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Dehydrogenation of LGeH by a Lewis *N*-Heterocyclic Carbene Borane Pair under the Formation of L′Ge and its Reactions with $B(C_6F_5)_3$ and Trimethylsilyl Diazomethane: An Unprecedented Rearrangement of a Diazocompound to an Isonitrile

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Herein we report the dehydrogenation of LGeH (**1**) [L = $CH\{(CMe)(2,6\text{-}i Pr_2C_6H_3N)\}_2$] by a frustrated Lewis NHC borane pair under the formation of an imidazolium borate salt (**2**) and the heterocyclic germylene L′Ge (**3**) [L′ = $CH\{(C{=}CH_2)(CMe)(2,6\text{-}i Pr_2C_6H_3N)_2\}$]. The reaction of **3** with $B(C_6F_5)_3$ in toluene results in the formation of a zwitterion containing a germylene moiety, $[B(C_6F_5)_3L''Ge]$ (**4**) [L″ = $CH\{(CCH_2)(CMe)(2,6\text{-}i Pr_2C_6H_3N)_2\}$]. Subsequent treatment of **4** with 1 equiv of 1,3-di-*tert*-butylimidazol-2-ylidene (NHC) gives $B(C_6F_5)_3L'''Ge$ (**5**) [L‴ = $CH\{(C{=}CH_2)(CCH_2B(C_6F_5)_3)(2,6\text{-}i Pr_2C_6H_3N)_2\}$] under formation of the imidazolium cation. Moreover compound **3** reacts with trimethylsilyl diazomethane ($N_2CHSiMe_3$) to form the diazogermylene $LGeC(N_2)SiMe_3$ (**6**) under C−H bond cleavage. Compound **6** slowly rearranges to the isonitriletrimethylsilyl germanium(II) amide $LGeN(SiMe_3)NC$ (**6a**). All compounds were characterized by microanalysis and multinuclear NMR spectroscopy. Compounds **4**, **6**, and **6a** were unequivocally identified by single crystal X-ray structure analysis.

Introduction

The Lewis acid−base concept is fundamental for understanding numerous chemical reactions.[1] This principle is essential for main group elements, as well as for transition metals.[2] In recent years, Stephan et al.,[3] Rieger et al.,[4] Erker et al.,[5] and Tamm et al.[6] were able to demonstrate that frustrated Lewis pairs of boranes (in particular tris(pentafluorophenyl)borane, $B(C_6F_5)_3)$[7] in combination with sterically demanding phosphanes, amines, imines, and *N*-heterocyclic carbenes (NHCs), respectively, are excellent nonmetallic systems for the activation of dihydrogen under mild conditions. NHCs and $B(C_6F_5)_3$ independently have also been employed for proton and hydride abstraction reactions.[8,9] Recently we reported on the synthesis of LGeCl,[10] and observed that one hydrogen from the backbone of one methyl group can be eliminated.[11] Therefore, it seemed possible that LGeH (**1**)[12] might be dehydrogenated with a Lewis NHC borane pair because of a reversible reaction. In the literature

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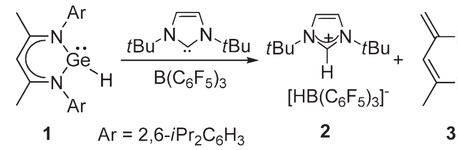
Table 1. Crystallographic Data for the Structural Analysis of **4**, **6**, and **6a**

