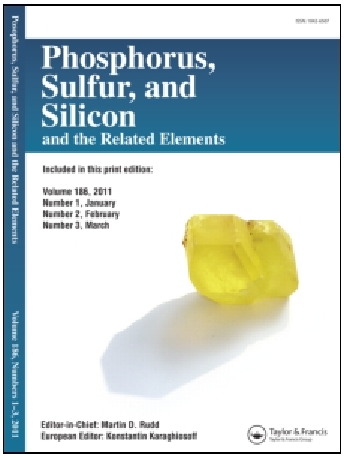

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NEW POLYCYCLIC ALUMINOPOLYSILOXANES

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When diphenyldihydroxysilane, $Ph_2Si(OH)_2$, is allowed to react with the aluminiumalkoxydihydride (tBu-O)AlH_2, the polycyclic compound $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$, **1**, is formed. The compound is made up of five eight membered cycles, the central one originating from formal donor-acceptor bonds between OH groups and Al atoms. The structure of **1** can be modified by reacting it with Lewis bases like Et_3N, Et_2O or C_5H_5N; in each case the basic structure of the polycycle is conserved, however serious changes are observed in the central Al_4O_4 ring depending upon the basicity (the hydrogen withdrawing properties) of the oxygen or nitrogen atom. It is intriguing that the *pseudo* host-guest behaviour of **1** is not the same for different bases and the 'shell' or 'basket' formed by the multiple phenyl groups and the shape of the Al-O-Si-skeleton is functioning as a selective trap such that the four OH groups accomodate two, three and four molecules of Et_3N (**2**), Et_2O (**3**) and C_5H_5N (**4**), respectively. The spatial consideration of the central part of the molecular unit for the incoming base i.e. an opening or closing effect is subjected to the steric requirements of the base employed. The replacement of hydrogen atoms in **1** by lithium atoms results in further cyclisation of the molecule to yield a higher polycyclic compound, $[(Ph_2Si)_2O_3]_4O_4Al_4Li_4$, which can be isolated as a tetrakis(diethylether) adduct (**5**) or as a tris(diethylether) bis(ammonia) adduct (**6**). Nevertheless the connection of the atoms in **1** is retained in compounds **5** and **6**. If the organic bases attacking **1** are replaced by the smaller and more acidic water molecule the new compound 7, $[(Ph_2Si)_2O_3]_6Al_6(OH)_3Al(OH)_6{*}3OEt_2$, is formed, the structure of which is completely different from **1**, **2**, **3** or **4**. In this case the starting molecule has been rearranged by the influence of water.

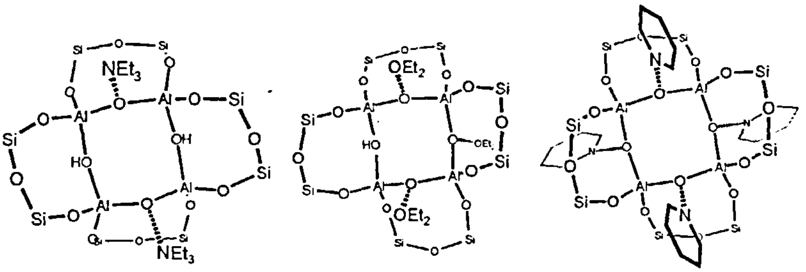
Keywords: alumosiloxanes; molecular polycycycles with Si, O, Al; host-guest chemistry; proton acidity of aluminiumhydroxyl groups

INTRODUCTION

Recently we have developped a new method for the synthesis of molecular alumosiloxanes with reactive hydroxyl groups[1]. The new parent compound $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$, 1, has the following characteristics: a) it has four OH groups which are linked exclusively to aluminium atoms and which are remarkably acidic, b) the three-dimensional arrangement of the OH groups together with the positions of the phenyl groups on the silicon atoms are limiting factors for the reaction partners with respect to their steric requirements and c) the polycyclic structure of 1 could be usefull to build even more complicated cage-like aggregates. We here report our first results on the reactions of 1 with the Lewis base H_2O in comparison to the reaction of 1 with the bases triethylamine[1], diethylether[1] and pyridine[2]. We also briefly review the reactions of 1 with phenyllithium[2] in the presence of different bases.

