Bull Soc Chim Fr (1995) 132, 585-589

Formation of organosilicon compounds. 114 [1]. Investigations concerning the amination of Si-chlorinated 1,3,5,7-tetrasilaadamantanes and formation of bis(1,3,5,7-tetrasilaadamantyl)methylamine

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(received 16 January 1995, accepted 4 April 1995)

Summary – The reaction of a mixture of Si-chlorinated 1,3,5,7-tetrasilaadamantanes (products of the gas phase pyrolysis of Me_3SiCl) with LiMe yields $ClMe_3Ad$ **2** and Cl_2Me_2Ad **3** (Ad = skeleton of 1,3,5,7-tetrasilaadamantane), the starting compounds for an investigation of the related silylamines. In contrast to reactions with NH_3, where no defined compounds could be isolated, the reaction of **2** with $MeNH_2$ leads to $Me_3(NHMe)Ad$ **5** and the reaction of **3** with $MeNH_2$ leads to $Me_2(NHMe)_2Ad$ **6**. The NMe-bridged $(Me_3Ad)_2NMe$ **7** is formed when heating **5** to 300°C. Analogously **6** yields $[Me_2(NHMe)Ad]_2NMe$ **8** and other compounds. $BrMe_3Ad$ **4** with $NaNH_2$ forms the products $Me_3(NH_2)Ad$ **9**, $(Me_3Ad)_2NH$ **10** and higher molecular compounds. The reaction of Cl_4Ad with $MeNH_2$ produces $(NHMe)_4Ad$ **11**. Compound **7** forms triclinic crystals in the space group $P\bar{1}$ with the lattice parameters $a = 959.6$ pm, $b = 1\,331.7$ pm, $c = 1\,371.5$ pm, $\alpha = 117.92°$, $\beta = 89.98°$, $\gamma = 103.23°$ and two formula units in the unit cell.

NMe-substituted 1,3,5,7-tetrasilaadamantane / crystal structure of bis(1,3,5,7-tetrasilaadamantyl)methylamine

Introduction

1,3,5,7-Tetrachloro-1,3,5,7-tetrasilaadamantane was first obtained in 1961 in small amounts (0.1% yield) from the reaction of Me_3SiCl and $SiCl_4$ with $AlCl_3$ at more than 500°C [2]. Preparative scale syntheses of tetrasilaadamantanes were later designed using by gas phase pyrolysis of Me_4Si and Me_3SiCl [3], the reaction of $(Me_2Si\text{-}CH_2)_3$ with $AlCl_3$ [4], and reactions of substituted 1,3,5-trisilacyclohexanes with $AlBr_3$ [5]. Si-substituted derivatives with the group SiX (X = Cl, H, OH, NEt_2, $OCH_2CH_2NMe_2$, NEt_2 [6]) and Si-fluorinated and C,Si-chlorinated derivatives, such as F_4AdCl_{12} and Cl_4AdCl_{12} [7], were also synthesized and the crystal structure of Me_4Ad [8] and its vibrational spectra were determined [9]. Investigations concerning the basicity of the NEt_2, derivatives Me_2 $(NEt_2)XAd$ (X = Me, Ph) [10] also exist.

Further derivatives of the parent substance bearing various substituents at the Si and even the C atoms of the Ad skeleton were isolated from the gas phase pyrolysis of Me_4Si. These products were accompanied by higher condensed silaadamantanes [11].

In the context of our investigations into CH_2-linked adamantanes of this type [12], we first intended to synthesize the compounds $Me_3(NHMe)Ad$, $Me_3(NH_2)Ad$ and $Me_2(NHMe)_2Ad$ and examine their properties. Moreover, we aimed to use these compounds to synthesize N-bridged 1,3,5,7-tetrasilaadamantanes.

