Si−NH−M Cage Compounds − Molecular Iminosilicates Containing Group 13 Metals and Their Functionalized Halogen Containing Derivatives

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Dedicated to Professor Jean-Marie Lehn on the occasion of his 60th birthday

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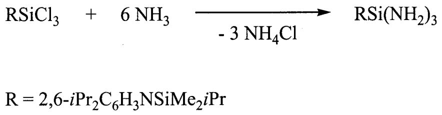
The reaction of a kinetically stable triaminosilane $RSi(NH_2)_3$ ($R = 2,6\text{-}iPr_2C_6H_3NSiMe_2iPr$) (**1**) with trialkyl group 13 metal compounds MR_3 (R = Me, Et; M = Al, Ga, In) leads to Si–NH–M cage molecules, which increase in solubility from aluminum to indium in common weakly-coordinating organic solvents like toluene. These compounds may be regarded as model systems for group 13 metal containing iminosilicates. X-ray studies show a prismatic cage framework which is isostructural and isoelectronic with known heterosiloxanes. Further functionalization of these compounds without cleavage of the cage molecule was achieved by reaction with elemental bromine and iodine.

Introduction

The importance of nitrido silicates in materials science has been growing during the last years. New nitrido silicate structures with different compositions have been synthesized by Schnick et al. using silicondiimide $[Si(NH)_2]_x$ and various metals at high temperatures.[1] In these systems nitrogen has an important influence on the final properties of the materials, so that hardness and thermal stability are dramatically increased in comparison to the oxygen congeners.[2] Recently Jansen et al.[3] and Riedel et al.[4] reported on ternary and quaternary ceramics containing silicon, boron, nitrogen, and carbon. These systems may be regarded as nitridosilicates which are even more thermally stable than Si_3N_4.

The reaction of a stable triaminosilane $RSi(NH_2)_3$ with trialkyls of group 13 metals MR_3 (M = Al, Ga, In; R = Me, Et) leads to cage molecules which are isostructural and isoelectronic with the analogous heterosiloxanes. Consequently, triaminosilanes may be regarded as interesting precursors for developing nitrogen containing molecular silicate chemistry. The methyl groups of the aluminum compound are accessible for substitution reactions with elemental bromine and iodine. Compounds containing two and four halogen atoms were isolated without cleavage of the cage structure. The halogen containing compounds can serve as precursors for the synthesis of functionalized structures.

In this context we have prepared several ring and cage compounds using stable silanetriols as starting materials.[6] At present, little is known about soluble molecular nitrogen containing silicates. Therefore, we have focused on the synthesis of cage molecules starting from stable triaminosilanes which are easily prepared by ammonolysis of the corresponding trichlorosilanes[9−11] (Scheme 1).



$$RSiCl_3 + 6\,NH_3 \xrightarrow[-\,3\,NH_4Cl]{} RSi(NH_2)_3$$

$R = 2,6\text{-}iPr_2C_6H_3NSiMe_2iPr$

Scheme 1

The isoelectronic properties of the amino and hydroxy groups should lead to similar reactivities for silanetriols and triaminosilanes. This was first shown in the reaction using alumazene, where structurally similar products for both types of compounds were formed.[12]

Results and Discussion

Synthesis and Structural Properties of Triaminosilanes

Reaction of silanetriols with trialkyls of group 13 metals leads to different types of heterosiloxanes with alternating Si−O−M units e.g. ring, cubic or prismatic compounds, whereas the reaction of $AlMe_3$ with hitherto known triaminosilanes leads only to insoluble products.[13]

Replacing one methyl group of the $SiMe_3$ substituent in $2,6\text{-}iPr_2C_6H_3NSiMe_3Si(NH_2)_3$ by an isopropyl group increases the solubility of the triaminosilane and of the resulting products. The synthesis and the crystal structure of $2,6\text{-}iPr_2C_6H_3NSiMe_2iPrSi(NH_2)_3$ (**1**) has been reported.[11]

The X-ray structural analysis of **1** shows the interesting effect of this exchange on the degree of oligomerization in the crystal. Compound **1** is connected via hydrogen bonds as a tetramer, in contrast to $2,6\text{-}iPr_2C_6H_3NSiMe_3Si(NH_2)_3$ which is dimeric in the crystal structure.

Reaction of $AlMe_3$ with 1

Reaction of $AlMe_3$ with **1** in toluene at 0 °C leads to the formation of a white microcrystalline solid **2**, which has a

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low solubility in common weakly coordinating solvents like pentane, hexane and toluene, but is soluble in coordinating solvents like tetrahydrofuran, dichloromethane or diethyl ether. Single crystals were obtained from a solution of [2,6-$i\mathrm{Pr_2C_6H_3NSiMe_2}i\mathrm{PrSi(NH)_3Al_2Me_3}]_2$ (**2**) in a THF/hexane mixture (20:80) by evaporating the solvent over two weeks.[11]

The M_6N_6 core in the molecular structure of **2**, shown in Figure 1 can be described as a bitruncated square bipyramid. It is formed by four $SiAl_2N_3$ six-membered rings in a boat conformation, sharing the three *stern* atoms and the three *prow* atoms with each neighboring ring system. Thus, two planar four-membered $SiAlN_2$ rings are formed. In all of these rings the metal and nitrogen atoms occupy alternating sites.

