enantiomeric (*S*)-(+)-phenylglycinol. These results show the crucial role of the chiral phenylglycinol, which serves not only for the transfer of chirality but also for the stabilization of the intermediate iminium.

The nitramine alkaloids (derivatives of 2-azaspiro[5.5]undecan-7-ol) are structurally analogous to the neurotoxic histrionicotoxin alkaloids,[11] compounds which have a 1-azaspiro[5.5]undecan-8-ol skeleton with unsaturated lipophilic side chains. The introduction of such essential side chains on the nitramine skeleton is therefore of particular interest. Intermediate **3** opens the way to a variety of substitutions which can be made a) at the carbon atoms adjacent to the nitrogen of the piperidine ring by selective opening of the oxazolidine and/or 1,3-oxazine in an iminium ion and b) on the cyclohexane ring by the sulfone reactivity.

Experimental Section

All new compounds were characterized by 2D ^{1}H and ^{13}C NMR as well IR spectra, $[\alpha]_D$ values, simple and high-resolution mass spectrometry, or elemental analysis.

(*R*)-(−)-phenylglycinol (6.9 g, 50 mmol) was added to a solution of citric acid (24 g) in distilled water (200 mL). The mixture was stirred vigourously until complete dissolution of the phenylglycinol and then cooled to 0–5 °C in an ice/water bath. A 25 % aqueous solution of glutaraldehyde (47 mL, 125 mmol) was added dropwise over 30 min, and then sodium *p*-toluenesulfinate (19.6 g, 110 mmol) was added simultaneously with CH_2Cl_2 (120 mL). The reaction mixture was stirred for 2 h at room temperature. The aqueous phase was neutralized with 5 N aqueous NaOH (80 mL) and extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layers were concentrated under vacuum, diluted with MeOH (50 mL), and treated with $ZnBr_2$ (2 g, 8.9 mmol) over 12 h. Evaporation of the solvent gave an oily crude residue which crystallized from MeOH to give 11.19 g (51 %) of **3** in two crops.

3: M.p. 222–223 °C; $[\alpha]_D - 77$ ($c = 1$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.12$ (m, 1 H, H-9), 1.50–2.10 (m, 6 H, H-5, Hs-8, H-9, Hs-10), 1.95–2.10 (m, 1 H, H-5), 2.15–2.35 (m, 2 H, Hs-4), 2.44 (s, 3 H, CH_3 Tol), 3.28 (dd, 1 H, $J = 13$, 4 Hz, H-7), 3.66 (dd, 1 H, $J = 9.5$, 8.5 Hz, H-13), 3.97 (dd, 1 H, $J = 11.5$, 4.5 Hz, H-11), 4.30 (dd, 1 H, $J = 3.5$, 1.5 Hz, H-6), 4.35 (dd, 1 H, $J = 8.5$, 6.5 Hz, H-13), 4.60 (dd, 1 H, $J = 9.5$, 6.5 Hz, H-12), 5.86 (s, 1 H, H-2), 7.20–7.45 (m, 7 H, Ar Hs), 7.78 (d, 1 H, $J = 8$ Hz, Tol H); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 16.4$ (C-4), 21.4 (CH_3 Tol), 21.4 (C-9), 23.6 (C-10), 27.2 (C-5), 28.2 (C-8), 40.7 (C-3), 62.6 (C-7), 63.2 (C-12), 70.4 (C-11), 73.0 (C-13), 78.5 (C-6), 91.3 (C-2), 127.3, 128.2, 129.5 (Ar CH), 136.9 (Ar C), 139.9 (Ar C), 144.3 (Ar C).

4: M.p. 211–213 °C (MeOH); $[\alpha]_D - 3$ ($c = 1$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.1$–1.2 (m, 1 H), 1.3–2.0 (m, 8 H), 2.0-2.2 (m, 4 H), 2.30 (s, 3 H, N-Me), 2.42 (s, 3 H, CH_3 Tol), 2.5–2.9 (br m, 2 H), 3.5–3.7 (m, 2 H), 7.32 (d, 1 H, $J = 8$ Hz, H Tol), 7.72 (d, 1 H, $J = 8$ Hz, H Tol); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 21.4$ (CH_3 Tol), 21.7 (CH_2), 22.3 (CH_2), 23.2 (CH_2), 28.8 (CH_2), 43.0 (C-3), 46.0 (N-Me), 55.3 (C-6), 65.4 (C-2), 68.6 (C-7), 81.9 (C-11), 128.1 (CH Tol), 129.6 (CH Tol), 137.2 (C Tol), 144.3 (C Tol).

