Steric Factors Affecting the Brønsted Acidity of Aluminosilsesquioxanes

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By reacting $AlMe_3$ with two equivalents of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiR_3$, the corresponding Brønsted acidic aluminosilsesquioxanes $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR_3)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)OSiR_3]$ [SiR_3 = $SiMe_3$ (**1a**), $SiMePh_2$ (**1b**)] are obtained. These complexes readily react with triethylamine to yield the corresponding ammonium salts $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR_3)]_2Al\}^-\{HNEt_3\}^+$ (**2a**,**b**). Hydrogen bonding between the acidic $SiO(H)\rightarrow Al$ proton and the pendant silyl ether function is effectively reduced by increasing the steric bulk of the silyl ether substituents, resulting in a higher acidity for **1b** compared to that of **1a**. With the silsesquioxane ligand $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$, which lacks pendant silyl ether functions, the acidic proton cannot satisfactorily be stabilized and this renders the putative Brønsted acid $[(c\text{-}C_5H_9)_8Si_8O_{13}]Al[(c\text{-}C_5H_9)_8Si_8O_{12}(OH)]$ unstable. In the absence of proton acceptors, the disproportionation product $[(c\text{-}C_5H_9)_8Si_8O_{13}]_3Al_2$ (**3**) is formed instead of the Brønsted acid. However, in the presence of triethylamine, the initially formed Brønsted acid readily transfers its proton to the amine, affording the ammonium salt $\{[(c\text{-}C_5H_9)_8Si_8O_{13}]_2Al\}^-\{HNEt_3\}^+$ (**4**).

Introduction

Acidic aluminum sites in zeolites, clays, and aluminosilicates play an important role in acid-catalyzed reactions.[1] In recent years, several soluble aluminum complexes based on incompletely condensed silsesquioxanes have been prepared and successfully employed as homogeneous models for aluminosilicates and zeolites.[2−5] This paper concerns the further development of molecular cluster analogues of zeolitic acidic sites, which are either inherently useful as catalysts or serve as model systems facilitating detailed mechanistic analysis. Recently, we reported the synthesis and characterization of the aluminosilsesquioxane $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)OSiMe_3]\}$ (**1a**),[4] the first homogeneous model of a hydrogen-bonded Brønsted acidic aluminosilicate site as found, for example, in zeolite HY.[1] The strong intramolecular hydrogen bond between the acidic $SiO(H)\rightarrow Al$ proton and the pendant silyl ether oxygen ($Si\mathit{O}SiMe_3$) was found to dramatically lower the Brønsted acidity of this complex. In an effort to produce more acidic aluminosilsesquioxanes, we have now synthesized aluminosilsesquioxane complexes with diminished intramolecular hydrogen bonding.

Results and Discussion

To reduce hydrogen bonding as observed in **1a**,[4] the silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ with a considerably more bulky silyl ether substituent was synthesized.[6] Brønsted acids of the type $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR_3)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)OSiR_3]\}$ [SiR_3 = $SiMe_3$ (**1a**); $SiMePh_2$ (**1b**)] may readily be prepared by treatment of silsesquioxane solutions with $AlMe_3$ in toluene, although the reaction rate strongly depends on the silyl ether substituent (Scheme 1). Whereas for SiR_3 = $SiMe_3$ the reaction reaches completion within minutes at 0 °C, when R is the more bulky $MePh_2$ group, significant retardation is seen and heating to reflux (1 h) is required in order to obtain the Brønsted acid $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)OSiMePh_2]\}$ (**1b**) in reasonable yield. In the presence of triethylamine, the Brønsted acids (**1a**,**b**) are selectively transformed into the corresponding ammonium salts $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR_3)]_2Al\}^-\{HNEt_3\}^+$ [SiR_3 = $SiMe_3$ (**2a**),[4] $SiMePh_2$ (**2b**); Scheme 1].