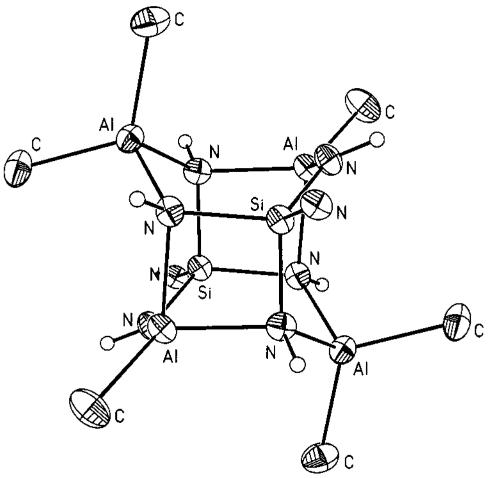
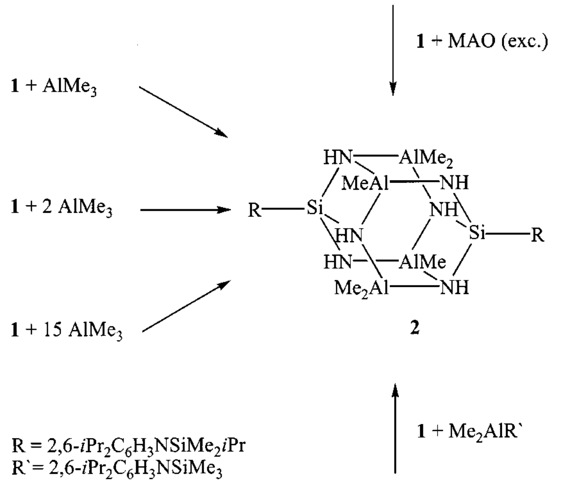


Figure 1. Central cage framework of the structure of **2** (organic substituents have been omitted for clarity)

The central framework of **2** is isostructural with the product of the reaction of diisobutyl aluminum hydride with the corresponding silanetriol.[6] In the mass spectrum the most intense peaks appear at *m/z* 433 (38%) and at 881 (100%) and are assigned to half of the molecular ion minus one methyl group and the molecular ion minus one methyl group respectively, which emphasizes the stability of **2** under these conditions.

Interestingly, this reaction is independent of the reaction temperature, time and the stoichiometry, but not of the solvent used. The reaction of **1** with $AlMe_3$ in different weakly coordinating solvents like hexane, pentane or toluene always gives **2**. In contrast to the corresponding silanetriol, the use of THF as solvent does not lead to a cubane but to a mixture of products, which could not be fully characterized.

The high selectivity in the formation of **2** is demonstrated in the reaction of MAO (methylaluminoxane), which contains some $AlMe_3$, and **1** to give single crystals of **2** and even the aminoalane $Me_2Al(i\mathrm{Pr_2C_6H_3NSiMe_3})$ reacts with **1** to give **2** in high yield. The different reaction pathways are summarized in Scheme 2.



$R = 2,6\text{-}i\mathrm{Pr_2C_6H_3NSiMe_2}i\mathrm{Pr}$
$R` = 2,6\text{-}i\mathrm{Pr_2C_6H_3NSiMe_3}$

Scheme 2

Reaction of GaR_3 (R = Me, Et) and $InMe_3$ with 1

In general indiumtrialkyls show a remarkably different reaction behavior, which is due to the difference in their heats of formation and those of the corresponding aluminum and gallium compounds [ΔH°_f kJ/mol + 173 (In), −42 (Ga), −81 (Al)].[14] The comparable reaction pathways of the Al- and Ga-alkyls is indicted by the similar reaction products obtained on hydrolysis.[15]

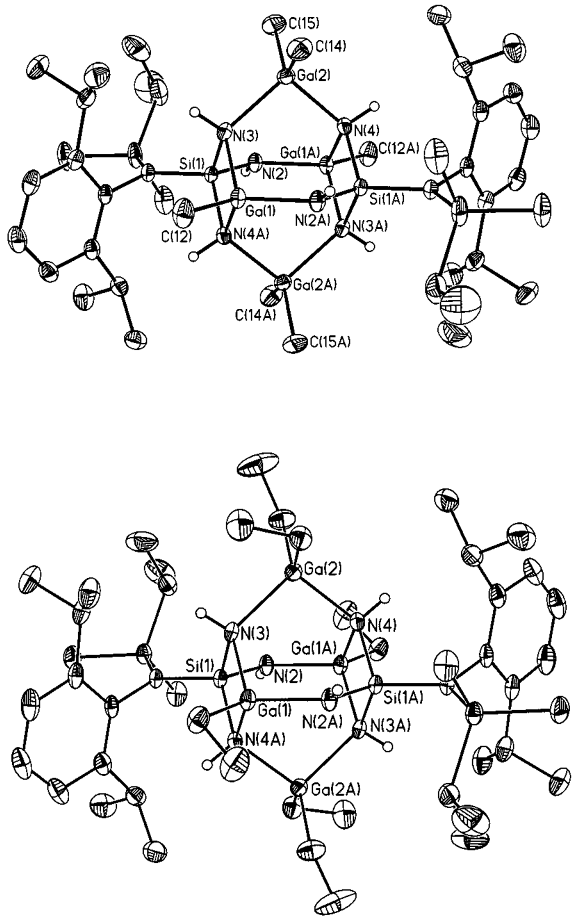


Figure 2. Crystal structures of **3** (top) and **4** (bottom) (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°] are given in Table 1. The ethyl groups in **4** are disordered

The reaction of MR_3 (M = Ga, In; R = Me, Et) with **1** in toluene at room temperature over 24 h yields a mixture of products, but heating the solutions at reflux for 1 h (in the case of the reaction of **1** with GaR_3) and 24 h (in the case of **1** with $InMe_3$) respectively leads to the formation of single crystals suitable for X-ray structural analysis. The molecular structures of $[RSi(NH)_3Ga_2Me_3]_2$ (**3**), $[RSi(NH)_3Ga_2Et_3]_2$ (**4**) and $[RSi(NH)_3In_2Me_3]_2$ (**5**) (R= 2,6-$i$$Pr_2C_6H_3NSiMe_2$$i$Pr) are shown in Figure 2 and Figure 3.