5: $[\alpha]_D - 17$ ($c = 1$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.7$–1.0 (m, 2 H), 1.0–1.8 (m, 8 H), 1.85 (d, 1 H, $J = 11$ hz, H-2), 2.0–2.1 (m, 2 H), 2.25 (td, 1 H, $J = 10$, 3 Hz, H-6), 2.67 (d, 1 H, $J = 11$ Hz, H-2), 2.8–2.9 (m, 1 H), 3.5–3.6 (m, 2 H), 3.80 (dd, 1 H, $J = 11$, 6 Hz), 4.08 (dd, 1 H, $J = 11$, 8 Hz), 7.0–7.4 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 20.3$ (CH_2) 22.8 (CH_2), 23.8 (CH_2), 28.1 (CH_2), 29.5 (CH_2), 35.9 (C-3), 51.8 (C-6), 62.1 (C-2), 62.7 (C-13), 71.0 (C-12), 79.0 (C-11), 127.8 (Ar CH), 128.4 (Ar CH), 128.6 (Ar CH), 147.5 (Ar C).

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[10] Isonitramine (−)-**1** could be obtained in a single step by treating **3** with Raney nickel at 80 °C and 25 bar in THF; however, the yield was modest (20 %, not optimized).

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Preparation of Lithium Oligosiloxane Aluminates and Acid Strength of Hydroxy Groups in a Molecular Aluminum Oligosiloxane

Michael Veith,* Maria Jarczyk, and Volker Huch

Dedicated to Professor Manfred Weidenbruch
on the occasion of his 60th birthday

As we recently reported, the molecular aluminum oligosiloxane **1**, which contains four aluminum atoms that are connected through OH bridges to form a ring, can be readily prepared in a one-step synthesis.[1] We observed that the hydrogen atoms of the OH groups are available for coordination with Lewis bases. Compound **1** can therefore be isolated as an adduct with three molecules of diethyl ether (a fourth is incorporated within the crystal lattice and does not

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coordinate with a hydrogen atom). It can also be allowed to react with triethylamine to give a 2:1 adduct that may be described as an ion pair with the formula $[\{(Ph_2Si)_2O_3\}_4Al_4(OH)_2O_2]^{2-}(Et_3NH^+)_2$. It was a logical consequence for us to investigate the effect that various other Lewis bases with different steric requirements and basic strengths have on **1**. In addition, we wanted to study whether the Loewenstein rule (according to which the AlO_4 tetrahedra in such compounds are always separated by silicon atoms) is also applicable to molecular aluminum/silicon–oxygen compounds,[2] or whether the hydroxy compound **1** can be converted into a lithium derivative without rearrangement. Roesky et al. recently described a molecular sodium siloxoaluminate of the general formula $[\{Na(thf)\}_4][\{EtAlO_3SiR\}_4]$ in which the O_3R tetrahedra centered by aluminum and silicon atoms were indeed linked through oxygen vertices in an alternating fashion.[3]

