Preparation and Structural Investigations of $(dippNSiMe_3Si)_2(Cp^*Ti)_2(NH)_6$ (dipp = 2,6-$i$$Pr_2C_6H_3$), $[dippNSiMe_3Si(NH_2)NH]_3$ and $[dippNSiMe_3Ge(NH_2)NH]_3$

Karsten Wraage,[a] Hans-Georg Schmidt,[a] Mathias Noltemeyer,[a] and Herbert W. Roesky*[a]

Dedicated to Professor John P. Fackler on the occasion of his 65th birthday

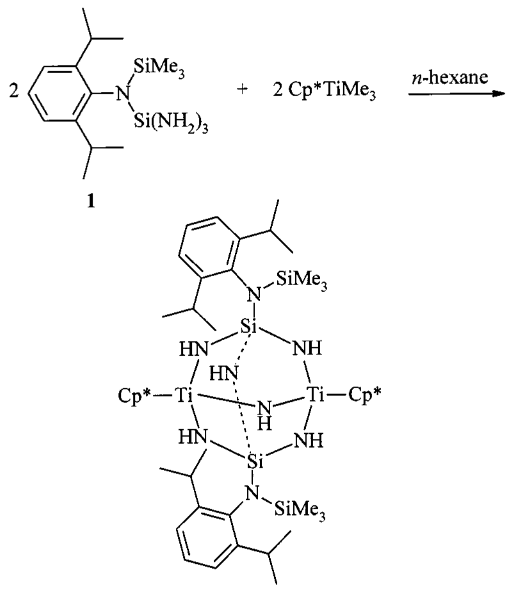
Keywords: Germanium / Nitrogen / Silicon / Titanium

The reaction of $dippNSiMe_3Si(NH_2)_3$ (**1**) (dipp = 2,6-$iPr_2C_6H_3$) with Cp^*TiMe_3 ($Cp^* = C_5Me_5$) and Me_3SnCl yields the new heterocyclic adamantane $(dippNSiMe_3Si)_2(Cp^*Ti)_2(NH)_6$ (**2**) containing the $Si_2Ti_2(NH)_6$ core and the silicon–nitrogen six-membered ring compound $[dippNSiMe_3Si(NH_2)NH]_3$ (**4**). $[dippNSiMe_3Ge(NH_2)_2]_2NH$ (**5**) reacts with $AlMe_3$ to give the germanium–nitrogen six-membered ring compound $[dippNSiMe_3Ge(NH_2)NH]_3$ (**6**). The compounds **2**, **4** and **6** have been structurally characterized by single-crystal X-ray structural analysis.

Introduction

Beyond the investigation of silanetriols as building blocks for new catalysts, the reactions of the isoelectronic triaminosilanes with organometallic precursors are of broad interest for materials research.[1][2] In 1995 we described the reaction of $dippNSiMe_3Si(NH_2)_3$ (**1**) with Cp^*TiMe_3 to yield a silicon−nitrogen−titanium four-membered ring system. Furthermore, we reported on the reaction of **1** and Me_3SnCl forming a compound with a monosubstituted nitrogen−tin bond. Moreover, in 1997 we published reactions of triaminosilanes with alumazene and $AlMe_3$. The reaction with alumazene forms a compound with an adamantane-like core.[3−5] Consequently, in 1998 we synthesized and published the first germanium compound containing more than one terminal amino group.[6]

Herein, we describe the reactions of $dippNSiMe_3Si(NH_2)_3$ with Cp^*TiMe_3 and Me_3SnCl under more drastic conditions and the reaction of $[dippNSiMe_3Ge(NH_2)_2]_2NH$ (**5**) with $AlMe_3$.



(1)

Scheme 1. Synthesis of compound **2**

Results and Discussion

Synthesis and Spectra

$dippNSiMe_3Si(NH_2)_3$ (**1**), prepared from $dippNSiMe_3SiCl_3$ and ammonia, reacts with Cp^*TiMe_3 in n-hexane under reflux with evolution of methane gas (Scheme 1) to give $(dippNSiMe_3Si)_2(Cp^*Ti)_2(NH)_6$ (**2**).

