Synthesis and Structures of the First Titanium(IV) Complexes with Cyclic Tetrasiloxide Ligands: Incomplete and Complete Cage Titanosiloxanes

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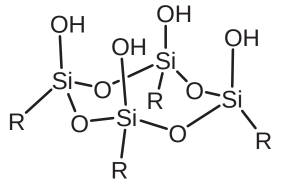
The first titanium(IV) complexes with cyclic tetrasiloxide ligands, $[Ti(L^1H)(OSiMe_3)]_2(H_2O)$ (**1**) and $(CpTiCl)_4(L^2)_2$ (**2**), were synthesized using the all-cis isomer of cyclotetrasiloxanetetraols $R_4(SiO)_4(OH)_4$ (L^1H_4: R = Ph, L^2H_4: R = ^{i}Pr) as ligand precursors. X-ray analysis revealed that **1** is a dinuclear complex with bridging siloxy and aqua ligands while **2** has a tetranuclear cage structure capped by two L^2 ligands.

Group 4 metal complexes immobilized on silica surfaces are industrially and commercially important catalysts.[1] However, the improvement of the catalysts is hindered by the complicated surface structures, which make the reaction processes unclear.[2] Several types of siloxido complexes have been synthesized using mono-, di-, and trisiloxide ligands, which can be considered as model compounds for the heterogeneous catalysts.[3–5] In particular, titanium complexes with a tridentate silsesquioxane ligand provided valuable information on the coordination geometry and reactivity for catalytic organic reactions.[5] Cyclic tetrasiloxide ligands are also potentially useful as a silica surface model but few complexes with such ligands have been reported so far.[6] Here, we report the first titanium(IV) complexes with the cyclic tetrasiloxide ligands. The ligand precursors used in this work, L^1H_4 and L^2H_4, are the all-cis isomer of cyclotetrasiloxanetetraols, which has four silanol groups on the same side of the $(SiO)_4$ eight-memberd ring (Figure 1).[7]



L^1H_4 (R = Ph), L^2H_4 (R = ^{i}Pr)

Figure 1. Structure of cyclic tetrasilanol ligands.

Our initial attempts were focused on the synthesis of a mononuclear complex with a tetrasiloxide ligand. The reaction of $Ti(OSiMe_3)_4$ and one equivalent of cyclic tetrasilanol L^1H_4 in Et_2O at 0 °C, however, afforded dititanium complex $[Ti(HL^1)(OSiMe_3)]_2(H_2O)\cdot 2Et_2O$ ($\mathbf{1}\cdot 2Et_2O$), which was isolated as colorless crystals in 60% yield.[8] No evidence of formation of the mononuclear complex was obtained even in the reaction carried out with excess amount of L^1H_4. The structure of **1** was determined by single crystal X-ray analysis (Figure 2).[9] Two titanium(IV) ions in **1** are sandwiched by two cyclic tetrasiloxide ligands. In the cyclic ligand L^1, two siloxido oxygen atoms, O(1) and O(3), are bound to Ti(1) and Ti(1)′, respectively, while O(4) bridges the two Ti centers. The remaining terminal oxygen atom O(2) is not bound to Ti and exists as a silanol group. The bridging Ti–O bonds (Ti(1)–O(4) = 2.0851(16) and Ti(1)′–O(4) = 2.0774(16) Å) is longer than the terminal Ti–O bonds (Ti(1)–O(1) = 1.8628(17) and Ti(1)′–O(3) = 1.8561(17) Å). Two titanium(IV) centers are further bridged by an aqua ligand (Ti(1)–O(10) = 2.3169(18) Å). Two trimethylsiloxide ligands occupy the trans positions of the bridging aqua ligand to complete the face-shared octahedrons. The nonbridging Ti–O bond distances in **1** are similar to those found in the octahedral siloxido titanium(IV) complexes, *cis*-$[Ti\{OSiPh_2(OSiPh_2)_2O\}_2(py)_2]$ (Ti–O = 1.836(5) and 1.874(5) Å) and $[\{Ti(acac)(thf)\}_2(\mu\text{-}O_2SiPh_2)_3]$ (Ti–O = 1.787(3)–1.836(4) Å).[4a,4c] The titanium(IV) centers in **1** are largely distorted from regular octahedral structure, which is demonstrated by nonlinear trans O–Ti–O angles: O(1)–Ti(1)–O(4)′ = 156.29(7), O(3)′–Ti(1)–O(4) = 153.82(7), and O(5)–Ti(1)–O(10) = 167.09(7)°.

