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Solubilizing functionalized molecular aluminosilicates†

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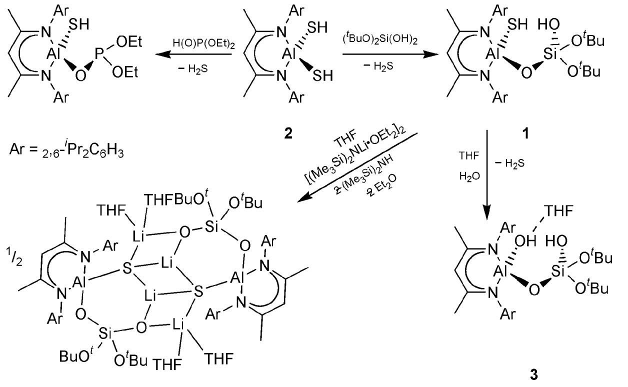
Molecular aluminosilicate **LAl(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$ 1** (**L** = [HC{C(Me)N(Ar)}$_2$]$^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) has been prepared from **LAl(SH)$_2$ 2** and (^{t}BuO)$_2$Si(OH)$_2$ in high yield. When reacted with one equiv. of water, the unique aluminosilicate containing two terminal hydroxy groups **LAl(OH·THF)(μ-O)Si(OH)(O^{t}Bu)$_2$ 3** can be isolated. However, when **2** is reacted with the bulkier silanol (^{t}BuO)$_3$SiOH, no reaction is observed. The desired **LAl(SH)(μ-O)Si(O^{t}Bu)$_3$ 6** can be prepared in a two-step synthesis between **LAlH$_2$ 4** and (^{t}BuO)$_3$SiOH giving first **LAl(H)(μ-O)Si(O^{t}Bu)$_3$ 5**, which reacts further with elemental sulfur to give **6** as the only product. Direct hydrolysis of **6** was conducted to obtain **LAl(OH)(μ-O)Si(O^{t}Bu)$_3$ 7**, however, such hydrolysis always resulted in a complete decomposition of the starting material. Therefore we used boric acid, which condenses in non-polar solvents and slowly evolve water, to hydrolyze **6** to **7** under mild conditions. Compounds **1**, **3** and **5–7** have been characterized by single-crystal X-ray diffraction.

Introduction

Aluminosilicates are widely found as natural minerals, and build up an important family of zeolitic materials.[1] They are useful as drying agents and as heterogeneous catalysts in a myriad of industrial processes.[2] Consequently, the development of molecular aluminosilicate compounds is a promising source of molecular models for catalytic materials, and secondary building units (SBU) for heterobimetallic systems, since current methods of synthesis are not able to tune precisely element distribution in the final material.[3] Molecular aluminosilicates offer advantages against the abundant aluminosiloxane-based systems,[4] because they obviously represent a more realistic approach as molecular models for zeolitic materials. In addition, thermal decomposition of Si–O based systems is cleaner than that of Si–C ones, leading to low carbon content materials.[5]

Recently, we have reported the preparation of aluminum silicate and phosphite precursors **LAl(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$** (**1**) (**L** = [HC{C(Me)N(Ar)}$_2$]$^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and **LAl(SH)(μ-O)P(OEt)$_2$** from **LAl(SH)$_2$** (**2**) and (^{t}BuO)$_2$Si(OH)$_2$ or HP(O)(OEt)$_2$, respectively, together with the corresponding lithium salts **[LAl(SLi)(μ-O)Si(OLi·2THF)(O^{t}Bu)$_2$]$_2$** and **LAl(SLi)(μ-O)P(OEt)$_2$]$_2$**.[6,7] The controlled hydrolysis of **1** led to a molecular aluminosilicate-hydroxide **LAl(OH·THF)(μ-O)Si(OH)(O^{t}Bu)$_2$** (**3**) (Scheme 1). It is known that the compound **LAl(OH)$_2$** is labile and decomposes easily, but the presence of an Al–(μ-O)–M (M = metal) bridge can stabilize the terminal OH group attached to the aluminum atom.[8] In compound **3**, such an hydroxy group is coordinated to a THF molecule, while acting as an acceptor for the proton from the OH group on the silicon atom. Although compound **3** is stable, trace amounts of impurities can cause its decomposition if stored for longer periods of time. Very few examples are known, where the proton from a terminal Al–OH moiety is involved in an intramolecular hydrogen bond.[9]



Scheme 1 Preparation of compounds **1**, **3**, **L(SH)(μ-O)P(OEt)$_2$** and **[LAl(SLi)(μ-O)Si(OLi·2THF)(O^{t}Bu)$_2$]$_2$**.

