Synthesis, Structures, and Reactivity of Alkylgermanium(II) Compounds Containing a Diketiminato Ligand[†]

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Received April 25, 2002

Reaction of $[HC(CMeNAr)_2]GeCl$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) with RLi (R = Me, nBu) in diethyl ether at −78 °C yielded the alkylgermanium(II) compounds $[HC(CMeNAr)_2]GeR$ (R = Me (**5**), nBu (**6**)), which are monomeric with a three-coordinate germanium center. Compound **5** was oxidized with sulfur and selenium to afford $[HC(CMeNAr)_2]GeMe(E)$ (E = S (**7**), Se (**8**)), in which a terminal Ge=E double bond is present. Treatment of **5** with trimethylsilyl azide in hexane at room temperature gave $[HC(C(CH_2)NAr)CMeNAr]GeMe(N(H)SiMe_3)$ (**9**), containing a Ge−N single bond; the expected compound $[HC(CMeNAr)_2]GeMe(NSiMe_3)$ with a Ge=N double bond was not observed. The latter reaction proceeds with migration of a hydrogen atom from a methyl group of the ligand backbone to the nitrogen atom bonded to the silicon atom with formation of a methylene moiety. X-ray structural data are provided for **5**, **6**, **8**, and **9**.

Introduction

The chemistry of divalent germanium compounds has received considerable attention over the past three decades due to their carbene-like properties.[1] Such compounds are generally reactive and tend to oligomerize or polymerize. However, Ge(II) compounds can be stabilized kinetically by sterically demanding ligands and/or thermodynamically by inter- and intramolecular coordination. Indeed, numerous nitrogen-containing bulky ligands have been used to stabilize these compounds.[2−9] Very recently, the chelating β-diketiminato ligands $[HC(CMeNR)_2]^-$ (R = Ph,[10] 2,4,6-Me$_3$C$_6$H$_2$,[11] 2,6-iPr$_2$C$_6$H$_3$[12−14]), where steric flexibility is afforded by variation of the substituents on the ligand backbone, were used to good advantage in the synthesis of such compounds.

Compounds of divalent germanium bonded to small alkyl substituents (such as Me, Et, and Bu) are highly reactive and therefore exist only as intermediates.[15,16] Recently, compounds of composition LGeR, where L is a bulky ligand and R is a small alkyl group, have been investigated. Jutzi and co-workers prepared the first examples of such compounds by oxidative addition of MeI to MamxGeR (Mamx = methylamino-methyl-m-xylyl; R = Me, nBu) but did not characterize the products by structural analysis.[7] We have synthesized $[HC(CMeNAr)_2]GeCl$ (**1**; Ar = 2,6-iPr$_2$C$_6$H$_3$).[12] By metathesis reactions compound **1** was converted to the first structurally characterized germanium(II) hydride and germanium(II) fluoride $[HC(CMeNAr)_2]GeF$ (**2**).[13] Moreover, the first structurally characterized compounds of multiply bonded heavier main group elements bearing a halide, $[HC(CMeNAr)_2]GeX(S)$ (X = F (**3**), Cl (**4**)),[14] were prepared. Herein, we report the preparation and the characterization of the alkylated germanium(II) compounds $[HC(CMeNAr)_2]GeR$ (Ar = 2,6-iPr$_2$C$_6$H$_3$, R = Me (**5**), nBu (**6**)) and the resulting chalcogen derivatives $[HC(CMeNAr)_2]GeMe(S)$ (**7**), $[HC(CMeNAr)_2]GeMe(Se)$ (**8**), $[HC(C(CH_2)NAr)CMeNAr]GeMe(N(H)SiMe_3)$ (**9**), and $[HC(CMeNAr)_2]GeMe_2(I)$ (**10**). Compounds **5**, **6**, **8**, and **9** were characterized by single-crystal X-ray structural analysis.

[†] Dedicated to Professor Anton Meller on the occasion of his 70th birthday.

