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

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Synthesis and characterization of alkylboronate tantalum(V) clusters: a multifunctional Lewis acid cage for host-guest purposes**

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The detection of a specific substrate from a complex mixture or the chemical transformation of a molecule to a desired product can be difficult to do with the same efficiency than Nature. Indeed, enzymes, Nature's catalysts, have well-defined cavities that allow great selectivity in the choice of molecular guests and, subsequently, on the reactivity.[1] In order to reach such ideals, scientists have been working on supramolecular structures bearing large cavities that can host specific molecules. For example some inorganic,[2] organometallic,[3] and organic[4] porous materials exhibit nice selectivity control over size and can host specific molecules. In the homogeneous phase, several compounds with large cavities, such as calix[4]arenes,[5] cucurbiturils,[6] or cyclodextrins[7] have shown similar selectivity for guest molecules. While most structures exhibit specific hosting behaviour based on size control, there have been few structures that rely on chemical interactions as well. For example, the functionalization of calix[4]arenes with donor groups allows transition metal coordination.[8] While the synthesis of multidentate Lewis acids is an important field in chemical synthesis mainly for catalytic purpose[9] or anion sensing,[10] the number of compounds having supramolecular features that allow substrate discrimination are more scarce.[11] We wish to report the discovery of tantalum clusters that possess Lewis acidic cavities made of alkylboronates. These have been shown to bind Lewis bases such as ketones and could be of great interest in recognition devices as well as in Lewis acid catalyzed reactions.

Boronic acids ($RB(OH)_2$; R = alkyl or aryl) are well known reagents for coupling reactions with late transition metals;[12] however, the use of alkylboronates (RBO_2^{2-}) as dianionic ligands in coordination chemistry is ill investigated. One major advantage of boronic acids is the large commercial availability of functional R groups, which would make the highly sought steric and electronic control of the complexes quite easy. There is only a short list of alkylboronate complexes reported in literature. They have for transition metal zirconium,[13] manganese,[14] copper,[15] palladium,[16] and platinum.[17] While group 10 complexes are transient species in Suzuki coupling, the structural features of the other boronate metal complexes put in evidence the tendency for this ligand to bridge transition metals in a similar fashion than their close carbon analogues, the carboxylates. The compounds formed when alkylboronates are used as ligand are stable enough to exhibit good magnetic properties[14a-c,15] and can even be used as catalyst for the epoxydation of alkenes.[14d]

Scheme 1. Synthesis of $\{[Cp^*Ta]_3(\mu^2\text{-}\eta^2\text{-}RB(O)_2)_3(\mu^2\text{-}O)(\mu^2\text{-}O)_2(\mu^3\text{-}O)\}$ (R = Ph, *i*Bu). The two bridging hydroxydes are also present.
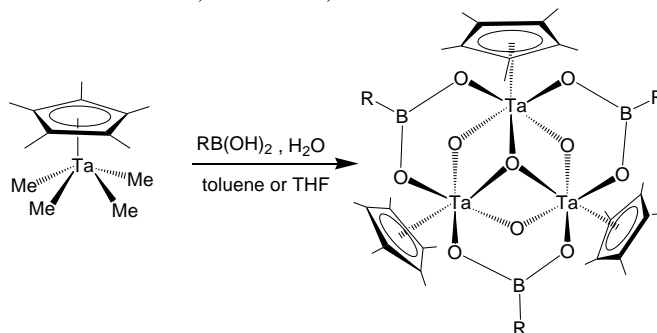
It is well known that alkyl tantalum(V) species are quite prone to protolysis with alcohols to form strong metal-oxygen bonds and liberate the corresponding alkane. Thus, the addition of 2 equiv of $RB(OH)_2$ (R = Ph, *i*Bu) and 1 equiv of water to a solution of Cp^*TaMe_4 in toluene yielded a colourless solution after stirring for 6 days.[18] Removal of the volatiles under reduced pressure followed afforded a white powder. Addition of pentane to a THF solution of the powder provided crystalline colourless $\{[Cp^*Ta]_3(\mu^2\text{-}\eta^2\text{-}PhB(O)_2)_3(\mu^2\text{-}O)_2(\mu^2\text{-}OH)(\mu^3\text{-}OH)\}$ (**1**) and $\{[Cp^*Ta]_3(\mu^2\text{-}\eta^2\text{-}PhB(O)_2)_3(\mu^2\text{-}O)(\mu^2\text{-}OH)_2(\mu^3\text{-}O)\}$ (**2**) in 57 % and 40% isolated yield respectively (scheme 1). Their molecular structures are depicted in figures 1 and 2.[19]