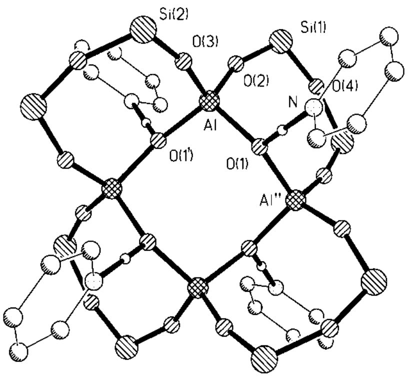
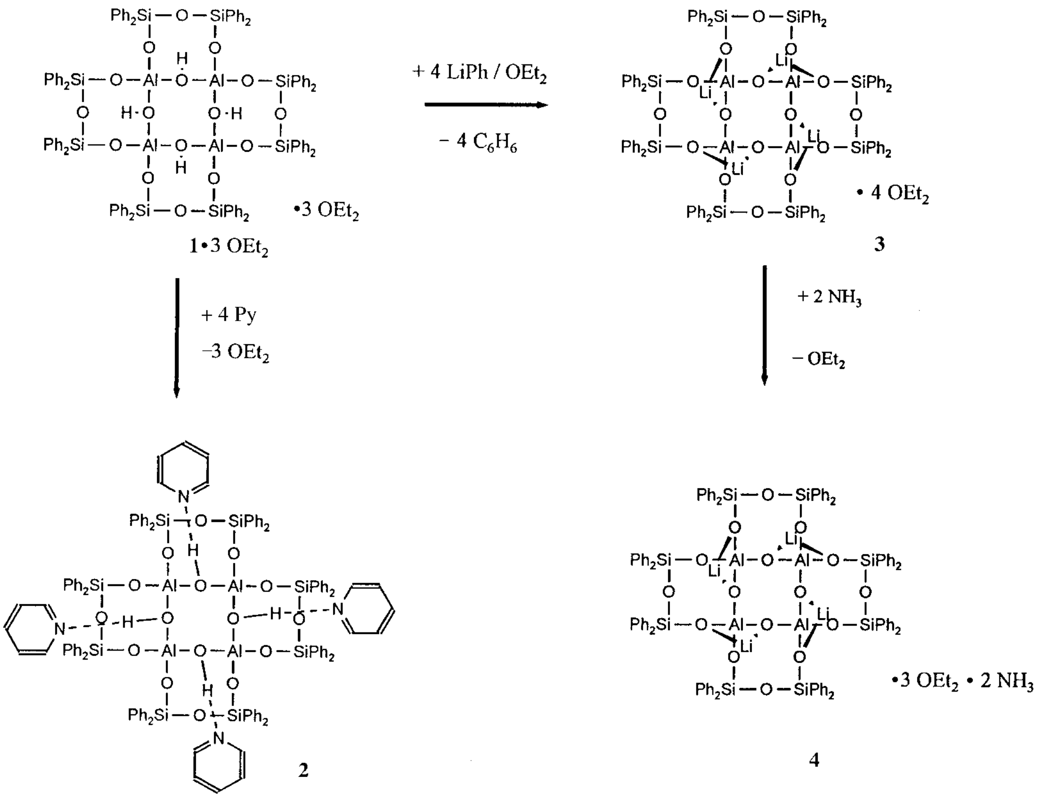


Figure 1. The framework of **2** in the crystal (for clarity the phenyl groups on the silicon atoms are not shown, see Figure 2). Selected bond lengths [Å] and angles [°]: Al–O(3) 1.703(2), Al–O(1) 1.768(2), Si(1)–O(2) 1.594(2), Si(2)–O(3) 1.586(2), Al–O(2) 1.714(2), Al–O(1') 1.770(2), Si(1)–O(4) 1.633(2), Si(2)–O(4') 1.632(2); O(3)-Al-O(2) 114.6(1), O(3)-Al-O(1) 106.6(1), O(2)-Al-O(1) 110.7(9), O(3)-Al-O(1') 109.7(1), O(2)-Al-O(1') 106.8(1), O(1)-Al-O(1') 108.3(1), Al-O(1)-Al'' 132.4(1), Si(1)-O(2)-Al 154.4(1), Si(2)-O(3)-Al 166.5(1).[8]

Adduct $\mathbf{1} \cdot 4\,OEt_2$ reacts smoothly with pyridine (Py) under elimination of the diethyl ether molecule to give the pyridine adduct **2**[4] in almost quantitative yield (Scheme 1).The IR spectrum of crystalline **2** has a narrow band at 3630 cm^{-1}, and the ^{29}Si NMR spectrum has only one signal. Based on the integration of the ^{1}H NMR signals and the elemental analysis, **2** contains one pyridine molecule per OH group. A section of the structure of **2** as determined from the X-ray structure analysis[4] is shown in Figure 1. The molecule has $S_4(\bar{4})$ crystallographic symmetry with four pyridine molecules linked to the central $Al_4(OH)_4$ ring through bridging hydrogen bonds. The O–N distance of the linear N–H ··· O bridge is 2.548(3) Å; the adjacent Al atoms along with the N and O atoms lie almost perfectly in a plane. In contrast to the triethylamine adduct (only two molecules per four OH groups) and the diethyl ether adduct (three molecules per four OH groups),[1] all OH groups in **2** are "coordinatively saturated". The fourfold incorporation of pyridine is attained in that half of the phenyl groups of the peripheral silyl groups are arranged parallel to each other and thus form a sandwich structure with the pyridine molecules (the average distance between the plane of the pyridine ring and the parallel phenyl



Scheme 1. Synthesis of compounds **2**–**4** from **1**.

groups is 3.6 Å, see Figure 2). The twofold symmetry of the $OSi(Ph)_2OSi(Ph)_2O$ handle is somewhat disturbed by the forced arrangement of the aryl groups. This manifests itself most clearly in the Si-O-Al angles of 154.4(1) and 166.6(1)°.