In the ^1H NMR spectrum of **1a**, the OH resonance is seen at $\delta = 8.50$, characteristic of a hydrogen-bonded acidic hydroxyl group.[7] In contrast, the OH resonance of **1b** is significantly shifted to higher field, appearing at $\delta = 4.90$. This high-field shift may conceivably be the result of either reduced hydrogen bonding or of decreased acidity of the hydroxyl group.[4,7] The observed higher frequency of the O−H stretching vibration of **1b** ($3366\ cm^{-1}$) compared to that of **1a** ($3150\ cm^{-1}$) is in line with decreased hydrogen bonding. Hence, it can be concluded that increasing the steric bulk of the pendant silyl ether function does indeed reduce hydrogen bonding and should render **1b** more acidic than **1a**.

To determine the relative acidities of **1a** and **1b**, the ammonium salt $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{HNEt_3\}^+$ (**2a**) was treated with an equimolar amount of the Brønsted acid $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)OSiMePh_2]\}$ (**1b**). As was assumed on the basis of the

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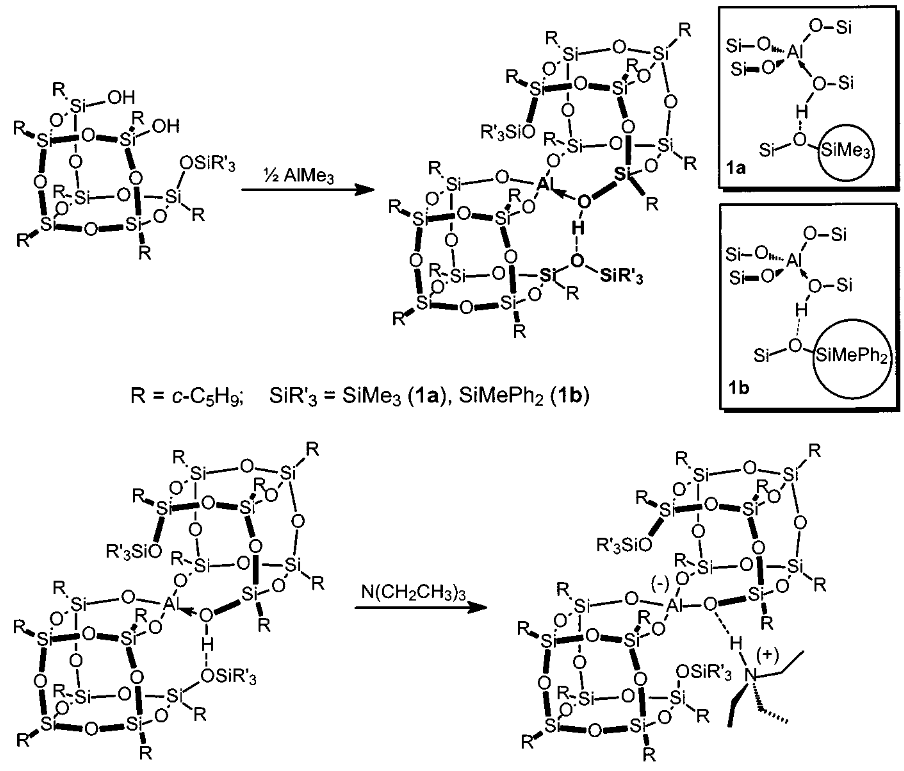


1a,b **2a,b**

Scheme 1

NMR and IR spectroscopic data, the equilibrium (^{1}H NMR) that was set up revealed that **1b** is indeed a stronger acid than **1a** ($\Delta pK_{a(\mathbf{1a}-\mathbf{1b})} = 1.1$).

The NMR spectra of the ammonium salts **2a**,**b** are significantly simplified compared to those of the corresponding asymmetric Brønsted acids **1a**,**b** and are consistent with a C_2 symmetric structure.[4] With shifts ranging from δ =

