Synthesis, Structure, and Characterization of $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ (R = Me, Et)

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The reaction between tetrakis(ethylamino)silane, $Si(NHEt)_4$ (**1**) and trialkylaluminium compounds AlR_3 [R = Me (**2**), R = Et (**3**)] results in partial deprotonation of **1** and subsequent formation of a new dimeric alumosilazane in high yield. Single-crystal X-ray analyses reveal the structure of two new four-membered ring compounds $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ [R = Me (**4**), R = Et (**5**)]. They are isostructural and crystallize in the triclinic space group $P\bar{1}$ (No. 2) with a = 8.3052(8) Å, b = 9.8323(9) Å, c = 10.324(1) Å, α = 115.498(4)°, β = 97.684(4)°, γ = 94.382(4)° (**4**) and a = 8.2319(3) Å, b = 9.3748(5) Å, c = 10.8221(6) Å, α = 107.035(2)°, β = 104.435(2)°, γ = 94.375(2)° (**5**). The alternating edge- and corner-sharing SiN_4- and $AlCN_3$-tetrahedra represent a new structural motif with μ-NHEt and μ-NEt groups in one double bridge. The compounds were further characterized by elemental analysis, mass spectrometry, and NMR and IR spectroscopy.

Introduction

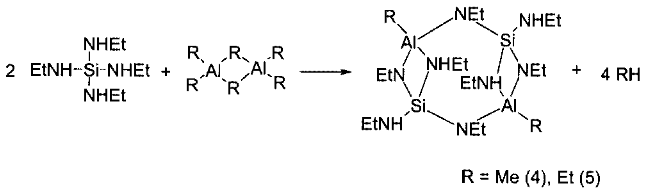
The design of new oxygen-free molecular precursors is crucial for the development of new nitride ceramics, porous non-oxide materials, and nanocomposites. Our interest is in the development of such precursors for the manufacture of porous non-oxide materials and gels, especially for catalytic applications in solid base catalysis.[1−4] For the synthesis of three-dimensional zeolitic frameworks such as nitridosilicates, molecular alumosilazanes may be suitable.[5,6] However, the known and well characterized triaminosilanes that form cage-type compounds in the reaction with $AlMe_3$ or $LiAlMe_4$ are expensive and require several synthesis steps.[7] We have therefore explored the reactions between AlR_3 and silanes such as $Si(NHEt)_4$, which on one hand is accessible in high yield from a one-step reaction between aminoethane and tetrachlorosilane,[8] and on the other hand is known to be transformable into $Si(NH)_2$ under mild conditions.[9] An important feature in comparison with other silane precursors is the absence of Si−C bonds. Si−C bonds are extremely stable, and so their cleavage and conversion into imides or nitrides under ammonothermal conditions requires high temperatures.

AlH_3 is known to form polymers of a wide compositional range in its reaction with $Si(NHMe)_4$. These are suitable precursors for the design of Si_3N_4/AlN nanocomposites.[10] Surprisingly, we found that AlR_3 (R = Me, Et) and $Si(NHEt)_4$ do not form polymers. Instead, molecular, crystalline compounds of the type $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2\text{-}Si(NHEt)]_2$ (R = Me, Et) with a fixed Al:Si ratio of 1:1 are obtained. They each have a cyclic four-membered ring structure, with bridging and terminal ethylamino ligands, and form through deprotonation of two ethylamino groups per $Si(NHEt)_4$. We report below on the preparation of the two isostructural compounds $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2\text{-}Si(NHEt)]_2$ (R = Me, Et) and on their structural and spectroscopic characterization by single-crystal X-ray analysis and spectroscopic methods.

Results and Discussion

Synthesis and Spectra

The compounds $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ [R = Me (**4**), R = Et (**5**)] are directly prepared by dropwise addition of trimethylaluminium ($AlMe_3$) or triethylaluminium ($AlEt_3$) to tetrakis(ethylamino)silane, $Si(NHEt)_4$ (**1**) (Scheme 1). The synthesis may be carried out either with or without solvent. If $AlEt_3$ is added slowly to the pure silane without solvent dilution the generation of gas bubbles is rather vigorous and the reaction vessel should be cooled.



Scheme 1

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After several minutes, ethane formation begins to slow down. The product is obtained after twelve hours, in the form of transparent crystals. Without the use of solvent dilution, in fact, the vessel is completely filled with white, crystalline product.

The reaction may also be carried out in pentane solution. In that case the solvent is removed in vacuo after twelve hours reaction time and the product is obtained as a white, crystalline solid.

Both compounds were characterized by mass spectrometry, IR and NMR spectroscopic studies, elemental analysis, and single-crystal X-ray diffraction.

