Diazomethane Derivatives Bearing Dialkylaluminium or Dialkylgallium Substituents – The Isomeric Diazomethane and Nitrile Imine Structures Realized by the Different Coordination Behavior of Aluminium and Gallium

Werner Uhl,*[a] Frank Hannemann,[a] Wolfgang Saak,[a] and Rudolf Wartchow[b]

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Lithium trimethylsilyldiazomethanide $Li(SiMe_3)CN_2$ reacted with the dialkylaluminium or -gallium halides R_2AlCl and R_2GaBr [$R = CH(SiMe_3)_2$] by the elimination of lithium halide and the formation of the corresponding aluminium or gallium diazo compounds. As shown by a crystal structure determination, the gallium derivative **1** adopts the nitrile imine structure, in which the gallium atom is coordinated by the terminal nitrogen atom of the diazo group. The N–N–C–Si moiety is almost ideally linear with N–N and C–N bond lengths of 125.5 and 115.9 pm on average. In contrast, the diazomethane structure was formed with dialkylaluminium chloride, and the aluminium atom in **2** is attached to the carbon atom of diazomethane. The almost linear N–N–C group (174.1°) has N–N and N–C distances of 120.0 and 126.4 pm, respectively, inverse to that of the gallium derivative. The bonding situations can best be described by the resonance structures $R–C≡N^+–N^-–GaR_2$ for **1** and $R_2Al–(R)C=N^+=N^-$ for **2**. The nitrile imine isomer of the aluminium compound could be detected by NMR spectroscopy as a by-product. Both compounds gave dimers in the solid state, a Ga_2N_2 four-membered heterocycle was formed of **1**, while an eight-membered $Al_2C_2N_4$ heterocycle resulted with **2**.

Diazomethane and its derivatives form a group of fascinating compounds due to their bonding situation and their singular chemical reactivity.[1] In many cases, they are used as a facile source of carbenes and for the synthesis of carbon−nitrogen heterocycles. As shown for the first time in 1933,[2] the methylene hydrogen atoms of diazomethane can be replaced by alkali metals, and those metalated diazomethane derivatives are very useful reagents for the syntheses of numerous diazomethane compounds containing main-group or transition-metal elements.[3−8] The lithiated compounds $Li−(H)CN_2$ and $Li−(Me_3Si)CN_2$ were theoretically investigated by the group of Boche.[8] By intramolecular rearrangements four isomeric structures are possible: $Li−(H)C=N^+=N^-$ (diazomethane), $C^-≡N^+−N(Li)H$ (*N*-isocyanoamine), $Li−C≡N^+−N^-−H$ and $H−C≡N^+−N^-−Li$ (nitrile imine), of which the second one was found to give the global minimum. The diazomethane formulation was intermediate, and both nitrile imine isomers were highest in energy. The energies of dimers were also calculated, and some aspects of their structures will be discussed below. Lithiated trimethylsilyldiazomethane was observed as a part of a complicated crystal structure by the same group.[8] Remarkably, it adopted the nitrile imine structure with the silyl group bound to the carbon atom and the lithium atom bound to the terminal nitrogen atom. The influence of the silyl group on the energy of the isomers could also be verified by theoretical calculations.[8] Previously, only one diazomethane compound of an element of the third main group was reported in literature, which has a tetracoordinated boron atom bound to the carbon atom of the CN_2 group.[6] The nitrile imine structure was found in two aluminium derivatives,[9] which have a phosphanyl group attached to the carbon atom and the terminal nitrogen atom coordinated by two alkylaluminium groups. We became interested in aluminium, gallium, or indium diazomethane derivatives for two reasons: (i) The nitrile imine molecular center is isosteric to an azido group. We recently succeeded in isolating a dialkylaluminium azide sterically highly shielded by bulky substituents, which formed a trimer with the unexpected head-to-tail coordination of the azido groups and a twelve-membered Al_3N_9 heterocycle.[10] Thus, we supposed that an unusual coordination behavior may be observed with the diazomethane derivatives, too. (ii) We hoped to use the reactivity of the diazomethane derivatives for the synthesis of novel organoaluminium or -gallium compounds. For instance, silylated diazomethane compounds inserted into the Al−Al bond of tetrakis[bis(trimethylsilyl)methyl]dialan(4), while a fragmentation reaction was observed with the corresponding gallium derivative.[11]

