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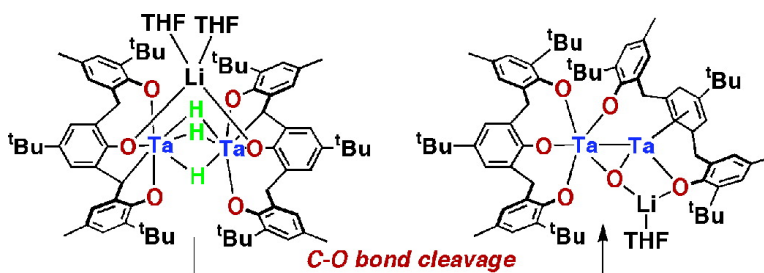
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# Aryl−Oxygen Bond Cleavage by a Trihydride-Bridging Ditantalum Complex

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Hydrodeoxygenation (HDO) is an important industrial process for the removal of oxygen from coal and biomass-derived feeds.[1] The study of C−O bond activation by metal complexes in solution is very attractive for understanding and improving the HDO process.[2−5] Of the O-containing compounds, phenol and its derivatives are among the most resistant toward HDO. There are few unequivocal examples of aryl−O bond cleavage by metal complexes. For example, Milstein described the insertion of Rh(I) and Pd(II) into the C−O bond of an aryl ether and a phenol under mild conditions.[2] A titanium complex reported by Schrock underwent C−O bond cleavage of the bis(anilide)−ether ligand.[3] On the other hand, activation of the sp[2] C−O bond of 1,2-hydrofuran and benzofuran by transition metals was also reported.[4]

Following our recent report on the reaction chemistry of [(ᵗBu-L)NbCl₂]₂ [H₃(ᵗBu-L) = 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxy-benzyl)-4-*tert*-butyl-phenol], which was treated with LiBHEt₃ under N₂ to produce the nitride Nb(V) complex along with the cleavage of N≡N,[6] we now report related results on the corresponding Ta system. Our studies have yielded a new Ta(V) hydride complex with some unusual reactivity, including HDO of the ligand.

**Scheme 1**
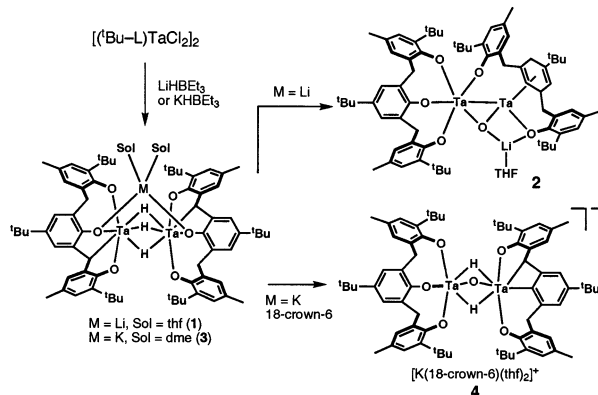
Treatment of [(ᵗBu-L)TaCl₂]₂ in toluene with 5 equiv of LiBHEt₃ in THF afforded yellow [(*bit*-ᵗBu-L)Ta]₂(μ-H)₃Li(thf)₂ (**1**) in 41% yield after workup, together with some brown crystals (**2**, vide infra) (Scheme 1). The formation of **1** is believed to proceed via a Ta(III)−Ta(III) intermediate which undergoes intramolecular addition of a methylene CH bond.[7] The molecular structure of **1** shows the dimer to be bridged by three hydrides (Figure 1), which were located and refined isotropically. Each $C_{ipso}$ carbon of the inner aryloxide of the *bit*-ᵗBu-L ligand forms close contact with the metal center [2.420(4) and 2.426(3) Å]. This is presumably a consequence of the conformational constraint imposed by the *bit*-ᵗBu-L framework in **1**. One lithium cation, solvated by two THF molecules, is connected to two inner aryloxides [O(2), O(5)] of the *bit*-ᵗBu-L ligands. Thus, the opposing *bit*-ᵗBu-L ligands on Ta(1) and Ta(2) are eclipsed, with a negligible O(2)−Ta(1)−Ta(2)−O(5) torsion
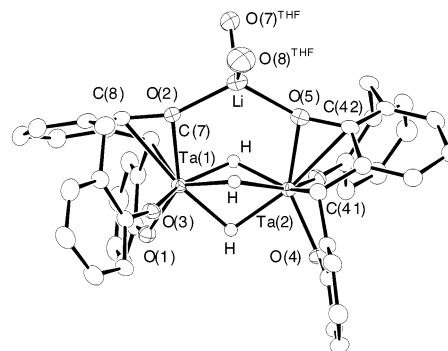
**Figure 1.** Molecular structure of **1**. Methyl and *tert*-butyl groups of the ligands and the THF groups (except for the oxygen atom) have been omitted for clarity.