REACTION OF 1 WITH ORGANIC LEWIS BASES

When the polycyclic compound 1, originating from the condensation reaction of $(tBuO\text{-}AlH_2)_2$ with $Ph_2Si(OH)_2$[1], is treated with the Lewis bases $N(Et)_3$, $O(Et)_2$ or pyridine, three different Lewis acid-base adducts are obtained, as may be seen from the Fig. 1. From NMR spectroscopic measurements as well as from X-ray structure



$((Ph_2Si)_2O_3)_4Al_4(OH)_4$ $*2NEt_3$
2

$((Ph_2Si)_2O_3)_4Al_4(OH)_4$ $*3OEt_2$
3

$((Ph_2Si)_2O_3)_4Al_4(OH)_4$ $*4py$
4

Atom connections from X-ray-structure determinations. The penyl groups on the silicon atoms are omitted for clarity. The dashed lines represent hydrogen bridges (hydrogen atoms not drawn).

FIGURE 1 Polycyclic skeletons of the three molecules **2**, **3**, **4**[3]

analyses it is evident, that **1** is accepting either two $N(Et)_3$, three $O(Et)_2$ or four pyridine molecules, respectively, to coordinate to the protons of the four OH-groups of the molecule **1** forming compounds **2**, **3** and **4**. A detailed inspection of the X-ray structure results on these molecules as well as molecular mechanics simulations[4] reveal that the steric requirements of the bases (which is decreasing in the order: $N(Et)_3 > O(Et)_2 > C_5H_5N$) as well as the molecular holes inside the polycycle **1** govern the number of coordinating bases and their structural positions with repect to the hosting molecule.

The different Lewis basicities have an important influence on the bonding of the basic centers of the coordinating molecules to the hydrogen atoms of the hydroxyl groups. The Al-O(H) distances within the inner eight membered cycles in the series **3**, **4**, **2** reflect this nicely

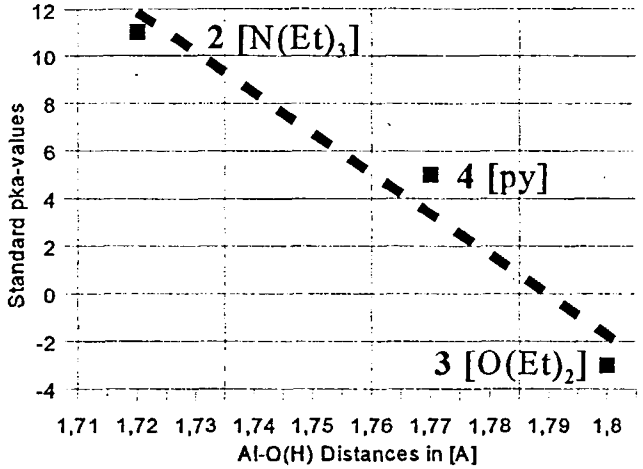


FIGURE 2 Dependance of Al-O(H)-distances [Å] from standard pk$_a$ values of N(Et)$_3$, C_5H_5N and O(Et)$_2$

as they decrease with increase of the basicity of the base under consideration taking standard pk$_a$ values as reference (see Fig. 2). On the same line the hydrogen atoms seem to shift more and more from the oxygen atoms of the hydroxyl groups to the nitrogen or oxygen atoms of the amine or ether which participate in the hydrogen bridges. This may finally end in a proton transfer as can be deduced from the very short Al-O($H_{coordinated}$) distances in 4 [1.72 Å, Al-O(H_{free}) 1.83 Å!], and there is also spectroscopic evidence[1] that the molecular complex 4 should be better formulated as an ion pair $\{[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2\}^{2-}$ $2\{H\text{-}N(Et)_3\}^+$. Interestingly the O---O respectively O---N distances correlate with the steric bulk of the organic bases (**2**: 2.72 Å, **3**:2.62 Å, 4:2.55Å), whereas the Al-O(H) distances are not affected.

HYDROGEN/LITHIUM EXCHANGE IN COMPOUND 1

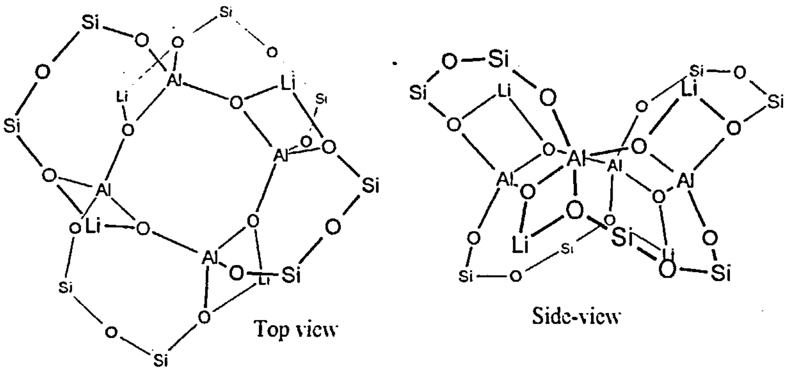
As can be anticipated from the reactions of **1** with organic bases (see above) treatment of **1** with strong organic nucleophiles like phenyllithium should lead to abstraction of the hydrogen atoms on the hydroxyl groups and the formation of the corresponding lithium compounds. This approach is working well, if certain conditions as low temperature and dilute solutions of **1** in diethylether are respected[2]. The results are assembled in Fig. 3.