Compound **2** was characterized by mass spectrometry, NMR-spectral studies and by single-crystal X-ray diffraction. The proton-NMR spectrum of **2** shows a multiplet (δ = 7.19) due to the aromatic protons of the dipp-ligand. Resonances at δ = 4.05, 3.70 and 1.25 can be attributed to the methylene and methyl protons of the iPr group, respectively. The signal of the methyl protons of the Cp* ligand appear as a singlet (δ = 1.91). The signal of the N−H protons is found at δ = 0.67, and the signals of the methyl protons of the $SiMe_3$ groups are observed at δ = 0.27 and 0.21. Thus, it is clear that the two $SiMe_3$ groups are in slightly different environments, and in solution the rigid structure is maintained.

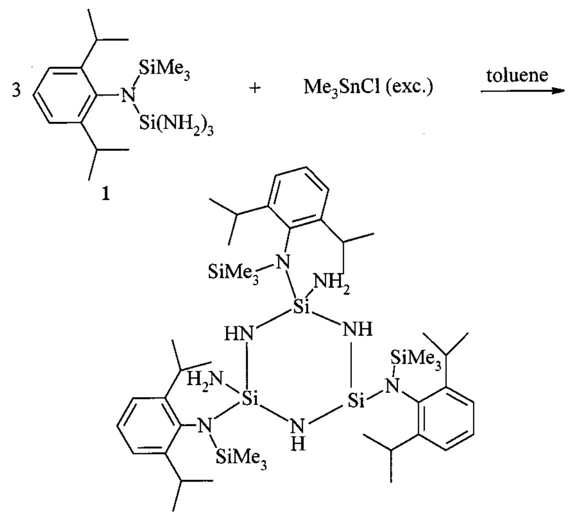
The mass spectrum of the compound shows the molecular ion peak [M^+] at m/z 1009 and a signal at m/z 994 due to the fragment [$M^+ - CH_3$].

[a] Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077, Göttingen, Germany
Fax: (internat.) + 49(0)551/393373

  1434−1948/99/0505−0863 $ 17.50+.50/0

Recently, we reported that compound **1** reacts with Me_3SnCl under smooth conditions to yield the monosubstituted derivative $dippNSiMe_3Si(NH_2)_2NHSnMe_3$ (**3**).[3] However, we were interested to obtain the fully substituted compound $dippNSiMe_3Si(NHSnMe_3)_3$.

Therefore we treated **1** with Me_3SnCl in toluene under reflux for 6 h and subsequent workup afforded compound $[dippNSiMe_3Si(NH_2)NH]_3$ (**4**) instead (Scheme 2).



(2)

4

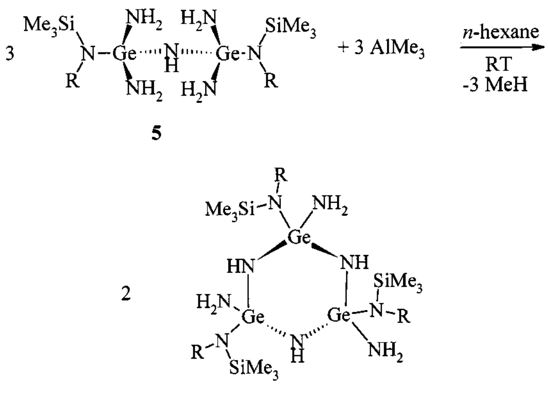
Scheme 2. Synthesis of compound **4**

Compound **4** was characterized by elemental analysis, NMR spectroscopy, mass spectrometry, and by single-crystal X-ray diffraction. The proton-NMR spectrum of **4** shows a multiplet ($\delta = 7.10$) due to the aromatic protons of the dipp ligand. Resonances at $\delta = 3.67$ and 1.31 can be attributed to the methylene and methyl protons of the *i*Pr group, respectively. The signals of N−H protons and unreacted NH_2 protons are found at $\delta = 0.65$ and 0.75, and the signals of the methyl protons of the $SiMe_3$ groups are observed at $\delta = 0.12$, 0.10 and 0.06.

The IR spectrum of **4** shows three absorptions ($\tilde{\nu} = 3401$, 3486 and 3152 cm^{-1}), which are due to the N−H stretching frequencies. The mass spectrum of **4** exhibits an intense peak at *m/z* 906 [$M^+ - NH_2$].

