Modeling Acidic Sites in Zeolites and Aluminosilicates by Aluminosilsesquioxanes

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Abstract: Protolysis of alkylaluminum compounds with silsesquioxanes is an efficient procedure to synthesize both Lewis and Brønsted acidic aluminosilsesquioxanes. Treatment of $AlEt_3$ with $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ and $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ gives the corresponding Lewis acidic aluminosilsesquioxanes, $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]Al\}_n$ (**1**) and $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]AlEt \cdot NEt_3$ (**2**). By allowing $AlEt_3$ to react with two equivalents of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$, the Brønsted acidic aluminosilsesquioxane $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OSiMe_3)(OH)]$ (**3**) is selectively formed. ^1H NMR and IR spectroscopy and density functional theory (DFT) calculations show that complex **3** contains a strong intramolecular hydrogen bond. Although the high strength of this hydrogen bond reduces the Brønsted acidity of **3** substantially, **3** can easily be deprotonated by amines to yield the corresponding ammonium salts $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-X^+$ ($X = Et_3NH$ **4a**, $PhN(H)Me_2$ **4b**, C_5H_5NH **4c**). The X-ray crystal structure of **4a** demonstrates that the ammonium cation is bonded to the aluminosilsesquioxane anion by a hydrogen bond. The corresponding lithium salt $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Li \cdot 2THF\}^+$ (**5**) could best be prepared by protolysis of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ with half an equivalent of $LiAlH_4$.

Keywords: aluminosilicates · aluminum · silicon · silsesquioxane · zeolite analogues

Introduction

Acidic aluminum sites in zeolites and clays play an important role in catalysis. Typical examples of processes catalyzed by solid acidic aluminum sites are isomerization and cracking of hydrocarbons.[1] The study of such catalysts in detail is, however, considerably hampered by the heterogeneity of these systems. Recently, an increasing number of metal complexes based on incompletely condensed silsesquioxanes[2] have been prepared and successfully used as homogeneous models for silica-grafted catalysts.[3, 4] Several studies have shown that the catalytic activity of these model systems resembles that of their supported analogues.[3] With this in mind we studied the applicability of soluble aluminosilsesquioxanes as models for both Lewis and Brønsted acidic aluminum sites as found in aluminosilicates and zeolitic materials.

The few well-defined aluminosilsesquioxane complexes known to date are either based on the cyclohexyl-substituted silsesquioxane $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$[5] or its monosilylated analogue $(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$.[6] In our study, we focused exclusively on the cyclopentyl-substituted analogues of these two silsesquioxanes and, as we will demonstrate here, the replacement of cyclohexyl groups by cyclopentyl substituents appears to have a pronounced influence on the structure of the aluminosilsesquioxane complexes formed.

Results and Discussion

The first aluminosilsesquioxane reported was prepared by Feher et al.[5a] who treated $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ with $AlMe_3$, to afford the dimeric aluminosilsesquioxane $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Al\}_2$. In contrast, the reaction of the cyclopentyl-substituted silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with $AlEt_3$ does not yield a dimer but instead gives a polymeric compound with an empirical formula of $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]Al\}_n$ (**1**, Scheme 1) that is completely insoluble in most common organic solvents (hexane, toluene, THF). Interestingly, in contrast to the crystalline **1**, the similar reaction of

