

Full paper / Mémoire

New types of alumosiloxanes by the reaction of the bicyclic compound $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ with water in the presence of donor ligands – A status report

Michael Veith^{a,b,*}, Fadime Şahin^a, Andreas Rammo^a, Volker Huch^a

^a Institute of Inorganic Chemistry, University of Saarland, P.O. Box 15 11 50, 66041 Saarbrücken, Germany

^b INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany

Received 4 December 2008; accepted after revision 10 June 2009

Available online 15 July 2009

Abstract

The selective synthesis of new types of alumosiloxanes can be achieved by the reaction of the bicyclic compound $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) with water in donor solvents like acetone or THF, leading to the polycyclic THF adduct $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**), and to the polycyclic alumosiloxane $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**), respectively. In the presence of the base triethylamine, the starting compound **3** gives rise to two other condensation products. At medium temperatures (50–60 °C) in toluene the dispiro “alumosilicate” $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH} \cdot \text{NEt}_3]\}_2$ (**9**) is formed and at higher temperatures under reflux in toluene, the product $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH} \cdot \text{NEt}_3]$ (**10**) is generated. The spirocyclic compounds **9** and **10** present the first isolated “alumosilicates” with six-membered $\text{O}(\text{SiO})_2\text{Al}$ cycles. These new types of alumosiloxanes and “alumosilicates” have been characterised by spectroscopic methods as well as by single crystal X-ray analyses. **To cite this article:** M. Veith et al., *C. R. Chimie* 12 2009.

© 2009 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

La synthèse sélective de nouveaux types d'alumosiloxanes peut être réalisée par la réaction du composé bicyclic $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) avec l'eau dans des solvants donneurs tels que l'acétone et le THF formant respectivement, l'adduit du THF d'un nouveau polycyclique $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**) et l'alumosiloxane polycyclique $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**). En présence de la base triéthylamine, le composé de départ **3** produit deux composés de condensation. A température modérée, dans le toluène, le dispiro « alumosilicate » $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH} \cdot \text{NEt}_3]\}_2$ (**9**) est formé, et à haute température, sous reflux du toluène, le produit $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH} \cdot \text{NEt}_3]$ (**10**) est créé. Les composés spirocycliques **9** et **10** sont les premiers « alumosilicates » isolés avec six membres cycliques $\text{O}(\text{SiO})_2\text{Al}$. Ces nouveaux types d'alumosiloxanes et d'« alumosilicates » ont été caractérisés par des méthodes spectroscopiques et également par diffractions aux rayons X. **Pour citer cet article :** M. Veith et al., *C. R. Chimie* 12 2009.

© 2009 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

* Corresponding author. INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany.

E-mail address: michael.veith@inm-gmbh.de (M. Veith).

Keywords: Alumosiloxanes; Polycyclic alumosiloxanes; Cyclo alumosiloxanes; Alumosilicates; Cyclo alumosilicates; Siloxanes; Cyclosiloxanes

Mots-clés : alumosiloxanes ; alumosiloxanes polycycliques ; cyclo alumosiloxanes ; alumosilicates ; cyclo alumosilicates ; siloxanes ; cyclosiloxanes

1. Introduction

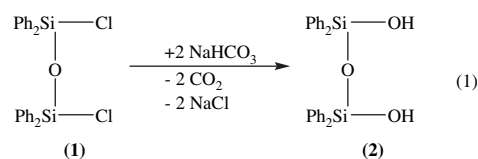
In recent years, several soluble alumosiloxanes have been prepared and successfully employed as homogeneous models for alumosilicates and zeolites [1,2]. Suitable starting materials for the synthesis of cyclic alumosiloxanes and - oxides are $\text{Ph}_2\text{Si}(\text{OH})_2$ and $(\text{HO})\text{SiPh}_2\text{OSiPh}_2(\text{OH})$, which readily react under self-condensation and/or ring expansion with aluminium alkyls and hydrides to afford mainly eight-membered spirocyclic or polycyclic compounds [3–6].

As we have already reported in detail, the polycyclic alumosiloxane $[\text{Ph}_2\text{SiO}]_8[\text{Al}(\text{O})\text{OH}]_4 \cdot 4 \text{Et}_2\text{O}$ can be obtained by the reaction of diphenylsilanediol with *tert*-butoxyalane [7] in diethylether as solvent [3]. As could be determined from single crystal X-ray analysis, an $\text{Al}_4(\text{OH})_4$ eight-membered ring in the centre of the molecular structure is coordinated by four disiloxane semicircles formed by condensation [4,8]. By using the reaction of *tert*-butoxyalane with $(\text{HO})\text{SiPh}_2\text{OSiPh}_2(\text{OH})$, we were able to isolate the bicyclic alumosiloxane $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**). Any analogy or difference in the reaction behaviour of the compound $[\text{Ph}_2\text{SiO}]_8[\text{Al}(\text{O})\text{OH}]_4 \cdot 4 \text{Et}_2\text{O}$ with Lewis bases like water or ammonia leading to various new polycyclic alumosiloxanes like $[(\text{Ph}_2\text{Si})_2\text{O}_3]_6(\text{OH})_3[\text{Al}(\text{OH})_6] \cdot 3 \text{Et}_2\text{O}$ [9] or $\{(\text{Ph}_2\text{SiO})_{12}[\text{Al}_5\text{O}_7(\text{OH})][\text{Al}(\text{OH})_2(\text{NH}_3)_2] \cdot \text{Et}_2\text{O}\}^-$ [8–10], compared to **3**, seemed to us of major interest. In this paper, we present our results concerning the reaction of **3** in different donor solvents in the presence and absence of water.