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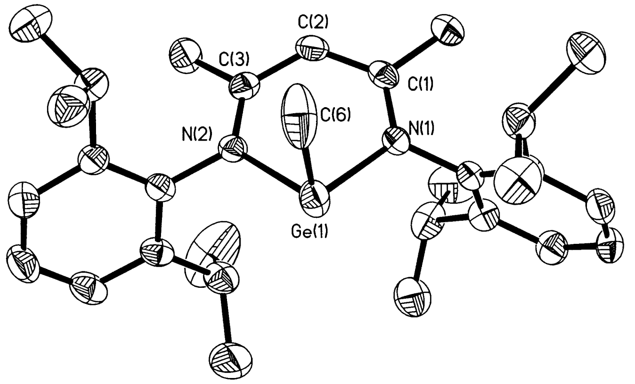
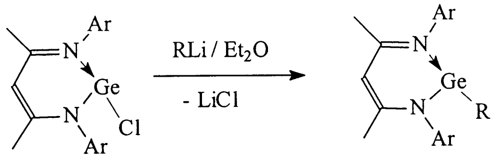


Figure 1. Thermal ellipsoid plot (50%) of **5**. Important structural data are given in Table 1.

Scheme 1



1 **5, 6**

R = Me (**5**), *n*Bu (**6**)

Ar = 2,6-*i*$Pr_2C_6H_3$

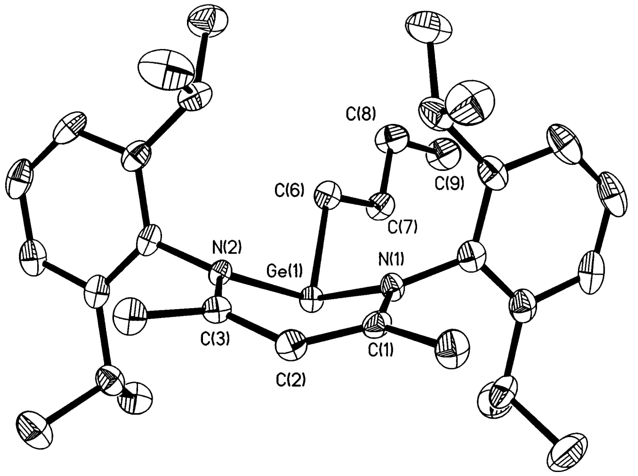


Figure 2. Thermal ellipsoid plot (50%) of **6**. Important structural data are given in Table 1.

Results and Discussion

Synthesis and Structures of Compounds 5 and 6. Although Ge(II) compounds are generally reactive and tend to oligomerize or polymerize, the preparation of a series of novel monomeric β-diketiminato germanium(II) compounds, [HC(CMeNAr)$_2$]GeX (Ar = 2,6-*i*$Pr_2C_6H_3$; X = Cl (**1**), F (**2**)),[12,13] as well as [HC(CMeNAr)$_2$]GeX(S) (X = F (**3**), Cl (**4**)), might suggest that the synthesis of a monomeric alkylated Ge(II) compound would be possible. Therefore, compound **1** was treated with MeLi and *n*BuLi in diethyl ether at −78 °C. After workup, the compounds [HC(CMeNAr)$_2$]GeR (R = Me (**5**), *n*Bu (**6**)) were isolated in high yield (Scheme 1).

Compounds **5** and **6** are stable under an inert atmosphere at temperatures below their melting points. They are soluble in common organic solvents such as pentane, diethyl ether, and dichloromethane.

For structural investigation, single crystals of **5** (red-orange) and **6** (deep red) were crystallized from hexane solution at −32 °C. The structures, determined by single-crystal X-ray diffraction, are shown in Figures 1 and 2. Selected bond lengths and angles are listed in Table 2; complete bond distances and angles are included in the Supporting Information.

The observed structures of **5** and **6** show that both compounds are monomeric, as expected, and that the germanium centers adopt similar three-coordinate sites. The sum of the bond angles at the metal center (280.81° in **5** and 285.4° in **6**) deviates strongly from that for tetrahedral symmetry. The Ge−N bond lengths in **5** (2.008(2) and 2.038(2) Å) and in **6** (2.023(2) and 2.025(2) Å) are in the normal range[2,3,17] but are slightly longer than those of the starting material **1** (1.988(2) and 1.997(3) Å).[12] Obviously, this results from the influence of the substituents at the metal center (the stronger electron-withdrawing property of chlorine compared to the alkyl groups). The Ge−C bond lengths in **5** (2.002(4) Å) and in **6** (2.014(3) Å) are in the normal range (1.962(6)−2.039(3) Å).[7]