Results and discussion

We decided to investigate the possibility of replacing the (^{t}BuO)$_2$Si(OH) group with a bulkier homologue (^{t}BuO)$_3$Si in order to determine the influence of the steric bulk of the silicate group on the stability and reactivity of the resulting products. In contrast with the facile synthesis of **1** from **LAl(SH)$_2$ 2**[10] and (^{t}BuO)$_2$Si(OH)$_2$, no reaction was observed between **2** and (^{t}BuO)$_3$SiOH, even under harsh conditions as reflux in toluene for six hours. However, the desired **LAl(SH)(μ-O)Si(O^{t}Bu)$_3$** (**6**) was obtained in a two-step synthesis starting from **LAlH$_2$** (**4**)[11] and one equiv. of tri-*tert*-butoxysilanol (^{t}BuO)$_3$SiOH. This reaction led to the unprecedented aluminosilicate-hydride **LAl(H)(μ-O)Si(O^{t}Bu)$_3$** (**5**) in 80% yield (Scheme 2). In this case, the product is formed

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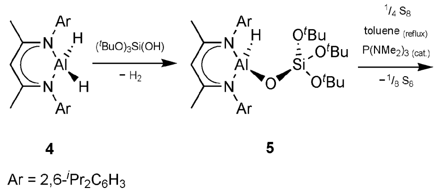
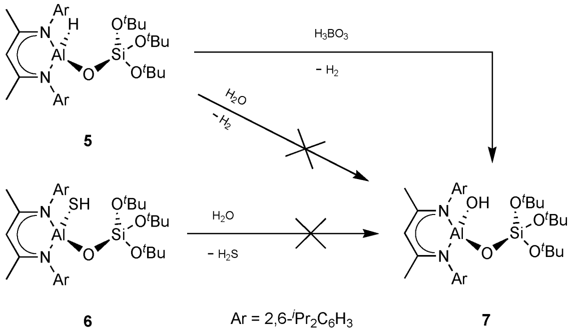


Scheme 2 Preparation of compounds **5** and **6**.

through an intermolecular elimination of H_2 and formation of an Al–O bond, to generate the aluminosilicate backbone.

In the next step—conversion of **5** into **6**—harsh conditions were needed. Reflux in toluene for 16 h of a mixture of **5**, two equiv. of elemental sulfur and a catalytic amount of hexamethylphosphoramide, resulted in the formation of **6** as the only product in good yield (80%) (see Scheme 2). On the other hand, all our efforts to convert **5** or **6** into **LAl(OH)(*μ*-O)Si(O*ᵗ*Bu)₃** (**7**) by a direct reaction with water—in a similar manner as the transformation of **1** to **3** occurs—always led to the decomposition of the starting material, although such reactivity has been observed before in related aluminum compounds.[12] To our surprise, N–Al bonds were more sensitive to the hydrolysis than the Al–H moiety, even when aluminum hydrides are usually considered to be very reactive towards hydrolytic reagents. In this case, steric hindrance provided by the bulky ligand **L** and the three *tert*-butoxy groups, as well as the electron rich ambient at the hydride surroundings may be responsible for the apparent hydride inertness. To overcome this difficulty, slow evolution of water through the auto-condensation of boric acid in toluene was used in the successful conversion of **5** to **7** (Scheme 3) in discrete yield (62%).



Scheme 3 Preparation of compound **7**.

For **7**, the free β-diketiminato ligand and **5** were found to be the main impurities. Thus, rinsing the crude product with pentane and recrystallization from a toluene–THF mixture led to single crystals containing the product and a persistent, yet small amount of **5** (*ca.* 8%). Due to the isomorphous nature of **5** and **7**, it is not possible to separate these two compounds by crystallization.