Synthetic investigations

Synthesis of $ClMe_3Ad$ (1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane) 2 *and Cl_2Me_2Ad 1,3-dichloro-3,5,7-trimethyl-1,3,5,7-tetrasila-adamantane* 3 *in the reaction of $Cl_nMe_{4-n}Ad$ with LiMe*

The product mixture resulting from the pyrolysis of Me_3SiCl [3] contains the compounds $Cl_nMe_{4-n}Ad$ **1** in a ratio of $Cl_4Ad/Cl_3MeAd/Cl_2Me_2Ad/ClMe_3Ad/Cl_3HAd = 3.1{:}3.7{:}1.5{:}0.2{:}1.5$ as determined by ^1H NMR spectroscopy. The synthesis and isolation of $ClMe_3Ad$ **2** and Cl_2Me_2Ad **3** by reacting **1** with LiMe are described in the *Experimental section.*

Synthesis of $Me_3(NHMe)Ad$ (1,3,5-trimethyl-7-methylamino-1,3,5,7-tetrasilaadamantane) 5

Compound **5** can be synthesized by passing gaseous $MeNH_2$ through a solution of $BrMe_3Ad$ **4** [4, 5] in THF :

$$\underset{\mathbf{4}}{BrMe_3Ad} + 2\ MeNH_2 \longrightarrow \underset{\mathbf{5}}{Me_3(NHMe)Ad} + MeNH_3Br$$

However, in nonpolar solvents such as hexane $ClMe_3Ad$ **2** reacts very slowly with $MeNH_2$ and the

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* Correspondence and reprints

reaction does not reach completion. In THF, the reaction rate is much faster but there is a considerable formation of siloxanes. In the reaction system $BrMe_3Ad/MeNH_2/THF$, this side reaction is even more predominant.

The reaction of $BrMe_3Ad$ **4** with NH_3 in THF led spontaneously to white, solid products together with a small amount of $Me_3(NH_2)Ad$ **9** and $(Me_3Ad)_2NH$ **10**. The white, solid products have not yet been identified.

Synthesis of $Me_2(NHMe)_2Ad$ (1,3-bis-methylamino-5,7-dimethyl-1,3,5,7-tetrasilaadamantane) 6

Compound **6** can be synthesized in the following manner, and was isolated in a yield of 61% as white crystals.

$$\underset{\mathbf{3}}{Cl_2Me_2Ad} + 4\ MeNH_2 \longrightarrow \underset{\mathbf{6}}{Me_2(NHMe)_2Ad} + 2\ MeNH_3Cl$$

Synthesis of $(Me_3Ad)_2NMe$ [bis(3,5,7-trimethyl-1,3,5,7-tetrasilaadamantan-1-yl)methylamino] 7

An important aim of our investigations was the synthesis of NH- or NMe-linked 1,3,5,7-tetrasilaadamantanes starting from monoadamantylamines. As no NH_2-substituted adamantane was available, **5** and **6** were heated and indeed yielded the linked products by eliminating volatile groups. Heating **5** for 72 h at 300°C in a sealed glass ampoule led to the formation of a mixture of $Me_3(NHMe)Ad$ **5** and $(Me_3Ad)_2NMe$ **7** in the ratio 1:5. After 24 h, only a 1:1 ratio was found. From a solution of the reaction products in *n*-pentane, a mixture of crystalline compounds precipitated at −30°C. Sublimation of this mixture between 130 and 150°C and 10^{-6} torr yielded the compounds Me_4Ad, $Me_3(NHMe)Ad$ **5** and $(Me_3)Ad)_2NMe$ **7** as a first fraction, and $(Me_3Ad)_2NMe$ **7** as a second, together with small amounts of a siloxane. Recrystallization of the second fraction from *n*-pentane (−30°C) led to crystals of **7** suitable for X-ray structural analysis.

The following reactions were also investigated :

a) A reaction of $BrMe_3Ad$ with $Me_3(NHMe)Ad$ **5** and NEt_3 under elimination of HBr as $NEt_3 \cdot HBr$ yields no **7**.

b) The reaction of $BrMe_3Ad$ and $Me_3(NHMe)Ad$ **5** with Na/K leads to some $(Me_3Ad)_2NMe$ **7**, but the reaction is not complete.

c) $BrMe_3Ad$ reacts with $NaNH_2$ in the following manner :

$$BrMe_3Ad + NaNH_2 \longrightarrow \underset{\mathbf{9}}{Me_3(NH_2)Ad} + \underset{\mathbf{10}}{(Me_3Ad)_2NH}$$

Several further products were formed but no $(Me_3Ad)_3N$ was identified.

Thermal properties of $Me_2(NHMe)_2Ad$ 6

Heating compound **6** in a sealed evacuated glass ampoule for three days at 300°C yields a glass-like substance of unknown structure as the main product, which is insoluble in common solvents. Heating of **6** at 180°C in a mass spectrometer yields $[Me_2(NHMe)Ad]_2NMe$ **8**.

