CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200903019

Stable N-Heterocyclic Carbene Adducts of Arylchlorosilylenes and Their Germanium Homologues

Alexander C. Filippou,* Oleg Chernov, Burgert Blom, Kai W. Stumpf, and Gregor Schnakenburg[a]

Abstract: The first N-heterocyclic carbene adducts of arylchlorosilylenes are reported and compared with the homologous germanium compounds. The arylsilicon(II) chlorides SiArCl(Im-Me_4) [Ar = C_6H_3-2,6-Mes_2 (Mes = C_6H_2-2,4,6-Me_3), C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-iPr$_3$)] were obtained selectively on dehydrochlorination of the arylchlorosilanes $SiArHCl_2$ with 1,3,4,5-tetramethylimidazol-2-ylidene (Im-Me_4). The analogous arylgermanium(II) chlorides GeArCl(Im-Me_4) were prepared by metathetical exchange of $GeCl_2$(Im-Me_4) with LiC_6H_3-2,6-Mes_2 or addition of Im-Me_4 to $GeCl(C_6H_3$-2,6-$Trip_2)$. All compounds were fully characterized. Density functional calculations on $ECl(C_6H_3$-2,6-$Trip_2)$(Im-Me_4), where E = Si, Ge, at different levels of theory show very good agreement between calculated and experimental bonding parameters, and NBO analyses reveal similar electronic structures of the two aryltetrel(II) chlorides. The low gas-phase Gibbs free energy of bond dissociation of $SiCl(C_6H_3$-2,6-$Trip_2)$(Im-Me_4) ($\Delta G^\circ_{calcd} = 28.1$ kJ mol^{-1}) suggests that the carbene adducts SiArCl(Im-Me_4) may be valuable transfer reagents of the arylsilicon(II) chlorides SiArCl.

Keywords: density functional calculations · carbene ligands · germylenes · Group 14 elements · silylenes

Introduction

Organosilicon(II) halides SiXR (X = halogen; R = alkyl, aryl, silyl) are very reactive species of major academic and industrial interest. Surface-confined chloromethylsilylenes (SiClMe),[1] for example, have been suggested to be key intermediates in the direct synthesis of chloromethylsilanes from Si–Cu and MeCl (Rochow–Müller synthesis),[2] and donor-stabilized chloromethylsilylenes have been implicated in the base-catalyzed disproportionation of chloromethyldisilanes leading to oligo- and polysilanes.[3] Furthermore, the halomethylsilylenes SiXMe (X = F–I) were shown to undergo reversible photoisomerization to 1-halosilenes (XHSi=CH_2) in Ar matrices at 10 K,[4] and were identified as intermediates in co-condensation reactions of silicon atoms with methyl halides in low-temperature inert-gas matrices, affording dihalodimethylsilanes.[4c,5] In general, haloorganosilylenes were generated in situ on thermolysis or photolysis of halodisilanes,[6] halotrisilanes,[7] or 7-silanorbonadienes.[8,9] The generated species were either trapped by chemical means or detected by low-temperature matrix-spectroscopic methods.[6–9] However, all attempts to isolate organosilicon(II) halides that can be manipulated at room temperature have been unsuccessful to date owing to their extremely high reactivity.[10]

Recent developments in the chemistry of low-coordinate germanium, tin, and lead compounds have shown that the organotetrel(II) halides EXR (E = Ge^{II}, Sn^{II}, Pb^{II}; X = halogen; R = sterically demanding alkyl or aryl group) have great synthetic potential providing access to tetrel compounds with unusual bonding modes.[11] In view of this potential, the isolation of related silicon compounds is expected to have far-reaching consequences in organosilicon chemistry. An advancement in this context is the present report, in which the electronic stabilizing effect of N-heterocyclic carbenes (NHC)[12] was used to obtain the first carbene adducts of arylchlorosilylenes SiArCl(Im-Me_4) (Ar = C_6H_3-2,6-Mes_2, C_6H_3-2,6-$Trip_2$; Im-Me_4 = 1,3,4,5-tetramethylimidazol-2-ylidene), which are compared to the homologous germanium compounds.

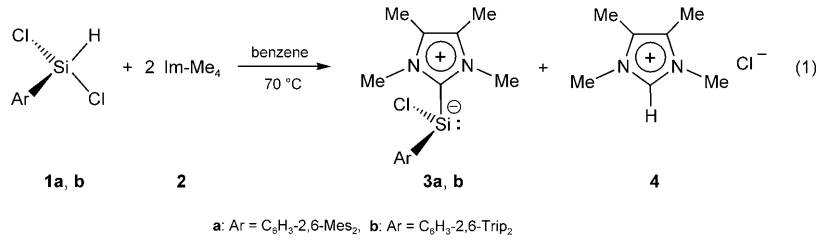
[a] Prof. Dr. A. C. Filippou, Dipl.-Chem. O. Chernov, B. Blom, Dipl.-Chem. K. W. Stumpf, Dr. G. Schnakenburg
Institut für Anorganische Chemie, Universität Bonn
Gerhard-Domagk-Str. 1, 53121 Bonn (Germany)
E-mail: filippou@uni-bonn.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903019.

WILEY InterScience DISCOVER SOMETHING GREAT
© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Results and Discussion

Addition of two equivalents of 1,3,4,5-tetramethylimidazol-2-ylidene (**2**)[13] to solutions of the arylchlorosilanes $SiArHCl_2$ [**1a**: Ar = C_6H_3-2,6-Mes_2 (Mes = C_6H_2-2,4,6-Me_3); **1b**: Ar = C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-iPr_3)][14] in benzene at 70 °C resulted in rapid precipitation of a solid, which was identified by NMR spectroscopy to be the imidazolium chloride (Im-Me_4H)Cl (**4**). NMR analysis of the benzene-soluble components revealed selective formation of the aryl-silicon(II) chlorides **3a** and **3b**, which were isolated as analytically pure, yellow, air-sensitive solids in 72 and 93% yield, respectively [Eq. (1)].



With rigorous exclusion of air, **3b** is stable for at least 120 h in solution in benzene at ambient temperature, whereas **3a** shows the first signs of decomposition within 24 h. For comparative reasons, the analogous germanium compounds GeArCl(Im-Me_4) [Ar = C_6H_3-2,6-Mes_2 (**7a**), Ar = C_6H_3-2,6-$Trip_2$ (**7b**)] were synthesized. Compound **7a** was obtained from $GeCl_2$(1,4-dioxane)[15] in two steps. $GeCl_2$(1,4-dioxane) was treated first with one equivalent of **2** to give the white carbene adduct $GeCl_2$(Im-Me_4) (**5**).[16] Metathetical exchange of **5** with LiC_6H_3-2,6-Mes_2[17] then afforded selectively the arylgermanium(II) chloride **7a** (Scheme 1). Compound **7b** was obtained upon addition of imidazol-2-ylidene **2** to GeCl(C_6H_3-2,6-$Trip_2$) (**6b-Ge**)[18] in toluene (Scheme 1). The Ge^{II} compounds were isolated in high yields as white, air-sensitive solids. Compounds **5** and **7b** melt at 104 and 162 °C, respectively, whereas **7a** starts to decompose at 185 °C.