Derivatives of Compound 5 and Their Structures. Chalcogen derivatives of the heavier group 14 elements M=E (M = Si, Ge, Sn; E = S, Se, Te) usually are prepared by reaction of the divalent group 14 compound with elemental chalcogens.[18−23] Compound **5** reacts with elemental sulfur in toluene at reflux to give the compound [HC(CMeNAr)$_2$]GeMe(S) (**7**) (Scheme 2). By a similar procedure, the selenium analogue [HC(CMeNAr)$_2$]GeMe(Se) (**8**) was prepared (Scheme 2) in 87% yield. However, alkylation of a halogen-containing Ge(IV) sulfide also is a possible route to X(R)Ge=S compounds. We recently synthesized the compound [HC(CMeNAr)$_2$]GeCl(S) (**11**),[14] a species with a formal double bond between the group 14 and 16 elements. Thus **11** was treated with MeLi to afford **7** (Scheme 2). To our surprise the Ge=S double bond in **7** remained intact in the presence of the small methyl group. Usually sterically bulky substituents are required for a stable X(R)Ge=S compound.

Of special interest is the nature of the germanium−chalcogenido interaction in **7** and **8**, which may be described by the resonance structures $\text{Ge}^{+}{-}\text{E}^{-} \leftrightarrow \text{Ge}{=}\text{E}$. This behavior of the Ge=S bond is supported by the reaction products using Tbt(Tip)Ge=S (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl) and reagents such as water and dienes.[22] To obtain more information about the germanium−sele-

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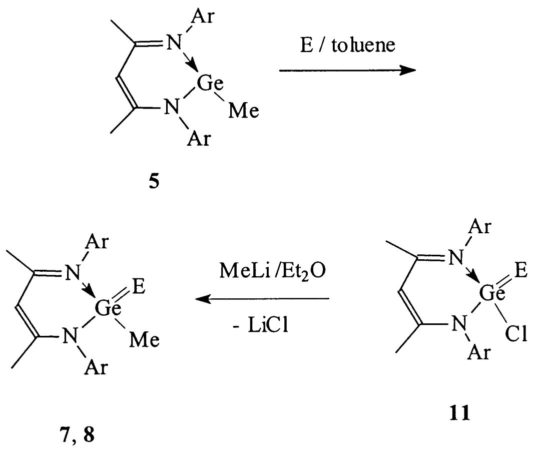
Table 1. Crystallographic Data for Compounds 5, 6, 8, and 9

	5	**6**	**8**	**9**
formula	$C_{30}H_{44}GeN_2$	$C_{33}H_{50}GeN_2$	$C_{30}H_{44}GeN_2Se$	$C_{33}H_{53}GeN_3Si$
fw	505.26	547.34	584.22	592.46
color	orange-red	deep red	yellow	pale yellow
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$Fdd2$	$P2_1/n$	$P2_1/m$
a (Å)	17.230 (3)	22.679 (5)	13.285 (3)	8.782 (2)
b (Å)	13.211 (3)	63.773 (13)	17.014 (3)	19.962 (4)
c (Å)	13.323 (2)	8.7734 (18)	13.752 (3)	10.500 (2)
β (deg)	109.011 (15)	90	106.01 (3)	114.58 (3)
V (Å^3)	2867.2 (9)	12689 (4)	2987.8 (11)	1673.9 (6)
Z	4	16	4	2
d_{calcd} (g cm^{-3})	1.170	1.146	1.299	1.175
μ (mm^{-1})	1.087	0.987	2.263	0.975
F(000)	1080	4704	1216	636
cryst size (mm)	1.00 × 0.60 × 0.30	0.50 × 0.4 × 0.3	0.80 × 0.80 × 0.60	0.60 × 0.50 × 0.40
2θ range (deg)	7.04−45.08	12.34−49.90	7.56−50.08	4.72−55.36
index range	$-15 \le h \le 18$, $-14 \le k \le 7$, $-14 \le l \le 14$	$-26 \le h \le 25$, $-74 \le k \le 74$, $-10 \le l \le 9$	$-15 \le h \le 15$, $-9 \le k \le 20$, $-16 \le l \le 16$	$-11 \le h \le 7$, $-26 \le k \le 26$, $-12 \le l \le 13$
no. of rflns collected	3944	21 238	8626	23 957
no. of indep rflns	3748 (R(int) = 0.0637)	4647 (R(int) = 0.0613)	5267 (R(int) = 0.0699)	4004 (R(int) = 0.0586)
R1, wR2 ($I > 2(\sigma)I$)	0.0388, 0.0986	0.0310, 0.0761	0.0339, 0.0879	0.0340, 0.0860
R1, wR2 (all data)	0.0432, 0.1028	0.0321, 0.0765	0.0384, 0.0916	0.0392, 0.0900
goodness of fit, F^2	1.026	1.092	1.028	1.026
no. of data/restraints/params	3748/0/309	4647/1/336	5267/0/318	4004/16/213
abs structure param		0.047(9)		
largest diff peak and hole, e Å^{-3}	0.601, −0.519	0.710, −0.493	0.820, −0.633	0.459, −0.586