	4	**6**	**6a**
empirical formula	$C_{47}H_{40}BF_{15}GeN_2$	$C_{33}H_{50}GeN_4Si$	$C_{33}H_{50}GeN_4Si$
CCDC No.	720891	734212	728257
T [K]	100(2)	100(2)	100(2)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [pm]	1216.90(13)	1074.32(4)	1077.8(3)
b [pm]	1371.36(15)	1200.91(5)	1204.0(4)
c [Å]	1504.04(16)	1450.66(6)	1444.5 (4)
α [deg]	109.9890(10)	106.9280(10)	107.113(3)
β [deg]	91.1810(10)	94.2460(10)	94.231(4)
γ [deg]	108.7890(10)	109.4780(10)	109.254(3)
V [nm^3]	2.2088(4)	1.65736(12)	1.6607(8)
Z	2	2	2
D_{calcd} [Mg m^{-3}]	1.505	1.209	1.207
μ [mm^{-1}]	0.794	0.987	0.985
F(000)	1016	644	644
θ range [deg]	1.69−25.39	1.91−26.74	1.50−25.35
reflections collected	43135	40967	24779
independent reflections	8111	7047	6039
data/restraints/parameters	8111/0/604	7047/0/365	6039/0/365
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0385, 0.0953	0.0258, 0.0677	0.0311, 0.0869
$R1$, $wR2$ (all data)[a]	0.0527, 0.0998	0.0273, 0.0685	0.0331, 0.0880
GoF	1.085	1.053	1.063
Residual density max./min. [e Å^{-3}]	0.391/−0.656	1.378/−0.287	0.900/−0.221

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

Scheme 1. Preparation of **2** and **3**

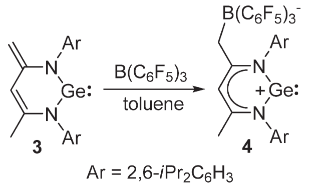


dehydrogenation of alkanes is reported using transition metal catalyst.[13] Herein we report on the dehydrogenation of LGeH by a frustrated Lewis NHC borane pair and the reaction of resulting heterocyclic germylene L′Ge (**3**) with $B(C_6F_5)_3$ and trimethylsilyl diazomethane.

Results and Discussion

In this paper we show the dehydrogenation of LGeH (**1**) with a frustrated Lewis NHC borane pair. A toluene solution of equimolar amounts of **1** and of $B(C_6F_5)_3$ under stirring changed the color from red to colorless after a few minutes. To this reaction mixture we added an equivalent of 1,3-di-*tert*-butylimidazol-2-ylidene,[14] and the reaction mixture immediately turned to brown-red with the formation of an insoluble white precipitate (Scheme 1). The latter was identified as $[(CHNt\mathrm{Bu})_2CH][HB(C_6F_5)_3]$ (**2**) and was recovered by filtration and dissolved in dichloromethane. The ^{1}H NMR spectrum of **2** indicates the formation of an imidazolium cation. The ^{11}B NMR resonance of **2** at −25.3 ppm is identical with a previously reported imidazolium borate salt.[3c,6] The soluble part of the reaction mixture was characterized to contain the heterocyclic germylene L′Ge (**3**).

Scheme 2. Preparation of **4**



We have shown that the heterocyclic germylene **3** cleaves one N−H bond of ammonia at room temperature upon formation of $LGeNH_2$.[11] Moreover, Driess et al. had independently demonstrated that **3** has a dipolar character.[15] Consequently we reacted **3** with $B(C_6F_5)_3$ at room temperature to afford the zwitterionic compound $[B(C_6F_5)_3L''Ge]$ (**4**), containing a germylene moiety (Scheme 2). Only two reports on the synthesis of germanium(II) cations are in the current literature, one was reported by Power and co-workers where they also used a β-diketiminate ligand.[16,17]

Compound **4** was isolated as air and moisture sensitive pale yellow crystals in 78% yield, which are insoluble in common hydrocarbon solvents but highly soluble in THF (Figure 1). In this solvent there is no equilibrium between **3** and **4** observed in contrast to the isoelectronic silicon analogue of **4**.[18] **4** crystallizes in the triclinic space group $P\bar{1}$ (Table 1) and consists of a planar six-membered C_3N_2Ge ring with an exocyclic $B(C_6F_5)_3$ group attached to C13. The β-diketiminate N−C and C−C ring bond lengths have average values

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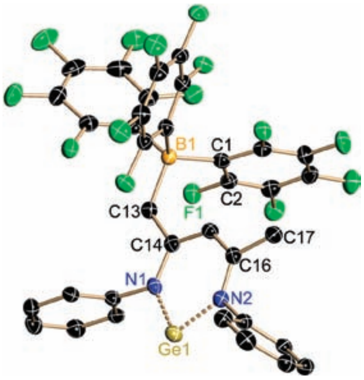


Figure 1. Molecular structure of **4**; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms and isopropyl groups are omitted for clarity.