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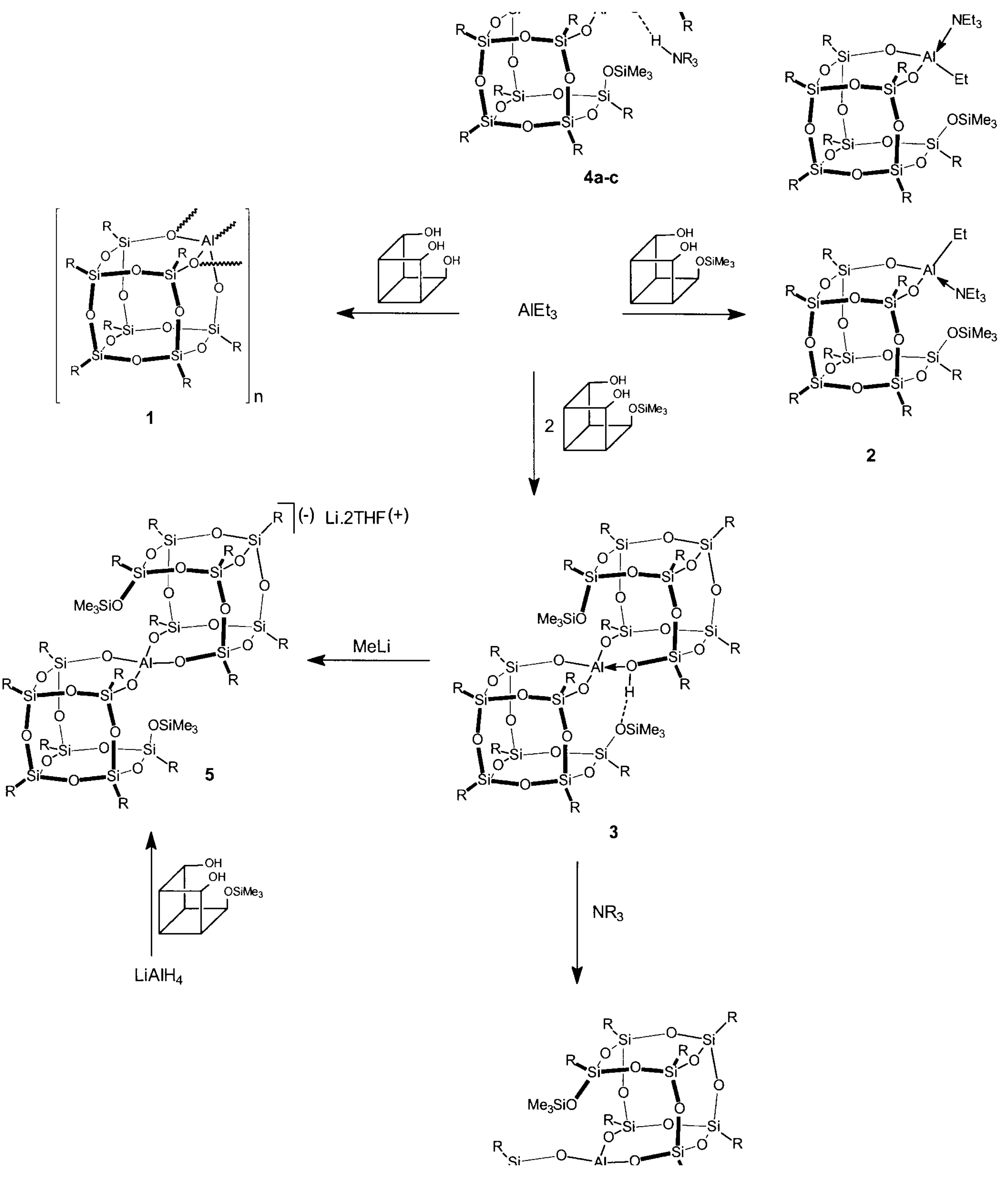

Scheme 1. Synthesis of aluminosilsesquioxanes **1**–**5**. R = *c*-C_5H_9.

$AlMe_3$ with the silsesquioxane $(c\text{-}C_6H_{11})_7Si_8O_{11}(OH)_2$ resulted in the formation of a highly porous polymer with high hydrocarbon sorption capacity.[4] The solid-state ^{29}Si NMR spectrum of **1** shows five sharp $(-O)_3Si(c\text{-}C_5H_9)$ resonances in a 1:2:2:1:1 ratio, which indicates C_2 symmetry of the silsesquioxane ligand in **1**. The proposed structure of **1** (Scheme 1) is comparable to that of its cyclohexyl-substituted analogue $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Al\}_2$;[5a] two siloxy functionalities bridge two neighboring aluminum sites while one siloxy group is monodentately bonded to a third aluminum center to form the polymeric structure. Clearly, the apparently small difference in steric bulk between cyclopentyl and cyclohexyl substituents is large enough to result in considerably different structures. When the protolysis of the disilanol $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ with an equimolar amount of $AlEt_3$ was carried out in the absence of Lewis bases, the reaction was nonselective and yielded a mixture of products. In the presence of NEt_3, the amine adduct **2** is selectively formed. The ^1H, ^{13}C, and ^{29}Si NMR spectra of **2** clearly show two isomers in a 10:8 ratio, indicating little preference for either of the two possible configurations (Scheme 1). It is clear that the aluminum sites in **1** and **2** are strong Lewis acids since they form either polymeric structures or coordinate even the sterically hindered triethylamine to relieve the electronic unsaturation.

