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Communication

A Tantalum(V) Carbene Complex: Formation of a Carbene–Bis(phenoxide) Ligand by Sequential Proton and Hydride Abstraction

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Proton and subsequent hydride abstraction from the bis(phenoxide) ligand of the trimethyltantalum(V) complex affords a cationic tantalum(V) carbene complex, in which two phenoxide groups are linked to the carbene center. The electrophilic nature of the carbene functionality is demonstrated by the reaction with PPh_3.

Bis(phenoxides), in which the two phenoxide rings are linked to a donor atom (X) such as S and P in the ortho positions, have been useful dianionic ancillary ligands in coordination chemistry and homogeneous catalysis.[1] In these types of hybrid [**OXO**] ligands that combine the hard phenoxide donors with the soft X donor into a chelating array, electronic and stereochemical parameters can be manipulated by modifications of X donor groups so as to accommodate many transition metals in a variety of oxidation states and induce interesting transformations.[2,3] With this in mind, we have begun to study the chemistry of carbene–phenoxide hybrid ligands, where a carbene functionality is introduced at the X donor site.[4] The strong two-electron donor ability of the carbene group was appealing to us.[5] In addition, this ligand system would provide the opportunity to study the effect of the σ-donor carbene functionality on the properties of electron-deficient metal complexes. In this Communication, we report the synthesis and molecular structure of the tantalum(V) complex having the tridentate dianionic bis(2-oxyphenyl)carbene ligand [**OCO**]$^{2-}$ (Scheme 1), in which two phenoxide groups are covalently jointed by a carbene C. This is a rare example of early-transition-metal complexes with σ-donor carbene ligands except N-heterocyclic carbenes.[4−7]

To avoid the need for preparation of a free carbene, we examined C−H activation of the [**OO**] ligand {H_2[**OO**] = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol)} that would provide the desired carbene-bridged bis(phenoxide) [**OCO**] complexes upon cyclometalation. There is considerable precedent for intramolecular C−H activation of 2,6-disubstituted phenoxides in metal complexes.[8] For instance, the 2,6-dimethylphenoxide ligand of a Ru complex was reported to undergo double C−H activation, giving an unusual bidentate carbene−phenoxide ligand.[9] We and others have found that the bridging methylene groups of multidentate phenoxide ligands are more susceptible to cyclometalation because within the chelate ring the methylene group and the metal center are brought into relatively close proximity.[10,11]

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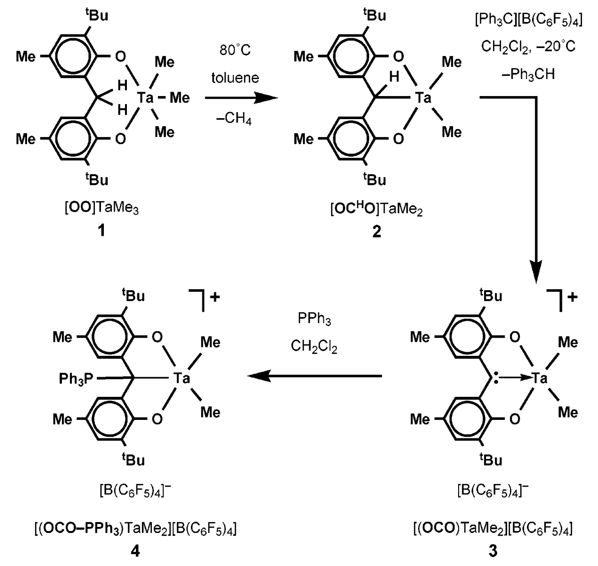
10.1021/ic0608492 CCC: $33.50

Scheme 1



A convenient starting material for this chemistry is the bis(phenoxide) trimethyl complex [**OO**]TaMe$_3$ (**1**), which was obtained as light-yellow crystals in 76% yield by the reaction of [**OO**]TaCl$_3$ with 3 equiv of MeMgBr in toluene.[12] Complex **1** is thermally unstable, and warming of a toluene solution of this complex at 80 °C for 3 days induced abstraction of a methylene proton from the ligand backbone with extrusion of methane to generate a cyclometalated species [**OC$^{\mathbf{H}}$O**]TaMe$_2$ (**2**) as colorless crystals in 79% yield. In the ^{1}H NMR spectrum of **2**, the Ta−Me protons appear as two distinct singlets at 0.51 and 0.77 ppm. The cyclometalated methine proton is observed as a singlet at 3.04 ppm. The resonances ascribed to the phenoxide groups are consistent with **2** having C_s symmetry.