2. Reaction of the bicyclic compound $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) with water in the presence of donor ligands

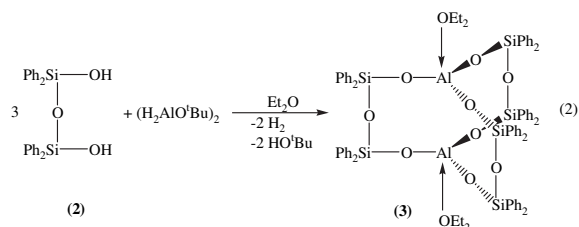
The starting compound, the bicyclic alumosiloxane $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**), can easily be obtained in a two-step reaction. In a solvent mixture of acetone and toluene, first the chloro substituents of 1,3-dichloro-1,1,3,3-tetra-phenyl-disiloxane (**1**) are replaced by hydroxyl groups. This reaction is carried out without direct water contact. To form the hydroxyl groups, sodium hydrogenocarbonate is used. In a salt

elimination reaction, sodium chloride and carbon dioxide are released (Eq. (1)).



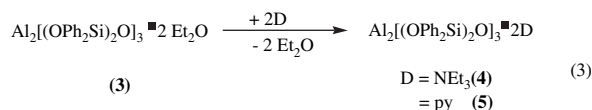
The pure 1,3-disiloxane **2** may be obtained either in crystalline form by concentration of the mother liquor or as a powder after removing the solvent under reduced pressure.

In the second step, the so formed 1,3-disiloxane is allowed to react with *tert*-butoxyalane. During a slow dropwise addition of the alane in diethylether, a strong development of hydrogen is observed (Eq. (2)).



The best yields of $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) (45%) are found when the reaction is not carried out in stoichiometric amounts as shown in Equation (2) but within double the amount of **2**.

In water free solvents, both diethylether molecules coordinating the Lewis-acidic aluminium in $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) can easily be substituted by nitrogen containing bases like triethylamine (yield: 76%) (Fig. 1) or pyridine (yield: 48%) (Eq. (3)).



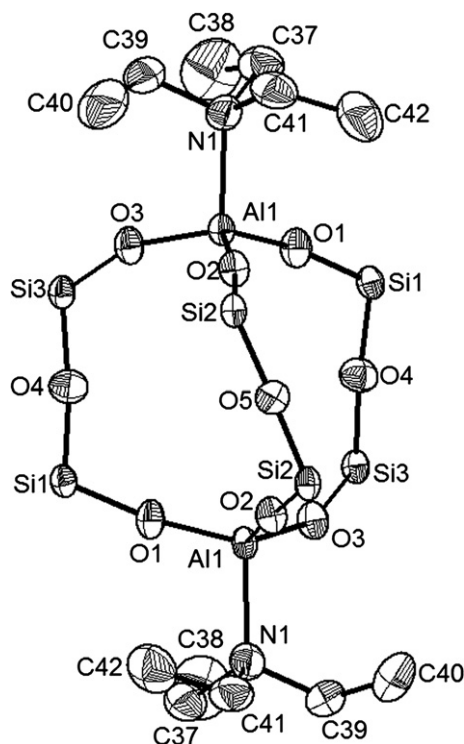


Fig. 1. The molecule structure of $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{NEt}_3$ (**4**) as determined by X-ray diffraction techniques. Thermal ellipsoids are plotted at the 50% level. Phenyl substituents at silicon and hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: Al(1)–O(1) 1.703(2), Al(1)–O(2) 1.700 (2), Al(1)–O(3) 1.706(2), Al(1)–N(1) 2.002(2), Si–O(Al) (av.) 1.597(3), Si–O(Si) (av.) 1.619(2), O(2)–Al(1)–O(1) 114.70(2), O(2)–Al(1)–O(3) 114.03(2), O(1)–Al(1)–O(3) 113.85(2), Si(1)–O(4)–Si(3') 173.09(2), Si(2)–O(5)–Si(2') 168.47(2), O–Si–O (av.) 111.28(1).

All donor stabilized compounds **3**–**5** have exact elemental analyses. Recorded CP-MAS NMR spectra show the expected ^{29}Si NMR shifts at -47.4 (**4**), -48.1 (**5**) compared to -50.7 ppm for the diethylether coordinated bicyclic **3**.

In Fig. 1, the molecular structure of the compound $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{NEt}_3$ (**4**) is shown as a representative for the donor adducts of the bicyclic $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{D}$ ($\text{D} = \text{Et}_2\text{O}$ (**3**), $^1\text{NEt}_3$ (**4**)² and py (**5**)³).

The skeleton of $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{NEt}_3$ (**4**) consists of a cage which is deduced from

a bicyclo[2.2.2]octane in which the two aluminium atoms take up the bridging positions and are connected by three disiloxane semicircles. A similar compound with the lighter homologous boron atoms in the place of the aluminium positions has already been described [11]. As expected, the most significant differences can be found in the coordination sphere of the homologous atoms boron and aluminium. Boron is able to form intramolecular back donations with the neighbouring oxygen atoms, resulting in a trigonal planar BO_3 coordination which needs no further base stabilisation despite the trigonal coordination sphere. The aluminium atoms however compensate their electron deficiency by formation of an additional coordination with triethylamine leading to a distorted tetrahedral coordination environment. The O–Al–O angles have an average value of $114.2(1)^\circ$ and the Al–O bonding lengths are well comparable to literature known values [5,12]. The O–Si–O–Si–O semicircles are strongly twisted. The shorter Si–O distances with an average value of $1.60(1)$ Å are found in the Al–O–Si groups (Si1–O1, Si2–O2, Si3–O3) whereas the longer ones are located in the Si–O–Si fragments (Si1–O4, Si2–O5, Si3–O4) with $1.619(2)$ Å on average.

