Synthesis and Structures of Germanium(II) Fluorides and Hydrides[†]

Yuqiang Ding, Haijun Hao, Herbert W. Roesky,* Mathias Noltemeyer, and Hans-Georg Schmidt

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

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Treatment of [{HC(CMeNAr)$_2$}GeCl] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**1**), 2,6-Me$_2$C$_6$H$_3$ (**2**)) with Me$_3$SnF in dichloromethane at room temperature afforded the corresponding fluoride [{HC(CMeNAr)$_2$}GeF] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**3**), 2,6-Me$_2$C$_6$H$_3$ (**4**)), while with NaBH$_4$ in THF under reflux for 12 h gave the hydride [{HC(CMeNAr)$_2$}GeH(BH$_3$)] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**5**), 2,6-Me$_2$C$_6$H$_3$ (**6**)). Reaction of **3** with Me$_3$SiN$_3$ in toluene provided [{HC(CMeNAr)$_2$}Ge(F)NSiMe$_3$] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**7**)). The BH$_3$ in **5** can be removed with Me$_3$P to afford [{HC(CMeNAr)$_2$}GeH] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**8**)). Treatment of **5** with tBuLi in diethyl ether led to [{HC(C(CH$_2$)NAr)CMeNAr}Ge(H)BH$_3$]Li(Et$_2$O)$_3$ (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**9**)), in which a hydrogen of one of the Me groups was eliminated, and this consequently resulted in the formation of a methylene group. Compounds **3**−**6** are the first examples of structurally characterized germanium(II) fluorides and hydrides. Single-crystal X-ray structural analyses indicate that compounds **3**, **5**, and **9** are monomeric and the germanium center resides in a trigonal-pyramidal environment in **3** and in distorted-tetrahedral environments in **5** and **9**.

Introduction

Organometallic fluorides and hydrides of the heavier group 14 elements are important due to their industrial applications, synthetic methodology, and theoretical implications.[1] To the best of our knowledge, the known compounds involve the metal preferentially in the +4 oxidation state. Currently, only two dimeric Sn(II) fluorides[2] and a dimeric Sn(II) hydride[3] have been reported as stable molecules. Although several Ge(IV) fluorides have been structurally characterized,[4] only one Ge(II) fluoride, [PhGeF],[5] was studied as a reactive intermediate. Moreover, there has also been a growing interest in Ge(IV) hydrides, after the germanium hydrides had been neglected for a long time compared to the silicon and tin hydrides.[1] This rapid development of Ge(IV) chemistry encouraged us to synthesize Ge(II) fluorides and hydrides. The related lower valent derivatives of group 14 elements can be stabilized with bulky substituents,[6] and therefore we have prepared a stable germanium(II) chloride (**1**) containing a bulky diketiminato ligand,[7] as well as other related compounds using this ligand.[8] Moreover, we have recently shown that the use of a bulky ligand enables the synthesis and characterization of a monomeric Al(I) compound.[9] Consequently we became interested in the preparation of the germanium(II) fluoride and hydride by using such bulky diketiminato ligands. Herein, we report on the synthesis and characterization of [{HC(CMeNAr)$_2$}GeCl] (Ar = 2,6-Me$_2$C$_6$H$_3$ (**2**)), [{HC(CMeNAr)$_2$}GeF] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**3**)), [{HC(CMeNAr)$_2$}GeF] (Ar = 2,6-Me$_2$C$_6$H$_3$ (**4**)), [{HC(CMeNAr)$_2$}GeH(BH$_3$)] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**5**)), and [{HC(CMeNAr)$_2$}GeH(BH$_3$)] (Ar = 2,6-Me$_2$C$_6$H$_3$ (**6**)), as well as the resulting derivatives [{HC(CMeNAr)$_2$}Ge(F)NSiMe$_3$] (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**7**)), [{HC(CMeNAr)$_2$}GeH] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**8**)), and [{HC(C(CH$_2$)NAr)CMeNAr}Ge(H)BH$_3$]Li(Et$_2$O)$_3$ (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**9**)). Compounds **3**, **5**, and **9** have been

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[†] Dedicated to Professor Max Herberhold on the occasion of his 65th birthday.

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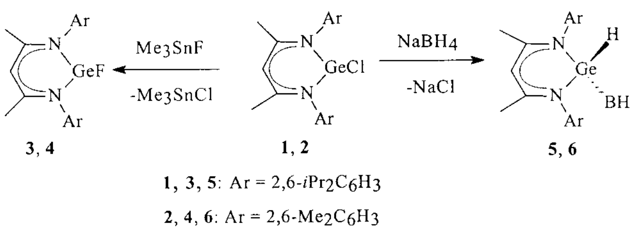
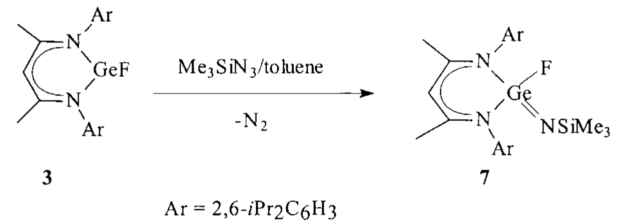
10.1021/om010358j CCC: $20.00

Scheme 1



Scheme 2



characterized by single-crystal X-ray structure analyses. The structures of **3** and **5** are the first examples of such species.