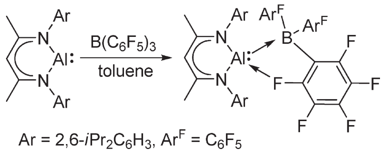
Table 2. Selected Bond Distances [Å] and Angles [deg] of **4**, **6**, and **6a**

Compound **4**			
Ge(1)−N(1)	1.881(2)	B(1)−C(13)	1.657(4)
Ge(1)−N(2)	1.873(2)	F(1)−C(2)	1.363(3)
N(1)−C(14)	1.361(3)	C(13)−C(14)	1.506(4)
N(2)−C(16)	1.361(3)	C(16)−C(17)	1.499(3)
B(1)−C(1)	1.661(4)		
N(1)−Ge(1)−N(2)	93.91(9)	N(1)−C(14)−C(13)	119.3(2)
Ge(1)−N(1)−C(14)	128.52(17)	B(1)−C(13)−C(14)	119.7(2)
Ge(1)−N(2)−C(16)	127.40(17)		
Compound **6**			
Ge(1)−N(1)	2.0111(12)	Ge(1)−C(25)	1.9969(14)
Ge(1)−N(2)	1.9974(12)	C(25)−Si(1)	1.8345(15)
N(1)−C(26)	1.3293(19)	C(25)−N(3)	1.3037(19)
N(2)−C(29)	1.3295(18)	N(3)−N(4)	1.1458(19)
N(1)−Ge(1)−N(2)	90.34(5)	N(1)−Ge(1)−C(25)	98.14(5)
Ge(1)−N(1)−C(26)	127.12(10)	Ge(1)−C(25)−Si(1)	118.37(7)
Ge(1)−N(2)−C(29)	127.69(10)	C(25)−N(3)−N(4)	175.74(15)
Compound **6a**			
Ge(1)−N(1)	1.9994(16)	Ge(1)−N(3)	1.9491(16)
Ge(1)−N(2)	1.9862(16)	N(3)−Si(2)	1.7699(17)
N(1)−C(2)	1.330(3)	N(3)−N(4)	1.350(2)
N(2)−C(4)	1.336(2)	N(4)−C(1)	1.154(3)
N(1)−Ge(1)−N(2)	90.84(7)	N(1)−Ge(1)−N(3)	97.61(6)
Ge(1)−N(1)−C(2)	126.74(13)	Ge(1)−N(3)−Si(2)	119.19(9)
Ge(1)−N(2)−C(4)	127.74(13)	N(3)−N(4)−C(1)	174.91(19)

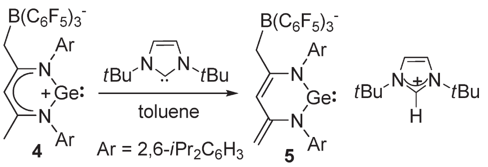
(1.36 and 1.39 Å) and are shorter than those of **3**, indicative for the delocalization of the π-electrons. The Ge−N bond lengths (1.873(2) and 1.881(2) Å) (Table 2) are comparable with those of the cation $[LGe]^+$.[16] The ^1H NMR spectrum exhibits a signal for the γ-CH proton at 6.50 ppm, which differs from that of germylene **3** (5.43 ppm). The ^{11}B NMR spectrum shows a singlet resonance at −14.82 ppm, and the ^{19}F NMR spectrum displays three resonances (−131.6, −167.2, and−163.40 ppm) for the *ortho*, *para*, and *meta* fluorine atoms, respectively.

