

## Structural Study of Acidic Metallocavitands and Characterization of their Interactions with Lewis Bases

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We report the synthesis and characterization of tantalum–boronate trimetallic clusters of the general formula  $\{[\text{Cp}^*\text{Ta}]_3(\mu^2\text{-RB}(\text{O})_2)_3(\mu^2\text{-OH})(\mu^2\text{-O})_2(\mu^3\text{-OH})\}$  (R = *i*-Bu (**Ta<sub>3</sub>-iBu**), C<sub>6</sub>H<sub>5</sub> (**Ta<sub>3</sub>-Ph**), 2,5-(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>) (**Ta<sub>3</sub>-2,5Me**), 3,5-(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>) (**Ta<sub>3</sub>-3,5Me**), and 3,5-(CF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>) (**Ta<sub>3</sub>-3,5CF<sub>3</sub>**)). Three of these complexes feature a Lewis acid type cavity allowing for substrate binding in both the solid and the liquid state using a unique electrostatic interaction and a hydrogen bond. We also report the synthesis of  $\{[\text{Cp}^*\text{Ta}]_2(\mu^2\text{-MesB}(\text{O})_2)_2[\text{MesB}(\text{OH})(\text{O})]_2(\mu^2\text{-OH})_2\}$  (Mes = 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**Ta<sub>2</sub>-Mes**)). All complexes have been characterized by NMR and X-ray diffraction studies, and the steric and electronic effects on the boronate ligands have been investigated. The physical properties of the interaction between the tantalum–boronate clusters and tetrahydrofuran and acetone have been studied by thermogravimetric analysis, FT-IR, and Density Functional Theory calculations to characterize the molecular interactions in the resulting adducts.

### Introduction

Mutidentate ligands have the ability to rigidify the backbone of transition metal complexes, inducing important properties, such as chirality and durability, as well as paving the way for new supramolecular architectures. The carboxylate moiety has been used abundantly as an organic framework for the synthesis of multimetallic complexes for catalytic purposes<sup>1</sup> or for the creation of metal-organic frameworks.<sup>2</sup> While there are numerous carboxylate complexes, the scarcity of their boron analogues, the alkylboronates, is remarkable. Some alkylboronate complexes have been reported in the literature related to the Suzuki–Miyaura coupling reactions,<sup>3</sup> but early metal analogues are rare. With

the exception of the metals of the platinum group,<sup>4–6</sup> only Zr,<sup>7</sup> Mn,<sup>8</sup> and Cu<sup>9</sup> boronate complexes were reported. One of the problems with the synthesis of boronate complexes is the weak B–C bond which is susceptible to oxidative coupling; it explains why the platinum group boronate complexes are only transient species. However, with early transition metals, a strong M–O bond stabilizes the ligand coordination to oxophilic transition metals while the high-oxidation state of the metal centers reduces the possibility

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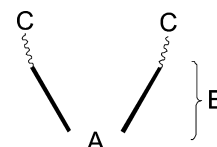
- (1) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861–2904.
- (2) (a) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191–214. (b) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276–288. (c) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (3) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

- (4) (a) Ahijado, M.; Braun, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 2954–2958. (b) Zhao, P.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 1876–1877.
- (5) Crociani, B.; Antonaroli, S.; Marini, A.; Matteoli, U.; Scrivanti, A. *Dalton Trans.* **2006**, 2698–2705.
- (6) (a) Pantcheva, I.; Osakada, K. *Organometallics* **2006**, *25*, 1735–1741. (b) Pantcheva, I.; Nishihara, Y.; Osakada, K. *Organometallics* **2005**, *24*, 3815–3817.
- (7) Balkwill, J. E.; Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Inorg. Chem.* **2002**, *41*, 3548–3552.
- (8) (a) Marlin, D. S.; Bill, E.; Weyhermüller, T.; Bothe, E.; Wiegardt, K. *J. Am. Chem. Soc.* **2005**, *127*, 6095–6108. (b) Duboc-Toia, C.; Hummel, H.; Bill, E.; Barra, A.-L.; Chouteau, G.; Wiegardt, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2888–2890. (c) Bossek, U.; Hummel, H.; Weyhermüller, T.; Wiegardt, K.; Russell, S.; van der Wolf, L.; Kolb, U. *Angew. Chem., Int. Ed.* **1996**, *35*, 1552–1554.
- (9) Bardwell, D. A.; Jeffery, J. C.; Ward, M. D. *Polyhedron* **1996**, *15*, 2019–2022.

of B–C bond cleavage, therefore making possible the use of boronate ligands as components of metal-organic supramolecular complexes.

Cavitands are a category of supramolecular assemblies having a bowl-shape structure able to host smaller molecules. The importance of cavitands, such as calixarenes, cucurbiturils, and cyclodextrins in supramolecular chemistry has been put forward in several review articles.<sup>10</sup> They show unique abilities to incorporate guest molecules and to serve as nanovessels for catalysis,<sup>11</sup> for drug delivery,<sup>12</sup> or for molecular recognition.<sup>13</sup> It is also possible to functionalize these macromolecules to increase their selectivity for some substrates or to incorporate molecular fragments to suit one's needs,<sup>14</sup> however, the functionalization can prove challenging and generally involves tedious and low yielding multistep syntheses. It is also possible to incorporate a metallic center within or in the periphery of the cavitand to form metallocavitands that serve as mimics to metalloenzymes.<sup>15</sup> However, the strategy involves also multistep syntheses of organic frameworks. We recently reported the facile one-step synthesis of a new metallocavitand interacting strongly with Lewis bases,  $\{[\text{Cp}^*\text{Ta}]_3(\mu^2\text{-PhB}(\text{O})_2)_3(\mu^2\text{-O})_2(\mu^2\text{-OH})(\mu^3\text{-OH})\}$  (**Ta<sub>3</sub>-Ph**), from  $\text{Cp}^*\text{TaMe}_4$  and phenylboronic acid.<sup>16</sup> This new species exhibits interesting features, including a conic cavity somewhat similar to calix[4]arenes, with a pseudo- $C_3$  symmetry. Even more unique is the presence of four acidic sites at the bottom of the cavity that can, in principle, interact with Lewis bases such as ketones. Since there is a large array of boronic acids commercially available, the possibilities of functionalizing the cavitands' upper-rim are numerous, opening the way to the easy synthesis of supramolecules to use as sensors or catalysts. These metallocavitands can possibly be used for three different functions:

(1) as Lewis acids for acid–base recognition and bond



**Figure 1.** General design of tantalum(V) boronate metallocavitand having: (A) a Lewis acid site, (B) a cavitand, and (C) a chemical sensor.

activation, (2) as cavitands for size-shape selectivity, and (3) as chemical sensors by having the appropriate functionalized boronate moiety (Figure 1).

In this work, we expand on our previous report by describing the synthesis and characterization of several new Ta(V) boronate clusters, demonstrating the generality of the concept. We will look in more depth at the steric and electronic levels of freedom that are available to form these metallocavitands. An analysis of the physical properties of the interaction between the tantalum clusters and acetone and tetrahydrofuran (THF) will be described, therefore putting forward the parameters for the construction of more complex assemblies with this supramolecular architecture and explaining the nature of the interaction with Lewis bases.

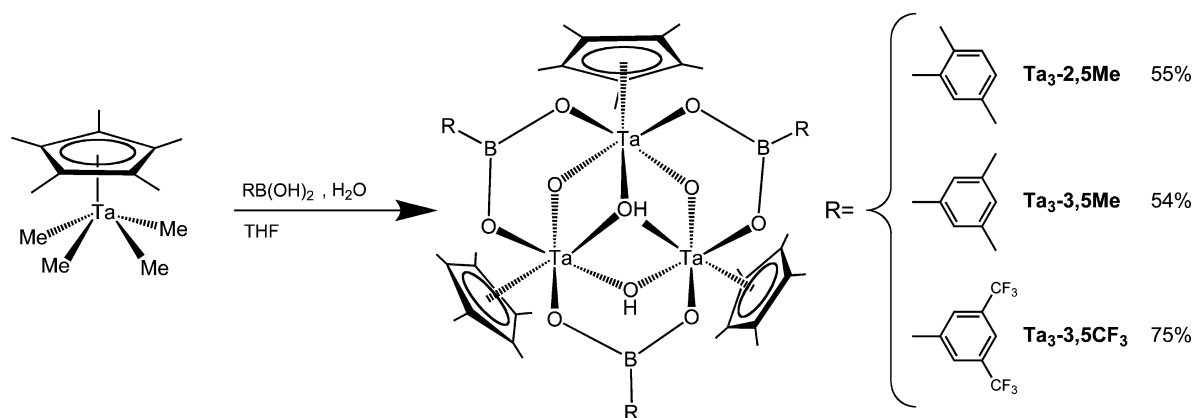
## Results

**Synthesis and Crystallographic Studies.** We reported that the addition of 2 equiv of  $\text{RB}(\text{OH})_2$  ( $\text{R} = \text{Ph}$  or  $i\text{Bu}$ ) to a solution of  $\text{Cp}^*\text{TaMe}_4$  in presence of 1 equiv of water yielded complexes **Ta<sub>3</sub>-Ph** and **Ta<sub>3</sub>-*i*Bu**, respectively.<sup>16</sup> While both complexes exhibit a typical  $\text{Ta}_3\text{O}_4$  core observed in various occasions,<sup>17</sup> only the aryl substituted complex is a metallocavitand, since folding of one alkyl chain in **Ta<sub>3</sub>-*i*Bu** fills the void made by the boronate coordination. To evaluate the level of freedom available with the steric bulk of substituents on the arylboronic acid, we carried out the synthesis of analogues using boronic acids displaying an increasing amount of steric bulk at the *ortho* and *meta* positions since the *para* position should be easy to modulate without affecting the structure of the cavity. 2,5-Dimethylphenylboronic acid and mesitylboronic acid were used to evaluate the effect of a gradual increase in bulk at the carbons situated in *ortho* to the boronate moiety, and 3,5-dimethylphenylboronic acid was used to assess the effects of bulkier substituents at positions far from the boron center. In addition, to study the possible electronic effects in the formation of the cages, electron withdrawing substituents on the aryl fragment of the boronate ligand were used. The reaction was carried out with 3,5-bis(trifluoromethyl)benzeneboronic acid and pentafluorobenzeneboronic acid.