The reaction to give compound **4** can be described as an "acid-catalyzed" condensation reaction. The intermediate **3** we had previously isolated and characterized is a product of the reaction of an amino group that functions as a Lewis base and the tin atom of Me_3SnCl as a Lewis acid. Finally, the cleavage of tin−chlorine and N−H bond takes place yielding HCl.[3] The condensation reaction occurred three times under evolution of ammonia. Due to steric reasons only the molecule containing the six-membered ring is formed.

$[dippNSiMe_3Ge(NH_2)_2]_2NH$ (**5**), prepared from $dippNSiMe_3GeBr_3$ and ammonia, reacts with $AlMe_3$ in *n*-hexane at room temperature with evolution of methane gas (Scheme 3) to yield $[dippNSiMe_3Ge(NH_2)NH]_3$ (**6**). So far we were not able to characterize any other by-products.



(3)

6

Scheme 3. Synthesis of compound **6**; R = dipp

Compound **6** was characterized by elemental analysis, NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis. The proton-NMR spectrum of **6** exhibits a multiplet ($\delta = 7.04$) due to the aromatic protons of the dipp ligands. Resonances at $\delta = 3.60$, 1.25 and 1.20 can be attributed to the methylene and methyl groups of the *i*Pr group, respectively. The signals of the N−H protons are found at $\delta = 0.70$ and 0.65. The integration ratio of the intensities of the two N−H resonances is 1:2. We assign the signal at $\delta = 0.70$ to the protons of the bridging N−H group. In the silicon-NMR spectrum we observed one signal ($\delta = 4.8$) associated with the $SiMe_3$ group.

The IR spectrum of **6** shows three bands ($\tilde{\nu} = 3309$, 3386, 3619 cm^{-1}) due the N−H stretching frequencies. The mass spectrum of **6** exhibits an intense peak at *m/z* 1040 [$M^+ - Me$].

X-ray Structures of 2, 4 and 6

The structure of compound **2** was determined by single-crystal X-ray structural analysis. Compound **2** crystallizes in the space group $P2_1/n$. The structure can be described as a distorted heterocyclic adamantane (Figure 1). The centroid distance of Ti−Cp* is 206 pm and the angles involving this distance are in the range of 116 to 119°. The dipp ligands and Cp* ligands are in staggered positions.

The titanium−nitrogen bond lengths are in the range of 189.9−196.4 pm and are comparable to those of the $Ti-N_2-Si$ four-membered ring, and the average Si−N bond length (171.9−175 pm) is comparable to that in **1** (169−172 pm).[3]

The N−Ti−N angles (99.7−101.0°) are somewhat smaller than the tetrahedral bond angles, but the N−Si−N bond angles (106.1−109.9°) are in the range of a regular tetrahedron.

The central unit of the structure of **4** can be described as a six-membered ring consisting of alternating silicon and nitrogen atoms (Figure 2).

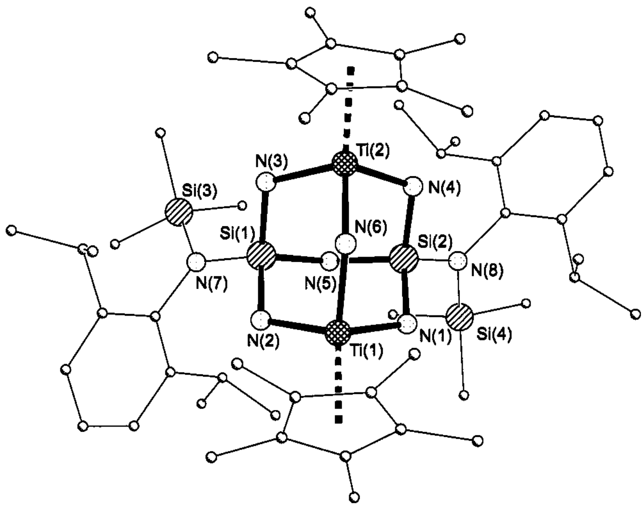


Figure 1. Crystal structure of **2**

Table 1. Selected bond lengths [pm] and angles [°] of compound **2**.