The EI mass spectrum of **4** shows the molecular ion peak [M^+] at *m*/*z* = 488 (19%) and a signal due to the [$M^+ - CH_3$] fragment at *m*/*z* = 473 (100%). The EI mass spectrum of **5** does not show the molecular ion peak, but a signal due to the [$M^+ - C_2H_5$] fragment is seen at *m*/*z* = 487 (100%). The molecular ion peak [$M^+ + H$] of **5** at *m*/*z* = 517 (35%) is only recorded if chemical ionization (isobutane) is used.

The ^{1}H NMR spectrum of **4** shows broad signals at δ = 2.88−3.14 and 1.06−1.40, due to the methylene and methyl protons in the amino ethane groups. The protons of the methyl groups bound to the aluminium center appear as a singlet (δ = −0.20 ppm). At 300 K the signals due to the methylene protons appear as two broad, overlapping peaks, whereas the methyl protons appear as three broad peaks. At lower temperatures (243 K, [D_8]toluene), on the other hand, the methyl protons are resolved as four triplets, two of which are separated (δ = 1.30 and 1.18 ppm) while two overlap with each other (δ = 1.09 and 1.04 ppm). The signals at δ = 2.88−3.14 appear at 243 K as a complicated structure of overlapping multiplets.

The ^{1}H NMR spectrum of **5** is very similar to that of **4**, but the broadening of the signals at 300 K is less pronounced. The methylene protons in the vicinity of the aluminium atom appear at δ = 0.37 ppm.

The temperature-dependent linewidth in the proton NMR spectra indicates inter- or intramolecular exchange of terminal and bridging groups on the NMR timescale in solution (benzene, toluene).

The molecular compounds each show two distinct absorptions in the IR spectrum, at 3413 (**4**) [3410 (**5**)] and 3262 (**4**) [3254 (**5**)] cm^{-1}. These are attributable to the N−H stretching frequency of the terminal ethylamino group, similar to that in $Si(NHEt)_4$ (3414 cm^{-1}), and the N−H stretching frequency of the μ-NHEt groups in the double bridge (Scheme 1).

The simultaneous presence of alkyl groups bound to aluminium and residual acidic protons in the aminoethane ligands is similar to the situation seen in an incomplete condensation reaction between a primary amine and an alkylaluminium compound and is not uncommon,[6] subsequent formation of alane-amine adducts, aminoalanes, and poly(*N*-alkylimino)alanes typically being observed in such reactions.[11] For **4** and **5**, further intramolecular condensation is difficult to achieve without complete rearrangement of the molecular structure, so further condensation of the terminal ethylamino and alkyl groups would probably result in polymerization. Obviously, this polymerization does not take place at room temperature because several alkyl groups are pointing outwards, acting as a protective shell for the cluster and hindering further polymerization.

X-ray Structures of [MeAl(μ-NHEt)(μ-NEt)$_2$Si(NHEt)]$_2$ (4) and [EtAl(μ-NHEt)(μ-NEt)$_2$Si(NHEt)]$_2$ (5)

Single-crystal X-ray structure determinations carried out at 100 K show that compounds **4** and **5** both crystallize in the $P\bar{1}$ space group, with one cagelike molecule per unit cell, situated on an inversion center. The basic structural motif in **4** and **5** is a heterocyclic eight-membered ring composed of alternating Al and Si atoms with interspersed N(Et) groups (Figure 1). Two additional NHEt groups, each bridging one pair of Si-Al atoms, produce a formally tricyclic ring system. The tetrahedral coordination of the Si and Al atoms is completed with an additional EtNH group for silicon and alkyl groups for aluminium, to give an overall neutral molecule. The cage is therefore made up of two pairs of edge-sharing $AlCN_3$ and SiN_4 tetrahedra linked through the corners to form a four-membered cycle (Figure 2). Two crystallographically and chemically different EtN groups can be distinguished. Both are μ_2-bridging ligands between Al and Si centers, but one has a common corner (top and bottom in Figure 2) of two tetrahedral units whereas the other is part of a common edge of two tetrahedra. The two μ_2-ligands forming a common edge of two tetrahedra are termed a "double-bridge" below.

