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Tetrahedral Sn-silsesquioxane: synthesis, characterization and catalysis[†]

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A tetrahedral stannasilsesquioxane complex was synthesized as a racemic mixture using $Sn(O^iPr)_4$ and silsesquioxanediol, and its structure was confirmed with X-ray crystallography, NMR, and EXAFS. The complex was a Lewis acid, and both *anti* and *syn*-binding with Lewis bases were possible with the formation of octahedral Sn complexes. It was also a Lewis acid catalyst active for epoxide ring opening and hydride transfer.

Polyhedral oligomeric silsesquioxane (POSS) are cage-structured siloxanes with aliphatic or aromatic groups attached to Si located at the vertices of the cage.¹ An incompletely condensed POSS possesses reactive silanols that can ligate metal cations effectively,² such as Ti,^{3,4} V,⁵ Al,⁶ and Ce⁷ to form a wide variety of metalla-silsesquioxanes which have been used as analogues of silica-supported or zeolitic heterogeneous catalysts.⁸ To be a realistic structural analogue of an active site in zeolite, the metal center of the metallasilsesquioxane should be tetrahedrally coordinated with three of the four ligands being siloxy bonds, and the fourth either a siloxy or an ancillary ligand that can be easily displaced during reaction.⁸

Although Ti and Sn complexes share many similar properties, and titanasilsesquioxanes have been extensively investigated, there is yet no similar investigation of Sn–silsesquioxanes, even though Sn-beta catalyzes many important reactions such as Baeyer–Villiger reaction,⁹ Meerwein–Ponndorf–Verley– Oppenauer redox equilibration,¹⁰ Diels–Alder reaction,¹¹ glucose

to fructose isomerization,^{12,13} and transformation of 5-(hydroxymethyl)furfural for biofuel processing.14 This could be due to the difficulties in synthesizing tetrahedral (T_d) stannasilsesquioxane. Synthesis starting with SnCl₄ were reported to be unsuccessful,¹⁵ even though well-defined T_d metallasilsesquioxanes could be formed from TiCl₄ and ZrCl₄ under similar conditions.¹⁶ To our knowledge, one T_d corner-capped CH₃-stannasilsesquioxane was synthesized successfully using CH₃SnCl₃,¹⁷ although an octahedral, dinuclear byproducts could be easily formed (Fig. S1a-e, ESI[†]). However, the difficulty in displacing the stable ancillary methyl ligand makes this T_d CH₃-stannasilsesquioxane unsatisfactory as a model for Sn-beta. Since single site Td metaloxo Lewis acid is an important class of catalyst,¹⁸ the synthesis and characterization of T_d stannasilsesquioxane with only siloxane ligands should be interesting. Here we report a successful synthesis scheme and the results of adsorptive and catalytic properties of the T_d Sn-oxo complex.

The Sn precursor in our scheme was $Sn(O^iPr)_4$ (Scheme 1). An incompletely condensed silsesquioxane **1**, $(c-C_6H_{11})_7Si_7O_9(OH)_3$, was converted to a disilanol with dimethylvinylchlorosilane *via* heterofunctional condensation following the method of Feher *et al.*¹⁹ and Sakugawa *et al.*²⁰ Triethylamine was added as a catalyst and to remove the HCl byproduct as the salt Et₃N·HCl.¹⁹ **2** was formed in good yield (>80%), and its structure and purity were confirmed with NMR (Fig. S2a–c, ESI†), ESI-MS, and crystal structure (Fig. S2d, ESI†). Addition of 0.5 eq. of $Sn(O^iPr)_4$ to **2** at 100 °C afforded a white powder, complex **3**. This synthesis scheme could be used with other silsesquioxanes with the general formula of $R_7Si_7O_9(OH)_3$. When R is i-butyl, the product **3b**, an i-butyl



Scheme 1 Synthesis of complex 3, $[(c-C_6H_{11})_7Si_7O_{11}(OSiC_2H_3Me_2)]_2Sn$.

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homolog of 3 was a viscous yellow oil. In this synthesis scheme, the spatial orientation of the disilanol in the silsesquioxane was found to be important. If instead of 2, another disilanol silsesquioxane $R_8Si_8O_{11}(OH)_2$ in which the OH groups pointed at different corners (Fig. S3b, ESI†), its reaction with $Sn(O^iPr)_4$ generated multiple octahedral products (Fig. S3a, ESI†).