Ti(1)−N(6)	189.9(4)	Ti(1)−N(2)	192.3(4)
Ti(1)−N(1)	195.7(4)	Ti(2)−N(4)	193.3(4)
Ti(2)−N(3)	196.4(4)	Ti(2)−N(6)	191.3(4)
Si(1)−N(2)	171.9(4)	Si(1)−N(3)	172.2(4)
Si(1)−N(5)	175.0(4)	Si(2)−N(4)	172.4(4)
Si(2)−N(1)	171.7(4)	Si(2)−N(5)	174.2(4)
N(6)−Ti(1)−N(2)	101.1(2)	N(6)−Ti(1)−N(1)	99.7(2)
N(2)−Ti(1)−N(1)	100.1(2)	N(6)−Ti(1)−Ti(2)	29.12(11)
N(2)−Ti(1)−Ti(2)	82.54(11)	N(1)−Ti(1)−Ti(2)	81.11(11)
N(6)−Ti(2)−N(4)	100.9(2)	N(6)−Ti(2)−N(3)	100.6(2)
N(4)−Ti(2)−N(3)	101.0(2)	N(6)−Ti(2)−Si(2)	83.44(12)
N(4)−Ti(2)−Si(2)	29.52(11)	N(3)−Ti(2)−Si(2)	81.00(12)
N(6)−Ti(2)−Ti(1)	28.89(11)	N(4)−Ti(2)−Ti(1)	83.07(11)
N(3)−Ti(2)−Ti(1)	81.87(11)	Si(2)−Ti(2)−Ti(1)	58.68(3)
N(2)−Si(1)−N(3)	109.3(2)	N(2)−Si(1)−N(5)	108.3(2)
N(3)−Si(1)−N(5)	106.4(2)	N(1)−Si(2)−N(4)	108.8(2)
N(1)−Si(2)−N(5)	106.1(2)	N(4)−Si(2)−N(5)	109.9(2)
N(1)−Si(2)−Ti(2)	91.33(13)	N(4)−Si(2)−Ti(2)	33.54(12)
N(5)−Si(2)−Ti(2)	88.68(13)	Si(2)−N(1)−Ti(1)	119.0(2)
Si(1)−N(2)−Ti(1)	118.5(2)	Si(1)−N(3)−Ti(2)	118.1(2)
Si(2)−N(4)−Ti(2)	116.9(2)	Si(2)−N(5)−Si(1)	117.3(2)
Ti(1)−N(6)−Ti(2)	122.0(2)		

Compound **4** crystallizes in the space group $P-1$. The silicon−nitrogen bond lengths within the ring are of nearly equal size (170 pm), and they are comparable to those in the starting material $dippNSiMe_3Si(NH_2)_3$ (average 171 pm). The bond angles N−Si−N (in the range of 102.63−104.46°) and Si−N−Si (in the range of 131.53−134.79°) are part of a distorted six-membered ring.

The atoms Si(1, 2, 3) and N(1, 3) are forming a plane while N(2) is out of the plane (61.57 pm), giving an envelope conformation.

The central unit of the structure of compound **6** is analogous to that of **4** (Figure 3).

Compound **6** crystallizes in the space group $P-1$. The Ge−N bond lengths in the ring are in the range of 181.9−182.8 pm. They are comparable to those described by George et al. in the six-membered ring of $[(tBuS)_2Ge(NH)]_3$.[7] The N−Ge−N bond angles are nearly 104° and the Ge−N−Ge angles (in the range of 124.8−127.6°) are part of a distorted $(GeN)_3$ six-membered ring system.