The solid-state structure of **2**, as revealed from an X-ray diffraction study, is shown in Figure 1. The molecule lies across a crystallographic mirror plane that passes through the atoms Ta, C(7), C(13), and C(14). The geometry at Ta is best described as distorted trigonal bipyramidal. The tridentate [**OC$^{\mathbf{H}}$O**] ligand is bound in a meridional fashion, with the phenoxide donors occupying axial positions [O(1)−Ta−O(2) = 148.2(2)°]. The two five-membered chelate ring planes of the ligand are folded along the Ta−C(7) vector with an angle of 163.9(1)°. The hydrogen atom [H(3)] of the methine C(7) carbon was located from Fourier difference maps and refined isotropically. The short Ta−H(3) distance (2.36 Å) and the acute Ta−C(7)−H(3) angle (87°) [Ta−C(7)−C(6), 110.6(3)°; C(6)−C(7)−C(6′), 123.2(5)°] implicate the presence of α-agostic interaction in the solid state, whereas this interaction might be weak in solution as evidenced by the J_{CH} coupling constant (112 Hz) for the methine C (101.6 ppm) from the ^{13}C NMR spectral data.[13]

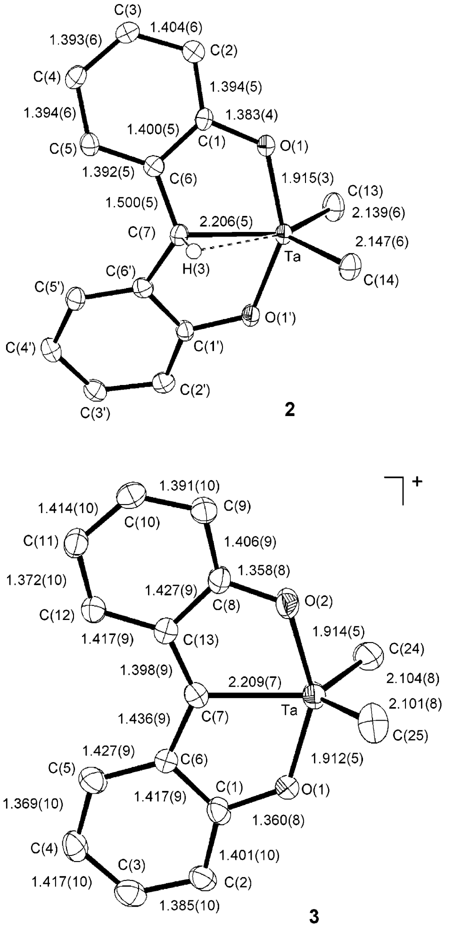


Figure 1. Molecular structures of **2** (above) and the cation part of **3** (below) showing the atom-labeling scheme and selected bond distances. For **2**, only the methine H atom is shown. Me and ^{t}Bu groups of the ligand are omitted for clarity.

To synthesize the alkylidene−bis(phenoxide) complex "[**OCO**]TaMe", we attempted a second α deprotonation of **2**.[14] However, prolonged thermolysis of **2** caused decomposition of the complex. Attempts to isolate any products in the presence of pyridine have met with failure. Owing to the difficulty in generating the *tetraanionic* [**OCO**] ligand via double deprotonation of the [**OO**] ligand, we turned our attention to hydride removal from **2** to prepare the desired *dianionic* [**OCO**] ligand. Treatment of **2** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] at −20 °C in CH$_2$Cl$_2$ afforded thermally unstable [(**OCO**)TaMe$_2$][B(C$_6$F$_5$)$_4$] (**3**) in 72% isolated yield,[15] in which α-hydride abstraction from the [**OC$^{\mathbf{H}}$O**] ligand by a trityl cation took place.[16,17] A color change from colorless

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(15) The half-life of **3** in a CH$_2$Cl$_2$ solution at room temperature was determined to be ca. 10 min. We have yet to identify any decomposition products.