The molecular structures of **3b**, **3b**·0.5 benzene, **5**·0.5 toluene, and **7b** were determined by single-crystal X-ray diffraction analyses (Figures 1 and 2). Compounds **3b** and **7b** (Figure 1) are isostructural and feature distinctly trigonal-pyramidal tetrel centers, indicating the presence of a stereochemically active lone pair of electrons at the tetrel atoms (**3b**: sum of angles at Si 299.2°, **7b**: sum of angles at Ge 293.8°).[19]

Notably, the degree of pyramidalization at the tetrel atom is close to those calculated for the anions EH_3^- (sum of angles at E: Si 285°, Ge 279–283°).[20,21] In comparison, the carbene carbon atom adopts an almost trigonal-planar coordination geometry in both compounds (sum of angles at C37: **3b** 357.9°, **7b** 357.7°). The Si–$C_{carbene}$ bond of **3b** (1.963(2) Å) compares well with those of the silicon(II) dihalides SiX_2(Idipp) (X = Cl, 1.985(4) Å; X = Br, 1.989(3) Å; Idipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[12b,c] and is slightly longer than the Si–C_{Ar} bond of **3b** (1.937(2) Å), which suggests the presence of a rather strong $C_{carbene}$→Si donor–acceptor single bond. The Si–C_{Ar} bond of **3b** (1.937(2) Å) is longer than those of the arylsilanes Si(C_6H_3-2,6-$Trip_2$)H_2Cl (1.859(4) Å)[14b] and Si(C_6H_3-2,6-$Trip_2$)Cl_3 (1.906(6) Å).[14a,22] Similarly, the Si–Cl bond of **3b** (2.1836(8) Å) compares well with those of the Si^{II} chlorides $SiCl_2$(Idipp) (2.166(8) Å)[12b,23] and SiCl[CPh(N*t*Bu)$_2$] (2.156(1) Å),[10] but is considerably longer than those of the arylchlorosilanes Si(C_6H_3-2,6-$Trip_2$)H_2Cl (2.032(8) Å)[14b] and Si(C_6H_3-2,6-Mes_2)Cl_3 (2.032(2) Å).[14a,23] All these bonding parameters suggest that the Si–C_{Ar} and Si–Cl bonds of aryl-silicon(II) chloride **3b** are weaker than those of arylchlorosilanes and indicate, in full agreement with the results of NBO analysis, that the silicon atom uses mainly p orbitals for bonding to the aryl and Cl groups in **3b** (vide infra).

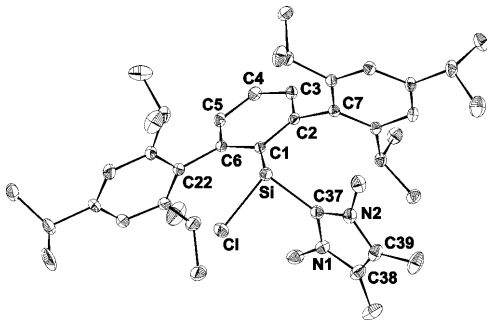
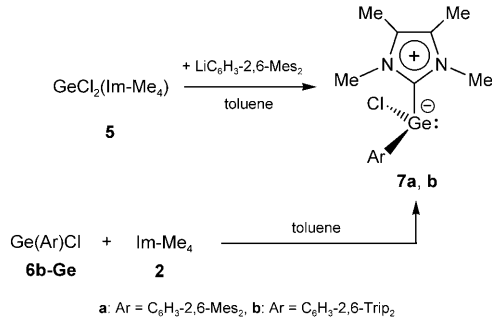


Figure 1. DIAMOND plot of the molecular structure of **3b** in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **3b** [**7b**]: Si–C1 1.937(2) [Ge–C1 2.035(3)], Si–C37 1.963(2) [Ge–C37 2.071(3)], Si–Cl 2.1836(8) [Ge–Cl 2.338(1)], N1–C37 1.355(2) [1.352(4)], N2–C37 1.352(2) [1.342(4)], N1–C38 1.386(3) [1.395(4)], N2–C39 1.389(3) [1.388(4)]; C1-Si-Cl 105.23(7) [C1-Ge-Cl 104.08(8)], C1-Si-C37 102.18(8) [C1-Ge-C37 100.4(1)], C37-Si-Cl 91.78(7) [C37-Ge-Cl 89.32(9)].



Scheme 1. Syntheses of N-heterocyclic carbene adducts of arylgermanium(II) chlorides.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

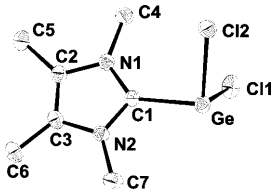


Figure 2. DIAMOND plot of the molecular structure of **5**·0.5 toluene in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge–C1 2.082(3), Ge–Cl1 2.3363(1), Ge–Cl2 2.3019(1); Cl1-Ge-Cl2 97.00(1), C1-Ge-Cl1 92.41(9), C1-Ge-Cl2 95.12(9).

Similar structural trends are found in the Ge^{II} compound **7b** (Figure 1). For example, the Ge–$C_{carbene}$ bond (2.071(3) Å) compares well with that of $GeCl_2$(Im-Me_4) (**5**; 2.082(3) Å; Figure 2) and is slightly longer than the Ge–C_{Ar} bond of **7b** (2.035(3) Å), indicative of a rather strong $C_{carbene}$→Ge donor–acceptor single bond in **7b**. Furthermore, the Ge–C_{Ar} bond (2.035(3) Å) and Ge–Cl bond (2.338(1) Å) of **7b** compare well with those of related Ge^{II} compounds,[16b,24] but are longer than those of arylchlorogermanes (Ge–C_{Ar} 1.94, Ge–Cl 2.18 Å).[25] As in the case of the homologous silicon compounds, these bonding parameters suggest that the Ge–C_{aryl} and Ge–Cl bonds of **7b** are weaker than those of arylchlorogermanes.

Additional structural information is provided by the solution NMR spectra of the carbene adducts. Compounds **3a**,**b** and **7a**,**b** contain a stereogenic tetrel center, which renders the *ortho* and *meta* positions of the mesityl and trisisopropylphenyl substituents chemically inequivalent. Therefore, a double set of signals is observed for the *ortho*- and *meta*-positioned nuclei of these substituents in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3a**,**b** and **7a**,**b** in C_6D_6 (see Experimental Section). This indicates that racemization of **3a**,**b** and **7a**,**b** does not occur in solution, whereas rotation of the aryl group about the E–C_{aryl} bond (E = Si, Ge) is rapid on the NMR timescale. Further support for the configurational stability of **3a**,**b** and **7a**,**b** is provided by the DFT calculations, which predict that the barrier for inversion of **3b** (109.2 kJ mol^{-1}, BP86/LANL2DZ) is similar to that of the silyl anion SiH_3^- (100 kJ mol^{-1}).[20,26]

The $^{13}C\{^1H\}$ NMR spectra of **3a**,**b** and **7a**,**b** display distinctive signals for the carbene carbon and tetrel-bonded C_{Ar} atoms. The $C_{carbene}$ signals (**3a**, δ = 165.2 ppm; **3b**, δ = 166.7 ppm; **7a**, δ = 170.5 ppm; **7b**, δ = 171.7 ppm) appear at considerably higher field than that of **2** (δ = 212.7 ppm),[13] and the C_{Ar} signals at considerably lower field (**3a** and **3b**, δ = 150.6 ppm; **7a** and **7b**, δ = 156.0 ppm) than those of the arylchlorotetrelanes $EArHCl_2$ (**1a**, δ = 128.8 ppm; **1b**, 130.3 ppm; $Ge(C_6H_3$-2,6-$Trip_2)HCl_2$, δ = 134.0 ppm[27]). The NMR signals indicate a major change in the electronic environment of the $C_{carbene}$ and tetrel atoms on formation of adducts **3a**,**b** and **7a**,**b**. In the case of **3a**, the silicon satellites of both carbon signals could be detected after a long accumulation time. The ^1J(Si,$C_{carbene}$) and ^1J(Si,C_{Ar}) coupling constants of 35 and 48 Hz, respectively, are smaller than that of **1a** (^1J(Si,C_{Ar}) = 96.8 Hz) and of Si–C(sp^2) single bonds in silanes (64–70 Hz),[28] and this reflects the differences in Si–C bond lengths (vide supra). Remarkably, the $^{29}Si\{^1H\}$ NMR spectra of the arylsilicon(II) chlorides **3a** and **3b** display a characteristic signal at slightly higher field (**3a**, δ = 1.34 ppm; **3b**, 0.77 ppm) than those of SiX_2(Idipp) (X = Cl, δ = 19.06 ppm; X = Br, δ = 10.9 ppm).[12b,c]

Gradient-corrected DFT calculations on **3b** and **7b** were carried out at different levels of theory, and the electronic structures of **3b** and **7b** were analyzed by the natural bond orbital (NBO) partitioning scheme.[29] The calculated bond lengths and angles compare well with the experimental values (Table 1), and even the conformation of both carbene adducts is well predicted by theory.[30]