Both **1** and **2** are trimetallic tantalum(V) clusters, where each metal is in a pseudo octahedral environment. The Cp* and the μ^3-O are *trans* to each other, while the bridging alkylboronates and oxo groups are *cis*. The absence of any counterion suggests that two of the tantalum bridging oxygen atoms are hydroxides. It was not possible, however, to locate the hydrogen atoms in the Fourier map. While at first

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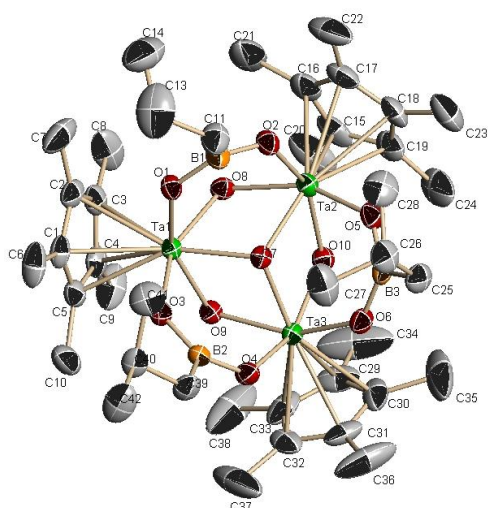
glance the core of **1** and **2** seems to possess C3 symmetry, both structures have a pseudo plane of symmetry crossing one of the tantalum atoms, consequence of the presence of a mixture of oxo and hydroxo groups. Consequently, in these complexes one of the Ta-Ta distances and two of the Ta-O distances are significantly different than the others. In the case of **1**, the odd distances are longer than the others. The Ta1-Ta3 bond length (3.4281(3) Å) is longer that the others (3.3460(2) Å and 3.3448(3) Å) and the Ta-μ^2-O(9) distances have an average of 2.075 Å compared to 1.998 Å for the Ta-μ^2-O(8) and Ta-μ^2-O(10) distances. Since a μ^2-OH has a longer bond length than a μ^2-O, it can be speculated that we are in presence of a $(\mu^2$-O)$_2(\mu^2$-OH)$(\mu^3$-OH) core. In the case of **2** the opposite relation was observed for the Ta-Ta distances, with the odd distance being the shortest of all three (3.3197(3) Å for Ta1-Ta3 vs. 3.3405(3) Å and 3.3395(3) Å). Also, the Ta-μ^2-O(9) average distance is shorter with an average of 2.071 Å compared to an average of 2.099 Å for the other Ta-μ^2-O distances. It can be speculated that we are in presence of a $(\mu^2$-O)$(\mu^2$-OH)$_2(\mu^3$-O) core.

