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Molecular Cages

Synthesis and Characterization of Tantalum(V) Boronate Clusters: Multifunctional Lewis Acid Cages for Binding Guests**

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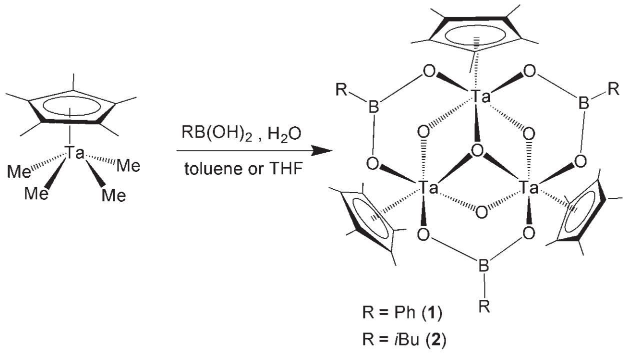
It is hard to match nature's ability to select a unique substrate from a complex mixture or to transform a molecule into a specific product. Enzymes accomplish these tasks by using well-defined cavities that control which guests are selected and how they react.[1] To develop synthetic analogues, scientists are studying supramolecular hosts with large cavities.[2] For example, inorganic,[3] organometallic,[4] and organic[5] porous solids can select guests on the basis of size and show useful selectivity in their binding. In solution, several compounds with large cavities, such as calix[4]-arenes,[6] cucurbiturils,[7] and cyclodextrins,[8] have shown high selectivity for particular guests. Most structures exhibit selective host behavior based on size control, and few have relied on specific chemical interactions as well. For example, the functionalization of calix[4]arenes with donor groups allows the introduction of transition metals and brings coordination into play.[9] Cages that allow guests to be bound by multiple Lewis acidic sites are rare,[10] despite the potential of multidentate Lewis acids in catalysis[11] and anion sensing.[12] We report the discovery of tantalum clusters that have Lewis acidic cavities made of alkyl boronates. These cavities bind Lewis bases such as ketones and have the potential to serve in recognition devices and as catalysts.

Boronic acids $RB(OH)_2$ are well-known reagents for coupling reactions with late transition metals;[13] however, the use of alkyl boronates RBO_2^{2-} as dianionic ligands in coordination chemistry is barely explored. A major advantage of boronic acids is their widespread commercial availability, which allows R to be easily modified to vary the steric and electronic properties. Few aryl boronate complexes of transition metals have been reported previously, and they are limited to zirconium,[14] manganese,[15] copper,[16] rhodium,[17] palladium,[18] and platinum.[19] Group 9 and 10 boronate complexes are transient species in Suzuki–Miyaura coupling reactions, and the structural features of the other boronate metal complexes reveal a tendency for aryl boronates to bridge transition metals in a fashion similar to that of their close carbon analogues, carboxylates. The compounds formed when aryl boronates are used as ligands are stable enough to offer promise as magnetic materials[15a–c, 16] and as catalysts for the epoxidation of alkenes.[15d]

It is well known that alkyl tantalum(V) species are prone to protolysis with alcohols to form strong metal–oxygen bonds and liberate the corresponding alkane. Thus, the addition of 2 equiv of $RB(OH)_2$ (R = Ph, *i*Bu) and 1 equiv of water to a solution of $[Cp^*TaMe_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) in toluene yielded a colorless solution after stirring for 6 days at 22 °C.[20] Removal of the volatile substances under reduced pressure followed by washing with pentane afforded a colorless solid. Addition of pentane to a solution of the solid in THF provided colorless crystals of $[(Cp^*Ta)_3(\mu^2\text{-}\eta^2\text{-}PhBO_2)_3(\mu^2\text{-}O)_2(\mu^2\text{-}OH)(\mu^3\text{-}OH)]\cdot 2\,THF$ (**1**·2THF) and $[(Cp^*Ta)_3(\mu^2\text{-}\eta^2\text{-}i\text{Pr}BO_2)_3(\mu^2\text{-}O)(\mu^2\text{-}OH)_2(\mu^3\text{-}O)]$ (**2**) in 57 and 40% yield of isolated product, respectively (Scheme 1). Their molecular structures are depicted in Figures 1 and 2.[21]



Scheme 1. Synthesis of **1** and **2**.