Comparison of the ¹H and ¹³C NMR spectra of 3 (Fig. S4a and b, ESI†) with those of POSS (Fig. S2a and b, ESI†) showed much similarity, suggesting retention of the silsesquioxane structural unit. Because the Sn center in 3 was chiral (the symmetry plane in 2 was lost), its ¹³C NMR spectrum showed seven *C*H resonances for the cyclohexyl groups in the 23–25 ppm region (Fig. S6b, ESI†). In addition, because of their diastereotopic nature, the two methyl groups in $-SiC_2H_3Me_2$ split into separate peaks in both ¹H and ¹³C NMR spectra. All 8 Si in each of the POSS unit became distinct and eight ²⁹Si signals of equal integrated areas (±20%) were observed (Fig. S4c, ESI†). The ¹¹⁹Sn NMR spectrum showed a resonance at -438 ppm (Fig. S4d, ESI†), consistent with T_d Sn.²¹

This T_d species was the predominant product, but occasionally another 119 Sn NMR signal at -330 ppm was detected. This resonance disappeared upon prolonged heating of the sample at 110 °C in toluene, and was never observed when the vinyl groups in 2 were replaced by methyl groups as in (c-C₆H₁₁)₇Si₇O₁₀(SiMe₃)(OH)₂. A parent peak at \sim 2230 m e⁻¹ with the expected isotope distribution was detected in ESI-MS (Fig. S4e, ESI†). Single crystals of 3 of a quality satisfactory for X-ray structural determination were obtained by slow addition of acetone to a chloroform solution of 3 in a J Young tube with subsequent crystallization over a 20 h period. The structure derived from such a single crystal (Fig. 1) showed a nearly perfect tetrahedral coordination of Sn to two silsesquioxane units via four siloxy bonds (Fig. 1, \angle O–Sn–O 109 \pm 3°). The Sn–O bond distance was determined as 1.94 Å, which was similar to the 1.91 Å determined for the tetrahedral Sn in Sn-beta²² and significantly shorter than 2.05 Å of hexa-coordinated SnO_2 . Extended X-ray absorption fine structure (EXAFS) analysis of 3 also confirmed the T_d coordination of Sn with a Sn-O bond distance of 1.93 Å (Table S3 and Fig. S5, ESI†), and the absorption edge was consistent with Sn(IV) (Table S2, ESI†).

Ligation to the Sn in 3 was investigated with external ligands of different basicity and bulkiness. In a mixture of diethylamine and 3,



At 2 eq. Et₂NH, complete conversion of T_d to O_h Sn was achieved. With the absence of unbound amine or unreacted 3, the ¹H and ¹³C NMR spectra became those of the new compound. Single crystal X-ray structure of this compound (Fig. 1) showed the two amines in the *anti* position and increased Sn–O bond distances to 1.98 and 2.00 Å. The elongated Sn–O bond indicated decreased backbonding to the oxygen atoms of the POSS ligand upon binding of Et₂NH. The Sn center was no longer a chiral center in this complex, and the distinct methyl peaks in ¹³C NMR were replaced by a single peak (Fig. S6b, ESI[†]).

Complete conversion of T_d to O_h Sn was also observed after adding 1 eq. ethylenediamine, as indicated by a sharp ¹¹⁹Sn NMR signal at -665 ppm (Fig. S7c, ESI[†]). Contrary to Et₂NH, the bidentate nature of ethylenendiamine favoured *syn*-binding, which was confirmed by the X-ray crystal structure of the bound complex (Fig. 1). In this structure, the Sn center remained chiral, and the asymmetry of the two POSS-ligands was retained. This was indicated by the split methyl peaks in the ¹H and ¹³C NMR (Fig. S7a and b, ESI[†]). Interestingly, it appeared that only one of three possible isomers was formed, and ethylenediamine coordinated to Sn in the "pocket" formed by the $-OSiC_2H_3Me_2$ substituents. This could be due to steric hindrance from the cyclohexyl groups in other isomers.