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 5, 6, and 8

complex	bond dist		bond angle	
5	Ge(1)−N(1)	2.008(2)	N(1)−Ge(1)−N(2)	90.87(9)
	Ge(1)−N(2)	2.038(2)	N(1)−Ge(1)−C(6)	97.13(13)
	Ge(1)−C(6)	2.002(4)	N(2)−Ge(1)−C(6)	92.81(12)
6	Ge(1)−N(1)	2.023(2)	N(1)−Ge(1)−N(2)	87.85(9)
	Ge(1)−N(2)	2.025(2)	N(1)−Ge(1)−C(6)	97.52(10)
	Ge(1)−C(6)	2.014(3)	N(2)−Ge(1)−C(6)	100.06(10)
8	Ge(1)−N(1)	1.931(2)	N(1)−Ge(1)−N(2)	95.24(8)
	Ge(1)−N(2)	1.947(2)	Se(1)−Ge(1)−N(1)	113.38(6)
	Ge(1)−C(6)	1.973(2)	Se(1)−Ge(1)- -N(2)	117.15(6)
	Ge(1)−Se(1)	2.1992(5)	Se(1)−Ge(1)−C(6)	120.94(10)
			N(1)−Ge(1)−C(6)	103.64(11)
			N(2)−Ge(1)−C(6)	102.70(10)

Scheme 2



7: E = S; **8**: E = Se; **11**: E = S
Ar = 2,6-iPr$_2$C$_6$H$_3$

nium interaction, the structure of compound **8** was determined by single-crystal X-ray diffraction.

Figure 3 shows its molecular structure. Compound **8** is monomeric, and the germanium center is four-coordinate in a distorted-tetrahedral environment. This geometry is similar to that of its sulfur analogue and to those of the compounds containing a terminal chalcogenido germanium unit.[14,19−23] The observed Ge−Se bond length in **8** (2.199(1) Å), which is shorter than the Ge−Se single-bond lengths in [Tbt(Mes)GeSe]$_2$ (Mes = 2,4,6-trimethylphenyl) (2.397(1) and 2.433(1) Å),[22] is in good agreement with those reported for Ge=Se (2.180(2)[22] to 2.247(7) Å[20]). The short Ge−Se bond length in **8** is indicative of a double bond or a Ge−Se σ bond with an additional percentage of ionic character. The Ge−N (1.931(2) and 1.947(2) Å) and Ge−C (1.973(2) Å) bond lengths are shorter than those of the starting material **5** (Ge(1)−N(1) = 2.008(2) Å, Ge(1)−N(2) = 2.038(2) Å, and Ge(1)−C(6) = 2.002(4) Å), as expected from the higher oxidation state of the product. The fact that the N(1)−Ge(1)−N(2) angle of **8** (95.24(8)°) is larger than that of **5** (90.87(9)°) may be explained in the same way.