X-ray structural analysis of 7

Crystals of the colorless compound **7** were examined with X-ray structural analysis (Stoe-Stadi IV four circle diffractometer Mo-K_α-radiation, graphite monochromator). The programs SHELXS-86 and SHELXL-93 [13] on a IBM 550 were used for evaluation. The crystallographic data are listed in table I, the atomic coordinates in table II and the bond lengths and bond angles in table III. Further information concerning the X-ray structural analysis are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-Technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen, Germany, under specification of the deposition number CSD 58897, the names of the authors and the citation of the journal.

Table I. Crystal data and structure refinement for **7**.

Empirical formula	$C_{19}H_{45}NSi_8$
Formula weight	512.28
Temperature	203 (2) K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.596 (4) Å, α = 117.92 (2) deg b = 13.317 (3) Å, β = 89.98 (2) deg c = 13.715 (4) Å, γ = 103.23 (2) deg
Volume	1 495.9 (9) $Å^3$
Z	2
Density (calculated)	1.137 mg/m^3
Absorption coefficient	0.367 mm^{-1}
F(000)	556
θ range for data collection	1.69-25.00°
Index ranges	$0 \leqslant h \leqslant 9$, $-15 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 16$
Reflections collected	5 171
Independent reflections	4 823 [R (int) = 0.0209]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4 823/0/253
Goodness-of-fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0300$, $wR2 = 0.0826$
R indices (all data)	$R1 = 0.0352$, $wR2 = 0.0868$
Largest diff peak and hole	0.290 and −0.264 e.$Å^{-3}$

Description of the structure

Compound **7** forms triclinic crystals in $P\bar{1}$ with the lattice parameters a = 959.6 pm, b = 1 331.7 pm, c = 1 371.5 pm, α = 117.92°, β = 89.98°, γ = 103.23°. The elementary unit contains two formula units. Figure 1 shows the structure of the molecule **7** in the crystal lattice.

The investigation of the structure verifies the linkage of two 3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane units with an NMe bridge in **7**. This is in agreement with the results from mass spectrometry and

Table II. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^{-2} \times 10^{-3}$) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	2 919(1)	6 172(1)	5 779(1)	37(1)
Si(2)	4 873(1)	8 577(1)	6 162(1)	36(1)
Si(3)	3 275(1)	6 708(1)	3 785(1)	30(1)
Si(4)	1 532(1)	8 039(1)	5 702(1)	45(1)
Si(5)	2 316(1)	1 993(1)	337(1)	31(1)
Si(6)	2 504(1)	4 683(1)	1 363(1)	27(1)
Si(7)	1 690(1)	3 001(1)	−1 212(1)	31(1)
Si(8)	−502(1)	2 809(1)	408(1)	31(1)
N(1)	3 406(2)	6 111(1)	2 366(1)	31(1)
C(1)	4 610(2)	7 369(2)	6 543(2)	41(1)
C(2)	3 026(2)	5 563(2)	4 245(2)	34(1)
C(3)	1 349(2)	6 849(2)	6 100(2)	48(1)
C(4)	4 943(2)	7 900(2)	4 626(2)	36(1)
C(5)	3 253(2)	9 183(2)	6 479(2)	48(1)
C(6)	1 712(2)	7 386(2)	4 178(2)	41(1)
C(7)	2 685(3)	4 977(2)	6 172(2)	57(1)
C(8)	6 555(2)	9 778(2)	6 939(2)	50(1)
C(9)	−56(3)	8 682(3)	6 036(2)	74(1)
C(10)	2 636(2)	4 514(2)	−69(1)	32(1)
C(11)	2 446(2)	1 894(2)	−1 064(2)	36(1)
C(12)	3 269(2)	3 530(2)	1 418(2)	33(1)
C(13)	525(2)	4 320(2)	1 506(2)	32(1)
C(14)	−255(2)	2 710(2)	−988(2)	35(1)
C(15)	349(2)	1 727(2)	525(2)	36(1)
C(16)	1 914(3)	2 916(2)	−2 599(2)	49(1)
C(17)	3 140(2)	891(2)	431(2)	47(1)
C(18)	−2 473(2)	2 518(2)	585(2)	42(1)
C(19)	3 979(2)	6 991(2)	1 995(2)	44(1)

Table III. Bond lengths [pm] and angles [deg] for **1**.