The NBO analyses suggest that compounds **3b** and **7b** have similar electronic structures (Table 2). The tetrel centers carry a lone pair of electrons in an NBO orbital of high s character and use hybrid orbitals of high p character for bonding to the Ar and Cl substituents. This reflects the reduced tendency of silicon and germanium for hybridization. In both compounds the E–$C_{carbene}$ bond is described as an almost completely filled (1.95 e) natural bond orbital, which is strongly polarized towards the carbon atom (**3b**: 78.7% C; **7b**: 79.3% C). This highlights the polar character of this bond, which is formed by overlap of an essentially pure p or-

Table 2. Selected results of the NBO analyses of **3b** and **7b** (B3LYP/I).[a]

E–X	Occ.	% (Si)	Hyb.	% (X)	Hyb.	WBI
Si–C1 (**3b**)	1.94	25.3	$sp^{5.04}$	74.7	$sp^{2.19}$	0.76
Si–Cl (**3b**)	1.97	19.7	$sp^{10.78}$	80.3	$sp^{3.01}$	0.71
Si–C37 (**3b**)	1.95	21.3	$sp^{7.99}$	78.7	$sp^{1.33}$	0.68
Si (LP) (**3b**)	1.86		$sp^{0.55}$			
Ge–C1 (**7b**)	1.94	25.8	$sp^{6.64}$	74.2	$sp^{2.42}$	0.74
Ge–Cl (**7b**)[31]						0.67
Ge–C37 (**7b**)	1.95	20.7	$sp^{11.30}$	79.3	$sp^{1.40}$	0.64
Ge (LP) (**7b**)	1.92		$sp^{0.31}$			

[a] NBO occupancy (Occ.), bond polarization in % (Si) and % (X), orbital hybridization (Hyb.) and Wiberg bond index (WBI). LP = lone pair.

Table 1. Calculated and experimental bond lengths [Å] and angles [°] of **3b** and **7b**.[a]

	3b						**7b**					
	Si–C1	Si–Cl	Si–C37	C1-Si-Cl	C1-Si-C37	C37-Si-Cl	Ge–C1	Ge–Cl	Ge–C37	C1-Ge-Cl	C1-Si-C37	C37-Ge-Cl
BP86/LANL2DZ	1.974	2.368	1.988	106.6	103.3	88.5	2.081	2.449	2.110	105.8	101.1	86.8
B3LYP/I	1.966	2.218	2.006	107.3	103.3	89.7	2.080	2.336	2.133	106.3	101.8	87.5
BP86/Ib	1.956	2.202	1.994	107.3	103.9	90.5	2.081	2.327	2.120	106.2	101.9	87.9
Exptl	1.937(2)	2.184(1)	1.963(2)	105.2(1)	102.2(1)	91.8(1)	2.035(3)	2.338(1)	2.071(3)	104.1(1)	100.4(1)	89.3(1)

[a] Basis set I: TZVPP for Si, Br and C1, 6-31G* for the other atoms; basis set Ib: TZ2P for all atoms (see Experimental Section).

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

bital of the tetrel atom with an $sp^{1.3}$ (**3b**) or $sp^{1.4}$ (**7b**) hybrid orbital of carbene atom C37.

Natural population analyses of **3b** and **7b** show that charge transfers of 0.33 e (**3b**) and 0.34 e (**7b**) occur on complexation of imidazol-2-ylidene (**2**) to the Lewis acids ECl(C_6H_3-2,6-$Trip_2$), which reduces the positive partial charge of the tetrel atom E from +0.98 in SiCl(C_6H_3-2,6-$Trip_2$) (**6b-Si**) to +0.72 in **3b** and from +0.96 in GeCl(C_6H_3-2,6-$Trip_2$) (**6b-Si**) to +0.70 in **7b** (Table 3).[32]

Table 3. NPA partial charges in **3b** and **7b** (B3LYP/I).

	E	Cl	C1	C37	Σ(Im-Me_4)
3b (E = Si)	+0.72	−0.50	−0.44	+0.08	+0.33
7b (E = Ge)	+0.70	−0.53	−0.39	+0.12	+0.34

The ZPVE-corrected calculated bond dissociation energy $D^0(0)$ of the silicon compound **3b** (94.3 kJ mol^{-1}, B3LYP/I) is lower than that of $SiBr_2$(Idipp) (123.7 kJ mol^{-1}),[12c] but higher than that of the germanium analogue **7b** (79.9 kJ mol^{-1}). Both carbene adducts are thermodynamically stable with respect to their dissociation products Im-Me_4 (**2**) and ECl(C_6H_3-2,6-$Trip_2$) [**6b-E** (E = Si, Ge)] at 298 K, as evidenced by the gas-phase Gibbs free energies of bond dissociation [$\Delta G°$ = 28.1 (**3b**) and 14.7 kJ mol^{-1} (**7b**)]. Given the low Gibbs free dissociation energy of **3b** it is conceivable that the carbene adducts **3a** and **3b** are valuable transfer reagents of the arylsilicon(II) chlorides SiArCl. Experiments are underway to verify this hypothesis.

Experimental Section

General: All experiments were carried out under an atmosphere of argon by using Schlenk or glove box techniques. Glassware was dried in an oven at approximately 110 °C and baked in vacuo prior to use. The solvents were refluxed over the appropriate drying agent (hexane: sodium wire/benzophenone/tetraglyme; benzene: sodium wire/benzophenone; toluene: sodium), purged several times with argon during reflux, and distilled under argon. All solvents were stored in a glove box. $SiArHCl_2$ [Ar = C_6H_3-2,6-Mes_2 (**1a**), C_6H_3-2,6-$Trip_2$ (**1b**)],[14] Im-Me_4 (**2**),[13] $GeCl_2$(1,4-dioxane),[15] LiC_6H_3-2,6-Mes_2,[17] and GeCl(C_6H_3-2,6-$Trip_2$) (**6b-Ge**)[18] were prepared according to published procedures and were shown by NMR spectroscopy[33–35] and elemental analyses to be pure. The C, H, N analyses of all compounds were carried out three times on an Elementar Vario Micro elemental analyzer. The individual C, H, N values did not differ by more than ±0.3. The mean C, H, N values are given below for each compound. The thermal behavior of analytically pure samples of **3a**, **3b**, **5**, **7a**, and **7b** was studied with a Büchi melting point apparatus. The melting point determination of each sample was carried out in duplicate. The samples were sealed in capillary tubes under vacuum (**3a**, **3b**) or under argon (**5**, **7a**, **7b**) and heated slowly until they melted or decomposed. All NMR spectra were recorded on Bruker Avance DMX-300, DPX-400, or DMX-500 NMR spectrometers in dry deoxygenated [D_6]benzene, [D_2]dichloromethane, [D]chloroform, or [D_8]tetrahydrofuran. The ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated against the residual proton and natural-abundance ^{13}C resonances of the deuterated solvent relative to tetramethylsilane ([D_6]benzene, δ_H = 7.15 ppm and δ_C = 128.0 ppm; [D_2]dichloromethane, δ_H = 5.32 ppm and δ_C = 53.8 ppm; [D]chloroform δ_H = 7.24 ppm and δ_C = 77.0 ppm; [D_8]THF, δ_H = 1.73 ppm and δ_C = 25.3 ppm). The solution ^{29}Si{^{1}H} NMR spectra of **3a** and **3b** were calibrated against external pure $SiMe_4$, which was filled in a sealed capillary and measured in a vacuum-sealed 5 mm NMR tube containing [D_6]benzene. The following abbreviations were used for the signal multiplicities of the NMR signals: s = singlet, d = doublet, sept = septet, and m = multiplet. The ^{1}H and ^{13}C NMR signals of **1a**, **1b**, **3a**, **3b**, **7a**, and **7b** were assigned by a combination of HMQC, HMBC, and DEPT experiments. This allowed unequivocal assignment of all proton and carbon resonances including those of the diastereotopic methyl groups of the isopropyl substituents, which were labeled with the subscript letters A and B, respectively.

