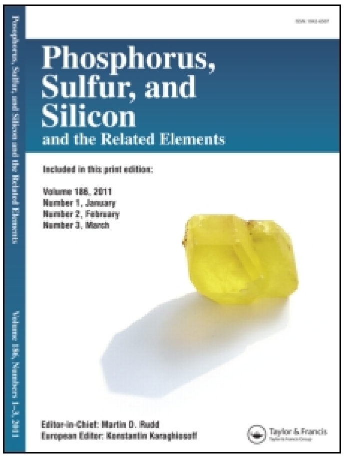

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ACCESS TO IMINOSILICATES FROM NOVEL TRIAMINOSILANES - A SHORT OVERVIEW

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In this paper we summarize our recent results concerning molecular iminosilicates containing group 13 metals. Furthermore, we report on the synthesis of the first Si-NH-In cage compound. These compounds are isostructural and isoelectronic to the known heterosiloxanes.

Keywords: Triaminosilanes, silicates, cage compounds, heterosiloxanes, heterosilazanes

INTRODUCTION

Silicates are used in a wide range of different applications e. g. in catalytic processes as carriers or catalysts as well as in material science as new ceramics.[1-3] Though catalytic processes performed on a silica surface are known for a long time, the understanding of the mechanism is quite unknown, but necessary for improving the catalytic properties.

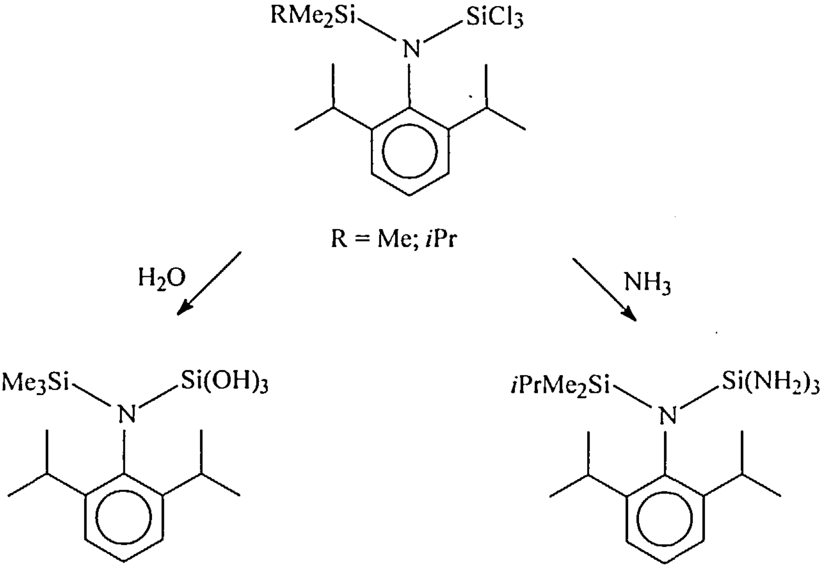
With several model compounds for silicates and zeolites prepared from kinetically stable silanetriols we contribute to the first step in the understanding of these processes.[4] The high interest is reflected in the still growing number of publications in this field.[5,6]

Parallel to the synthesis of different heterosiloxanes we are working on isoelectronic heterosilazanes, that could be regarded as molecular iminosilicates.[7-10]

Herein, we report on our results so far of preparing cage-shaped molecules with different compositions using stable triaminosilanes.

RESULTS AND DISCUSSION

Kinetically stable silanetriols are synthezised by hydrolysis of the corresponding trichlorosilanes in the presence of anilin and Et_3N respectively. Parallel to this synthesis the ammonolysis of trichlorosilanes in liquid ammonia leads to the isoelectronic triaminosilanes (**1** and **2**, scheme 1).[4,11,12]