Si(1)-C(7)	187.4(2)	C(7)-Si(1)-C(3)	111.00(11)
Si(1)-C(3)	187.8(2)	C(7)-Si(1)-C(1)	111.40(10)
Si(1)-C(1)	187.8(2)	C(3)-Si(1)-C(1)	108.22(10)
Si(1)-C(2)	188.0(2)	C(7)-Si(1)-C(2)	110.51(10)
Si(2)-C(5)	187.2(2)	C(3)-Si(1)-C(2)	107.45(9)
Si(2)-C(4)	187.2(2)	C(1)-Si(1)-C(2)	108.13(9)
Si(2)-C(8)	187.7(2)	C(5)-Si(2)-C(4)	108.31(10)
Si(2)-C(1)	187.8(2)	C(5)-Si(2)-C(8)	110.18(10)
Si(3)-N(1)	174.2(2)	C(4)-Si(2)-C(8)	110.72(10)
Si(3)-C(2)	187.5(2)	C(5)-Si(2)-C(1)	107.79(11)
Si(3)-C(6)	187.6(2)	C(4)-Si(2)-C(1)	107.59(9)
Si(3)-C(4)	188.1(2)	C(8)-Si(2)-C(1)	112.10(10)
Si(4)-C(9)	186.9(2)	N(1)-Si(3)-C(2)	111.57(8)
Si(4)-C(5)	187.4(2)	N(1)-Si(3)-C(6)	112.10(8)
Si(4)-C(6)	187.7(2)	C(2)-Si(3)-C(6)	107.13(9)
Si(4)-C(3)	187.8(2)	N(1)-Si(3)-C(4)	111.19(8)
Si(5)-C(11)	186.9(2)	C(2)-Si(3)-C(4)	107.77(9)
Si(5)-C(17)	187.2(2)	C(6)-Si(3)-C(4)	106.82(9)
Si(5)-C(12)	187.7(2)	C(9)-Si(4)-C(5)	111.27(11)
Si(5)-C(15)	188.1(2)	C(9)-Si(4)-C(6)	111.33(11)
Si(6)-N(1)	174.7(2)	C(5)-Si(4)-C(6)	107.83(10)
Si(6)-C(10)	187.7(2)	C(9)-Si(4)-C(3)	110.63(13)
Si(6)-C(12)	187.8(2)	C(5)-Si(4)-C(3)	107.53(10)
Si(6)-C(13)	188.4(2)	C(6)-Si(4)-C(3)	108.09(9)
Si(7)-C(16)	186.7(2)	C(11)-Si(5)-C(17)	110.12(10)
Si(7)-C(14)	187.3(2)	C(11)-Si(5)-C(12)	108.33(8)
Si(7)-C(11)	187.4(2)	C(17)-Si(5)-C(12)	110.97(9)
Si(7)-C(10)	188.3(2)	C(11)-Si(5)-C(15)	107.12(9)
Si(8)-C(14)	187.5(2)	C(17)-Si(5)-C(15)	111.80(9)
Si(8)-C(15)	187.9(2)	C(12)-Si(5)-C(15)	108.36(9)
Si(8)-C(18)	188.1(2)	N(1)-Si(6)-C(10)	110.31(8)
Si(8)-C(13)	188.3(2)	N(1)-Si(6)-C(12)	112.84(8)
N(1)-C(19)	148.2(2)	C(10)-Si(6)-C(12)	107.01(8)
		N(1)-Si(6)-C(13)	112.03(8)
		C(10)-Si(6)-C(13)	106.84(8)
		C(12)-Si(6)-C(13)	107.50(8)
		C(16)-Si(7)-C(14)	111.78(10)
		C(16)-Si(7)-C(11)	111.35(9)
		C(14)-Si(7)-C(11)	107.18(9)
		C(16)-Si(7)-C(10)	110.19(9)
		C(14)-Si(7)-C(10)	107.49(9)
		C(11)-Si(7)-C(10)	108.70(8)
		C(14)-Si(8)-C(15)	108.27(9)
		C(14)-Si(8)-C(18)	110.45(9)
		C(15)-Si(8)-C(18)	111.64(9)
		C(14)-Si(8)-C(13)	108.16(8)
		C(15)-Si(8)-C(1)	107.06(9)
		C(18)-Si(8)-C(13)	111.12(9)
		C(19)-N(1)-Si(3)	114.53(12)
		C(19)-N(1)-Si(6)	118.37(12)
		Si(3)-N(1)-Si(6)	124.71(9)
		Si(2)-C(1)-Si(1)	112.29(10)
		Si(3)-C(2)-Si(1)	113.17(9)
		Si(4)-C(3)-Si(1)	112.28(11)
		Si(2)-C(4)-Si(3)	113.33(10)
		Si(2)-C(5)-Si(4)	112.65(10)
		Si(3)-C(6)-Si(4)	113.43(10)
		Si(6)-C(10)-Si(7)	113.53(9)
		Si(5)-C(11)-Si(7)	112.76(9)
		Si(5)-C(12)-Si(6)	113.20(10)
		Si(8)-C(13)-Si(6)	113.43(9)
		Si(7)-C(14)-Si(8)	112.46(10)
		Si(8)-C(15)-Si(5)	112.34(9)