Results and Discussion

We have reported the preparation and solid structure of [{HC(CMeNAr)$_2$}GeCl] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**1**)). The compound [{HC(CMeNAr)$_2$}GeCl] (Ar = 2,6-Me$_2$C$_6$H$_3$ (**2**)), an analogue of **1**, was prepared in a way similar to that of **1**. With the change of the substituent on the aryl from isopropyl to methyl, compound **2** became less soluble than that of **1**. Both **1** and **2** are soluble in polar solvents (such as CH_2Cl_2, and THF), while **1** is soluble but **2** shows only limited solubility in hydrocarbons. However, compound **2** is soluble in hot (70 °C) toluene.

Treatment of **1** and **2**, respectively, with Me_3SnF in dichlormethane at ambient temperature for 2 days smoothly afforded the corresponding fluorides [{HC(CMeNAr)$_2$}GeF] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**3**), 2,6-Me$_2$C$_6$H$_3$ (**4**)) in high yield (88% and 80%) (Scheme 1). Colorless crystals of **3** suitable for single-crystal X-ray analysis were obtained from a hexane solution at room temperature. Both **3** and **4** are thermally stable. No decomposition was observed at temperatures below the corresponding melting points (182−184 and 186−189 °C, respectively) under an inert atmosphere. EI-MS of **3** and **4** both gave the corresponding monomeric molecular ion peak M^+. The ^{19}F NMR spectrum consisted of a singlet resonance for Ge−F (50.58 and 54.46 ppm, respectively). The IR spectra exhibit Ge−F stretching frequencies (543 and 539 cm^{-1}, respectively) close to those found in $[(CF_3)GeF_2]^-$ (545 cm^{-1})[4b] and $[GeF_6]^{2-}$ (563 cm^{-1}).[10] The ^{1}H NMR spectra and elemental analyses are also in accordance with **3** and **4** as formulated.

We preliminarily examined the reactivity of **3** with trimethylsilyl azide (Scheme 2). The reactions of germylenes with trimethylsilyl azide have been well-studied and established as a route to compounds containing the Ge=N double bond.[11] Refluxing the solution of **3** and trimethylsilyl azide in toluene for 3 h gave the pale yellow compound **7**, [{HC(CMeNAr)$_2$}Ge(F)NSiMe$_3$] (Ar = 2,6-iPr$_2$C$_6$H$_3$). Compound **7** was characterized by MS, multinuclear (^{19}F, ^{29}Si, and ^{1}H) NMR, and elemental analysis. In the mass spectrum the molecular ion M^+ was observed at *m/e* 597 (10%) followed by $[M - F]^+$ (*m/e* 578, 100%) with the correct isotope pattern. The ^{19}F NMR chemical shift of **7** is found at low field (71.04 ppm) compared with that of the starting material **3** (50.58 ppm). The ^{29}Si NMR resonates at 13.79 ppm. The ^{1}H NMR spectrum and elemental analysis are in accordance with the proposed formula of **7**.

Germanium(IV) hydrides generally were prepared by the substitution of X^- by H^-. Treatment of **1** with $LiAlH_4$ in diethyl ether at room temperature did not give the expected Ge(II) hydride, but instead the known aluminum hydride [{HC(CMeNAr)$_2$}AlH$_2$] (Ar = 2,6-iPr$_2$C$_6$H$_3$)[12] was formed by a metathesis reaction. However, reflux of the suspension of **1** and $NaBH_4$ in THF for 12 h enabled us to get the adduct of germanium hydride with BH_3, [{HC(CMeNAr)$_2$}Ge(H)BH$_3$] (Ar = 2,6-iPr$_2$C$_6$H$_3$ (**5**)) (Scheme 1). After removal of all the volatiles of the reaction mixture the residue was extracted with diethyl ether. Storage of the slightly green extract at −32 °C for 24 h afforded colorless crystals of **5** suitable for single-crystal X-ray analysis. Compound **6**, [{HC(CMeNAr)$_2$}Ge(H)BH$_3$] (Ar = 2,6-Me$_2$C$_6$H$_3$), was prepared in a similar manner.

There is current interest in the base behavior of monomeric low-coordinated group 14 element compounds with reference to Lewis acids. Several such examples using carbene, silylene, and stannylene[13] were reported. Lappert et al. have published the first example of a Lewis acid (BH_3) adduct of a monomeric intramolecularly base-stabilized germylene,[14] and Dias et al. reported on the adduct of a germylene with BPh_3.[15] Compounds **5** and **6** feature the adduct with BH_3 and that of a hydride containing germane.