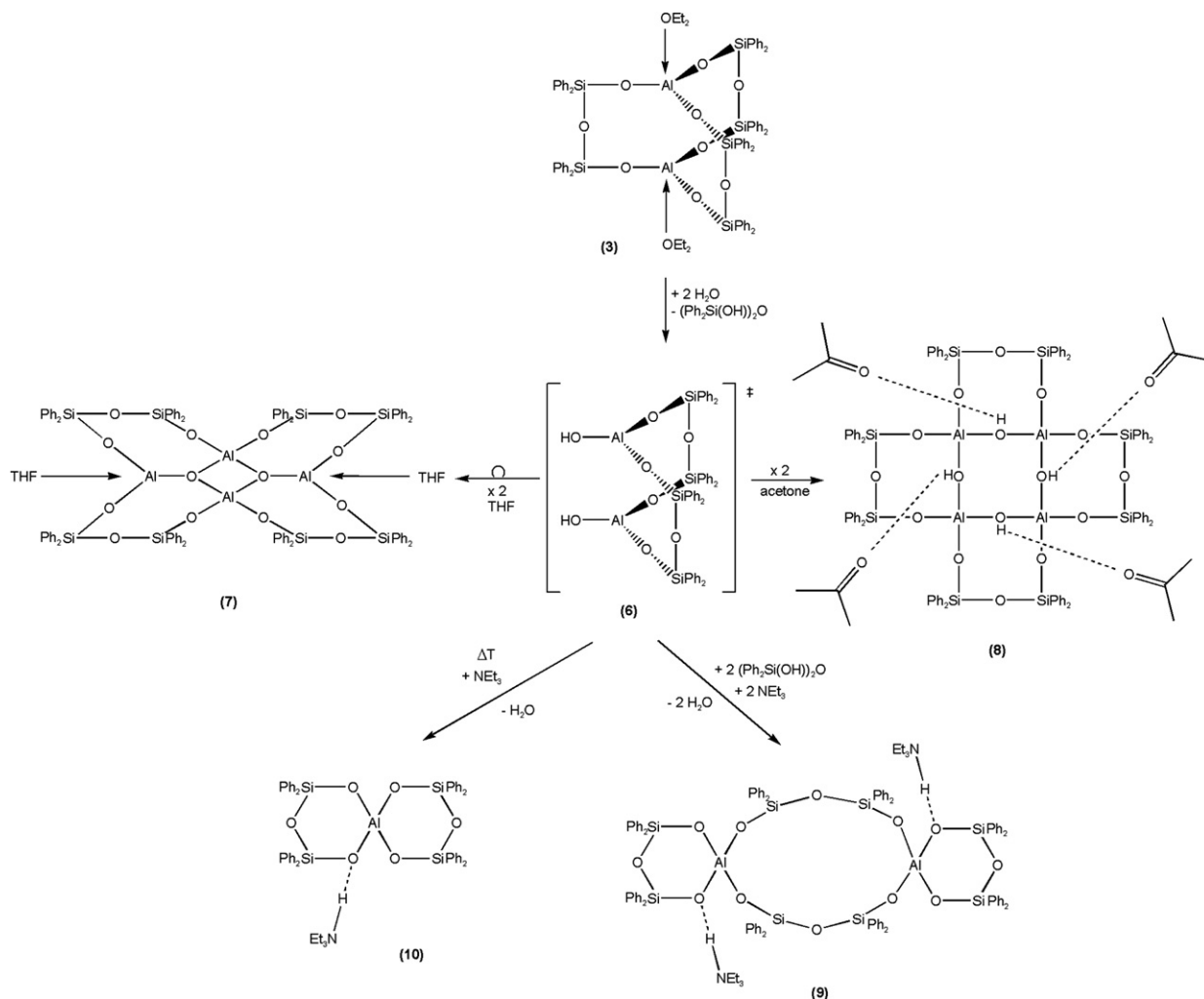
The ethyl groups of the triethylamine donor molecules take a staggered confirmation. Although triethylamine ($\text{p}K_{\text{a}} = 10.8$) presents a stronger Lewis base than pyridine ($\text{p}K_{\text{a}} = 5.2$) [13], interestingly in $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{NEt}_3$ (**4**) the Al1–N1 distances with $2.002(2)$ Å are longer than in $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{py}$ (**5**) with $1.974(4)$ Å on average.³ This fact can be easily explained by the more sterical hindrance of triethylamine. In **4**, the triethylamine groups show more sterical interactions with the phenyl groups at the silicon atoms compared to the plane pyridine molecule in **5**, as may be seen from closer inspection of the structures.

An overall view of the reactions of compound $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) with water is shown in Scheme 1 which summarizes our findings and proposes an intermediate $[(\text{Ph}_2\text{SiO})_2\text{O}]_2[\text{Al}(\text{OH})_2]$ (**6**) which could explain the different reaction products. The rearrangement reactions of $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) leading to $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**) and $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**) can most likely be

¹ $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**), $\text{C}_{80}\text{H}_{80}\text{Si}_6\text{O}_{11}\text{Al}_2$, 1439.94 g/mol, triclinic, Space group *P*-1, $a = 14.511(3)$ Å, $b = 14.494(3)$ Å, $c = 22.233(4)$ Å, $\alpha = 70.815(9)^\circ$, $\beta = 71.463(9)^\circ$, $\gamma = 60.000(8)^\circ$, $V = 3756.6(11)$ Å³, $Z = 2$, 21 932 reflections, 896 parameters, $R = 0.2750$ ($R_w = 0.5767$) (due to the disorder of the molecule in the crystal).

² $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{NEt}_3$ (**4**), $\text{C}_{84}\text{H}_{90}\text{Al}_2\text{N}_6\text{O}_9\text{Si}_6$, 1494.08 g/mol, monoclinic, space group *C*2/c, $a = 25.3630(7)$ Å, $b = 14.5394(3)$ Å, $c = 23.3481(7)$ Å, $\beta = 114.818(2)^\circ$, $V = 7814.7(4)$ Å³, $Z = 4$, 74 509 reflections, 480 parameters, $R = 0.0568$ ($R_w = 0.1540$).