Synthesis of SiCl(C_6H_3-2,6-Mes_2)(Im-Me_4) (3a): Si(C_6H_3-2,6-Mes_2)HCl_2 (**1a**, 207 mg, 0.50 mmol) was dissolved in benzene (10 mL) and the colorless solution was heated to 70 °C. A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (**2**) (129 mg, 1.04 mmol, 2.08 equiv) in benzene (5 mL) was added dropwise to the solution of the silane over 10 min. During addition an orange solid precipitated, and the reaction solution turned yellow. After the addition was complete, the suspension was concentrated in vacuo to about 3 mL, and pentane (15 mL) was added. The orange precipitate was isolated by filtration and treated with benzene (15 mL). The obtained suspension was filtered via cannula. The benzene-insoluble, orange solid was dried in vacuo and was shown by NMR spectroscopy to contain mainly the imidazolium salt (Im-Me_4H)Cl (**4**).[36] The yellow filtrate was evaporated to dryness to give a yellow solid, which was washed with pentane (5 mL) and dried in vacuo (1 h, 25 °C, 0.05 mbar) to afford compound **3a** as a yellow solid. Yield 180 mg (0.36 mmol, 72 %). Compound **3a** starts to decompose on heating at 120 °C. Recrystallization of the solid from toluene afforded an analytically pure sample of the toluene hemisolvate of **3a**. Elemental analysis calcd (%) for $C_{31}H_{37}ClN_2Si{\cdot}0.5\,C_7H_8$ (547.23): C 75.72, H 7.55, N 5.12; found: C 75.47, H 7.44, N 5.11; ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ = 1.18 (s, 6H, $C^{4,5}$-*Me*, Im-Me_4), 2.11 (s, 6H, 2×C^2-*Me*, Mes), 2.18 (s, 6H, 2×C^4-*Me*, Mes), 2.57 (s, 6H, 2×C^6-*Me*, Mes), 3.02 (s, 6H, 2×N-*Me*, Im-Me_4), 6.63 (s, 2H, 2×C^3-*H*, Mes), 6.88 (s, 2H, 2×C^5-*H*, Mes), 6.93 (d, ^3J(H,H) = 7.5 Hz, 2H, $C^{3,5}$-*H*, C_6H_3), 7.19 ppm (t, ^3J(H,H) = 7.5 Hz, 1H, C^4-*H*, C_6H_3); ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ = 7.9 (s, $C^{4,5}$-*Me*, Im-Me_4), 21.13 and 21.17 (2s, 2×C^4-*Me* + 2×C^2-*Me*, Mes), 22.0 (s, 2×C^6-*Me*, Mes), 34.0 (s, 2×N-*Me*, Im-Me_4), 124.5 (s, $C^{4,5}$-Me, Im-Me_4), 126.1 (s, C^4-H, C_6H_3), 128.0 (s, 2×C^3-H, Mes), 128.6 (s, 2×C^5-H, Mes), 129.2 (s, $C^{3,5}$-H, C_6H_3), 135.1 (s, 2×C^4, Mes), 135.8 (s, 2×C^2, Mes), 136.7 (s, 2×C^6, Mes), 141.8 (s, 2×C^1, Mes), 146.2 (s, $C^{2,6}$, C_6H_3), 150.6 (s, ^1J(^{13}C,^{29}Si) = 48 Hz, Si-C^1, C_6H_3), 165.2 ppm (s, ^1J(^{13}C,^{29}Si) = 33 Hz, Si-C^2, Im-Me_4); ^{29}Si{^{1}H} NMR (C_6D_6, 59.63 MHz, 298 K): δ = 1.34 ppm (s).

Synthesis of SiCl(C_6H_3-2,6-$Trip_2$)(Im-Me_4) (3b): Si(C_6H_3-2,6-$Trip_2$)HCl_2 (**1b**, 910 mg, 1.56 mmol) was dissolved in benzene (25 mL), and the solution was heated to 70 °C. A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (**2**, 396 mg, 3.19 mmol, 2.05 equiv) in benzene (10 mL) was added dropwise over 15 min. During addition a precipitate formed, and the mixture turned orange. After the addition was complete, the solvent was removed in vacuo and the residue washed twice with benzene: hexane (1:1; 10 mL). The washings were discarded. The obtained yellow solid was extracted with benzene (40 mL), and the extract filtered to remove an insoluble, white solid (260 mg), which was shown by NMR spectroscopy to be the imidazolium salt (Im-Me_4H)Cl (**4**).[36] The filtrate was evaporated to dryness, and the residue washed with 10 mL of hexane and dried in vacuo (1 h, 30 °C, 0.05 mbar) to afford organosilicon(II) chloride **3b** as a yellow solid. Yield: 970 mg (1.45 mmol, 93 %). Compound **3b** starts to decompose on heating at 172 °C. Elemental analysis calcd (%) for $C_{43}H_{61}ClN_2Si$ (669.48): C 77.14, H 9.18, N 4.19, Cl 5.30; ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ = 1.13 (s, 6H, $C^{4,5}$-*Me*, Im-Me_4), 1.173 (d, ^3J(H,H) = 6.8 Hz, 6H, 2×C^2-CH$Me_A$$Me_B$, Trip), 1.183 (d, ^3J-(H,H) = 6.8 Hz, 6H, 2×C^2-CH$Me_A$$Me_B$, Trip), 1.271 (d, ^3J(H,H) = 6.9 Hz, 2×C^4-CH$Me_A$$Me_B$, Trip), 1.277 (d, ^3J(H,H) = 6.9 Hz, 2×C^4-CH$Me_A$$Me_B$, Trip) 1.31 (d, ^3J(H,H) = 6.8 Hz, 6H, 2×C^6-CH$Me_A$$Me_B$, Trip), 1.74 (d, ^3J-(H,H) = 6.8 Hz, 6H, 2×C^6-CH$Me_A$$Me_B$, Trip), 2.87 (sept, ^3J(H,H) = 6.9 Hz, 2H, 2×C^4-C*H*$Me_A$$Me_B$, Trip), 3.02 (sept, ^3J(H,H) = 6.8 Hz, 2H, 2×C^2-C*H*$Me_A$$Me_B$, Trip), 3.14 (s, 6H, 2×N*Me*, Im-Me_4), 3.43 (sept, ^3J-(H,H) = 6.8 Hz, 2H, 2×C^6-C*H*$Me_A$$Me_B$, Trip), 7.03 (d, ^4J(H,H) = 1.6 Hz, 2H, 2×C^3-*H*, Trip), 7.10–7.13 (m, 3H, $C^{3,5}$-*H* + C^4-*H*, C_6H_3), 7.24 ppm (d, ^4J(H,H) = 1.6 Hz, 2H, 2×C^5-*H*, Trip); ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6,

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

298 K): $\delta = 7.9$ (s, $C^{4,5}$-*Me*, Im-Me_4), 23.0 (s, 2×C^2-CHMe_A*Me*$_B$, Trip), 23.7 (s, 2×C^6-CHMe_A*Me*$_B$, Trip), 24.4 (s, 2×C^4-CH*Me*$_A$Me$_B$, Trip), 24.7 (s, 2×C^4-CHMe_A*Me*$_B$, Trip), 26.5 (s, 2×C^6-CH*Me*$_A$Me$_B$, Trip), 26.9 (s, 2×C^2-CH*Me*$_A$Me$_B$, Trip), 31.0 (s, 2×C^2-*C*HMe_AMe$_B$, Trip), 31.7 (s, 2×C^6-*C*HMe_AMe$_B$, Trip), 33.8 (s, 2×N-*Me*, Im-Me_4), 34.7 (s, 2×C^4-*C*HMe_AMe$_B$, Trip), 120.1 (s, 2×C^3-H, Trip), 121.0 (s, 2×C^5-H, Trip), 124.4 (s, C^4-H, C_6H_3), 125.1 (s, $C^{4,5}$-Me, Im-Me_4), 130.8 (s, $C^{3,5}$-H, C_6H_3), 140.0 (s, 2×C^1, Trip), 145.0 (s, $C^{2,6}$, C_6H_3), 147.3 (s, 2×C^2, Trip), 147.4 (s, 2×C^4, Trip), 147.5 (s, 2×C^6, Trip), 150.6 (s, Si-C^1, C_6H_3), 166.7 ppm (s, $^1J(^{13}C,^{29}Si) = 37$ Hz, Si-C^2, Im-Me_4); $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 298 K): $\delta =$ 0.77 ppm (s).