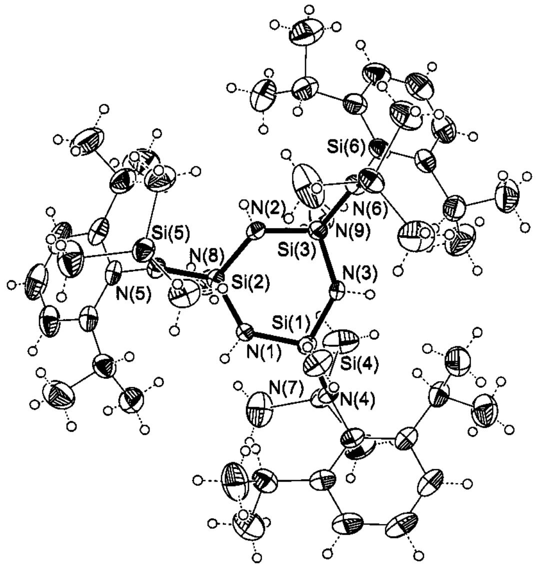


Figure 2. Crystal structure of **4**

Table 2. Selected bond lengths [pm] and angles [°] of compound **4**

Si(1)−N(1)	170.5(2)	Si(1)−N(3)	170.3(2)
Si(2)−N(1)	170.3(2)	Si(2)−N(2)	170.6(2)
Si(3)−N(2)	171.1(2)	Si(3)−N(3)	170.5(2)
N(3)−Si(1)−N(1)	103.95(9)	N(1)−Si(2)−N(2)	104.46(9)
N(3)−Si(3)−N(2)	102.63(9)	Si(1)−N(3)−Si(3)	134.79(11)
Si(2)−N(1)−Si(1)	131.53(12)	Si(2)−N(2)−Si(3)	124.04(11)

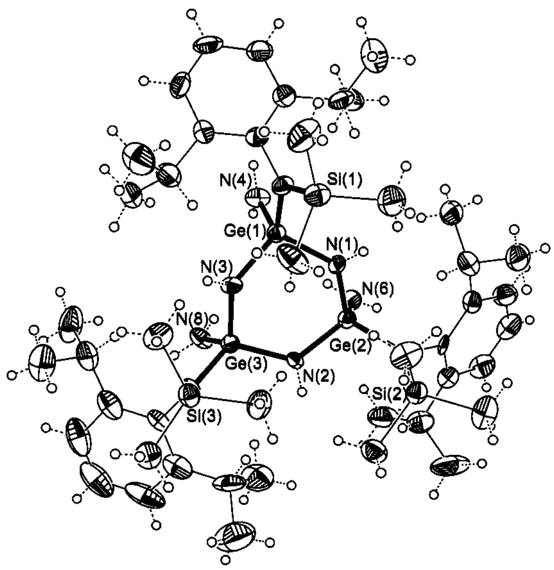


Figure 3. Crystal structure of **6**

The atoms Ge(1, 2) and N(2, 3) are forming a plane while Ge(3) and N(1) are out of the plane (19.2 and −19.2 pm), giving a chair conformation.

Conclusion

In summary, we have shown that silicon and germanium compounds containing terminal NH_2 groups are interesting

Table 3. Selected bond lengths [pm] and angles [°] of compound **6**

Ge(1)−N(1)	181.9(7)	Ge(1)−N(3)	182.8(8)
Ge(1)−N(4)	183.2(9)	Ge(2)−N(2)	182.4(8)
Ge(2)−N(6)	181.8(9)	Ge(3)−N(2)	182.4(8)
Ge(2)−N(1)	182.7(7)	Ge(3)−N(8)	182.1(9)
Ge(3)−N(3)	180.7(7)	N(1)−Ge(1)−N(3)	104.0(3)
N(2)−Ge(2)−N(1)	104.7(4)	N(2)−Ge(3)−N(3)	104.4(4)
Ge(1)−N(1)−Ge(2)	124.8(5)	Ge(1)−N(3)−Ge(3)	127.6(4)
Ge(2)−N(2)−Ge(3)	127.3(4)		

starting materials for preparing new inorganic ring systems with functional groups. A marked difference in reactivity has been observed while Cp*$TiMe_3$ yields the $Si_2Ti_2(NH)_6$ adamantane core, the main-group reagents Me_3SnCl and $AlMe_3$ lead to six-membered $(SiN)_3$ and $(GeN)_3$ condensation products.

Experimental Section

General: Due to the water and air sensitivity of the compounds, oxygen and moisture were excluded during all procedures. ^{1}H-NMR data were recorded with a Bruker AM 200 FT NMR spectrometer, IR data were recorded with a BIO RAD Digilab FTS 7 spectrometer and mass data with a Finnigan MAT 95 and a Varian MAT CH5 spectrometer. Elemental analyses were performed by the analytical laboratory of the institute. The starting materials dippNSiMe_3Si$(NH_2)_3$ and Cp*$TiMe_3$ were prepared by literature methods.[3][8] Me_3SnCl and dippNH_2 were commercially available.