Both **5** and **6** were characterized by elemental analysis, EI-MS, IR, and ^{1}H and ^{11}B NMR. In the ^{1}H NMR spectra of **5** and **6** the protons of the backbone ligand can be clearly distinguished, while the resonance was silent for the proton on the germanium atom, even at low temperature (193 K). The ^{1}H NMR spectrum of **5** exhibits a broad resonance for BH (toluene-d_8, 0.78 ppm) and indicates that there are three hydrogen atoms on the boron atom (213 K). The ^{11}B NMR spectra of **5** (C_6D_6, δ −41.94, q, $J(^{11}B-^1H) = 95$ Hz) and **6** (C_6D_6, δ −43.04, q, $J(^{11}B-^1H) = 95$ Hz) are similar to that of the complex reported by Lappert,[14] confirming that there are three hydrogen atoms on the boron atom. The IR absorptions at 1928 cm^{-1} for **5** and 1949 cm^{-1} for **6**, however, are indicative for the existence of GeH. The reason for the undistinguishable GeH resonance in the ^{1}H NMR prob-

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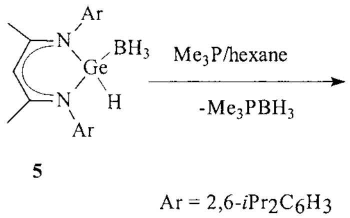
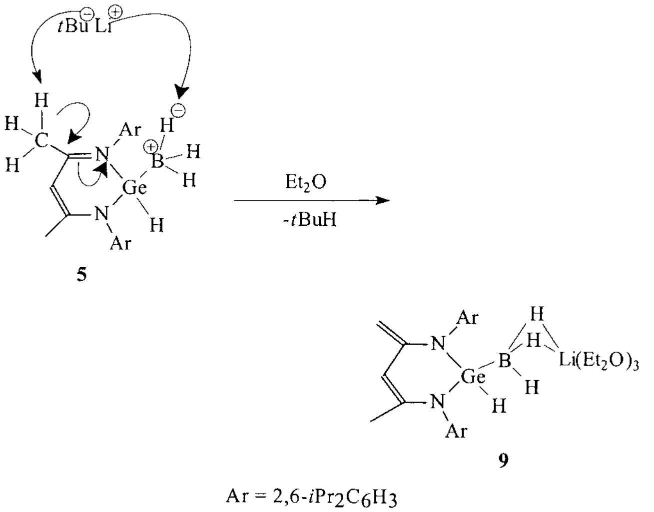
Scheme 3



Scheme 4



ably is due to the rapid hydrogen exchange on the NMR time scale, or there is an overlap of the resonance with those of the aryl protons. Although the exact mechanism of the formation of **5** is unclear, H^- migration from BH_4^- to the germanium(II) center may be involved. The formula of **5** was confirmed by the crystal structure (Figure 2).

Although several adducts of monomeric low-valent group 14 element compounds with Lewis acids have been prepared,[13−15] the reactivity of these compounds has not been studied so far. We were preferentially interested in removing the Lewis acids of these adducts to obtain the free base. For this purpose PMe_3 was used. Treatment of a solution of **5** in hexane with PMe_3 at room temperature was accompanied by a smooth color change from pale yellow to orange. After removal of the solvent, the resulting Me_3PBH_3 was trapped as a white solid. The composition of Me_3PBH_3 was confirmed by ^1H, ^{11}B, and ^{31}P NMR. Recrystallization of the residue with *n*-hexane afforded orange crystals of **8** (Scheme 3). Compound **8** was characterized by elemental analysis, MS, IR, and multinuclear NMR (^1H, ^{11}B, ^{31}P). The ^{11}B and ^{31}P NMR was silent, as expected. Interestingly, the GeH resonance was found (δ 8.04) in the ^1H NMR of **8**. The IR absorption at 1726 cm^{-1} was assigned to the Ge−H stretching frequency.

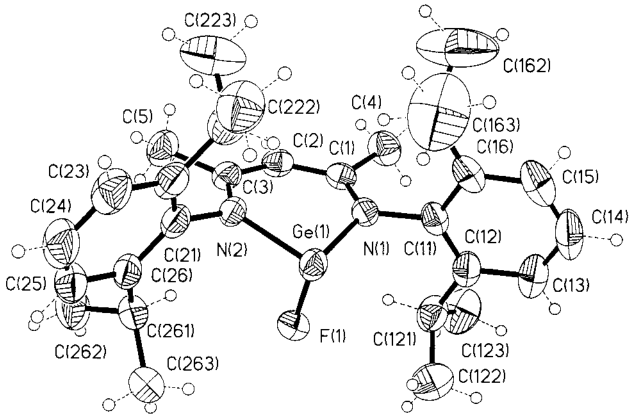


Figure 1. Molecular structure of **3** in the crystal (50% probability thermal ellipsoids).