The reaction scheme and the yields for the synthesis of  $\{[\text{Cp}^*\text{Ta}]_3(\mu^2\text{-2,5-(CH}_3)_2(\text{C}_6\text{H}_3)\text{B}(\text{O})_2)_3(\mu^2\text{-OH})_2(\mu^2\text{-O})(\mu^3\text{-O})\}$  (**Ta<sub>3</sub>-2,5Me**),  $\{[\text{Cp}^*\text{Ta}]_3(\mu^2\text{-3,5-(CH}_3)_2(\text{C}_6\text{H}_3)\text{B}(\text{O})_2)_3(\mu^2\text{-O})_2(\mu^2\text{-OH})(\mu^3\text{-OH})\}$  (**Ta<sub>3</sub>-3,5Me**), and  $\{[\text{Cp}^*\text{Ta}]_3(\mu^2\text{-3,5-(CF}_3)_2(\text{C}_6\text{H}_3)\text{B}(\text{O})_2)_3(\mu^2\text{-O})_2(\mu^2\text{-OH})(\mu^3\text{-OH})\}$  (**Ta<sub>3</sub>-3,5CF<sub>3</sub>**)

- (10) (a) Liu, S.; Gibb, B. C. *Chem. Commun.* **2008**, 3709–3716. (b) Biroš, S. M. *J. Chem. Soc. Rev.* **2007**, *36*, 93–104. (c) Houk, K. N.; Leach, A. G.; Kim, S. P.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 4872–4897.
- (11) Few leading references: (a) Shenoy, S. R.; Pinacho Crisóstomo, F. R.; Iwasawa, T.; Rebek, J. *J. Am. Chem. Soc.* **2008**, *130*, 5658–5659. (b) Zelder, F. H., Jr. *J. Chem. Commun.* **2006**, 753–754. (c) Gissot, A., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 7424–7425.
- (12) Few leading references: (a) Kuykendall, D. W.; Zimmerman, S. C. *Nat. Nanotechnol.* **2007**, *2*, 201–202. (b) Memisoglu-Bilensoy, E.; Dogan, A. L.; Hincal, A. A. *J. Pharm. Pharmacol.* **2006**, *58*, 585–589.
- (13) Few leading references: (a) Schramm, M. P.; Rebek, J., Jr. *Chem.—Eur. J.* **2006**, *12*, 5924–5933. (b) Pinalli, R.; Suman, M.; Dalcanele, E. *Eur. J. Org. Chem.* **2004**, 451–462. (c) Arimori, S.; Davidsson, M. G.; Fyles, T. M.; Hibbert, T. G.; James, T. D.; Kociok-Köhn, G. I. *Chem. Commun.* **2004**, 1640–1641.
- (14) Few leading references: (a) Srinivasan, K.; Laughrey, Z. R.; Gibb, B. C. *Eur. J. Org. Chem.* **2008**, 3265–3271. (b) Azov, V. A.; Schlegel, A.; Diederich, F. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1926–1940. (c) Aakeröy, C. B.; Schultheiss, N.; Desper, J. *Org. Lett.* **2006**, *8*, 2607–2610. (d) Harvey, P. D. *Coord. Chem. Rev.* **2002**, *233–234*, 289–309.
- (15) Few leading references: (a) Frischmann, P. D.; MacLachlan, M. J. *Comments Inorg. Chem.* **2008**, *29*, 26–45. (b) Lenthall, J. T.; Steed, J. W. *Coord. Chem. Rev.* **2007**, *251*, 1747–1760. (c) Jeunesse, C.; Armspach, D.; Matt, D. *Chem. Commun.* **2005**, 5603–5614.
- (16) Sigouin, O.; Garon, C. N.; Delaunais, G.; Yin, X.; Woo, T. K.; Fontaine, F.-G. *Angew. Chem., Int. Ed.* **2007**, *46*, 4979–4982.

- (17) (a) Blaurock, S.; Hey-Hawkins, E. *Eur. J. Inorg. Chem.* **2002**, 2975–2984. (b) Jernakoff, P.; De Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362–1364.

Scheme 1. Synthesis of  $\text{Ta}_3\text{-2,5Me}$ ,  $\text{Ta}_3\text{-3,5Me}$ , and  $\text{Ta}_3\text{-3,5CF}_3$ 

are shown in Scheme 1, and the solid state structure of the new products and of  $\text{Ta}_3\text{-Ph}$  obtained by slow evaporation of acetone are illustrated in Figures 2–5.

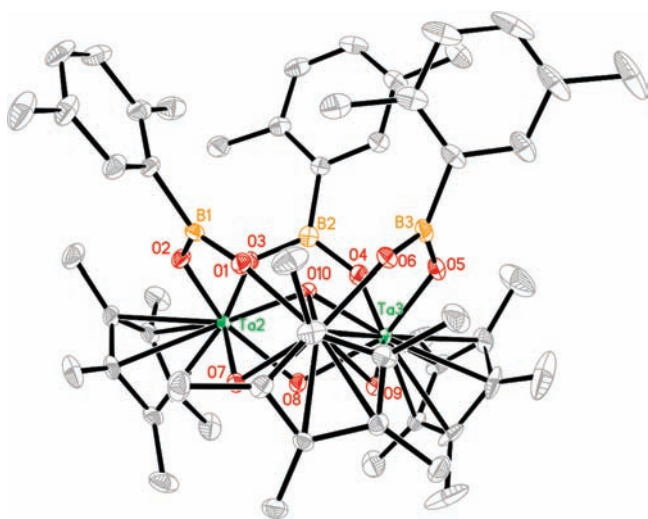


Figure 2. ORTEP diagram (50% probability) of  $\text{Ta}_3\text{-2,5Me}$ . Hydrogen atoms have been omitted for clarity.

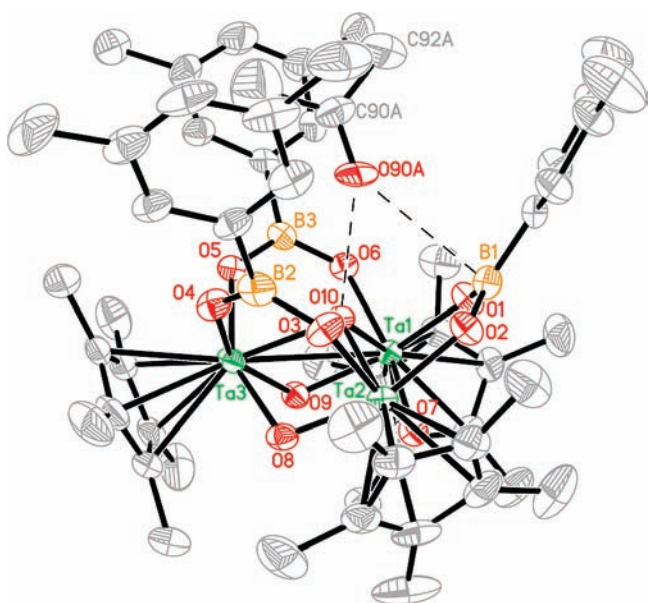


Figure 3. ORTEP diagram (50% probability) of  $\text{Ta}_3\text{-3,5Me}\cdot\text{acetone}$ . Only one model for the disordered aryl group on B3 is shown. Hydrogen atoms have been omitted for clarity.

It can be seen from the resolution of the molecular structures of these products that a trimetallic core similar to the one observed with  $\text{Ta}_3\text{-Ph}$  and  $\text{Ta}_3\text{-}i\text{Bu}$  is obtained. In these trimetallic complexes, the tantalum centers are in a pseudo-octahedral environment with the Cp\* ligands *trans* to the  $\mu^3\text{-OH}$  while the bridging boronates are *cis* to the  $\mu^2\text{-O}$  oxygens. The resulting Ta<sub>3</sub>O<sub>4</sub> core possesses a C<sub>2</sub> symmetry caused by the OH groups creating a mirror plane passing through a tantalum center and thus preventing higher symmetry. As a result, one Ta–Ta distance (Ta1–Ta3) and two Ta–O distances (Ta1–O9, Ta3–O9) are significantly different from the others. The numbering scheme used in this report for the inorganic core can be seen in Figure 6, and a list of relevant interatomic distances are shown in Table 1.

Compounds  $\text{Ta}_3\text{-3,5Me}$ ,  $\text{Ta}_3\text{-3,5CF}_3$ , and  $\text{Ta}_3\text{-Ph}$  crystallize with an acetone molecule within the cavity, having weak van der Waals contacts with one of the boron atoms (3.032 Å for  $\text{Ta}_3\text{-3,5Me}$ , 2.928 Å for  $\text{Ta}_3\text{-3,5CF}_3$ , and 3.042 Å for  $\text{Ta}_3\text{-Ph}$ )<sup>18</sup> and with the  $\mu^3\text{-OH}$  (2.641 Å for  $\text{Ta}_3\text{-3,5Me}$ , 2.740 Å for  $\text{Ta}_3\text{-3,5CF}_3$ , and 2.646 Å for  $\text{Ta}_3\text{-Ph}$ ).  $\text{Ta}_3\text{-3,5Me}$  and  $\text{Ta}_3\text{-3,5CF}_3$  show some level of disorder, with one aryl ring disordered in the former complex and rotational

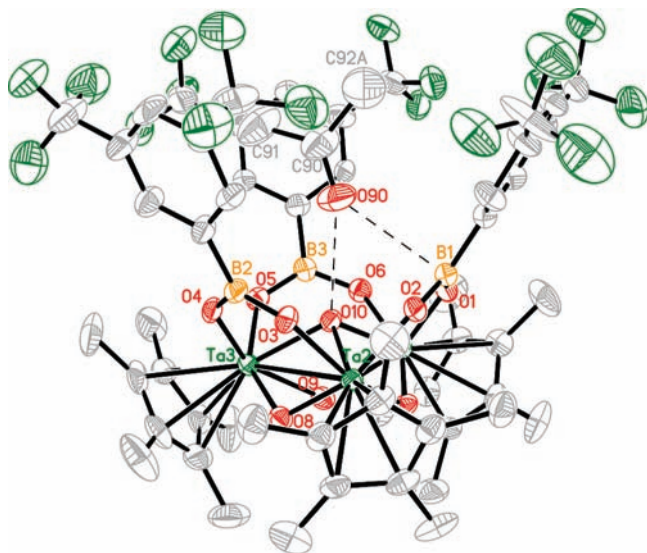
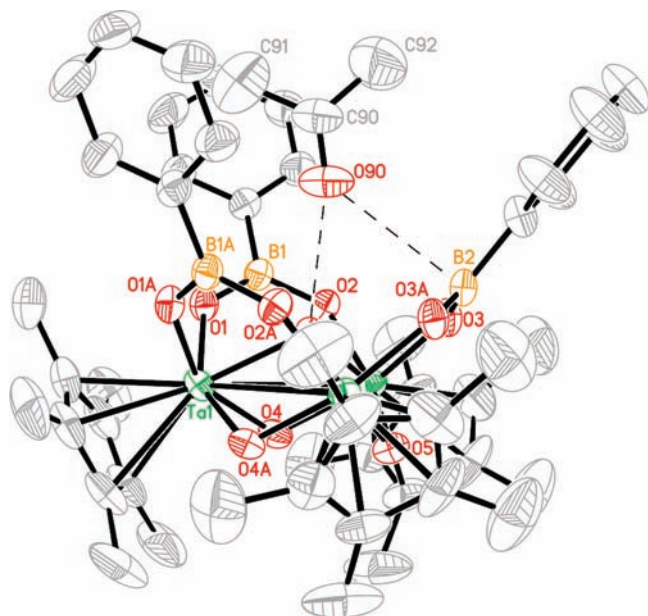
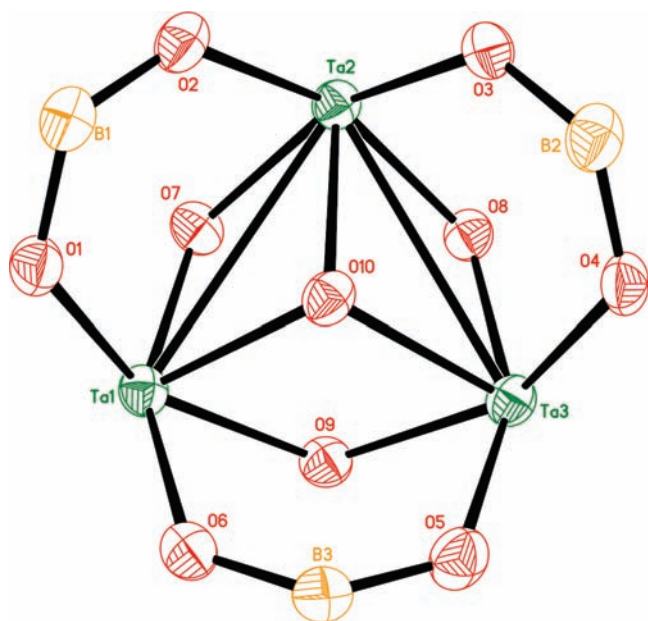