Compound **3** might be compared with the monomeric aluminum(I), LAl,[19] although the difference of the two species is one proton. This is demonstrated in the reactivity of **3** and LAl, respectively, with $B(C_6F_5)_3$ (Scheme 3). **3** assembled as a zwitterionic germanium(II) species **4** and the LAl forms a compound with a boron−aluminum bond.[20] Preliminary studies of **4** with 1,3-di-*tert*-butylimidazol-2-ylidene (NHC) show the deprotonation of the second methyl group from the backbone with formation of compound $B(C_6F_5)_3L'''Ge$ (**5**) under complete conversion (Scheme 4). The 1,3-di-*tert*-butylimidazol-2-ylidene reacts (Schemes 1 and 3) under formation of the imidazolium cation. However, the counteranion is different. The neutral compound **3** is formed to give the anion $[HB(C_6F_5)_3]^-$, whereas in **5** we assume that the borate anion forms a stable ion pair with the imidazolium cation.

Scheme 3. Reaction of LAl with $B(C_6F_5)_3$



Scheme 4. Preparation of **5**



The anion of **5** gives rise to the expected resonance with the γ-CH proton at 5.87 ppm, which is comparable with that of **3**. The deprotonation of the second methyl group leads to the exocyclic carbon−carbon double bond. The two vinylic protons exhibit two non-equivalent singlets (δ 3.63, 2.96 ppm), indicating that the germanium(II) atom is neutral in **5**. This is the first time we have shown that the double C−H bond activation of the two methyl groups at the ligand backbone has occurred by NHC. So far there is only one C−H bond activation of the methyl group at the ligand backbone reported.[21] Unfortunately we were not able to prove this result by an X-ray crystal structural analysis of **5** because of the lack of single crystals.

Recently we reported on the cleavage of N−H[11] and O−H[22] bonds using the heterocyclic germylene L′Ge (**3**). Now we reacted **3** with trimethylsilyl diazomethane under formation of the diazogermylene $LGeC(N_2)SiMe_3$ (**6**) by a C−H bond cleavage (Scheme 5). Here it is also noted that the trimethylsilyl diazomethane reacts with LGeH (**1**) with an unprecedented end-on nitrogen insertion of diazo nitrogen into the Ge−H bond under formation of germanium(II)-

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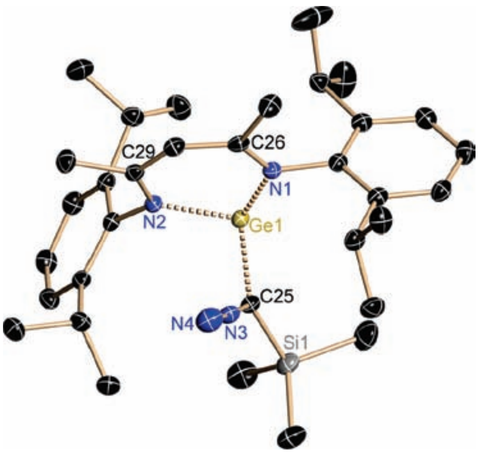
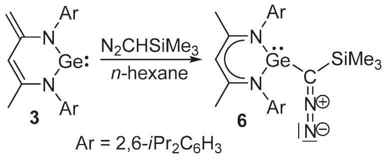


Figure 2. Molecular structure of **6**; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity.

Scheme 5. Preparation of **6**



substituted hydrazone.[23] **6** is readily soluble in hydrocarbon and ether solvents and has been fully characterized.

The germanium complex **6** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 2). The germanium atom is coordinated to two nitrogen atoms of the ligand (N1, N2) and to the carbon atom (C25) of the diazolyl group. The Ge1−C25 (1.9969(14) Å) and Si1−C25 (1.8345(15) Å) bond lengths are close to the normal values for σ bonds of 1.99 and 1.87 Å, respectively. Also the C25−N3 bond length with 1.3037(19) Å is in the range of a carbon−nitrogen double bond (1.29 Å); the N3−N4 bond length (1.1458(19) Å) lies between a nitrogen−nitrogen double and triple bond (N═N 1.25 Å, N≡N 1.10 Å). The Ge1−C25−Si1 angle of 118.37(7)° is consistent with an sp^2 hybridized carbon atom (C25). These values are closely related to those of a reported diazogermylene compound.[24] Compound **6** has one $SiMe_3$ group and displays a singlet in the ^{29}Si NMR spectrum (δ −2.43 ppm).