Complexes **1** and **2** are both trimetallic tantalum(V) clusters in which each metal atom is in a pseudooctahedral environment. The Cp* and μ^3-O ligands are *trans* to each other, while the bridging alkyl boronates and μ^2-O groups have a *cis* arrangement. The absence of any counterion suggests that two of the tantalum-bridging oxygen atoms belong to hydroxy groups. However, it was not possible to locate the hydrogen atoms in the Fourier map. At first glance,

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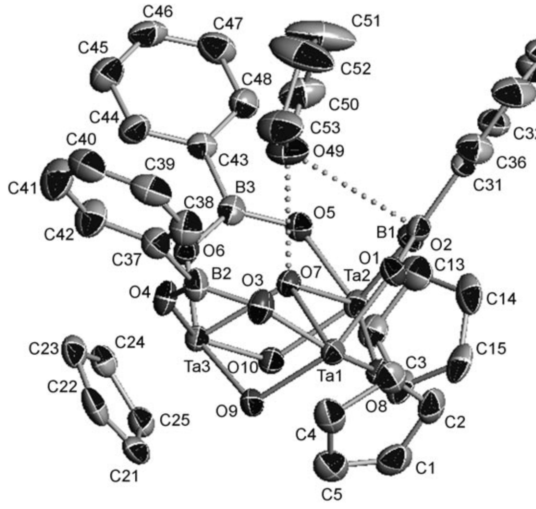

Figure 1. ORTEP view of the structure of **1**·2 THF. Hydrogen atoms, methyl groups of Cp*, and one THF molecule have been removed for clarity.

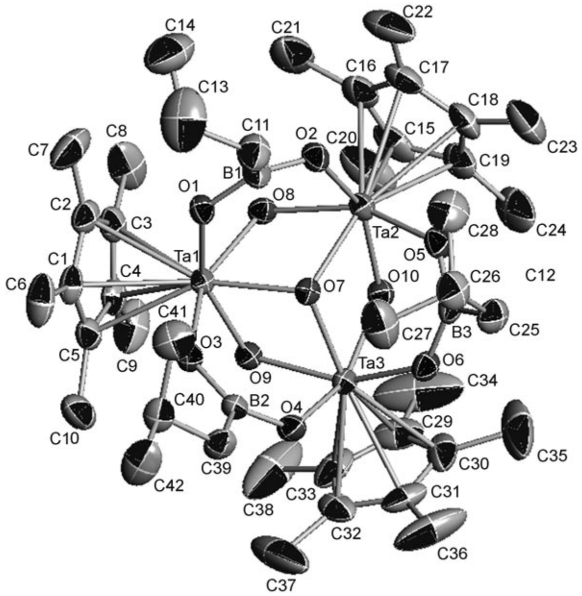

Figure 2. ORTEP view of the structure of **2**. Hydrogen atoms have been removed for clarity.

the core of complexes **1** and **2** seems to have C_3 symmetry, but in fact both structures have a pseudoplane of symmetry crossing one of the tantalum atoms. This lower symmetry is a consequence of the presence of a mixture of oxo and hydroxo ligands. As a result, one of the Ta–Ta distances and two of the Ta–O distances are significantly different from the others. In the case of complex **1**, the odd distances are longer than the others; specifically, the Ta1–Ta3 distance (3.4281(3) Å) is longer than the others (3.3460(2) and 3.3448(3) Å), and the average Ta–μ^2-O9 distance (2.075 Å) is longer than the Ta–μ^2-O8 and Ta–μ^2-O10 distances (1.998 Å). On the basis of density functional theory calculations,[22] and because a μ^2-OH ligand has a longer bond than a μ^2-O ligand, we suggest that the complex has a $(\mu^2\text{-O})_2(\mu^2\text{-OH})(\mu^3\text{-OH})$ core. In the case of complex **2**, observation of the opposite relation suggests the presence of a $(\mu^2\text{-O})(\mu^2\text{-OH})_2(\mu^3\text{-O})$ core.

