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Trapping Unstable Terminal Ta−O Multiple Bonds of Monocyclopentadienyl Tantalum Complexes with a Lewis Acid

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Summary: Hydrolysis of Ta−Cl or Ta−C bonds with the water-coordinated adduct [$H_2O\cdot B(C_6F_5)_3$] *allowed the synthesis of borane-stabilized complexes* [$TaCp^*R_2\{O\cdot B(C_6F_5)_3\}$] *(R = Cl,* CH_2Ph*, Me) with a tantalum−oxo multiple bond. The chloro derivative in the presence of pyridine releases the adduct* [$py\cdot B(C_6F_5)_3$] *with formation of the oxo-bridged compound* [$TaCp^*Cl_2(\mu\text{-}O)]_2$*. DFT calculations have been carried out to determine the electronic properties of the Ta−O and O−B bonds.*

Introduction

Organometallic oxides play an important role in numerous catalytic processes[1] and also serve as molecular models[2,3] for catalyst−substrate surface interactions. The isolobal similarities between the oxo ligand and alkylidene (CR_2), imido (NR), and cyclopentadienyl ligands (C_5R_5) justify the known relationships among the fragments [$M(C_5R_5)_2$] (M = group 4), [$M(C_5R_5)(L)$] (M = group 5; L = CR_2, NR), and [MLL′] (M = group 6; L, L′ = CR_2, NR, O).[4−6] However, the tendency to form terminal metal−oxo bonds is most favored along the diagonal from vanadium to osmium.[4] Consequently, the mononuclear 16-electron group 5 compounds [$M(C_5R_5)(O)X_2$], considering the oxo group as a 4-electron-donor ligand, have thus far only been unequivocally characterized for vanadium.[7] It has been reported that analogous unstable diiodide and dibromide tantalum compounds are mononuclear,[8] although the related dichloride compound was formulated as a dinuclear complex with μ-O bridges.[9,10] On the other hand, hydrolysis of [$TaCp^*Cl_4$] led to the formation of tri- and tetranuclear oxo-bridged complexes.[11] The scarcity of terminal oxo tantalum complexes is in contrast with the straightforward preparation to obtain mononuclear compounds with the isolobal imido[4,12] ligand and prompted us to look for an appropriate procedure to synthesize mononuclear tantalum complexes containing oxo ligands. We have studied the reactions of monocyclopentadienyl tantalum compounds with the water adduct [$H_2O\cdot B(C_6F_5)_3$], which was proved to be a useful oxo transfer reagent yielding previously unknown oxo compounds.[13]

Results and Discussion

Hydrolysis of the monocyclopentadienyl compounds [$TaCp^*Cl_4$], [$TaCp^*(CHPh)(CH_2Ph)_2$], and [$TaCp^*Me_4$] with 1 equiv of [$H_2O\cdot B(C_6F_5)_3$] afforded the mononuclear oxo complexes [$TaCp^*R_2\{O\cdot B(C_6F_5)_3\}$] (R = Cl (**1**), CH_2Ph (**2**), Me (**3**)) in moderate yields: **1** was obtained after 3 h in refluxing toluene and **2** and **3** were produced after stirring for 1 h at room temperature (Scheme 1). Compound **2** was also obtained by alkylation of **1** with 1 equiv of [$Mg(CH_2Ph)_2(THF)_2$] in toluene, but any attempt to obtain **3** through similar alkylation reactions failed. Complex **1** is thermally stable, but **2** and **3** decompose on heating over 100 and 80 °C, respectively, although all complexes are air stable in solution for several hours. The ^{11}B NMR spectra of complexes **1**−**3** showed a broad resonance around 0 ppm (δ 1.42 (**1**), −0.40 (**2**), −0.65 (**3**)), and the ^{19}F NMR spectra showed a multiplet corresponding to the *m*-fluorine nuclei of the C_6F_5 groups below −155 ppm (δ −156.1 (**1**), −157.1 (**2**), −157.3 (**3**)) that indicated the presence of a tetracoordinated boron atom.