The presence of an apical μ^3-OH in **1** was confirmed by calculations. This conformation is more stable than the $(\mu^2$-O)$(\mu^2$-OH)$_2(\mu^3$-O) core by 12.0 kcal/mol when a solvent molecule is present inside the cavity, as observed in the X-ray structure of **1.**THF (*vide infra*). In the absence of a THF molecule, the conformation remains stable but by only 1.2 kcal/mol. In the case of **2**, the $(\mu^2$-O)$(\mu^2$-OH)$_2(\mu^3$-O) conformation was more stable by 0.6 kcal/mol. The small difference in energy in the absence of solvent for both conformation could explain the ambiguity previously observed in the localisation of the hydrogen for {[Cp*TaCl]$_3(\mu^2$-Cl)$(\mu^2$-O)$_2(\mu^3$-OH)$(\mu^3$-O)} [20], the only one compound with a {[Cp*Ta]$_3(\mu^2$-O)$_3(\mu^3$-O)} core structure to be reported.[20,21]
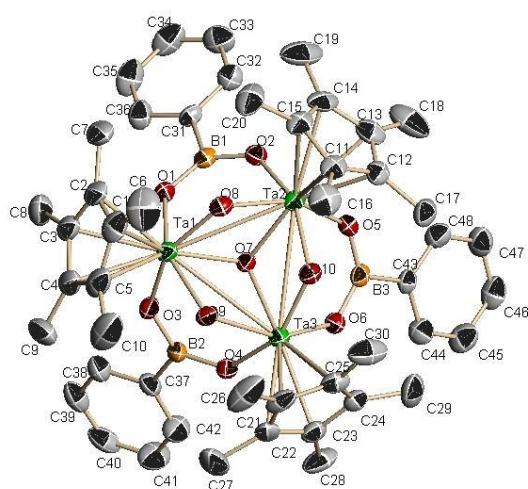
Figure 1. ORTEP diagram of **1·**2THF. The hydrogen atoms and the THF molecules have been removed for clarity. Selected bond distances (Å): Ta(1)-Ta(2) 3.3460(2), Ta(2)-Ta(3) 3.3448(3), Ta(1)-Ta(3) 3.4281(3), Ta(1)-O(1) 1.976(2), Ta(1)-O(3) 1.963(3), Ta(2)-O(2) 1.978(2)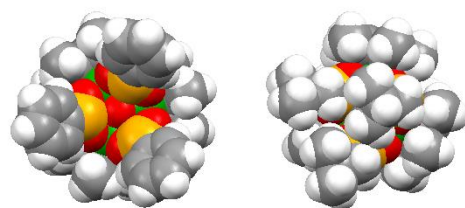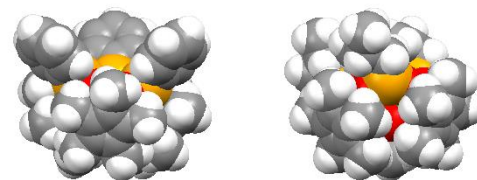, Ta(2)-O(5) 1.999(3), Ta(3)-O(6) 1.968(2), Ta(3)-O(4) 1.987(3), Ta(1)-O(8) 1.984(3), Ta(1)-O(9) 2.068(3), Ta(2)-O(8) 2.011(2), Ta(2)-O(10) 2.012(2), Ta(3)-O(10) 1.987(3), Ta(3)-O(9) 2.081(3), Ta(1)-O(7) 2.182(2), Ta(2)-O(7) 2.182(3), Ta(3)-O(7) 2.197(2).
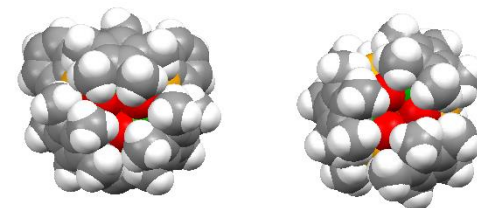

Figure 2. ORTEP diagram of **2**. The hydrogen atoms have been removed for clarity. Selected bond distances (Å): Ta(1)-Ta(2) 3.3405(3), Ta(2)-Ta(3) 3.3395(3), Ta(1)-Ta(3) 3.3197(3), Ta(1)-O(1) 1.966(2), Ta(1)-O(3) 1.959(3), Ta(2)-O(2) 1.943(2), Ta(2)-O(5) 1.948(3), Ta(3)-O(6) 1.957(3), Ta(3)-O(4) 1.953(3), Ta(1)-O(8) 2.089(2), Ta(1)-O(9) 2.073(2), Ta(2)-O(8) 2.108(3), Ta(2)-O(10) 2.103(1), Ta(3)-O(10) 2.096(2), Ta(3)-O(9) 2.068(3), Ta(1)-O(7) 2.085(2), Ta(2)-O(7) 2.065(3), Ta(3)-O(7) 2.084(2).