Symmetry transformations used to generate equivalent atoms.

NMR spectroscopy. The bond lengths in **7** largely agree with those of the parent compound 1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane **12** [8]. Deviations of the average value of the Si-C distances in the $SiCH_2Si$ groups of the skeleton (**7** : 187.64 pm; **12** : 188.9 pm) probably arise from compound **7** being measured at 203 K, whereas **12** was examined at room temperature. Even the lengths of the bonds directly adjacent to the NMe bridge in **7** are not recognizably modified.

The comparison of the bond lengths and bond angles in compound **7** with those of the less sterically loaded molecule $(Me)_3SiN(Me)_2$ **14** [14] and $(Me_3Si)_2NH$ **15** [15] shows the following picture : Si–N : **7** 174.2 (2) pm, **14** 171.94 pm, **15** 175.5 pm; Si–C : **7** 187.64 pm, **14** 186.3 pm, **15** 186.7 pm; NSiC : **7** 111.4°, **14** 110.3°; CSiC : **7** 106.84°, **14** 108.7°, **15** 107.5° ; SiNSi : **7** 124.7°, **15** 125.5°. Obviously, there is no deterioration in **7** due to steric influence.

Discussion

The aim of the investigation was to gain a ready access to 1,3,5,7-tetrasilaadamantylamines in order to establish a route to N-bridged derivatives. Extensive investigations exist concerning N-bridged silanes [15]. Our results show that the starting compound $Me_3(NHMe)Ad$ **5** can be synthesized by reacting $MeNH_2$ with $ClMe_3Ad$ **2**, and $Me_2(NHMe)_2Ad$ **6** with Cl_2Me_2Ad **3**. In contrast, reactions with NH_3 yield white compounds which cannot be characterized. In the reaction of $BrMe_3Ad$ with $NaNH_2$, white polymers are the main products although $Me_3(NH_2)Ad$ **9** and $(Me_3Ad)_2NH$ **10**

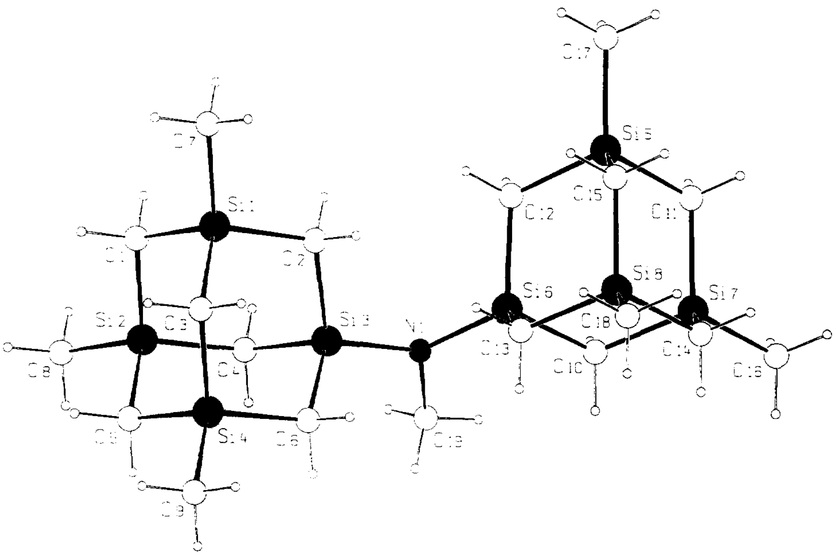

Fig 1. Crystal structure of compound **7**.