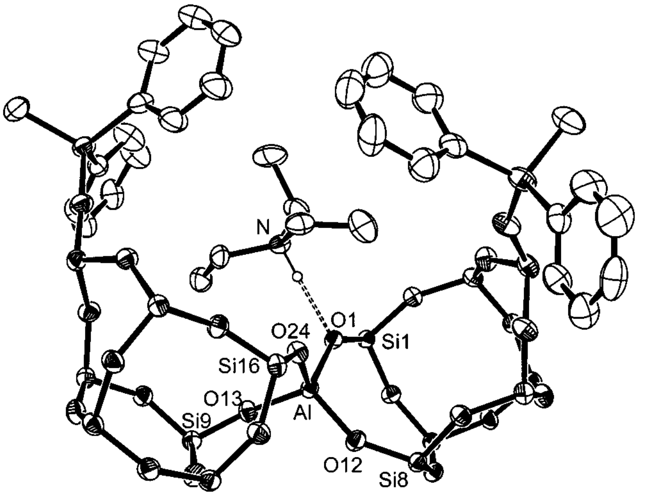


Figure 1. Molecular structure of **2b**; cyclopentyl substituents are omitted for the sake of clarity; thermal ellipsoids are scaled to enclose 30% of the electron density; selected bond lengths [Å]: Al−O1 1.764(4), Al−O12 1.721(4), Al−O13 1.731(4), Al−O24 1.743(4), Si1−O1 1.604(4), Si8−O12 1.586(4), Si9−O13 1.586(4), Si16−O24 1.587(4), N−O1 2.885(6); angles [deg]: O1−Al−O12 112.4(2), O13−Al−O24 109.0(2), O1−Al−O24 104.1(2), O12−Al−O13 111.8(2)

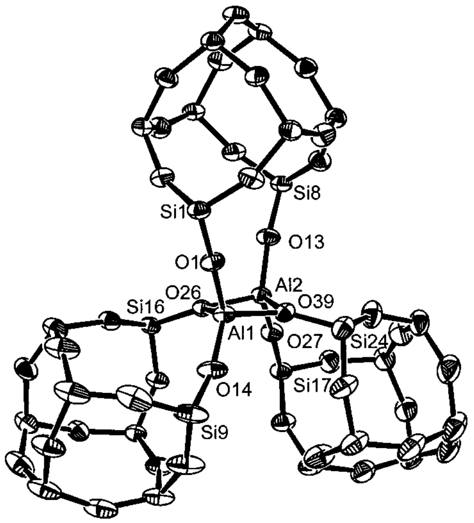
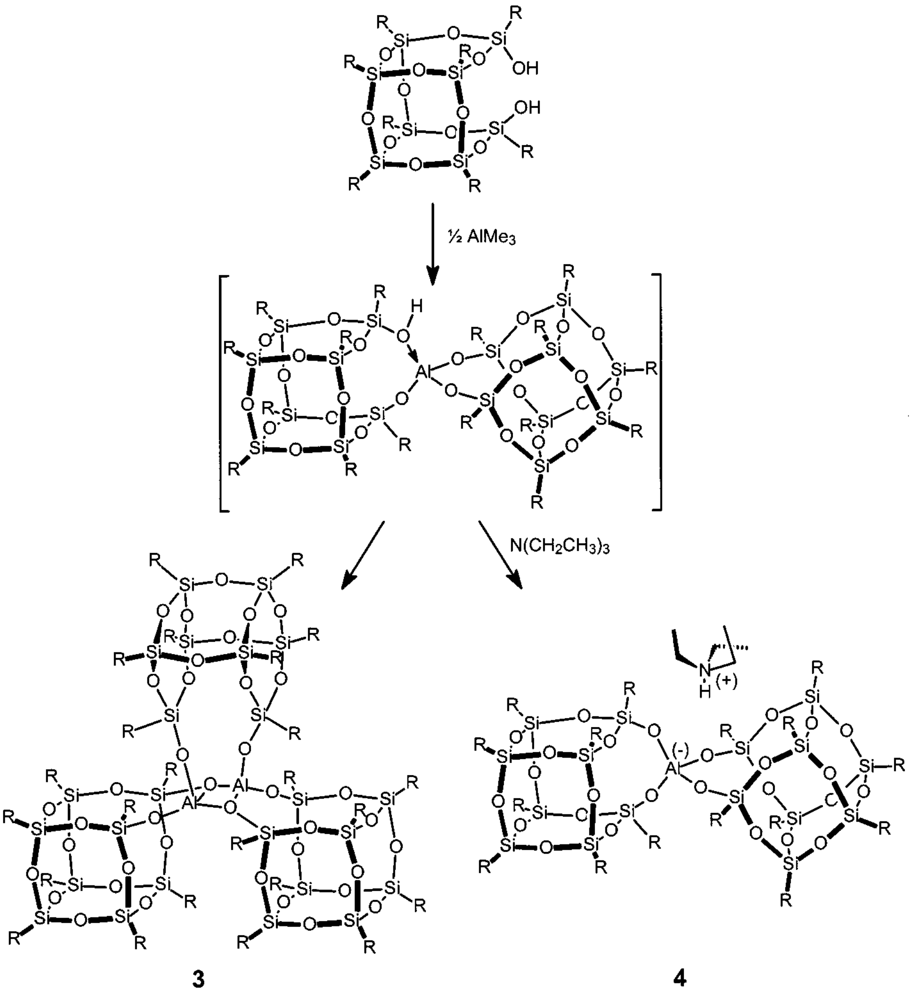