Reaction of $AlEt_3$ with two equivalents of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ selectively affords the bis(silsesquioxane) aluminum complex **3**, a homogeneous model for a Brønsted acidic aluminum site present in zeolites and aluminosilicates. The ^{29}Si NMR spectrum of **3** displays two $SiMe_3$ signals and fourteen distinct $(-O)_3Si(c\text{-}C_5H_9)$ resonances, corresponding to an asymmetric structure in which all silicon atoms are nonequivalent. The OH resonance in the ^1H NMR spectrum of **3** is found at $\delta = 8.50$, and such deshielding is characteristic for acidic and/or hydrogen-bonded hydroxy groups. For example, the OH resonance ($\delta = 6.95$ ppm)[2] for the hydrogen-bonded silsesquioxane $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ is considerably shifted to low field compared to the OH resonances of the less acidic, nonbridged silsesquioxanes $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ ($\delta = 2.93$)[7] and $(c\text{-}C_6H_{11})_7Si_7O_8(OH)$ ($\delta = 3.00$),[2a] and, for example, the silanols $Me_2Si(OSiMe_2)_2CHSiMe_2OH$ ($\delta = 1.38$) and $Me_2Si(Si(OH)Me_2)_2(SiMe_2)_3$ ($\delta = 2.74$).[8] In agreement with the ^1H resonance of **3**, the low O–H stretching vibration frequency of $3150\,cm^{-1}$ indicates strong hydrogen bonding within **3**. As a comparison, the O–H vibration of acidic, hydrogen-bonded hydroxy groups in zeolite HY is found at $3550\,cm^{-1}$, shifted to lower frequency compared to the vibration of nonbridged acidic OH ($3650\,cm^{-1}$) and nonacidic terminal OH groups ($3750\,cm^{-1}$).[9] The much stronger shift to lower frequency observed for **3** indicates substantially more efficient hydrogen bonding in **3** than in zeolite HY.[9] Further proof for a strong hydrogen bond came from a DFT computational study.[10] The calculated structure of **3** is shown in Figure 1. For computational reasons, in these calculations the silsesquioxane alkyl groups had to be replaced by hydrogen atoms. Although even small differences in steric bulk were found to have a significant influence on the structure of the complex, this approximation seems reasonable for the computation of an internal feature such as an intramolecular hydrogen bond. With a $H_3SiO\cdots O(H)Al$ distance of 2.84 Å (Figure 1), the $OSiH_3$ group is clearly bent towards the hydroxy group bonded to aluminum, thus enabling the formation of a hydrogen bond. Although the X-ray crystal structure analysis of **3** encountered serious problems which prevented complete refinement of the structure,[3c, 11] one of the $OSiMe_3$ groups in **3** was clearly bent towards the AlOH hydroxyl ($Me_3SiO\cdots O(H)Al = 2.74(2)$ Å),[12a] in a very similar fashion to the calculated structure.

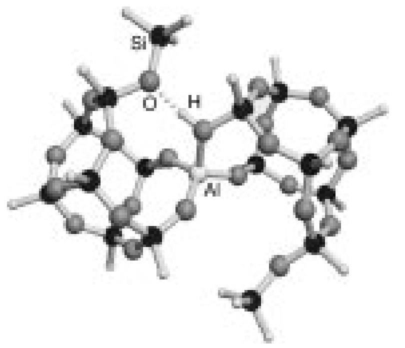

Figure 1. Calculated structure of $[H_7Si_7O_{11}(OSiH_3)]Al[H_7Si_7O_{10}(OSiH_3)(OH)]$. $H_3SO\cdots O(H)Al$ 2.84 Å; Al–O(H) 1.94 Å, Al–O_{av}, 1.75 Å.