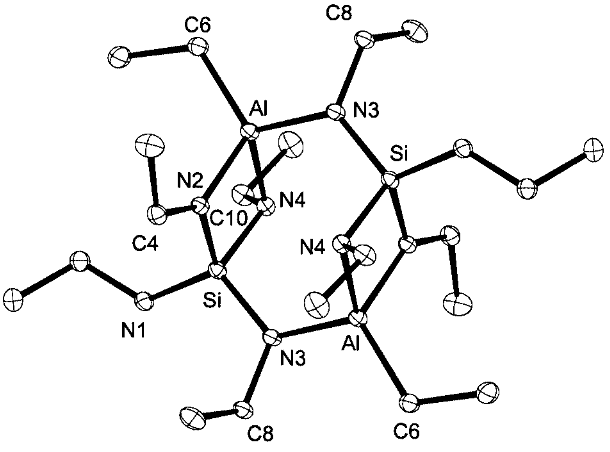

Figure 1. Crystal structure of **5** (hydrogen atoms are omitted for clarity); selected bond length [Å] and angles [°] are given in Table 1

The deviation of the coordination from an ideal tetrahedron (Figures 1 and 3, Table 1) is noticeable for the aluminium center, since the double bridges give rise to compression of one of the tetrahedron angles (N2−Al−N4) to only 80.4(1)°, whereas all other angles except for one (N3−Al−N4: 107.6(1)°] are expanded (113.5−119.4°). The Al−C6 bond length is 1.971(2) Å in **5** and 1.967(4) Å in **4,** close to Al−C distances typically observed in organoaluminium compounds ($LiAlEt_4$: *d*(Al−C) = 2.023 Å[12]). The Al−N bond lengths to the bridging EtN nitrogens [Al−N2: 1.849(2), Al−N3: 1.851(2) Å in **5**; 1.858(3) and 1.856(3) Å

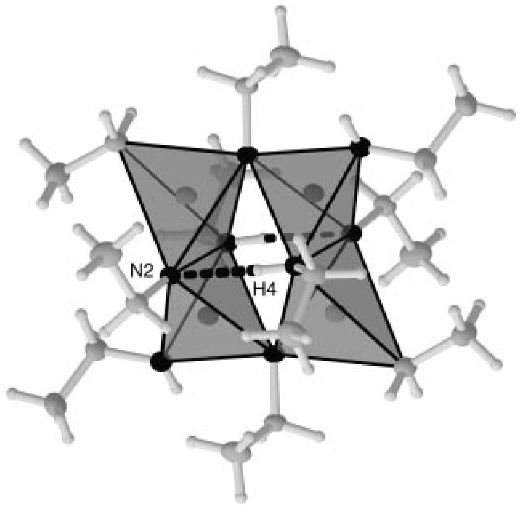

Figure 2. Polyhedral representation of **5**; the proton in position H4 was located in the Fourier map and refined without constraints; the dashed line indicates a secondary interaction between EtNH and EtN groups in neighboring double bridges

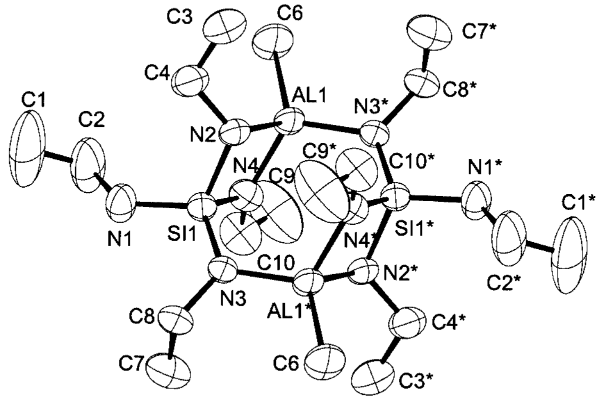

Figure 3. Molecular structure of **4**

Table 1. Selected bond lengths [Å] and angles [°] in compound **5**

Al−N2	1.849(2)	Al−N3	1.851(2)
Al−N4	2.006(2)	Al−C6	1.971(2)
Si−N1	1.700(2)	Si−N2	1.699(2)
Si−N3	1.704(2)	Si−N4	1.833(2)
N4−H4	0.80(2)	N1−H1	0.80(3)
N2−Al−N3	115.2(1)	N2−Al−C6	119.4(1)
N3−Al−C6	113.5(1)	N2−Al−N4	80.4(1)
N3−Al−N4	107.6(1)	C6−Al−N4	116.1(1)
N2−Si−N1	114.1(1)	N2−Si−N3	118.3(1)
N1−Si−N3	110.8(1)	N2−Si−N4	89.6(1)
N1−Si−N4	112.2(1)	N3−Si−N4	110.1(1)
C4−N2−Si	125.3(1)	C8−N3−Si	119.7(1)
C4−N2−Al	134.9(1)	C8−N3−Al	118.2(1)
Si−N2−Al	99.9(1)	Si−N3−Al	119.8(1)
C10−N4−Si	118.3(1)		
Si−N4−Al	90.0(1)		
C10−N4−Al	121.1(1)		

in **4**] are significantly shorter than the bond to the EtNH ligand [Al−N4: 2.006(2) Å in **5**, 1.992(3) Å in **4**].