can be detected by mass spectrometry. In contrast with NH_3, the reactivity of $MeNH_2$ is much lower. $(NHMe)_4Ad$ **11**, $Me(NHMe)_3Ad$ **13**, $Me_2(NHMe)_2Ad$ **6** and $Me_3(NHMe)Ad$ **5** were thus obtained as isolable products in the reaction of $MeNH_2$ with the mixture of $Cl_nMe_{4-n}Ad$ resulting from the gas phase pyrolysis of Me_3SiCl. Compounds **5** and **6** are suitable intermediate states on the way to the formation of higher condensed derivatives, which is evident from the formation of $(Me_3Ad)_2NMe$ **7** from **5** and $[Me_2(NHMe)Ad]_2NMe$ **8** from **6**. The formation of **8** was observed during the mass spectroscopy experiments at 150°C. The investigation of the structure of **7** shows that no steric effects result from the linking of two Ad-skeletons. Therefore, and supported by model considerations, we also expect the formation of cyclic derivatives such as $(AdNMe)_3$ to be possible under experimental conditions still to be established.

Experimental section

The results of the mass spectrometry experiments on compound **5-11** are given in table IV together with their molecular masses.

^1H NMR (C_6D_6) [ppm] : $(CH_3)_3(NHMe)Ad$ **5** : CH_2 −0.31, −0.12; CH_3 0.32; NMe 2.55. $(CH_3)_2(NHMe)_2Ad$ **6** : CH_2 −0.40, −0.20, −0.03; CH_3 0.25; NMe 2.47. $(CH_3Ad)_2NMe$ **7** : CH_2 −0.32, 0.09; CH_3 0.27; NMe 2.48.

Formation and Investigation of Cl_2Me_2Ad 3

6 g of the mixture $Cl_nMe_{4-n}Ad$ **1**, which is a product from the gas phase pyrolysis of Me_3SiCl, was dissolved in 200 mL THF and cooled to −40°C. TMEDA (3.4 mL) was added and 11 mL (15 mmol) of a 1.35 M solution of LiMe (80% of the calculated amount) was added dropwise over 3 h. The reaction mixture was then stirred for 24 h at 20°C and subsequently investigated by ^1H NMR spectroscopy. The molar ratio of Cl_3MeAd and $ClMe_3Ad$ **2** was determined by integration (Cl_4Ad and Cl_3HAd were no longer present) in order to calculate the required quantity of LiMe for the formation of Cl_2Me_2Ad **3**. A further 7.4 mL (10 mmol) LiMe was added dropwise at −40°C, and the reaction mixture was stirred for 24 h. The THF was then removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 and filtered. The solvent was then removed again and the residue dried at 10^{-3} torr and 20°C. The raw product consisted of the main product Cl_2Me_2Ad and a minor amount of $ClMe_3Ad$, siloxanes and TMEDA. This mixture was then separated by sublimation at 120-160°C and 10^{-3} torr, and Cl_2Me_2Ad **3** and $ClMe_3Ad$ **2** were obtained in a ratio of 9.4:0.6 (determined by ^1H NMR spectroscopy). The isolated amount of the mixture of **3** and **2** is 4.2 g.

Synthesis and isolation of $ClMe_3Ad$ 2

For the synthesis of **2** from $Cl_nMe_{4-n}Ad$ **1**, we proceeded in the same way as for **3 1** (4.9 g) was dissolved in 200 mL THF and then 32 mmol LiMe was added at −40°C. Sublimation of the reaction product at 100-140°C and 10^{-3} torr yielded $ClMe_3Ad/Me_4Ad$ in a ratio of 4.3:1. Altogether, 1.9 g of this mixture was isolated.

Synthesis of $Me_3(NHMe)Ad$ 5

$BrMe_3Ad$ (3.0 g, 9.3 mmol) was dissolved in 150 mL hexane and an excess of $MeNH_2$ gas (dried over Na/K) was passed through the solution. The solution became cloudy due to the precipitation of $MeNH_3Br$. The solution was refluxed for 2 h, and then filtered at 20°C. Some of the solvent was removed *in vacuo* until white crystals precipitated, which were readily soluble in hexane. Yield of **5** = 1.3 g (4.9 mmol), 53%.