Figure 4. ORTEP diagram (50% probability) of  $\text{Ta}_3\text{-3,5CF}_3\cdot\text{acetone}$ . Only one model for the disordered CF<sub>3</sub> is shown. Hydrogen atoms have been omitted for clarity.

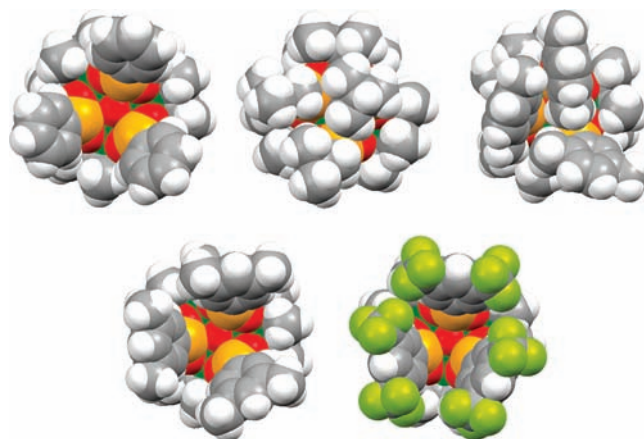


**Figure 5.** ORTEP diagram (50% probability) of **Ta<sub>3</sub>-Ph·acetone**. Only one model for the disordered acetone is shown. Hydrogen atoms have been omitted for clarity.



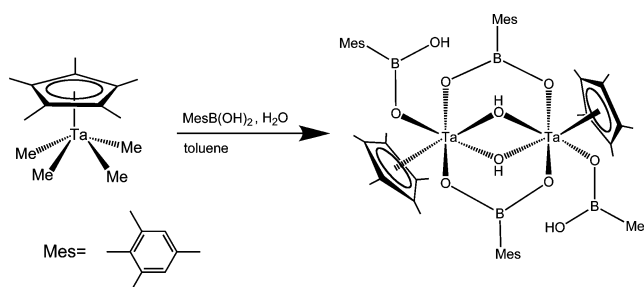
**Figure 6.** Labeling scheme for the inorganic core of Ta<sub>3</sub> complexes.

disorder in the trifluoromethyl groups in the latter complex, leading in both cases to two different orientations for the acetone bound inside the cavity. These results indicate that the presence of functional groups in the *meta* position of the aryl ring does not prevent the inclusion of Lewis bases. However, some structural distortion was observed for the aryl groups which are rotated to a certain degree out of the



**Figure 7.** Spacefilling of (top to bottom, left to right) **Ta<sub>3</sub>-Ph**, **Ta<sub>3</sub>-iBu**, **Ta<sub>3</sub>-2,5Me**, **Ta<sub>3</sub>-3,5Me**, and **Ta<sub>3</sub>-3,5CF<sub>3</sub>**.

### Scheme 2. Synthesis of Ta<sub>2</sub>-Mes

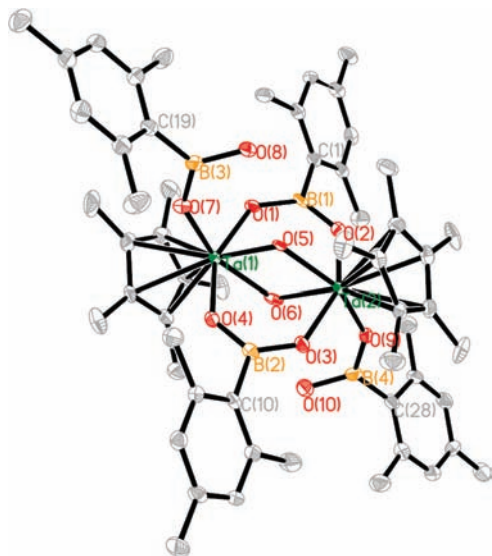


O–B–O plane for **Ta<sub>3</sub>-3,5Me** (13.7°<sub>av</sub>) and for **Ta<sub>3</sub>-3,5CF<sub>3</sub>** (6.1°<sub>av</sub>), whereas the aryl groups are close to coplanarity with the O–B–O plane in **Ta<sub>3</sub>-Ph** (0.9°<sub>av</sub> and 4.4°<sub>av</sub> for THF and acetone containing structures, respectively). To limit the repulsion between the *ortho* substituents, the aryl groups in compound **Ta<sub>3</sub>-2,5Me** are majorly distorted, as can be seen by the torsion angles of 26.0(4)°, 46.8(3)°, and 54.9(3)°. These torsions result in the cavity of the cluster being completely obstructed and therefore unavailable for Lewis acid–base interactions, since none is observed in the solid state structure. Spacefilling diagrams of the above complexes putting in evidence the cavities are illustrated in Figure 7.

The complex {[Cp\*Ta]<sub>2</sub>(μ<sup>2</sup>-MesB(O)<sub>2</sub>)<sub>2</sub>[MesB(OH)(O)]<sub>2</sub>(μ<sup>2</sup>-OH)<sub>2</sub>} (**Ta<sub>2</sub>-Mes**) was obtained in moderate isolated yield (60%) from the reaction of Cp\*TaMe<sub>4</sub> with mesitylboronic acid (Scheme 2). X-ray diffraction studies on **Ta<sub>2</sub>-Mes** showed that a boronic acid bearing substituents on both *ortho* carbons of the aryl fragment displays too much steric bulk to form a trimetallic cluster, as observed in the Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing in Figure 8. Instead, a dimer reminiscent of (Cp\*)<sub>2</sub>Zr(η<sup>2</sup>-MesBO<sub>2</sub>)<sub>2</sub><sup>7</sup> or [V<sub>2</sub>O<sub>3</sub>(nicotinate)<sub>3</sub>]<sup>19</sup> is obtained, where two μ<sup>2</sup>-boronates bridge two Cp\*Ta centers. Interestingly, the steric bulk of the mesityl group did not allow for four bridging boronates

**Table 1.** Distances of Interest in Structurally Characterized Ta<sub>3</sub> Complexes

Complex	dTa1–Ta2 (Å)	dTa2–Ta3 (Å)	dTa1–Ta3 (Å)	dTa1–O9(Å)	dTa3–O9(Å)	dC90–O90(Å)
<b>Ta<sub>3</sub>-iBu</b>	3.341	3.340	3.320	2.073	2.068	
<b>Ta<sub>3</sub>-Ph·acetone</b>	3.333	3.333	3.453	2.092	2.092	1.161
<b>Ta<sub>3</sub>-Ph·THF</b>	3.346	3.345	3.428	2.092	2.092	
<b>Ta<sub>3</sub>-2,5Me</b>	3.370	3.412	3.214	1.972	1.975	
<b>Ta<sub>3</sub>-3,5Me</b>	3.376	3.408	3.303	1.974	1.963	1.212
<b>Ta<sub>3</sub>-3,5CF<sub>3</sub></b>	3.310	3.296	3.503	2.145	2.144	1.225



**Figure 8.** ORTEP diagram (50% probability) of **Ta<sub>2</sub>-Mes**. Hydrogen atoms have been omitted for clarity.

so each metal center features a boronate ligand coordinated in an  $\eta^1$  fashion and a bridging hydroxo group. The mesityl groups of both the  $\eta^1$  and the  $\eta^2$  boronate moieties are suffering major rotations out of the O–B–O plane. Torsion angles of  $62.9(8)^\circ$  ( $\eta^1$ ),  $75.0(8)^\circ$  ( $\eta^1$ ),  $50.7(8)^\circ$  ( $\eta^2$ ), and  $48.1(8)^\circ$  ( $\eta^2$ ) from the O–B–O plane can be observed in the molecule, and this results in the aromatic rings all aligning in the same plane within the molecule (Figure 9). The rotations out of the plane for the  $\eta^2$  ligands of **Ta<sub>2</sub>-Mes** are slightly less than those observed for  $(\text{Cp}^*)_2\text{Zr}(\eta^2\text{-MesBO}_2)_2$  ( $66.8^\circ$ ).<sup>7</sup> Effectively, this creates  $\pi$ -stacking in the crystal lattice with the interplane distances of around 3.5 Å, where solvent molecules provide support in-between adjacent complexes, since the lattice of the crystal is destroyed when THF is removed upon exposure to air.

The reaction done with pentafluorobenzeneboronic acid resulted in a mixture of products as evidenced by the many Cp\* environments between  $\delta$  2.0–2.3 ppm observed in the <sup>1</sup>H NMR spectrum of the solid crystalline product in C<sub>6</sub>D<sub>6</sub>. The <sup>19</sup>F NMR spectrum of the reaction mixture revealed the only fluorine-containing species to be C<sub>6</sub>F<sub>5</sub>H when compared to a commercial sample. Separation of the several inorganic products was unsuccessful, but recrystallization attempts yielded two species that were characterized by X-ray diffraction studies. Although the data collected through these studies was of mediocre quality and therefore unpublished, we were able to determine that the two major boron products obtained were derivatives of boric acid, as observed in Figure 10. We are still uncertain and are working to assess whether the loss of the C<sub>6</sub>F<sub>5</sub> groups happens before or after the formation of the inorganic core of the trimetallic complex.