angle of 6.4(1)°. The short Ta−Ta distance of 2.9313(4) Å is presumably imposed by the hydride bridges.

The cyclometalation of the ligand was also confirmed by its ¹H NMR spectrum. The metal-bound methine group appears as a singlet at 3.88 ppm in the ¹H NMR spectrum at room temperature. The remaining methylene protons of the ligand are observed as a pair of AB doublets at 4.77 and 3.46 ppm. In addition, the bridging hydrides appear equivalent at 10.8 ppm, and no change is seen at −80 °C. On warming up to 60 °C, although **1** partially decomposes, these resonances due to methine, methylene, and hydride protons are observed to coalesce. This is consistent with the methylene CH activation process being reversible. Thus, the cyclometalated-hydride complex **1** could provide a masked form of a low-valent tantalum dimer.[8]

Complex **1** is thermally unstable and gradually undergoes rearrangement. Over 6−8 weeks in solution, **1** is transformed into the brown compound **2** in 18% isolated yield.[9] Unlike **1**, the brown compound **2** displays $C_1$ symmetry in solution, as shown by its ¹H NMR spectrum, and in the solid state, as demonstrated by X-ray crystallography. The rearrangement leading to **2** includes C−O bond scission, accompanied by the migration of three hydrides to one phenyl and two methine carbons.

The dimer **2** (Figure 2) contains two different Ta atoms: Ta(1) is bonded to an η⁶-phenyl ring, two aryloxides, and a μ-oxo atom, whereas Ta(2) is bonded to four aryloxides and a μ-oxo atom. The phenyl ring coordinated to Ta(1) is puckered with a dihedral angle of 18° between the planes defined by C(9)−C(8)−C(13)−C(12) and C(9)−C(10)−C(11)−C(12), which implies appreciable sp³ character at C(9) and C(12). The Ta−C bonds also reflect this trend, with shorter Ta(1)−C(9) [2.20(1) Å] and −C(12) [2.311(9) Å] bonds than the other four Ta−C interactions (2.38−2.41 Å). Additionally, the C−C bonds in this phenyl ring are atypical, with short C(8)−C(13) and C(10)−C(11) distances of 1.38(2) and 1.36(2) Å, respectively, and longer other C−C distances ranging from 1.42(1) to 1.49(1) Å. These parameters suggest a significant contribution from a cyclohexadiene-diyl resonance structure. This coordination environment is similar to that observed previously for
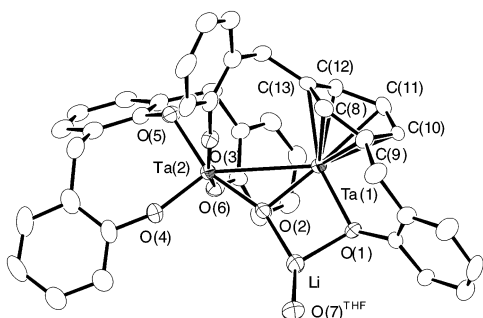
**Figure 2.** Molecular structure of **2**. Methyl and *tert*-butyl groups of the ligands and the THF group (except for the oxygen atom) have been omitted for clarity.

