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## **ARTICLE TYPE**

## Synthesis and Characterization of Tantalum Silsesquioxane Complexes

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- <sup>5</sup> Tantalum polyhedral oligosilsesquioxane (POSS) complexes have been synthesised and characterized. X-ray structures of these complexes revealed that the coordination number of the tantalum center greatly affects the cube-like silsesquioxane framework.
- Over the past several years, single-site, supported tantalum 10 species have been observed to catalyze a number of interesting and noteworthy transformations. For example, Basset and coworkers have developed silica-supported tantalum hydride catalysts for alkane metathesis,<sup>1</sup> and chiral tantalum catalysts for 15 enantioselective epoxidations.<sup>2</sup> This laboratory has found that supported tantalum species are highly efficient alkene epoxidation catalysts that can employ hydrogen peroxide as the oxidant.<sup>3</sup> With growing interest in single-site tantalum catalysts for various transformations, it is important to develop molecular, 20 structural models for such species and probe their spectroscopic and structural properties. In this way it may be possible to establish structure-activity relationships, which are crucial for the design and development of more efficient catalysts. Along these lines, molecular models for silica-bound metal centers have been <sup>25</sup> based on calixarene<sup>4</sup> and siloxide<sup>5</sup> ligands, but most interest has
- centered on incompletely condensed polyhedral oligosilsesquioxane (POSS) ligands, which have been studied as close analogues of the surface silanol groups present on silica.<sup>6,7</sup>
- While many metal-POSS derivatives have been prepared and <sup>30</sup> studied (e.g., with Ti, Zr, Hf, V, Cr, Mo, Re, Fe, Rh, Pt, Au, Zn, Al, Ga, and Sn) as structural molecular models and as related homogeneous catalysts for some of them,<sup>8</sup> there are only two reports in the literature of Ta silsesquioxane complexes which differ substantially in their structures.<sup>9,10</sup> While the complex
- <sup>35</sup> described by Edelmann and co-workers appears to possess a cube-like, cage structure with tantalum as part of the cage, the system described by Basset and co-workers possesses a Ta that is coordinated to a completely condensed POSS. However, no Xray structural characterization of tantalasilsesquioxane complexes
- <sup>40</sup> has so far been reported. In this contribution we describe the synthesis and characterization of four new tantalasilsesquioxane complexes, along with their X-ray crystal structures.
  - The reaction of  $Cp*TaCl_4^{11}$  (Cp\*
- pentamethylcyclopentadienyl) with 1 equiv of the silsesquioxane <sup>45</sup> **1** in toluene at 110 °C for 12 h produced complex **2**, isolated as a white powder in 79% yield after dropwise addition of acetonitrile into a solution of **2** in toluene (Scheme 1).† The <sup>1</sup>H NMR spectrum displays a singlet at 2.10 ppm for the Cp\* moiety and

three doublets at 1.19, 1.12 and 1.09 ppm for the *i*-butyl ligands 50 (3:3:1 H).



Treatment of 2 with 1.2 equiv of methyl lithium in diethyl ether at -30 °C resulted in formation of 3 in 94% (Scheme 2). In 55 addition to the expected resonances for the Cp\* and *i*-butyl groups, the <sup>1</sup>H NMR spectrum of **3** displays a singlet at 0.71 ppm for the methyl ligand. The chloride ligand of 2 can also be displaced by the "less-coordinating" trifluoromethanelsulfonate (OTf) and BAr<sup>F</sup> ( $[B(C_6F_5)_4]^-$ ) anions, to give 4 and 5, 60 respectively. Complex 4 was obtained as a white powder in quantitative yield by the reaction of 2 with 1 equiv of silver trifluoromethanesulfonate (AgOTf) in toluene at room temperature. The <sup>19</sup>F NMR spectrum of 4 displays a singlet at 75.6 ppm, confirming substitution of the chloride ligand by 65 triflate. In order to access a tantalasilsesquioxane cation, 2 was treated with 1.15 equiv of  $LiB(C_6F_5)_4$  2Et<sub>2</sub>O in dichloromethane to afford 5 as a white powder in 85% yield after crystallization from acetonitrile at -30 °C. After removal of the residual solvent under vacuum, the <sup>1</sup>H NMR spectrum of 5 in  $C_6D_6$  displays only 70 resonances for the *i*-butyl and Cp\* groups. No solvent appears to be coordinated to the Ta (Fig. S1). Moreover, the <sup>19</sup>F NMR spectrum displays 3 singlets between -130 ppm and -165 ppm, confirming the presence of the BAr<sup>F</sup> anion. As has been observed for Ti silsesquioxane complexes with the same silsesquioxane 75 backbone, the  ${}^{29}Si{}^{1}H$  NMR spectrum of the complexes 3, 4 and 5 display three signals between -60 and -70 ppm.<sup>12</sup> However, only two resonances at -63.3 ppm and -66.9 ppm are observed in the  ${}^{29}Si{}^{1}H$  NMR spectrum of the complex 2, likely due to the overlap of two signals.