The ^{1}H NMR spectrum of **1** in toluene-d_8 at −30 °C showed a singlet signal at $\delta = -0.15$ ppm which is assignable to the two equivalent trimethylsiloxy ligands. The phenyl signals appeared in the range of $\delta = 6.9$–8.4 ppm. Three signals at $\delta = 7.77$, 8.02, and 8.35 ppm in intensity ratio 1:2:1 are assignable to the *o*-H of the phenyl groups. Relatively broad signals at $\delta = 8.64$ and 5.36 ppm is assignable to the bridging aqua ligand and noncoordinated silanol groups, respectively. These results demonstrate

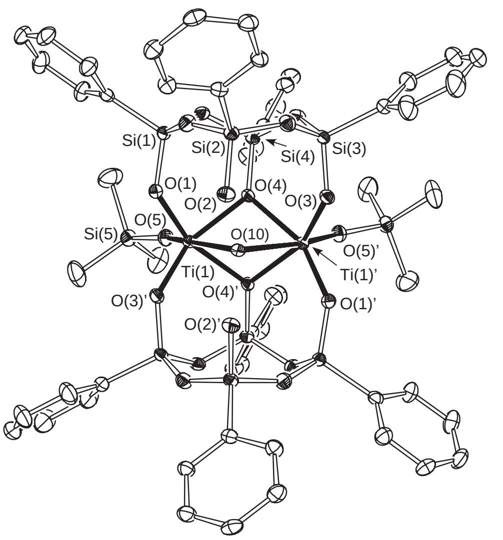


Figure 2. ORTEP drawing of **1** (thermal ellipsoids at the 50% probability level). Selected interatomic distances (Å): Ti(1)–O(1), 1.8628(17); Ti(1)–O(3)′, 1.8561(17); Ti(1)–O(4), 2.0851(16); Ti(1)–O(4)′, 2.0774(16); Ti(1)–O(5), 1.7813(18); Ti(1)–O(10), 2.3169(18); Ti(1)–Ti(1)′, 3.1435(8).

that **1** bears a C_{2v} symmetry in solution.

Complex **1** is thermally unstable in solution at room temperature under inert atmosphere to decompose to unidentified products within 2 days. The tetrasilanol ligand with bulky isopropyl groups (L^2H_4) was thus used to stabilize titanium complexes with the cyclic tetrasiloxide ligand. The reaction between L^2H_4 and $Ti(OSiMe_3)_4$, however, gave a complex mixture of decomposition products. In contrast to the reaction with $Ti(OSiMe_3)_4$, refluxing a 1:1 mixture of L^2H_4 and $(CpTiCl_2)_2O$ in toluene resulted in the formation of $(CpTiCl)_4\{{}^i\mathrm{Pr}_4(SiO)_4O_4\}_2\cdot(C_7H_8)$ (**2**•toluene) which was isolated as light yellow crystals in 63% yield.[10] X-ray crystal structure analysis revealed that complex **2** consists of two L^2 ligands and four CpTiCl units (Figure 3).[11] The titanium fragment should be derived from the starting complex $(CpTiCl_2)_2O$, i.e., the bridging oxo ligand was lost during the reaction. Four CpTiCl units link two L^2 ligands to form a cage structure consisting of two $(SiO)_4$ eight-membered rings and four $Si_4O_6Ti_2$ 12-membered rings. There is a pseudo-C_4 axis through each center of the $(SiO)_4$ rings. The Ti–O(siloxido) bond distances in **2** are in the range of 1.801(2)–1.811(2) Å which are comparable to those in titanium(IV) siloxido complexes with the tripodal piano stool structure.[4d,5d]

The ^{1}H NMR spectrum of **2** in benzene-d_6 at room temperature showed a singlet signal at $\delta = 6.77$ ppm assignable to Cp and three signals at $\delta = 1.00$, 1.23, and 1.27 ppm assignable to the isopropyl group on the L^2 ligand.[10] Only one ^{29}Si NMR signal was also observed at $\delta = -67.7$ ppm for the cyclic siloxane ligands. These results indicate that the C_{4h} symmetrical structure of **2** is retained in solution.

In summary, the first titanium(IV) complexes with cyclic tetrasiloxide ligands, **1** and **2**, were synthesized using all-cis isomer of tetrasilanols, L^1H_4 and L^2H_4, respectively. It is emphasized that the cyclic tetrasiloxide ligands have the multinucleating character suitable for synthesis of a novel class of titanosiloxanes.