The likely presence of an apical μ^3-OH ligand in **1** was supported by calculations,[22] which indicate that the proposed core is more stable than the alternative $(\mu^2\text{-O})(\mu^2\text{-OH})_2(\mu^3\text{-O})$ core by 11.47 kcal mol^{-1} when a solvent molecule is present inside the cavity, as observed in the X-ray structure of **1**·2 THF (see below). In the absence of THF, the proposed structure (μ^3-OH) remains stable but by only 1.16 kcal mol^{-1}. In the case of **2**, the $(\mu^2\text{-O})(\mu^2\text{-OH})_2(\mu^3\text{-O})$ core was estimated to be slightly less stable than the alternative (μ^3-OH) by 0.18 kcal mol^{-1}. The small difference in energy in the absence of included solvent could explain the ambiguity previously observed in the localization of the hydrogen atom for $[(\text{Cp*TaCl})_3(\mu^2\text{-Cl})(\mu^2\text{-O})_2(\mu^3\text{-OH})(\mu^3\text{-O})]$,[23] the only reported compound with a $(\text{Cp*Ta})_3(\mu^2\text{-O})_3(\mu^3\text{-O})\}$ core.[23,24]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** and **2** at −40 °C in [D$_8$]toluene revealed the presence of a plane of symmetry. Indeed, the observation of two sets of resonances for the Cp* and R groups in a 2:1 ratio is in full accordance with the solid-state structure. Also present in the ^{1}H NMR spectra is a signal integrating for two protons (at $\delta = 1.96$ ppm for **1** and at $\delta = 1.16$ ppm for **2**), which was assigned to the hydroxo ligands, since it was not associated with any carbon by HMQC spectroscopy. As the temperature rises, the OH signal becomes broader and shifts to lower field. It ends up at $\delta = 5.9$ ppm at 25 °C for **1**, whereas it was not located for **2**. At the same time, it was possible to observe coalescence of the two Cp* resonances, which merge to one broad signal at 25 °C. These observations seem to indicate a fluxional process, which probably involves migration of the hydroxide hydrogen atom; however, more studies will be needed to elucidate this phenomenon in detail.

Whereas both structures have the same core featuring bridging boronate ligands, the PhBO$_2$ fragment in **1** is coplanar (the angles between the $C_{ipso}BO_2$ plane and the $Ta_A\text{-}BO_2\text{-}Ta_B$ plane are between 2.4(1) and 5.0(2)°). This produces a cup-shaped structure with a prominent open cavity (Figure 3). A similar feature is absent in complex **2**, because the *i*Bu groups close the cavity. A unique characteristic of the cavity is the presence of three accessible Lewis acidic sites provided by the boronate boron atoms.[25] The B–B distances in complex **1** are in the range 4.73–4.81 Å, and the tilting of

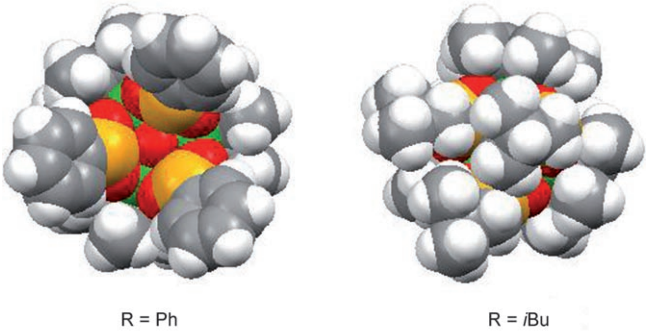

Figure 3. Space-filling views of **1** (R = Ph) and **2** (R = *i*Bu), obtained from crystallographic data. The μ-O hydrogen atoms are omitted. C gray, H white, B orange, O red, Ta green.

the boronate groups orients the p orbital of boron towards the opening of the cavity, while the back is protected by the Cp* ligand. Further shaping of the cavity in **1** should be trivial, given the large number of commercially available aryl boronic acids functionalized at the *meta* or *para* positions. Such modifications would not sterically affect the coordination sites themselves but could change the morphology of the upper rim.