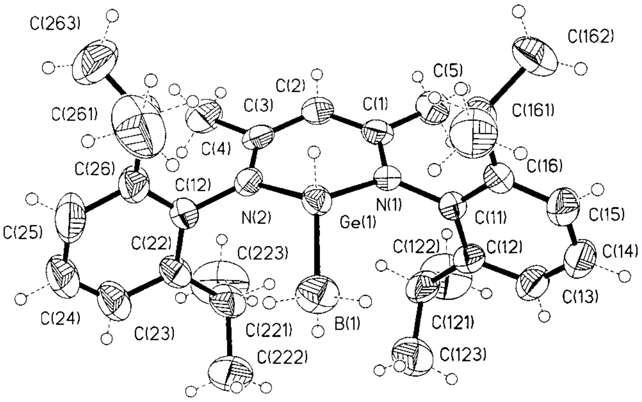


Figure 2. Molecular structure of **5** in the crystal (50% probability thermal ellipsoids).

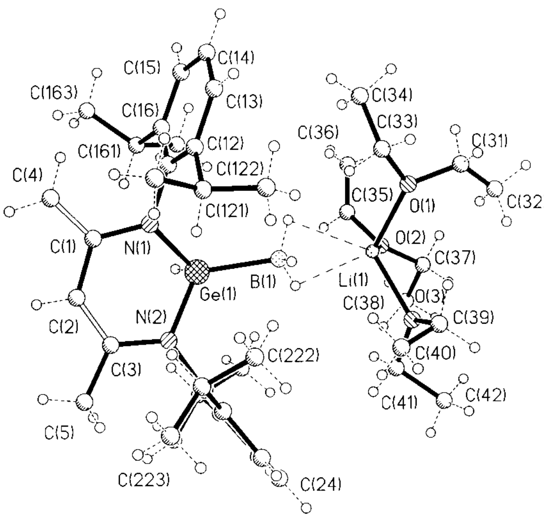


Figure 3. Molecular structure of **9** in the crystal (50% probability thermal ellipsoids).

The reactivity of compound **5** was preliminarily studied with *t*BuLi (Scheme 4). Treatment of a solution of **5** in diethyl ether with *t*BuLi at room temperature led to the formation of [{HC(C(CH_2)NAr)CMeNAr}Ge(H)BH_3] (Ar = 2,6-*i*$Pr_2C_6H_3$) (**9**). The reaction proceeds with elimination of a hydrogen atom from a methyl group of the ligand backbone and formation of a methylene moiety. This may be due to the relative inertness of the Ge−H bond or due to the bulky ligand protecting the germanium center. Compound **9** was characterized by elemental analyses, MS, and multinuclear (^1H, ^{11}B, ^7Li) NMR. In the ^1H NMR spectrum of **9** (toluene-d_8) the resonances clearly show the existence of GeH (δ 6.70, b, 1 H), the β-CH_2 moiety (δ 3.92, s, 1 H and δ 3.20, s, 1 H), and the BH_3 group (δ −0.65 to −1.15, b, 3 H), as well as the coordinated diethyl ether molecule (δ 2.85, q, 12 H, OCH_2Me and δ 0.79, t, 18 H, OCH_2Me). Colorless crystals of **9** suitable for X-ray diffraction analysis were obtained from a diethyl ether solution at

Table 1. Crystallographic Data for Compounds 3, 5, and 9

	3	5	9
formula	$C_{29}H_{41}FGeN_2$	$C_{29}H_{45}BGeN_2$	$C_{41}H_{73}BGeLiN_2O_3$
fw	509.23	505.07	732.35
color	colorless	colorless	colorless
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	13.805(3)	10.713(2)	11.245(2)
b (Å)	16.060(4)	15.306(3)	19.132(5)
c (Å)	14.408(3)	20.340(4)	21.115(10)
α (deg)	90	105.11(3)	90
β (deg)	116.580(15)	101.30(3)	92.52(2)
γ (deg)	90	100.68(3)	90
V (Å^3)	2856.7(10)	3057.6(11)	4538(3)
Z	4	4	4
d_{calcd} (g cm^{-3})	1.184	1.097	1.072
μ (mm^{-1})	1.096	1.019	0.709
F(000)	1080	1080	1588
cryst size (mm)	1.10 × 0.30 × 0.30	0.60 × 0.40 × 0.20	1.10 × 0.80 × 0.80
2θ range (deg)	3.54−25.05	3.51−25.00	3.52−25.04
index range	$-16 \le h \le 16$ $-14 \le k \le 19$ $-17 \le l \le 17$	$-12 \le h \le 11$ $-16 \le k \le 15$ $-16 \le l \le 21$	$-13 \le h \le 12$ $-8 \le k \le 22$ $-9 \le l \le 25$
no. of rflns collected	9557	9237	7135
no. of indep rflns	5040 (R(int) = 0.0201)	8487 (R(int) = 0.1173)	7100 (R(int) = 0.1543)
R1, wR2 ($I > 2\sigma(I)$)	0.0359, 0.0849	0.0640, 0.1530	0.0689, 0.1705
R1, wR2 (all data)	0.0475, 0.0917	0.0959, 0.1826	0.1106, 0.2043
goodness of fit, F^2	1.051	1.064	1.041
no. of data/restaints/params	5040/0/308	8479/9/621	7100/1/481
largest diff peak, e Å^{-3}	0.503 to −0.333	1.188 to −0.897	0.585 to −1.001