**Metallocavitands as Lewis Base Guests.** Evidence of the hosting behavior in solution of **Ta<sub>3</sub>-Ph** is provided by the shielding of the <sup>1</sup>H NMR resonances of the inclusion species, which is mainly a consequence of the anisotropic shielding from the aromatic rings. For example, it was observed that the methyl groups of acetone have a chemical shift of 1.36 ppm in benzene-*d*<sub>6</sub> when acetone is a guest species, compared

to the chemical shift of 1.55 ppm for the free molecule. It is therefore informative to look at the <sup>1</sup>H chemical shift of acetone in the presence of the tantalum clusters to probe supramolecular properties in solution.

<sup>1</sup>H NMR measurements were conducted for all the complexes synthesized throughout this study (Table 2). Other than **Ta<sub>3</sub>-Ph**, the trimetallic clusters that show a distinct cavity in the solid state (**Ta<sub>3</sub>-3,5Me** and **Ta<sub>3</sub>-3,5CF<sub>3</sub>**) were found to interact with 1 equiv of acetone in solution, as witnessed by the chemical shift sliding upfield by 0.10 and 0.11 ppm, respectively, from the uncoordinated value ( $\delta$  1.55 ppm). Electron withdrawing groups on the arylboronate ligands did not seem to have a clear effect on the coordination of acetone in solution versus a complex bearing electron donating substituents. Indeed the chemical shift values observed for these complexes are equivalent to each other, and both are lower in magnitude to the shift which is observed for product **Ta<sub>3</sub>-Ph** (0.19 ppm). Conversely, studies conducted with **Ta<sub>3</sub>-2,5Me** revealed no chemical shift displacement versus the reference uncoordinated acetone value. This supports the observation in the solid state that no cavity is present in the molecule, and the conformation observed in the crystal lattice is maintained in solution as well.

It was not possible to determine equilibrium constants at room temperature by <sup>1</sup>H NMR, but upon cooling down a toluene-*d*<sub>8</sub> solution of **Ta<sub>3</sub>-Ph** and **Ta<sub>3</sub>-3,5Me**, the coalescence of the acetone resonance was observed at  $-70^\circ\text{C}$  and broad peaks were resolved at  $-90^\circ\text{C}$  for free (1.39 ppm) and included acetone (0.74 and 0.98 ppm, for **Ta<sub>3</sub>-Ph** and **Ta<sub>3</sub>-3,5Me**, respectively). The upfield signal for the bound acetone in **Ta<sub>3</sub>-Ph** suggests a stronger interaction than in **Ta<sub>3</sub>-3,5Me**, which is confirmed by an association constant of  $1.3 \pm 0.5 \times 10^3 \text{ M}^{-1}$  for **Ta<sub>3</sub>-Ph** which is about 1 order of magnitude greater than what is observed for **Ta<sub>3</sub>-3,5Me** ( $0.8 \pm 0.4 \times 10^2 \text{ M}^{-1}$ ). The low solubility of **Ta<sub>3</sub>-3,5CF<sub>3</sub>** in cold toluene prevented the determination of the association constant.

To quantify the interaction between acetone and THF with complexes having an open cavity at the solid state, a thermogravimetric analysis coupled to mass spectrometry (TGA-MS) was performed on complexes **Ta<sub>3</sub>-Ph**, **Ta<sub>3</sub>-3,5Me**, **Ta<sub>3</sub>-3,5CF<sub>3</sub>**, and on **Ta<sub>3</sub>-2,5Me** which does not possess a cavity. A ground, solvent-free sample of the complex was triturated with acetone or THF. The excess solvent was allowed to evaporate for 10 min on the benchtop and under a continuous flow of air on the scale until the mass of the solid was stabilized.

Any adsorbed solvent molecules on the powder particles of **Ta<sub>3</sub>-Ph** are instantly lost in the first minutes of the experiment when the mass stabilizes. Upon reaching  $46.5^\circ\text{C}$ , a gradual mass reduction process is observed, peaking at  $89.0^\circ\text{C}$  and finishing at  $126^\circ\text{C}$  for acetone, and peaking at  $110^\circ\text{C}$  and finishing at  $138^\circ\text{C}$  for THF (Figures 11 and 12, run A). The mass losses observed during these processes total 4.7% (4.2% calculated) for acetone and 8.1% (4.8% calculated) for THF, which are the mass losses expected for one and two molecules of solvent, respectively.

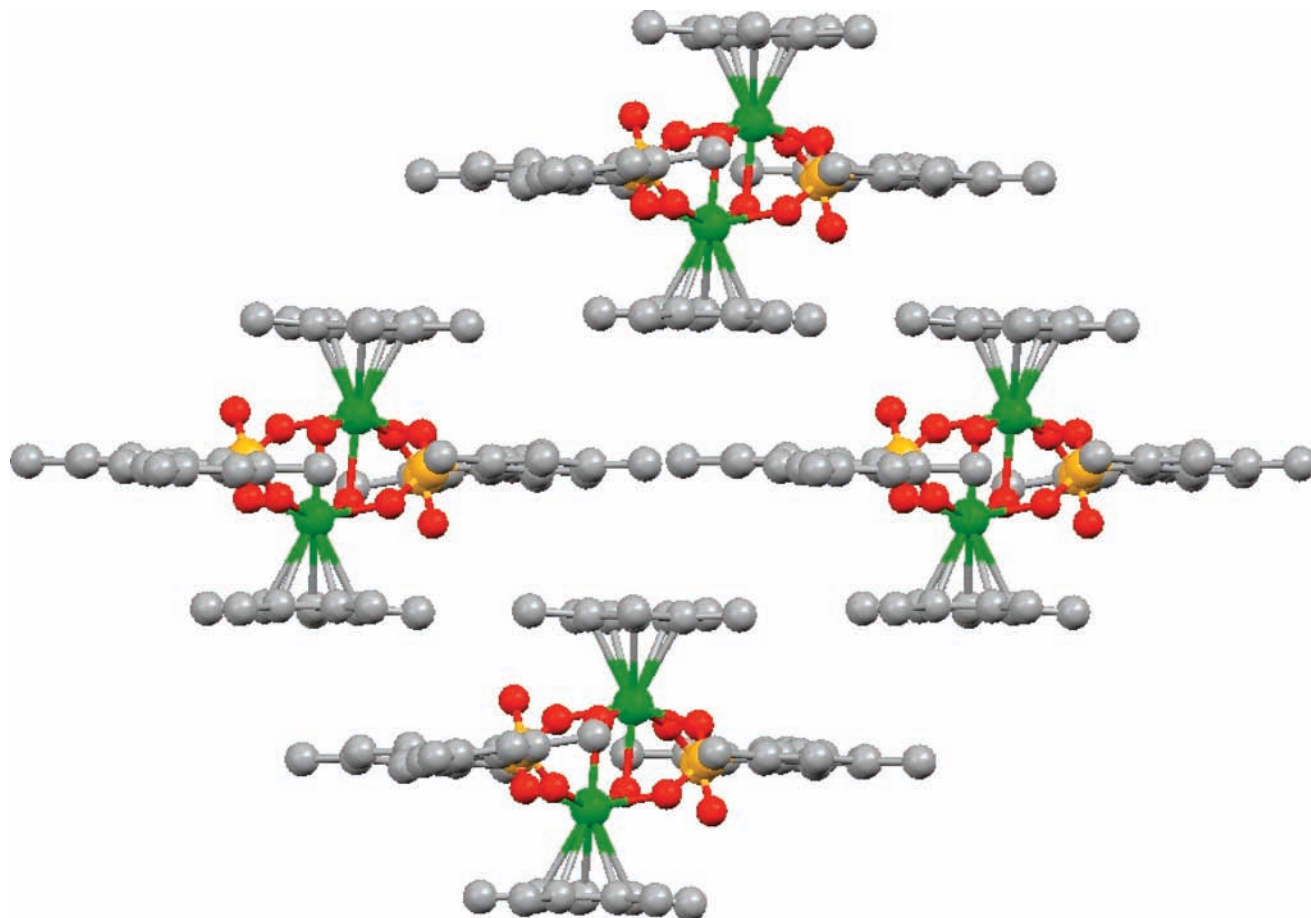


Figure 9. Packing diagram of  $\text{Ta}_2\text{-Mes}\cdot\text{THF}$ .

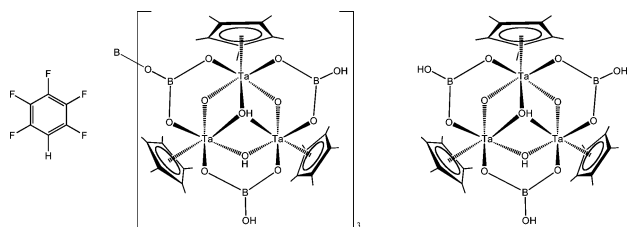


Figure 10. Major products obtained from the reaction of 2 equiv of  $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$  with  $\text{Cp}^*\text{TaMe}_4$ .