When a supernatant solution of **6** is stored for a longer period of time (about 3 months) at room temperature, a silyl group, as well as germanium moiety, shift from the diazo carbon atom to the end-on nitrogen atom of the diazogermylene has been observed (Scheme 6). Thus, the diazo group is converted into an isonitrile species. A comparable migration of a silyl group of azides and the lithium salt of trimethylsilyl diazomethane is known for organolanthanides.[25]

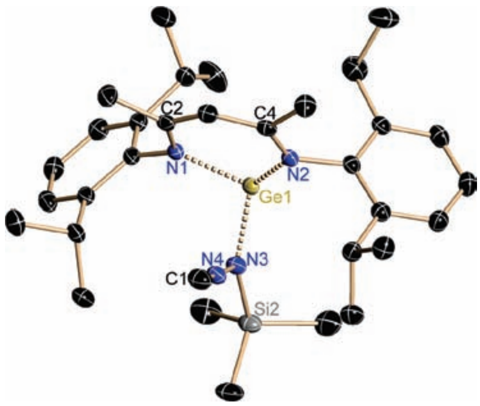
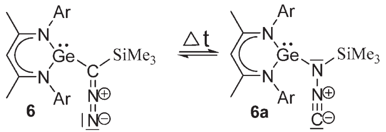


Figure 3. Molecular structure of **6a**; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity.

Scheme 6. Equilibrium between **6** and **6a**



The above-described silyl group and germanium substituent migration has been confirmed by X-ray structure analysis of **6a**. Compounds **6** and **6a** are isostructural (Figure 3). The germanium atom in **6a** is coordinate to three nitrogen atoms whereas the bond length of Ge1−N3 (1.9491(16) Å) is marginally shorter than the average Ge−N bond lengths of the bidentate ligand (Ge1−N1 (1.9994(16) Å, Ge1−N2 (1.9862(16) Å). The N3−Si2 (1.7699(17) Å) bond length is in the range of a standard N−Si bond (1.74 Å). The N4−C1 bond length (1.154(3) Å) correlates with a normal N−C triple bond (N≡C 1.156 Å) while the N3−N4 bond (1.350(2) Å) lies between a N−N single and double bond (N−N 1.45 Å, N═N 1.25 Å). The ^{29}Si NMR spectrum of **6a** exhibits a singlet (δ 12.50 ppm).

Conclusion

In summary we have shown the synthesis of the *N*-heterocyclic germylene L′Ge (**3**) from dehydrogenation of germylene hydride, LGeH (**1**) by using a frustrated Lewis *N*-heterocyclic carbene borane pair. The sequential cleavage of C−H and Ge−H bonds without a catalyst is shown herein. Germylene **3** reacts with $B(C_6F_5)_3$ at room temperature under C−B bond formation to the zwitterionic germanium(II) compound **4**. The reaction of 1,3-di-*tert*-butylimidazol-2-ylidene (NHC) with **4** results in a C−H bond cleavage of the backbone methyl group and the formation of an exocyclic carbon carbon double bond. Moreover compound **3** reacts with $N_2CHSiMe_3$ to form the diazogermylene compound **6** by cleavage of a C−H bond, and after about 3 months it rearranges to the isonitriletrimethylsilyl germanium(II) amide $LGeN(SiMe_3)NC$ (**6a**).

Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk techniques or a MBraun MB 150-GI glovebox. All solvents were dried by MBraun solvent purifying system prior to use. The starting material **1** was prepared using literature procedures.[12b] Other

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chemicals were purchased and used as received. ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the case of the ^{1}H and ^{13}C NMR spectra. ^{11}B and ^{29}Si NMR spectra were referenced to $BF_3 \cdot Et_2O$ and $SiMe_4$, respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument and are not corrected.