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 3, 5, and 9

Compound **3**			
Ge(1)−N(1)	1.977(19)	C(2)−C(3)	1.393(3)
Ge(1)−N(2)	1.978(18)	C(1)−C(4)	1.508(3)
Ge(1)−F(1)	1.805(17)	C(3)−C(5)	1.510(3)
C(1)−N(1)	1.333(3)	C(3)−N(2)	1.3334(3)
C(1)−C(2)	1.387(3)		
N(1)−Ge(1)−N(2)	91.04(8)	Ge(1)−N(1)−C(1)	126.12(15)
N(1)−Ge(1)−F(1)	93.67(8)	Ge(1)−N(2)−C(3)	125.85(16)
N(2)−Ge(1)−F(1)	93.16(8)		
Compound **5**			
Ge(1)−N(1)	1.917(4)	C(1)−C(2)	1.390(8)
Ge(1)−N(2)	1.933(4)	C(2)−C(3)	1.398(8)
Ge(1)−H(1)	1.110	C(1)−C(5)	1.499(9)
Ge(1)−B(1)	2.015(7)	C(3)−C(5)	1.513(8)
C(1)−N(1)	1.355(7)	C(3)−N(2)	1.325(7)
N(1)−Ge(1)−N(2)	94.5(2)	Ge(1)−N(1)−C(1)	120.3(4)
N(1)−Ge(1)−B(1)	118.3(3)	Ge(1)−N(2)−C(3)	120.8(4)
N(2)−Ge(1)−B(1)	117.9(3)		
Compound **9**			
Ge(1)−N(1)	1.875(4)	C(1)−C(2)	1.443(8)
Ge(1)−N(2)	1.879(4)	C(2)−C(3)	1.380(7)
Ge(1)−B(1)	2.016(8)	C(1)−C(4)	1.384(9)
B(1)−Li(1)	2.382(14)	C(3)−C(5)	1.480(8)
C(1)−N(1)	1.377(7)	C(3)−N(2)	1.380(7)
N(1)−Ge(1)−N(2)	96.41(19)	G(1)−B(1)−Li(1)	161.0(6)
N(1)−Ge(1)−B(1)	115.8(3)	Ge(1)−N(1)-C(1)	119.8(3)
N(2)−Ge(1)−B(1)	116.7(3)	Ge(1)−N(2)−C(3)	117.6(3)

−32 °C within 2 days. Although the mechanism for the formation of **9** is unclear, the most likely one is given in Scheme 4.

Another important finding for compounds **5**, **6**, **8**, and **9** is their distinct difference in the NMR and IR spectra compared to the Ge(IV) congeners. In the ^1H NMR spectra the $Ge^{IV}H$ resonances are generally observed in the range of 4−6 ppm,[1f,j,16] whereas in **8** (8.04 ppm, C_6D_6) and **9** (6.70 ppm, toluene-d_8) they are shifted to lower field. The GeH resonances of **5** and **6** probably appeared in the range of 6.9−7.2 ppm, overlapping with those of the aryl protons. The low-field shift of the GeH resonance in **5**, **6**, **8**, and **9** compared to those of Ge(IV) compounds indicates the distinct influence of the free electron pair on the hydrogen atom of the Ge(II) compounds. As a consequence, the Ge−H bond in the Ge(II) compounds is more covalent compared to that in the corresponding Ge(IV) species, due to the higher electron density around the Ge(II). This is also seen in the IR spectra comparing the Ge−H stretching frequencies. In the compound Mes_2HGe(Li-crown-4),[16] the electron density is increased compared to neutral $Ge^{IV}H$ compounds exhibiting a low Ge−H absorption at 1980 cm^{-1}. The germanium(II) hydrides **5**, **6**, and **8** show absorptions even at lower wavenumbers (1927, 1949, and 1726 cm^{-1}). This applies especially to compound **8**, without the coordinating BH_3.

X-ray Diffraction Analysis for 3, 5, and 9. The solid-state structures of compounds **3**, **5**, and **9** were determined by single-crystal X-ray diffraction and are shown in Figures 1−3. Crystallographic data are given in Table 1, and selected bond lengths and bond angles are listed in Table 2; additional bond distances and angles are included in the Supporting Information.

Figures 1−3 show that compounds **3**, **5**, and **9** are monomeric. The germanium center is three- (in **3**) and four-coordinated (in **5** and **9**). The sum of the angles at the metal center in **3** (277.87°) deviates strongly from the sp^3 tetrahedral value. Thus, the geometry of **3** may be described pyramidal rather than distorted tetrahedral. However, the sums of the angles N(1)−Ge(1)−N(2), N(1)−Ge(1)−B(1), and N(2)−Ge(1)−B(1) around the metal center in **5** (330.7°) and in **9** (328°) are tetrahedral.