Compounds **1**, **3** and **5–7** were isolated as crystalline and stable solids. The formation of the products was confirmed by MS-EI, where the parent ions were observed at *m/z* 684 (**1**), 668 (**3**), 708 (**5**), 740 (**6**) and 724 (**7**). In addition, the $[M - X]^+$ fragment was observed at *m/z* 651 in compounds **1** ($[M - SH]^+$) and **3** ($[M - OH]^+$), whereas for **6** ($[M - SH]^+$) and **7** ($[M - OH]^+$), it was observed at *m/z* 707. Moreover, subsequent losses of *m/z* 56 were present in all compounds, and were assigned to isobutene elimination, a common loss in compounds containing *tert*-butoxy moieties.[13] Absorption of the (Al)S–H moiety was found at $\tilde{\nu} = 2560$ for **1**, and 2571 cm^{-1} for **6**, respectively; whereas the characteristic band for a vibration of (Al)O–H group was found in at $\tilde{\nu} = 3541$ (**3**) and 3504 (**7**) cm^{-1} in the IR spectra. The Al–H stretching vibration in **5** absorbs at $\tilde{\nu} = 1821$ cm^{-1}. Finally, absorption of the (Si)O–H group was found at $\tilde{\nu} = 3462$ (**1**) and 3357 cm^{-1} (**3**). The presence of two different substituents on the aluminum center in **1**, **3** and **5–7** was confirmed also by the presence of signals corresponding to the symmetry C_s (two septets and four doublets) instead of only one septet and two doublets for the isopropyl groups observed for compound **2** with a C_{2v} symmetry in the ^{1}H NMR spectra. The Al–S*H* protons exhibited singlet signals at $\delta = -0.45$ and -0.29 ppm, for **1** and **6**, respectively, and are shifted downfield in comparison to **2** (−0.88 ppm).[10] Corresponding signals for Al–O*H* were found at $\delta = 0.95$ for **3**, and 1.40 ppm for **7**, which are comparable to that found in **LAl(OH)(*μ*-O)Ti(SH)Cp₂**[8] ($\delta = 1.07$ ppm), and considerably shifted downfield when compared to **[LAl(OH)]₂O**[13] ($\delta = -0.30$ ppm), **LAl(OH)₂**[14] ($\delta = 0.20$ ppm), and **LAlMe(OH)**[15] (0.50 ppm). The latter may be explained by the steric bulk of the *tert*-butoxy group which shields the OH moieties and also by the fact, that in both compounds, the protons from the OH moieties are involved in a hydrogen bond. Likewise, Si–O*H* chemical shifts vary considerably between **1** ($\delta = 1.53$ ppm) and **3** ($\delta = 2.79$ ppm), presumably upon substitution of the Al–SH by Al–OH group and thus different hydrogen bonding pattern. In addition, the base peak of all compounds belonged to a singlet signal that integrated either for 18 (**1**, **3**) or 27 (**5–7**) protons, corresponding to the *tert*-butoxy groups bonded to the silicon atom. Finally, a set of resonances associated to protons of the β-diketiminato ligand was also found in all the compounds prepared. All compounds are soluble in common organic solvents such as toluene, THF, CH_2Cl_2 and partially soluble in hexane. All compounds are stable at ambient temperature in the solid state, but decomposed at higher temperatures (especially during melting). We have also observed partial decomposition of the compounds in solution at low concentrations, even if freshly dried solvents are used.

Molecular description of compounds 1, 3 and 5–7

Single crystals of all compounds were obtained either from saturated hexane–toluene (**1**, **3** and **5**) or toluene–THF (**6** and **7**) solutions at −30 °C. Compound **1** crystallizes in the rhombohedral space group $R\bar{3}$ with one molecule of **1** and one third of a highly disordered hexane molecule in the asymmetric unit, whereas compound **3** crystallizes in the monoclinic space group $P2_1/n$ with one THF molecule in the asymmetric unit, and finally the isomorphous compounds **5–7** crystallize in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit, respectively (Table 1). Further crystal data for compounds **1** and **3** can be found elsewhere.[6] We were not able to crystallize clean **7**, therefore crystal data of compound **7** contaminated by 8% of the starting material **5** were used in the discussion (Fig. 1).

The X-ray analysis confirmed the presence of terminal Al–SH (compounds **1** and **6**) and Al–OH (compounds **3** and **7**) moieties and a terminal hydride in compound **5**. In all cases, the protons from the SH and OH moieties are part of an intra or intermolecular hydrogen bond. Thus in **1**, **6** and **7** the proton of the Al–EH moiety is involved in an intramolecular Al–E–H···O*ᵗ*Bu hydrogen bond

Table 1 Crystal data and structure refinement for compounds **5–7**

	5	**6**	**7**
Formula	$C_{41}H_{69}AlN_2O_4Si$	$C_{41}H_{69}AlN_2O_4SSi$	$C_{41}H_{69}AlN_2O_{4.92}Si$
FW	709.05	741.11	723.77
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.061(2)	12.068(2)	12.061(2)
b/Å	19.621(3)	19.698(3)	19.651(3)
c/Å	18.028(3)	18.023(2)	18.008(3)
β/°	90.40(2)	90.72(2)	90.24(2)
V/Å^3	4266(1)	4284(1)	4268(1)
Z	4	4	4
Size/mm^3	0.28 × 0.25 × 0.24	0.26 × 0.24 × 0.15	0.32 × 0.28 × 0.08
ρ_{calcd}/g cm^{-3}	1.104	1.149	1.126
μ/mm^{-1}	0.115	0.164	0.117
F(000)	1552	1616	1581
θ range/°	1.69–25.00	1.53–25.37	1.69–25.03
Index ranges	$-14 \le h \le 14$	$-14 \le h \le 14$	$-14 \le h \le 14$
	$-23 \le k \le 23$	$-23 \le k \le 23$	$-23 \le k \le 23$
	$-21 \le l \le 21$	$-21 \le l \le 21$	$-21 \le l \le 21$
No. of reflections collected	44 647	34 989	44 646
No. of independent reflections (R_{int})	7485 (0.0794)	7829 (0.0812)	7520 (0.0598)
Data/restraints/parameters	7485/0/467	7829/0/476	7520/140/517
GOF on F^2	1.058	1.008	1.027
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0591, 0.1232	0.0578, 0.1241	0.0519, 0.1245
R_1,[a] wR_2[b] (all data)	0.0861, 0.1368	0.0889, 0.1396	0.0694, 0.1343
Largest diffraction peak/hole (e Å^{-3})	0.352/–0.224	0.437/–0.261	0.363/–0.238

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/(F_o^2)^2]^{1/2}$.

with the oxygen atom from one free O^{t}Bu group as acceptor (**1**, E = S, 2.48(3); **6**, E = S, 2.43(3); **7**, E = O, 2.48(2) Å). The proton of the Si–OH hydroxy group in **1** forms an intermolecular hydrogen bridge to the free O^{t}Bu group of another molecule of **1** forming a centrosymmetric dimer, whereas in compound **3**, it is part of a hydrogen bridge SiO–H · · · O(H)Al (2.06(2) Å). Finally, the proton from the Al–OH group in **3** is obviously interacting with the THF molecule located partially in between the ^{i}Pr groups of the ligand **L**. In spite of the disorder over two positions present in the THF molecule, their orientations and the difficulties in removing the THF under vacuum confirm the presence of the AlO–H · · · OC_4H_8 (2.10(2), 2.13(1) Å) hydrogen bond.

The analysis of the values for the Al–O–Si angle revealed, that the presence of an extra O^{t}Bu group in compounds **5–7** does not have a determining effect over its size, but that it is rather influenced by the group attached to the aluminum center. Thus, the largest values for the Al–O–Si angles correspond to the presence of the Al–SH moiety in the molecules of **1** 146.5(1)° and **6** (140.6(1)°), followed by the angle in **5** 138.5(1)° containing the Al–H moiety, whereas the presence of the Al–OH group results in both cases in the smallest values (136.4(1)° in **7** to 132.8(1)° in **3**). This can be explained by the presence of the strong hydrogen bonds Si–OH · · · OH–Al in **3** and Al–OH · · · O^{t}BuSi in **7**, which diminish the values for the Al–O–Si angles. A similar effect of an intramolecular hydrogen bond on the size of the Al–O–Si angle has been observed in [(^{i}PrOH)Al{(μ-O)Si(O^{t}Bu)$_3$}$_3$] cocrystalized with [{(^{i}PrO)$_2$Al(μ-O^{i}Pr)$_2$}$_3$Al].[16] In this compound, the presence of a hydrogen bond between the OH proton of the coordinated isopropanol and the oxygen atom from one of the three O^{t}Bu groups of one of the three (μ-O)Si(O^{t}Bu)$_3$ moieties, reduces the value of the corresponding Al–O–Si angle to 141.3(1)°, whereas the other two angles in the same molecule are significantly more obtuse: 158.7(2) and 159.2(2)°. In compounds **1**, **3** and **5–7**, the aluminum and silicon centers have a distorted tetrahedral geometry, where the silicon environment in all compounds features lower degree of distortion. In case of aluminum, the N1–Al1–N2 angle has always the largest deviation from the ideal value of 109.5° (the observed values are in the range of 95.8(1)° in **5**, to 97.5(1)° in **1**). While the first number is significantly smaller than in the parent compound **4** (96.4(1)°), the second is comparable to that in **2** (97.3(1)°). This demonstrates that the substituents attached to the aluminum center do not have the determining effect on the size of the N–Al–N angle. In both **3** and **7**, the Al–(μ-O) bond length is comparable to the Al–OH, while there is a significant difference between the Si–(μ-O) and Si–OH bond lengths in **1** and **3**, as the latter are 0.02 Å (**1**) and 0.025 Å (**3**) longer. For better comparison, selected bonds and angles for compounds **1**, **3** and **5–7** are listed in Table 2.

From the space filling diagram of compound **5** (Fig. 2), it can be seen that the three *tert*-butoxy groups bound to the silicon atom, as well as the isopropyl moieties from the β-diketiminato ligand generate a hydrophobic shell that surrounds the Al–H unit and limits considerably its reactivity, as we suggested previously. Moreover, the silicon-bonded *tert*-butoxy groups offer an interesting advantage, due to isobutene elimination upon heating treatment, and could lead to carbon-free materials after suitable treatment.[5e,17]

Experimental

General comments

All experiments were performed under an inert atmosphere of nitrogen using standard Schlenk techniques and a MBraun

Table 2 Crystal data and structure refinement for compounds **1**, **3** and **5–7**

	1·1/3hexane[a]	**3**·THF[b]	**5**[c]	**6**[a]	**7**[b]
Al(1)–X	2.222(1)	1.715(3)	1.54(2)	2.225(1)	1.706(2)
Al(1)–O(1)	1.720(2)	1.711(2)	1.715(2)	1.706(2)	1.717(2)
Al(1)–N(1)	1.885(2)	1.891(3)	1.908(2)	1.899(2)	1.901(2)
Al(1)–N(2)	1.891(2)	1.894(3)	1.908(2)	1.903(2)	1.901(2)
Si(1)–O(1)	1.591(2)	1.602(2)	1.600(2)	1.604(2)	1.603(2)
Si(1)–O(2)	1.611(2)	1.627(3)	1.617(2)	1.629(2)	1.623(1)
Si(1)–O(3)	1.624(2)	1.623(3)	1.624(2)	1.616(2)	1.618(2)
Si(1)–O(4)	1.637(2)	1.625(3)	1.624(2)	1.620(2)	1.630(2)
X–H(*z*)	1.31(3)	0.74(1)	—	1.11(3)	0.84(1)
(Si)O(*x*)–H(2)	0.77(2)	0.75(1)	—	—	—
N(1)–Al(1)–N(2)	97.5(1)	97.3(1)	95.8(1)	97.3(1)	96.3(1)
O(1)–Al(1)–X	112.9(1)	106.3(1)	115.7(9)	114.6(1)	114.2(1)
Al(1)–O(1)–Si(1)	146.5(1)	132.8(1)	138.5(1)	140.6(1)	136.4(1)
O(1)–Si(1)–O(2)	109.3(1)	110.4(1)	112.7(1)	105.8(1)	114.1(1)
O(1)–Si(1)–O(3)	106.3(1)	112.5(1)	106.4(1)	112.8(1)	112.9(1)
O(1)–Si(1)–O(4)	112.9(1)	106.7(1)	113.8(1)	113.5(1)	106.4(1)
O(2)–Si(1)–O(3)	112.7(1)	109.8(1)	112.4(1)	112.4(1)	105.4(1)
O(2)–Si(1)–O(4)	105.2(1)	112.2(2)	105.2(1)	106.5(1)	105.7(1)
O(3)–Si(1)–O(4)	110.6(1)	105.2(1)	106.3(1)	105.8(1)	112.2(1)
Si(1)–O(*x*)–H(2)	123(3)	114(1)	—	—	—
Al(1)–X–H(*z*)	92(1)	111(1)	—	99(2)	118(2)

[a] X = S(1), *z* = 1. [b] X = O(5), *z* = 5. [c] X = H(1); for **1** *x* = 4, for **3** *x* = 2.

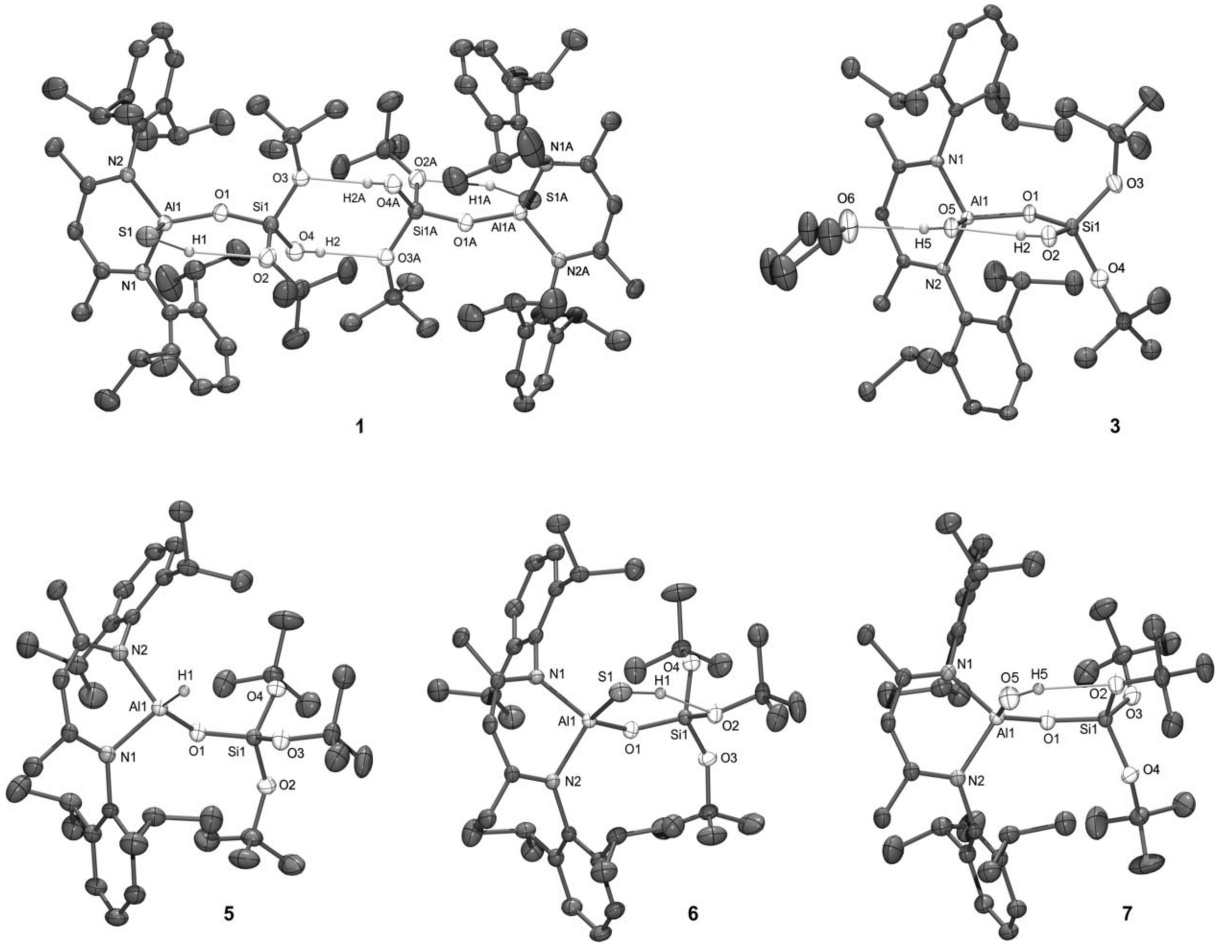


Fig. 1 POV-Ray drawing of the molecular structures of compounds **1**, **3** and **5–7**. Thermal ellipsoids at 50% probability. All carbon-bound hydrogen atoms, and solvating hexane molecule (in **1**) have been omitted for clarity. Only the major position of disordered groups is shown: THF in **3** and ^{t}Bu in **1** and **7**. The hydridic hydrogen atom of **5** in the crystal of **7** could not be localized due to its low content (8%).

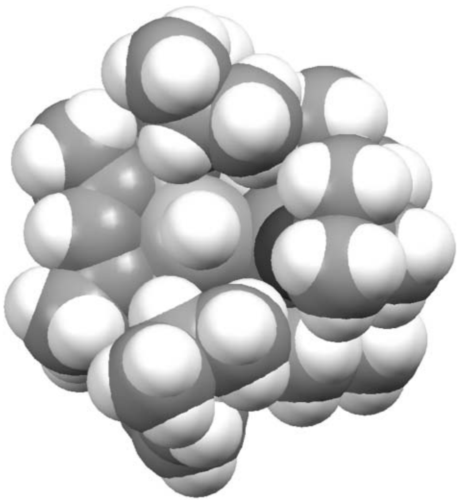


Fig. 2 Space filling plot of **5** showing the Al–H proton surrounded by two ^{i}Pr, one ^{t}Bu group and the carbon backbone of the ligand.

Unilab glove box. The solvents were purified according to the conventional procedures and were freshly distilled prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received. (^{t}BuO)$_3$SiOH,[18] (^{t}BuO)$_2$Si(OH)$_2$,[18] **L**Al(SH)$_2$ (**2**)[10] and **L**AlH$_2$ (**4**)[11] were prepared according to literature procedures. Elemental analyses (C, N and H) were performed using an CE-440 Exeter Analytical instrument. ^{1}H, ^{13}C, ^{27}Al and ^{29}Si NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer. Benzene-d$_6$ was dried using Na–K alloy and distilled *in vacuo*. Chloroform-d was stirred with phosphorous pentoxide and filtered prior to use. IR spectra were recorded from 4000–250 cm^{-1} on a Bruker Tensor 27 FT-IR instrument with all samples being pressed into CsI disks. Mass spectra (EI-MS) were measured on a JMS-AX505HA spectrometer. Melting points were measured in sealed glass capillary tubes.

Preparation of LAl(EH)(μ-O)Si(OH)(O^{t}Bu)$_2$ (E = S (1), O (3)). The preparation of compounds **1** and **3** has been described previously.[6]

Preparation of LAl(H)(μ-O)Si(O^{t}Bu)$_3$ (5). Toluene (40 mL) was added to the mixture of freshly sublimed (^{t}BuO)$_3$SiOH (2.82 g, 10.68 mmol) and **2** (3.89 g, 8.74 mmol) at −78 °C. After the addition was complete, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The solvent was removed *in vacuo* and the remaining white solid was washed with hexanes (2 × 10 mL) and filtered off. Yield: 4.98 g (80.4%). mp: 201 °C. EI-MS: *m/z* 708 [M]$^+$, 651 [M − C$_4$H$_8$ − H]$^+$, 595 [M − 2 C$_4$H$_8$ − H]$^+$, 539 [M − 3 C$_4$H$_8$ − H]$^+$, 523 [M − 3 C$_4$H$_8$ − O − H]$^+$. ^{1}H NMR (300.53 MHz, C$_6$D$_6$, 20 °C, TMS) δ/ppm: 7.15–7.11 (m, 6 H, Ar–*H*), 4.90 (s, 1 H, γ-*H*), 3.44 (sept, $^3J_{\text{H–H}} = 6.8$ Hz, 2 H, C*H*Me$_2$), 3.34 (sept, $^3J_{\text{H–H}} = 6.8$ Hz, 2 H, C*H*Me$_2$), 1.54 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.52 (s, 6 H, *Me*), 1.48 (d, $^3J_{\text{H–H}} =$ 6.8 Hz, 6 H, CH*Me*$_2$), 1.17 (s, 27 H, ^{t}Bu) 1.14 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.13 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6 H, CH*Me*$_2$). ^{13}C NMR (75.57 MHz, C$_6$D$_6$, 20 °C, TMS) δ/ppm: 170.4 (*C*N), 144.4, 143.7, 140.7, 127.0, 124.4 (*Ar*), 96.7 (γ-*C*), 71.3 (*C*Me$_3$), 31.5 (C*Me*$_3$), 28.2 (*C*HMe$_2$), 25.9, 25.2, 24.5, 24.1 (CH*Me*$_2$), 23.4 ppm (*Me*). ^{27}Al NMR (78.30 MHz, C$_6$D$_6$, 25 °C, AlCl$_3$·6H$_2$O): no shifts observed. ^{29}Si NMR (29.94 MHz, C$_6$D$_6$, 20 °C, TMS) δ/ppm: −106. IR (CsI disc) $\tilde{\nu}$/cm^{-1}: 3063 w, 2967 vs, 1821 s (ν, Al–H), 1523 vs, 1439 sh, 1388 vs, 1319 s, 1254 s, 1197 s, 1058 vs, 1030 sh, 938 vw, 877 w, 830 w, 804 s, 766 w, 706 s, 667 s, 595 vw, 534 vw, 510 sh, 485 w, 456 sh, 389 w, 357 sh, 285 vw. Anal. calcd for C$_{41}$H$_{69}$AlN$_2$O$_4$Si (709.06): C 69.45, H 9.81, N 3.95. Found: C 69.26, H 9.63, N 4.03%.

Preparation of LAl(SH)(μ-O)Si(O^{t}Bu)$_3$ (6). Toluene (20 mL) was added to a mixture of **5** (2.02 g, 2.84 mmol) and sulfur (0.182 g, 5.69 mmol), and after complete dissolution of the sulfur, P(NMe$_2$)$_3$ (0.03 mL, 0.02 mmol) was added. The reaction mixture was heated at reflux for 12 h, and then allowed to cool to ambient temperature. The volatiles were removed *in vacuo*. To remove the excess of sulfur used in the synthesis, the crude product was recrystallized from a toluene–hexane mixture (1 : 1) as large colourless crystals. Yield: 1.68 g (80.7%). mp: 205–206 °C (dec.). EI-MS m/z: 740 [M]$^+$, 707 [M − SH]$^+$, 651 [M − C$_4$H$_8$ − SH]$^+$, 595 [M − 2 C$_4$H$_8$ − SH]$^+$, 539 [M − 3 C$_4$H$_8$ − SH]$^+$, 523 [M − 3 C$_4$H$_8$ − O − SH]$^+$. ^{1}H NMR (300.53 MHz, CDCl$_3$, 20 °C, TMS) δ/ppm: 7.22–7.12 (m, 6 H, Ar–*H*), 5.33 (s, 1 H, γ-*H*), 3.72 (sept, $^3J_{\text{H–H}} = 6.8$ Hz, 2H, C*H*Me$_2$), 3.19 (sept, $^3J_{\text{H–H}} = 6.8$ Hz, 2H, C*H*Me$_2$), 1.78 (s, 6 H, *Me*), 1.33 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6H, CH*Me*$_2$), 1.31 (d, $^3J_{\text{H–H}} =$ 6.8 Hz, 6H, CH*Me*$_2$), 1.23 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6H, CH*Me*$_2$), 1.06 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6H, CH*Me*$_2$), 0.90 (s, 27H, ^{t}Bu), −0.29 (s, 1 H, S*H*). ^{13}C NMR (75.57 MHz, CDCl$_3$, 20 °C, TMS) δ/ppm: 171.6 (*C*N), 145.6, 143.2, 140.4, 127.0, 125.0, 123.9 (*Ar*), 98.6 (γ-*C*), 71.5 (*C*Me$_3$), 31.3 (C*Me*$_3$), 28.9 (*C*HMe$_2$), 27.9, 27.3, 24.9, 24.4 (CH*Me*$_2$), 24.1 (*Me*). ^{27}Al NMR (78.30 MHz, CDCl$_3$, 20 °C, AlCl$_3$·6H$_2$O) δ/ppm: 72. ^{29}Si NMR (29.94 MHz, CDCl$_3$, 20 °C, TMS) δ/ppm: −115. IR (CsI disc) $\tilde{\nu}$/cm^{-1}: 3063 w, 2970 s, 2929 sh, 2871 w, 2571 vw (ν, S–H), 1523 s, 1438 s, 1385 s, 1319 s, 1251 s, 1195 s, 1057 vs, 937 w, 880 w, 832 w, 804 w, 767 w, 706 s, 643 w, 545 sh, 472 s, 393 w, 335 w, 285 w. Anal. calcd for C$_{41}$H$_{69}$AlN$_2$O$_4$SSi (741.13): C 66.44, H 9.38, N 3.78. Found: C 66.23, H 9.19, N 3.77%.

Preparation of LAl(OH)(μ-O)Si(O^{t}Bu)$_3$ (7). A mixture of **5** (0.97 g, 1.36 mmol) and anhydrous boric acid (0.086 g, 1.40 mmol) was set in a flask, and toluene (25 mL) was added *via* cannula. The reaction mixture was stirred for 12 h. The reaction finishes when the initial suspension becomes a slightly green solution. After removing all volatiles, hexanes were added and the mixture was filtered off. The product was redissolved in a mixture toluene–THF (1 : 1, 6 mL) and stored at −20 °C overnight. The resulting colourless prismatic crystals were filtered off, washed with cold THF and dried *in vacuo*. Yield: 0.61 g (62%), mp: 205–206 °C (dec.). EI-MS *m/z*: 724 [M]$^+$, 707 [M − OH]$^+$, 651 [M − C$_4$H$_8$ − OH]$^+$, 595 [M − 2 C$_4$H$_8$ − OH]$^+$, 539 [M − 3 C$_4$H$_8$ − OH]$^+$. ^{1}H NMR (300.53 MHz, C$_6$D$_6$, 20 °C, TMS) δ/ppm: 7.19–7.00 (m, 6 H, Ar–*H*), 4.95 (s, 1 H, γ-*H*), 3.93 (sept, $^3J_{\text{H–H}} = 6.8$ Hz, 2H, C*H*Me$_2$), 3.24 (sept, $^3J_{\text{H–H}} = 6.8$ Hz, 2H, C*H*Me$_2$), 1.52 (s, 6 H, *Me*), 1.51 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.43 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6H, CH*Me*$_2$), 1.40 (s, 1H, O*H*), 1.25 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6H, CH*Me*$_2$), 1.12 (s, 27H, ^{t}Bu), 1.09 (d, $^3J_{\text{H–H}} = 6.8$ Hz, 6H, CH*Me*$_2$). IR (CsI disc) $\tilde{\nu}$/cm^{-1}: 3504 w (ν, O–H), 3059 w, 2919 s, 2860 w, 1545 s, 1412 s, 1297 s, 1258 s, 1215 s, 1195 s, 1019 s, 929 w, 859 w, 813 w, 750 s, 709 w, 653 sh, 613 w, 572 s, 445 w, 383 w, 315 w. Due to the purity of the sample, elemental analysis was not performed.

X-Ray structure determination

Crystals were mounted on Nylon loops and rapidly placed in a stream of cold nitrogen. Diffraction data were collected on a Bruker-APEX three-circle diffractometer using MoKα radiation ($\lambda = 0.71073$ Å) at −100 °C. Structures were solved by direct methods (SHELXS-97)[19] and refined against all data by full-matrix least-squares on F^2.[20] The hydrogen atoms of C–H bonds were placed in idealized positions, whereas the hydrogen atoms from the OH and SH moieties were localized from the difference electron density map and their position was refined with U_{iso} tight to the parent atom with distance restraints (SADI) when applicable. The disordered hexane (in the crystal of **1**) and THF (in the crystal of **3**) molecules as well as the disordered ^{t}Bu moieties (in the crystals of **1** and **7**) were refined using geometry and distance restraints (SAME, SADI) together with the restraints for the U_{ij} values (SIMU, DELU). The twin law for **3** was determined as 1 0 0 0 −1 0 0 0 −1 and the ratio of the twin domains was refined to 85 : 15. The hexane content in the crystal of **1** was refined to two hexane molecules per a cavity centered around the $\bar{3}$ axis. Thus, there is 1/3 of hexane in the asymmetric unit, which is disordered over three independent positions (18 for the whole cavity and two hexane molecules). The sum of the occupancies was controlled using the SUMP command implemented in the in SHELXL program. The hydridic hydrogen atom of **5** in the crystal of **7** could not be localized due to its low content (8%), but it is included in the sum and moiety formulas.

Conclusions

To summarize, we have prepared five unique soluble functionalized molecular aluminosilicates. The compounds prepared are stable even at 150 °C in the solid state, and do not suffer self-condensation, although they contain reactive Al–EH (E = O, S) and Si–OH functional groups. Compounds **1**, **3** and **5–7** are promising starting materials for the preparation of soluble molecular heterobimetallic aluminosilicates. Preparation of such compounds is a subject of an ongoing research.

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