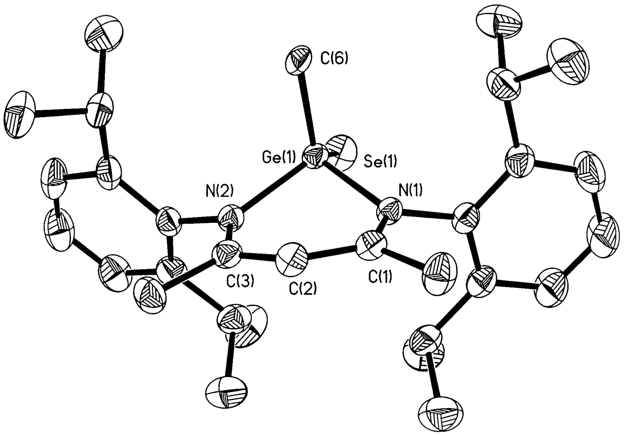
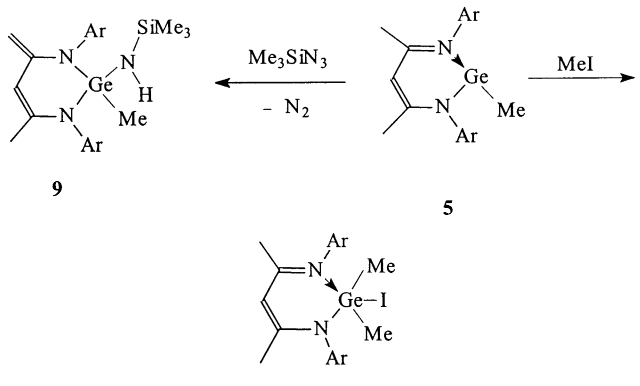


Figure 3. Thermal ellipsoid plot (50%) of **8**. Important structural data are given in Table 1.

^{77}Se NMR may act as a good probe for the germanium−selenium interaction. The ^{77}Se chemical shift for the Ge−Se single bond in (H$_3$Ge)$_2$Se is −612 ppm

Scheme 3



9

5

10

Ar = 2,6-iPr$_2$C$_6$H$_3$

(relative to Me$_2$Se).[24] In contrast, to the best of our knowledge, the available data for germanium selenones, R$_2$Ge=Se, show resonances at a much lower field (800−1100 ppm).[20,22,23] In the ^{77}Se NMR of compound **8** the resonance was observed at −349 ppm. This finding that the ^{77}Se chemical shift for **8** (−349 ppm) is between that for a single bond (−600 ppm) and those for a double bond (800−1100 ppm) indicates that the bonding in **8** is appropriately described as intermediate between Ge$^+$−E$^-$ and Ge=E resonance structures.

The reaction of germylenes with trimethylsiyl azide has been studied and established as a route to compounds containing the Ge=N double bond.[3,17] However, treatment of **5** with trimethylsilyl azide in hexane at room temperature gave the Ge−N single-bonded compound [HC(C(CH$_2$)NAr)CMeNAr]GeMe(N(H)SiMe$_3$) (**9**), instead of [HC(CMeNAr)$_2$]GeMe(NSiMe$_3$) (Scheme 3). The reaction proceeds with migration of a hydrogen atom from a methyl group of the ligand backbone to the nitrogen atom on silicon with formation of a methylene group. The EI-MS spectrum showed the molecular ion peak M$^+$ (m/e 593) with the calculated isotopic pattern. In the ^{1}H NMR spectrum of **9** (toluene-d_8) the resonances clearly show the existence of NH (δ 0.25, b, 1 H) and the β-CH$_2$ moiety (δ 3.22, s, 1 H and δ 3.86, s, 1 H). The IR (Nujol) NH absorption is observed at 3361 cm^{-1}. The NH resonance and the IR stretching frequency are comparable with those of compounds containing a GeN(H)SiMe$_3$ group.[17] Although the mechanism for the formation of **9** is unclear, a likely one is given in Scheme 4.