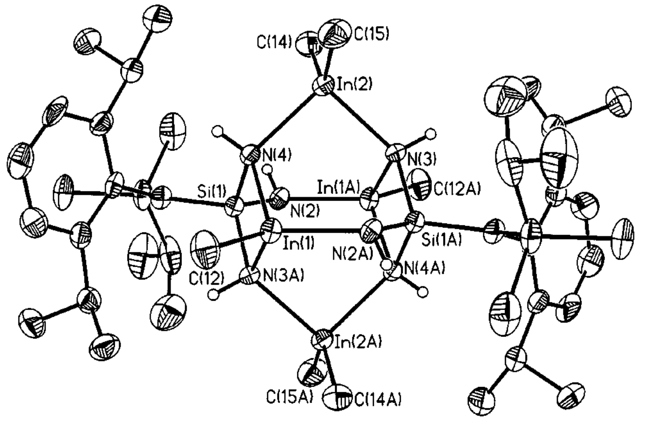


Figure 3. Crystal structure of **5** (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°] are given in Table 1

The similarity of the X-ray structures (**3**, **4**, **5**) to that of compound **2** is obvious. We preferentially describe the crystal structures of compounds **3** and **4** as representative examples for a detailed discussion of bond lengths and angles. Selected bond lengths and angles for **2**, **3**, **4**, and **5** are given in Table 1. The planes described by Ga(1)Si(1)N(2)Ga(1A)-Si(1A)N(2A) and Ga(2)N(3)N(4)Ga(2A)N(3A)N(4A) form a dihedral angle of 90.7°. The N atoms can be divided into two types, having μ- and μ_3-bridging sites. The bond lengths of the μ_3-bridging N atoms are significantly longer than of the others (N(3)−Si(1) 177 pm, N(2)−Si(1) 168 pm, N(3)−Ga(1) 203 pm, N(2)−Ga(1) 189 pm). These differences and the cage constraints determine the angles in the polyhedron. Therefore the expected tetrahedral coordination spheres at N, Si and Ga are distorted. The angles within the four-membered rings vary from 80.4° to 94.6°, the angles in the six-membered rings are in the range 106.6° to 122.7°. The bond lengths and angles of **3** and **4** are equal within experimental error (Table 1). The crystallographic data of compounds **2**, **3**, **4**, and **5** are given in Table 2.

Interestingly, the mass spectral data of **3**, **4**, and **5** lead to results similar to those obtained for compound **2**, where cleavage of the cage into two monomeric species under EI-conditions is observed. However, the solution NMR spectra show a series of signals consistent with the solid state structures of **2**, **3**, **4**, and **5** respectively.

Comparison of 2, 3, 4, and 5

Trialkyls of group 13 metals react with **1** independent of stoichiometry to give the isostructural cage compounds **2**, **3**, **4**, and **5**. A comparable reaction pathway for the corresponding silanetriols is not yet known, however heterosiloxanes which are isoelectronic and isostructural to **3** and **5** have been reported and underline the similar reaction behavior of **1**.

A few further observations should be briefly mentioned. All cage compounds have a remarkably high thermal stability and decompose at temperatures around 280 °C. Furthermore, their solubility increases from the aluminum to the indium compounds, which may be explained by the lower charge density at the indium centers as compared to the aluminum cage molecule. Although the reaction in coordinating solvents does not lead to the expected products, treatment of the isolated **2**, **3**, **4**, and **5** with THF, ether or dichloromethane does not result in the cleavage of the cage.

Table 1. Comparison of bond lengths [pm] and angles [°] of **2**, **3**, **4, 5**

	2 (M = Al)	**3** (M = Ga)	**4** (M = Ga)	**5** (M = In)
M(1)−N(2)	182.9(2)	189.1(2)	188.6(2)	208.8(5)
M(1)−N(3)	195.4(2)	204.4(2)	203.3(2)	223.3(6)
M(1)−N(4)	193.9(2)	200.9(2)	200.9(2)	219.9(5)
M(2)−N(4)	194.0(2)	201.1(2)	201.5(2)	220.4(5)
M(2)−N(3)	195.1(2)	202.8(2)	203.0(2)	221.2(5)
Si(1)−N(2)	168.4(2)	169.2(2)	167.9(2)	168.0(6)
Si(1)−N(3)	177.5(2)	177.4(2)	177.4(2)	175.5(5)
Si(1)−N(4)	178.0(2)	178.7(2)	177.7(2)	177.2(5)
N(2)−M(1)−N(4)	106.59(9)	106.51(8)	106.65(7)	103.1(2)
N(4)−M(1)−N(3)	82.52(8)	80.35(8)	80.44(7)	73.8(3)
N(2)−M(1)−Si(1)	114.39(7)	113.24(6)	113.20(6)	108.1(2)
N(4)−M(2)−N(3)	100.47(8)	98.43(8)	99.48(7)	95.5(2)
N(2)−Si(1)−N(3)	108.8(1)	109.1(1)	108.68(9)	109.8(3)
N(3)−Si(1)−N(4)	92.50(9)	94.48(9)	94.61(8)	97.9(3)
N(2)−Si(1)−M(1)	122.05(7)	123.91(7)	122.65(6)	126.4(2)
Si(1)−N(2)−M(1)	123.5(1)	122.8(1)	124.1(1)	125.5(3)
Si(1)−N(3)−M(2)	121.7(1)	123.2(1)	122.71(9)	128.1(3)
Si(1)−N(3)−M(1)	92.22(9)	92.12(9)	92.08(8)	93.8(2)
M(2)−N(3)−M(1)	114.16(9)	113.48(9)	112.84(8)	108.1(2)
Si(1)−N(4)−M(2)	118.5(1)	119.6(1)	119.72(9)	120.2(3)
M(1)−N(4)−M(2)	115.9(1)	114.95(9)	113.82(8)	114.9(2)