Reaction of Lithium Trimethylsilylmethyldiazomethanide with R_2AlCl and R_2GaBr [$R = CH(SiMe_3)_2$]

The reactive intermediate $Li−(Me_3Si)CN_2$ was obtained according to a literature procedure[3] by treating trimethylsilyldiazomethane with *n*-butyllithium at −100°C. The alkylgallium and -aluminium halides were added at this temperature, and the reaction mixtures were warmed slowly

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[a] Fachbereich Chemie der Universität,
Postfach 2503, D-26111 Oldenburg, Germany
Fax: (internat.) + 49(0)441/798-3352
[b] Institut für Anorganische Chemie der Universität,
Callinstraße 9, D-30167 Hannover, Germany
Fax: (internat.) + 49(0)511/762-3006

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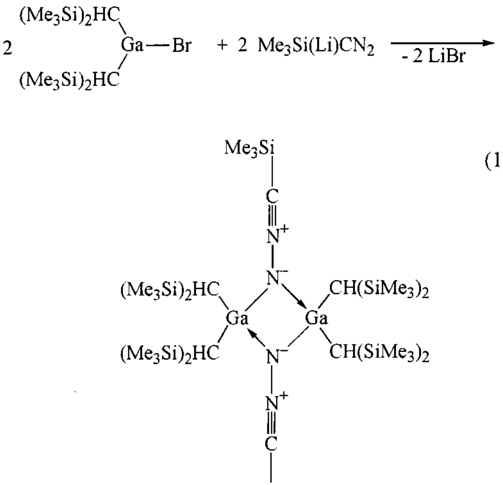
to room temperature. Dialkylgallium bromide gave a mixture of compounds, from which the diazomethane product **1** was isolated in a yield of 38% (Equation 1). Compound **1** was identified by elemental analysis and a crystal structure determination (see below) as the nitrile imine isomer of diazomethane, in which the alkylgallium group is attached to the terminal nitrogen atom. The main component of the mother liquor was identified by NMR spectroscopy as the trialkylgallium derivative $Ga[CH(SiMe_3)_2]_3$,[12] which due to its high solubility in organic solvents could, however, not be isolated in a pure form. Three resonances were observed in the ^{1}H-NMR spectrum of **1**, which could be assigned to the methyl protons of the bis(trimethylsilyl)methyl groups, the protons of the $SiMe_3$ groups of diazomethane and the methine protons. The latter have a chemical shift of $\delta = -0.22$, which is just intermediate between the characteristic ranges of bis(trimethylsilyl)methyl compounds with coordination numbers of three and four at the central gallium atoms.[13−15] The IR spectrum showed an intensive absorption at 2120 cm^{-1}, which was attributed to the stretching vibration of the C−N group with a high π-bond order.[16] The molar mass of **1** cryoscopically determined in benzene is intermediate between those calculated of the monomer and the dimer, thus an equilibrium may exist between the monomeric and dimeric formula units, which is shifted in dilute solutions to the monomer.