Figure 2. Perspective ORTEP plot of **3**; cyclopentyl substituents are omitted for the sake of clarity; thermal ellipsoids are scaled to enclose 30% of the electron density; selected bond lengths [Å]: Al1−O1 1.684(7), Al2−O13 1.674(7), Al1−O14 1.676(7), Al2−O27 1.665(7), Al1−O26 1.833(6), Al2−O26 1.835, Al1−O39 1.826(7), Al2−O39 1.837(7), O1−Si1 1.568(7), O13−Si8 1.584(7), O14−Si9 1.576(7), O27−Si17 1.602(7), O26−Si16 1.649(6), O39−Si24 1.653(7); angles [deg]: O1−Al1−O14, 117.4(4), O1−Al1−O26 111.3(3), O1−Al1−O39 112.1(3), O14−Al1−O26 115.2(3), O14−Al1−O39 112.4(4), O26−Al1−O39 83.7(3), O13−Al2−O27 118.7(4), O13−Al2−O26 111.3(3), O13−Al2−O39 110.6(3), O27−Al2−O26 110.8(3), O27−Al2−O39 116.6(3), O26−Al2−O39 83.4(3), Al1−O26−Al2 95.5(3), Al1−O39−Al2 95.6(3), Si1−O1−Al1 176.4(5), Si8−O13−Al2 173.2(5), Si9−O14−Al1 162.8(5), Si17−O27−Al2 173.7(5), Si16−O26−Al1 129.1(4), Si16−O26−Al2 133.1(4), Si24−O39−Al1 136.8(4), Si24−O39−Al2 126.9(4)



Scheme 2

9.69−9.27, the Et_3NH resonances for **2a**,**b** are virtually identical. It is interesting to note that for **2b** the $HNEt_3$ methylene protons appear as a doublet of multiplets ($^3J_{HH}$ = 68 Hz), whereas for **2a** only a single multiplet is observed. This effect may possibly be attributed to a difference in hydrogen bonding between the ammonium proton and the Al−O−Si oxygen in **2a**,**b**. The X-ray structure of **2a** reveals that the ammonium ion is hydrogen bonded to the aluminosilsesquioxane fragment.[4] In contrast, the molecular structure of the slightly more bulky cyclohexyl analogue of **2a** consists of a nonbonded ion pair.[3] Although still hydrogen bonded, due to its larger steric bulk the ammonium cation in **2b** (Figure 1) is coordinated significantly less effectively than in **2a**. Therefore, the $^3J_{HH}$ coupling, and thus the N−H bond strength, can be expected to increase on going from **2a** to **2b**, as is indeed observed.

The above results support the proposition that hydrogen bonding between the $SiO(H)\rightarrow Al$ proton and the silyl ether function is effectively reduced by increasing the steric bulk of the pendant silyl ether function, which, in turn, results in increased acidity of the complex. If instead a silsesquioxane ligand lacking such a silyl ether function is used, such hydrogen bonding will be prevented, which may result in an even stronger Brønsted acid. To test this hypothesis, we studied the silsesquioxane $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$, which is accessible by a similar route as its cyclohexyl-substituted analogue, as recently reported by Feher et al.[8] Treatment of toluene solutions of $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ with half an equivalent of $AlMe_3$ led to a rapid reaction. The only aluminosilsesquioxane compound recovered after crystallization was the bimetallic $[(c\text{-}C_5H_9)_8Si_8O_{13}]_3Al_2$ (**3**), and not the expected Brønsted acid, $[(c\text{-}C_5H_9)_8Si_8O_{13}]Al[(c\text{-}C_5H_9)_8Si_8O_{12}(OH)]$ (Scheme 2). However, when the reaction of $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ with $AlMe_3$ was carried out in the presence of NEt_3, the ammonium salt $\{[(c\text{-}C_5H_9)_8Si_8O_{13}]_2Al\}^-\{HNEt_3\}^+$ (**4**) was formed (Scheme 2). The fact that in the presence of an amine the ammonium salt **4** is obtained suggests that, in the absence of a proton acceptor, the proton of the initially formed Brønsted acid is highly reactive. Consequently, the unstable Brønsted acid disproportionates into the thermodynamically more stable complex **3**.