Table 2. Crystallographic data for **2**, **3**, **4, 5, 6a/6b** and **7a/7b**

	2	**3**	**4**
Formula	$C_{40}H_{84}Al_4N_8Si_4$	$C_{40}H_{84}Ga_4N_8Si_4$	$C_{46}H_{96}Ga_4N_8Si_4$
M	897.43	1068.39	1152.54
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
Cell dimensions	a = 1029.6(2) pm;	a = 1034.5(2) pm;	a = 2368.1(6) pm;
	b = 1154.2(2) pm;	b = 1163.1(2) pm;	b = 1080.5(3) pm;
	c = 1206.8(2) pm	c = 1212.7(2) pm	c = 2326.6(5) pm
	α = 94.86(3)°;	α = 94.86(3)°;	β = 102.56(2)°
	β = 106.90(1)°;	β = 106.90(1)°;	
	γ = 103.99(1)°	γ = 103.99(1)°	
Volume	1.3129(4) nm^3	1.3366(5) nm^3	5.810(3) nm^3
Z	1	1	4
δ_{calcd}	1.135 Mg/m^3	1.327 Mg/m^3	1.318 Mg/m^3
μ(Mo-K_α)	0.215 mm^{-1}	2.118 mm^{-1}	1.954 mm^{-1}
F(000)	488	560	
Crystal size [mm^3]	0.20 × 0.20 × 0.10	0.35 × 0.25 × 0.25	0.20 × 0.20 × 0.20
2θ-range	4.62 to 50.06°	3.56 to 52.86°	3.52 to 52.74°
Reflections coll	18464	13748	13287
Reflections obs.	4614	5437	5937
	(R_{int} = 0.0397)	(R_{int} = 0.0226)	(R_{int} = 0.0342)
Data/restraints/parameter	4614/3/273	5437/3/273	5937/11/320
GoF on F^2	1.057	1.040	1.127
*R*1 (all data)	0.0599	0.0338	0.0360
*wR*2 (all data)	0.1072	0.0724	0.0685
Highest maximum and minimum	742 and −495 e·nm^{-3}	1889 and −993 e·nm^{-3}	370 and −555 e·nm^{-3}

	5	**6a/6b**	**7a/7b**
Formula	$C_{40}H_{84}In_4N_8Si_4$	0.78 $C_{38}H_{78}Al_4Br_2N_8Si_4$ 0.22 $C_{36}H_{72}Al_4Br_4N_8Si_4$ 0.50 C_7H_8	0.85 $C_{38}H_{78}Al_4I_2N_8Si_4$ 0.15 $C_{36}H_{72}Al_4I_4N_8Si_4$ 0.59 C_6H_6
M	1248.43	0.78 (1027.18) + 0.22 (1156.92) + 0.5 (92.14)	0.85 (1121.18) + 0.15 (1344.92) + 0.59 (78.11)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Cell dimensions	a = 1011.6(2) pm;	a = 1111.2(2) pm	a = 1109.3(2) pm
	b = 1093.9(2) pm;	b = 1511.3(3) pm;	b = 1508.4(3) pm;
	c = 1335.0(2) pm	c = 1754.6(4) pm	c = 1788.0(4) pm
	α = 99.08(1)°;		
	β = 96.42(1)°;	β = 100.28(3)°	β = 101.00(3)°
	γ = 111.08(1)°		
Volume	1.3352(4) nm^3	2.8993(10) nm^3	2.9369(10) nm^3
Z	1	4	2
δ_{calcd}	1.553 Mg/m^3	1.315 Mg/m^3	1.410 Mg/m^3
μ(Mo-K_α)	1.830 mm^{-1}	1.882 mm^{-1}	1.407 mm^{-1}
F(000)	632	1203	1278
Crystal size [mm^3]	0.20 × 0.20 × 0.10	0.40 × 0.40 × 0.30	0.20 × 0.10 × 0.10
2θ-range	4.38 to 46.50°	3.58 to 50.00°	4.62 to 54.00°
Reflections coll.	28307	34689	76585
Reflections obs.	(R_{int} = 0.0641)	5098 (R_{int} = 0.0445)	6399 (R_{int} = 0.0682)
Data/restraints/parameter	3842/3/273	6098/283/343	6399/167/308
GoF on F^2	1.166	1.036	1.044
*R*1 (all data)	0.0616	0.0421,	0.0619,
*wR*2 (all data)	0.1065	0.0872	0.1264
Highest maximum and minimum	2041 and −779 e·nm^{-3}	608 and −609 e·nm^{-3}	1374 and −942 e·nm^{-3}