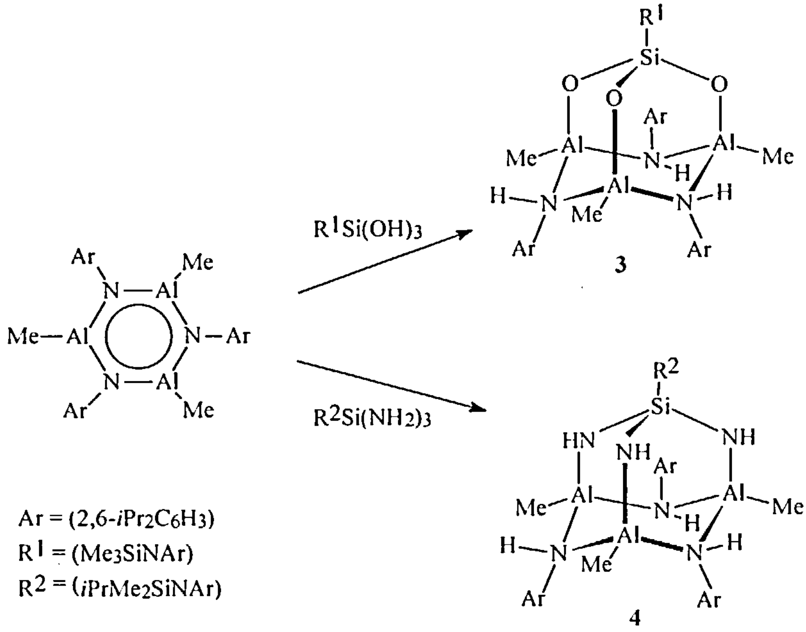


1

2

SCHEME 1.

These compounds are characterized by single crystal X-ray studies. Our expectation that **1** and **2** show a comparable reaction behavior was confirmed by the addition of **1** and **2** respectively to the alumazene ring system (scheme 2). The isostructural adamantane-like molecules were obtained in good yields. The hydrogen atoms migrate to the N-atoms of the ring. A change of the coordination number from three to four on aluminum and nitrogen respectively is favored.



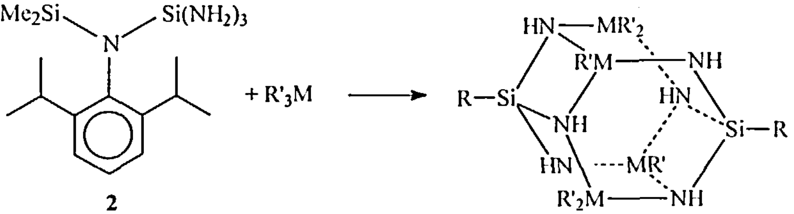
Ar = (2,6-iPr$_2$C$_6$H$_3$)
R^1 = (Me$_3$SiNAr)
R^2 = (iPrMe$_2$SiNAr)

SCHEME 2.

X-ray structures of **3** and **4** show the change of the ring conformation from a planar six-membered ring to a chair-conformation.[9] **3** and **4** are the first examples using an alumazene and this chemistry opens up an interesting new field. Furthermore, **3** is the first mixed nitrogen-oxygen molecular silicate.

The reaction of triorganyles of group 13 metals with **1** in toluene leads to prismatic cage compounds. Consequently, we were interested in preparing isostructural molecules using **2** instead of **1**.

By the reaction of Me_3M (M = Al, Ga, In) and Et_3Ga with **2** in toluene we were able to synthesize the predicted compounds in good yields by varying the reaction temperature (scheme 3 and table 1).



2

R = $2,6\text{-}iPr_2C_6H_3NSiMe_2iPr$
5 : M = Al, R' = Me
6 : M = Ga, R' = Me
7 : M = Ga, R' = Et
8 : M = In, R' = Me

SCHEME 3.