A distinctly different behaviour was observed with triethylamine. Addition of triethylamine to 3 caused merging of the two methyl group signals of $-SiC_2H_3Me_2$ in both ¹H and ¹³C NMR spectra (Fig. 2), and broadening and/or disappearance of four of the methine carbon peaks in the ¹³C spectra (Fig. S8a, ESI†), and four of the Si peaks in the ²⁹Si (Fig. S8b, ESI†). This fluxional behaviour^{23,24} was attributed to interaction of Et₃N with 3, which led to rapid racemization of the chiral Sn center and exchange of the positions of the methyl groups. However, the binding of this amine with Sn was weak and rapidly reversible as indicated by the broad NMR peaks of the unbound amine at low equivalents of added amine (Fig. S8c, ESI†).



Fig. 1 X-ray crystal structures of 3 showing tetrahedral coordination of Sn, $3 \cdot (Et_2NH)_2$, and $3 \cdot (H_2NCH_2CH_2NH_2)$. Cyclohexyl groups are not shown for clarity. Ellipsoids show 50% of the occupancy.



Fig. 2 The methyl NMR signals of $SiC_2H_3Me_2$ of **3** with 0 (bottom) or 2 eq. (top) triethylamine. Left: ¹H NMR right: ¹³C NMR.

A similar behaviour was observed with a bulky secondary base (2,2,6,6-tetramethyl piperidine) or a less basic alcohol (PhCH₂OH). It is likely that steric hindrance of 3 contributed to the weak binding of these ligands. The steric barrier however can be overcome when a very strong base was used. Sterically bulky 1,8-diazabicyclo[5.4.0]undec-7ene (DBU), with a pK_b 6 times higher than that of triethylamine,²⁵ bound to Sn in a 1:1 stoichiometry as indicated by a complete conversion of 3 to a new species with a one equivalent of the base. Even in the presence of two equivalents of DBU, only one molecule would bind to 3, resulting in a pentacoordinated complex with a ¹¹⁹Sn NMR signal at -596 ppm (Fig. S9c, ESI†). ¹H and ¹³C NMR spectra indicated loss of asymmetry (Fig. S9a and b, ESI†), which suggests symmetrical square pyramidal configuration of the complex, as opposed to an alternative trigonal bipyramidal.

The observed behaviour of bases and benzyl alcohol indicated that Sn in 3 was a Lewis acid and accessible. In fact, the remarkable e-withdrawing tendency of the POSS ligands was expected to make the Sn very electron deficient²⁶ Together with the fact that syn-binding was possible as indicated by ethylenediamine, it is likely that 3 would be a catalyst for bond-forming reactions. To this end, we tested 3 as a catalyst for epoxide ring opening and hydride transfer reactions. The ring-opening of styrene oxide with benzyl alcohol (Scheme 2) was conducted using 0.5 mol% 3. All epoxide was consumed after 16 h at 80 °C, producing a primary alcohol product with 50% yield (by ¹H NMR). The by-products were: phenylacetaldehyde (2%), which was formed by isomerization of styrene oxide, and its reduction product, phenethyl alcohol (10%), most likely formed by hydride transfer from benzyl alcohol, which also produced benzaldehyde (6%). At the conclusion of the reaction, addition of another aliquot of reactants resulted in continued reaction until complete consumption of the epoxide after 16 h, indicating preservation of catalytic activity.

3 was also active for hydride transfer reactions, and achieved nearly complete conversion of *p*-nitrobenzaldehyde to *p*-nitrobenzyl alcohol in 1 h in the presence of a 2-fold excess of benzyl alcohol in toluene at 100 $^{\circ}$ C (a Meerwein–Ponndorf reaction).

In summary, we have succeeded in the first synthesis of a stannasilsesquioxane with a tetrahedrally coordinated Sn. Surrounded by four siloxy bonds, the Sn center was similar to that in a Sn-beta zeolite. It acted as a Lewis acid, and coordinated to basic molecules bearing lone pair electrons. Diethylamine or ethylenediamine adducts were stable octahedral Sn complexes, but bulkier ligands bound weakly. The stannasilsesquioxane was a Lewis acid catalyst active for epoxide ring opening and hydride transfer reactions. However, the hydrolytic sensitivity of the Sn–siloxy bonds made



Scheme 2 Reactions catalysed by 3.

the complex unstable in an aqueous medium. The vinyl groups in the complex offer opportunities to heterogenize the complex by hydrosilylation, which will be a topic for future studies.

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