Synthesis of $GeCl_2$(Im-Me_4) (5): A Schlenk tube was charged with $GeCl_2$(1,4-dioxane) (1.00 g, 4.32 mmol), and the germanium compound was suspended in toluene (15 mL). A solution of **2** (536 mg, 4.32 mmol) in toluene (20 mL) was added slowly via cannula to the suspension at room temperature under rapid stirring. The reaction mixture was stirred for 1 h at room temperature and the resulting clear, slightly yellow solution was filtered from a tiny amount of an orange insoluble material. The filtrate was concentrated in vacuo to about 5 mL, upon which a white solid precipitated. The white solid was separated from the light yellow mother liquor by filtration at −60 °C, washed with pentane (2×5 mL) at −60 °C, and dried in vacuo at room temperature for 2 h to afford compound **5** as a white, microcrystalline powder. Yield: 1.02 g (3.81 mmol, 88 %). M.p.: 104 °C; elemental analysis calcd (%) for $C_7H_{12}Cl_2GeN_2$ (267.68): C 31.41, H 4.52, N 10.47, Cl 26.49; found: C 31.62, H 4.47, N 10.31, Cl 26.2 %; ^1H NMR (300.1 MHz, C_6D_6, 298 K): $\delta = 1.07$ (s, 6H, $C^{4,5}$-*Me*), 3.19 ppm (s, 6H, 2×N-*Me*); ^1H NMR (400.1 MHz, [D_8]THF, 298 K): $\delta = 2.19$ (s, 6H, $C^{4,5}$-*Me*), 3.93 ppm (s, 6H, 2×N-*Me*); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): $\delta = 7.5$ (s, 2×$C^{4,5}$-*Me*), 33.0 (s, 2×N-*Me*), 125.7 (s, $C^{4,5}$-Me), 166.1 ppm (s, Ge-C^2).

Synthesis of GeCl(C_6H_3-2,6-Mes_2)(Im-Me_4) (7a): A suspension of $GeCl_2$-(Im-Me_4) (**5**, 370 mg, 1.382 mmol) in 15 mL of toluene was cooled to −78 °C. A precooled (−78 °C) solution of Li(C_6H_3-2,6-Mes_2) (443 mg, 1.383 mmol) in toluene (15 mL), was added rapidly via cannula to the first suspension with stirring. The reaction mixture was stirred for 1 h at −78 °C, at which point an almost colorless solution and a white insoluble solid were present. The Schlenk tube was then transferred to a −20 °C cooling bath and stirring was continued for a further 1 h, upon which the reaction solution turned light blue. The mixture was then warmed to 0 °C and stirred at this temperature for an additional 2 h to afford a Prussian blue colored solution with a white precipitate. On stirring the reaction mixture at room temperature for 0.5 h the color of the solution turned orange and a white precipitate was present. Pentane (15 mL) was added to the mixture, and the suspension was filtered via cannula at room temperature. The residue was extracted with a toluene:pentane mixture (2:1, 2×10 mL) and the filtrates were combined, leaving 120 mg of a white residue (LiCl) in the reaction vessel. The clear orange filtrate was concentrated in vacuo at room temperature to about 2 mL. Pre-cooled (0 °C) pentane (5 mL) was added to the filtrate via cannula to precipitate a light yellow solid, which was filtered off, washed with pentane (2×10 mL), and dried in vacuo for 0.5 h at room temperature to afford the product as a white powder. Yield: 667 mg (1.22 mmol, 88 %). Compound **7a** starts to decompose at 185 °C, turning brown. Elemental analysis calcd (%) for $C_{31}H_{37}ClGeN_2$ (545.67): C 68.23, H 6.83, N 5.14, Cl 6.50; found: C 68.91, H 6.86, N 4.71, Cl 5.7; ^1H NMR (300.1 MHz, C_6D_6, 298 K): $\delta = 1.15$ (s, 6H, $C^{4,5}$-*Me*, Im-Me_4), 2.09 (s, 6H, 2×C^2-*Me*, Mes), 2.17 (s, 6H, 2×C^4-*Me*, Mes), 2.51 (s, 6H, 2×C^6-*Me*, Mes), 2.91 (s, 6H, 2×N-*Me*, Im-Me_4), 6.64 (s, 2H, 2×C^3-*H*, Mes), 6.87 (s, 2H, 2×C^5-*H*, Mes), 6.98 (d, $^3J(H,H) = 7.5$ Hz, 2H, $C^{3,5}$-*H*, C_6H_3), 7.24 ppm (t, $^3J(H,H) = 7.5$ Hz, 1H, C^4-*H*, C_6H_3); ^1H NMR (400.1 MHz, [D_8]THF, 298 K): $\delta = 1.92$ (s, 6H, 2×*Me*, Mes), 2.02 (s, 6H, $C^{4,5}$-*Me*, Im-Me_4), 2.18 (s, 6H, 2×*Me*, Mes), 2.25 (s, 6H, 2×*Me*, Mes), 3.30 (s, 6H, 2×N-*Me*, Im-Me_4), 6.64 (s, 2H, 2×C-*H*, Mes), 6.74 (d, $^3J(H,H) = 7.5$ Hz, 2H, $C^{3,5}$-*H*, C_6H_3), 6.77 (s, 2H, 2×C-*H*, Mes), 7.16 ppm (t, $^3J(H,H) = 7.5$ Hz, 1H, C^4-*H*, C_6H_3); $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 298 K): $\delta = 7.8$ (s, $C^{4,5}$-*Me*, Im-Me_4), 21.1 (s, 2×C^4-*Me*, Mes), 21.2 (s, 2×C^2-*Me*, Mes), 21.9 (s, 2×C^6-*Me*, Mes), 34.0 (s, 2×N-*Me*, Im-Me_4), 124.2 (s, $C^{4,5}$-Me, Im-Me_4), 126.7 (s, C^4-H, C_6H_3), 128.1 (s, 2×C^3-H, Mes), 128.7 (s, 2×C^5-H, Mes), 129.1 (s, $C^{3,5}$-H, C_6H_3), 135.3 (s, 2×C^4, Mes), 135.7 (s, 2×C^2, Mes), 136.7 (s, 2×C^6, Mes), 141.3 (s, 2×C^1, Mes), 147.1 (s, $C^{2,6}$, C_6H_3), 156.0 (s, Ge-C^1, C_6H_3), 170.5 ppm (s, Ge-C^2, Im-Me_4).