In the solid-state structure of **1**·2THF, one of the solvent molecules is located inside the cavity and interacts with one boronate ligand, while the other THF molecule does not interact with complex **1**. Although the B–O bond of 2.99 Å is significantly longer than those observed in borane–THF adducts (1.467–1.659 Å) and different from the other B–O bond in **1**·2THF (3.41–3.53 Å), it is much shorter than the sum of the van der Waals radii (3.5 Å).[26] Moreover, the distance is similar to those seen previously in complexes in which THF molecules are squeezed between bridging alkyl boronate esters (B–O 2.67–2.91 Å).[27] The orientation of THF in the solid-state structure and the computational details suggest that the THF molecule also interacts with the μ^3-OH ligand (O–O 2.70 Å). Such a double interaction of an oxygen atom with a Lewis acid and a hydrogen-bond donor is to our knowledge unique. It has the effect of increasing the interaction between the cavity and the guest, which is normally weakly bound. Indeed, as observed by ^{1}H NMR spectroscopy, a ground sample of **1**·2THF must be kept at 0.01 Torr/95 °C for 2 h to completely remove bound THF, while the unbounded solvent molecule is removed cleanly under reduced pressure at room temperature. No solvent molecule was located in the solid-state structure of **2**, since the *i*Bu groups block the cavity.

The interaction between host **1** and THF is also present in solution. A important feature of the ^{1}H NMR spectrum of a solvent-free sample of **1** in the presence of 1 equiv of THF in [D$_6$]benzene is shielding of the α- and β-hydrogen atoms of THF by $\Delta\delta = 0.32$ and 0.14 ppm, respectively. This demonstrates that THF remains bound in solution. It is most likely that the shielding is a consequence of the anisotropic cone of the phenyl rings, because similar shifts were not observed in **2**, in phenylboronic acid, or in the trimeric phenylboronic anhydride. To determine whether other Lewis bases can also be bound within the cavity, selected reagents were added to a 0.005 M solution of THF-free **1** in [D$_6$]benzene. When 1 equiv of acetone was added, it was immediately possible to observe by ^{1}H NMR spectroscopy an upfield shift of $\Delta\delta =$ 0.2 ppm for the methyl resonance, which suggests that the new guest is bound inside the cavity. When additional equivalents of acetone were added, downfield shift of the resonance suggested that rapid exchange occurs between the bound and unbound molecules in solution. Somewhat bulkier ketones, such as Me(Ph)CO or *t*Bu(Me)CO, also appeared to interact, since the chemical shifts of the methyl resonances were shielded by $\Delta\delta = 0.09$ and 0.12 ppm, respectively. Weak Lewis bases such as chloroform, diethyl ether, and toluene did not appear to bind.

We have demonstrated that boronic acids can be used as templating agents to form supramolecular structures with interesting host properties. The ease of synthesis of these materials is a notable advantage. By tuning the steric and electronic properties of the R group of the boronic acid, it should be possible to increase the selectivity of binding, to introduce additional sites of interaction, and even to add chirality. Several potential applications of these hosts are now being investigated, including their use as catalysts in Lewis acid activated organic transformations and as anion sensors.

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[20] It was possible to observe by ^{1}H NMR spectroscopy the presence of the anhydride $(RBO)_3$ and various Cp^*TaMe_x resonances when the reaction was carried out under strictly anhydrous conditions. Complete experimental details can be found in the Supporting Information.

[21] CCDC-637124 and CCDC-637125 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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