For silicon, compression of the tetrahedral environment along the double bridge is less severe [N2−Si−N4: 89.6(1)°] and the other N−Si−N angles are between 110 and 114°, with one exception [N2−Si−N3: 118.3(1)°]. As in the $AlCN_3$ tetrahedron, the Si−N bond length to the μ_2-bridging EtNH group is longer [Si−N4: 1.833(2) Å (**5**); 1.826(3) Å (**4**)] than the other Si−N bonds [1.699(2)−1.704(2) Å].

An interesting feature is that only 50% of the original EtNH groups are deprotonated. Bridging EtN groups are clearly different from the bridging EtNH ligands in geometry. In the former, the nitrogen atoms (N2 and N3) show a distorted trigonal planar coordination [C4−N2−Si: 125.3(1)°, C4−N2−Al: 134.9(1)°, Si−N2−Al: 99.9(1)°, sum: 360.1°; C8−N3−Si: 119.7(1)°, C8−N3−Al: 118.2(1)°, Si−N3−Al: 119.8(1)° sum: 357.7° (359.7° for **4**)] whereas in the latter N4 has a pseudotetrahedral arrangement of non-hydrogen atoms [C10−N4−Si: 118.3(1)°, Si−N4−Al: 90.0(1)°, C10−N4−Al: 121.1(1)°, sum: 329.4° (332.2° for **4**)].

The simultaneous presence of bridging EtNH and EtN groups is a unique structural feature of the new cluster. The proton H4, attached to N4, was located in the difference Fourier map and refined without constraints to give an N4−H4 distance of 0.80(2) Å. Interestingly, the distance between H4 and the non-covalently bonded N2 in the neighboring double bridge is only 2.49(2) Å (Figure 2, dashed line), so a secondary interaction between the EtNH and the EtN ligand in the neighboring double bridge is probably the reason for the unusual structural motif. The H4 location is also ideal for an intramolecular exchange of the proton from the EtNH to the EtN ligand, which is unprecedented and would explain some of the broadening in the NMR spectra.

The position of the proton in the terminal EtNH group attached to silicon was also located in the course of the structural refinement.

Although differentiation between aluminium and silicon and location of the hydrogen position are not trivial, the assignment of positions is evident from the synthesis and the geometrical considerations outlined above. The good solubilities of **4** and **5** in non-polar solvents such as pentane are also in agreement with the overall zero charge on the molecule deduced from the structural analysis, especially since the ethyl groups point outwards from the cluster to provide an overall hydrophobic shell. Hydrophobic interactions between those groups therefore also largely determine the lattice energy and packing of the clusters in the crystal structure.

Overall, the structures of the new compounds are a remarkable new element in alane chemistry. Tetrameric iminoalanes commonly possess cubane-type skeletons.[11] However, for an Al_2Si_2 skeleton the cubane structure, for reasons of charge-matching, would not only require one unusual terminal EtN ligand ($[RAl(\mu_3\text{-}NEt)_2Si(NEt)]_2$) but would also produce neighboring aluminium tetrahedra, obviously less favorable than alternating silicon and aluminium tetrahedra. Interestingly, the latter can be seen as a molecular analogy of Löwenstein's rule, which states that the Al:Si ratio in zeolites can never exceed 1.0 because Al−O−Al linkages are avoided.[13]

Conclusion

We have shown that heterocyclic precursors containing aluminium and silicon in a fixed ratio of 1:1 are accessible as crystalline compounds in high yield. They represent preorganized structural building units for the assembly of tetrahedral framework materials such as nitrido zeolites. Preliminary investigations in our group show that they are suitable precursors for the generation of porous aluminium silicon imide materials with high accessible surface area by use of ammonothermal transamination in supercritical ammonia.

Experimental Section

Synthesis of 4 and 5: All operations were performed either in a glove box (Argon, $O_2 < 1$ ppm, $H_2O < 1$ ppm) or with use of a vacuum line and dry solvents. Tetrakis(ethylamino)silane was obtained from aminoethane and silicon chloride (9:1) and purified by distillation in vacuo (99.7%, GC).[8]

Typically, AlR_3 (5 mmol) was added dropwise at room temperature either to a stirred solution of $Si(NHEt)_4$ (5 mmol, 1 g) in pentane or to pure $Si(NHEt)_4$. The liquid mixture was stirred at room temperature for 12 hours. For reactions carried out in the absence of solvent the vessel was completely filled with white, crystalline product after 12 h. For reactions carried out in pentane, the solvent was removed in vacuo and a solid product was obtained [yield: 98%, 1.198 g (**4**), 100%, 1.292 g (**5**)].