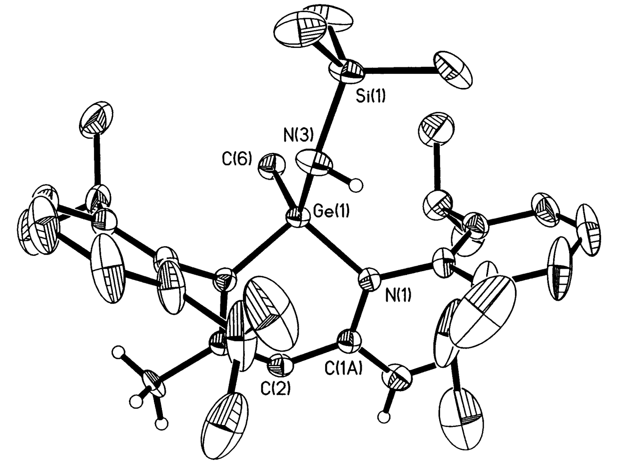
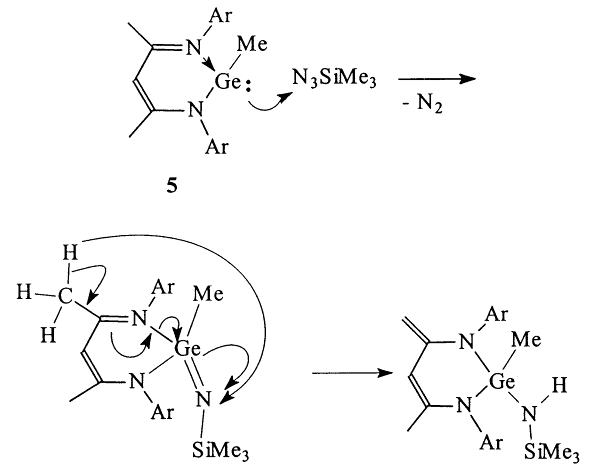


Figure 4. Thermal ellipsoid plot (50%) of the molecular backbone of **9**. H atoms are not shown. Important structural data are given in Table 1.

Scheme 4



5

9

Ar = 2,6-iPr$_2$C$_6$H$_3$

To obtain more evidence for the formula of **9** given above, pale yellow crystals of **9** were obtained from a hexane solution at −32 °C and investigated by X-ray diffraction analysis. The result shows that the molecule lies on a crystallographic mirror plane, although only parts of the structure fulfill this symmetry. Refinement in the lower symmetric space group $P2_1$ shows the same disorder and no improvement. Due to this disorder, the affected bond lengths are not very accurate and will not be discussed here. Nevertheless, some important structural information for **9** was generated. Crystallographic data for **9** are listed in Table 1. The molecular framework of **9** is shown in Figure 4. It is monomeric in the solid state, and the germanium is four-coordinate. The hydrogen bond to N3 could clearly be found in the electron density map. These findings, despite the disorder, as well as the results of NMR, IR, EI-MS, and elemental analysis, support the formula given for **9**.

The oxidative addition reaction of MeI with **5** in dichloromethane afforded [HC(CMeNAr)$_2$]GeMe$_2$(I) (**10**) (Scheme 3). Compound **10** is poorly soluble in THF and has a high melting point (217−219 °C) compared to that of the starting material **5**.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques or in a glovebox under a nitrogen atmosphere. Diethyl ether and toluene were freshly distilled from Na and hexane from K prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. A Bruker AM 200 instrument was used to record ^{1}H, ^{29}Si, and ^{77}Se NMR spectra (200.1 MHz), with reference to TMS, TMS, and Me$_2$Se, respectively. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls between KBr

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[24] McFahrlane, H. C. E.; McFarlane, W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 417.

plates. Mass spectra were obtained on a Finnigan Mat 8230 instrument. The compound [HC(CMeNAr)$_2$]GeCl[12] was prepared by literature procedures. Other chemicals were purchased from Aldrich and used as received.