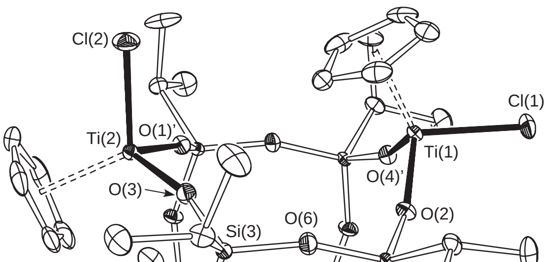


Figure 3. ORTEP drawing of **2** (thermal ellipsoids at the 50% probability level). Selected interatomic distances (Å): Ti(1)–O(2), 1.807(2); Ti(1)–O(4)′, 1.801(2); Ti(1)–Cl(1), 2.2807(17); Ti(2)–O(1)′, 1.808(2); Ti(2)–O(3), 1.811(2); Ti(2)–Cl(2), 2.269(2).

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8 **1**: ^{1}H NMR (300 MHz, $C_6D_5CD_3$, −30 °C) δ −0.15 (s, 18H, OSi*Me*$_3$), 5.36 (s, 2H, SiO*H*), 6.98–7.30 (m, 24H, Ar), 7.77 (d, 4H, $J = 6.6$ Hz, *o*-Ph), 8.02 (d, 8H, $J = 3.3$ Hz, *o*-Ph), 8.35 (d, 4H, $J = 4.5$ Hz, *o*-Ph), 8.64 (s, 2H, H_2O); ^{13}C NMR (125.7 MHz, $C_6D_5CD_3$, −10 °C) δ 1.5 (OSi*Me*$_3$), 128.1, 128.3, 130.8, 131.0, 131.1, 131.6, 131.7, 131.9, 134.4, 134.9, 135.7; ^{29}Si NMR (99.3 MHz, $C_6D_5CD_3$, −10 °C) δ −70.3 (cyclic-*Si*$_4$O$_4$), −66.8 (cyclic-*Si*$_4$O$_4$), −60.4 (cyclic-*Si*$_4$O$_4$), 20.4 (O*Si*Me$_3$).

9 Crystals suitable for X-ray structure analysis were grown from THF/hexane. **1**•2THF: Anal. Calcd for $C_{62}H_{78}O_{21}Si_{10}Ti_2$: C, 48.49; H, 5.12%. Found: C, 48.01; H, 5.12%. IR (KBr) 3300 cm^{-1} (br, ν_{OH}). Crystal data: $C_{62}H_{78}O_{21}Si_{10}Ti_2$, $M_r = 1535.9$, orthorhombic, $P2_12_12$, $a = 14.4561(9)$, $b = 18.1710(9)$, $c = 14.1250(10)$ Å, $V = 3710.4(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.375$ g/cm^3, $R_1 = 0.044$ ($I > 2.0\sigma(I)$), $wR_2 = 0.115$ (all data).

10 **2**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.0 (sep, 2H, $J = 7.3$ Hz, C*H*Me$_2$), 1.23 (d, 6H, $J = 7.3$ Hz, CH*Me*$_2$), 1.27 (d, 6H, $J = 7.3$ Hz, CH*Me*$_2$), 6.77 (s, 5H, Cp); ^{13}C NMR (125.7 MHz, C_6D_6) δ 13.7 (*C*HMe$_2$), 17.5 (CH*Me*$_2$), 17.7 (CH*Me*$_2$), 119.2 (Cp); ^{29}Si NMR (99.3 MHz, C_6D_6) δ −67.7 (cyclic-*Si*$_4$O$_4$).

11 **2**•toluene: Anal. Calcd for $C_{51}H_{84}Cl_4O_{16}Si_8Ti_4$: C, 40.53; H, 5.60%. Found: C, 40.29; H, 5.50%. Crystal data: $C_{51}H_{84}Cl_4O_{16}$-Si_8Ti_4, $M_r = 1511.2$, triclinic, $P\bar{1}$, $a = 13.071(8)$, $b = 13.186(11)$, $c = 13.487(11)$ Å, $V = 1794(2)$ Å^3, $Z = 1$, $D_{calcd} = 1.423$ g/cm^3, $R_1 = 0.044$ ($I > 2.0\sigma(I)$), $wR_2 = 0.131$ (all data).

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