Compound 4: $C_{18}H_{50}Al_2N_8Si_2$ (488.80) Calcd. C 44.23, H: 10.31, N 22.93, Al 11.04, Si 11.49; found C 44.15, H 10.19, N 23.11, Al 11.15, Si 11.81. MS(EI): *m/z* (%) = 488 (19) [M^+], 473 (100) [$M^+ - CH_3$]. ^1H NMR (300 MHz, 300 K, [D_6]benzene, ppm): $\delta = -0.20$ (s, 6 H, $\mathrm{AlC}H_3$), 1.06−1.40 (m, 24 H, N-$\mathrm{CH_2{-}C}H_3$), 2.88−3.14 (m, 16 H, N-$\mathrm{C}H_2\mathrm{{-}CH_3}$). IR (KBr): $\tilde{\nu} = 3413 cm^{-1}$(m), 3262 (m)(N−H), 2960(s), 2927(s), 2862(s)(C−H), 2683(w), 2589(w), 1475(m), 1449(m), 1395(s), 1371(s), 1298(m), 1265(m), 1192(s), 1125(s), 1065(s), 929(s), 887(s), 864(s), 779(s), 699(m), 657(m).

Compound 5: $C_{20}H_{54}Al_2N_8Si_2$ (516.86) Calcd. C 46.48, H 10.53, N 21.68, Al 10.44, Si 10.87; found C 46.11, H 10.26, N 21.39, Al 10.59, Si 11.31. MS(CI, *i*-butane): *m/z* (%) = 517 (35) [$M^+ + H$], 487 (100) [$M^+ - C_2H_5$]. ^1H NMR (300 MHz, 300 K, [D_6]benzene, ppm): $\delta = 0.37$ (m, 4 H, $\mathrm{AlC}H_2\mathrm{CH_3}$), 1.01−1.49 (m, 30 H, $\mathrm{CH_2{-}C}H_3$), 2.70−3.03 (m, 16 H, N-$\mathrm{C}H_2\mathrm{{-}CH_3}$). IR (KBr): $\tilde{\nu}$ = 3410(m) cm^{-1}, 3254(m) (N−H), 2958(s), 2895(s), 2861(s) (C−H), 2680(w), 2589(w), 1449(s), 1393(s), 1371(s), 1350(s), 1296(w), 1265(s), 1188(s), 1125(s), 1065(s), 991(m), 926(s), 861(s), 780(s), 692(m), 628(m), 542(m).

Crystal Data Collection and Refinement of the Structure of 4: $C_{18}H_{50}Al_2N_8Si_2$, M_r = 488.80 g·mol^{-1}, triclinic, space group $P\bar{1}$ (No.2), a = 8.3052(8) Å, b = 9.8323(9) Å, c = 10.3240(10) Å, α = 115.498(4)°, β = 97.684(4)°, γ = 94.382(4)°, V = 745.60(12) Å^3, Z = 1, $D_{calcd.}$ = 1.089 g·cm^{-3}, μ = 0.198 mm^{-1}, $F(000)$ = 536 e, T = 100 K. Convergence of the 141 variable parameters by full-matrix, least-squares refinement on F^2 reaches $R_1 = 0.0766$ [$I > 2\sigma(I)$] and wR_2= 0.2515 with a goodness-of-fit of 0.870.The data were collected on a Siemens SMART-CCD diffractometer by use of graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å).

Crystal Data Collection and Refinement of the Structure of 5: $C_{20}H_{54}Al_2N_8Si_2$, M_r = 516.86 g·mol^{-1}, triclinic, space group $P\bar{1}$ (No.2), a = 8.2319(3) Å, b = 9.3748(5) Å, c = 10.8221(6) Å, α = 107.035(2)°, β = 104.435(2)°, γ = 94.375(2)°, V = 763.20(6) Å^3, Z = 1, $D_{calcd.}$ = 1.125 g·cm^{-3}, μ = 0.196 mm^{-1}, $F(000)$ = 568 e, T = 100 K. Convergence of the 158 variable parameters by full-matrix, least-squares refinement on F^2 reaches $R_1 = 0.0671$ [$I > 2\sigma(I)$] and wR_2= 0.1471 with a goodness-of-fit of 1.007. The data were collected on a Nonius Kappa-CCD diffractometer by use of graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å).

CCDC-190148 (**5**) and CCDC-190147 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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