³ $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{pyr}$ (**5**), $\text{C}_{82}\text{H}_{70}\text{Al}_2\text{N}_2\text{O}_9\text{Si}_6 \cdot \frac{1}{2} \text{C}_7\text{H}_8$, 1495.97 g/mol, monoclinic, space group *C*2/c, $a = 24.7042(7)$ Å, $b = 14.1960(3)$ Å, $c = 45.1013(11)$ Å, $\beta = 98.053(3)^\circ$, $V = 15661.1(7)$ Å³, $Z = 8$, 119 128 reflections, 1077 parameters, $R_1 = 0.0824$ ($R_w = 0.1645$).



Scheme 1. Overall view of the reaction of compound **3**, $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$, with donor solvents in the presence of water.

understood by the presence of water. First a molecule disiloxane-1,3-diol is cleaved from **3** and substituted by a hydroxyl group at each aluminium atom. Starting from this intermediate $[(\text{Ph}_2\text{SiO})_2\text{O}]_2[\text{Al}(\text{OH})_2]$ (**6**), the stoichiometries and structures of the subsequently formed products **7–10** can be easily rationalised. When the reaction of $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) is carried out in acetone as solvent, two molecules of **6** dimerise to form the oligoalumosiloxane $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH})_4)] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**) (yield: 33%) (Fig. 2),⁴ whereas in THF, the

polycycle $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**) (yield: 44%) (Fig. 3)⁵ is formed through condensation and rearrangement of two entities of **6**.

In a recent publication [14] we presented the synthesis and the molecular structure of compound $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{py}$ showing the same isostructural skeleton as the molecule $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**) (Fig. 3). With the exception of the different donor atoms, both molecules show comparable bond lengths and bond angles. As shown by single crystal X-ray analysis,

⁴ $(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4 \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**), $\text{C}_{108}\text{H}_{108}\text{Al}_4\text{O}_{20}\text{Si}_8$, 2058.58 g/mol, tetragonal, space group *I*-4, $a = 18.850(3) \text{ \AA}$, $b = 18.850(3) \text{ \AA}$, $c = 15.460(4) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 5493.1(19) \text{ \AA}^3$, $Z = 2$, 52 727 reflections, 332 parameters, $R = 0.0265$ ($R_w = 0.0658$).

⁵ $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 4 \text{THF}$ (**7**), $\text{C}_{112}\text{H}_{120}\text{Al}_4\text{O}_{18}\text{Si}_8$, 2086.72 g/mol, triclinic, space group *P*-1, $a = 13.1656(15) \text{ \AA}$, $b = 15.1942(17) \text{ \AA}$, $c = 15.6210(18) \text{ \AA}$, $\alpha = 69.616(4)^\circ$, $\beta = 80.353(5)^\circ$, $\gamma = 66.087(4)^\circ$, $V = 2676.5(5) \text{ \AA}^3$, $Z = 1$, 39 619 reflections, 628 parameters, $R_1 = 0.0639$ ($R_w = 0.1751$).

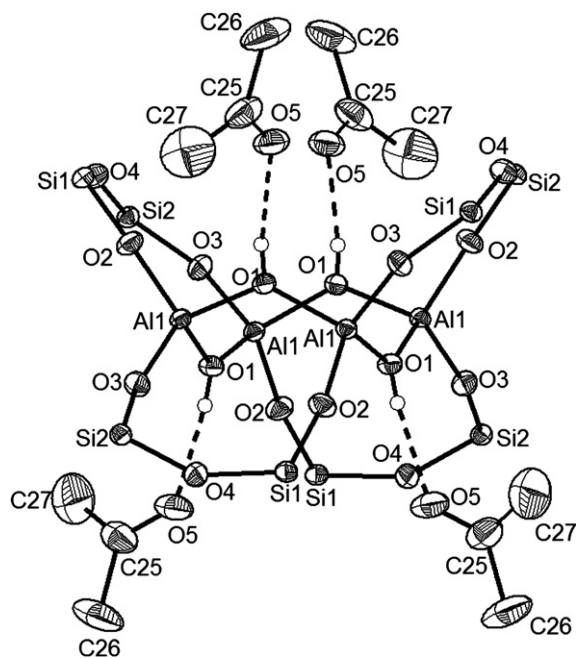


Fig. 2. The molecule structure of $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**) as determined by X-ray diffraction techniques. Thermal ellipsoids are plotted at the 50% level. Phenyl substituents and hydrogen atoms are omitted for clarity. Selected bond length [\AA] and angles [deg]: Al(1)–O(1) 1.792(2), Al(1)–O(2) 1.698(2), Al(1)–O(3) 1.707(2), O(5)–C(25) 1.214(2), C(25)–C(27) 1.474(3), C(25)–C(26) 1.508(2), O(2)–Al(1)–O(1) 108.85(1), O(2)–Al(1)–O(3) 117.10(2), O(3)–Al(1)–O(1) 106.66(2), O(2)–Si(1)–O(4)' 111.53(2), O(3)–Si(2)–O(4) 113.15(2), Si(1)–O(2)–Al(1) 170.25(2), Si(2)–O(3)–Al(1) 158.01(2), Si(2)–O(4)–Si(1)' 147.87(2).

7 presents a polyalumosiloxane of point symmetry i ($\bar{1}$), whose centre is formed of a planar (angle sum 180°) four-membered Al_2O_2 ring [14], which often can be found as bridging unit between silsesquioxanes [15,16]. From a formal point of view, $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**) can be described as a polycycle, in which four $\text{Al}_2\text{O}_4\text{Si}_2$ eight-membered rings are connect at two common aluminium corners with the peculiarity that always two rings are fused at a common Al–O edge. As expected, the highest amount of ring strain occurs in the central four-membered Al_2O_2 ring at the aluminium atoms. Whereas the O1–Al2–O1 angle is $85.59(7)^\circ$, the Al2–O1–Al2' angle has a value of $94.40(1)^\circ$. The Al2–O1 and the Al2'–O1 distances of the central Al_2O_2 ring average to a bond length of $1.804(3) \text{\AA}$. Apparently, there is a strong dilatation in comparison to the Al1–O1 bond in **7** with $1.743(2) \text{\AA}$. The bond length of the donor–acceptor–interaction between aluminium and the oxygen atom of the THF molecule has a value of $1.847(2) \text{\AA}$ corresponding to comparable bond lengths of other Al–O interactions [17–19]. The endocyclic oxygen atoms (O1 and O1') are in the centres of the triangles formed by