Synthesis of 2 and 3. A solution of $B(C_6F_5)_3$ (0.51 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a stirred solution of **1** (0.49 g, 1.0 mmol) in toluene (10 mL) at room temperature. Immediately the red color of the reaction mixture changed to colorless. The reaction mixture was stirred for additional 10 min. After that a solution of 1,3-di-*tert*-butylimidazol-2-ylidene (0.18 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to the reaction mixture. During this time the reaction mixture turned to brown-red with the formation of a white precipitate. After another 10 min the solvent was removed in vacuum, and the residue was extracted with *n*-hexane (15 mL). The extracted brown-red solution contained compound **2**. The insoluble part was collected and identified as imidazolium borate salt **3**. Both are formed almost quantitatively, and the NMR data matches with the previously reported samples.[3c,9]

Synthesis of 4. A solution of $B(C_6F_5)_3$ (0.51 g, 1.0 mmol) in toluene (10 mL) was added to a solution of **3** (0.49 g, 1.0 mmol) in toluene (10 mL) at room temperature. The brown-red color of the solution of **3** vanished slowly, and pale yellow crystals of **4** were formed after 2 days at room temperature. Yield: 0.78 g (78%). Mp 265 °C. ^{1}H NMR (500 MHz, THF-D_8): δ 7.37−7.44 (m, 6H, Ar-*H*), 6.50 (s, 1H, γ-C*H*), 2.73 (sept, 2H, $CH(CH_3)_2$), 2.61 (sept, 2H, $CH(CH_3)_2$), 2.47 (s, 2H, CH_2), 1.84 (s, 3H, CH_3), 1.39 (d, 6H, $CH(CH_3)_2$), 1.25 (d, 6H, $CH(CH_3)_2$), 1.19 (d, 6H, $CH(CH_3)_2$), 1.15 (d, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, THF-D_8): δ 180.93, 166.74 (*C*N), 145.62, 137.35, 130.25, 129.65, 128.89, 126.02 (Ar−C), 149.13, 139.52, 137.41 (C_6F_5), 108.96 (γ-*C*), 29.42 ($CH(CH_3)_2$), 29.32 ($CH(CH_3)_2$), 27.50 ($CH(CH_3)_2$), 25.85 ($CH(CH_3)_2$), 25.62 ($CH(CH_3)_2$), 25.46 ($CH(CH_3)_2$), 25.30 (CH_3) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, THF-D_8): δ −14.82. $^{19}F\{^1H\}$ NMR (188.31 MHz, THF-D_8): δ −131.60 (d, 6F, *o*-F), −163.40 (t, 6F, *m*-F), −167.28 (t, 3F, *p*-F). EI-MS (70 eV): *m*/*z* (%): 475 (100) $[M-(B(C_6F_5)_3, Me)]^+$. Anal. Calcd for $C_{47}H_{40}BF_{15}GeN_2$ (1001.26): C, 56.38; H, 4.03; N, 2.80. Found: C, 56.27; H, 3.82; N, 2.68.

Synthesis of 5. A solution of 1,3-di-*tert*-butylimidazol-2-ylidene (0.18 g, 1.0 mmol) in toluene (10 mL) was added to a solution of **4** (0.49 g, 1.0 mmol) in toluene (10 mL) at room temperature. Immediately the reaction mixture turns to red in color. After 10 min the solvent was removed in vacuum, and the product was isolated as a red oil. ^{1}H NMR (500 MHz, C_6D_6): δ 7.32 (s, 1H, NC*H*), 6.99−7.20 (m, 6H, Ar-*H*), 6.33 (s, 2H, NC*H*), 5.87 (s, 1H, γ-C*H*), 3.86 (sept, 2H, $CH(CH_3)_2$), 3.63(s, 1H, C*H*), 3.60 (sept, 2H, $CH(CH_3)_2$), 2.96 (s, 1H, C*H*), 2.45 (s, 2H, CH_2), 1.70 (d, 6H, $CH(CH_3)_2$), 1.35 (d, 12H, $CH(CH_3)_2$), 1.32 (d, 6H, $CH(CH_3)_2$), 0.75 (s, 18H, $C(CH_3)_3$) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, C_6D_6): δ −13.66. $^{19}F\{^1H\}$ NMR (188.31 MHz, C_6D_6): δ −130.65 (br, 6F, *o*-F), −163.77 (t, 6F, *m*-F), −167.32 (br, 3F, *p*-F). From the analytical data we do not obtain satisfactory results.