The oxo−borane adduct **1** was also formed by reaction of $B(C_6F_5)_3$ with the oxo-bridged dinuclear compound

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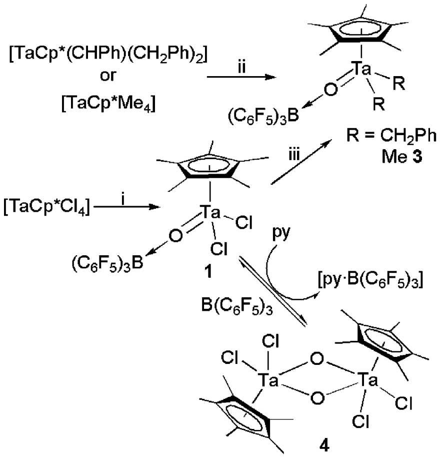
Scheme 1[a]



[a] Reagents and conditions: (i) [$H_2O{\cdot}B(C_6F_5)_3$], toluene, reflux; (ii) [$H_2O{\cdot}B(C_6F_5)_3$], toluene, −78 °C; (iii) [$Mg(CH_2Ph)_2(THF)_2$], toluene, −78 °C.

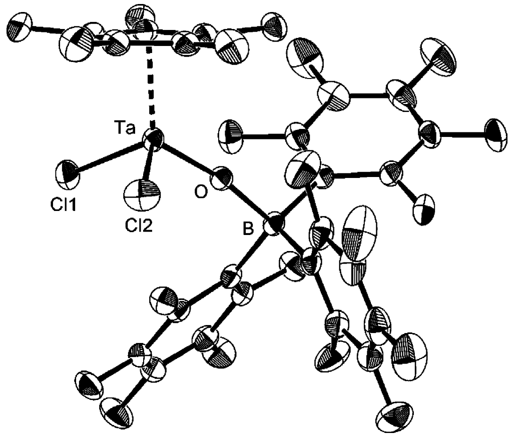


Figure 1. ORTEP diagram of [$TaCp^*Cl_2\{O{\cdot}B(C_6F_5)_3\}$] (**1**). Hydrogen atoms have been omitted, and thermal ellipsoids are shown at the 50% level.

[$TaCp^*Cl_2(\mu\text{-}O)]_2$ (**4**). This is a reversible process, reforming **4** with elimination of the acid−base adduct [py·$B(C_6F_5)_3$] when complex **1** was treated with pyridine. Compounds **2** and **3** remained unchanged in the presence of pyridine at room temperature, although they decomposed when heated over 40 °C with formation of [py·$B(C_6F_5)_3$]. The three compounds remained unchanged when equimolar amounts of oxygen donor ligands such as THF and Et_2O were added, but they decomposed in the presence of excess amounts, preventing their use as solvents.

The molecular structure of compound **1** was determined by X-ray diffraction studies (Figure 1). Its most notable feature, a Ta−O bond distance of 1.784(2) Å, is the longest yet reported for mononuclear compounds, which were previously found to range from 1.73 to 1.77 Å, and even longer than those found in the saturated 18-electron compounds [$TaCp^*Cl(O)\{\eta^2\text{-}C(Me){=}NR\}$] (1.731(7) Å)[14] and [$TaCp_2^*H(O)$] (1.73(2) and 1.69(4) Å),[15] with terminal 4- and 2-electron donor oxo groups, respectively. This value of the Ta−O bond length is a