Complex **3** is an interesting model for a Brønsted acidic aluminum site in aluminosilicates and zeolites. The strong hydrogen bonding in **3** reduces its Brønsted acidity substantially, which is supported by the incapacity of **3** to catalyze even the isomerization of 1-hexene. However, **3** is significantly more acidic than aluminum-free silsesquioxanes. For example, unlike $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ and $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$,[7] **3** is readily deprotonated by amines (NEt_3, $PhNMe_2$, pyridine) to give the corresponding ammonium salts **4a–c** ($R_3N = Et_3N$ **4a**, $PhNMe_2$ **4b**, pyridine **4c**). Deprotonation of complex **3** by alkyllithium reagents (MeLi, BuLi) was complicated by competitive $SiMe_3$ abstraction, a reaction that was also observed during attempted lithiation of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$.[7] However, the corresponding aluminosilsesquioxane lithium salt **5** can easily be synthesized by treatment of $LiAlH_4$ with two equivalents of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ in THF. Since only two THF molecules are coordinated to the lithium atom in **5** it can be concluded that, to fill its coordination sphere, the lithium is also bonded to the silsesquioxane framework.[13] The single $SiMe_3$ resonance in the ^1H, ^{13}C, and ^{29}Si NMR spectra of **4a–c** and **5** is consistent with a tetrahedrally coordinated aluminum center which has local C_2 symmetry. In analogy with $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2M$ (M = Ti, Zr),[3c] for example, the ^{13}C and ^{29}Si NMR spectrum of **4a–c** show seven equally intense resonances (assigned to methine CH and silsesquioxane $(-O)_3Si(c\text{-}C_5H_9)$), which indicates that the local mirror symmetry of the silsesquioxane ligands is lost. On the other hand, with five methine CH (1:2:2:1:1 ratio) and $(-O)_3Si(c\text{-}C_5H_9)$ (1:2:2:1:1 ratio) resonances, the C_2 symmetry of the silsesquioxane ligands is retained in **5**.

Recently, Edelmann et al. reported the cyclohexyl-substituted analogue of **4a**, $\{[(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Et_3NH\}^+$, which was synthesized by dehydrochlorination of (*c*-

$C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ with $AlCl_3$ in the presence of NEt_3.[6] Comparison of the X-ray crystal structures of **4a** (Figure 2, Table 1)[12b] and its cyclohexyl-substituted analogue $\{[(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Et_3NH\}^+$ clearly reveals the difference in steric congestion between cyclopentyl and cyclohexyl-substituted aluminosilsesquioxanes. Whereas in the latter structure the aluminosilicate anion and the ammonium cation form a separated ion pair,[6] less steric crowding in **4a** allows the formation of a contact ion pair in which the ammonium proton forms a hydrogen bond with one of the Al-O-Si oxygens in the aluminosilicate anion (N···O12 = 2.775(6) Å). The coordination of the ammonium ion is accompanied by slight elongation of the Al–O12 (1.771(4) Å) and Si8–O12 (1.621(4) Å) bonds, compared to the other three Al–O (av 1.730(4) Å) and Si–OAl bonds (1.588(4) Å). Although the Si–O distances and Si-O-Si angle span a wide range, they are not exceptional for silsesquioxane compounds.[2–6]

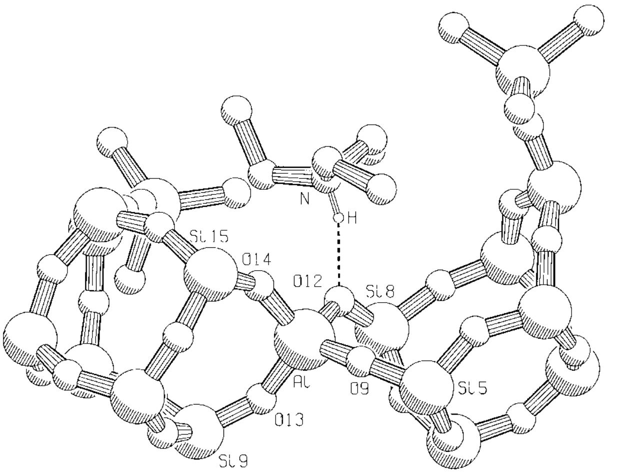

Figure 2. Perspective view of the molecular structure of **4a**. Hydrogen atoms and cyclopentyl groups have been omitted for clarity.

Table 1. Selected interatomic distances [Å] and bond angles [°] for **4a**.

Al–O9	1.727(5)	Al-O9-Si5	150.9(3)
Al–O12	1.771(4)	Al-O12-Si8	128.1(2)
Al–O13	1.722(5)	Al-O13-Si9	148.8(3)
Al–O14	1.742(4)	Al-O14-Si15	144.5(3)
Si5–O9	1.586(5)	O9-Al-O12	107.5(2)
Si8–O12	1.621(4)	O9-Al-O13	114.0(2)
Si9–O13	1.594(5)	O9-Al-O14	109.6(2)
Si15–O14	1.585(4)	O12-Al-O13	110.2(2)
N–O12	2.775(6)	O12-Al-O14	105.1(2)
		O13-Al-O14	110.0(2)