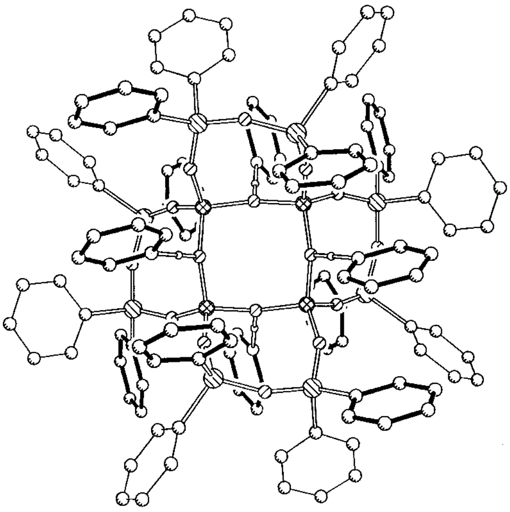


Figure 2. The parallel arrangement of the phenyl groups on the silicon atoms and the interstitial pyridine molecules in **2** (thick lines).

The Al−O(H) bond lengths are particularly informative with respect to the H···N interaction and the relative acidic strength of the OH groups. They are equal within the limits of the standard deviation (av 1.769(1) Å) and lie between the corresponding lengths in the adducts with diethyl ether (av 1.800 Å) and triethylamine (av 1.728 Å). In agreement with the pK_a values of diethyl ether (−3.0), pyridine (5.2), and triethylamine (10.8),[5] there is a correlation with the Al−O bond lengths; as expected, the strongest base effects the strongest attraction on the hydrogen atoms. This leads to a negative partial charge on the oxygen atoms and thus to a shortening of the Al−O bond. However, the lengths of the bridging hydrogen bonds (2.65 Å in **1**·4O_2Et, 2.72 Å in the triethylamine adduct, and 2.55 Å in **2**) do not correlate with the base strengths. It appears that the steric requirements of the bases are reflected in these distances; pyridine clearly requires less space than diethyl ether or triethylamine. This is plausible when space-filling models of the molecules are considered.

With the reaction of **1**·4OEt_2 with phenyllithium it is possible to replace all four hydrogen atoms of the hydroxy groups with lithium atoms[6] (Scheme 1). Product **3** reacts further with NH_3 in toluene; the formation of **4** is accompanied by the incorporation of two NH_3 molecules and the elimination of a diethyl ether molecule[7] (large molar amounts of NH_3 lead to mixtures of products, which could not yet be separated). The quantitative reaction can be inferred from the IR spectra of the reaction products: In the case of **3** no peaks between 3700 and 3150 cm^{-1} are found, and for **4** there is an intense peak at 3389 cm^{-1}, which can be attributed to the N−H vibrations of the NH_3 molecules coordinated to two lithium atoms (there is a signal at $\delta = -382.4$ in the ^{15}N NMR spectrum). X-ray structure analyses were performed on both compounds,[6, 7] the results of which are depicted in Figures 3 and 4.