Table 2.  $^1\text{H}$  Chemical Shift of Bound and Free Acetone in Adducts of  $\text{Ta}_3$  Complexes in a  $\text{C}_6\text{D}_6$  Solution

complex	$\delta$ (ppm)
free acetone	1.55
$\text{Ta}_3\text{-Ph}$	1.36
$\text{Ta}_3\text{-}i\text{Bu}$	1.54
$\text{Ta}_3\text{-}2,5\text{Me}$	1.53
$\text{Ta}_3\text{-}3,5\text{Me}$	1.45
$\text{Ta}_3\text{-}3,5\text{CF}_3$	1.44

These results show that acetone, which has a boiling point of  $56^\circ\text{C}$ , is strongly imprisoned in the cavity of  $\text{Ta}_3\text{-Ph}$  for its optimal evaporation temperature is  $89.0^\circ\text{C}$ , which is  $33^\circ\text{C}$  more than its boiling point. The same can be said with THF, which has a boiling point of  $66^\circ\text{C}$  and leaves the complex optimally at  $102^\circ\text{C}$ ,  $36^\circ\text{C}$  above its boiling point.  $\text{Ta}_3\text{-}3,5\text{Me}$ , with its electron donating methyl groups in *meta* position, could not retain acetone in the solid state (Figure 11, run B). Indeed, all acetone interacting with the complex is lost during the initialization time since no mass loss is

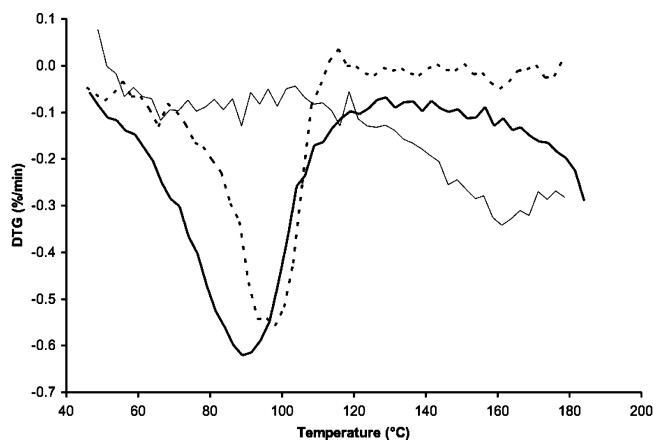
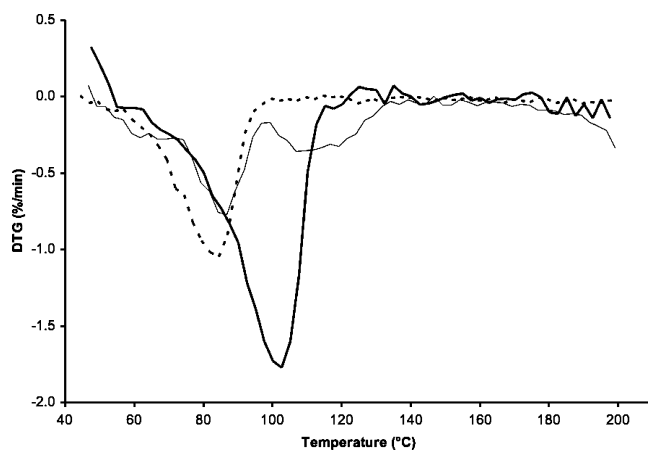


Figure 11. TGA of (A)  $\text{Ta}_3\text{-Ph}$  (thick solid line), (B)  $\text{Ta}_3\text{-}3,5\text{Me}$  (solid line), and (C)  $\text{Ta}_3\text{-}3,5\text{CF}_3$  (dashed line) with acetone.

observed until the complex starts to decompose at  $150^\circ\text{C}$ . This is an interesting result since the complex demonstrates hosting capacities in solution. However,  $\text{Ta}_3\text{-}3,5\text{Me}$  can retain THF in the solid state, as a mass loss of 4.9% (calculated and observed) corresponding to 1 equiv of THF exiting the cage occurs optimally at  $87^\circ\text{C}$  (Figure 12, run B). Isostructural complex  $\text{Ta}_3\text{-}3,5\text{CF}_3$ , with its electron withdrawing trifluoromethyl groups in *meta* position, lost 2.9% of its total mass during the experiment with acetone (3.2% expected) and had its mass reduction process peak at  $96.0^\circ\text{C}$  (Figure 11, run C). This is  $7^\circ\text{C}$  above the value observed for  $\text{Ta}_3\text{-Ph}$  for a total of  $40^\circ\text{C}$  above the boiling



**Figure 12.** TGA of (A) **Ta<sub>3</sub>-Ph** (thick solid line), (B) **Ta<sub>3</sub>-3,5Me** (solid line), and (C) **Ta<sub>3</sub>-3,5CF<sub>3</sub>** (dashed line) with THF.

**Table 3.** Calculated Binding Energies between Ta<sub>3</sub> Complexes and Substrate

complex	substrate molecule	$\Delta E_b^a$ (kcal mol <sup>-1</sup> )	$\Delta E_{ES}^b$ (kcal mol <sup>-1</sup> )	$\Delta E_{ES}^{*c}$ (kcal mol <sup>-1</sup> )
<b>Ta<sub>3</sub>-3,5Me</b>	acetone	-13.4	-17.8	-16.1
<b>Ta<sub>3</sub>-Ph</b>	acetone	-13.8	-17.4	-15.6
<b>Ta<sub>3</sub>-Ph</b>	THF	-14.8	-22.3	-19.7
<b>Ta<sub>3</sub>-3,5CF<sub>3</sub></b>	acetone	-15.9	-19.7	-18.4
<b>Ta<sub>3</sub>-F</b>	acetone	-17.6	-21.0	-18.7

<sup>a</sup> Binding energy calculated at the B3LYP/Lan12DZ level of theory. <sup>b</sup> Electrostatic interaction energy calculated using NPA point charges (see text for more details). <sup>c</sup> Electrostatic interaction energy, including the preparation energy, or the energy required to distort the adduct forming species from their free geometry to the geometry in the adduct complex.

point of acetone. Interestingly, experiments conducted with THF as the guest molecule reached a total mass loss of 4.0% (calculated and observed) and had the mass reduction peak at 85 °C, which is significantly lower than the result observed with **Ta<sub>3</sub>-Ph** and similar to the result obtained with **Ta<sub>3</sub>-3,5Me** (Figure 12, run C). Such difference might be the consequence of the larger volume of THF compared to acetone and of a smaller cavity caused by the trifluoromethyl groups.

Increasing the Lewis acidity at the boron center seems to improve the solvent trapping potential of the cages when steric factors are kept to a minimum. The tests done with the metallocavitands substituted in both *meta* positions of the aryl substituents revealed a certain level of selectivity is attainable by modifying the shape of the opening since **Ta<sub>3</sub>-3,5Me** can host THF effectively whereas acetone is easily lost. When the trimetallic species does not feature an opening, such as with **Ta<sub>3</sub>-2,5Me**, TGA results show no loss of mass until decomposition of the complex, and the same is observed for test runs with silica and carbon exposed to acetone.

We have also attempted to quantify the binding between acetone and the cavitand complexes with Density Functional Theory (DFT) calculations at the B3LYP/Lan12DZ level of theory (Table 3). Geometry optimizations have been performed on **Ta<sub>3</sub>-3,5Me**, **Ta<sub>3</sub>-Ph**, and **Ta<sub>3</sub>-3,5CF<sub>3</sub>** (untruncated) with and without acetone bound. From this, the binding energies,  $\Delta E_b$ , were calculated to be -13.4, -13.8, and -15.9 kcal mol<sup>-1</sup> for **Ta<sub>3</sub>-3,5Me**, **Ta<sub>3</sub>-Ph**, and **Ta<sub>3</sub>-3,5CF<sub>3</sub>**, respectively. This trend agrees with the TGA results in that the peak evaporation temperature was found to be

higher for **Ta<sub>3</sub>-3,5CF<sub>3</sub>** than for **Ta<sub>3</sub>-Ph**, while **Ta<sub>3</sub>-3,5Me** was found not to bind acetone in the solid state. It should be noted that because of the large size of the complexes, it was not feasible to perform harmonic frequency analysis on the full systems, so the binding energies reported do not include zero-point vibrational or free energy corrections. However, we have performed the frequency analysis on a model system  $\{[\text{CpTa}]_3((\text{C}_6\text{H}_5)\text{B}(\text{O})_2)_3(\mu^2\text{-OH})_2(\mu^2\text{-O})(\mu^3\text{-O})\}$  in which the Cp\* ligands of **Ta<sub>3</sub>-Ph** are replaced with Cp groups. Binding of acetone to this cluster in the gas phase has a  $\Delta S_b$  of -41 cal mol<sup>-1</sup> K<sup>-1</sup> and a  $\Delta G_b$  of -1.6 kcal mol<sup>-1</sup> at 298 K. Since acetone dissociation from the complex should occur when  $\Delta G_b$  becomes positive, the calculated enthalpy and entropy of the reaction are in good agreement with the temperature of acetone desorption observed by TGA.

We have also examined the binding energy of **Ta<sub>3</sub>-Ph** with THF and found it to be -14.8 kcal mol<sup>-1</sup>, which is 1.0 kcal mol<sup>-1</sup> stronger than that calculated for acetone. This also agrees with the TGA results which give a peak evaporation temperature of 89 °C for acetone and 102 °C for THF. On the other hand, the binding energy of THF with **Ta<sub>3</sub>-Ph** ( $\Delta E_b = -14.8$  kcal mol<sup>-1</sup>) is less than that of acetone with **Ta<sub>3</sub>-3,5CF<sub>3</sub>** (-15.9 kcal mol<sup>-1</sup>), whereas the peak TGA evaporation temperatures suggest it should be higher.

**Nature of the Interaction Between the Metallocavitand and the Lewis Base.** The FTIR spectra at the solid state of compounds **Ta<sub>3</sub>-Ph**, **Ta<sub>3</sub>-3,5Me**, and **Ta<sub>3</sub>-3,5CF<sub>3</sub>** have one sharp peak around 3645 cm<sup>-1</sup> (3644 cm<sup>-1</sup> for **Ta<sub>3</sub>-Ph**, 3645 cm<sup>-1</sup> for **Ta<sub>3</sub>-3,5Me**, and 3650 cm<sup>-1</sup> for **Ta<sub>3</sub>-3,5CF<sub>3</sub>**) that can be attributed to the  $\nu_{\text{O-H}}$  stretching frequency. Upon addition of acetone, the sharp signal is lost, and one very broad signal centered around 3200 cm<sup>-1</sup> with a half-width close to 200 cm<sup>-1</sup> is observed. However, the broadness of the last signal and the overlap with the C-H stretching frequencies between 3100 and 2700 cm<sup>-1</sup> prevents a more detailed analysis.

The carbonyl stretching frequency of acetone was monitored as well, once inserted into the cavity. With **Ta<sub>3</sub>-Ph**, the carbonyl band shifts to 1708 cm<sup>-1</sup> and a shoulder appears at 1717 cm<sup>-1</sup>, relative to the carbonyl band at the gas phase which is expected to be at 1740 cm<sup>-1</sup>.<sup>20</sup> Complexes **Ta<sub>3</sub>-3,5CF<sub>3</sub>** and **Ta<sub>3</sub>-3,5Me** display similar carbonyl absorption spectra (Table 4). To gain further insight on the nature of the interaction and of the two different stretching frequencies observed for the C=O, computational studies were performed on this system. Since the full systems are too large to perform frequency calculations, a truncated model system  $\{[\text{CpTa}]_3((\text{C}_6\text{H}_5)\text{B}(\text{O})_2)_3(\mu^2\text{-OH})_2(\mu^2\text{-O})(\mu^3\text{-O})\}$  was utilized in which the Cp\* ligands of **Ta<sub>3</sub>-Ph** are replaced with Cp groups. The carbonyl stretching frequency was calculated to be 1676 cm<sup>-1</sup>, which is significantly lower than the experimental value of 1708 cm<sup>-1</sup>. However, using this somewhat modest basis set, the same band in free acetone is calculated to be

(18) Since all acetone molecules are disordered, only the average values without the esds are given in most crystallographic data.