The order of the corresponding N−Ge−N angles is **9** (96.41(19)°) > **5** (94.5(2)°) > **3** (91.04(8)°) > **1** (90.89(10)°), while the order of the Ge−N bond lengths is **9**

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(16) Castel, A.; Riviere, P.; Satgé, J.; Ko, H. Y. *Organometallics* **1990**, *9*, 205.

(1.875(4), 1.879(4) Å) < **5** (1.917(4), 1.933(4) Å) < **3** (1.977(19), 1.979(18) Å) < **1** (1.988(2), 1.997(3) Å). This indicates that the metal center in **9** is more closely bound to the ligand. This perhaps results from the coordination of the Lewis acid (BH_3) to the germanium center in **9** and **5** combined with the weak electron-withdrawing property of the chlorine atom in **1** compared to the fluorine atom in **3**.

Veith[17] and Lappert[8c] et al. have reported that the coordinative N→Ge bonds in the intramolecular N→Ge complexed germylene are longer (2.045−2.110 Å) than those related $Ge^{IV}-N$ bonds. However, the Ge−N bond lengths observed in **3** (1.997(19), 1.978(18) Å), in **5** (1.917(4), 1.933(4) Å), and in **9** (1.875(4), 1.879(4) Å) are comparable to σ $Ge^{IV}-N$ bonds. Similar results were observed in close analogues of **3**, **5**, and **9** in which conjugated ligand backbones are involved.[8c,15] Previous studies have suggested that the conjugated ligand backbones play an important role in improving the stability.[18] The same applies to compounds **1**−**9** and affects the Ge−N bond lengths in **3**, **5**, and **9**. Because of the delocalization of the electrons in the backbones of the ligand, the bond length differences of the C−C bond (0.006 Å in **3**, 0.002 Å in **5**, 0.064 Å in **9**), the C−N bond (0.001 Å in **3**, 0.030 Å in **5**, 0.003 Å in **9**), and the Ge−N bond (0.002 Å in **3** and 0.016 Å in **5** and 0.004 Å in **9**) are very small.

The C(1)−C(4) (1.384(9) Å) bond length is much shorter than that of C(3)−C(5) (1.480(8) Å) in **9** and those in **3** (1.508(3), 1.510(3) Å) and **5** (1.499(9), 1.513(8) Å). This indicates that C(1)−C(4) and C(2)−C(3) bonds in **9** have double-bond character! The B−Li distance in **9** is longer than the covalent radius (2.03 Å). The observed Ge−F bond length (1.805(17) Å) in **3** is in the normal range (1.781−1.835 Å),[4b,c] although there is no germanium(II) fluoride available for comparison with **3**. The Ge−B bond lengths of **5** and **9** (2.015(7) and 2.016(8) Å, respectively) are slightly shorter than that of a comparable adduct of a germylene with BH_3 (2.041(11) Å).[14]

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques or in a glovebox under a nitrogen atmosphere. Diethyl ether was freshly distilled from Na and *n*-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 ^1H (200.1 MHz), ^{19}F (188.3 MHz), ^{11}B (80.25 MHz), and ^7Li (97.21 MHz) NMR spectra, with reference to TMS, $BF_3 \cdot OEt_2$, and LiCl, respectively. Mass spectra were obtained on a Finnigan Mat 8230. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls on KBr plates. The compound $[HC(CMeNAr)_2]Li \cdot OEt_2$ was prepared by literature procedures.[7] Other chemicals were purchased from Aldrich and used as received.

[$\{HC(CMeNAr)_2\}GeCl$] (Ar = 2,6-$Me_2C_6H_3$ (2)). A solution of $[HC(CMeNAr)_2Li(OEt_2)]$ (0.412 g, 1.0 mmol) in diethyl ether (20 mL) was reacted at −78 °C with $GeCl_2 \cdot$(dioxane) (0.271 g, 1.0 mmol) to yield **2**. Pure **2** was obtained after extraction with hot (70 °C) toluene (15 mL). Yield: 60%. Mp: 221−224 °C. Anal. Calcd for $C_{21}H_{25}ClGeN_2$: C, 61.00; H, 6.09; Cl, 8.57; N, 6.77. Found: C, 61.05; H, 6.03; Cl, 8.62; N, 6.70. EI-MS: *m/e* 414 (M^+), 379 ($[M - Cl]^+$). ^1H NMR ($CDCl_3$): δ 1.85 (s, 6 H, β-*Me*), 2.17 (s, 6 H, Ar *Me*), 2.49 (s, 6 H, Ar *Me*), 5.50 (s, 1 H, γ-C*H*), 7.08−7.29 (m, 6 H, Ar *H*).