In summary, aluminosilsesquioxanes appear to be interesting models for either Lewis or Brønsted acidic aluminum sites in aluminosilicates and zeolites. The Lewis acidic aluminosilsesquioxanes (**1**, **2**) form either oligomeric structures or Lewis base adducts to relieve the electronic unsaturation. Brønsted acid **3** contains an intramolecular hydrogen bond comparable to that found in zeolite HY, for example. Although the Brønsted acidity of **3** is reduced substantially by the strength of the hydrogen bond, aluminosilsesquioxane **3** can still be easily deprotonated by amines to yield the corresponding ammonium salts (**4a**–**c**). This work provides the first significant study on the relation between the structures and steric bulk of silsesquioxane complexes. Unexpectedly, the apparently small difference in steric bulk between silsesquioxane cyclopentyl and cyclohexyl substituents appears to have a significant effect on the structure of the corresponding aluminosilsesquioxane complexes.

Experimental Section

General information: All manipulations were performed under an argon atmosphere in a glove box (Braun MB-150 GI) and with Schlenk techniques. Solvents were distilled from Na (toluene), K (THF) or Na/K alloy (hexanes, $[D_6]$benzene) and stored under argon. Acetonitrile, triethylamine, *N*,*N*-dimethylaniline, pyridine, and $[D_1]$chloroform were dried over 4 Å molecular sieves. The IR spectrum of **3** was recorded on a Shimadzu FTIR-8300 spectrophotometer. NMR spectra were recorded on a Varian GEMINI 300 MHz (^1H 300 MHz, ^{13}C 75 MHz) and a Bruker AC400 MHz (^{29}Si 79.5 MHz) spectrometer at 25 °C. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C) or an external standard (^{29}Si TMS = 0 ppm). $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$[2] and $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$[14] were prepared following literature procedures.

$\{[(c\text{-}C_5H_9)_7Si_7O_{12}]Al\}_n$ (1): At room temperature, $AlEt_3$ (3.0 mmol, 1.6 mL, 1.9 M in toluene) was added to a solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (2.6 g, 3.0 mmol) in THF (30 mL). Immediately, gas evolution and precipitation of a white solid was observed. After 10 min at room temperature, the solid was collected, washed with THF (2 × 5 mL) and dried in vacuum to yield **1** as a microcrystalline material (2.4 g, 2.67 mmol, 89%). Magic angle spinning (2.5 kHz) solid-state ^{29}Si NMR: $\delta = -61.74, -62.94, -64.79, -65.34, -69.49$ ($O_3SiC_5H_9$, 1:2:2:1:1 ratio); $(C_{35}H_{63}AlO_{12}Si_7)_n$: calcd C 46.74, H 7.06; found C 46.44, H 7.44.

$[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]AlEt\cdot NEt_3$ (2): At 0 °C, a solution containing NEt_3 (0.5 mL, 3.6 mmol) and $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (2.80 g, 2.95 mmol) in toluene (25 mL) was treated with $AlEt_3$ (3.0 mmol, 1.6 mL, 1.9 M in toluene). Gas evolved immediately. The solution was allowed to warm to room temperature and was stirred for one additional hour. The solvent was removed in vacuum. The remaining sticky solid was dissolved in hexane (10 mL) which was subsequently evaporated. This procedure was repeated twice until a non-sticky solid was obtained (2.40 g, 2.18 mmol, 74%). Slow crystallization from hexane (5 mL) at −30 °C yielded **2** as colorless crystals (0.94 g, 0.85 mmol, 29%). The ^1H and ^{13}C NMR spectra showed the two stereoisomers in a 1:0.8 ratio. ^1H NMR ($[D_6]$benzene): $\delta =$ 2.55 (q, $^3J(H,H) = 7$ Hz, 6H; $N(CH_2CH_3)_3$,), 2.42 (q, $^3J(H,H) = 7$ Hz, 6H; $N(CH_2CH_3)_3$), 1.98 (m, 28H; $CH_2{-}C_5H_9$), 1.75 (m, 56H; $CH_2{-}C_5H_9$), 1.56 (m, 28H; $CH_2C_5H_9$), 1.50 (t, $^3J(H,H) = 8$ Hz, 3H; $AlCH_2CH_3$), 1.48 (t, $^3J(H,H) = 8$ Hz, 3H; $AlCH_2CH_3$), 1.21 (m, 14H; $CH\text{-}C_5H_9$), 1.00 (t, $^3J(H,H) = 7$ Hz, 9H; $N(CH_2CH_3)_3$), 0.90 (t, $^3J(H,H) = 7$ Hz, 9H; $N(CH_2\text{-}CH_3)_3$), 0.39 (s, 9H; $Si(CH_3)_3$), 0.27 (s, 9H; $Si(CH_3)_3$), 0.22 (q, $^3J(H,H) =$ 8 Hz, 2H; $AlCH_2CH_3$), 0.11 (q, $^3J(H,H) = 8$ Hz, 2H; $AlCH_2CH_3$); $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): $\delta = 47.45$, 47.28 (s, $N(CH_2CH_3)_3$), 28.72, 28.57, 28.48, 28.43, 28.15, 28.06, 28.01, 27.76, 27.69, 27.48, 27.43, 27.39, 27.30 (s, $CH_2{-}C_5H_9$), 25.69, 25.43, 24.75, 24.67, 24.20, 24.08, 23.57, 23.39, 23.27 (s, $CH{-}C_5H_9$), 10.40, 10.01 (s, $AlCH_2CH_3$), 9.33, 9.06 (s, $N(CH_2CH_3)_3$), 2.22, 2.15 (s, $Si(CH_3)_3$), 0.79, 0.42 (s, $AlCH_2CH_3$); ^{29}Si NMR (toluene): $\delta = 7.14$, 6.85 (s, $SiMe_3$), −65.26, −65.37, −65.44, −65.78, −66.03, −66.60, −66.83, −66.94, −68.05, −68.62 (s, $O_3SiC_5H_9$); $C_{46}H_{92}AlNO_{12}Si_8$ (1102.91): calcd C 50.10, H 8.41, N 1.27; found C 49.43, H 8.22, N 1.14.