[HC(CMeNAr)$_2$]GeMe (**Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 5**). A solution of MeLi (1.4 mL, 1.6 M in diethyl ether, 2.24 mmol) was added dropwise to a stirred solution of [HC(CMeNAr)$_2$]GeCl (**1**; 1.05 g, 2.0 mmol) in diethyl ether (40 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for 3 h. After removal of all volatiles, the residue was extracted with *n*-hexane (30 mL). Storage of the extract in a −32 °C freezer for 3 days afforded orange-red crystals of **5** (0.90 g, 89%). Mp: 131−132 °C. Anal. Calcd for $C_{30}H_{44}GeN_2$ (506.3): C, 71.31; H, 8.78; N, 5.54. Found: C, 71.56; H, 8.84; N, 5.53. EI-MS (70 eV): *m*/*e* (%) 506 (M^+, 5), 491 ($M^+ - Me$, 100). ^{1}H NMR (C_6D_6): δ 0.64 (s, 3 H, Ge*Me*), 1.16 (d, 6 H, CHMe_2), 1.17 (d, 6 H, CHMe_2), 1.29 (d, 6 H, CHMe_2), 1.38 (d, 6 H, CHMe_2), 1.55 (s, 6 H, β-*Me*), 3.45−3.50 (sept, 2 H, C*H*Me_2), 3.65−3.73 (sept, 2 H, CHMe_2), 4.80 (s, 1 H, γ-C*H*), 7.10−7.15 (m, 6 H, 2,6-*i*Pr$_2$C$_6$$H_3$).

[HC(CMeNAr)$_2$]Ge*n*Bu (**Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 6**). Deep red crystals of **6** can be obtained in a way similar to that for **5** in high yield (85%). Mp: 152−155 °C. Anal. Calcd for $C_{33}H_{50}GeN_2$ (547.3): C, 72.41; H, 9.21; N, 5.12. Found: C, 72.01; H, 9.10; N, 5.01. EI-MS (70 eV): *m*/*e* (%) 547 (M^+, 5), 491 ($M^+ -$ *n*Bu, 100). ^{1}H NMR (C_6D_6): δ 0.65 (t, 3 H, $(CH_2)_3Me$), 0.80−1.05 (m, 6 H, (CH_2)$_3$Me), 1.12 (d, 6 H, CHMe_2), 1.16 (d, 6 H, CHMe_2), 1.35 (d, 6 H, CHMe_2), 1.42 (d, 6 H, CHMe_2), 1.52 (s, 6 H, β-*Me*), 3.45−3.60 (sept, 2 H, C*H*Me_2), 3.65−3.82 (sept, 2 H, CHMe_2), 4.72 (s, 1 H, γ-C*H*), 7.05−7.15 (m, 6 H, 2,6-*i*Pr$_2$C$_6$$H_3$).

[HC(CMeNAr)$_2$]GeMe(S) (**Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 7**). A solution of **5** (0.506 g, 1.0 mmol) in toluene (20 mL) was added to a stirred suspension of elemental sulfur (0.032 g, 1.0 mmol) and the mixture refluxed for 4 h. After removal of the volatiles, the residue was washed with *n*-hexane (2 × 5 mL) and then extracted with toluene (15 mL). Adding *n*-hexane (5 mL) to the extract and keeping the solution at room temperature for 3 days afforded pale yellow crystals of **7** in a yield of 65%. The physical data are in agreement with those in ref 14.

[HC(CMeNAr)$_2$]GeMe(Se) (**Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 8**). A solution of **5** (0.506 g, 1.0 mmol) in toluene (20 mL) was added to a stirred suspension of elemental selenium (0.079 g, 1.0 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for 2 days. After filtration a yellow solution was obtained. Concentration (ca. 10 mL) and storage of the yellow solution in a −32 °C freezer for 24 h afforded yellow crystals of **8** (yield 0.508 g, 87%). Mp: 210−213 °C dec. Anal. Calcd for $C_{30}H_{44}GeN_2Se$: C, 61.67; H, 7.58; N, 4.79. Found: C, 61.29; H, 7.47; N, 4.80. EI-MS: *m*/*e* 584 (M^+), 569 ($M^+ - Me$), 506 ($M^+ - Se$). ^{1}H NMR (C_6D_6): δ 1.06 (d, 6 H, CHMe_2), 1.09 (d, 6 H, CHMe_2), 1.10 (s, 3 H, Ge*Me*), 1.25 (d, 6 H, CHMe_2), 1.46 (s, 6 H, β-*Me*), 1.63 (d, 6 H, CHMe_2), 2.92−3.02 (sept, 2 H, C*H*Me$_2$), 3.80−3.90 (sept, 2 H, C*H*Me$_2$), 4.81 (s, 1 H, γ-C*H*), 7.01−7.15 (m, 6 H, 2,6-*i*Pr$_2$C$_6$$H_3$). ^{77}Se NMR ($C_6D_6$): δ −349.