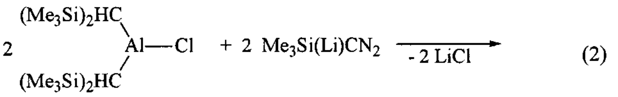


(1)

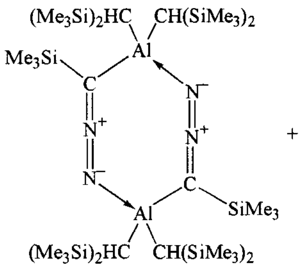
1

The reaction with dialkylaluminium chloride was different from that of the gallium analogue. Two compounds were formed. Only one could be isolated by recrystallization in a pure form (**2**): The second one (**3**) could be enriched by repeated recrystallization to a maximum concentration of only 70% besides **2** (Equation 2). The impure compound **3** crystallizes as colorless needles similar to **1** and has the resonances of the trimethylsilyl group attached to the carbon atom of diazomethane in the ^{1}H- and ^{13}C-NMR spectra at $\delta = 0.11$ and -0.8, respectively, which is similar to the chemical shifts observed for the corresponding group in **1**. In addition, two singlets are observed in each spectrum for the methine and methyl protons of the bis(trimethylsilyl)methyl group. Due to these strong similarities, we assume that compound **3** is the aluminium analogue of the gallium derivative **1** with the nitrile imine structure. Compound **2** was characterized by a crystal structure determination and has another constitution derived from the diazomethane isomer with the aluminium atom bound to the carbon atom of the CN_2 group. The compound is a dimer in the solid state (see below) and in solution, as shown by the cryoscopic determination of its molar mass in benzene. Due to the coordination of the central aluminium atom by two $CH(SiMe_3)_2$ groups and one carbon and one nitrogen atom of the diazomethane fragment, the trimethylsilyl groups become diastereotopic and, in contrast to **1** and **3**, give two resonances in the ^{1}H- and ^{13}C-NMR spectra. The protons of the N_2CSiMe_3 group shows a resonance at $\delta = 0.32$. It is shifted to lower field than the corresponding signals of **1** and **3**, which are part of the linear $Me_3Si{-}C{\equiv}N^+{-}N^-$ moieties. In the IR spectrum of **2**, three absorptions are observed between 2135 and 2220 cm^{-1}, which can be assigned to the stretching vibrations of both C=N=N groups of the heterocycle.[16] Remarkably, the ratio between both aluminium compounds in the mixture remains constant in solution, and no rearrangement by the 1,3 shift of the dialkylaluminium group to form a thermodynamically more favored product was observed even in hot benzene. Thus, the formation of the mixture may not be caused by the migration of alkylaluminium groups in any stage of the reaction, but may reflect the distribution of the lithiated diazomethane species in their complicated equilibrium in solution. With gallium, only the nitrile imine isomer was isolated in a low yield of 38%, and we observed the formation of the corresponding trialkylgallium derivative besides some further minor by-products. A diazomethane isomer similar to compound **2** could not be detected. This isomer may be formed as an intermediate, but possibly it is not stabilized by the formation of a strong dimer due to the lower Lewis acidity of gallium than of aluminium and decomposes by the release of nitrogen, for instance. A following redistribution reaction may yield GaR_3 as the main product. The lower stability of the gallium compounds due to the formation of only weak dimers is in agreement with the partial dissociation of **1** in benzene and its low decomposition point as discussed below.

Both products **1** and **2** were heated and irradiated with UV light, in order to investigate their stability and to prove their ability to lose nitrogen and to form carbene intermediates. Solutions in benzene can be stored at 60°C for many hours without any detectable secondary reaction. The crystals of compound **1** completely decomposed at temperatures as low as 117°C by the formation of a gaseous product, while the aluminium compound **2** was more stable and did not decompose below 200°C. But in each case the thermal decomposition yielded mixtures of many unknown products, from which none could be isolated in a pure form. A similar result was obtained upon irradiation of solutions with UV light, which led to the formation of oily residues with many unknown products.



$$2\,[(Me_3Si)_2HC]_2Al{-}Cl + 2\,Me_3Si(Li)CN_2 \xrightarrow[-2\,LiCl]{} \quad (2)$$



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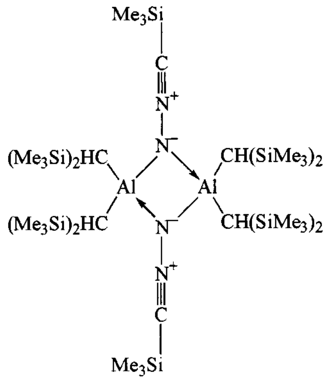