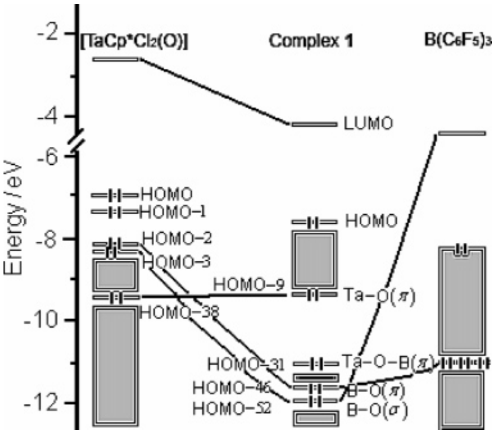


Figure 2. Molecular orbital diagram for the formation of complex **1** from [$TaCp^*Cl_2(O)$] and $B(C_6F_5)_3$. The principal contributions for the Ta−O and O−B bonds are shown.

consequence of the coordination of the oxygen atom to the borane ligand, although it is clearly shorter than the values found in complexes with Ta−O−Ta bridges (1.82−2.10 Å). The O−B bond distance of 1.546(4) Å is within the range observed for neutral oxo−borane compounds (1.496−1.591 Å)[16,17] and the Ta−O−B angle deviates slightly from linearity (169.6(2)°), probably due to the steric requirements of the Cp* and $B(C_6F_5)_3$ ligands. This value contrasts with the Nb−O−B angle in [$NbCp_2'Cl(O{\cdot}BF_3)$] (140.07°),[18] where a bond order of 2 was proposed to abide by the 18-electron rule.

DFT Calculations. Starting from the optimized structure, we have carried out a DFT analysis of the electronic properties of complex **1**, focusing our attention on the nature of the Ta−O and O−B bonds. In fact, these bonds are the most strongly affected in forming the oxo−borane complex. The stabilization energy of the oxo−borane complex **1**, with respect to the isolated borane $B(C_6F_5)_3$ and the unknown terminal oxo complex [$TaCp^*Cl_2(O)$], of 50.4 kcal mol^{-1} reflects the high stabilization of the process and its exergonic nature. Hence, the LUMO of **1**, which belongs essentially to an atomic orbital (d type) of the Ta, is stabilized by ca. 33 kcal mol^{-1} with respect to the equivalent orbital in the borane-free metal complex, favoring its reactivity as an electron acceptor.

The energetic stabilization mainly comes from σ and π B−O interactions (Figure 2). The B−O σ bond (HOMO-52) is essentially due to the interaction between an oxygen lone pair of the borane-free complex (HOMO-3) and the LUMO of the borane. The B−O π bond (HOMO-46) is due to the interaction between one of the three equivalent sp^2 orbitals from the borane and HOMO-2 of the borane-free metal complex, which is essentially an oxygen orbital with an electron pair. Another important contribution to the stabilization of **1** (HOMO-31) is the π charge delocalization through the Ta, O, and B three-atom system (Figure 3). Conversely, the Ta−O π bond in **1** is weakly destabilized in comparison with the borane-free oxo compound.

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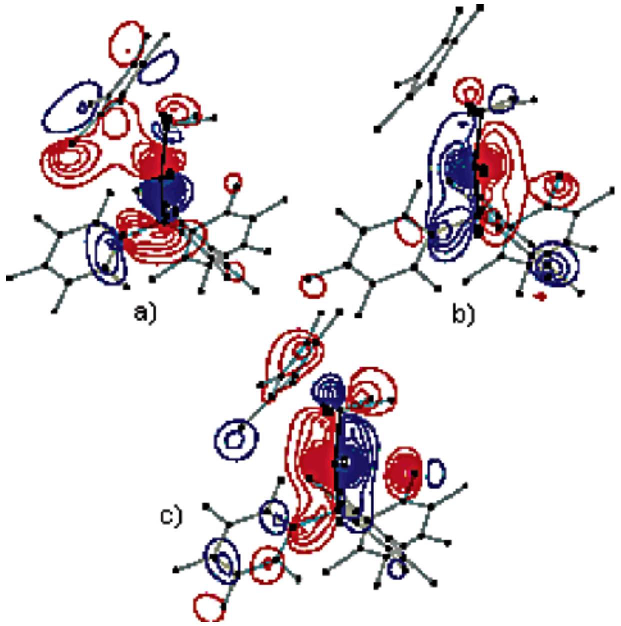

Figure 3. Illustration of some representative occupied molecular orbitals involving bonding relations between Ta, O, and B: (a) O−B (σ) (HOMO-52); (b) O−B (π) (HOMO-46); (c) Ta−O−B (π) (HOMO-31).