Figure 2 shows the molecular structure of **3**. The tetrahedral aluminum centers are connected by two bridging μ-OSi groups and by one silsesquioxane ligand, which is bonded in an η^1-fashion to each aluminum atom. The average η^1-O_{Si}−Al bond length of 1.675(7) Å compares well with those in $[(Ph_3SiO)_2Al(OtBu)]_2$ [av. η^1-O_{Si}−Al = 1.690(3)

Å][9a] and $[(Ph_2Si)_2O_3]_4Al_4(OH)_4{\cdot}4OEt_2$ [av. $\eta^1\text{-}O_{Si}{-}Al$ = 1.698(3) Å][9a] and is significantly shorter than, for example, that in the Lewis base adduct $[(c\text{-}C_6H_{11})_7Si_7O_{12}]AlO{=}PPh_3$ [av. $\eta^1\text{-}O_{Si}{-}Al$ = 1.717(4) Å][2] or those in the anionic $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR'_3)]_2Al\}^-\{HNEt_3\}^+$ {av. $\eta^1\text{-}O_{Si}{-}Al$: 1.741(5) Å [$SiR'_3$ = $SiMe_3$ (**2a**)],[4] 1.740(4) [SiR'_3 = $SiMePh_2$ (**2b**)]}. With an average distance of 1.833(7) Å, the $(\mu\text{-}O_{Si}){-}Al$ bonds are normal for bridging $(\mu\text{-RO}){-}Al$ bonds.[9] The Si−O bond lengths [av. 1.605(7) Å] are similar to those found in the silsesquioxane compounds $(c\text{-}C_6H_{11})_8Si_8O_{13}[N(H)Ph]_2$ [1.609(2)−1.630(2) Å] and $(c\text{-}C_6H_{11})_8Si_8O_{13}S$ [1.610(2)−1.693(2) Å].[10]

Concluding Remarks

In summary, the strength of the intramolecular hydrogen bond found in **1a−b** may be effectively tuned by altering the steric bulk of the silyl ether substituent. Increased steric bulk leads to less effective hydrogen bonding, which, in turn, renders the complex more acidic. However, when the acidic proton is not satisfactorily stabilized (as, for example, by hydrogen bonding), then the Brønsted acid becomes unstable and is liable to undergo further reactions.

Experimental Section

General Remarks: All manipulations were performed under an argon atmosphere using glove box (Braun MB-150 GI) and Schlenk techniques. Solvents were distilled from Na (toluene), K (THF), or Na/K alloy (hexanes, $[D_6]$benzene) and stored under argon. Triethylamine and $[D_1]$chloroform were dried over 4 Å molecular sieves. − IR spectra were recorded on a Nicolet Avatar 360 spectrophotometer equipped with an ATR (golden gate) device. − NMR spectra were recorded on a Varian Mercury 400 MHz (^1H, 400 MHz; ^{13}C, 100 MHz) or a Varian Inova 500 MHz (^{29}Si, 99 MHz) spectrometer at 25 °C. Chemical shifts are reported in ppm and are referenced to residual solvent resonances (^1H, ^{13}C) or an external standard (^{29}Si, TMS, δ = 0). − $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$[2] and $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$[11] were prepared according to literature procedures. $(c\text{-}C_5H_9)_8Si_8O_{12}$ was prepared by the Pt-catalyzed hydrosilylation of $(c\text{-}C_5H_9)_7Si_8O_{12}H$ in refluxing cyclopentene. $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ was prepared by treating $(c\text{-}C_5H_9)_8Si_8O_{12}$ with CF_3SO_3H as described by Feher et al.[8]