Synthesis of $Me_2(NHMe)_2Ad$ 6

An excess of $MeNH_2$ gas (dried over Na/K) was passed through a solution of 1.4 g (4.7 mmol) **6** in 30 mL THF at 20°C. The reaction mixture was then refluxed for 3 h. The solvent was removed by distillation and the residue was dissolved in *n*-pentane and filtered. Some of the solvent was removed *in vacuo*. From this solution, **6** crystallized as white crystals. Yield of **6** = 0.8 g (2.9 mmol), 61%.

Table IV. Results of the mass spectrometric investigation.

Compound	Detected mass ($_{det}$)			$m_{det} - m_{calc}$	Relative intensity (%)
5	$Si_4NC_{10}H_{25}$	M^+	271.10570	0.7	24.7
	$Si_4NC_9H_{22}$	M^+-CH_3	256.08160	1.3	100
	$Si_4C_9H_{21}$	M^+-$NHCH_3$	241.06970	2.3	41.1
6	$Si_4N_2C_{10}H_{26}$	M^+	286.11640	0.8	36.2
	$Si_4N_2C_9H_{23}$	M^+-CH_3	271.09330	0.5	100
	$Si_4NC_9H_{22}$	M^+-$NHCH_3$	256.0807	2.2	36.1
	$Si_4C_7H_{17}$	M^+-$N_2C_3H_9$	213.04074	0.7	23.9
7	$Si_8NC_{19}H_{45}$	M^+	511.17062	3.5	100
	$Si_8NC_{18}H_{42}$	M^+-CH_3	496.14716	0.6	80.3
	$Si_7NC_{18}H_{41}$	M^+-$SiCH_4$	467.1600	2.4	3.2
8	$Si_8N_3C_{19}H_{47}$	M^+	541.1908	1.5	100
	$Si_8N_3C_{18}H_{44}$	M^+-CH_3	526.1720	−1.3	60.3
	$Si_8N_3C_{17}H_{41}$	M^+-$2CH_3$	511.1448	0.5	12.9
	$Si_8N_3C_{17}H_{41/2}$		255.57273		18.1
9	$Si_4NC_9H_{23}$	M^+	257.0898	1.0	2.2
	$Si_4NC_8H_{20}$	M^+-CH_3	242.0669	0.4	50.2
	$Si_4C_9H_{21}$	M^+-NH_2	241.072	0.0	29.7
	$Si_4NC_7H_{17}$	M^+-$2CH_3$	227.0429	0.9	5.3
10	$Si_8NC_{18}H_{43}$	M^+	497.1500	5.0	29.5
	$Si_8NC_{17}H_{40}$	M^+-CH_3	482.1300	1.5	100
	$Si_8NC_{16}H_{37}$	M^+-$2CH_3$	467.1080	8.0	4.1
	$Si_7NC_{14}H_{32}$	M^+-SiC_4H_{11}	410.0900	2.0	8.1
11	$Si_4N_4C_{10}H_{28}$	M^+	316.1389	0.2	5.4
	$Si_4N_4C_9H_{25}$	M^+-CH_3	301.1260	44.1	44.1
	$Si_4N_3C_9H_{24}$	M^+-$NHCH_3$	286.1062	1.5	100
13	$Si_4N_3C_{10}H_{27}$	M^+	301.1260	2.2	50.4
	$Si_4N_3C_9H_{24}$	M^+-CH_3	286.1062	1.5	100

Synthesis of $(Me_3Ad)_2NMe$ 7 from $Me_3(NHMe)Ad$ 5

$Me_3(NHMe)Ad$ **5** (1.3 g, 4.9 mmol) was sealed in an evacuated glass ampoule and heated at 300°C for 24 h. The ampoule was then opened under N_2 and the reaction product determined to be a mixture of $Me_3(NHMe)Ad$ **5** and $(Me_3Ad)_2NMe$ **7** in a ratio of 1:1 by ^1H NMR spectroscopy. Annealing for 72 h led to a ratio **5**/**7** of 1:5. Fractional sublimation between 130 and 150°C and 10^{-6} torr made it possible to isolate a mixture of Me_4Ad, $Me_3(NHMe)Ad$, $(Me_3Ad)_2NMe$ and a small amount of siloxanes from the first fraction. By extracting the second fraction with *n*-pentane and cooling the solution to −30°C, we obtained white crystals of **7**.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for the financial support of our work.

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