Conclusions

The water adduct $[H_2O{\cdot}B(C_6F_5)_3]$ may be used as an efficient oxo transfer reagent to isolate previously unknown or very unstable mononuclear oxo tantalum compounds while maintaining the oxygen attached to the borane fragment. This new Ta−O−B system implies a weakening of the Ta−O and B−C bonds through σ and π B−O interactions with an overall stabilization of the new compounds. Further studies on the stabilization of unstable multiple metal−oxo bonds and the reactivity of these new complexes are being carried out.

Experimental Section

All manipulations were carried out under an argon atmosphere, and solvents were distilled from appropriate drying agents. NMR spectra were recorded at 300.13 (^{1}H), 188.31 (^{19}F), 75.47 (^{13}C), and 128.38 MHz (^{11}B) at room temperature on a Varian Unity 300 (^{1}H, ^{13}C, ^{19}F) or Bruker Advance 400 spectrometer (^{11}B). Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H and ^{13}C) or external $CFCl_3$ (^{19}F) and $BF_3{\cdot}OEt_2$ (^{11}B). Elemental analyses were performed on a Perkin-Elmer 240C. The compounds [TaCp*Cl$_4$],[19] [TaCp*(CHPh)(CH$_2$Ph)$_2$],[20] and [TaCp*Cl$_2$(O)]$_2$[10] were prepared by literature methods. $[H_2O{\cdot}B(C_6F_5)_3]$[21] was prepared in situ and used without further purification by adding 1 equiv of H_2O to a toluene solution of $B(C_6F_5)_3$ at −30 °C and stirring the mixture at room temperature for 90 min.

[TaCp*Cl$_2${O·B(C$_6$F$_5$)$_3$}] (1). A solution of $[H_2O{\cdot}B(C_6F_5)_3]$ (0.76 mmol) in toluene (15 mL) was added slowly to a suspension of [TaCp*Cl$_4$] (0.35 g, 0.76 mmol) in toluene (10 mL) at ambient temperature. When the addition was complete, the solution was refluxed for 3 h. Afterward, the solution was filtered and the volatiles were removed under vacuum. The yellow solid was washed with hexane (2 × 20 mL), yielding **1** as a pale yellow solid (0.45 g, 65%). Data for **1**: ^{1}H NMR (CDCl$_3$) 2.37 (C$_5$Me$_5$); ^{11}B NMR (CDCl$_3$) 1.42 (O·B(C$_6$F$_5$)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) 12.2 (C$_5$*Me*$_5$), 130.3 (*C*$_5$Me$_5$), 136.2 (m, *C*$_6$F$_5$), 138.2 (m, *C*$_6$F$_5$), 146.9 (m, *C*$_6$F$_5$), 148.9 (m, *C*$_6$F$_5$); ^{19}F NMR (CDCl$_3$) −131.7 (*o*-C$_6$F$_5$), −156.1 (*p*-C$_6$F$_5$), −162.7 (*m*-C$_6$F$_5$). Anal. Calcd for $C_{28}H_{15}BCl_2F_{15}OTa$ (915.07): C, 36.75; H, 1.65. Found: C, 37.03; H, 1.70.

[TaCp*(CH$_2$Ph)$_2${O·B(C$_6$F$_5$)$_3$}] (2). Method A. A solution of $[H_2O{\cdot}B(C_6F_5)_3]$ (0.85 mmol) in toluene (20 mL) was added to a solution of [TaCp*(CHPh)Bz$_2$] (0.50 g, 0.85 mmol) at −78 °C. The solution was then warmed to ambient temperature and stirred for 60 min, changing from red to yellowish. The resulting solution was then filtered, and the volatiles were removed under vacuum to a volume of ca. 2 mL. Hexane (30 mL) was added, the solution was filtered off, and the yellow solid was characterized as **2** (0.87 g, 85%).