TABLE 1 Physical data for some molecular iminosilicates

	yield (%)	reaction temp. (°C) (time (h))	decomposition temp. (°C)	mass spectra (EI, m/z) (%):
5:	75	RT (12)	280	½ M^+-Me (38); M^+-Me (100)
6:	80	RT (12); 120 (1)	280	½ M^+-Me (48); M^+-Me (100)
7:	75	RT (14); 120 (1)	285	½ M^+-Et (68); M^+-Et (100)
8:	77	RT (1); 120 (12)	285	½ M^+-Me (68); M^+-Me (100)

Compounds **5**, **6** and **7** were characterized by single crystal X-ray investigations.[8,10] **8** is characterized by ^{1}H NMR, electron ionization mass spectra, IR measurements and elemental analysis. All compounds are showing nearly the same central cage structure. Besides the high decomposition temperature the stability of these compounds even in the gas phase is remarkably as can be followed from the high percentage of molecular ion minus one organyl group in the mass spectra (table 1). The ^{1}H NMR spectra (**5**, **6** and **7**) in solution are consistent with the structures found in the solid state. Interestingly the formation of the products is independent from the stoichiometry of the starting materials. The variation of the molar ratios in the range 1 : 1 to 1 : 2 to 1 : 12 using **2** and Me_3Al leads always to **5**.

Presently we are investigating the possibilities of using these compounds for preparing supramolecular structures. In contrast to the analogues oxygen compounds two routes are possible: either to substitute the methyl groups at the aluminum atoms or to metalate at the imino groups.

Moreover these compounds can function as precursors for ternary and quartanary ceramics. Recent publications[13-16] show the extraordinary properties of these materials and it would be an interesting advancement using single-source precursors for the preparation of such materials

CONCLUSION

The isoelectronic properties of triaminosilanes and silanetriols lead to a similiar reaction pathway. The addition of **1** and **2** respectively to the quasiaromatic alumazene ring system yields isostructural adamantane-like molecules. The reactions of Me_3M (M = Al, Ga, In) with **2** in toluene under various conditions lead to prismatic cage molecules which could be regarded as molecular iminosilicates. Their capability to act as single-source precursors for the preparation of advanced materials is under investigation.

ACKNOWLEDGMENT

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EXPERIMENTAL

General techniques: All reactions were performed using general 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 THF-d8 as the solvent, referenced to $SiMe_4$ externally. Elemental analysis were performed by the Analytische Laboratorium des Instituts für Anorganische Chemie, Göttingen.

Preparation of 8: A solution of Me_3In (0.53 g, 4.6 mmol) in toluene (10 cm^3) was added dropwise to a solution of **2**[8] (0.80 g, 2.3 mmol) in toluene (15 cm^3) at room temperature. After stirring the solution for 1 h it was refluxed for 12 h. The solvent was removed *in vacuo*, and the remaining solid was taken up in pentane (5 cm^3). A colorless solid was filtered off. Yield 0.98 g (80 %), decomp. 285 °C; ^1H NMR (200 MHz, THF-d8): δ -0.92 (s, 6 H, $InCH_3$), -0.42 (s, 12 H $In(CH_3)_2$), 0.14 (s, 12 H, $Si(CH_3)_2iPr$), 0.80 (s, b, 2 H, Si(N*H*)InMe), 1.15 (s, b, 4 H, $Si(NH)_2(In_2Me_3)_2$), 1.02 (d, $^3J(H\,H)$ = 6.8 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): ν 3499, 3414, 3360, 1313 , 802 ; MS (EI) *m/z* (%) : 609 [1/2 M^+ - Me, 36], 1233 [M^+ - Me, 100], calculated and found isotopic pattern are consistent; Analysis: Found: C, 38.8; H, 6.8; $C_{40}H_{84}In_4N_8Si_4$ requires C, 38.47; H, 6.78 %.

REFERENCES

[1] W. Hölderich, M. Hesse and F. Näumann, *Angew. Chem.*, **100**, 232 (1988); *Angew. Chem. Int. Ed. Engl.*, **27**, 226, (1988).

[2] C. S. John, D. M. Clark and I. E. Maxwell, *Perspectives in Catalysis Chemistry for the 21st Century.* (Ed. J. M. Thomas, K. I. Zamaraev), Blackwell Scientific Publ., London, Edinburgh, Boston, Melbourne, Paris, Berlin, Vienna, (1992).

[3] M. Ichikawa, L. R. Rao and A. Fukoka, *Catalytic Science and Technology*, **Vol. 1**, VCH, Weinheim, (1991).