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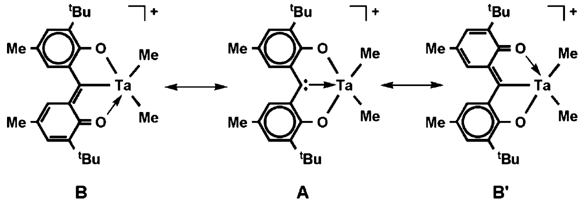
to deep green accompanied the formation of **3**. The formulation of **3** is supported by combustion analysis, NMR spectroscopy, and single-crystal X-ray diffraction. Diagnostic spectroscopic features for **3** include a ^{13}C NMR singlet at 255.5 ppm, which can be assigned to a carbene C.[18] Loss of the α-hydride results in an increase in symmetry from C_s to C_{2v}, where two Ta−Me groups of **3** are equivalent. The aryl ring proton and carbon resonances are shifted downfield compared with those of **2**. An X-ray analysis revealed that the structure of **3** comprises well-separated cations and anions (Figure 1).[19]

As with **2**, the structure of **3** also exhibits a distorted trigonal-bipyramidal Ta center. The carbene C is bonded to Ta with Ta(1)−C(7) = 2.209(7) Å, which is similar to the Ta−C(cyclometalated) distance of **2** [2.206(5) Å]. This distance is significantly longer than those found in high-oxidation-state Schrock-type alkylidenes and falls in the range for known Ta^{V}−C single bonds.[7,20−22] Noteworthy is planarity at C(7), with the sum of the angles being 359.9(6)°. Additionally, the two phenyl rings of the ligand are almost coplanar with the O(1), O(2), C(7), and Ta(1) atoms, an alignment that presumably optimizes resonance donation into the carbene p orbital by the oxyphenyl π electrons. The short C−O and C(7)−C distances of **3** relative to those of **2** reflect this interaction. Further, short/long alternations for C−C bonds within the aryl rings indicate significant contributions from *o*-quinone methide resonance forms (**B** and **B′** in Scheme 2).

Although the trityl cation is widely used as a powerful alkide-abstracting reagent,[23] the reaction of **2** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] proceeds via α-hydride abstraction to generate **3** and triphenylmethane quantitatively according to NMR spectroscopy. The preference for hydride abstraction over methide abstraction is likely a thermodynamic result. Another plausible explanation is that an initial electron transfer from the [**OC$^{\mathbf{H}}$O**] ligand to the trityl cation facilitates subsequent α-hydrogen abstraction from the ligand-centered radical species. For electron-rich transition-metal complexes, abstraction of α-hydride by the trityl cation has been proposed to occur by an electron-transfer mechanism.[16] Further studies are required to determine the mechanistic details for the formation of **3**.

Scheme 2



Preliminary investigations into the reactivity of **3** reveal that this complex does not react with simple olefins. The addition of PPh$_3$ to a CH$_2$Cl$_2$ solution of **3** yielded the phosphine adduct [(**OCO**−PPh$_3$)TaMe$_2$][B(C$_6$F$_5$)$_4$] (**4**). The formation of **4** is accompanied by a color change to orange. The ^{13}C{^{1}H} NMR spectrum exhibits a definitive doublet for the P-bound carbon at 78.5 ppm with $^{1}J_{PC}$ = 14 Hz, while the Ta−Me carbons are observed as two singlets at 67.5 and 76.5 ppm. Attack of PPh$_3$ on **3** indicates the electrophilic nature of the carbene functionality.[17]

In summary, the present work has demonstrated the synthesis and structure of the cationic dimethyltantalum(V) complex with the [**OCO**] ligand. The dianionic tridentate [**OCO**] ligand is formed by the sequential proton and hydride abstraction from the backbone of the [**OO**] ligand. The carbene moiety of **3** is stabilized via π bonding to the oxyphenyl groups. This is reminiscent of the stabilization of N-heterocyclic carbenes by the electron-donating effects of adjacent N atoms.[5a] The electrophilic nature of carbene **3** has been shown in the reaction with PPh$_3$. Extension of this work to include other transition-metal complexes and reactivity studies of **3** are in progress.

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Supporting Information Available: X-ray crystallographic files (CIF) and complete synthetic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Two crystallographically independent, but chemically equivalent, molecules are present in the asymmetric unit. The second molecule has the Ta−C(carbene) distance of 2.216(7) Å, and the sum of the angles around the carbene C is 359.9(7)°.

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