$[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)(OSiMe_3)]$ (3): A solution of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (3.87 g, 4.08 mmol) in toluene (25 mL) was cooled to 0 °C and $AlEt_3$ (2.1 mmol, 1.1 mL, 1.9 M in toluene) was added. The solution was warmed to room temperature and stirred for an additional hour. Evaporation of the volatiles yielded **3** as a white foam in nearly quantitative yield. Recrystallization by slow diffusion of acetonitrile into a concentrated toluene solution yielded **3** (0.8 g, 0.4 mmol, 20%) as colorless crystals. IR (C_4Cl_6): $\tilde{\nu} = 3150\ cm^{-1}$ (OH); ^1H NMR ($[D_6]$benzene): $\delta = 8.50$ (s, 1H; OH), 1.67 (m, 112H; $CH_2{-}C_5H_9$), 1.14 (m, 14H; $CH{-}C_5H_9$), 0.44 (s, 18H; $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): $\delta = 28.47$, 28.31, 28.11, 27.98, 27.87, 27.84, 27.66, 27.60, 27.52, 27.44, 27.23 (s, $CH_2{-}C_5H_9$),

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25.31, 24.50, 23.97, 22.84 (s, CH–C_5H_9), 2.47 (s, $Si(CH_3)_3$); ^{29}Si NMR (toluene): $\delta = 8.02$, 7.93 (s, $SiMe_3$), –58.72, –62.01, –63.46, –64.53, –65.10, –65.18, –65.25, –66.26, –66.49, –67.09, –67.33, –67.56, –68.30, –68.45 (s, $O_3SiC_5H_9$); $C_{76}H_{145}AlO_{24}Si_{16}$ (1919.33): calcd C 47.56, H 7.62; found C 47.26, H 7.67.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Et_3NH\}^+$ (4a): At 0°C, a solution of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (4.03 g, 4.25 mmol) in toluene (40 mL) was treated with $AlEt_3$ (1.1 mL, 1.9 M in toluene, 2.1 mmol) followed by NEt_3 (0.7 mL, 5.0 mmol). The solution was allowed to warm to room temperature and stirred for an additional hour. After evaporation of the solvent, the sticky product was dried in vacuum and traces of toluene were removed by dissolving the product in hexane (10 mL) and evaporation of the volatiles. Crystallization from a cooled (–30°C) hexane (10 mL) solution yielded **4a** (1.83 g, 0.91 mmol, 43 %) as a white microcrystalline material. ^{1}H NMR ([D_1]chloroform): $\delta = 9.72$ (s, 1H; NH), 3.26 (m, 6H; $N(CH_2CH_3)_3$), 1.76 (m, 28H; CH_2–C_5H_9), 1.51 (m, 84H; CH_2–C_5H_9), 0.99 (m, 23H; CH–C_5H_9 + $N(CH_2CH_3)_3$), 0.16 (s, 18H; $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ([D_1]chloroform): $\delta = 45.71$ (s, $N(CH_2CH_3)_3$), 28.25, 28.12, 28.02, 27.88, 27.81, 27.66, 27.55, 27.36, 27.16, 27.11, 27.02, 26.95, 26.86 (s, CH_2–C_5H_9), 25.27, 25.23, 24.39, 24.17, 23.80, 22.86, 22.48 (s, CH–C_5H_9), 8.96 (s, $N(CH_2CH_3)_3$), 2.11 (s, $Si(CH_3)_3$); ^{29}Si NMR (toluene): $\delta = 6.65$ (s, $SiMe_3$), –65.15, –65.34, –65.43, –65.56, –65.75, –67.86, –68.46 (s, $O_3SiC_5H_9$); $C_{82}H_{160}AlNO_{24}Si_{16}$ (2020.52): calcd C 48.74, H 7.98, N 0.69; found C 48.73, H 8.25, N 0.62.