Figure 3. Space filling views of [Cp*Ta(μ^2-η^2-RB(O)$_2$)$_3(\mu^2$-O)$_3(\mu^3$-O)]$_3$ (R= Ph (**1**), (**2**)) obtained from crystallographic data. The μ-O hydrogens were omitted.

The ^{1}H and ^{13}C{^{1}H} NMR spectra at -40°C in toluene-d_8 put in evidence the presence of a plane of symmetry in **1** and **2**. Indeed, the presence of two set of resonances for the Cp* and the R groups in a 2:1 ratio is in accordance with the solid state structure. Also present in the ^{1}H NMR spectra, is a signal integrating for two protons at 1.96 ppm for **1** and at 1.16 ppm for **2**, which was assigned to the hydroxides since it was not associated to any carbon by HMQC spectroscopy. However, as the temperature rises, the OH signal becomes broader and starts shifting to lower field, to end at 5.9 ppm at 25°C for **1**, while it was not located for **2** at room temperature. At the same time, it is possible to observe the coalescence of the two Cp* resonances which merge to one broad signal at 25°C. While these observations seem to

indicate an important fluxional process, which probably involves migration of the hydrogen atom on the hydroxide, more studies will be needed in order to get more detailed information on this phenomenon.

Whereas both structures have the same core featuring bridging alkylboronate ligands, the planarity of the $PhBO_2$ fragment in **1** (the angles between the $C_{ipso}BO_2$ plane and the $Ta_A-BO_2-Ta_B$ plane is between 2.4(1) and 5.0(2)º) induces a cup shape structure with the $PhBO_2$ group serving as templating agent and the $\{[Cp^*Ta]_3(\mu^2-O)_3(\mu^3-O)\}$ core serving as support. As observed in the views of figure 3, **1** possesses a large accessible area, which is absent in **2**, consequence of the *i*Bu groups closing the cavity. The unique feature of this cavity is the presence of three accessible Lewis acids. Indeed, the B-B distances in **1** are between 4.73 and 4.81 Å and the tilting of boronates orientates the p_z orbital of the boron towards the opening of the cavity, while the back is protected by the cyclopentadienyl ligands. Shaping the cavity in **1** should be quite trivial considering the number of boronic acids available with aryl groups functionalized at the *meta* or *para* position. Such modification would not strerically affect the ligand's coordination but could change the morphology of the upper rim.
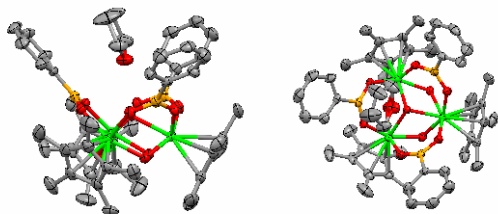

Figure 4. ORTEP diagram of **1** with a THF molecule included in the Lewis-acid cavity.

In the solid state structure of **1**.2THF, one of the solvent molecules is located inside this cavity (fig. 4). While the 2.99 Å boron-oxygen bond length is significantly longer than the observed bond lengths in borane-THF adducts, which vary between 1.467 and 1.659 Å, it is significantly shorter than the summation of the van der Waals radii of 3.5 Å.[22] Indeed, the 2.99 Å distance compares well to weak bonding interactions previously reported when THF molecules are squeezed between bridging alkylboronate esters, where the B-O distances range between 2.67 and 2.91 Å.[23] The orientation of the THF in the solid state structure and the computational details indicate that the THF molecule interacts as well with the μ^3-OH. Such double interaction of an oxygen with a Lewis acid and a hydrogen bond is to our knowledge unique and has for effect to strengthen the interaction between the solvent molecule and the cavity whereas each independent interaction would not be strong enough to retain the solvent molecule inside the cavity. Indeed, a grinded sample of **1**.2THF needs to be put under reduced pressure at 0.01 Torr at 95ºC for 2 hours in order to remove completely the bonded THF molecule while the unbounded one is removed cleanly after only few minutes at room temperature.

