6 complexes deserve some comments. High oxidation aryloxide complexes are usually light-colored. For example, **1** is yellow. In contrast, intense colors are noted for the C_6O_6 complexes. The UV−visible spectra of **2**, **3**, and **4** contain broad absorptions in the region between 500 and 700 nm with extinction coefficients from 8300 to 12 000 M^{-1} cm^{-1}, which are assigned to the HOMO→LUMO transitions.[9] Since the HOMO has mainly hexatriene π orbital character and the LUMO gains contribution from tantalum d orbitals in addition to the π* orbital of the hexatriene unit, the observed absorptions are attributable to ligand-to-metal charge transfer transition.[16]

We have shown that multielectron reductive chemistry of transition metals can be applicable to the chaining of CO. The sequence of reductive coupling beginning with the hydride complex **1** ceases with the C_6O_6 complex, which was not found to react with CO. Prevention of further CO homologation is possibly due to the lack of d-electrons available for reducing CO. The C_6O_6 complexes are remarkably stable as long as they are not exposed to O_2 and water. Coordination to tantalum is ascribed to stabilizing an acyclic CO linkage.

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Supporting Information Available: Experimental procedures in PDF format. X-ray structural data of **2**, **3**, and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Each THF ligand can be situated above and below the $Ta_4C_6O_6$ plane.
(16) To gain more insight into the electronic structures of the complexes, DFT calculations were performed. See SI for details of these results.

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