[HC(C(CH$_2$)NAr)CMeNAr]GeMe(N(H)SiMe$_3$) (**Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 9**). A solution of Me_3SiN_3 (0.106 g, 0.1 mmol) in *n*-hexane (10 mL) was added to a stirred solution of **5** (0.506 g, 1.0 mmol) in *n*-hexane (20 mL) at room temperature. After the addition, the reaction mixture was stirred for 12 h, during which time the color changed from orange-red to pale yellow. Concentration (ca. 10 mL) and storage of the solution in a −32 °C freezer for 24 h afforded yellow crystals of **9** (yield 0.362 g, 61%). Mp: 188−191 °C. Anal. Calcd for $C_{33}H_{53}GeN_3Si$: C, 66.90; H, 9.02; N, 7.09. Found: C, 66.85; H, 9.09; N, 7.19. EI-MS: *m*/*e* 593 (M^+), 578 ($M^+ - Me$, 100). ^{1}H NMR (toluene-d_8): δ −0.36 (s, 9 H, SiMe_3), 0.25 (s, 1 H, N*H*), 0.79 (s, 3 H, Ge*Me*), 1.25 −1.50 (m, 24 H, CHMe_2), 1.58 (s, 3 H, β-*Me*), 3.22 (s, 1 H, β-CH_2), 3.40 (sept, 2 H, C*H*Me$_2$), 3.50 (sept, 2 H, C*H*Me$_2$), 3.75 (sept, 2 H, C*H*Me$_2$), 3.85 (sept, 2 H, C*H*Me$_2$), 3.86 (s, 1 H, β-CH_2), 5.25 (s, 1 H, γ-C*H*), 7.10−7.20 (m, 6 H, 2,6-*i*Pr$_2$C$_6$$H_3$). ^{29}Si NMR (toluene-$d_8$): δ 5.94. IR (Nujol): 3361 cm^{-1} (NH).

[HC(CMeNAr)$_2$]GeMe$_2$(I) (**Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 10**). A solution of MeI (0.142 g, 0.1 mmol) in dichloromethane (10 mL) was added to a stirred solution of **5** (0.506 g, 1.0 mmol) in dichloromethane (20 mL) at room temperature. After the addition the reaction mixture was stirred for 10 h, during which time the color changed from orange-red to yellow. Removing the volatiles, washing the residue with *n*-hexane (2 × 5 mL), and drying under vacuum afforded a pale yellow powder of **10** (0.589 g, 91%). Mp: 217−219 °C. Anal. Calcd for $C_{31}H_{47}GeIN_2$ (647.2): C, 57.53; H, 7.32; N, 4.33. Found: C, 57.66; H, 7.13; N, 4.58. EI-MS (70 eV): *m*/*e* (%) 521 ($M^+ - I$, 20), 505 ($M^+ - I - CH_4$, 100). ^{1}H NMR (CD_3CN): δ 0.83 (s, 6 H, GeMe_2), 1.19 (d, 12 H, CHMe_2), 1.28 (d, 12 H, CHMe_2), 2.02 (s, 6 H, β-*Me*), 2.80−3.00 (sept, 4 H, C*H*Me_2), 5.85 (s, 1 H, γ-C*H*), 7.38−7.50 (m, 6 H, 2,6-*i*Pr$_2$C$_6$$H_3$).

X-ray Crystallography. Single crystals of **5**, **6**, **8**, and **9** were taken from the flask under nitrogen gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether.[25] Data were collected on a Stoe AED2 four-circle diffractometer (**5** and **8**) at 200(2) K or on a Stoe-Siemens-Huber four-circle diffractometer (**6** and **9**) equipped with a Siemens SMART area detector at 133(2) K. Monochromated Mo Kα radiation (λ = 0.710 73 Å) was used. The structures were solved by direct methods (SHELXS-96[26]) and refined against F^2 using SHELXL-97.[27] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon were included in geometrically ideal positions and refined with the riding model. The hydrogen atom bonded to nitrogen (**9**) was refined with a distance restraint. All disordered groups were refined with distance restraints and restraints for the anisotropic displacement parameters.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Figures showing ORTEP diagrams and tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0203328

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