Synthesis of 2: To a solution of 0.46 g (2 mmol) of Cp*$TiMe_3$, in *n*-hexane (8 ml), was added dropwise a solution of 0.65 g (2 mmol) of **1**, dissolved in 6 mL of *n*-hexane, at room temperature while stirring. The reaction mixture was warmed up to 69 °C until the gas evolution ceased (3 h). The solvent was removed in vacuo and recrystallization of **2** from *n*-hexane (5 mL) afforded single crystals of **2**; yield 0.8 g (79%) (m.p. 260 °C). −$C_{50}H_{88}N_8Si_4Ti_2$ (1008.71): calcd. C 61.39, H 9.38; found C 61.81, H 9.48. − IR (Nujol): $\tilde{\nu}$ = 3365 cm^{-1}, 3409, 3481 (N−H). − ^{1}H NMR (200 MHz, C_6D_6): δ = 0.21 [s, 9 H, Si(C*H*$_3$)$_3$], 0.27 [s, 9 H, Si(C*H*$_3$)$_3$], 0.67 (s, 6 H, N*H*), 1.25 [m, 24 H, CH(C*H*$_3$)$_2$], 1.91 (s, 30 H, C*H*$_3$, Cp*), 3.70 [sept, 2 H, C*H*(CH$_3$)$_2$], 4.05 [sept, 2 H, C*H*(CH$_3$)$_2$], 7.19 (m, 6 H, aromatic *H*). − ^{29}Si NMR (49 MHz, C_6D_6): δ = −38.7 (*Si*NH), 3.1 (*Si*Me$_3$). − MS (EI); *m*/*z* (%): 1009 (100) [M$^+$].

Synthesis of 4: 0.65 g (2 mmol) of **1** and 1.19 g (6 mmol) of Me_3SnCl were dissolved in 20 mL of toluene. Then the reaction mixture was warmed up to 111 °C for 6 h. Removal of solvent and Me_3SnCl in vacuo afforded a white solid and recrystallization of the crude product from *n*-hexane (3 mL) gave colorless single crystals of **4**; yield 0.48 g (78%) (m.p. 260 °C). − $C_{45}H_{87}N_9Si_6$ (922.07): calcd. N 13.68, Si 18.28; found N 12.65, Si 18.14. − IR (Nujol): $\tilde{\nu}$ = 3401 cm^{-1}, 3486, 3152 (N−H). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.06 [s, 9 H Si(C*H*$_3$)$_3$], 0.10 [s, 9 H Si(C*H*$_3$)$_3$], 0.12 [s, 9 H Si(C*H*$_3$)$_3$], 0.65 [s, 3 H, Si(N*H*)NH$_2$], 0.75 [s, 6 H, Si(NH)N*H*$_2$], 1.31 [m, 36 H, CH(C*H*$_3$)$_2$], 3.67 [m, 6 H, C*H*(CH$_3$)$_2$], 7.10 (m, 9 H, aromatic *H*). − ^{29}Si NMR (49 MHz, $CDCl_3$): δ −43.1 [*Si*(NH)NH$_2$], −41.4 [*Si*(NH)NH$_2$], −39.8 [*Si*(NH)NH$_2$], 4.2 (*Si*Me$_3$), 4.7 (*Si*Me$_3$), 5.3 (*Si*Me$_3$). − MS (EI); *m*/*z* (%): 906 (80) [M$^+$ − NH$_2$], 905 (100) [M$^+$ − NH$_2$ − H].

Synthesis of 6: To a solution of 0.62 g (2 mmol) of **5** in *n*-hexane (10 mL) was added dropwise 0.53 mL of a solution of $AlMe_3$ in *n*-hexane (1.6 M) at room temperature. After 2 h, the evolution of methane ceased. Subsequently, the solvent was removed in vacuo and the colorless solid recrystallized from *n*-hexane/trichloromethane (1:1) to give single crystals of **6**; yield 0.6 g (67%) (m.p. 177 °C). − $C_{45}H_{87}Ge_3N_9Si_3$ (1055.64): calcd. H 8.24, Ge 20.63; found H 7.94, Ge 19.63. − IR (KBr): $\tilde{\nu}$ = 3309 cm^{-1}, 3386, 3619 (N−H). − ^{1}H NMR (200 MHz, C_6D_6): δ = 0.21 [s, 27 H, Si(C*H*$_3$)$_3$], 0.65 [s, 6 H, Ge(N*H*$_2$)NH], 0.70 [s, 3 H, Ge(NH$_2$)N*H*], 1.20 [d, 18 H, CH(C*H*$_3$)$_2$], 1.25 [d, 18 H, CH(C*H*$_3$)$_2$], 3.60 [sept, 6 H, C*H*(CH$_3$)$_2$], 7.04 (m, 9 H, aromatic *H*). − ^{29}Si NMR (49 MHz, C_6D_6): δ = 4.8 (*Si*Me$_3$). − MS (EI); *m*/*z* (%): 73 (90) [SiMe$_3$], 1040 (100) [M$^+$ − Me].