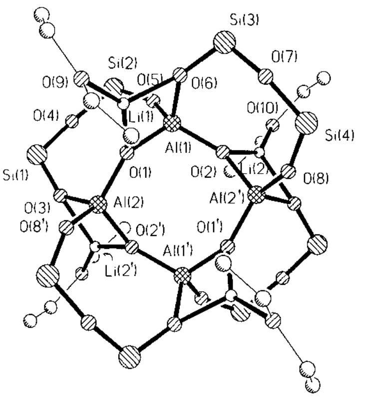


Figure 3. Section from the structure of **3** in the crystal (for clarity the phenyl groups on the silicon atoms are not shown). Selected bond lengths [Å] and angles [°]: Al(1)−O(2) 1.720(4), Al(1)−O(1) 1.729(4), Al(1)−O(5) 1.734(4), Al(1)−O(6) 1.799(4), Al(2)−O(1) 1.727(4), Al(2)−O(2′) 1.734(4), Al(2)−O(8′) 1.736(4), Al(2)−O(3) 1.786(4), Si(1)−O(3) 1.616(4), Si(1)−O(4) 1.618(5), Si(2)−O(5) 1.593(4), Si(2)−O(4) 1.631(5), Si(3)−O(6) 1.605(4), Si(3)−O(7) 1.617(5), Si(4)−O(8) 1.593(4), Si(4)−O(7) 1.630(5), O(1)−Li(1) 1.85(1), O(2)−Li(2) 1.84(1), O(3)−Li(2′) 2.03(1), O(6)−Li(1) 1.95(1), Li(1)−O(9) 1.91(1), Li(2)−O(10) 1.88(1); O(2)-Al(1)-O(1) 118.9(2), O(1)-Al(2)-O(2′) 116.4(2), Al(2)-O(1)-Al(1) 133.6(2), Al(1)-O(2)-Al(2′) 134.6(2).[8]

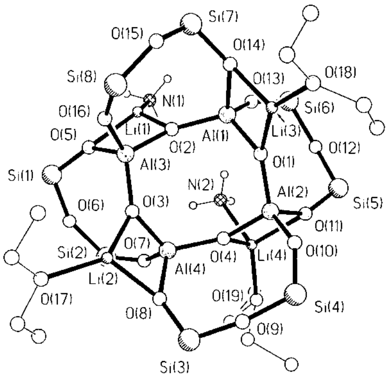


Figure 4. Section from the structure of **4** in the crystal that is analogous to that in Figure 3. Selected bond lengths [Å] and angles [°]: Al(1)−O(2) 1.715(3), Al(1)−O(13) 1.734(4), Al(1)−O(1) 1.746(3), Al(1)−O(14) 1.791(3), Al(2)−O(4) 1.733(3), Al(2)−O(1) 1.738(3), Al(2)−O(10) 1.748(3), Al(2)−O(11) 1.786(4), Al(3)−O(3) 1.727(3), Al(3)−O(2) 1.733(4), Al(3)−O(16) 1.743(4), Al(3)−O(5) 1.789(3), Al(4)−O(4) 1.714(3), Al(4)−O(3) 1.744(3), Al(4)−O(7) 1.757(3), Al(4)−O(8) 1.781(4), O(1)−Li(3) 1.85(1), O(2)−Li(1) 1.87(1), O(3)−Li(2) 1.85(1), O(4)−Li(4) 1.90(1), N(1)−Li(1) 2.00(1), N(2)−Li(4) 2.09(2); O(2)-Al(1)-O(1) 117.1(2), O(4)-Al(2)-O(1) 114.9(2), O(3)-Al(3)-O(2) 114.9(2), O(4)-Al(4)-O(3) 119.3(2), Al(2)-O(1)-Al(1) 127.1(2), Al(1)-O(2)-Al(3) 137.8(2), Al(3)-O(3)-Al(4) 128.5(2), Al(4)-O(4)-Al(2) 141.0(2).[8]

Compound **3** has the same central cyclic structural unit as **1**, but is supplemented by four annelated AlO_2Li rings. Each lithium atom is additionally connected to a diethyl ether ligand molecule, so that approximately trigonal-planar LiO_3 units are formed. Alternatively, the inner unit can also be described as consisting of four AlO_4 tetrahedra connected through common vertices with one edge of each tetrahedron being bridged by a lithium atom. The similarity to lithium aluminium silicates is also reflected by the formula $[\{Ph_2SiO\}_8][\{LiAlO_2\}_4]\cdot 4OEt_2$. The point symmetry of the molecule in the crystal is $C_2(2)$; however, the deviation from

$S_4(\bar{4})$ symmetry is only slight. Moreover, **3** crystallizes enantiomerically pure in a noncentrosymmetric space group. The Al–O bond lengths in the central Al_4O_4 ring alternate systematically according to whether the bond is situated within the AlO_2Li ring (av 1.732(3) Å) or outside it (av 1.723(3) Å). Otherwise, the distances are similar to those in the triethylamine adduct of **1**,[1] which suggests equivalent charge states on the oxygen atoms. Of all the Li–O distances, Li–O(Al)$_2$ is, as expected, the shortest (av 1.85(2) Å), followed by Li–O(Et)$_2$ (av 1.89(2) Å) and finally Li–O(Al,Si) (av 1.99(2) Å).