X-ray crystal structure analysis of 4a: Single crystals suitable for an X-ray structure analysis were grown in an NMR tube by slow evaporation of a saturated solution of **4a** in $CDCl_3$. Slightly disordered $CDCl_3$ molecules were found in the lattice, which frustrated the refinement. Enraf-Nonius CAD-4F diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 130$ K, $0.25 \times 0.30 \times 0.50$ mm, $C_{82}H_{160}AlNO_{24}Si_{16} \cdot CDCl_3$, $M_r = 2140.90$, monoclinic, $P2_1/n$, $a = 14.655(1)$ $b = 32.976(3)$, $c = 23.042(2)$ Å, $\beta = 98.448(6)^\circ$, $V = 11014.5(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.291\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 3.30\ cm^{-1}$, $\omega/2\theta$ scans, total data $(\pm h, -k, -l) = 22548$, The structure was solved by direct methods with SHELXS97[15] and subsequent difference Fourier maps. A final refinement on F^2 converged at $wR(F^2) = 0.2574$ for 21572 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0865$ for 13093 reflections with $F_o \geq 4.0\sigma(F_o)$ and 1150 parameters. Max. residual electron density –1.21 and 1.14 e Å^{-3}.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{C_6H_5N(H)Me_2\}^+$ (4b): The general procedure was similar as for **4a**. Starting from $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (3.00 g, 3.17 mmol), $AlEt_3$ (1.5 mmol, 0.8 mL, 1.9 M in toluene), and *N,N*-dimethylaniline (0.4 mL, 3.5 mmol) yielded after recrystallization from hexane **4b** as a white microcrystalline material (1.99 g, 0.98 mmol, 65 %). ^{1}H NMR ([D_6]benzene): $\delta = 12.71$ (s, 1H; $PhN(H)Me_2$), 7.41 (m, 2H; $C_6H_5N(H)Me_2$), 7.31 (m, 2H; $C_6H_5N(H)Me_2$), 7.03 (m, 1H; $C_6H_5N(H)Me_2$), 3.19 (s, 6H; $PhNH(CH_3)_2$), 1.68 (m, 112H; CH_2-C_5H_9), 1.22 (m, 14H; CH-C_5H_9), 0.10 (s, 18H; $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ([D_6]benzene): $\delta = 130.54$ (s, $C_6H_5N(H)Me_2$), 121.85 (s, $C_6H_5N(H)Me_2$), 28.77, 28.51, 28.35, 28.23, 28.11, 28.02, 27.93, 27.83, 27.70, 27.61, 27.51, 27.39, 27.35, 27.39 (s, CH_2–C_5H_9), 25.64, 25.52, 24.43, 24.34, 24,28, 23.28, 23.04 (s, CH–C_5H_9), 2.12 (s, $Si(CH_3)_3$); ^{29}Si NMR (toluene): $\delta = 7.21$ (s, $SiMe_3$), –64.63, –65.05, –65.18, –65.36, –65.62, –67.91, –68.16 (s, $O_3SiC_5H_9$); $C_{84}H_{156}AlNO_{24}Si_{16}$ (2040.51): calcd C 49.44, H 7.71, N 0.69; found C 49.48, H 7.77, N 0.73.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{C_5H_5NH\}^+$ (4c): The general procedure was similar as for **4a**. Starting from $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (3.48 g, 3.67 mmol), $AlEt_3$ (1.9 mmol, 1.0 mL, 1.9 M in toluene), and pyridine (0.3 mL, 3.7 mmol) yielded after recrystallization from hexane **4c** as a white microcrystalline material (2.28 g, 1.09 mmol, 58 %). The product contained one equivalent of lattice hexane. ^{1}H NMR ([D_6]benzene): $\delta = 18.22$ (s, 1H; C_5H_5NH), 9.33 (s, 2H; C_5H_5–NH), 7.35 (s, 2H; C_5H_5NH), 7.09 (s, 1H; C_5H_5NH), 1.98 (m, 28H; CH_2–C_5H_9), 1.75 (m, 56H; CH_2–C_5H_9), 1.57 (m, 28H; CH_2–C_5H_9), 1.23 (m, 14H; CH–C_5H_9), –0.10 (s, 18H; $Si(CH_3)_3$); ^{13}C