$[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]Al[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)(OSiMePh_2)]$ (1b): To a solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMe_2Ph$ (3.22 g, 3.00 mmol) in toluene (25 mL) was added $AlMe_3$ (0.75 mL, 2.0 M solution in *n*-heptane, 1.5 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was refluxed for a further 1 h. The volatiles were then evaporated and the product was recrystallized from hexane (7 mL) at room temperature, yielding **1b** (2.33 g, 1.07 mmol, 72%) as colorless crystals. − ^1H NMR ($[D_6]$benzene): δ = 0.88 (m, 6 H, $SiCH_3$), 1.17 (m, 14 H, $CH{-}C_5H_9$), 1.65 (m, 112 H, $CH_2{-}C_5H_9$), 4.90 (s, 1 H, OH), 7.30 (m, 6 H, Ph), 7.85 (m, 4 H, Ph). − $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): δ = 0.03 (s, $SiCH_3$), 22.67, 22.87, 22.90, 23.62, 24.93 (s, $CH{-}C_5H_9$), 27.27, 27.36, 27.43, 27.52, 27.98, 28.09, 28.50 (s, $CH_2{-}C_5H_9$), 128.07, 130.26, 134.57 (Ph). − $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene): δ = −67.48, −66.91, −64.66, −64.29, −63.53 [s, $(\equiv O)_3SiC_5H_9$], −9.89 (s, $SiMePh_2$) (1:1:1:2:2:1 ratio). − $C_{96}H_{153}AlO_{24}Si_{16}$ (2167.61): calcd. C 53.19, H 7.11; found C 53.03, H 7.24.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Al\}^-\{Et_3NH\}^+$ (2b): At 0 °C, $AlMe_3$ (0.5 mL, 2.0 M solution in *n*-heptane, 1.0 mmol) was added to a stirred solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ (2.15 g, 2.01 mmol) and NEt_3 (0.3 mL, 2.2 mmol) in toluene (30 mL). After stirring at room temperature for 1 h, the volatiles were evaporated. The crude product was recrystallized from hexane (15 mL) at 0 °C, yielding **2b** (1.20 g, 0.53 mmol, 53%) as colorless crystals. − ^1H NMR ($[D_6]$benzene): δ = 0.73 (s, 6 H, $SiCH_3$), 0.89 [m, 9 H, $HN(CH_2CH_3)_3$], 1.23 (m, 14 H, $CH{-}C_5H_9$), 1.65 (m, 112 H, $CH_2{-}C_5H_9$), 2.63 [dm, $^3J(H,H)$ = 68 Hz, 6 H, $HN(CH_2CH_3)_3$], 7.23 (m, 12 H, Ph), 7.70 (m, 8 H, Ph), 9.29 (s, 1 H, $HNEt_3$). − $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): δ = 0.21 (s, $SiCH_3$), 8.84 (s, NCH_2CH_3), 23.05, 23.31, 24.31, 24.50, 24.63, 25.51, 25.91 (s, $CH{-}C_5H_9$, 1:1:1:1:1:1:1 ratio), 27.05, 27.13, 27.25, 27.33, 27.46, 27.62, 28.06, 28.12, 28.30, 28.57, 28.67, 28.93 (s, $CH_2{-}C_5H_9$), 45.59 (s, NCH_2CH_3), 127.99, 128.04, 129.87, 134.43, 134.50, 137.57, 137.86, (s, Ph). − $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene): δ = −67.03, −66.46, −64.48, −64.23, −64.14, −63.61 [s, $(\equiv O)_3SiC_5H_9$], −11.79 (s, $SiMePh_2$) (1:1:1:2:1:1:1 ratio). − $C_{102}H_{168}AlNO_{24}Si_{16}$ (2268.81): calcd. C 54.00, H 7.46; found C 53.63, H 7.52.