[4] N. Winkhofer, A. Voigt, H. Dorn, H. W. Roesky, A. Steiner, D. Stalke and A. Reller, *Angew. Chem.*, **106**, 1414 (1994); *Angew. Chem. Int. Ed. Engl.*, **33**, 1352 (1994); R. Murugavel, V. Chandrasekhar, A. Voigt, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, **14**, 5298 (1995); M. L.

Montero, I. Usón and H. W. Roesky, *Angew. Chem.*, **106**, 2198 (1994); *Angew. Chem. Int. Ed. Engl.*, **33**, 2103 (1994); M. L. Montero, A. Voigt, H. W. Roesky, M. Teichert and I. Usón, *Angew. Chem.*, **107**, 2761 (1995); *Angew. Chem. Int. Ed. Engl.*, **34**, 2504 (1995); A. Voigt, R. Murugavel, E. Parisini and H. W. Roesky, *Angew. Chem.*, **108**, 823 (1996); *Angew. Chem. Int. Ed. Engl.*, **35**, 748 (1996); V. Chandrasekhar, R. Murugavel, A. Voigt, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, **15**, 918 (1996).

[5] M. Veith, M. Jarczyk and V. Huch, *Angew. Chem.*, **109**, 140 (1997); *Angew. Chem. Int. Ed. Engl.*, **36**, 117 (1997).

[6] M. R. Mason, M. S. Mashuta and J. F. Richardson, *Angew. Chem.*, **109**, 187 (1997); *Angew. Chem. Int. Ed. Engl.*, **36**, 239 (1997).

[7] The following results are presented at the IRIS VIII Symposium, Loughbourough, England, (1997); **2-7** were published in [8-10].

[8] C. Rennekamp, A. Gouzyr, A. Klemp, H. W. Roesky, C. Brönneke, J. Kärcher and R. Herbst-Irmer, *Angew. Chem.*, **109**, 413 (1997); *Angew. Chem. Int. Ed. Engl.*, **36**, 404 (1997).

[9] H. Wessel, C. Rennekamp, D.-S. Waezsada, H. W. Roesky, M. L. Montero and I. Usón, *Organometallics*, in the press (1997).

[10] Carsten Rennekamp, Hyung-Suh Park, Helge Wessel, Herbert W. Roesky, Peter Müller and Isabel Usón, *J. Chem. Soc. Dalton Trans.*, submitted (1997).

[11] K. Ruhlandt-Senge, R. A. Bartlett, M. M. Olmstead and P. P. Power, *Angew. Chem.*, **105**, 459 (1993); *Angew. Chem. Int. Ed. Engl.*, **32**, 425 (1993).

[12] K. Wraage, A. Künzel, M. Noltemeyer, H.-G. Schmidt and H. W. Roesky, *Angew. Chem.*, **107**, 2954 (1995); *Angew. Chem. Int. Ed. Engl.*, **34**, 2645 (1995).

[13] T. Schlieper and W. Schnick, *Z. Anorg. Allg. Chem.*, **621**, 1037 (1995); T. Schlieper, W. Milius and W. Schnick, *ibid.*, **621**, 1380 (1995); T. Schlieper and W. Schnick, *ibid.*, **621**, 1535 (1995).

[14] H. Huppertz and W. Schnick, *Angew. Chem.*, **108**, 2115 (1996); *Angew. Chem. Int. Ed. Engl.*, **35**, 1983 (1996); H. Huppertz and W. Schnick, *Chem. Eur. J.*, **3**, 249 (1997).

[15] H.-P. Baldus and M. Jansen, *Angew. Chem.*, **109**, 338 (1997); *Angew. Chem., Int. Ed. Engl.*, **36**, 328 (1997).

[16] R. Riedel, A. Greiner, G. Miehe, W. Dreßler, H. Fuess, J. Bill and F. Aldinger, Angew. Chem., **109**, 657 (1997); *Angew. Chem. Int. Ed. Engl.*, **36**, 603 (1997).