$(\eta^6$-C$_6$Et$_6$)Ta(O-2,6-$^i$Pr-C$_6$H$_3$)$_2$.[10] Thus, **2** may be viewed as an oxo-bridged dimer containing two Ta(IV) centers with a cyclohexadiene-diyl fragment. Although the Ta–Ta distance of 3.0943(4) Å is long, it is in the range observed for tantalum–tantalum bonding interactions.[11] This could explain the observed diamagnetism.

Formation of **1** as a lithium salt prompted us to explore the effect of other alkali cations. A similar reaction of [($^t$Bu-L)TaCl$_2$]$_2$ with KBHEt$_3$, followed by recrystallization from DME, afforded [(*bit*-$^t$Bu-L)Ta]$_2$($\mu$-H)$_3$K(dme)$_2$ (**3**). An X-ray crystal structure determination revealed a dimer similar to **1** with crystallographic 2-fold symmetry. Treatment of **3** with 18-crown-6 in THF produced light yellow crystals of **4** in 73% yield. Like **2**, the solid structure of **4** shows the $\mu$-oxo ditantalum moiety associated with C–O bond cleavage of the ligand (Figure 3). One hydride has migrated back to the methine carbon, restoring the tridentate $^t$Bu-L ligand bound to Ta(2). The two other hydrides remain intact and bridge the Ta–Ta unit. These were located in the diffraction experiment and give resonances at 10.3 and 12.1 ppm in the $^1$H NMR spectrum. As a result, the aryl–alkyl-bis(aryloxide) ligand coordinates to Ta(1). The Ta–Ta distance of 2.8944(6) Å is shortened relative to that of **1**, reflecting the small Ta(1)–O(1)–Ta(2) angle of 96.5(3)°.
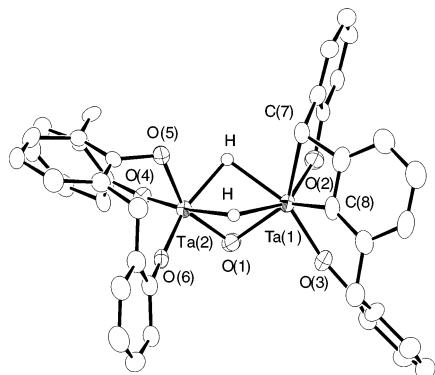


**Figure 3.** Structure of the anion part of **4**. Methyl and *tert*-butyl groups of the ligands have been omitted for clarity.

Isolation of **4** provides insight into the transformation of **1** into **2**, and a proposed mechanism is shown in Scheme 2. The first step is likely the migration of one hydride to the methine carbon of the *bit*-$^t$Bu-L ligand to form a dihydride Ta(IV)–Ta(IV) intermediate. Subsequent C–O scission occurs across the metal–metal bond, in which two electrons stored in the metal–metal bonding are used

to yield an oxo-dihydride dimer analogous to that found in **4**. The final formation of **2** requires the migration of two hydrides to a methine and an aryl carbon, respectively. As the conversion of **1** to **2** was monitored by NMR spectroscopy, the formation of the dihydride species, which exhibits resonances similar to those of **4**, was noticed as an intermediate. This is consistent with the proposed mechanism. The overall transformation implies an internal redox process and does not require electrons to be added to or removed from **1**. Further work to clarify the promising behavior of cyclometalated hydride dimers is in progress.

***Scheme 2***
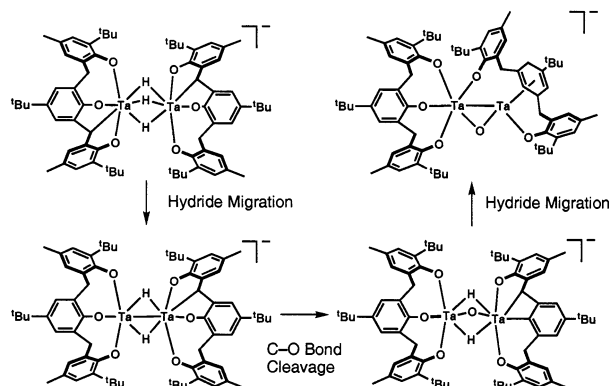
**Supporting Information Available:** Experimental procedures, analytical data, spectroscopic data (PDF), and X-ray crystallographic files (in CIF format) for **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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