[$\{HC(CMeNAr)_2\}GeF$] (Ar = 2,6-*i*$Pr_2C_6H_3$ (3)). A solution of **1** (0.526 g, 1.0 mmol) in dichloromethane (20 mL) was added to a stirred suspension of Me_3SnF (0.201 g, 1.1 mmol) in dichloromethane (10 mL), and the reaction mixture was stirred at room temperature for 2 days. After removal of all volatiles the residue was extracted with *n*-hexane (20 mL). Storage of the extract at −32 °C for 24 h afforded colorless needle-shaped crystals of **2** (yield 0.45 g, 88%). Mp: 182−184 °C. Anal. Calcd for $C_{29}H_{41}FGeN_2$: C, 66.21; H, 7.79; N, 5.32. Found: C, 66.01; H, 7.97; N, 5.22. EI-MS: *m/e* 510 (M^+), 475 ($[M - Me - F]^+$). ^1H NMR (C_6D_6): δ 1.07 (d, 6 H, CH*Me*$_2$), 1.17 (d, 6 H, CH*Me*$_2$), 1.22 (d, 6 H, CH*Me*$_2$), 1.40 (d, 6 H, CH*Me*$_2$), 1.60 (s, 6 H, β-*Me*), 3.05−3.20 (sept, 2 H, C*H*Me$_2$), 3.70−3.82 (sept, 2 H, C*H*Me$_2$), 5.05 (s, 1 H, γ-C*H*), 7.05−7.10 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{19}F NMR (C_6D_6): δ 50.58. IR (Nujol): 543 cm^{-1} (GeF).

[$\{HC(CMeNAr)_2\}GeF$] (Ar = 2,6-$Me_2C_6H_3$ (4)). The procedure is the same as that described for **3**. Yield: 80%. Mp: 186−189 °C. Anal. Calcd for $C_{21}H_{25}FGeN_2$: C, 63.53; H, 6.35; N, 7.06. Found: C, 63.59; H, 6.31; N, 7.15. EI-MS: *m/e* 398 (M^+), 379 ($[M - F]^+$). ^1H NMR ($CDCl_3$): δ 1.83 (s, 6 H, β-*Me*), 2.13 (s, 6 H, Ar *Me*), 2.41 (s, 6 H, Ar *Me*), 5.40 (s, 1 H, γ-C*H*), 7.05−7.15 (m, 6 H, Ar *H*). ^{19}F NMR ($CDCl_3$): δ 54.46. IR (Nujol): 539 cm^{-1} (GeF).

[$\{HC(CMeNAr)_2\}GeH(BH_3)$] (Ar = 2,6-*i*$Pr_2C_6H_3$ (5)). A solution of **1** (0.526 g, 1.0 mmol) in THF (20 mL) was added to a stirred suspension of $NaBH_4$ (excess) in THF (10 mL), and the reaction mixture was refluxed for 12 h. After removal of all volatiles the residue was extracted with diethyl ether (20 mL). Storage of the slightly green extract in a −32 °C freezer for 24 h afforded colorless crystals of **5** (yield 0.44 g, 87%). Mp: 193−195 °C. Anal. Calcd for $C_{29}H_{49}BGeN_2$: C, 68.96; H, 8.98; N, 5.55. Found: C, 68.89; H, 9.03; N, 5.67. EI-MS: *m/e* 491 ($[M - BH_3 - H]^+$). ^1H NMR (C_6D_6): δ 1.06 (d, 6 H, CH*Me*$_2$), 1.09 (d, 6 H, CH*Me*$_2$), 1.25 (d, 6 H, CH*Me*$_2$), 1.45 (s, 6 H, β-*Me*), 1.47 (d, 6 H, CH*Me*$_2$), 2.85−3.05 (sept, 2 H, C*H*Me$_2$), 3.25−3.45 (sept, 2 H, C*H*Me$_2$), 4.88 (s, 1 H, γ-C*H*), 6.95−7.15 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{11}B NMR (C_6D_6): δ −41.94. IR (Nujol): 2370, 2333, 1927 cm^{-1} (BH_3, GeH).

[$\{HC(CMeNAr)_2\}Ge(H)BH_3$] (Ar = 2,6-$Me_2C_6H_3$ (6)). The procedure is the same as that for **5**. Yield: 81%. Mp: 184−187 °C. Anal. Calcd for $C_{21}H_{29}BGeN_2$: C, 64.20; H, 7.44; N, 7.13. Found: C, 64.37; H, 7.51; N, 7.18. EI-MS: *m/e* 379 ($[M - BH_3]^+$). ^1H NMR ($CDCl_3$): δ 1.82 (s, 6 H, β-*Me*), 2.24 (s, 6 H, Ar *Me*), 2.26 (s, 6 H, Ar *Me*), 5.32 (s, 1 H, γ-C*H*), 7.08−7.15 (s, 6 H, Ar *H*). ^{11}B NMR (C_6D_6): δ −43. IR (Nujol): 2351, 2327, 1949 cm^{-1} (BH_3, GeH).