Synthesis of 6 and 6a. A solution of $N_2CHSiMe_3$ (0.7 mL, 2 M, in *n*-hexane) was added to a solution of **3** (0.49 g, 1.0 mmol) in *n*-hexane (10 mL) at room temperature. Then the flask was kept at room temperature for 3 days and after that yellow crystals of **6** were obtained, which are suitable for X-ray structural analysis. Yield: 0.53 g (88%). Mp 244 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.09−7.17 (m, 6H, Ar-*H*), 4.51 (s, 1H, γ-C*H*), 3.63 (sept, 2H, $CH(CH_3)_2$), 3.60 (sept, 2H, $CH(CH_3)_2$), 1.62 (s, 6H, CH_3), 1.58 (d, 6H, $CH(CH_3)_2$), 1.43 (d, 6H, $CH(CH_3)_2$), 1.25 (d, 6H, $CH(CH_3)_2$), 1.13 (d, 6H, $CH(CH_3)_2$), −0.07 ($Si(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ 166.43 (*C*N), 146.92, 143.76, 139.99, 127.56, 124.98, 124.76 (Ar−*C*), 95.35 (γ-*C*), 31.91 (CN_2), 29.60 ($CH(CH_3)_2$), 27.39 ($CH(CH_3)_2$), 25.34 ($CH(CH_3)_2$), 25.32 ($CH(CH_3)_2$), 24.68 ($CH(CH_3)_2$), 23.68 ($CH(CH_3)_2$), 0.03 ($Si(CH_3)_3$) ppm. $^{29}Si\{^1H\}$ NMR (99.35 Hz, C_6D_6): δ −2.43 ($Si(CH_3)_3$) ppm EI-MS (70 eV): *m*/*z* (%): 561 (100) $[M\text{-}iPr)]^+$. Anal. Calcd for $C_{33}H_{50}GeN_4Si$ (603.50): C, 65.68; H, 8.35; N, 9.28. Found: C, 64.96; H, 8.62; N, 8.87. For **6a**: After keeping the supernatant solution of **6** for about 3 months at room temperature we observed the conversion of **6** to **6a**. Mp 210 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.06−7.18 (m, 6H, Ar-*H*), 4.75 (s, 1H, γ-C*H*), 3.89 (sept, 2H, $CH(CH_3)_2$), 3.39 (sept, 2H, $CH(CH_3)_2$), 1.66 (s, 6H, CH_3), 1.57 (d, 6H, $CH(CH_3)_2$), 1.37 (d, 6H, $CH(CH_3)_2$), 1.26 (d, 6H, $CH(CH_3)_2$), 1.07 (d, 6H, $CH(CH_3)_2$), −0.04 ($Si(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ 167.04 (*C*N), 147.39, 143.37, 139.81, 127.80, 125.34, 124.53 (Ar−*C*), 97.23 (γ-*C*), 29.76 ($CH(CH_3)_2$), 28.59 (N*C*), 27.35 ($CH(CH_3)_2$), 25.85 ($CH(CH_3)_2$), 25.22 ($CH(CH_3)_2$), 24.44 ($CH(CH_3)_2$), 23.93 ($CH(CH_3)_2$), 0.03 ($Si(CH_3)_3$) ppm. $^{29}Si\{^1H\}$ NMR (99.35 Hz, C_6D_6): δ 12.50 ($Si(CH_3)_3$) ppm EI-MS (70 eV): *m*/*z* (%): 604 (100) $[M]^+$.

Crystallographic Details for Compounds 4, 6, and 6a. The data sets of **4**, **6**, and **6a** were collected on a Bruker TXS-Mo rotating anode equipped with INCOATEC Helios mirror optics (Mo Kα λ = 0.71073 Å). The crystal was mounted in a shock-cooled oil drop at the tip of a fiber.[26] The data was integrated with SAINT V7.46A (**4**, **6a**) and SAINTV7.60A (**6**),[27] and an empirical absorption correction (SADABS-2008/2) was applied.[28] The structure was solved by direct methods (SHELXS)[29] and refined on F^2 using the full-matrix least-squares methods of SHELXL.[30] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp^2 (sp^3) carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom.

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Supporting Information Available: X-ray data for **4**, **6**, and **6a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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