Scheme 2 Synthesis of 3-5. i) MeLi (1.6 M in diethyl ether), diethyl ether, -30 °C to RT, 3 h; ii) AgOTf, toluene, RT, 3 h; iii)  $LiB(C_6F_5)_4 2Et_2O$ , dichloromethane, -30 °C to RT, 3 h.

- Single crystal X-ray diffraction studies of the new tantalasilsesquioxane complexes 2-5 confirmed the structures proposed in Schemes 1 and 2. Crystals of 2 and 3 suitable for X-ray diffraction were obtained from saturated solutions of the compounds in hexanes and pentane, respectively, at -30 °C. Slow 10 evaporation of a solution of 4 in benzene at 20 °C afforded crystals of 4, and crystals of 5 were obtained by slow diffusion of pentane into a solution of 5 in toluene at -30 °C. The structures of these complexes are represented in Fig. 1-4 and selected bonds and angles are summarized in Table 1.
- <sup>15</sup> The crystal structures of **4** and **5** confirmed that the triflate anion coordinates to the Ta center, while the BAr<sup>F</sup> anion is not coordinated. In general, a four-legged piano stool geometry for the tantalum center (compounds **2-4**) leads to a distorted cubelike structure, whereas the three-legged piano stool structure of **5**
- <sup>20</sup> gives a regular, cube-like silsesquioxane framework. For complexes 2-5, the Ta-O(Si) distances are between 1.843(4) and 1.9694(18) Å and are similar to the Ta-O(Si) bond distances (1.806-2.041 Å) previously reported for tantalum complexes with -OSi(O'Bu)<sub>3</sub>,<sup>3a</sup> -OSi<sup>1</sup>Bu<sub>3</sub>,<sup>13</sup> -OSi<sup>Ph<sub>3</sub><sup>14</sup> or -OSi<sup>1</sup>BuPh<sub>2</sub><sup>15</sup> ligands.</sup>



<sup>30</sup> Fig. 1 Molecular structure of 2 displaying thermal ellipsoids at the 50% probability level. H-atoms and *i*-butyl groups have been omitted for clarity.



**Fig. 2** Molecular structure of **3** displaying thermal ellipsoids at the 50% <sup>35</sup> probability level. H-atoms and *i*-butyl groups have been omitted for clarity.



**Fig. 3** Molecular structure of **4** displaying thermal ellipsoids at the 50% probability level. H-atoms, *i*-butyl groups and a C<sub>6</sub>H<sub>6</sub> molecule have been <sup>40</sup> omitted for clarity.

25

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Fig. 4 Molecular structure of cation 5 displaying thermal ellipsoids at the 50% probability level. H-atoms, *i*-butyl groups and  $[B(C_6F_5)_4]$ <sup>-</sup> have been omitted for clarity.