[$\{HC(CMeNAr)_2\}Ge(F)NSiMe_3$] (Ar = 2,6-*i*$Pr_2C_6H_3$ (7)). A solution of **3** (0.510 g, 1.0 mmol) and Me_3SiN_3 (0.115 g, 1.0 mmol) in toluene (25 mL) was refluxed for 3 h. After removal of all volatiles, washing of the residue with *n*-hexane (2 × 5 mL) afforded a pale yellow powder of **7**. Storage of the slightly yellow solution of **7** in a −32 °C freezer gave pale yellow crystals of **7** (yield 0.471 g, 79%). Mp: 167−169 °C. EI-MS: *m/e* 597 (M^+), 578 ($[M - F]^+$). ^1H NMR (C_6D_6): δ 0.00 (s, 9 H, Si*Me*$_3$), 1.11 (d, 6 H, CH*Me*$_2$), 1.21 (d, 6 H, CH*Me*$_2$), 1.23 (d, 6 H, CH*Me*$_2$), 1.51 (d, 6 H, CH*Me*$_2$), 1.54 (s, 6 H, β-*Me*), 3.08−3.12 (sept, 2 H, C*H*Me$_2$), 3.72−3.78 (sept, 2 H, C*H*Me$_2$), 4.98 (s, 1 H, γ-C*H*), 7.04−7.08 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{19}F NMR (C_6D_6): δ 71.05. ^{29}Si NMR (C_6D_6): δ 13.85.

[$\{HC(CMeNAr)_2\}GeH$] (Ar = 2,6-*i*$Pr_2C_6H_3$ (8)). A solution of PMe_3 (2 mL, 1.0 M in toluene) was added to a solution of **5** (1.052 g, 2.0 mmol) in *n*-hexane (30 mL) at room temperature and stirred for 12 h. The color turned from pale yellow to

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orange. After removal of all volatiles, the residue was extracted with *n*-hexane (20 mL). Storage of the extract in a −32 °C freezer for 24 h afforded orange crystals of **8** (yield 0.776 g, 79%). Mp: 173−175 °C. Anal. Calcd for $C_{29}H_{42}GeN_2$: C, 70.90; H, 8.62; N, 5.70. Found: C, 70.51; H, 8.65; N, 5.67. EI-MS: *m*/*e* 491 ($[M-1]^+$), (100%). ^{1}H NMR (C_6D_6): δ 1.15 (d, 6 H, CH*Me*$_2$), 1.17 (d, 6 H, CH*Me*$_2$), 1.27 (d, 6 H, CH*Me*$_2$), 1.35 (d, 6 H, CH*Me*$_2$), 1.54 (s, 6 H, β-*Me*), 3.24−3.42 (sept, 2 H, C*H*Me$_2$), 3.43−3.62 (sept, 2 H, C*H*Me$_2$), 4.92 (s, 1 H, γ-C*H*), 7.02−7.15 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$), 8.08 (s, 1 H, Ge*H*). IR (Nujol): 1726 cm^{-1} (GeH).

[{HC(C(CH$_2$)NAr)CMeNAr}Ge(H)BH$_3$]Li(Et$_2$O)$_3$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ (9)). A solution of *t*BuLi (2 mL, 1 M in toluene) was added to a solution of **5** (1.012 g, 2.0 mmol) in diethyl ether (30 mL) at −78 °C, and the reaction mixture was warmed to room temperature. After the mixture was stirred for an additional 3 h and stored in a −32 °C freezer for 2 days, colorless crystals of **9** were obtained (yield 1.039 g, 71%). Mp: 138−140 °C. Anal. Calcd for $C_{41}H_{73}BGeLiN_2O_3$: C, 67.24; H, 10.05; N, 3.82. Found: C, 67.31; H, 9.98; N, 3.91. EI-MS: *m*/*e* 491 ($[M-Li(Et_2O)_3-H]^+$) (100%). ^{1}H NMR (toluene-d_8): δ −0.65 to −1.15 (b, 3 H, B*H*$_3$), 0.79 (t, 18 H, OCH$_2$*Me*), 1.30−1.50 (m, 24 H, CH*Me*$_2$), 1.70 (s, 3 H, β-*Me*), 2.85 (q, 12 H, OC*H*$_2$-Me), 3.19 (s, 1 H, β-C*H*$_2$), 3.65 (sept, 2 H, C*H*Me$_2$), 3.75 (sept, 2 H, C*H*Me$_2$), 3.92 (s, 1 H, β-C*H*$_2$), 3.97 (sept, 2 H, C*H*Me$_2$), 4.05 (sept, 2 H, C*H*Me$_2$), 5.38 (s, 1 H, γ-C*H*), 6.70 (b, 1 H, Ge*H*), 7.04−7.10 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{11}B NMR (toluene-d_8): δ −43.68. ^{7}Li NMR (toluene-d_8): δ −1.41.

X-ray Crystallography. Single crystals of **3**, **5**, and **9** were taken from the flask under nitrogen gas and mounted on a glass fiber in rapidly cooled perfluoropolyether.[19] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector at 200(2) K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (SHELXS-96)[20] and refined against F^2 using SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically with similarity and rigid bond restraints. All hydrogen atoms were included in the refinement in geometrically ideal positions.

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Supporting Information Available: 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 **3**, **5**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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