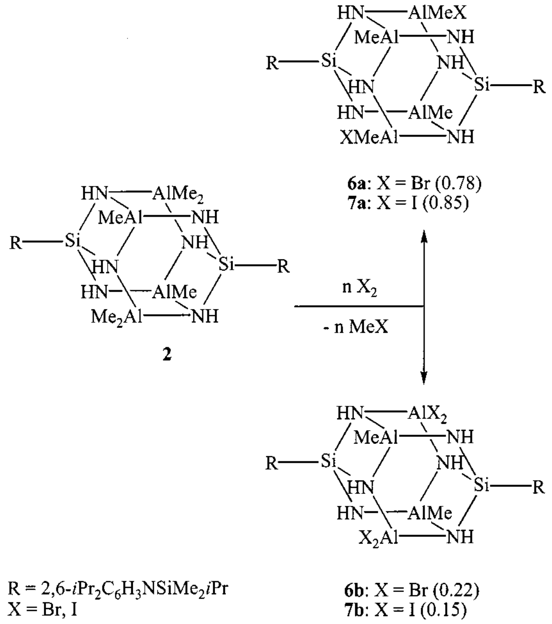
Treatment of 2 with Bromine and Iodine

A toluene solution of **2** was titrated at 0 °C with a small excess of bromine and iodine. Evaporation of the bromomethane and iodomethane, respectively, at room temperature, resulted in the formation of a mixture of products **6a/6b** and **7a/7b** (Scheme 3). Single crystals of **6a/6b** and **7a/7b** were obtained by recrystallization from warm toluene (60 °C). [16]

The solution and refinement of these structures show the presence of two different products, a mono- and a bis-halogen containing species at Al(1) and Al(1a). Molecular structures of **6a/6b** and **7a/7b** are shown in Figure 4 and Figure 5.

The halogenation has almost no influence on the prismatic core structure. Bond lengths and angles of the cages are equal within experimental error to those in **2** (see Table 1).

We observed that increasing the amount of halogen bound to the aluminum results in lower solubility, which in turn leads to preferred crystallization of the bis-halogen containing products (**6b,7b**) which have a high content in the crystal. ^{1}H NMR data and elemental analysis (of **6a/6b** and **7a/7b)** are consistent with the solid state structures,



6a: X = Br (0.78)
7a: X = I (0.85)

6b: X = Br (0.22)
7b: X = I (0.15)

R = 2,6-iPr$_2$C$_6$H$_3$NSiMe$_2$$i$Pr
X = Br, I

Scheme 3

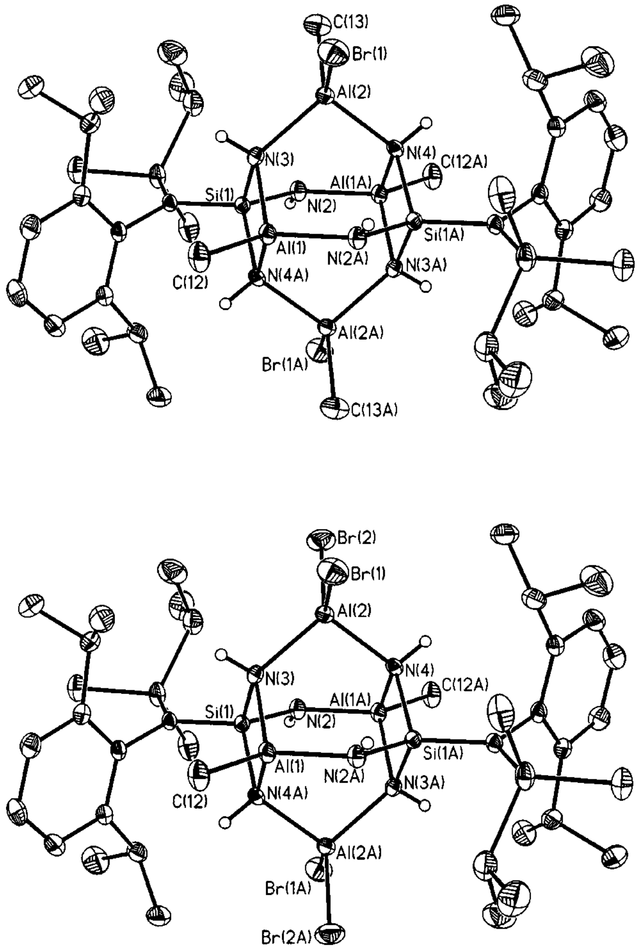


Figure 4. Crystal structures of **6a** (top) and **6b** (bottom) (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°] for **6a**: Al(2)−Br(1) 232.27(9), Al(2)−C(13) 197.1(13), C(13)−Al(2)−Br(1) 110.0(5); **6b**: Al(2)−Br(2) 220.6(5), Br(2)−Al(2)−Br(1) 113.4(2)