The coordination number of the tantalum center greatly affects the structure of the cube-like silsesquioxane framework, as can be seen in examination of the Ta-O-Si and O-Ta-O angles. For **5**, the three Ta-O-Si angles are similar (145.0(3)-153.3(3)°) whereas three distinct angles are observed in the structures of **2-4**. For **2-4**, <sup>10</sup> the angle for the Ta-O-Si linkage that is *trans* to the anionic donor ligand (Cl, Me or OTf) outside the cage is greatest (165.4(5)-177.1(1)°). In each complex, one of the remaining Ta-O-Si angles is intermediate in value (143.5(1)-147.0(5)°), while the other is more acute (117.1(1)-133.1(5)°). Literature values for

- <sup>15</sup> Ta-O-Si angles in tantalum siloxide complexes vary between 162 and  $175^{\circ}$ ,<sup>3a,13,14,15</sup> whereas in complexes **2-5**, the Ta-O-Si angles are distributed over a wider range (117-177°). This phenomenon is probably due to a combination of electronic and steric effects enforced by the Ta-Cp\*X fragment in the cube-like framework.
- <sup>20</sup> For **5**, the three O-Ta-O angles have similar values (102.1(2)-105.4(2)°). Similar O-M-O (M = Zr, Hf) angles have previously been reported for isoelectronic Zr-POSS<sup>16</sup> (103.4(6)°) and Hf-POSS<sup>17</sup> (102.7(2)°) compounds with the same three-legged piano stool geometry. To the best of our knowledge, no other cationic <sup>25</sup> tantalum complex with a three-legged piano stool geometry has
- been reported in the literature.

The O-Ta-X (X = O, Cl, Me, OTf) angles for **2-4** exhibit two distinctly different values. In general, the *trans*-like O-Ta-X angle involving the donor atom outside the cage (X) is larger (145-

<sup>30</sup> 153°) than the other *trans* O-Ta-O angle (125-140°). This structural feature is commonly observed for the four-legged piano stool coordination geometry.<sup>18</sup> The remaining bond angles associated with *cis* arrangements of the silsesquioxane and X donor atoms are rather acute (*ca.* 80-90° for the O-Ta-O angles) <sup>35</sup> as expected, with the *cis* O-Ta-X angles being smaller.

| 2           |            |                   |            |
|-------------|------------|-------------------|------------|
| Cl(1)-Ta(1) | 2.4624(9)  | O(9)-Si(6)-O(10)  | 109.37(14) |
| O(1)-Ta(1)  | 1.947(3)   | O(9)-Si(6)-O(11)  | 108.14(14) |
| O(2)-Ta(1)  | 1.939(2)   | O(10)-Si(6)-O(11) | 108.86(14) |
| O(3)-Ta(1)  | 1.929(3)   | O(3)-Ta(1)-O(1)   | 140.02(11) |
|             |            | O(3)-Ta(1)-O(2)   | 86.66(10)  |
|             |            | O(2)-Ta(1)-O(1)   | 85.06(10)  |
|             |            | O(3)-Ta(1)-Cl(1)  | 83.67(8)   |
|             |            | O(2)-Ta(1)-Cl(1)  | 148.70(8)  |
|             |            | O(1)-Ta(1)-Cl(1)  | 83.49(8)   |
|             |            | Si(1)-O(1)-Ta(1)  | 117.13(14) |
|             |            | Si(3)-O(2)-Ta(1)  | 169.99(17) |
|             |            | Si(2)-O(3)-Ta(1)  | 146.91(16) |
| 3           |            |                   |            |
| C(1)-Ta(1)  | 2.275(2)   | O(12)-Si(6)-O(7)  | 111.42(11) |
| O(1)-Ta(1)  | 1.9318(18) | O(12)-Si(6)-O(8)  | 107.66(10) |
| O(2)-Ta(1)  | 1.9694(18) | O(7)-Si(6)-O(8)   | 107.99(10) |
| O(3)-Ta(1)  | 1.9433(18) | O(1)-Ta(1)-O(3)   | 131.56(8)  |
| C(2)-Ta(1)  | 2.453(3)   | O(1)-Ta(1)-O(2)   | 85.50(8)   |
| C(3)-Ta(1)  | 2.490(3)   | O(3)-Ta(1)-O(2)   | 84.06(8)   |
| C(4)-Ta(1)  | 2.455(3)   | O(1)-Ta(1)-C(1)   | 81.44(8)   |
| C(5)-Ta(1)  | 2.425(3)   | O(3)-Ta(1)-C(1)   | 80.81(9)   |
| C(6)-Ta(1)  | 2.406(3)   | O(2)-Ta(1)-C(1)   | 145.08(8)  |
|             |            | Si(1)-O(1)-Ta(1)  | 143.54(11) |
|             |            | Si(3)-O(2)-Ta(1)  | 177.12(13) |
|             |            | Si(4)-O(3)-Ta(1)  | 129.66(11) |
| 4           |            |                   |            |
| O(1)-Ta(1)  | 2.223(8)   | O(9)-Si(6)-O(13)  | 109.2(4)   |
| O(4)-Ta(1)  | 1.894(8)   | O(9)-Si(6)-O(12)  | 109.5(4)   |
| O(5)-Ta(1)  | 1.912(7)   | O(13)-Si(6)-O(12) | 108.2(4)   |
| O(6)-Ta(1)  | 1.895(8)   | O(4)-Ta(1)-O(6)   | 125.2(3)   |
|             |            | O(4)-Ta(1)-O(5)   | 88.9(3)    |
|             |            | O(6)-Ta(1)-O(5)   | 89.0(3)    |
|             |            | O(4)-Ta(1)-O(1)   | 77.3(3)    |
|             |            | O(6)-Ta(1)-O(1)   | 80.4(3)    |
|             |            | O(5)-Ta(1)-O(1)   | 152.7(3)   |
|             |            | Si(3)-O(4)-Ta(1)  | 133.1(5)   |
|             |            | Si(2)-O(5)-Ta(1)  | 165.4(5)   |
|             |            | Si(1)-O(6)-Ta(1)  | 147.0(5)   |
| 5           |            |                   |            |
| O(1)-Ta(1)  | 1.855(5)   | O(3)-Si(3)-O(6)   | 109.2(3)   |
| O(12)-Ta(1) | 1.843(4)   | O(3)-Si(3)-O(10)  | 108.8(2)   |
| O(4)-Ta(1)  | 1.867(4)   | O(6)-Si(3)-O(10)  | 108.0(3)   |

Table 1 Selected bond lengths [Å] and angles [°] for 2-5

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108.0(3)O(4)-Ta(1) 1.867(4) J(6)-S1(3)-O(10) O(4)-Ta(1)-O(12) 102.14(18) O(4)-Ta(1)-O(1) 105.4(2)104.34(18) O(12)-Ta(1)-O(1) 152.1(3) Si(1)-O(1)-Ta(1)Si(5)-O(4)-Ta(1) 145.0(3) 153.3(3) Si(7)-O(12)-Ta(1) To evaluate the influence of a neutral donor ligand in the

10 evaluate the influence of a neutral donor ligand in the 40 coordination sphere of the tantalum, a saturated acetonitrile solution of **5** was cooled to -30 °C to provide colorless crystals of the acetonitrile adduct **5(CH<sub>3</sub>CN)** (Fig. 5). Selected bond lengths and angles are summarized in Table 2.

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Fig. 5 Molecular structure of cation 5(CH<sub>3</sub>CN) displaying thermal ellipsoids at the 50% probability level. H-atoms, i-butyl groups.  $[B(C_6F_5)_4]^-$  and a CH<sub>3</sub>CN molecule have been omitted for clarity.

5 Table 2 Selected bond lengths [Å] and angles [°] for 5(CH<sub>3</sub>CN)

| O(1)-Ta(1) | 1.897(8) | O(13)-Si(6)-O(5)  | 110.0(4) |
|------------|----------|-------------------|----------|
| O(2)-Ta(1) | 1.917(7) | O(13)-Si(6)-O(12) | 108.6(4) |
| O(3)-Ta(1) | 1.879(7) | O(5)-Si(6)-O(12)  | 107.9(4) |
| Ta(1)-N(1) | 2.255(9) | O(3)-Ta(1)-O(2)   | 123.5(3) |
|            |          | O(3)-Ta(1)-O(1)   | 90.4(3)  |
|            |          | O(1)-Ta(1)-O(2)   | 90.4(3)  |
|            |          | O(3)-Ta(1)-N(1)   | 76.2(3)  |
|            |          | O(1)-Ta(1)-N(1)   | 151.5(3) |
|            |          | O(2)-Ta(1)-N(1)   | 76.9(3)  |
|            |          | Si(1)-O(1)-Ta(1)  | 161.9(4) |
|            |          | Si(4)-O(2)-Ta(1)  | 141.0(4) |
|            |          | Si(8)-O(3)-Ta(1)  | 146.1(4) |

Notably, as for 2-4, the *cis* O-Ta-X ( $X = N(CH_3CN)$ ) angles are acute (76.3(3) and 76.9(3)°) whereas the two cis O-Ta-O angles are close to 90°. For the *trans* O-Ta-X (X = O, N) angles, 10 as expected, a behavior similar to that for 2-4 was observed with a O-Ta-N angle larger than the O-Ta-O angle (151.5(3) vs. 123.5(3)°). Removal of the solvent under vacuum results in loss of the coordinated acetonitrile ligand, as indicated by <sup>1</sup>H NMR spectroscopy (benzene- $d_6$ ), and elemental analysis. Thus, the 15 acetonitrile appears to be very weakly bound and due to its high lability, further characterization of 5(CH<sub>3</sub>CN) was precluded.

To evaluate the validity of complexes 2-5 as molecular models for silica-bound tantalum centers with a Cp\* ligand, a comparison was made between 3 and a similar, previously reported surface-

- 20 bound Ta species. Basset and co-workers investigated the grafting of Cp\*TaMe<sub>4</sub> on silica partially dehydroxylated at 700 °C, and determined the activity of the grafted complex toward alkane metathesis.<sup>1d</sup> While for complex **3**, the Ta is coordinated by one Cp\*, one methyl and three siloxide ligands, the grafted
- 25 material possesses a Cp\*TaMe<sub>3</sub>(OSi-silica) structure. Interestingly, the <sup>13</sup>C NMR spectrum of TaCp\*Me<sub>4</sub> displays a signal at 74 ppm assigned to the methyl ligands whereas both complex 3 and the grafted system display more upfield signals at 53.6 and 58 ppm, respectively. Comparison of the bond distances
- 30 for **3** and the grafted system is also informative. The EXAFS data for the silica-supported Ta species indicates a Ta-O(Si) distance of 1.931 Å, a Ta-C(Me) distance of 2.142 Å and 2.456 Å for the Ta-C(Cp\*) distances. For 3, the bond distances are in the same range (1.932(2)-1.969(2) Å for Ta-O(Si), 2.275(2) Å for the Ta-
- 35 C(Me) and 2.406(3)-2.490(3) Å for the Ta-C(Cp\*) distances

(Table 1)). Structural and spectroscopic characteristics of the complex model 3 are in good agreement with the data for the grafted Ta analog and thus confirm the validity of such molecular models in structural studies of analogous, grafted systems.

In summary, four new tantalasilsesquioxane complexes have been synthesized and characterized. To the best of our knowledge, the crystal structures of these compounds are the first for polyhedral oligosilsesquioxane complexes with a Ta center. Complexes 2-4 display a four-legged piano stool geometry 45 around the tantalum center whereas 5 possesses a three-legged piano stool arrangement. These complexes are relevant structural molecular models for Cp\*Ta fragments grafted onto a silica surface. Further modifications to the structures of these tantalasilsesquioxane complexes are currently being investigated.

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#### Notes and references

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†Electronic Supplementary Information (ESI) available: General experimental details, synthetic procedures for compounds 2-5, <sup>1</sup>H NMR of 5 (Table S1) and crystallographic details (Table S1-S5). CCDC 897182-897186. For ESI and crystallographic data in CIF or other 65 electronic format see DOI: 10.1039/b000000x/

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### Synthesis and Characterization of Tantalum Silsesquioxane Complexes

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X-ray structures of four new Ta-POSS complexes reveal that the coordination number of the tantalum greatly affects the cube-like silsesquioxane framework.

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