Crystal Structure Determination of Compounds 2, 4 and 6: Data collection and processing: Intensity data were collected using the ω-2θ scan method at 153(2) K for **2**, 193(2) K for **4** and 150(2) K for **6** with a Siemens AED2 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) and according to the Learnt-Profile Method.[9] Of the 11865 reflections measured of compound **2** (3.51° ≤ θ ≤ 22.56°) 8424 were unique (merging *R* = 0.0468), of the 12450 reflections measured of compound **4** (3.51° ≤ θ ≤ 22.55°) 7708 were unique (merging *R* = 0.0238) and of the 16520 reflections measured of compound **6** (3.52° ≤ θ ≤ 25.04°) 11734 were unique (merging *R* = 0.1137). All of the reflections were used in the refinement. − X-ray crystallographic study: The structures were solved by direct methods (SHELXS-90)[9] and refined against F^2 by means of the full-matrix least-squares technique using SHELXL 93 and SHELXL 97.[10][11] The weighting schemes were $w^{-1} = \sigma^2(F_o^2) + (0.080\cdot P)^2 + 18.55\cdot P$ for **2**, $w^{-1} = \sigma^2(F_o^2) + (0.040\cdot P)^2 + 1.95\cdot P$ for **4** and $w^{-1} = \sigma^2(F_o^2) + (0.20\cdot P)^2 + 0\cdot P$ for **6** with $P = (F_o^2 + 2F_c^2)/3$ were applied in the final cycles of refinement. The converged residuals were $R1$ = 0.0791 for reflections with $I > 2\sigma(I)$, and $wR2$ = 0.1798 for all data of **2**, the converged residuals were $R1$ = 0.0791 for reflections with $I > 2\sigma(I)$, and $wR2$ = 0.0.0909 for all data of **4** and the converged residuals were $R1$ = 0.1066 for reflections with $I > 2\sigma(I)$, and $wR2$ = 0.2625 for all data of **6**. A final Fourier difference map showed the largest peak and hole 904 and −520 e nm^{-3} for **2**, 331 and −358 e nm^{-3} for **4** and 218.3 and 142.2 e nm^{-3} for **6**. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located in positions riding on the corresponding C atoms.

Acknowledgments

This work was financially supported by the Deutsche Forschungsgemeinschaft.

[1] R. Murugavel, A.Voigt, M. G.Walawalkar, H. W. Roesky, *Chem. Rev.* **1996**, *96*, 2205.

[2] R. Murugavel, V. Chandrasekhar, H. W. Roesky, *Acc. Chem. Res.* **1996**, *29*, 183.

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

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

[5] H. Wessel, C. Rennekamp, D.-S. Waeszada, H.W. Roesky, M.L. Montero, I. Uson, *Organometallics* **1997**, *16*, 3243.

[6] K. Wraage, L. Lameyer, D.Stalke, H. W. Roesky, *Angew. Chem.* **1998**, accepted.

[7] C. George, A. P. Purdy, *Acta Crystallogr., Sect. C* **1996**, *52*, 2489.

[8] M. Mena, P. Royo, R. Serrano, M.A. Pellinghelli, A. Tiripicchio, *Organometallics* **1989**, *8*, 476.

[9] G.M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[10] G.M. Sheldrick, *SHELXL-93*, University of Göttingen, Germany, **1993**.

[11] G. M. Sheldrick, Universität Göttingen, **1997**.
[12] Further details of the crystal structure investigations are available on request from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK on quoting the depository numbers CCDC-111763 for **2**, -111764 for **4** and -111765 for **6**, the names of the authors, and the journal citation (Fax: int. code + 44-1223/336−033; E-mail: deposit@ccdc.cam.ac.uk).

Received December 7, 1998
[I98418]