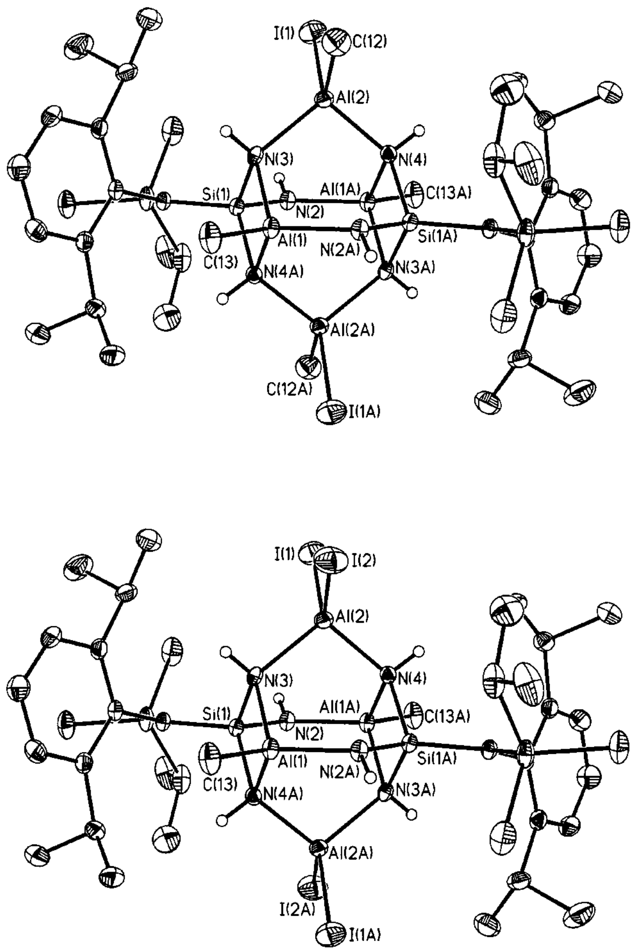


Figure 5. Crystal structures of **7a** (top) and **7b** (bottom) (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°] for **7a**: Al(2)−I(1) 257.0(1), Al(2)−C(12) 197.1(1), C(12)−Al(2)−I(1) 108.4(5); **7b:** Al(2)−I(2) 236.9(5), I(2)−Al(2)−I(1) 113.9(2)

whereas the mass spectra show several fragments which may be assigned to different halogen containing species.

The crystal structures of **6a/6b** and **7a/7b** are similar and interestingly the halogen atoms in **6a** and **7a** are located in a pseudo-trans position. At 0 °C a small excess (≈0.05 mmol) of the halogen gives the solution a characteristic color, which disappears at room temperature after 24 h. The bis-halogen containing products **6b** and **7b** are formed at higher temperatures. The second bromination step takes place at the same aluminum atom as the first, so both methyl groups at Al(1) and Al(1a) are substituted. Remarkably, only two compounds (**6a/6b**), containing two and four bromine atoms are observed, while an intermediate with three bromine atoms was not observed under these conditions.

By variation of the stoichiometry and the reaction time, we tried to synthesize the mono-, bis- and tris-bromine containing products and the related iodine compounds. X-ray structural analysis of the products showed that the crystals contain a variety of different molecules with the typical cage framework but they could not be refined, whereas under the reported reaction conditions **6a/6b** were formed several times in similar ratios.

Conclusion

By introducing a bulky substituent, we achieved to synthesize kinetically stable triaminosilanes which serve as starting materials to generate soluble iminosilicates. Based on our observations it should be possible to synthesize a variety of molecular iminosilicates and to extend this new area of chemistry. With the halogenation reaction, we present the first compounds in which there is further functionalization of the cage without cleavage of the framework. We are currently studying the use of these molecules as precursors for generating supramolecular systems under mild conditions by salt elimination reactions.

Experimental Section

General Techniques: All reactions were performed using Schlenk and dry box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. − All NMR spectra were obtained in 5 mm tubes using dry degassed [D$_8$]THF as the solvent, referenced to SiMe$_4$ externally. The solubilities of the cage compounds are not sufficient for ^{13}C NMR spectroscopy. − Elemental analyses were performed by the Analytisches Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen.

Compound **1**[11] and GaEt$_3$[17] were prepared according to literature methods. Other compounds are commercially available.

Preparation of 2 (Molar Ratio of 1 to AlMe$_3$ 1:2): A solution of AlMe$_3$ (2.3 mL, 2M in heptane) was added dropwise to a solution of **1** (0.8 g, 2.3 mmol) in toluene (20 mL) at −80 °C. As soon as gas evolution had ceased, the reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed in vacuo and the remaining yellowish oil stirred in hexane. A white precipitate was filtered off. Compound **2** was obtained in 75% yield (0.77 g).

Preparation of 2 (Molar Ratio of 1 to AlMe$_3$ 1:1): Analogous preparation method. Yield 75%.

Preparation of 2 from 1 and Me$_2$Al(*i*Pr$_2$C$_6$H$_3$NSiMe$_3$): A solution of **1** (0.8 g, 2.2 mmol) in hexane (30 mL) was added dropwise to a solution of Me$_2$Al(*i*Pr$_2$C$_6$H$_3$NSiMe$_3$) (0.7 g, 2.2 mmol) in hexane (20 mL) at 0 °C. As soon as gas evolution had ceased, the reaction mixture was warmed to room temperature and stirred for 12 h. Finally the reaction mixture was heated to 30 °C for 1 h. The solvent was evaporated to 15 mL and the residue was filtered off. Yield 0.4 g **2** (82%).