NMR ([D_6]benzene): $\delta = 143.88$ (s, C_5H_5N), 127.57 (s, C_5H_5N), 126.31 (s, C_5H_5N), 28.68, 28.58, 28.44, 28.31, 28.20, 28.08, 28.01, 27.91, 27.73, 27.61, 27.47, 27.37, 27.30 (s, CH_2–C_5H_9), 25.29, 24.82, 24.44, 24.19, 23.22, 23.18 (s, CH–C_5H_9, 2:1:1:1:1:1 ratio), 1.83 (s, $Si(CH_3)_3$); ^{29}Si NMR (toluene): $\delta = 8.15$ (s, $SiMe_3$), –64.44, –65.28, –65.52, –65.98, –68.45, –68.69 (s, $O_3SiC_5H_9$, 1:1:2:1:1:1). Gradual loss of hexane from the lattice prevented satisfactory elemental analysis.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Li \cdot 2\,THF\}^+$ (5): To a stirred solution of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (4.49 g, 4.74 mmol) in THF (25 mL), $LiAlH_4$ (1.4 mL, 1.7 M in THF, 2.3 mmol) was added at 0°C. After gas evolution had ceased, the volatiles were removed in vacuum to leave a sticky white solid. The crude product was dissolved in diethyl ether (10 mL) and filtered to remove traces of insoluble material. Concentration and cooling to –30°C gave **5** as colorless crystals (2.30 g, 1.11 mmol, 48 %). ^{1}H NMR ([D_1]chloroform): $\delta = 3.74$ (m, 4H; THF-α-CH_2), 1.83 (m, 4H; THF-β-CH_2), 1.71 (m, 14H; $CH_2C_5H_9$), 1.51 (m, 42H; $CH_2C_5H_9$), 0.91 (m, 7H; CHC_5H_9), 0.20 (s, 9H; $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ([D_1]chloroform): $\delta = 67.98$ (s, THF-α-CH_2), 28.09, 28.06, 27.67, 27.62, 27.59, 27.56, 27.39, 27.34, 27.29, 27.26, 27.15, 27.09, 26.98, 26.95, 26.93 (s, $CH_2C_5H_9$), 25.60 (s, THF-β-CH_2), 24.24 23.68, 23.37, 22.40, 22.37 (s, CHC_5H_9, 1:2:2:1:1), 1.62 (s, $Si(CH_3)_3$); ^{29}Si NMR (toluene): $\delta = 0.10$ (s, $SiMe_3$), –63.40, –64.79, –65.33, –67.07, –67.89 (s, $O_3SiC_5H_9$, 1:2:2:1:1); $C_{84}H_{160}AlLiO_{26}Si_{16}$ (2069.48): calcd C 48.75, H 7.79; found C 48.76, H 7.75.

DFT computational studies: Density functional theory (DFT) formed the basis of our calculations as implemented by the Amsterdam density functional (ADF) code.[16] The exchange correlation functionals in the local-density approximation[17] were augmented by generalized gradient approximations to the exchange[18] and correlation.[19] All the corrections were applied self-consistently. We chose a double ς basis set of Slater type orbitals with polarization functions for hydrogen, oxygen, silicon, and aluminum. The inner electrons were treated with a frozen-core approximation, for silicon and aluminum these were taken up to the 2p and for oxygen up to the 1s electrons. A quasi Newtonian approach[20] to geometry optimization is combined with the direct inversion in the iterative subspace (DIIS) method.[21] Full geometry optimization was used in all calculations in this work. The convergence criteria used in these calculations are 10^{-3} Hartree for the energy, 5×10^{-3} Hartree/Å for the gradients and 5×10^{-3} Å for the Cartesian displacement. ADF code makes use of the natural symmetry properties of the different clusters. The silsesquioxanes were approximated by substitution of the large cyclopentyl groups on the silicon atoms by hydrogen atoms.

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