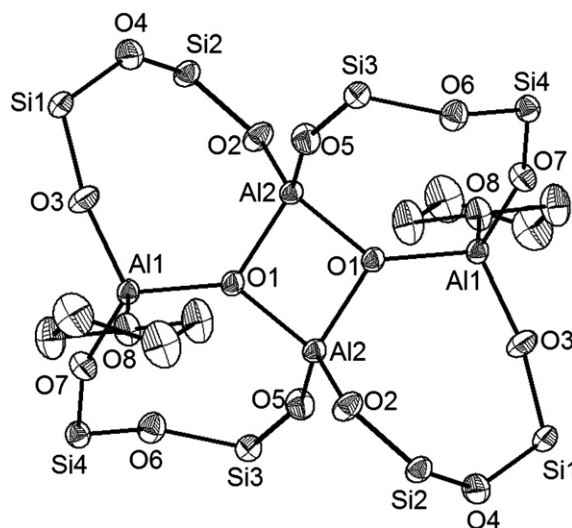


Fig. 3. X-ray diffraction of compound $[(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4] \cdot 2 \text{THF}$ (**7**). Thermal ellipsoids are plotted at the 50% level. Phenyl substituents and hydrogen atoms are omitted for clarity. Selected bond length [\AA] and angles [deg]: Al(1)–O(1) 1.743(2), Al(1)–O(7) 1.692(2), Al(1)–O(8) 1.847(2), Al(2)–O(1) 1.804(2), Al(2)–O(1') 1.804(2), Al(2)–O(5) 1.698(2), Si(3)–O(5) 1.602(2), Si(3)–O(6') 1.637(2), Si(4)–O(6) 1.633(2), Si(4)–O(7) 1.601(2), O(1)–Al(2)–O(1') $85.60(2)$, Al(2)–O(1)–Al(2') $94.40(2)$, O–Si–O (av.) $111.19(2)$.

the aluminium atoms (Al1, Al2 and Al2') and show an almost trigonal planar coordination sphere (sum of Al–O–Al angles: $359.2(1)^\circ$).

In the presence of water, the bicyclic $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3 \cdot 2 \text{Et}_2\text{O}$ (**3**) surprisingly reacts in acetone as solvent to the pentacyclic molecule $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**) (Fig. 2). This molecular alumpolysiloxane $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4]$, which forms the centre of the molecule has been synthesized long time ago by the reaction of diphenylsilanediol and *tert*-butoxyalane in diethylether [3]. The structure of $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4]$ and its reactivity have already been described in detail in former publications [4,8,9,14,20,21]. The single crystal X-ray determination of $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**) shows that four acetone molecules interact with the hydrogen atoms of the central Al(OH)-groups by formation of hydrogen bridges (Fig. 2). To ethers, amine alcohols and other donors, we have thus added another representative in the form of a ketone [9].

Compound $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**) has S_4 point symmetry in the crystal as has $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4] \cdot 4 \text{py}$ [4].

The description of acetone acting as a simple donor may be seen from the carbon–oxygen (C25–O5) distance of $1.214(2) \text{\AA}$ which is typical for a C=O double bond in the coordinating acetone molecules. As

