

## 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)<sub>n</sub>, 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,<sup>1</sup> while the chaining of CO beyond two is rare due to the great tendency of neutral (CO)<sub>n</sub> toward dissociation into CO.<sup>2–4</sup>

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.<sup>5</sup> 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.<sup>6</sup> Recently, U(III) complexes have been demonstrated to undergo reductive cyclo-trimerization and -tetramerization of CO under mild conditions.<sup>7</sup> Here we describe reduction of CO with a ditantalum hydride complex, resulting in head-to-head C–C coupling of six CO molecules.

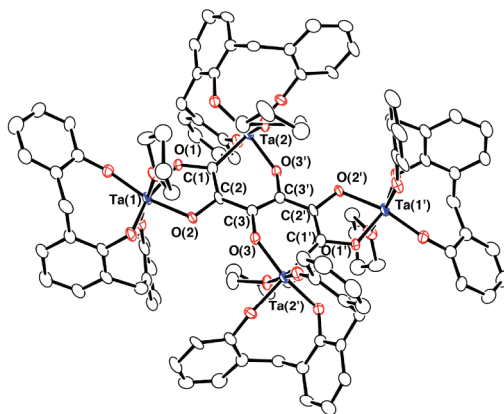
We have previously reported the synthesis of **1** by the reaction of [(OOO)TaCl<sub>2</sub>]<sub>2</sub> with KBHEt<sub>3</sub> (H<sub>3</sub>[OOO] = 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-*tert*-butylphenol, the C–H activated ligand is denoted as [OOCO]<sup>4–</sup>), in which a methylene linker of the [OOO] ligand backbone undergoes cyclometalation.<sup>8</sup> 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<sub>6</sub>O<sub>6</sub> 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<sub>6</sub>O<sub>6</sub>]<sup>8–</sup> 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.<sup>9</sup> The presence of hydride ligands in **2** was further established by other means.

The reaction of metal hydrides with proton (H<sup>+</sup>) sources is a well-known reaction, and formation of H<sub>2</sub> and a solvated metal complex has been used as a diagnostic test for metal hydrides.<sup>10</sup> Performing protonation of **2** with [Me<sub>3</sub>NH][BPh<sub>4</sub>] in THF resulted in H<sub>2</sub> gas evolution and the generation of **3** with concomitant precipitation of K[BPh<sub>4</sub>] 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<sub>6</sub>O<sub>6</sub> unit within a shell comprised of four Ta fragments. There is a crystallographic inversion center between C(3) and C(3')

renders the two halves of the molecule equivalent. The C<sub>6</sub>O<sub>6</sub> unit is bound to Ta(1) and Ta(1') in a κ<sup>2</sup>O,O mode, while it is bound to Ta(2) and Ta(2') in a κ<sup>2</sup>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<sub>2</sub> release, THF binds to the Ta to offset the loss of the hydride ligands.



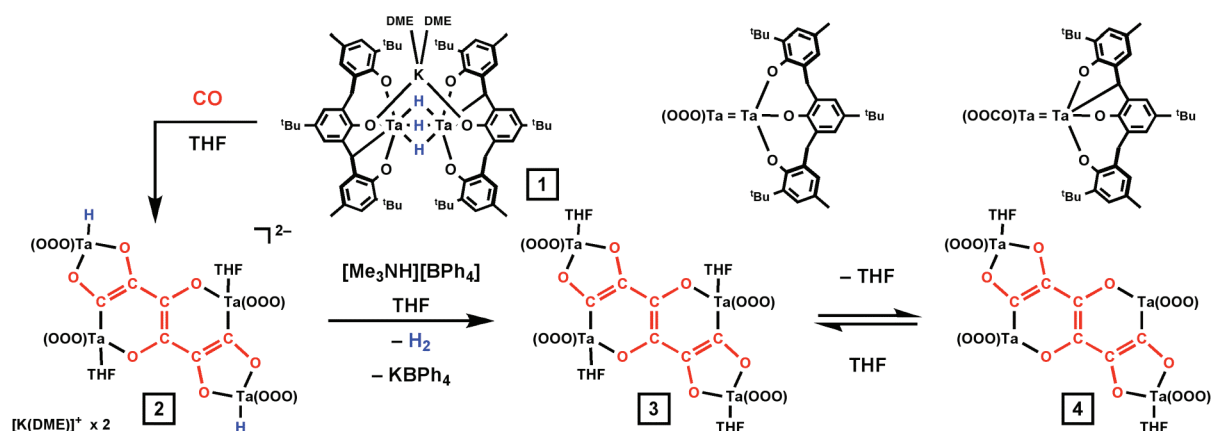
**Figure 1.** Molecular structure of **3**. All methyl and *tert*-butyl groups attached to the aryloxides have been omitted for clarity.

A close look at the bond distances within the Ta<sub>4</sub>C<sub>6</sub>O<sub>6</sub> 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.<sup>11,12</sup> The C–O distances [average 1.379(9) Å] are comparable to enolate C–O bond distances.<sup>12,13</sup> 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–hexaoxolate form as shown in Scheme 1.

Complexes **2** and **3** are further characterized by NMR spectroscopy. The <sup>1</sup>H NMR spectrum of **2** at 253 K in THF-*d*<sub>8</sub> exhibits the number of the peaks expected for a molecule with C<sub>i</sub> 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.<sup>11,14</sup> As the temperature is raised, these signals are severely broadened. For **3**, the low-temperature <sup>1</sup>H NMR spectrum indicated the presence of isomers<sup>15</sup> in equilibrium. Warming the sample results in observation of a time-average C<sub>2h</sub> 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<sub>6</sub>O<sub>6</sub> unit, the isotopically enriched product **2**-<sup>13</sup>C was analogously prepared by treatment of **1** with <sup>13</sup>CO. Subsequent protonation of **2**-<sup>13</sup>C yielded **3**-<sup>13</sup>C. The <sup>13</sup>C NMR spectrum of **2**-<sup>13</sup>C exhibits three resonances for the C<sub>6</sub>O<sub>6</sub> unit at 143.1, 160.2, and 219.3 ppm, but C–C coupling is not adequately

Scheme 1



resolved even at low temperatures owing to a broadening of resonances associated with a reversible THF-dissociation process. In the <sup>13</sup>C NMR spectrum of **3**-<sup>13</sup>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<sub>6</sub>O<sub>6</sub> 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.<sup>9</sup> Dissociation of the two THF ligands creates two trigonal-bipyramidal Ta centers, while the other Ta metals remain octahedral. The Ta<sub>4</sub>C<sub>6</sub>O<sub>6</sub> 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<sub>6</sub>O<sub>6</sub> 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<sub>6</sub>O<sub>6</sub> 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<sup>−1</sup> cm<sup>−1</sup>, which are assigned to the HOMO→LUMO transitions.<sup>9</sup> 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.<sup>16</sup>

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<sub>6</sub>O<sub>6</sub> 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<sub>6</sub>O<sub>6</sub> complexes are remarkably stable as long as they are not exposed to O<sub>2</sub> 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<sub>4</sub>C<sub>6</sub>O<sub>6</sub> 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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