Preparation of 2 from 1 and MAO: A solution of **1** (1.8 g, 5.1 mmol) in hexane (30 mL) was added dropwise to a solution of MAO in toluene (30.0 g, 10%, 517 mmol Al) at room temperature. The reaction mixture was stirred for 20 h. The flask was kept at room temperature for 21 d and single crystals suitable for X-ray structural analysis were formed. Yield 0.11 g **2** (5%), decomp. 280−285 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = −1.37 (s, 6 H, AlCH_3), −0.83 [s, 12 H Al(CH_3)$_2$], 0.08 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.89 [s, b, 6 H, Si(NH)$_3$], 1.15 [d, ^3J(H,H) = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.20 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.32 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.38 [sept, ^3J(H,H) = 7.1 Hz, 2 H, CH(Me)$_2$], 3.52 [sept, ^3J(H,H) = 6.8 Hz, 4 H, CH(Me)$_2$], 7.23 [s, 6 H, Ar−H). − IR ([cm^{-1}], KBr, Nujol): $\tilde{\nu}$ = 3407, 3345, 3328, 1383, 825, 753. − MS (EI); *m/z* (%): 433 (38) [1/2 M$^+$ − Me], 882 (100) [M$^+$ − Me]. − C$_{40}$H$_{84}$Al$_4$N$_8$Si$_4$ (897.43): calcd. C 52.54, H 9.44; found C 52.3, H 8.6.

Preparation of 3: A solution of GaMe$_3$ (0.53 g, 4.60 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (0.80 g, 2.30 mmol) in toluene (15 mL) at room temperature. After stirring the solution for 12 h it was heated at reflux for 1 h. The reaction mixture was cooled (2 °C), and crystals suitable for X-ray structural analysis were obtained. The solvent was removed in vacuo, and the remaining solid was washed with pentane (5 mL). A colorless solid was filtered off. Yield 0.98 g (80%), decomp. 280 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = −0.90 (s, 6 H, GaCH_3), −0.57 [s, 12 H Ga(CH_3)$_2$], 0.04 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.82 [s, b, 2 H, Si(NH)GaMe], 1.05 [s, b, 4 H, Si(NH)$_2$(Ga$_2$Me$_3$)$_2$], 0.95 [d, ^3J(H,H) = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.05 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.18 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.42 [sept, ^3J(H,H) = 7.1 Hz, 2 H, CH(Me)$_2$], 3.48 [sept, ^3J(H,H) = 6.8 Hz, 4 H, CH(Me)$_2$], 7.09 (s, 6 H, Ar−H). − IR ([cm^{-1}], KBr, Nujol): $\tilde{\nu}$ = 3410, 3360, 3342, 1309, 827, 773. − MS (EI); *m/z* (%): 511 (48) [1/2 M$^+$ − Me], 1053 (100) [M$^+$ − Me]. − C$_{40}$H$_{84}$Ga$_4$N$_8$Si$_4$ (1068.39): calcd. C 44.97, H 7.92; found C 45.0, H 7.8.

Preparation of 4: A solution of GaEt$_3$ (1.07 g, 6.80 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (1.20 g, 3.40 mmol) in toluene (10 mL) at room temperature, and stirred for 14 h followed by 1 h of heating at reflux. The reaction mixture was cooled to room temperature and after 24 h single crystals suitable for X-ray structural analysis were obtained. After the solvent was removed in vacuo the residue was stirred in pentane (5 mL), and a colorless solid was filtered off. Yield 1.47 g (75%), decomp. 285 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = −0.05 [m, 4 H Ga(CH_2Me)], 0.52 [m, 8 H Ga(CH_2Me)$_2$], 0.15 [s, 12 H, Si(CH_3)$_2$-*i*Pr], 0.82 [s, b, 2 H, Si(NH)GaMe], 1.05 [s, b, 4 H, Si(NH)$_2$(Ga$_2$Me$_3$)$_2$], 1.17 [d, ^3J(H,H) = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.27 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.41 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.66 [sept, ^3J(H,H) = 7.1 Hz, 2 H, CH(Me)$_2$], 3.66 [sept, ^3J(H,H) = 6.8 Hz, 4 H, CH(Me)$_2$], 7.27 (s, 6 H, Ar−H). − IR ([cm^{-1}], KBr, Nujol): $\tilde{\nu}$ = 3411, 3360, 3342, 1363, 828, 751. − MS (EI); *m/z* (%): 547 (68) [1/2 M$^+$ − Et], 1123 (100) [M$^+$ − Et]. − C$_{46}$H$_{96}$Ga$_4$N$_8$Si$_4$ (1152.54): calcd. C 47.94, H 8.40; found C 48.2, H 8.20.

Preparation of 5: A solution of InMe$_3$ (0.53 g, 4.60 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (0.80 g, 2.30 mmol) in toluene (15 mL) at room temperature. After stirring the solution for 1 h it was heated at reflux for 12 h. The solvent was removed in vacuo, and the remaining solid was washed with pentane (5 mL). A colorless solid was filtered off and dissolved in warm toluene (10 mL) at 60 °C. Formation of single crystals suitable for X-ray measurements was observed after 24 h. Yield 0.98 g (80%), decomp. 285 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = −0.92 (s, 6 H, InCH_3), −0.42 [s, 12 H In(CH_3)$_2$], 0.14 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.80 [s, b, 2 H, Si(NH)InMe], 1.15 [s, b, 4 H, Si(NH)$_2$(In$_2$Me$_3$)$_2$], 1.02 [d, ^3J(H,H) = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.05 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.20 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.40 [sept, ^3J(H,H) = 7.1 Hz, 2 H, CH(Me)$_2$], 3.46 [sept, ^3J(H,H) = 6.8 Hz, 4 H, CH(Me)$_2$], 7.09 (s, 6 H, Ar−H). − IR ([cm^{-1}], KBr, Nujol): $\tilde{\nu}$ = 3499, 3414, 3360, 1313, 802. − MS (EI); *m/z* (%): 609 (36) [1/2 M$^+$ − Me], 1233 (100) [M$^+$ − Me]. − C$_{40}$H$_{84}$In$_4$N$_8$Si$_4$ (1248.43): calcd. C 38.47, H 6.78; found C 38.8, H 6.8.