Hydrogen/metal exchange

Synthesis of compound 5:

$$\underset{1}{((Ph_2Si)_2O_3)_4Al_4(OH)_4} + 4\,LiPh \xrightarrow[+4OEt_2\ (-4\ C_6H_6)]{} \underset{5}{((Ph_2Si)_2O_3)_4Al_4O_4Li_4{*}4OEt_2}$$

Structure of the backbone of compound 5 (phenyl and ether molecules omitted):



Top view

Side-view

FIGURE 3 Synthesis and structure of compound **5**

The lithium compound **5** contains four lithium atoms; thus all hydrogen atoms of hydroxyl groups in the starting compound **1** have been replaced by lithium atoms. Each litium atom in compound **5** (X-ray structure determination) has a further diethylether molecule bonded to it, the coordination sphere at the lithium atoms being almost trigonal planar by the interaction of three oxygen atoms. The molecule has crystallographic S_4 symmetry and is constituted of a central eight membered Al_4O_4 ring, to which four four membered LiO_2Al rings and four eight membered $Al_2Si_2O_4$ rings are fused (the compound contains nine cycles alltogether). It should be mentioned that no rearrangement of the parent polycycle is observed during the hydrogen/lithium exchange. The compound **5** can be formulated also as $[(Ph_2Si)_2O_2]_4(LiAlO_2)_4$ which shows its close relationship to lithiumalumosilicates. The molecular skeleton of **5** is remarkably stable as the coordinating ether molecules can be partly replaced even by very reactive bases like NH_3 without destroying the polycycles: $[(Ph_2Si)_2O_3]_4Al_4\,(OLi\,)_4{*}3O(Et)_2{*}2NH_3$, **6**, is obtained which contains two lithium atoms coordinated by diethylether, one by NH_3 and another one by one diethylether and one NH_3 molecule as follows from X-ray diffraction determination. One of the lithium atoms is thus almost tetrahedrally coordinated by three oxygen and one nitrogen atom.

REACTION OF 1 WITH WATER

As we have seen above the steric requirements of Lewis bases like diethylether or triethylamine versus the polycycle **1** seem to prevent from the attack to the Lewis acidic aluminium atoms. The attack of the bases, instead, is restricted to the hydrogen atoms of the hydroxyl groups to which they form hydrogen bridges. This could of course be different for smaller Lewis bases like water, which could either attack the OH-groups or the aluminium atoms.(see also Fig. 4). Furthermore water could facilitate proton transfer.

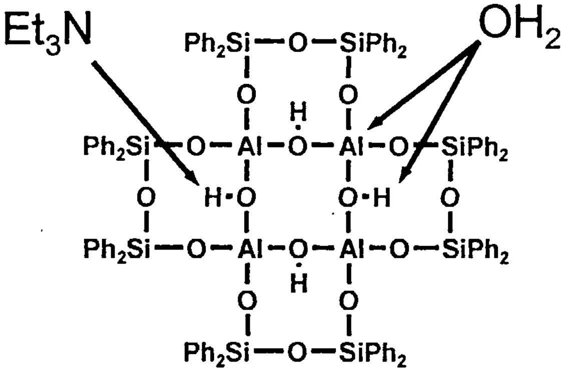
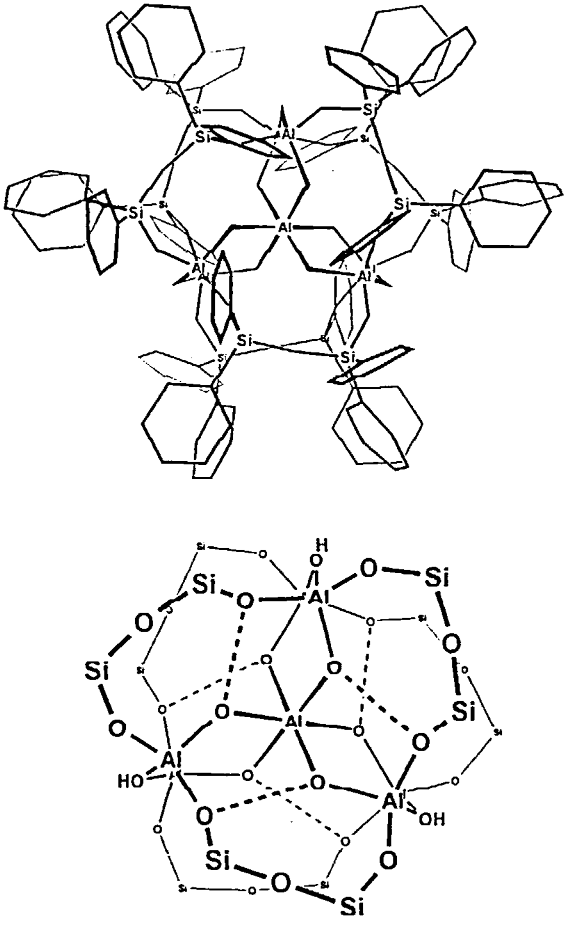