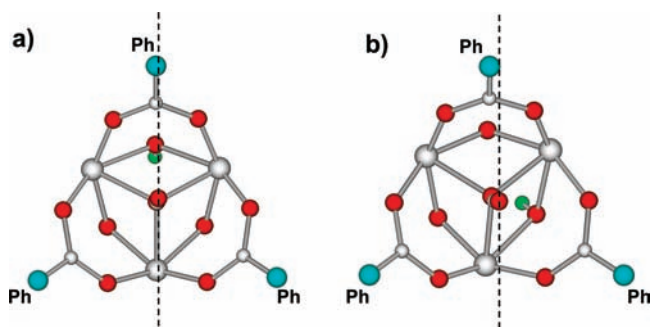
(19) Lin, W.; Ayyappan, P. *Polyhedron* **2003**, *22*, 3037–3042.

(20) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Company: San Francisco, CA, 1960; p 139.

**Table 4.** Carbonyl Stretching Frequencies for Acetone with Ta<sub>3</sub> Complexes

complex	experimental carbonyl band (cm <sup>-1</sup> )		calculated carbonyl band (cm <sup>-1</sup> )
	major component	shoulder	
gaseous acetone	1740		1699
Ta <sub>3</sub> -Ph	1708	1717	1676 <sup>a</sup>
Ta <sub>3</sub> -3,5Me	1703	1715	
Ta <sub>3</sub> -3,5CF <sub>3</sub>	1706	1713	

<sup>a</sup> Carbonyl stretch frequency calculated on a truncated model of Ta<sub>3</sub>-Ph, where the Cp\* have been replaced by Cp ligands (see text for more details).



**Figure 13.** (a) Lowest energy isomer and (b) higher-energy isomer of the Ta<sub>3</sub>-Ph adduct with acetone. The dashed line represents the intersection between the plane of the acetone molecule in the adduct with the plane made by the three Ta atoms. The H atom of the  $\mu^2$ -OH group is shown in green. The Cp ligands and the Ph groups of the Ta<sub>3</sub> clusters and the Me groups of acetone are not shown for clarity.

1699 cm<sup>-1</sup> which is also significantly lower than the experimental value of 1740 cm<sup>-1</sup>. Thus, the shift in the frequency  $\Delta\nu_{\text{CO}}$  is calculated to be -23 cm<sup>-1</sup> which is in reasonable agreement with the shift of -32 cm<sup>-1</sup> observed experimentally.

A distinct shoulder in the carbonyl stretching frequencies suggests that the acetone is bound to the cavitand in at least two distinct configurations. However, all attempts to locate a second distinct binding mode of acetone in our calculated model system or any of the full systems always led back to the most stable binding geometry. In this way, we found the cavities of these complexes somewhat more restrictive than expected. To explain the observed shoulder, we considered the more subtle possibility that the acetone is binding to the cavity in the same way but differently with respect to the bridging  $\mu$ -OH group of the complex. This is depicted in Figure 13, where the dotted line represents the plane of the bound acetone molecule and the hydrogen atom of the bridging  $\mu$ -OH group we are discussing is shown in green. The more symmetric isomer shown in Figure 13a is 0.2 kcal mol<sup>-1</sup> more stable than the asymmetric isomer shown in Figure 13b. Such a difference in energy is small enough for the two isomers to be present via the Boltzmann population at ambient temperature. Moreover, the calculated red-shift in the carbonyl stretching mode is smaller ( $\Delta\nu_{\text{CO}} = 20$  vs 23 cm<sup>-1</sup>) for the less stable isomer, that would be the one corresponding to the shoulder.

The nature of the bonding between the Lewis base and the Ta cavitand is important to understand if one wants to optimize the interaction. Both the acetone and THF interact

with the Ta cavitand through a hydrogen bond with the  $\mu^3$ -OH moiety in the center of the cavity (the ORTEP structures in Figures 2–5 do not show the hydrogen atoms). Without the positions of the hydrogen atoms from the X-ray data, the length of the C=O bond in acetone can be used as a diagnostic parameter to estimate the strength of the hydrogen bond. The crystal structures (as well as the computed structures) reveal that the C=O bond length of acetone only increases by less than 5% relative to the free acetone (Table 1). According to a study done by Novak on the correlation of spectroscopic and crystallographic data, such parameters correspond to a hydrogen bond that is somewhere between weak and intermediate.<sup>21</sup> This suggests that the hydrogen bond alone does not account for the calculated binding energies that were in the range of -13 to -15 kcal mol<sup>-1</sup>.

We have quantified the amount of orbital interaction and charge transfer between cavitand complexes and the acetone. The Mayer bond order<sup>22</sup> between the O atom of acetone and the H atom of the  $\mu^3$ -OH moiety for the model complex was found to be only 0.17, which is too small to account for the binding energies calculated. It might be thought that the acetone may be interacting with the B atoms that project into the mouth of the cavity as depicted in Figures 2–5. However, the B–O distances are fairly long, at >3 Å and the calculated Mayer bond orders of 0.01–0.04 suggest there is negligible interaction. This is also corroborated by the absence of shift upon addition of acetone by <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy.

We have also quantified the amount of charge transfer that occurs upon association of the Lewis acid substrate and the Ta cavitands. Analysis of fragment molecular orbital populations of the acetone–Ta<sub>3</sub> model complex, indicates there is a small charge transfer of ~0.14 e<sup>-</sup> from acetone to the Ta<sub>3</sub> complex upon the adduct formation. Among all occupied orbitals of acetone, the highest occupied molecular orbital HOMO-3 (55% CO character) makes the largest contribution (0.07 electrons) toward the charge transfer to the Ta<sub>3</sub> cluster. This further suggests that the charge transfer occurs primarily through the O–H hydrogen bond.

Without significant orbital overlap and charge transfer, the attractive interaction between the Lewis base and the Ta cavitands must be dominated by electrostatic interactions. This suggests that the cavitand possesses a favorable electrostatic “pocket” for the Lewis base. To estimate the electrostatic interaction energy, we have calculated the Natural Population Analysis charges on the free substrate and substrate free Ta complex in the geometry they are in when they form the adduct. We then evaluated the Coulomb interaction energy using these point charges in the geometry of the adduct. The electrostatic interaction energies calculated in this way,  $\Delta E_{\text{ES}}$ , are given in Table 3 for various cavitand/substrate pairs. They range from -17.4 to -22.3 kcal mol<sup>-1</sup> which compares well with the calculated binding energies that range from -13.4 to -15.9 kcal mol<sup>-1</sup>. The

(21) Novak, A. Hydrogen Bonding in Solids. Correlation of Spectroscopic and Crystallographic Data. In *Structure & Bonding*; Springer: Berlin, 1974; Vol. 18, pp 177–216.

(22) Mayer, I. *Chem. Phys. Lett.* **1983**, 97, 270–274.



electrostatic interaction energies are expected to be higher, to offset the unfavorable steric interactions and the energy required to perturb the geometry of the free species to that in the adduct. We can easily correct for the latter, which is commonly known as the preparation energy, by evaluating the energy of the individual adduct forming species in their respective free geometries and comparing it to the energy of the individual species in the geometry they are in the adduct complex. The preparation energies range between 1.3 to 2.3 kcal/mol and the preparation corrected electrostatic interaction energies are given in Table 3 as  $\Delta E_{ES}^*$ . The largest discrepancy between  $\Delta E_{ES}^*$  and the binding energy  $\Delta E_b$  occurs for the **Ta<sub>3</sub>-Ph**·THF complex. For this complex the electrostatic interaction energy is the strongest, but the binding energy is in the middle of the pack. This suggests that the hydrogen bonding interaction between the  $\mu^3$ -OH group and THF is weaker than with acetone and that the steric interactions upon adduct formation are stronger. The weaker hydrogen bond with the THF adduct is supported by the slightly smaller O–H bond order of 0.15 for the THF adduct versus 0.17 for the acetone adduct.

To investigate what structural features of cavitand complexes are important in the attractive interaction we have analyzed the NPA charges.<sup>23</sup> The acetone and THF molecules bind with their oxygen atoms directed into the cavity. This suggests that a cavity with a positive electrostatic potential exists to interact favorably with the electronegative end of the substrate. Certainly, the positive charge of the  $\mu^3$ -OH hydrogen atom that forms the hydrogen bond with the substrate contributes. However, the strength of this hydrogen bond does not account for all of the binding energy, as already established. The B atoms near the bottom of the cavity have large positive charges. For example, the NPA charges on B in **Ta<sub>3</sub>-Ph** are calculated to be approximately +1.2 e (It is notable that the ESP charges on the boron atoms from a CHELPG calculation are also high,  $\sim +0.9e$ ). To see if the charges on the boron atoms have a strong influence on the binding energy, we set their charges to zero and recalculated the electrostatic binding energy. With the charges set to zero, the electrostatic energy became highly repulsive with  $\Delta E_{ES} = +33.2$  kcal mol<sup>-1</sup>. These calculations strongly suggest that the boron atoms at the mouth of the cavity play a critical role in the binding of Lewis bases. Moreover, it suggests that functionalizing the boron to make it more electropositive will strengthen the substrate binding. To test this, we have calculated the binding energy for Ta<sub>3</sub>-F where the Ph group in Ta<sub>3</sub>-Ph is replaced by F and found the overall binding energy to be very strong at -17.6 kcal mol<sup>-1</sup>.

## Discussion

There is a large number of cavitands reported in the literature for various host–guest purposes, but most species rely on similar frameworks having C<sub>4</sub> (calix[4]arene, resorcin[4]arene), C<sub>5</sub> (cucurbit[5]uril), C<sub>6</sub> ( $\alpha$ -cyclodextrin,

cucurbit[6]uril), or higher symmetry ( $\beta$ - and  $\gamma$ -cyclodextrin). The pseudo C<sub>3</sub> symmetry featured in this work is relatively unique and opens new opportunities that are not easily accessible to other structures, such as chirality, which would be induced by having three different boronate moieties.<sup>24</sup> The association constant measured for acetone and **Ta<sub>3</sub>-Ph** at -90 °C ( $1.3 \pm 0.5 \times 10^3$  M<sup>-1</sup>) is comparable to many host–guest systems with small molecules but is several orders of magnitude lower than the strongest binding constants observed for Lewis bases in cavitands (10<sup>5</sup> to 10<sup>8</sup> M<sup>-1</sup>).<sup>11–13,25</sup> However, it should be noted that THF and acetone are not very strong bases, especially compared to the best systems with DABCO and quinuclidine,<sup>25</sup> and the system we are presenting is intrinsically neutral and no anion- $\pi$  interaction is present,<sup>15b</sup> which is usually the predominant force in strong interactions within cavitands. Also, the opening of the cavity observed in **Ta<sub>3</sub>-Ph** is quite large and the possibility of van der Waals contacts between the walls of the host and the confined guest, as can be observed with cucurbiturils, is limited. Indeed, the metallocavitands can be described as having a conic structure with an approximate diameter of the upper rim of 10 Å, which is relatively similar in size to calix[4]arenes ( $\sim 8$  Å).<sup>26</sup> However, the system we are presenting is one of the simplest: each wall of the cavity is composed of a phenylboronate. We demonstrated that it was possible to functionalize the cavitand by having additional moieties in *meta* position of the arylboronate; the functionalization of the *para* position should therefore be trivial. The modulation of the size of the cavity and the design of architectures with functional groups on the upper-rim would be possible in one synthetic step from one of the many boronic acids commercially available. This fact alone makes this new family of clusters an interesting target for the design of novel supramolecules.