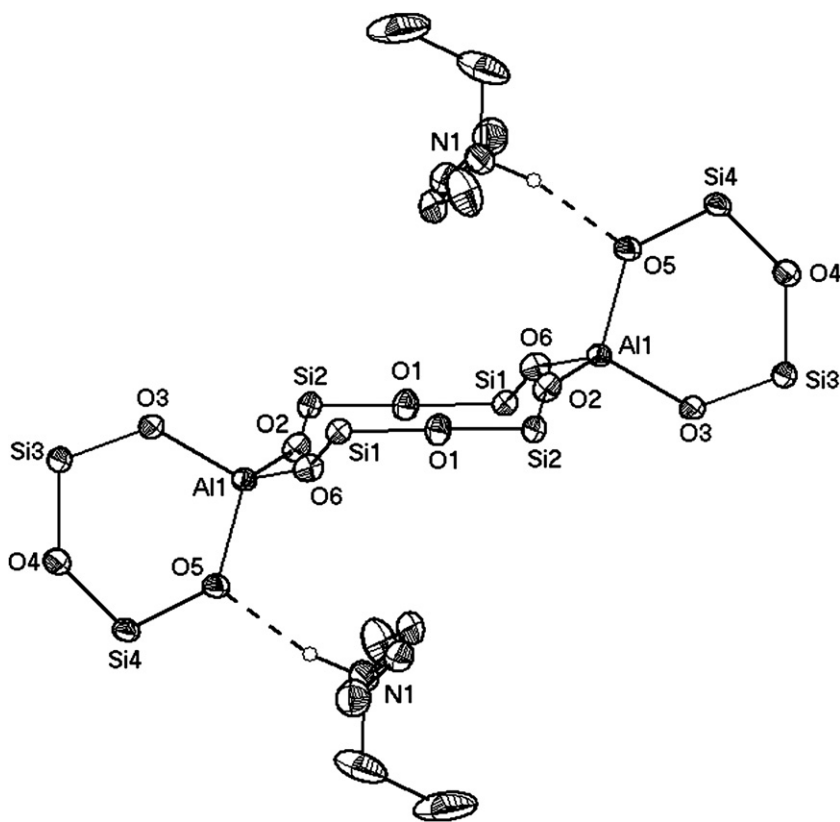


Fig. 4. Molecule structure of compound **9**, $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]\}_2$, determined by X-ray diffraction techniques. Thermal ellipsoids are plotted at the 50% level. Phenyl substituents and hydrogen atoms are omitted for clarity. Selected bond length [\AA] and angles [deg]: Al(1)–O(2) 1.727(1), Al(1)–O(3) 1.744(1), Al(1)–O(5) 1.788(1), Al(1)–O(6') 1.724(1), Si(1)–O(6) 1.599(1), Si(3)–O(3) 1.604(1), Si(4)–O(5) 1.626(1), Si–O(1) (av.) 1.629(1), Si–O(4) (av.) 1.642(1), O(2)–Al(1)–O(3) 111.81(2), O(3)–Al(1)–O(5) 105.22(2), O(6')–Al(1)–O(2) 108.94(2), Si(2)–O(1)–Si(1) 159.59(8), Si(3)–O(3)–Al(1) 130.82(7), Si(4)–O(4)–Si(3) 131.29(2), Si(4)–O(5)–Al(1) 129.86(2).

the C–C bonds vary quite remarkably from C25–C26 with 1.508(2) \AA to C25–C27 value with 1.474(3) \AA , we looked for further verification of our structural description. To find out if the acetone molecules interact through their keto form or through their enol form, IR- and CP-MAS spectra were recorded. Both spectra give evidence of the presence of the acetone molecule in its keto form: in the IR spectrum, the typical keto absorbance occurs at 1689 cm^{-1} . In the recorded ^{13}C -CP-MAS spectrum, the carbon resonances appear at 27.9 ppm for the carbon atoms of the methyl groups and only one signal occurs at 212.7 ppm for the sp^2 -hybridized C25(O) atom. In the case of a C=C double bond, three ^{13}C signals should occur: one in the range of 0–35 ppm for a methyl group and two signals in the range of 80–180 ppm for the methylene group and the quaternary carbon atom, respectively [22].

The C=O \cdots HO(Al) distances of 2.627(6) \AA , which are comparable to C=O \cdots HO interactions between acetone and alcohols [23–27], indicate relatively

strong oxygen–hydrogen bonds [28] leading to similar Al1–O1 and Al1–O1' distances (1.792(9) and 1.796(9) \AA) in the central $\text{Al}_4(\text{OH})_4$ eight-membered ring of molecule $[(\text{Ph}_2\text{SiO})_8(\text{AlO}(\text{OH}))_4]\cdot 4 \text{Me}_2\text{C}=\text{O}$ (**8**). According to the point symmetry in the crystal structure, only one ^{29}Si NMR signal occurs in the CP-MAS spectrum at -45.6 ppm, consistent with ^{29}Si shifts in similar alumosiloxane compounds [3,4].

Usually, in order to circumvent the ring strain energy, alumosiloxane chains form at least eight-membered cycles. So the strain energy of six-membered cyclo-siloxanes is 16–21 kJ mol^{-1} , while cyclotetrasiloxanes and larger ring systems have almost no strain energy [29,30].

Apart from some halogen substituted alumosiloxanes [31–34], highly strained five- and six-membered cycles with oxygen, aluminium and silicon are only known using di- and trisilane units [6,31,33]. We have now found that the starting compound $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3\cdot 2 \text{Et}_2\text{O}$ (**3**) may be transformed to two new and original condensation

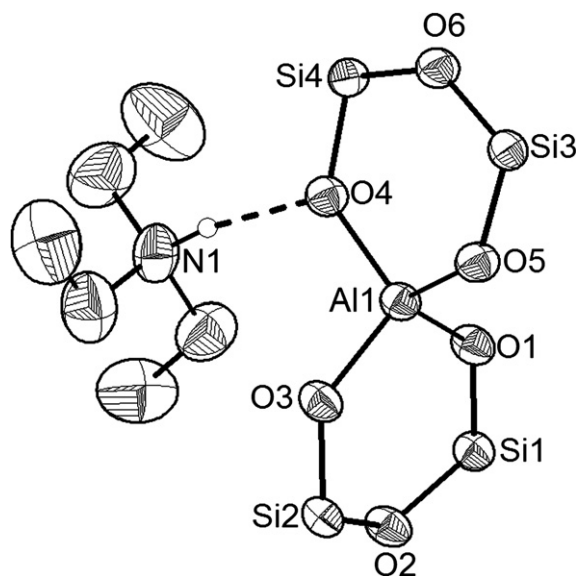


Fig. 5. The molecule structure of compound **10**, $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]$, determined by X-ray diffraction techniques. Thermal ellipsoids are plotted at the 50% level. Phenyl substituents and hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: Al(1)–O(1) 1.744(2), Al(1)–O(3) 1.745(2), Al(1)–O(4) 1.773(2), Al(1)–O(5) 1.740(2), Si(4)–O(4) 1.628(2), Si–O(Al) (av.) 1.605(3), Si–O(Si) (av.) 1.641(4), O(1)–Al(1)–O(3) 105.89(2), O(3)–Al(1)–O(4) 109.61(2), O(5)–Al(1)–O(1) 110.89(2), O(5)–Al(1)–O(4) 106.55(2).

products in the presence of the base triethylamine. At low temperatures (50–60 °C) in toluene, the dispiro “alumosilicate” $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]\}_2$ (**9**) (yield: 57%)⁶ is formed (Fig. 4), whereas at higher temperatures under reflux in toluene, the product $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]$ (**10**) (yield: 77%)⁷ (Fig. 5) is generated (see Scheme 1).