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Crystal Structures of 1 and 2

The molecular structure of compound **1** is depicted in Figure 1. The ligand derived from the starting diazomethane compound adopts the almost linear nitrile imine form, and with their terminal nitrogen atoms two of these ligands bridge two dialkylgallium fragments to yield a dimer with a Ga_2N_2 heterocycle. The geminal coordination of the terminal nitrogen atoms by two gallium atoms is similar to the situation in trimeric diisobutylaluminium nitrile imide[9] or to the structures of dialkylaluminium and -gallium azides,[17] which were derived from their IR-spectroscopic characterization. Further examples of a geminal bridging by azido groups could be verified by crystal structure determinations.[17] A different coordination was, however, found for the sterically highly shielded trimer of $[(Me_3Si)_2CH]_2AlN_3$, for which a 1,3 coordination of the azido group by the formation of a twelve-membered heterocycle was observed.[10] This unusual structure may be caused by the electrostatic repulsion between the positively charged aluminium atoms and a steric interaction between the bulky substituents. The electrostatic repulsion should be lower in the case of the more electronegative gallium. The formation of dimers with Al_2N_2 or Ga_2N_2 heterocycles comparable to compound **1** has not been observed before for this type of ambident ligands.

The angles N−N−C and N−C−Si in both independent molecules of **1** are on average 178.7° and 176.5°, respectively. The C−Si bonds to the terminal trimethylsilyl group of the ligand (184.5 pm on average) are not shorter than the expected value. The C−N bond lengths (115.9 pm) correspond to a normal C≡N triple bond[18], and the N−N bonds (125.5 pm on average) are a little longer than typical N=N double bonds,[19] which may indicate some π character of the bond or an electrostatic contribution to the N−N bond strength. These results are in excellent agreement with the theoretically obtained parameters of 114.6 and 127.8 pm for hydrogen-substituted nitrile imine or 114.6 and 121.4 pm for dimeric LiN_2CH with a central Li_2N_2 heterocycle.[8] They impressively confirm the formulation of compound **1** as a nitrile imine derivative with a main contribution of the resonance structure $R{-}C{\equiv}N^+{-}N^-{-}GaR_2$, which gives a dimer by the interaction of a lone electron pair at the negatively charged nitrogen atom with a second gallium atom. The nitrogen atoms in the heterocycles have almost ideally planar surroundings, and the sum of the bond angles are between 358.6° and 360.0°. The heterocycles are slightly folded, and the angles between the normals of the planes GaN_2 are 12.3 and 12.1°. Similar to other compounds with a four-membered heterocycle like $R_4Ga_2(\mu\text{-}OH)_2$[14] or a $R_4Ga_2(\mu\text{-}F)_2$,[15] the most acute angles in the ring are observed at the gallium atoms (76.3°); the inner ring angles at the nitrogen atoms are 102.9°.