FIGURE 4 Different pathways for the base attack of H_2O compared to $N(Et)_3$ at acidic sites in molecule 1

We have slowly added a saturated solution of water in toluene to the ether adduct of 1. After several days we almost got a quantitative yield of colourless crystals which seemed to have a different Al/Si ratio compared to 1 (0.6 compared to 0.5). The X-ray structure determination on single crystals revealed an unprecedented polycyclic molecular alumosiloxane 7 with the composition $[(Ph_2Si)_2O_3]_6Al_6(OH)_3[Al(OH)_6]*3O(Et)_2$. The molecule has almost D_3 symmetry in the crystal and may be described by several models, one approach being discussed in more detail in the following.

In Fig. 5 a general view of the polycycle 7 as well as of the skeleton of the main atoms is given (omitting the diethylether molecules which are coordinated to the three bridging OH groups), while Fig. 6 shows the OH interactions in the molecule 7.



$[(Ph_2Si]_2O_3]_6Al_6(OH)_3[Al(OH)_6] * 3O(Et)_2$

FIGURE 5 Graphic representation of the molecular structure of compound 7 (above: general view, below: skeleton). The ether molecules are not drawn in each case. The dashed lines represent the hydrogen bridges.

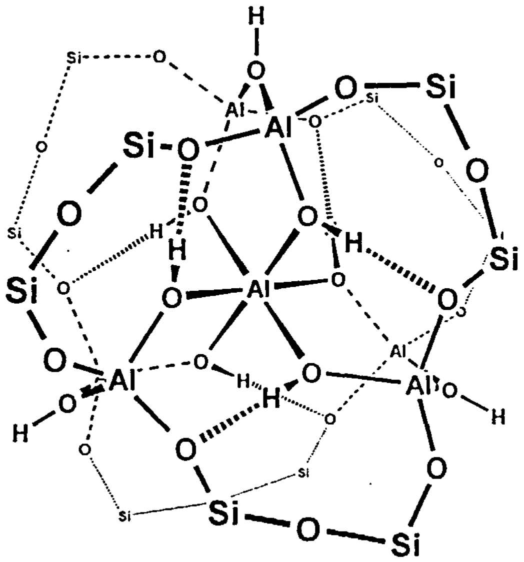


FIGURE 6 Hydrgen bridges O---H-O within the skeleton of polycycle of 7

From inspection of Fig. 5 and 6 the following description of the molecular structure can be given: there are two identical eighteen membered $Al_3Si_6O_9$ cycles which are connected at the aluminium sites through oxygen bonding via three OH groups with terminal hydrogen atoms, to each of which a diethylether molecule is coordinnated (not drawn in the figures). The molecular formula of this part of the molecule is $[(Ph_2Si)_2O_3]_6Al_6(OH)_3*3O(Et)_2$ and its formal charge is 3+. This part of the molecule is reminiscent of the starting compound 1 which also has the $[(Ph_2Si)_2O_3]$ hemicycles and the connecting aluminium atoms. The second part of the molecule is made up of an isolated aluminium atom which is in the center of an octahedron of hydroxyl groups. This entity has a formal charge of 3- and is linked to the six aluminium atoms of the first part of the molecule through oxygen bonding. Furthermore the hydrogen atoms of the hydroxyl groups are bridging to oxygen atoms of the eighteen membered rings (see Fig.6). On this line the macrocyclic molecule **7** may be described as a molecular complex of $[Al(OH)_6]^{3-}$ in a hole of a cationic cage-like alumopolysiloxane.

Acknowledgments

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