The compound $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]$ (**10**) is a spirocyclic “alumosilicate” in which two $(\text{Ph}_2\text{SiO})_2\text{O}$ chains are connected by a central aluminium atom. The dihedral angle between the two six-membered rings is almost 90° (88.4(1)°). The O–Al–O angles range from 105.9(1)° (O1–Al1–O3) to 113.2(1)° (O3–Al1–O5) and are comparable to other alumo spiro silicate compounds like $[\text{PyH}]\{\text{Al}[\text{OSiPh}_2(\text{OSiPh}_2)_2\text{O}]_2\}$ [5] or $[\text{HNEt}_3]\{\text{Al}[(\text{Cy}_7\text{Si}_7\text{O}_{12}(\text{SiMe}_3))_2]\}_2$ [35]. The negative charge of the spirocyclic $[(\text{O}–\text{SiPh}_2–\text{O}–\text{SiPh}_2–\text{O})_2\text{Al}]$

is compensated by a triethylammonium cation which is linked through a N–H···O hydrogen bridge to the oxygen atoms O(4) of the anion (N1···O4 = 2.842(1) Å) [5,6,35–37]. The coordination of the ammonium ion is accompanied by a slight elongation of the Al1–O4 (1.773(2) Å) and the Si4–O4 (1.628(2) Å) bonds, compared to the other three Al1–O(1,3,5) (av. 1.743(3) Å) and Si–O(Al) and Si–O(Si) bonds (Si1–O1, Si2–O3, Si3–O5) (av. 1.605(3) Å) [35,36].

The formation of compound $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]\}_2$ (**9**) can be rationalised by a ring opening reaction of the bicyclic $\text{Al}_2[(\text{OPh}_2\text{Si})_2\text{O}]_3\cdot 2\text{Et}_2\text{O}$ (**3**) and the addition of a further molecule of 1,3-dihydroxy-1,1,3,3-tetra-phenyl-disiloxane in the presence of triethylamine (see Scheme 1). By linking a six-, a twelve- and a six-membered ring through spirocyclic aluminium atoms, a molecule is created as shown in Fig. 4. Whereas the six-membered $\text{O}(\text{SiO})_2\text{Al}$ cycles almost form planar rings (sum of angles: 718.296°), the twelve-membered alumosiloxane ring is not planar (common to higher cyclic siloxane ring systems). As may be seen in Fig. 4, two Si1–O1–Si2 parts of the molecule are almost in a plane to which the $\text{O}_2\text{Al}(\text{OSi})_2\text{O}$ molecule fragments are arranged above and below. The molecule has a crystallographic inversion centre. The doubly charged anion is compensated by two triethylammonium cations. As found for **10**, the formation of an O–H···N bridge leads to a significant change in the Al–O (Al–O5 1.788(2) Å, av. 1.731(2) Å) bonds and to an elongation for the Si4–O5(Al) bond length found at 1.626(2) Å, compared to the Si3–O3(Al) bond length with 1.604(2) Å in the six-membered alumosiloxane ring. The second conspicuous fact is the influence of the more electropositive aluminium atom in comparison to the silicon atoms concerning the bond lengths in the six- and the twelve-membered rings. In the six-membered rings, the Si–O(Al) bonds (Si3–O3, Si4–O5) have an average length of 1.615(1) Å while the Si–O bond lengths in the disiloxane chain (Si3–O4, Si4–O4) have 1.642(1) Å on average. The same effect can be observed in the larger ring fragment. Whereas the Si–O(Al) bonds (Si1–O6, Si2–O2) show very short average lengths of 1.596(1) Å, the Si–O bond lengths in the Si1–O1–Si2 groups are significant longer (1.629(1) Å on average) [38].

⁶ $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]\}_2$ (**9**), $\text{C}_{108}\text{H}_{112}\text{Si}_8\text{O}_{12}\text{Al}_2\text{N}_2$, 1908.68 g/mol, triclinic, space group *P*-1, $a = 13.8375(3)$ Å, $b = 16.3265(4)$ Å, $c = 23.4351(5)$ Å, $\alpha = 91.1520(10)^\circ$, $\beta = 91.5570(10)^\circ$, $\gamma = 107.2190(10)^\circ$, $V = 5053.0(2)$ Å³, $Z = 2$, 98 220 reflections, 1203 parameters, $R = 0.0446$ ($R_w = 0.0993$).

⁷ $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]$ (**10**), $\text{C}_{54}\text{H}_{55}\text{AlNO}_6\text{Si}_4$, 953.35 g/mol, triclinic, space group *P*-1, $a = 14.4359(3)$ Å, $b = 18.7978(4)$ Å, $c = 18.9746(4)$ Å, $\alpha = 90.7510(10)^\circ$, $\beta = 90.0050(10)^\circ$, $\gamma = 94.9100(10)^\circ$, $V = 5129.67(19)$ Å³, $Z = 4$, 93 905 reflections, 1206 parameters, $R = 0.0542$ ($R_w = 0.1342$).

In both compounds $[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]\}_2$ (**9**) (Fig. 4) and $[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Al}[(\text{Ph}_2\text{SiO})_2\text{OH}\cdot\text{NEt}_3]$ (**10**) (Fig. 5), elemental C-, H- and N analyses of which have found to be correct, the recorded ^{29}Si -CP-MAS spectra clearly show differences due to the structural and electronic environments of the respective atoms. Chemical shifts for ^{29}Si -NMR are dependent upon the ring size, as becomes apparent from a deshielding of around 14 ppm being found in the six-membered rings compared to the twelve-membered ring in **9** (−39.3 and −53.6 ppm). In compound **10**, the coordination of triethylamine leads, as expected, to a splitting into three ^{29}Si -CP-MAS signals at −35.7, −39.2 and −53.3 ppm.

Acknowledgements

The authors gratefully acknowledge support by the Fonds der Chemischen Industrie as well as by the “Europäisches Graduiertenkolleg” GRK 532 financed by the Deutsche Forschungsgemeinschaft (DFG).

The authors hereby state that there are no conflicts of interest.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.crci.2009.06.003.