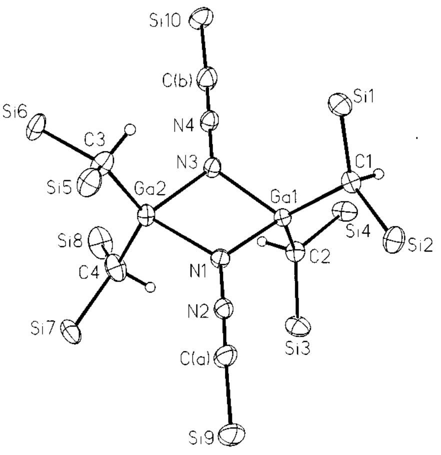

Figure 1. Molecular structure and numbering scheme of compound **1**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; only one of both independent molecules is shown; selected bond lengths [pm] and angles [°] (values of the second molecule in square brackets): Ga1−N1 200.7(3) [200.3(3)], Ga1−N3 202.5(3) [203.0(3)], Ga1−C1 200.5(4) [201.3(4)], Ga1−C2 202.2(4) [199.7(4)], Ga2−N1 202.9(3) [202.2(3)], Ga2−N3 202.6(3) [201.3(3)], Ga2−C3 200.0(4) [201.2(4)], Ga2−C4 201.9(4) [201.6(4)], N1−N2 126.0(4) [125.8(4)], N2−C(a) 115.3(5) [114.8(5)], N3−N4 124.2(4) [125.9(5)], N4−C(b) 117.2(5) [116.3(6)], C(a)−Si9 185.0(4) [185.7(4)], C(b)−Si10 183.5(4) [183.8(5)]; Ga1−N1−Ga2 103.0(1) [103.3(1)], Ga1−N3−Ga2 102.5(1) [102.7(1)], N1−Ga1−N3 76.7(1) [76.2(1)], N1−Ga2−N3 76.2(1) [76.2(1)], Ga1−N1−N2 128.5(3) [128.4(2)], Ga1−N3−N4 129.4(3) [126.4(3)], Ga2−N1−N2 127.1(2) [127.0(2)], Ga2−N3−N4 128.1(3) [129.5(3)], N1−N2−C(a) 178.4(4) [178.6(4)], N3−N4−C(b) 179.5(4) [178.3(4)], N2−C(a)−Si9 176.9(4) [175.8(4)], N4−C(b)−Si10 174.9(4) [178.4(5)]

The nitrile imine structure has been observed before in the complicated lithium compound $(LiN_2CSiMe_3)_6$-$[LiC_2N_3(SiMe_3)_2]_2(Et_2O)_7$[8] and in two aluminium compounds, $(R_2PCN_2Al\textit{i}Bu_2)_3$ and $[R_2PCN_2(AlCl\textit{t}Bu_2)_2]^-$ ($R = NMe_2$).[9] While the nitrile imine fragments of the aluminium compounds have structural parameters similar to **1**, the C−N and N−N bonds are almost equally long in the lithium derivative. Furthermore, few nitrile imine derivatives of non-metals are known.[20] Their bond lengths and angles (C−N 117.2 pm and N−N 125.6 pm on average) resemble those observed for compound **1**. But their $X{-}CN_2$ groups with X the central atom of the terminal ligand deviate more significantly from linearity and show angles X−C−N between 137.3 and 165.1°.

Although compound **2** (Figure 2) also forms dimers in the solid state, a completely different structure is found, which is not derived from the nitrile imine, but from the diazomethane skeleton. The aluminium atom is bound to the diazomethane carbon atom, and an eight-membered centrosymmetric $Al_2C_2N_4$ heterocycle is formed by the interaction of the terminal diazomethane nitrogen atom with the aluminium atom of a second molecule. The Al−C bonds (Al−C3) within the ring have a length of 196.1(4) pm, which is in the range usually observed. The diazomethane group is almost linear with an angle C−N−N of 174.1°. The ratio of the C−N and N−N bond lengths in this group is inverted relative to those of **1**. The N−N bond is shorter than in **1** [120.0(6) pm] corresponding to an N=N double bond[19] and the C−N bond is longer [126.4(5) pm] indicating the formation of a C=N double bond.[18] Thus, the bonding in this part of the molecule is best described by the resonance structure $R_2Al-(R)C=N^+=N^-$. Usually, diazomethane[21] and its *C*-metalated, monomeric derivatives[5−7] show larger differences between their C−N and N−N bond lengths with longer C−N distances and very short N−N bonds, which are in the characteristic range of N≡N triple bonds. The exocyclic bond Si5−C3 [177.2(4) pm] is much shortened relative to the corresponding Si−C bond in compound **1** (184.5 pm), which may indicate some additional hyperconjugative interaction between the trimethylsilyl group and the carbon atom. The terminal nitrogen atom of the diazomethane group is coordinated to the aluminium atom of a second fragment with a long[22] Al−N distance of 208.4(6) pm. The angle Al−N1−N2 approaches linearity with 158.9°. All Al−C distances are, however, in the expected range. The eight-membered heterocycle is almost planar, and the largest deviation of an atom from the mean plane is observed for N2 with only 6.5 pm.