Preparation of 6a/6b: Bromine was added dropwise at 0 °C to a suspension of **2** (0.70 g, 0.78 mmol) in toluene (25 mL) until no color change was observed. One further drop of bromine was added. The solution was stirred for 1 h at 0 °C. The MeBr was then removed in vacuo and the solution was allowed to warm to room temperature. Further solvent was removed (15 mL) and a white precipitate was formed, which was dissolved again by stirring the solution at 60 °C. Single crystals suitable for X-ray structural analysis were obtained after keeping the solution for 4 d at room temperature. Yield 0.39 g (43%), decomp. 295 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): (**6a**) δ = −1.07 (s, 6 H, AlCH_3), −0.83 [s, 6 H, Al(CH_3)Br], 0.10 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.76 [s, br, 6 H, Si(NH)$_3$], 1.13 [d, $^{3}J(H,H)$ = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.16 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.32 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.38 [sept, $^{3}J(H,H)$ = 7.1 Hz, 2 H, CH(Me)$_2$], 3.52 [sept, $^{3}J(H,H)$ = 6.8 Hz, 4 H, CH(Me)$_2$], 7.23 (m, 6 H, Ar−H); (**6b**) −1.17 (s, 6 H, AlCH_3), 0.08 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.89 [s, br, 6 H, Si(NH)$_3$], 1.15 [d, $^{3}J(H,H)$ = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.20 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.40 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.40 [sept, $^{3}J(H,H)$ = 7.1 Hz, 2 H, CH(CH$_3$)$_2$], 3.50 [sept, $^{3}J(H,H)$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 7.20 (m, 6 H, Ar−H). − IR ([cm^{-1}], KBr, Nujol): $\tilde{\nu}$ = 3408, 3348, 3330, 1381, 824, 752. − MS (EI); *m/z* (%): 1012 (100) [M^{+}_{6a} − Me]; 1141 (12) [M^{+}_{6b} − Me]. − $C_{44.56}H_{84.68}Al_4Br_{2.44}N_8Si_4$ (1101.80): calcd. C 46.58, H 9.41; found C 45.1, H 9.0.[16]

Preparation of 7a/7b: A solution of iodine in toluene (0.1 M) was added dropwise at 0 °C to a suspension of **2** (0.55 g, 0.61 mmol) in toluene (25 mL) until no color change was observed. One further drop of this solution was then added. The solution was stirred for 30 min at 0 °C and 1 h at room temperature. The MeI formed, as well as 15 mL of the solvent, were removed in vacuo and a white precipitate was formed. It was dissolved again by stirring the solution at 60 °C. Single crystals suitable for X-ray structural analysis were obtained from the solution after 4 d at room temperature. Yield 0.22 g (47%), decomp. 280−285 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): (**7a**) δ = −1.07 (s, 6 H, AlCH_3), −0.83 [s, 6 H, Al(CH_3)I], 0.10 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.76 [s, br, 6 H, Si(NH)$_3$], 1.13 [d, $^{3}J(H,H)$ = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.16 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.32 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.38 [sept, $^{3}J(H,H)$ = 7.1 Hz, 2 H, CH(Me)$_2$], 3.52 [sept, $^{3}J(H,H)$ = 6.8 Hz, 4 H, CH(Me)$_2$], 7.23 (m, 6 H, Ar−H); **(7b):** δ **=** −1.17 (s, 6 H, AlCH_3), 0.08 [s, 12 H, Si(CH_3)$_2$*i*Pr], 0.89 [s, b, 6 H, Si(NH)$_3$], 1.15 [d, $^{3}J(H,H)$ = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.20 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.40 [d, $^{3}J(H,H)$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.40 [sept, $^{3}J(H,H)$ = 7.1 Hz, 2 H, CH(Me)$_2$], 3.50 [sept, $^{3}J(H,H)$ = 6.8 Hz, 4 H, CH(Me)$_2$], 7.20 (m, 6 H, Ar−H). − IR ([cm^{-1}], KBr, Nujol): $\tilde{\nu}$ = 3407, 3345, 3328, 1383, 825, 753. − MS (EI); *m/z* (%): 1106 (100) [M^{+}_{7a} − Me], 1329 (6) [M^{+}_{7b} − Me]. − $C_{41.24}H_{80.64}Al_4I_{2.30}N_8Si_4$ (1200.83): calcd. C 41.25, H 6.72; found C 40.1, H 6.3.[16]

X-ray Crystallography: Crystallographic data: Crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[18] Diffraction data were collected on a Stoe-Siemens-Huber four-circle-diffractometer coupled to a Siemens CCD area-detector at 133(2) K, with graphite-monochromated Mo-K_a radiation (λ = 71.073 pm).

The structures were solved by direct methods using SHELXS-97[19] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[20] All nonhydrogen atoms were refined anisotropically. In all structures the hydrogen atoms bound to N(2), N(3) and N(4) were found in the difference Fourier map and refined freely, all other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The disordered ethyl groups in **4** were modeled with the help of similarity restraints for 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The cocrystallized products in the structures of **6a/b** and **7a/b** were treated as disorders and refined with the help of similarity and rigid bond restraints. The occupancies of **6a** and **6b** refined to a ratio of 80% to 20%, the ratio of **7a** and **7b** was found to be 85% to 15%.

Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC-140493 to CCDC-140498. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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