The formation of acid–base pairs in cavitands is not something new; a recent report by Rebek on deep cavitand having acid functionalities show that the barrier of tumbling of amines within an acid-containing cavitand is raised by 6.5 kcal mol<sup>-1</sup>.<sup>25</sup> In our system, the positive electrostatic “pocket” at the bottom of the cavity, caused by the presence of the boron atoms, and the hydrogen bond with the  $\mu^3$ -OH favor the inclusion of Lewis bases with binding energies between -13 and -16 kcal mol<sup>-1</sup> for acetone and THF. Although there is no bond formed between the boron and the oxygen atom of the guests, the weak van der Waals contact with boron is significant enough to orientate the acetone and the THF within the cavity. Indeed, in all solid-state structures and in the computational models, only one orientation is observed for guests, where both lone pairs on oxygen are oriented toward the hydroxide and one boron

(24) **Ta<sub>3</sub>-Ph** is stable in presence of water and of various boronic acids, and no boronate exchange has yet been observed, other than the decomposition of the complex obtained from the reaction with C<sub>6</sub>F<sub>5</sub>B(OH)<sub>2</sub> (vide supra). However, the step by step post-functionalization of a *para*-X-phenylboronate cluster (X = Br, I) and the resolution of the racemic mixture would be possible.

(25) Purse, B. W.; Butterfield, S. M.; Ballester, P.; Shivanyuk, A., Jr. *J. Org. Chem.* **2008**, *73*, 6480–6488.

(26) Average value determined by looking at 795 structures of calix[4]arene in the Cambridge Crystallographic Database.

(23) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746.

atom. Nevertheless, the interaction between acetone and **Ta<sub>3</sub>-Ph** is stronger than with most examples of multidentate Lewis acids coordinating with ketones.<sup>27</sup> In a previous report, Gabbai reported that multidentate organomercurials exhibited specific interactions with ketones in solution.<sup>28</sup> However, the interactions at the solid state were weaker; the acetone would evaporate when left for a few minutes on the benchtop, and no physical analyses were made.

## Concluding Remarks

The complexes described herein are an important addition to the family of boronate ligands coordinated to transition metals for they not only greatly expand the family of reported complexes but also further our understanding of the assembly and stability of these complexes. Several of the trimetallic species feature an interesting electrophilic cavity, which has been shown to interact with Lewis bases.

Most inclusion complexes having large association constants rely mainly on multiple interactions, such as hydrogen bonding or ionic interactions, or larger pores for guest selectivity. However, the synthetic challenges to obtain these organic hosts are numerous, which can limit the accessibility of the desired molecular architecture. Here, we have described the simplest supramolecular structures that can be made and still have significant binding energy. While the association constants and the binding energies are comparable to known organic cavitands, it should be kept in mind that the reported complexes bear no special functional groups and a relatively small cavity. It is possible to increase the volume of the cavity or to add functional groups just by modifying the nature of the arylboronic acid, in only one step. We are currently working in adding functional groups on the metallocavitands for the design of sensors and catalysts.

## Experimental Section

**General Comments.** The syntheses of the tantalum clusters were conducted under an atmosphere of nitrogen using standard glovebox techniques. All subsequent manipulations and workup were done under normal atmosphere. Toluene was purified using a MBraun SPS. Benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> were purified by vacuum distillation from Na/K alloy. The elemental analyses were performed at the Laboratoire d'analyse élémentaire de l'Université de Montréal. Cp\*TaMe<sub>4</sub>,<sup>29</sup> **Ta<sub>3</sub>-Ph**, and **Ta<sub>3</sub>-iBu**,<sup>16</sup> were prepared according to literature procedures. The boronic acids were purchased from Aldrich, Alfa Aesar, and Frontier Scientific and were used as received. NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer at 400.0 MHz (<sup>1</sup>H) and 100.0 MHz (<sup>13</sup>C) or on a Bruker NMR AC-300 at 300 MHz (<sup>1</sup>H) and 75.5 MHz (<sup>13</sup>C). The temperatures of the VT NMR experiments were measured using a thermocouple inside the probe which was calibrated with methanol prior to its use.

**Synthesis of {[Cp\*Ta]<sub>3</sub>(μ<sup>2</sup>-η<sup>2</sup>-2,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>B(O)<sub>2</sub>)<sub>3</sub>(μ<sup>2</sup>-OH)<sub>2</sub>(μ<sup>2</sup>-O)(μ<sup>3</sup>-O)} (Ta<sub>3</sub>-2,5Me).** A solution of water (9.6 μL, 0.531 mmol) and 2,5-(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>)B(OH)<sub>2</sub> (159 mg, 1.06 mmol) in THF (5 mL) was added to a solution of Cp\*TaMe<sub>4</sub> (200 mg, 0.531 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 5 h under vacuum at 90 °C for the <sup>1</sup>H NMR experiments or recrystallized from acetone. Isolated yield: 143 mg, 55%. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 7.76 (s, 3 H), 6.95 (m, 6 H), 2.26 (ov s, 9 H), 2.24 (ov s, 9 H), 2.11 (br, 15 H), 2.03 (br, 30 H). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ 140.7, 135.5, 132.5, 129.6, 129.3, 122.1, 22.6, 21.3, 11.6. <sup>11</sup>B{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): 30.3. Anal. Calcd for C<sub>54</sub>H<sub>74</sub>B<sub>3</sub>O<sub>10</sub>Ta<sub>3</sub>: C, 44.47; H, 5.11. Found: C, 45.42; H, 5.23.

**Synthesis of {[Cp\*Ta]<sub>3</sub>(μ<sup>2</sup>-η<sup>2</sup>-3,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>B(O)<sub>2</sub>)<sub>3</sub>(μ<sup>2</sup>-OH)(μ<sup>2</sup>-O)<sub>2</sub>(μ<sup>3</sup>-OH)}·acetone (Ta<sub>3</sub>-3,5Me).** A solution of water (9.6 μL, 0.531 mmol) and 3,5-(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>)B(OH)<sub>2</sub> (159 mg, 1.06 mmol) in THF (5 mL) was added to a solution of Cp\*TaMe<sub>4</sub> (200 mg, 0.531 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 5 h under vacuum at 90 °C for the <sup>1</sup>H NMR experiments or recrystallized from acetone. Isolated yield: 139 mg, 54%. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 7.83 (br s, 4 H), 7.68 (s, 2H), 6.86 (s, 2 H), 6.75 (s, 1 H), 2.25 (ov s, 12 H), 2.24 (ov s, 6 H), 2.19 (br s, 30 H), 2.11 (br s, 15 H). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ 139.5, 137.7, 136.1, 135.7, 135.4, 133.9, 133.5, 133.1, 131.5, 131.4, 131.2, 130.7, 130.2, 126.4, 122.5, 122.0, 29.9, 21.7, 21.6, 21.4, 21.0, 11.9, 11.6. <sup>11</sup>B{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): 24.0. Anal. Calcd for C<sub>54</sub>H<sub>74</sub>B<sub>3</sub>O<sub>10</sub>Ta<sub>3</sub>: C, 44.47; H, 5.11%. Found: C, 44.37; H, 5.28%.

**Synthesis of {[Cp\*Ta]<sub>3</sub>(μ<sup>2</sup>-η<sup>2</sup>-3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>B(O)<sub>2</sub>)<sub>3</sub>(μ<sup>2</sup>-OH)(μ<sup>2</sup>-O)<sub>2</sub>(μ<sup>3</sup>-OH)}·acetone (Ta<sub>3</sub>-3,5CF<sub>3</sub>).** A solution of water (7.2 μL, 0.399 mmol) and 3,5-(CF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>)B(OH)<sub>2</sub> (210 mg, 0.814 mmol) in THF (5 mL) was added to a solution of Cp\*TaMe<sub>4</sub> (150 mg, 0.399 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 yellow precipitate was washed once with acetone (2 mL) in normal atmosphere. The white powder was dried for 5 h under vacuum at 90 °C for the <sup>1</sup>H NMR experiments or recrystallized from acetone. Isolated yield: 146 mg, 75%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 8.31 (s, 4 H), 8.25 (s, 2 H), 7.89 (s, 3 H), 2.30 (ov s, 30 H), 2.27 (ov s, 15 H). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 145.1, 136.6, 131.7, 129.9, 127.2, 125.2, 124.7, 124.5, 124.0, 121.8, 13.1, 12.9. <sup>11</sup>B{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): 27.6. <sup>19</sup>F{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ -64.1. Anal. Calcd for C<sub>54</sub>H<sub>56</sub>B<sub>3</sub>O<sub>10</sub>F<sub>18</sub>Ta<sub>3</sub>: C, 36.39; H, 3.17%. Found: C, 36.88; H, 3.11%.

**Synthesis of {[Cp\*Ta]<sub>2</sub>(μ<sup>2</sup>-η<sup>2</sup>-MesB(O)<sub>2</sub>)<sub>2</sub>(η<sup>1</sup>-MesB(O)(OH))<sub>2</sub>(μ<sup>2</sup>-OH)<sub>2</sub>} (Ta<sub>2</sub>-Mes).** A solution of water (9.6 μL, 0.531 mmol) and 2,4,6-(CH<sub>3</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>2</sub>)B(OH)<sub>2</sub> (175 mg, 1.07 mmol) in toluene (5 mL) was added to a solution of Cp\*TaMe<sub>4</sub> (200 mg, 0.531 mmol) in toluene (5 mL) under nitrogen at -78 °C. The resulting yellow solution was stirred for 4 days at room temperature until it turned colorless. The solvent was then removed under reduced pressure. Colorless crystals were obtained from a concentrated THF solution. Isolated yield: 133 mg, 38%. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, -40 °C): δ 7.00 (s, 2H), 6.86 (s, 2H), 2.71 (s, 6H), 2.49 (s, 6H), 2.31 (d, <sup>4</sup>J<sub>H-H</sub> = 8.8 Hz, 6H), 1.90 (s, 15H). <sup>11</sup>B{<sup>1</sup>H} NMR (chloroform-*d*): 31.2. Anal. Calcd for C<sub>56</sub>H<sub>78</sub>B<sub>4</sub>O<sub>10</sub>Ta<sub>2</sub>: C, 51.10; H, 5.97%. Found: C,

- (27) (a) Wuest, J. D. *Acc. Chem. Res.* **1999**, *32*, 81–89. (b) Maruoka, K. *Pure Appl. Chem.* **2002**, *74*, 123–128. (c) Simard, M.; Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 370–372.  
 (28) (a) Tschinkl, M.; Schier, S.; Riede, J.; Gabbai, F. P. *Organometallics* **1999**, *18*, 1747–1753. (b) Beckwith King, J.; Tsunoda, M.; Gabbai, F. P. *Organometallics* **2002**, *21*, 4201–4205.  
 (29) Sanner, R. D.; Carter, S. T., Jr. *J. Organomet. Chem.* **1982**, *240*, 157–162.