The fundamental structure of the framework of **4** is similar to that of **3**; the Al–O bond lengths of the central Al_4O_4 ring alternate also here. In contrast to the situation in **3**, the four lithium atoms are quite differently coordinated. Atoms Li(2) and Li(3) are coordinated by diethyl ether, which results in a slightly distorted trigonal-planar environment, whereas Li(1) is coordinated by an ammonia molecule, and Li(4) by both an ammonia and a diethyl ether molecule. Thus, Li(4) has the coordination number four. The asymmetrical ligand distribution leads to the point symmetry C_1 in the crystal. As in **3**, the shortest Li–O bond length is that between Li and O atoms of the central Al_4O_4 ring (1.846(9) – 1.865(9) Å). The Li–O(Et$_2$) bond lengths (1.89(1) – 1.94(1) Å) are longer (as are Li–N bond lengths with 2.00(1) Å), and the Li–O(Al,Si) distances are the longest (2.01(1) – 2.03(1) Å). Due to the higher coordination number on Li(4), all bond lengths here are somewhat longer (e.g. Li(4)–N(2) 2.09(2) Å).

As shown unequivocally by the X-ray structure analyses of **3** and **4**, the fundamental framework is not altered by the incorporation of the lithium atoms into **1**. It thus appears that the Loewenstein rule does not apply for the molecular lithium oligosiloxane aluminates considered here. Their formation is apparently more "kinetically" than "thermodynamically controlled". Moreover, attack by bases occurs more readily than in the case of **1** (**3** contains four diethyl ether donors, and the corresponding adduct of **1** only three). The oxygen atoms of the OSi(Ph)$_2$OSi(Ph)$_2$O handle readily coordinate to the lithium atoms, which leads to the observed cyclizations. It is expected that larger metal atoms would form coordinate bonds with even more oxygen atoms.

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Keywords: aluminum · N ligands · O ligands · polycycles · silicon

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[4] **2**: **1** · 4 OEt$_2$[1] (0.380 g, 0.18 mmol) in benzene (10 mL) was stirred with pyridine (0.056 g, 0.71 mmol) at room temperature for 2 h. The solvent was then removed under reduced pressure until crystals of **2** precipitated (0.366 g, 95 %). Correct elemental analysis. NMR: [D$_6$]benzene, 296 K, TMS; ^{1}H NMR (200 MHz): $\delta = 6.02$ (m, 8 H, Py), 6.65 (m, 4 H, Py), 7.03 (m, 48 H, Ph), 7.53 (m, 16 H, Ph), 7.85 (m, 8 H, Py), 7.90 (m, 16 H, Ph); ^{13}C NMR (50.3 MHz): $\delta = 123.87$ (s, Py), 127.39 – 128.11 (m, Ph), 134.89 (s, Ph), 135 (s, Ph/Py), 137.59 (s, Ph), 139.19 (s, Ph), 139.62 (s, Ph), 146.86 (s, Py); ^{29}Si NMR (39.7 MHz): $\delta = -45.98$ (s, SiPh$_2$). Crystal structure analysis:[8] $C_{116}H_{104}Al_4N_4O_{16}Si_8$, $M = 2142.73\ \mathrm{g\,mol^{-1}}$, tetragonal, space group $I\bar{4}$, $a = b = 1912.3(3)$, $c = 1561.7(3)$ pm, $V = 5711(2) \times 10^6\ \mathrm{pm^3}$, $Z = 2$, $\rho_{calcd} = 1.246\ \mathrm{Mg\,m^{-3}}$, $F(000)$ 2240, $T = 293$ K, $2 < 2\,\Theta < 48°$; of 18188 reflections 4517 were independent ($R_{int} = 0.054$), and 4010 with $I > 2\sigma(I)$; $R_1 = 0.035$, $wR_2 = 0.081$.

[5] D. D. Perrin, B. Dempsey, E. P. Serjeant, *pK_a Prediction for Organic Acids and Bases*, Chapman & Hall, London, **1981**.