Synthesis of GeCl(C_6H_3-2,6-$Trip_2$)(Im-Me_4) (7b): A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (**2**, 47 mg, 0.38 mmol) in toluene (15 mL) was added to an orange solution of GeCl(C_6H_3-2,6-$Trip_2$) (**6b-Ge**, 219 mg, 0.37 mmol) in toluene (10 mL). Upon addition the reaction solution decolorized. The solvent was removed in vacuo and the residue was washed with hexane (3 mL) and dried in vacuo for 1 h at ambient temperature to afford the product **7b** as a white, microcrystalline solid. Yield: 213 mg (0.30 mmol, 80 %). M.p. 162 °C; elemental analysis calcd (%) for $C_{43}H_{61}ClGeN_2$ (714.01): C 72.33, H 8.61, N 3.92; found: C 72.60, H 8.43, N 3.73 %; ^1H NMR (500.1 MHz, C_6D_6, 298 K): $\delta = 1.140$ (d, ^3J-(H,H) = 6.8 Hz, 6H, 2×C^2-CH*Me*$_A$Me$_B$, Trip), 1.145 (s, 6H, $C^{4,5}$-*Me*, Im-Me_4), 1.168 (d, $^3J(H,H) = 6.8$ Hz, 6H, 2×C^2-CHMe_A*Me*$_B$, Trip), 1.276 (d, $^3J(H,H) = 6.8$ Hz, 6H, 2×C^4-CH*Me*$_A$Me$_B$, Trip), 1.283 (d, $^3J(H,H) = 6.9$ Hz, 6H, 2×C^4-CHMe_A*Me*$_B$), 1.295 (d, $^3J(H,H) = 6.8$ Hz, 6H, 2×C^6-CH*Me*$_A$Me$_B$, Trip), 1.72 (d, $^3J(H,H) = 6.8$ Hz, 6H, 2×C^6-CHMe_A*Me*$_B$, Trip), 2.87 (sept, $^3J(H,H) = 6.9$ Hz, 2H, 2×C^4-C*H*Me_AMe$_B$, Trip), 3.02 (sept, $^3J(H,H) = 6.8$ Hz, 2H, 2×C^2-C*H*Me_AMe$_B$, Trip), 3.07 (s, 6H, 2×N*Me*, Im-Me_4), 3.38 (sept, $^3J(H,H) = 6.8$ Hz, 2H, 2×C^6-C*H*Me_AMe$_B$, Trip), 7.05 (d, $^4J(H,H) = 1.7$ Hz, 2H, 2×C^3-*H*, Trip), 7.14–7.17 (m, 3H, $C^{3,5}$-*H* + C^4-*H*, C_6H_3, this signal group overlaps partially with the residual proton signal of the deuterated solvent), 7.24 ppm (d, $^4J(H,H) = 1.7$ Hz, 2H, 2×C^5-*H*, Trip); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): $\delta = 7.8$ (s, $C^{4,5}$-*Me*, Im-Me_4), 22.8 (s, 2×C^2-CHMe_A*Me*$_B$, Trip), 23.7 (s, 2×C^6-CHMe_A*Me*$_B$, Trip), 24.4 (s, 2×C^4-CH*Me*$_A$Me$_B$, Trip), 24.7 (s, 2×C^4-CHMe_A*Me*$_B$, Trip), 26.6 (s, 2×C^6-CH*Me*$_A$Me$_B$, Trip), 26.9 (s, 2×C^2-CH*Me*$_A$Me$_B$, Trip), 31.1 (s, 2×C^2-*C*HMe_AMe$_B$, Trip), 31.7 (s, 2×C^6-*C*HMe_AMe$_B$, Trip), 33.9 (s, 2×N-*Me*, Im-Me_4), 34.7 (s, 2×C^4-*C*HMe_AMe$_B$, Trip), 120.3 (s, 2×C^3-H, Trip), 120.9 (s, 2×C^5-H, Trip), 124.8 (s, $C^{4,5}$-Me, Im-Me_4), 125.2 (s, C^4-H, C_6H_3), 130.7 (s, $C^{3,5}$-H, C_6H_3), 139.3 (s, 2×C^1, Trip), 146.0 (s, $C^{2,6}$, C_6H_3), 147.2 (s, 2×C^2, Trip), 147.4 (s, 2×C^6, Trip), 147.5 (s, 2×C^4, Trip), 156.1 (s, Ge-C^1, C_6H_3), 171.7 ppm (s, Ge-C^2, Im-Me_4).

Crystal structure determination of 3b, 3b·0.5 benzene, 5·0.5 toluene and 7b: Yellow single crystals of **3b** were grown by cooling a concentrated toluene solution from ambient temperature to +4 °C. Diffusion of pentane into a [D_6]benzene solution of **3b** afforded yellow crystals of the benzene hemisolvate of **3b**. Colorless single crystals of the toluene hemisolvate of **5** were obtained upon cooling a concentrated toluene solution from ambient temperature to −60 °C, and colorless single crystals of **7b** upon slow cooling of a warm saturated hexane solution to room temperature. The data collection of **3b, 3b**·0.5 benzene and **7b** was performed on a NONIUS KappaCCD diffractometer (area detector), and that of **5**·0.5 toluene on a STOE IPDS2T diffractometer, with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Both diffractometers were equipped with a low-temperature device (Cryostream, Oxford Cryosystems, 123(2) K). Intensities were measured by fine-slicing ω- and ϕ-scans and corrected for background, polarization and Lorentzian effects. A numerical (**5**·0.5 toluene, **7b**) or semiempirical (**3b, 3b**·0.5 benzene) absorption correction from equivalent reflections was applied for all data sets by using Blessing's method.[37] The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[38] The hydrogen atoms were included isotropically by using the riding model on the bound carbon atoms. The illustrations of the molecular structures were prepared with Diamond 2.1c.[39]

CCDC-749955 (**3b**), CCDC-749956 (**3b**·0.5 benzene), CCDC-749957 (**5**·0.5 toluene), and CCDC-749954 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic structure calculations: All calculations were carried out at the nonlocal density functional level of theory (DFT) by using the exchange functional of Becke and the correlation functional of Perdew (BP86)[40] or the hybrid three-parameter functional of Becke and the correlation functional of Lee, Yang and Parr (B3LYP).[41] The following basis sets were used: 1) basis set I, which is a combination of the TZVPP basis[42]

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

for the silicon, bromine and carbene carbon atoms and the 6-31G* basis set[43] for all other atoms; b2) basis set Ib, which corresponds to basis set "TZ2P" of the program package ADF2007 without frozen-core approximation;[44] 3) the LANL2DZ basis set as implemented in Gaussian03.

All geometry optimizations using basis set I were carried out without symmetry restraints with the program package Gaussian 03 by using its standard convergence criteria.[45] The optimized geometries were verified as minima on the potential-energy surface by evaluation of their harmonic vibrational frequencies, which were used to calculate the zero-point vibrational energies of Im-Me_4 (**2**), **3b**, **6b-Si, 6b-Ge** and **7b**. Geometry optimization of **3b** and **7b** at the BP86/Ib level of theory was carried out with the program ADF 2007.01[46] and the implemented basis set "TZ2P". No frozen-core approximation was used and scalar relativistic effects were considered by means of the zero-order regular approximation (ZORA).

The NBO analyses of **3b** and **7b** were performed with the NBO 5.0 program.[29] Atomic charges in all structures were obtained by the natural population analysis (NPA) method within the NBO approach. The NBO method interprets a many-electron molecular wave function in terms of localized electron-pair bonding units and leads to a natural Lewis structure which describes best the system.

The Gibbs free energies of bond dissociation of **3b** and **7b** were calculated at the B3LYP/I level of theory and corrected for the difference in the zero-point vibrational energies (ZPVE, B3LYP/I). Thermal corrections were carried out under standard conditions ($T=298.15$ K, and $P=1$ atm).

The transition state of the isomerization of **3b** was calculated by using the Berny algorithm implemented in Gaussian. The starting geometry was obtained from a partially optimized geometry with the restriction of a planar-coordinated Si atom. IRC calculations in both directions were carried out to assure the right trajectory of the transition state.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for the generous financial support of this work. We also thank C. Schmidt, K. Prochnicki, and H. Spitz for recording the solution NMR spectra and A. Martens for the elemental analyses.

[1] a) K. M. Lewis, D. McLeod, B. Kanner, J. L. Falconer, T. C. Frank in *Catalyzed Direct Reactions of Silicon* (Eds.: K. M. Lewis, D. G. Rethwisch), Elsevier, Amsterdam, Chapter 6, **1993**.

[2] D. Seyferth, *Organometallics* **2001**, *20*, 4978.

[3] a) R. F. Trandell, G. Urry, *J. Inorg. Nucl. Chem.* **1978**, *40*, 1305; b) R. Richter, G. Roewer, U. Böhme, K. Busch, F. Babonneau, H. P. Martin, E. Müller, *Appl. Organomet. Chem.* **1997**, *11*, 71; c) J. Belzner, H. Ihmels, *Adv. Organomet. Chem.* **1998**, *43*, 1; d) H. Hildebrandt, B. Engels, *Z. Anorg. Allg. Chem.* **2000**, *626*, 400.