Method B. A toluene solution (15 mL) of [Mg(CH$_2$Ph)$_2$(THF)$_2$] (0.32 mmol) was slowly added to a toluene solution (25 mL) of [TaCp*Cl$_2${O·B(C$_6$F$_5$)$_3$}] (0.30 g, 0.32 mmol) at −78 °C. When the addition was complete, the solution was warmed to ambient temperature and stirred for 2 h. The solution was then filtered, and the volatiles were removed under vacuum, leaving a yellow solid that was washed with hexane (2 × 20 mL) to yield **2** (0.33 g, 60%).

Data for **2**: ^{1}H NMR (CDCl$_3$) 1.92 (s, 15 H, C$_5$*Me*$_5$), 1.97 (d, ^2J(H−H) = 14.3 Hz, 2 H, Ta−C*H*$_2$Ph), 2.93 (d, ^2J(H−H) = 14.3 Hz, 2 H, Ta−C*H*$_2$Ph), 6.75 (m, 2 H, *m*-C$_6$*H*$_5$), 6.94 (m, 1 H, *p*-C$_6$*H*$_5$), 7.13 (m, 2 H, *o*-C$_6$*H*$_5$); ^{11}B NMR (CDCl$_3$) −0.40 (O·B(C$_6$F$_5$)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) 10.8 (C$_5$*Me*$_5$), 70.0 (*C*H$_2$Ph), 125.2 (*C*$_5$Me$_5$), 125.6 (*C*$_6$H$_5$), 127.9 (*C*$_6$H$_5$), 128.8 (*C*$_6$H$_5$), 135.2 (m, *C*$_6$F$_5$), 138.4 (m, *C*$_6$F$_5$), 141.7 (*C*$_6$H$_5$), 146.1 (m, *C*$_6$F$_5$), 149.2 (m, *C*$_6$F$_5$); ^{19}F NMR (CDCl$_3$) −132.4 (*o*-C$_6$F$_5$), −157.1 (*p*-C$_6$F$_5$), −162.7 (*m*-C$_6$F$_5$). Anal. Calcd for $C_{42}H_{29}BF_{15}OTa$ (1026.43): C, 49.15; H, 2.85. Found: C, 49.43; H, 3.00.

[TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}] (3). A toluene solution (20 mL) of $[H_2O{\cdot}B(C_6F_5)_3]$ (1.06 mmol) was added to a solution of [TaCp*Me$_4$] (0.40 g, 1.06 mmol) in toluene (15 mL) at −78 °C. When the addition was finished, the solution was warmed to ambient temperature and was stirred for 60 min. Afterward, the solution was filtered and concentrated to ca. 2 mL. Hexane (40 mL) was added, the solution was filtered off, and the white solid was characterized as **3** (0.72 g, 82%). Data for **3**: ^{1}H NMR (δ, CDCl$_3$) 0.63 (s, 6 H, Ta−*Me*), 2.00 (s, 15 H, C$_5$*Me*$_5$); ^{11}B NMR (δ, CDCl$_3$) −0.65 (O·B(C$_6$F$_5$)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) 10.9 (C$_5$*Me*$_5$), 63.7 (Ta−*Me*), 123.1 (*C*$_5$Me$_5$), 135.2 (m, *C*$_6$F$_5$), 137.7 (m, *C*$_6$F$_5$), 138.7 (m, *C*$_6$F$_5$), 141.0 (m, *C*$_6$F$_5$), 145.9 (m, *C*$_6$F$_5$), 149.4 (m, *C*$_6$F$_5$); ^{19}F NMR (δ, CDCl$_3$) −133.1 (*o*-C$_6$F$_5$), −157.3 (*p*-C$_6$F$_5$), −163.1 (*m*-C$_6$F$_5$). Anal. Calcd for $C_{30}H_{21}BF_{15}OTa$ (874.23): C, 41.22; H, 2.42. Found: C, 40.87; H, 2.30.