[6] **3**: Phenyllithium (2.63 mmol, 1.6 M in diethyl ether/cyclohexane) was added dropwise to **1** · 4 OEt$_2$[1] (1.398 g, 0.65 mmol) in diethyl ether (20 mL) and stirred for 30 min, and a clear solution formed. After a further 30 min a precipitate was formed, which was then recrystallized from diethyl ether. Yield: 0.989 g (70 %). Correct elemental analysis. ^{1}H NMR: $\delta = 0.70$ (t, 24 H, OEt), 2.80 (q, 16 H, OEt), 7.15 (m, 48 H, Ph), 7.97 (m, 16 H, Ph), 8.16 (m, 16 H, Ph); ^{13}C NMR: $\delta = 14.34$ (s, OEt), 65.36 (s, OEt), 127.5 – 129.06 (m, Ph), 134.91 (s, Ph), 135.61 (s, Ph), 139.50 (s, Ph), 141.37 (s, Ph); ^{29}Si NMR: $\delta = -45.93$ (s, SiPh$_2$). Crystal structure analysis:[8] $C_{112}H_{120}Al_4Li_4O_{20}Si_8$, $M = 2146.48\ \mathrm{g\,mol^{-1}}$, monoclinic, space group $I2$, Flack parameter: 0.046, $a = 1812.2(4)$, $b = 1531.9(3)$, $c = 2244.1(4)$ pm, $\beta = 90.22°$, $V = 6230(2) \times 10^6\ \mathrm{pm^3}$, $Z = 2$, $\rho_{calcd} = 1.144\ \mathrm{Mg\,m^{-3}}$, $F(000) = 2256$, $T = 293$ K, $2 < 2\,\Theta < 48°$; of 14713 reflections 9565 were independent ($R_{int} = 0.041$), and 6036 with ($I > 2\sigma(I)$; $R_1 = 0.069$, $w\mathrm{R}_2 = 0.164$.

[7] **4**: **3** (172 mg, 0.079 mmol) was stirred in toluene (5 mL) with NH_3 (0.2 mmol in toluene) for 30 min at room temperature. The solvent was then removed under reduced pressure and the residue recrystallized from a small amount of diethyl ether. Yield 135 mg (81 %). Correct elemental analysis. ^{1}H NMR: $\delta = -0.90$ (s, 6 H, NH$_3$), 0.69 (t, 18 H, OEt), 2.81 (q, 12 H, OEt), 7.15 (m, 48 H, Ph), 7.53 (m, 16 H, Ph), 8.15 (m, 16 H, Ph); ^{13}C NMR: $\delta = 14.84$ (s, OEt), 65.80 (s, OEt), 127.7 – 129.4 (m, Ph), 134.93 (s, Ph), 135.66 (s, Ph), 139.81 (s, Ph), 141.45(s, Ph); ^{29}Si NMR: $\delta = -45.83$ (s, SiPh$_2$); ^{15}N NMR (20.3 MHz): $\delta = -384.2$ (s, NH$_3$). Crystal structure analysis:[8] $C_{108}H_{116}Al_4Li_4N_2O_{19}Si_8$, $M = 2106.49\ \mathrm{g\,mol^{-1}}$, triclinic space group $P\bar{1}$, $a = 1564.1(3)$, $b = 1591.2(2)$, $\mathrm{c} = 2689.2(7)$ pm, $\alpha = 91.93(2)$, $\beta = 92.12(3)$, $\gamma = 118.70(2)°$, $V = 5857(2) \times 10^6\ \mathrm{pm^3}$, $Z = 2$, $\rho_{ber} = 1.194\ \mathrm{Mg\,m^{-3}}$, $F(000) = 2212$, $T = 293$ K, $1.7 < 2\,\Theta < 45°$; of 37024 reflections 14208 were independent ($R_{int} = 0.066$), and 10208 with $I > 2\sigma(I)$; $R_1 = 0.070$, $wR_2 = 0.205$.

[8] General information regarding the crystal structure analyses: Stoe-IPDS-diffractometer. The structures were solved by direct methods (SHELXS-86) and refined (SHELXL-93) with anisotropic temperature factors for all non-hydrogen atoms; hydrogen atoms were in fixed geometrical positions. Further details concerning the crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-407811 (**2**), 407812 (**3**), and 407813 (**4**).