[4] a) H. P. Reisenauer, G. Mihm, G. Maier, *Angew. Chem.* **1982**, *94*, 864; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 854; b) G. Maier, G. Mihm, H. P. Reisenauer, D. Littmann, *Chem. Ber.* **1984**, *117*, 2369; c) G. Maier, J. Glatthaar, H. P. Reisenauer, *J. Organomet. Chem.* **2003**, *686*, 341.

[5] G. Maier, J. Glatthaar, *Organometallics* **2007**, *26*, 425.

[6] a) R. L. Jenkins, A. J. Vanderwielen, S. P. Ruis, S. R. Gird, M. A. Ring, *Inorg. Chem.* **1973**, *12*, 2968; b) T. J. Barton, D. S. Banasiak, *J. Am. Chem. Soc.* **1977**, *99*, 5199; c) M. P. Clarke, I. M. T. Davisdon, *J. Chem. Soc. Chem. Commun.* **1988**, 241; d) J. Heinicke, B. Gehrhus, S. Meinel, *J. Organomet. Chem.* **1994**, *474*, 71.

[7] a) M. J. Michalczyk, M. J. Fink, D. J. De Young, C. W. Carlson, K. M. Welsh, R. West, J. Michl, *Silicon Germanium Tin Lead Compd.* **1986**, *9*, 75; b) N. Wiberg, W. Niedermayer, *J. Organomet. Chem.* **2001**, *628*, 57; c) T. Tanaka, M. Ishinohe, A. Sekiguchi, *Chem. Lett.* **2004**, *33*, 1420.

[8] M. Okimoto, A. Kawachi, Y. Yamamoto, *J. Organomet. Chem.* **2009**, *694*, 1419.

[9] Reduction of the tribromosilane $SiBr_3C(SiMe_3)_3$ with lithium/naphthalene has been also proposed to afford a bromosilylene ($SiBrC(SiMe_3)_3$) on the basis of NMR and trapping experiments: M. E. Lee, H. M. Cho, M. S. Ryu, C. H. Kim, W. Ando, *J. Am. Chem. Soc.* **2001**, *123*, 7732. However, the proposed structure was questioned (M. Flock, A. Dransfeld, *Chem. Eur. J.* **2003**, *9*, 3320) and a silylenoid intermediate was suggested recently to rationalize the outcome of the trapping experiments: M. E. Lee, H. M. Cho, Y. M. Lim, J. K. Choi, C. H. Park, S. E. Jeong, U. Lee, *Chem. Eur. J.* **2004**, *10*, 377.

[10] Recently, a donor-stabilized silicon(II) chloride with an N-chelating ligand has been reported: C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem.* **2006**, *118*, 4052; *Angew. Chem. Int. Ed.* **2006**, *45*, 3948.

[11] Reduction of EXR by alkali metals has been shown to give a series of unprecedented compounds featuring "*trans*-bent" tetrel–tetrel multiple bonds: a) P. P. Power, *Chem. Commun.* **2003**, 2091; b) P. P. Power, *Organometallics* **2007**, *26*, 4362. Similarly, a wide variety of metal complexes featuring triple bonds to linearly coordinated tetrel atoms has been obtained upon activation of EXR by electron-rich dinitrogen or trimethylphosphane complexes of Group 6 transition metals: c) A. C. Filippou, P. Portius, A. I. Philippopoulos, H. Rohde, *Angew. Chem.* **2003**, *115*, 461; *Angew. Chem. Int. Ed.* **2003**, *42*, 445; d) A. C. Filippou, H. Rohde, G. Schnakenburg, *Angew. Chem.* **2004**, *116*, 2293; *Angew. Chem. Int. Ed.* **2004**, *43*, 2243; e) A. C. Filippou, G. Schnakenburg, A. I. Philippopoulos, N. Weidemann, *Angew. Chem.* **2005**, *117*, 6133; *Angew. Chem. Int. Ed.* **2005**, *44*, 5979; f) A. C. Filippou, N. Weidemann, A. I. Philippopoulos, G. Schnakenburg, *Angew. Chem.* **2006**, *118*, 6133; *Angew. Chem. Int. Ed.* **2006**, *45*, 5987; g) G. Balázs, L. J. Gregoriades, M. Scheer, *Organometallics* **2007**, *26*, 3058; h) A. C. Filippou, N. Weidemann, G. Schnakenburg, *Angew. Chem.* **2008**, *120*, 5883; *Angew. Chem. Int. Ed.* **2008**, *47*, 5799.

[12] Recently, N-heterocyclic carbenes have been shown to stabilize silicon centers in low oxidation states: a) Y. Wang, Y. Xie, P. Wei, R. B. Bruce, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069; b) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Hemm, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683; c) A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, *121*, 5797; *Angew. Chem. Int. Ed.* **2009**, *48*, 5687.

[13] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561.

[14] a) R. S. Simons, S. T. Haubrich, B. V. Mork, M. Niemeyer, P. P. Power, *Main Group Chem.* **1998**, *2*, 275; b) N. Weidemann, G. Schnakenburg, A. C. Filippou, *Z. Anorg. Allg. Chem.* **2009**, *635*, 253.

[15] J. Kouvetakis, A. Haaland, D. J. Shorokhov, H. V. Volden, G. V. Girichev, V. I. Solokov, P. Matsunaga, *J. Am. Chem. Soc.* **1998**, *120*, 6738.

[16] A few examples of N-heterocyclic carbene adducts of germanium dihalides are known: a) A. J. Arduengo III, H. V. R. Dias, C. Calabrese, F. Davidson, *Inorg. Chem.* **1993**, *32*, 1541; b) P. A. Rupar, V. N. Stavorevov, P. J. Ragogna, K. M. Baines, *J. Am. Chem. Soc.* **2007**, *129*, 15138; c) P. A. Rupar, M. C. Jennings, K. M. Baines, *Organometallics* **2008**, *27*, 5043.

[17] K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11353: LiC_6H_3-2,6-Mes_2 is composed of dimers in the solid-state. The monomeric formula was used in the text for simplicity reasons.

[18] L. Pu, M. Olmstead, P. P. Power, B. Schiemenz, *Organometallics* **1998**, *17*, 5602.

[19] The bonding parameters of **3b** and **3b**·0.5 benzene are almost identical. Therefore, only the bonding parameters of **3b** are presented and discussed in the text.

[20] K. Aarset, A. G. Császár, E. L. Sibert III, W. D. Allen, H. F. Schaefer III, W. Klopper, J. Noga, *J. Chem. Phys.* **2000**, *112*, 4053, and references therein.