The interaction between the cluster and the Lewis base is also present in solution. One important feature of the ¹H NMR of **1** in presence of one equiv of THF in benzene-d_6 is the 0.32 ppm shielding for the α-H and the 0.14 ppm shielding for the β-H of the THF resonances (Table 1). This is a clear indication that the molecule remains inside the cavity of **1** in solution. While it is most likely that the shielding is a consequence of the anisotropic cone of the phenyl rings, the same phenomena was not observed in **2**, in the phenylboronic acid or in the trimeric phenylboronic anhydride. In order to verify if other Lewis bases could also lodge inside the cavity, common reagents were added to a 0.005 M solution of **1** in benzene-d_6. When one equiv of acetone was added, it was immediately possible to observe by ¹H NMR spectroscopy a chemical shift of 1.36 ppm for the methyl resonance, a 0.2 ppm upfield shift from the usual chemical shift of acetone in benzene-d_6, suggesting that the ketone is positioning itself inside the cavity. Interestingly, when additional equivalents of acetone were added, the resonance was shown to shift downfield, suggesting that a rapid exchange is occurring between the bound and unbound molecules in solution. Since there are more than one boronate moieties available for bonding, it can be speculated that even if the thermodynamic stability of the interaction between **1** and the ketone is important, the additional coordinating sites makes it kinetically labile. Such properties could be useful in order to regenerate **1** and isolate the complexed molecule in potential catalytic or sensor applications. When bulkier ketones, such as (Me)(Ph)CO or (*t*Bu)(Me)CO, were added to the cavity, they were also shown to interact with **1** since the chemical shifts of the methyl resonances were shielded by 0.09 and 0.12 respectively. Trimethylphosphine interacts with the cavity even if it does not bind boronic acids nor does hydrogen bonding easily. Since triethylamine interacts with the boronic acid as well, it could not be concluded that the shifting of both ¹H NMR ethyl resonances could be attributed to its coordination inside the cavity. Finally, when weak Lewis bases like chloroform, diethylether or toluene were added to a solution of **1** in toluene, no shifting was observed.

Table 1. ¹H NMR chemical shift of common reagents in presence of compounds **1**, **2**, PhB(OH)₂ and (PhBO)₃

Molecule	δ[a]	**1**[b]	**2**[b]	PhB(OH)₂[c]	Ph(BO)₃[d]
C₆H₅Me	2.11	2.10	2.10	2.10	2.10
	7.02	7.03	7.03	7.00	7.03
	7.13	7.12	7.12	7.12	7.11
OEt₂	1.11	1.11	1.11	1.10	1.11
	3.26	3.25	3.26	3.24	3.25
THF	1.40	1.08	1.41	1.37	1.40
	3.57	3.43	3.57	3.54	3.56
NEt₃	0.96	0.78	0.96	0.75	0.70

	2.40	2.26	2.39	2.19	2.18
PMe_3	0.79	0.52	0.79	0.77	0.77
$(Me)_2CO$	1.55	1.36	1.54	1.52	1.54
(Me)(Ph)CO	2.07	1.98	2.07	2.06	2.06
	7.02	6.96	7.01	7.01	7.01
	7.10	7.05	7.09	7.09	7.08
	7.75	7.60	7.75	7.73	7.74
(*t*Bu)(Me)CO	0.88	0.76	0.88	0.86	0.87
	1.72	1.63	1.71	1.70	1.71
$CHCl_3$	6.15	6.11	6.12	6.13	6.12

[a] ^{1}H NMR chemical shift in ppm in pure benzene-d_6.[24] [b] 1 equiv of the additive in a 0.005 M benzene-d_6 solution. [b] 1 equiv of the additive in a 0.03 M benzene-d_6 solution. [b] 1 equiv of the additive in a 0.01 M benzene-d_6 solution.

We have demonstrated that boronic acids can be used as templating agent to form supramolecular structures with interesting host properties. The vast availability of substrates and the ease of synthesis of these materials make possible the exploration of several derivatives of **1** and **2**. By tuning the steric environment and the electronic properties of the R group of the boronic acid, it could be possible to induce more selective host guest properties, to introduce additional functional group and even to add chirality on the rim. Several perspective uses of **1** are now being investigated, including its use as catalyst for Lewis-acid activated organic transformations and for anion sensor applications.