$[(c\text{-}C_5H_9)_8Si_8O_{13}]_3Al_2$ (3): At 0 °C, $AlMe_3$ (0.5 mL, 2.0 M in *n*-heptane, 1.0 mmol) was added to a stirred solution of $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ (1.98 g, 2.00 mmol) in toluene (10 mL). After stirring overnight at room temperature, the volatiles were removed in vacuo and the remaining white solid was crystallized from hexane (5 mL) to yield **3** (1.00 g, 0.33 mmol, 66%) as colorless crystals. − ^1H NMR ($[D_6]$benzene): δ = 1.23 (m, 8 H, $CH{-}C_5H_9$), 1.75 (br. m, 64 H, $CH_2{-}C_5H_9$). − $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): δ = 22.62, 22.69, 22.93, 23.20, 23.78, 24.44, 25.52 (s, $CH{-}C_5H_9$), 27.39, 27.45, 27.64, 27.76, 28.01, 28.58 ($CH_2{-}C_5H_9$). − $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene): δ = −69.89, −69.51, −68.85, −68.40, −68.23, −67.56, −67.40, −65.78, −64.98, −60.56. − $C_{120}H_{216}Al_2O_{39}Si_{24}$ (3011.04): calcd. C 47.87, H 7.23; found C 47.93, H 7.29.

$\{[(c\text{-}C_5H_9)_8Si_8O_{13}]_2Al\}^-\{Et_3NH\}^+$ (4): The procedure used was similar to that described for **2b**, starting from $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ (0.64 g, 0.65 mmol). The crude product was recrystallized from hexane (6 mL) at 0 °C, yielding **4** (0.42 g, 0.20 mmol, 61%) as colorless crystals. − ^1H NMR ($[D_6]$benzene): δ = 0.92 [m, 9 H, $N(CH_2CH_3)_3$], 1.06 (m, 4 H, $CH{-}C_5H_9$), 1.21 (m, 12 H, $CH{-}C_5H_9$), 1.80 (m, 128 H, $CH_2{-}C_5H_9$), 2.78 [m, 6 H, $N(CH_2CH_3)_3$], 9.94 (s, 1 H, $HNEt_3$). − $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): δ = 8.26 [s, $N(CH_2CH_3)_3$], 22.89, 23.87, 26.42 (s, $CH{-}C_5H_9$, 2:4:2 ratio), 27.44, 27.52, 27.58, 27.61, 27.84, 28.67, 28.43, 28.72 (s, $CH_2{-}C_5H_9$), 45.02 [s, $N(CH_2CH_3)_3$]. − $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene): δ = −68.66, −67.39, −65.17 (s, 2:1:1 ratio). − $C_{86}H_{160}AlNO_{26}Si_{16}$ (2100.56): calcd. C 49.17, H 7.68; found C 49.75, H 7.84.

X-ray Crystal Structure Analyses of 2b and 3: Single crystals of **2b** and **3** suitable for X-ray structure analysis were grown from saturated hexane solutions. Data were collected on a Bruker AX SMART 1 K CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å).

For **2b**: $C_{102}H_{168}AlNO_{24}Si_{16}{\cdot}(C_6H_{14})$ (M_r: 2345.59): T = 203(2) K, 0.2 × 0.1 × 0.1 mm, monoclinic, $P2_1/n$, a = 24.947(2) Å, b = 19.032(2) Å, c = 28.629(3) Å, β = 111.718(2)°, V = 12628(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.234 gcm^{-3}, μ(Mo-K_α) = 2.32 cm^{-1}. A total of 81069 reflections were collected, of which 13217 were considered unique. The structure was solved by direct methods using SHELXS-97[12] and subsequent difference Fourier maps. A final refinement on F^2 converged at R_1 = 0.0595, wR_2 = 0.1662.

For **3**: $C_{120}H_{216}Al_2O_{39}Si_{24}$ (M_r: 3011.05): $T = 236(2)$ K, $0.1 \times 0.1 \times 0.02$ mm, triclinic $P1$(bar), $a = 19.047(4)$ Å, $b = 19.355(4)$ Å, $c = 24.662(6)$ Å, $\alpha = 105.540(4)°$, $\beta = 91.650(5)°$, $\gamma = 103.428(5)°$, $V = 8480(3)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.179$ gcm^{-3}, μ(Mo-K_α) = 2.52 cm^{-1}. A total of 66657 reflections were collected, of which 15296 were considered unique. The structure was solved by direct methods using SHELXS-97[12] and subsequent difference Fourier maps. A final refinement on F^2 converged at $R_1 = 0.0831$, $wR_2 = 0.2347$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143922 (**26**) and -143923 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax (internat.): +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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