Reaction of [TaCp*Cl$_2${O·B(C$_6$F$_5$)$_3$}] (1) with Pyridine. In an NMR tube charged with a C$_6$D$_6$ solution of [TaCp*Cl$_2${O·B(C$_6$F$_5$)$_3$}] (0.020 g, 0.021 mmol) was added pyridine (0.021 mmol). After 1 h, quantitative transformation to [TaCp*Cl$_2$(O)]$_2$ (**4**) and [py·B(C$_6$F$_5$)$_3$] was observed. ^{1}H NMR for **4** (C$_6$D$_6$): 2.21 (s, 15 H, C$_5$*Me*$_5$). NMR data for [py·B(C$_6$F$_5$)$_3$](C$_6$D$_6$): ^{1}H, 6.36 (m, 2 H, *m*-C$_6$*H*$_5$N), 6.70 (d, 1 H, J = 5.7 Hz, *p*-C$_6$*H*$_5$N), 7.97 (d, 2 H, J = 5.3 Hz, *p*-C$_6$*H*$_5$N); ^{19}F, −161.6 (*m*-C$_6$F$_5$), −154.3 (*p*-C$_6$F$_5$), −130.2 (*o*-C$_6$F$_5$).

Reaction of [TaCp*Cl$_2$(O)]$_2$ (4) with B(C$_6$F$_5$)$_3$. A valved NMR tube was charged with a solution of **4** (0.020 g, 0.024 mmol) and B(C$_6$F$_5$)$_3$ (0.025 g, 0.050 mmol) in C$_6$D$_6$. After 10 min, NMR spectroscopy revealed that the reactants had totally transformed into **1**. NMR for **1** (C$_6$D$_6$): ^{1}H, 1.67 (s, 15 H, C$_5$*Me*$_5$); ^{19}F, −162.7 (*m*-C$_6$F$_5$), −156.0 (*p*-C$_6$F$_5$), −131.6 (*o*-C$_6$F$_5$).

X-ray Structure Determination of 1. Suitable crystals for X-ray diffraction studies were obtained by slow evaporation of a chloroform solution of **1**. Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-250000. Crystal data and refinement

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details: $C_{28}H_{15}BCl_2F_{15}OTa$, Nonius Kappa CCD, formula weight 915.06, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.6113(1)$ Å, $b = 11.2399(1)$ Å, $c = 13.7102(2)$ Å, $\alpha = 88.8081(5)°$, $\beta = 69.2081(5)°$, $\gamma = 74.7048(5)°$, $V = 1469.76(3)$ Å^3, $T = 173$ K, $Z = 2$, $D_{calcd} = 2.068$ g/cm, μ(Mo Kα) = 4.041 mm^{-1}, 33 311 reflections measured, wR2(F^2) = 0.0593 (5385 independent reflections ($R_{int} = 0.050$)), R1 = 0.0226 (5226 data with $I_o > 2\sigma(I_o)$), GOF = 1.102. Additional crystallographic data are available in the Supporting Information.

DFT Calculations. The HF method with B3Lyp hybrid exchange-correlation energy functional[22] implemented in the Gaussian suite of programs[23] was used for the theoretical study of the structural and electronic properties of the complex. All the electronic properties as well as the geometry optimization were performed with this method using the double-ζ basis set LanL2DZ. Computed (optimized) geometry and Cartesian coordinates of **1**, [TaCp*Cl_2(O)], and B(C_6F_5)$_3$ are available in the Supporting Information.

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Supporting Information Available: Crystal data for **1**, as a CIF file, and text and tables giving computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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