Experimental Section

Synthesis of {[Cp*Ta]$_3$(μ^2-η^2-PhB(O)$_2$)$_3$(μ^2-O)$_2$(μ^2-OH)(μ^3-OH)}.THF (**1**).
A solution of water (14.5 μL, 0.797 mmol) and PhB(OH)$_2$ (193 mg, 1.59 mmol) in THF (5 mL) was added to a solution of (η^5-C$_5$Me$_5$)TaMe$_4$ (300 mg, 0.797 mmol) in THF (5 mL) under nitrogen at -78°C. The resulting yellow solution was stirred for 6 days at room temperature until it turned colorless. The solvent was then removed under reduced pressure. The resulting white precipitate was washed once with acetone (2 mL) in normal atmosphere. The white powder was dried for 16 hours under vacuum at 90°C for the ^{1}H NMR experiments or recrystallized from the diffusion of pentane to a solution of **1** in THF. Yield: 57%. ^{1}H NMR (toluene-d_8, -40°C): δ 8.38 (d, $^3J_{H-H}$ = 6.8 Hz, 4H, C$_{ortho}$), 8.33 (d, $^3J_{H-H}$ = 6.8 Hz, 2H, C$_{ortho}$), 7.39 (m, 5H, C$_{meta}$+C$_{para}$), 7.29 (m, 4H, C$_{meta}$+C$_{para}$), 3.21 (m, THF), 2.28 (s, 15H, Cp*^{B}), 2.15 (s, 30H, Cp*^{A}), 1.94 (s, 2H, OH), 0.36 (m, THF). ^{13}C NMR (toluene-d_8, -40°C): δ122.22 (Cp*^{B}), 122.22 (Cp*^{A}), 68.05 (THF), 25.03 (THF), 12.39 (Cp*^{B}), 12.00 (Cp*^{A}). ^{11}B NMR (chloroform-d, -30°C): δ 27.7. Anal. Calc. for C$_{48}$H$_{62}$B$_3$O$_{10}$Ta$_3$.C$_4$H$_8$O: C, 43.18; H, 4.88. Found: C, 43.34; H, 4.76 %.

Synthesis of {[Cp*Ta]$_3$(μ^2-η^2-*i*BuB(O)$_2$)$_3$(μ^2-O)(μ^2-OH)$_2$(μ^3-O)} (**2**).
A solution of water (14.5 μL, 0.797 mmol) and *i*BuB(OH)$_2$ (163 mg, 1.59 mmol) in toluene (30 mL) was added to a solution of (η^5-C$_5$Me$_5$)TaMe$_4$ (300 mg, 0.797 mmol) in toluene (5 mL) under nitrogen at -78°C. The resulting yellow solution was stirred for 6 days at room temperature until the solution turned colorless. The solvent was then removed under vacuum. The resulting white precipitate was washed once with pentane (2 mL) and dried for an hour under vacuum. Yield: 40% ^{1}H NMR (toluene-d_8, -40°C): δ 2.1 (m, 3H, CH$_2$*CH*(CH$_3$)$_2$), 2.03 (s, 30H, Cp*^{B}), 1.81 (s, 15H, Cp*^{B}), 1.24 (m, 9H, CH$_2$CH(*CH$_3$*)$_2$), 1.12 (s, 2H, OH), 0.98 (m, 6H, *CH$_2$*CH(CH$_3$)$_2$). ^{13}C NMR (toluene-d_8, -40°C): δ 121.67 (Cp*^{B}), 121.27 (Cp*^{A}), 26.59 (*i*Bu), 26.51 (*i*Bu), 26.24 (*i*Bu), 11.59 (Cp*^{A}), 11.08 (Cp*^{B}). ^{11}B NMR (chloroform-d, -30°C): δ 30.8. Anal. Calc. for C$_{42}$H$_{74}$B$_3$O$_{10}$Ta$_3$: C, 38.38; H, 5.68. Found: C, 38.14; H, 5.57 %.

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[18] 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 in strict anhydrous conditions.

[19] CCDC-XXXX and CCDC-XXXX contains 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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