**Table 5.** Crystal Data, Data Collection, and Structure Refinement for Ta<sub>3</sub> Complexes and Ta<sub>2</sub>-Mes

	Ta <sub>3</sub> -2,5Me	Ta <sub>3</sub> -3,5Me	Ta <sub>3</sub> -3,5CF <sub>3</sub>	Ta <sub>3</sub> -Ph·acetone	Ta <sub>2</sub> -Mes
formula	C <sub>54</sub> H <sub>72</sub> B <sub>3</sub> O <sub>10</sub> Ta <sub>3</sub>	C <sub>54</sub> H <sub>72</sub> B <sub>3</sub> O <sub>10</sub> Ta <sub>3</sub> , C <sub>3</sub> H <sub>6</sub> O	C <sub>54</sub> H <sub>54</sub> B <sub>3</sub> O <sub>10</sub> F <sub>18</sub> Ta <sub>3</sub> , C <sub>3</sub> H <sub>6</sub> O	C <sub>54</sub> H <sub>74</sub> B <sub>3</sub> O <sub>12</sub> Ta <sub>3</sub> , C <sub>3</sub> H <sub>6</sub> O	C <sub>56</sub> H <sub>48</sub> B <sub>4</sub> O <sub>10</sub> Ta <sub>2</sub> , 2(C <sub>3</sub> H <sub>8</sub> O)
fw	1457.4	1514.47	1838.33	1548.50	1460.53
size (mm)	0.30 × 0.24 × 0.20	0.18 × 0.11 × 0.10	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.2	0.15 × 0.16 × 0.06
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.2618(5)	12.313(3)	12.554(3)	12.2119(8)	13.6909(19)
<i>b</i> (Å)	20.0522(7)	12.435(3)	12.669(3)	17.2175(11)	16.068(2)
<i>c</i> (Å)	18.4914(6)	20.171(3)	21.659(6)	14.6516(10)	16.587(2)
$\alpha$ (deg)	90	87.105(3)	83.460(3)	90	97.783(2)
$\beta$ (deg)	90.34(1)	83.411(3)	78.659(3)	111.5270(10)	110.322(2)
$\gamma$ (deg)	90	74.300(3)	74.210(3)	90	107.834(2)
<i>V</i> (Å <sup>3</sup> )	5288.1(3)	2952.9(12)	3243.3(14)	2865.7(3)	3135.3(7)
<i>Z</i>	4	2	2	2	2
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
<i>D</i> <sub>calc.</sub> (mg·m <sup>-3</sup> )	1.831	1.703	1.882	1.727	1.547
<i>F</i> <sub>000</sub>	2844	1484	1772	1456	1480
temp (K)	100(2)	200(2)	200(2)	200(2)	100(2)
no. of unique/total reflns	12872/64497	13711/34427	15322/38820	7188/35331	12270/33865
<i>R</i> <sub>int</sub>	0.0266	0.0379	0.0722	0.0243	0.0474
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0179 w <i>R</i> 2 = 0.0466	<i>R</i> 1 = 0.0318 w <i>R</i> 2 = 0.0629	<i>R</i> 1 = 0.0489 w <i>R</i> 2 = 0.1214	<i>R</i> 1 = 0.0243 w <i>R</i> 2 = 0.0579	<i>R</i> 1 = 0.0371 w <i>R</i> 2 = 0.0836

51.53; H, 6.37%. The low solubility of Ta<sub>2</sub>-Mes prevented from taking a <sup>13</sup>C{<sup>1</sup>H} NMR spectrum.

**Reaction of Cp\*TaMe<sub>4</sub> with C<sub>6</sub>F<sub>5</sub>B(OH)<sub>2</sub>.** A solution of water (9.6 μL, 0.531 mmol) and C<sub>6</sub>F<sub>5</sub>B(OH)<sub>2</sub> (225 mg, 1.07 mmol) in THF (5 mL) was added to a solution of Cp\*TaMe<sub>4</sub> (200 mg, 0.531 mmol) in THF (5 mL) under nitrogen at -78 °C. The resulting dark yellow solution was stirred for 2 days at room temperature until it turned pale yellow. The solvent was then removed under reduced pressure. The resulting yellow precipitate was dissolved in acetone (2 mL) in normal atmosphere and recrystallized into clear colorless crystals. Yield: 138 mg. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub> ppm): δ 2.0–2.3 (m).

**Binding Constant Determination.** The binding constants were determined by <sup>1</sup>H NMR. Solutions of the cavitand were prepared at known concentrations in deuterated toluene, and roughly 1 equiv of acetone was added to the mixture. An initial spectrum was recorded at room temperature with a 30 s pulse delay to improve the accuracy of the integrations, and the exact concentration of acetone in solution was obtained. A second spectrum was recorded at -90 °C with 30 s pulse delay, and concentrations for the trapped and free acetone were obtained. The binding constants were then calculated from the equation: [Ta·acetone]/[Ta]<sub>free</sub>[acetone]<sub>free</sub>. All experiments were duplicated with separate samples.

**Crystallographic Data.** Crystallographic data are reported in Table 5. Single crystals were coated with Paratone-N oil, mounted using a glass fiber and frozen in the cold nitrogen stream of the goniometer. The data were collected on a Bruker SMART APEX II diffractometer. The data were reduced (SAINT)<sup>30</sup> and corrected for absorption (SADABS).<sup>31</sup> The structure was solved and refined using SHELXS-97 and SHELXL-97.<sup>32</sup> All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions, but the hydrogen atoms on the hydroxyl ligands are missing since they were not located. Neutral atom scattering factors were taken from the International Tables for X-Ray Crystallography.<sup>33</sup> All calculations and drawings were performed using

the SHELXTL package.<sup>34</sup> The final model was checked for either missed symmetry or voids in the crystal structure using the PLATON software.<sup>35</sup> None was found. The crystal structures gave a satisfactory checkcif report.

**Thermogravimetric Analyses.** TG-MS measurements were performed using a Netzsch STA 449C thermogravimetric analyzer coupled with a Netzsch Aeolos QMS 403C mass spectrometer. For complexes with acetone binding, the experiments were conducted over a range of 150 °C, from 34 to 184 °C. THF experiments were conducted from 35 to 200 °C. The temperature was increased at a rate of 5 °C/min.

**FTIR.** Spectra were recorded using a Nicolet Magna 850 Fourier transform infrared spectrometer (Thermo Scientific, Madison, WI) with a liquid nitrogen cooled narrow-band mercury cadmium telluride (MCT) detector and a Golden Gate ATR accessory (Specac Ltd., London, U.K.). In this apparatus, the infrared beam is focused to a diameter of about 500 μm on the diamond crystal with ZnSe lenses (4× magnification). Each spectrum was obtained from 128 scans at a resolution of 4 cm<sup>-1</sup> using a Happ-Genzel apodization. No further spectral operations were performed on obtained spectra.

**Computational Section.** DFT calculations have been performed using Gaussian 03<sup>36</sup> program at the B3LYP<sup>37</sup>/LanL2DZ<sup>38</sup> level. Geometry optimizations and electronic structure analysis calculations were completed using the spin-restricted method. Wave function stability calculations<sup>39</sup> were performed to confirm that the calculated wave functions corresponded to the true electronic ground state. Tight self-consistent field (SCF) convergence criteria (10<sup>-8</sup> a.u.) were used for all calculations. Harmonic frequency calculations were used to determine the nature of the stationary points, vibrational frequencies, and the thermodynamic parameters (at 298 K and 1 atm.) for the cyclopentadienyl (Cp) models of the Ta clusters. The analysis of the electronic structure was performed using Gaussian 03 calculations at the same level of theory as geometry optimizations. Orbital populations and compositions were calculated using Mulliken population analysis (MPA) using the AOMix program.<sup>40</sup> Mayer bond orders<sup>22</sup> were calculated using the AOMix-L program. Atomic charges were evaluated by using the natural population analysis (NPA).<sup>23</sup>

(30) SAINT, Version 7.07a; Bruker AXS Inc.: Madison, WI, 2003.

(31) Sheldrick, G. M. SADABS, Version 2004/1; Bruker AXS Inc.: Madison, WI, 2004.

(32) Sheldrick, G. M. SHELXS-97 and SHELXL-97. Programs for the refinement of crystal structures; University of Göttingen: Göttingen, Germany, 1997.

(33) International Tables for Crystallography; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, pp 219–222, and pp. 500–502.

(34) SHELXTL, Version 6.12; Bruker AXS Inc.: Madison, WI, 2001.

(35) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; University of Utrecht: Utrecht, The Netherlands, 2005.

The energies of electrostatic interactions were evaluated using the point-charge approximation:

$$E_{ES} = \sum_{a \in Ta} \sum_{b \in X} \frac{q_a^{NPA} q_b^{NPA}}{r_{ab}} \quad (\text{in atomic units})$$

where  $q^{NPA}$  are NPA-derived atomic charges in the two non-interacting fragments,  $Ta_3$  and the substrate, with the geometry of

- (36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Lyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (37) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.
- (38) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.
- (39) Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047–9052.

the adduct.  $r_{ab}$  are the corresponding interatomic distances in the adduct structure.

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**Supporting Information Available:**  $^1\text{H}$  NMR and FTIR spectra of selected compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data have been deposited with CCDC (CCDC No. 704431 for **Ta<sub>2</sub>-Mes**, CCDC No. 704432 for **Ta<sub>3</sub>-2,5Me**, CCDC No. 704433 for **Ta<sub>3</sub>-3,5Me·acetone**, CCDC No. 704434 for **Ta<sub>3</sub>-Ph·acetone**, and CCDC No. 704435 for **Ta<sub>3</sub>-3,5CF<sub>3</sub>·acetone**). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk), or via the Internet at [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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- (40) Gorelsky, S. I. *AOMix*, version 6.36; University of Ottawa: Ottawa, Canada, 2007.