References

- [1] M.L. Montero, I. Uson, H.W. Roesky, *Angew. Chem.* 106 (1994) 2198; *Angew. Chem. Int. Ed.* 33 (1994) 2103.
- [2] M.L. Montero, A. Voigt, M. Teichert, I. Uson, H.W. Roesky, *Angew. Chem.* 107 (1995) 2761; *Angew. Chem. Int. Ed.* 34 (1995) 2504.
- [3] M. Veith, M. Jarzyk, V. Huch, *Angew. Chem.* 109 (1997) 140; *Angew. Chem. Int. Ed.* 36 (1997) 117.
- [4] M. Veith, M. Jarzyk, V. Huch, *Angew. Chem.* 110 (1998) 109; *Angew. Chem. Int. Ed.* 37 (1998) 105.
- [5] Y.K. Gun'ko, R. Reilly, V.G. Kessler, *New J. Chem.* 25 (2001) 528.
- [6] C. Krempner, H. Reinke, K. Weichert, *Organometallics* 26 (2007) 1386.
- [7] M. Veith, S. Faber, H. Wolfanger, V. Huch, *Chem. Ber.* 129 (1996) 381.
- [8] M. Veith, A. Rammo, M. Jarzyk, V. Huch, *Monatsh. Chem.* 130 (1999) 15.
- [9] M. Veith, M. Jarzyk, V. Huch, *Phosphorus Sulfur Silicon* 124 and 125 (1997) 213.
- [10] M. Veith, *Adv. Organomet. Chem.* 54 (2006) 49.
- [11] A.T. O'Dowd, T.R. Spalding, G. Ferguson, J.F. Gallagher, D. Reed, *J. Chem. Soc., Chem. Commun.* (1993) 1816.
- [12] J.B. Jones, *Acta Crystallogr. B* 24 (1968) 355.
- [13] D.D. Perrin, B. Dempsey, E.P. Serjeant (Eds.), *pK_a Prediction of Organic Acids and Bases*, Chapman & Hall, London, 1981, p. 130.
- [14] M. Veith, A. Rammo, V. Huch, J. Biegler, *Z. Anorg. Allg. Chem.* 633 (2007) 246.
- [15] M.D. Skowronska-Ptasinska, R. Duchateau, R.A. van Santen, G.P.A. Yap, *Eur. J. Inorg. Chem.* 1 (2001) 133.
- [16] F.J. Feher, T.A. Budzichowski, K.J. Weller, *J. Am. Chem. Soc.* 111 (1989) 7288.
- [17] S.J. Obrey, S.G. Bott, A.R. Barron, *Organometallics* 20 (2001) 5119.
- [18] H. Zhu, E.Y.-X. Chen, *Inorg. Chem.* 46 (2007) 1481.
- [19] J.M. Pietryga, J.D. Gorden, C.L.B. Macdonald, A. Voigt, R.J. Wiacek, A.H. Cowley, *J. Am. Chem. Soc.* 123 (2001) 7713.
- [20] M. Veith, H. Hreleva, M. Gasthauer, A. Rammo, V. Huch, *Z. Anorg. Allg. Chem.* 632 (2006) 985.
- [21] M. Veith, H. Hreleva, J. Biegler, V. Huch, A. Rammo, *Phosphorus Sulfur Silicon* 179 (2004) 651.
- [22] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, 6 Aufl.). Thieme, Stuttgart, New York, 2002, p. 165ff.
- [23] O.I. Shchegolikhina, Y.A. Pozdnyakova, Y.A. Molodtsova, S.D. Korkin, S.S. Bukalov, L.A. Leites, K.A. Lyssenko, A.S. Peregudov, N. Auner, D.E. Katsoulis, *Inorg. Chem.* 41 (2002) 6892.
- [24] G.C. Valle, G.G. Bombi, B. Corain, M. Favarato, P. Zatta, *J. Chem. Soc., Dalton Trans.* (1989) 1513.
- [25] I. Csöregy, T. Brehmer, S.I. Nitsche, W. Seichter, E. Weber, J. Inclusion Phenom. *Macrocycl. Chem.* 47 (2003) 113.
- [26] E. Weber, W. Seichter, K. Skobridis, D. Alivertis, V. Theodorou, P. Bombicz, I. Csöregy, *J. Inclusion Phenom. Macrocycl. Chem.* 55 (2006) 131.
- [27] S.P. Draffin, P.J. Duggan, G.D. Fallon, *Acta Crystallogr. E* 60 (2004) o1520.
- [28] J.E. Huheey, E.A. Keiter, *Anorganische Chemie*, 101 Aufl.). Walter de Gruyter, Berlin, 1995, p. 347.
- [29] M.A. Hossain, M.B. Hursthouse, A. Ibrahim, M. Mazid, A.C. Sullivan, *J. Chem. Soc., Dalton Trans.* (1989) 2347.
- [30] M.A. Hossain, M.B. Hursthouse, M.A. Mazid, A.C. Sullivan, *J. Chem. Soc., Chem. Commun.* (1988) 1305.
- [31] C. Ercolani, A. Camilii, G. Sartori, *J. Chem. Soc.* (1966) 606.
- [32] M. Bonamico, *Chem. Commun.* 5 (1966) 135.
- [33] M. Bonamico, G. Dessy, *Inorg. Phys. Theor., J. Chem. Soc. (A)* (1968) 291.
- [34] V.E. Shlover, Y.T. Struchkov, M.M. Levitskii, A.A. Zhdanov, *Zh. Strukt. Khim.* 27 (1986) 129.
- [35] F.T. Edelmann, Y.K. Gun'ko, S. Giessmann, F. Olbrich, *Inorg. Chem.* 28 (1999) 210.
- [36] R. Duchateau, R.J.H. Harmsen, H.C.L. Abbenhuis, R.A. Van Santen, A. Meetsma, S.K.-H. Thiele, M. Kranenburg, *Chem. Eur. J.* 5 (11) (1999) 3130.
- [37] M.D. Skowronska-Ptasinska, R. Duchateau, R.A. van Santen, G.P.A. Yap, *Organometallics* 20 (2001) 3519.
- [38] R. Tacke, C. Burschka, J. Heermann, I. Richter, B. Wagner, R. Willeke, *Eur. J. Inorg. Chem.* (2001).