[21] Q.-S. Li, R.-H. Lü, Y. Xie, H. F. Schaefer III, *J. Comput. Chem.* **2002**, *23*, 1642, and references therein.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[22] According to a CSD survey of arylchlorosilanes, the mean length of a Si–C(sp^2) single bond is 1.87 Å, and that of a Si–Cl bond 2.09 Å.
[23] The unweighted mean values x_u of the Si–Cl bond lengths of $SiCl_2$(Idipp) and Si(C_6H_3-2,6-$Trip_2$)Cl_3 are given. The standard deviation σ (value in parentheses) was calculated by using the equation $\sigma^2 = \Sigma(x_i - x_u)^2/n^2 - n$, where x_i is the individual value and n is equal two for $SiCl_2$(Idipp) and three for Si(C_6H_3-2,6-Mes_2)Cl_3.
[24] a) J. G. Winter, P. Portius, G. Kociok-Köhn, R. Steck, A. C. Filippou, *Organometallics* **1998**, *17*, 4176, and references therein.
[25] The mean Ge–C_{Ar} and Ge–Cl bond lengths are given, which were obtained from a CSD survey of four-coordinate arylchlorogermanes.
[26] The inversion barriers of silyl anions depend strongly on the substituents; π-donor and σ-acceptor substituents increase the barrier, whereas π-acceptor substituents lower the barrier: a) J. B. Lambert, M. Urdaneta-Pérez, *J. Am. Chem. Soc.* **1978**, *100*, 157; b) R. A. Eades, D. A. Dixon, *J. Chem. Phys.* **1980**, *72*, 3309; c) A. C. Hopkinson, M. H. Lien, *Tetrahedron* **1981**, *37*, 1105; d) J. R. Damewood, Jr., C. M. Hadad, *J. Phys. Chem.* **1988**, *92*, 33; e) B. Goldfuss, P. v. R. Schleyer, *Organometallics* **1997**, *16*, 1543; f) M. Flock, C. Marschner, *Chem. Eur. J.* **2002**, *8*, 1024.
[27] Ge(C_6H_3-2,6-$Trip_2$)HCl_2 was obtained selectively from **6b-Ge** and HCl and fully characterized: N. Weidemann, Dissertation, Humboldt-Universität zu Berlin (Berlin), Cuviller, Göttingen, **2008**.
[28] a) G. C. Levy, D. M. White, J. D. Cargioli, *J. Magn. Reson. (1969–1992)* **1972**, *8*, 280; b) A. G. Brook, F. Abdesaken, G. Gutekunst, N. Plavac, *Organometallics* **1982**, *1*, 994.
[29] NBO 5.0 Program, E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**.
[30] The Supporting Information contains additional calculated and experimental bonding parameters of **2**, **3b**, **6b-Si**, **6b-Ge**, and **7b**, the illustrations and the Cartesian atomic coordinates of the calculated structures.
[31] In the leading resonance structure the Ge–Cl bond was found to be ionic with an almost empty acceptor NBO residing on the Ge atom (occupation: 0.38e; hybridization $sp^{34.82}$).
[32] The negative charge on the ECl(C_6H_3-2,6-$Trip_2$) fragment in **3b** and **7b** (−0.33 and −0.34, respectively) indicates that the polarity of the E–$C_{carbene}$ bond in **3b** and **7b** is reversed relative to that of the E–C multiple bonds of silenes and germenes ($R_2E{=}CR_2$): a) J. Escudié, C. Couret, H. Ranaivonjatovo, *Coord. Chem. Rev.* **1998**, *178–180*, 565; b) H. Ottosson, A. M. Eklöf, *Coord. Chem. Rev.* **2008**, *252*, 1287.
[33] NMR spectroscopic data of **1a**: ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ = 2.08 (s, 12H; 2×C^{2,6}-*Me*, Mes), 2.15 (s, 6H; 2×C^4-*Me*, Mes), 5.33 (s, $^1J(^1H,^{29}Si)$ = 299 Hz, 1H; Si-*H*), 6.82 (s, 4H; 2×C^{3,5}-*H*, Mes), 6.84 (d, $^3J(H,H)$ = 7.5 Hz, 2H; C^{3,5}-*H*, C_6H_3), 7.18 ppm (t, $^3J(H,H)$ = 7.5 Hz, 1H; C^4-*H*, C_6H_3); ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ = 21.16 (s, 2×C^4-*Me*, Mes)**, 21.20 (s, 2×C^{2,6}-*Me*, Mes), 128.5 (s, 2×$C^{3,5}$-H, Mes), 128.8 (s, Si-C^1, C_6H_3)**, 129.3 (s, $C^{3,5}$-H, C_6H_3)*, 132.9 (s, C^4-H, C_6H_3)*, 136.4 (s, 2×$C^{2,6}$, Mes)*, 137.71 (s, 2×C^1, Mes)*, 137.76 (s, 2×C^4, Mes)*, 149.6 ppm (s, $C^{2,6}$, C_6H_3)**; ^{29}Si{^{1}H} NMR (C_6D_6, 59.63 MHz, 298 K): δ = −8.8 ppm (s, $^1J(^{29}Si,^{13}C)$ = 96.8 Hz). The ^{13}C NMR signals marked with an asterisk were incorrectly assigned in reference [14a]. The signals marked with a double asterisk were either missing or had an incorrect chemical shift in reference [14a].
[34] NMR spectroscopic data of **1b**: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K): δ = 1.08 (d, $^3J(H,H)$ = 6.9 Hz, 12H; 2×C^{2,6}-CHMe_AMe$_B$, Trip), 1.25* (d, $^3J(H,H)$ = 6.9 Hz, 12H; 2×C^4-CHMe_2, Trip), 1.37* (d, $^3J(H,H)$ = 6.9 Hz, 12H; 2×C^{2,6}-CHMe$_A$$Me_B$, Trip), 2.85 (sept, $^3J(H,H)$ = 6.9 Hz, 6H; 2×C^{2,6}-C*H*Me$_A$Me$_B$ + 2×C^4-C*H*Me$_2$, Trip), 5.39 (s, $^1J(^1H,^{29}Si)$ = 300.4 Hz, 1H; Si-*H*), 7.10–7.18 (m, 3H; C^{3,5}-*H* + C^4-*H*, C_6H_3), 7.20 ppm (s, 4H; 2×C^{3,5}-*H*, Trip); ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ = 22.6 (s, 2×C^{2,6}-CHMe$_A$$Me_B$, Trip), 24.2 (s, 2×C^4-CHMe_2, Trip), 25.9 (s, 2×C^{2,6}-CHMe_AMe$_B$, Trip), 31.2 (s, 2×C^{2,6}-*C*HMe$_A$Me$_B$, Trip), 34.7 (s, 2×C^4-*C*HMe$_2$, Trip), 120.8 (s, 2×$C^{3,5}$-H, Trip), 130.3 (s, Si-C^1, C_6H_3),** 130.5 (s, C^4-H, C_6H_3), 130.7 (s, $C^{3,5}$-H, C_6H_3), 135.7* (s, 2×C^1, Trip), 147.1 (s, 2×$C^{2,6}$, Trip), 148.2 (s, $C^{2,6}$, C_6H_3),* 149.6 ppm (s, 2×C^4, Trip)*. The NMR signals marked with an asterisk were incorrectly assigned in reference [14a]. The signal marked with a double asterisk was missing in reference [14a].
[35] The Supporting Information of the following references contains corrected ^{1}H and ^{13}C NMR spectroscopic data of LiC_6H_3-2,6-Mes_2 and GeCl(C_6H_3-2,6-$Trip_2$) (**6b-Ge**): a) reference [14b]; b) A. C. Filippou, N. Weidemann, A. I. Philippopoulos, G. Schnakenburg, *Angew. Chem.* **2006**, *118*, 6133; *Angew. Chem. Int. Ed.* **2006**, *45*, 5987.
[36] NMR spectroscopic data for **4**: ^{1}H NMR (CD_2Cl_2, 300.1 MHz, 298 K): δ = 2.19 (s, 6H; C^{4,5}-*Me*), 3.86 (s, 6H; 2×N*Me*), 10.80 ppm (s, 1H; C^2-*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.47 MHz, 298 K): δ = 8.4 (s, C^{4,5}-*Me*), 33.9 (s, 2×N-*Me*), 126.9 (s, $C^{4,5}$), 137.9 ppm (s, C^2); ^{1}H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ = 2.17 (s, 6H; C^{4,5}-*Me*), 3.82 (s, 6H; 2×N*Me*), 10.46 ppm (s, 1H, C^2-*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz, 298 K): δ = 8.3 (s, C^{4,5}-*Me*), 33.6 (s, 2×N-*Me*), 126.6 (s, $C^{4,5}$), 136.9 ppm (s, C^2).
[37] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33.
[38] SHELXS97 and SHELXL97, G. M. Sheldrick, University of Göttingen, Göttingen, **1997**.
[39] DIAMOND 2.1c, K. Brandenburg, Crystal Impact GbR, Bonn, **1999**.
[40] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
[41] a) A. D. Becke , *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[42] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.
[43] P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213.
[44] E. van Lenthe, E. J. Baerends, *J. Comput. Chem.* **2003**, *24*, 1142.
[45] Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople,Gaussian, Inc., Pittsburgh, PA, **2003**.
[46] ADF2007.01, SCM, E. J. Baerends, J. Autschbach, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, F. E. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, G. van Kessel, F. Kootstra, E. van Lenthe, D. A. McCormack, A. Michalak, J. Neugebauer, V. P. Nicu, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev, T. Ziegler, Theoretical Chemistry, Vrije Universiteit, Amsterdam, **2007**.

Received: November 2, 2009
Published online: January 14, 2010

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim