*Supporting information for:*

# Synthesis and Characterization of Tantalum Silsesquioxane Complexes

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**General considerations**

All manipulations of air sensitive compounds were conducted under a nitrogen atmosphere using standard Schlenk techniques or using a nitrogen atmosphere glovebox. Solvents were stored in PTFE valved flasks after drying using Vacuum Atmosphere solvent purification systems or by distillation under nitrogen from appropriate drying agents. $C_6D_6$ was purchased from Cambridge Isotope Laboratories, dried over Na/K alloy, and then degassed by several freeze-pump-thaw cycles. NMR spectra were recorded on Bruker spectrometers at room temperature unless otherwise noted. Spectra were referenced internally by solvent peaks for $^{1}H$ and $^{13}C\{^{1}H\}$ NMR, and tetramethylsilane for $^{29}Si$-$^{1}H$ HMBC experiments. X-ray analyses were carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements of **2-5** and **5($CH_3CN$)** were made on an APEX CCD area detector with Mo Kα radiation (λ = 0.71069 Å) monochromated with QUAZAR multilayer mirrors. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

Cp*$TaCl_4$[1] and $LiB(C_6F_5)_4{\cdot}2Et_2O$[2] were prepared according to literature methods. Incompletely condensed silsesquioxane **1** was purchased from Hybrid Plastics Inc. and dried overnight under vacuum at 50 °C prior to use. All other chemicals were purchased from commercial sources and used without further purification.

**Synthesis of 2**

Toluene (20 mL) was added to a solid mixture of **1** (0.300 g, 0.38 mmol) and Ta$Cp^*Cl_4$ (0.174 g, 0.38 mmol). Stirring at 90 °C for 12 h afforded a slightly yellow solution, which was evaporated under reduced pressure. The residue was redissolved in 1 mL of toluene. Acetonitrile was added dropwise to the yellow solution to precipitate **2** and this mixture was kept at -30 °C for 12 h to achieve complete precipitation. After filtration, washing with cold acetonitrile and drying under vacuum, **2** (0.340 g, 79%) was obtained as a white powder. Crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of **2** in hexanes at -30 °C.

Anal. Calcd for $C_{38}H_{78}ClO_{12}Si_7Ta$: C, 40.04; H, 6.90. Found: C, 40.25; H, 6.89.$^{1}H$ NMR (600 MHz, $C_6D_6$, 25 °C) δ = 2.23-2.15 (m, 7H), 2.10 (s, 15H), 1.19 (d, 18H, 6.6 Hz), 1.12 (d, 18H, 6.6 Hz), 1.09 (d, 6H, 6.6 Hz), 0.95 (d, 6H, 6.6 Hz), 0.92 (d, 6H, 7.2 Hz), 0.84 (d, 2H, 7.2 Hz). $^{13}C\{^{1}H\}$ NMR (600 MHz, $C_6D_6$, 25 °C) δ = 125.40, 25.94, 25.67, 25.57, 24.29, 24.07, 23.02, 22. 91, 11.74. $^{29}Si\{^{1}H\}$ NMR (600 MHz, $C_6D_6$, 25 °C) δ = -63.3, -66.9.

**Synthesis of 3**

To 0.200 g (0.175 mmol) of **2** in 5 mL of diethyl ether at -30 °C, was added methyllithium solution (1.6 M in diethyl ether) (132 µL, 0.211 mmol) via syringe. The resulting solution was stirred at room temperature for 2 h. After filtration to remove LiCl, the solution was evaporated under reduced pressure. The residue was dissolved in 2 mL of toluene and filtered through a plug of celite. Acetonitrile was then added dropwise to the yellow solution to precipitate **3** and this mixture was kept at -30 °C for 12 h to achieve complete precipitation. After filtration and drying under vacuum, **3** (0.185 g, 94%) was obtained as a white powder. Crystals suitable for X-ray diffraction were obtained by cooling a saturated solution of **3** in pentane at -30 °C.

Anal. Calcd for $C_{39}H_{81}O_{12}Si_7Ta$: C, 41.84; H, 7.29. Found: C, 41.54; H, 7.40.$^{1}$H NMR (600 MHz, $C_6D_6$, 25 °C) δ = 2.22-2.10 (m, 7H), 1.91 (s, 15H), 1.20 (d, 18H, 6.6 Hz), 1.13 (d, 18H, 6.6 Hz), 1.11 (d, 6H, 7.8 Hz), 0.91 (d, 6H, 6.6 Hz), 0.88 (d, 6H, 6.6 Hz), 1.20 (d, 2H, 7.2 Hz), 0.71 (s, 3H). $^{13}$C{$^{1}$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = 122.51, 53.56, 26.78, 26.47, 26.30, 25.24, 24.91, 24.85, 23.97, 23.68, 11.87. $^{29}$Si{$^{1}$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = -65.0, -67.3, -67.8.

**Synthesis of 4**

To 0.100 g (0.088 µmol) of **2** in 3 mL of toluene, was added silver trifluoromethanesulfonate (0.023 g, 0.088 µmol) and the mixture was stirred at room temperature for 2 h. After filtration to remove AgCl, the filtrate was evaporated under vacuum and analytically pure **4** (0.110 g, 100%) was obtained as a white powder. Crystals suitable for X-ray diffraction were obtained were obtained as colorless needles after slow evaporation of a solution of **4** in benzene at 20 °C.

Anal. Calcd for $C_{39}H_{78}F_3O_{15}SSi_7Ta$: C, 37.36; H, 6.27. Found: C, 37.22; H, 6.11.$^{1}$H NMR (600 MHz, $C_6D_6$, 25 °C) δ = 2.22-2.06 (m, 7H), 2.12 (s, 15H), 1.17 (d, 18H, 6.6 Hz), 1.11 (d, 18H, 7.2 Hz), 1.08 (d, 6 H, 6.6 Hz), 1.02 (d, 6H, 7.2 Hz), 0.97 (d, 7.2 Hz), 0.81 (d, 2H, 6.6 Hz). $^{13}$C{$^{1}$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = 127.96, 26.54, 26.35, 26.27, 25.12, 24.86, 24.79, 23.50, 23.36, 12.10. $^{29}$Si{$^{1}$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = -63.1, -66.8, -67.4. $^{19}$F{$^{1}$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = -75.6.

**Synthesis of 5**

To 0.300 g (0.263 mmol) of **2** in 5 mL of dicholoromethane, $Li[B(C_6F_5)_4]\cdot 2Et_2O$ (0.252 g, 0.302 mmol) was added and the mixture was stirred at room temperature for 3 h. After

filtration to remove LiCl, the filtrate was evaporated under vacuum. The complex **5** was then crystallized from acetonitrile at -30 °C. Crystals of **5(CH$_3$CN)** suitable for X-ray diffraction were obtained by this method. After removal of the solvent and drying under vacuum, **5** (400 mg, 85%) was obtained as a white powder. Crystals of **5** suitable for X-ray diffraction were obtained by diffusion of pentane into a solution of **5** in toluene at -30 °C.

Anal. Calcd for $C_{62}H_{78}BF_{20}O_{12}Si_7Ta$: C, 41.75; H, 4.41. Found: C, 41.87; H, 4.74. $^1$H NMR (600 MHz, $C_6D_6$, 25 °C) δ = 1.99-1.90 (m, 7H), 1.89 (s, 15H), 1.04 (d, 18H, 6.6 Hz), 0.98 (m, 24H), 0.79 (d, 6H, 7.2 Hz), 0.73 (d, 6H, 7.2 Hz), 0.71 (d, 2H, 7.2 Hz). $^{13}$C{$^1$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = 129.10, 26.00, 25.94, 24.62, 24.55, 23.07, 22.73, 22.37, 10.83. $^{29}$Si{$^1$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = -68.4, -67.8, -59.7. $^{19}$F{$^1$H} NMR (600 MHz, $C_6D_6$, 25 °C) δ = -130.7, -161.9, -165.6.

**Fig. S1** $^1$H NMR spectrum of **5** in $C_6D_6$ at 25 °C.

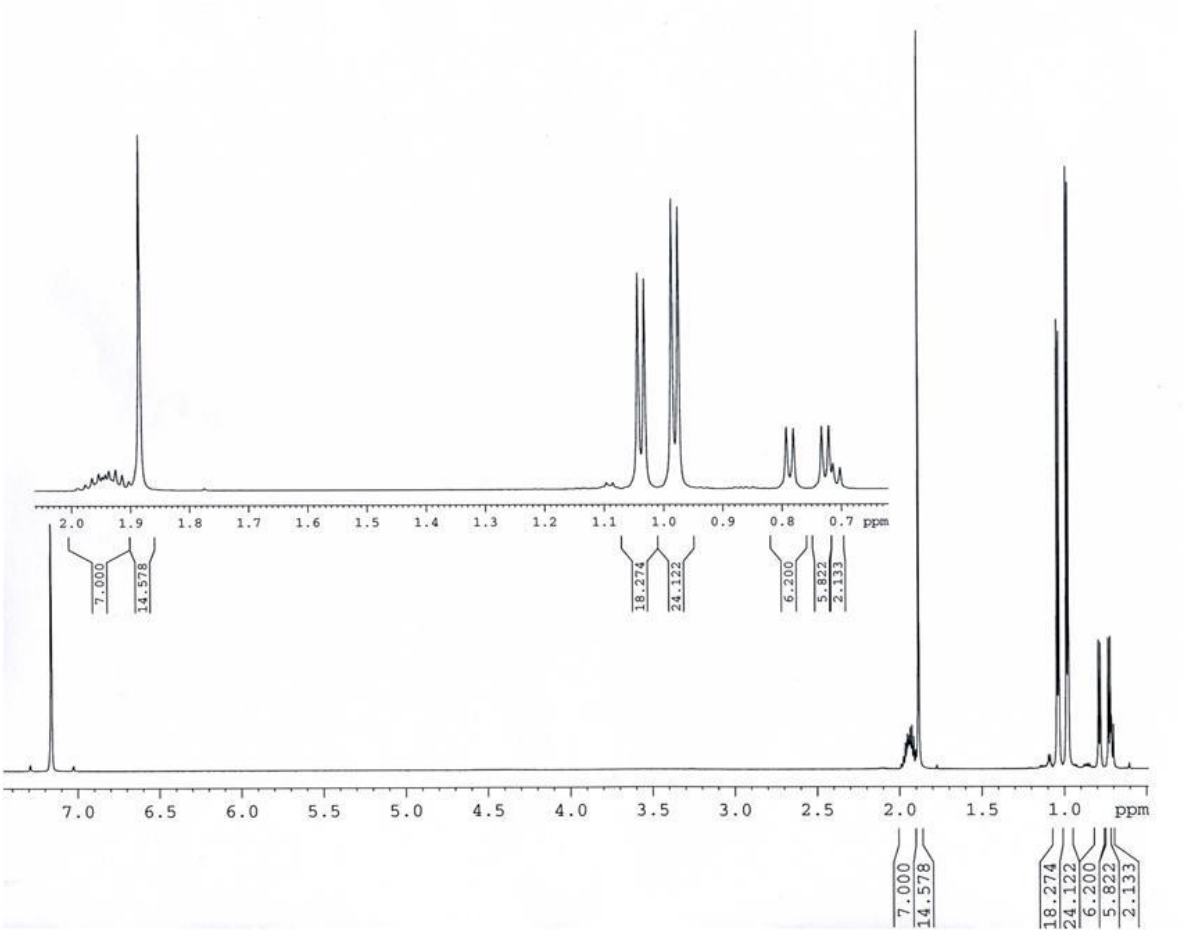

**Table S1** Crystal data and structure refinement for **2**

| | | |
|---|---|---|
| Empirical formula | C38 H78 Cl O12 Si7 Ta | |
| Formula weight | 1140.04 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 14.690 Å | α = 105.25° |
| | b = 19.058 Å | β = 107.43° |
| | c = 21.339 Å | γ = 100.37° |
| Volume | 5277.2 Å $^3$ | |
| Z | 4 | |
| Density (calculated) | 1.336 Mg/m$^3$ | |
| Absorption coefficient | 2.340 mm$^{-1}$ | |
| F(000) | 2048 | |
| Crystal size | 0.14 x 0.14 x 0.10 mm$^3$ | |
| Theta range for data collection | 1.51 to 25.40°. | |
| Index ranges | -17<=h<=17, -22<=k<=22, -25<=l<=25 | |
| Reflections collected | 59433 | |
| Independent reflections | 19091 [R(int) = 0.0229] | |
| Completeness to theta = 25.40° | 98.2 % | |
| Max. and min. transmission | 0.7997 and 0.7353 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 19091 / 0 / 1101 | |
| Goodness-of-fit on $F^2$ | 1.137 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0286, wR2 = 0.0895 | |
| R indices (all data) | R1 = 0.0367, wR2 = 0.1117 | |
| Largest diff. peak and hole | 1.336 and -1.844 e. Å $^{-3}$ | |

**Table S2** Crystal data and structure refinement for **3**

| | | |
|---|---|---|
| Empirical formula | C39 H81 O12 Si7 Ta | |
| Formula weight | 1119.62 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 10.4766(7) Å | α = 78.832(3)° |
| | b = 11.7685(7) Å | β = 79.710(3)° |
| | c = 22.1260(15) Å | γ = 79.243(3)° |
| Volume | 2600.4(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.430 $Mg/m^3$ | |
| Absorption coefficient | 2.327 $mm^{-1}$ | |
| F(000) | 1164 | |
| Crystal size | 0.80 x 0.10 x 0.10 $mm^3$ | |
| Theta range for data collection | 1.79 to 25.41°. | |
| Index ranges | -12<=h<=12, -14<=k<=14, -26<=l<=26 | |
| Reflections collected | 67291 | |
| Independent reflections | 9559 [R(int) = 0.0326] | |
| Completeness to theta = 25.41° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8024 and 0.2603 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9559 / 0 / 552 | |
| Goodness-of-fit on $F^2$ | 1.066 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0231, wR2 = 0.0559 | |
| R indices (all data) | R1 = 0.0249, wR2 = 0.0575 | |
| Largest diff. peak and hole | 1.608 and -1.660 $e.Å^{-3}$ | |

**Table S3** Crystal data and structure refinement for **4**·$C_6H_6$

| | | |
|---|---|---|
| Empirical formula | C45 H84 F3 O15 S Si7 Ta | |
| Formula weight | 1331.78 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71069 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 13.252(5) Å | α = 90.000(5)° |
| | b = 10.146(5) Å | β = 93.033(5)° |
| | c = 44.599(5) Å | γ = 90.000(5)° |
| Volume | 5988(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.477 $Mg/m^3$ | |
| Absorption coefficient | 2.078 $mm^{-1}$ | |
| F(000) | 2752 | |
| Crystal size | 0.10 x 0.03 x 0.03 $mm^3$ | |
| Theta range for data collection | 1.58 to 25.71° | |
| Index ranges | -16<=h<=13, -9<=k<=12, -53<=l<=54 | |
| Reflections collected | 40832 | |
| Independent reflections | 11160 [R(int) = 0.0660] | |
| Completeness to theta = 25.71° | 97.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9394 and 0.8167 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11160 / 12 / 668 | |
| Goodness-of-fit on $F^2$ | 1.330 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0905, wR2 = 0.1828 | |
| R indices (all data) | R1 = 0.1167, wR2 = 0.1898 | |
| Largest diff. peak and hole | 2.594 and -6.870 e.$Å^{-3}$ | |

**Table S4** Crystal data and structure refinement for **5**

| | | |
|---|---|---|
| Empirical formula | C62 H78 B F20 O12 Si7 Ta | |
| Formula weight | 1782.12 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 13.3982(17)Å | α= 97.778(7)°. |
| | b = 29.185(4)Å | β= 90.888(8)°. |
| | c = 40.772(5)Å | γ = 92.306(8)°. |
| Volume | 15780(3)Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.500 Mg/m$^3$ | |
| Absorption coefficient | 1.600 mm$^{-1}$ | |
| F(000) | 7204 | |
| Crystal size | 0.14 x 0.08 x 0.02 mm$^3$ | |
| Theta range for data collection | 1.41 to 31.75 °. | |
| Index ranges | -19<=h<=17, -34<=k<=39, -56<=l<=56 | |
| Reflections collected | 307718 | |
| Independent reflections | 84272 [R(int) = 0.0702] | |
| Completeness to theta = 25.00° | 100 % | |
| Absorption correction | None | |
| Max. and min. transmission | 0.9687 and 0.8070 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 84272 / 6 / 3785 | |
| Goodness-of-fit on $F^2$ | 1.067 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0693, wR2 = 0.1650 | |
| R indices (all data) | R1 = 0.1111, wR2 = 0.1800 | |
| Largest diff. peak and hole | 5.407 and -2.960 e.Å$^{-3}$ | |

**Table S5** Crystal data and structure refinement for **5(CH$_3$CN)·CH$_3$CN**

| | | |
|---|---|---|
| Empirical formula | C66 H84 B F20 N2 O12 Si7 Ta | |
| Formula weight | 1865.75 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71069 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 14.324(5) Å | α = 102.447(5)° |
| | b = 14.832(5) Å | β = 90.694(5)° |
| | c = 19.356(5) Å | γ = 94.252(5)° |
| Volume | 4003(2) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.548 Mg/m$^3$ | |
| Absorption coefficient | 1.581 mm$^{-1}$ | |
| F(000) | 1892 | |
| Crystal size | 0.05 x 0.05 x 0.05 mm$^3$ | |
| Theta range for data collection | 1.41 to 23.30°. | |
| Index ranges | -15<=h<=15, -16<=k<=16, -21<=l<=21 | |
| Reflections collected | 26149 | |
| Independent reflections | 11281 [R(int) = 0.0539] | |
| Completeness to theta = 25.27° | 95.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9253 and 0.9253 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 13907 / 30 / 1003 | |
| Goodness-of-fit on F$^2$ | 1.072 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0830, wR2 = 0.2084 | |
| R indices (all data) | R1 = 0.1189, wR2 = 0.2439 | |
| Largest diff. peak and hole | 4.209 and -2.517 e.Å$^{-3}$ | |

## References


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[2] J. B. Lambert, S. Zhang and S. M. Ciro, *Organometallics* **1994**, *13*, 2430.