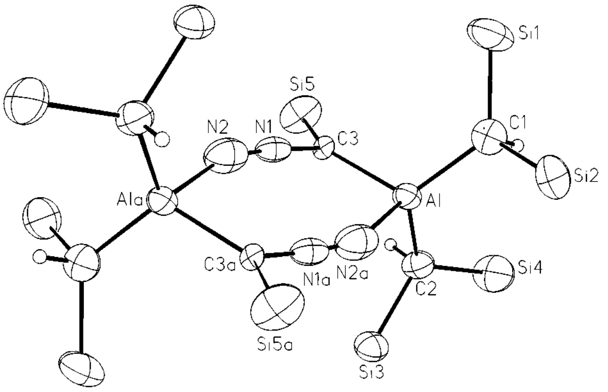

Figure 2. Molecular structure and numbering scheme of compound **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; selected bond lengths [pm] and angles [°]: Al−C3 196.1(4), Al−N2*a* 208.4(6), Al−C1 197.4(8) and 203.5(6) (disordered), Al−C2 198.8(5), C3−Si5 177.2(4), C3−N1 126.4(5), N1−N2 120.0(6); C3−Al−N2*a* 92.0(2), Al−C3−Si5 133.5(2), Al−C3−N1 113.7(3), N1−C3−Si5 112.2(3), C3−N1−N2 174.1(4), N1−N2−Al*a* 158.9(4); the atoms labeled *a* are generated by $-x + 2$, $-y$, $-z + 2$

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (diisopropyl ether from Na/benzophenone, *n*-hexane and cyclopentane with $LiAlH_4$, pentafluorobenzene over molecular sieve). Bis[bis(trimethylsilyl)methyl]gallium bromide was synthesized as described in ref.[23] The corresponding aluminium chloride was obtained according to ref.[24] Commercially available solutions of trimethylsilyldiazomethane and *n*-butyllithium in *n*-hexane were used without further purification.

Synthesis of the Gallium Diazomethane Derivative 1: 0.9 mL (1.79 mmol) of a 2 M solution of trimethylsilyldiazomethane in hexane was diluted with 10 mL of hexane and cooled to −100°C. A cooled (−60°C) mixture of 1.12 mL (1.79 mmol) of a 1.6 M solution of *n*-butyllithium in hexane and 10 mL of the same solvent was added over a period of 10 min. After stirring for 15 min at −100°C, the lithium trimethylsilyldiazomethanide intermediate was treated with a cooled (−50 to −60°C) solution of 0.837 g (1.79 mmol) of $[(Me_3Si)_2CH]_2GaBr$ in 25 mL of hexane over a period of 20 min. The mixture was slowly warmed to room temperature and filtered. The solvent was removed in vacuo, and the residue was recrystallized twice from diisopropyl ether (20/−50°C). Yield 0.341 g (38%), colorless needles, which usually include small quantities of diisopropyl ether (less than 0.2 mol each monomeric formula unit of **1**), m.p. (argon, sealed capillary): 117°C (dec). − ^1H NMR (C_6D_6, 300 MHz): $\delta = 0.39$ [36 H, $SiMe_3$ of $CH(SiMe_3)_2$], 0.15 (9 H, $SiMe_3$ of diazomethane), −0.22 (2 H, $GaCHSi_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 9.6$ ($GaCSi_2$), 5.3 [$SiMe_3$ of $CH(SiMe_3)_2$], −0.3 ($SiMe_3$ of diazomethane); the carbon atom signal of the CN_2 group was not detected. − IR (CsBr, paraffin): $\tilde{\nu} = 2120$ vs cm^{-1} νCN; 1464 vs, 1377 vs paraffin; 1335 vs, 1285 vs, 1248 vs δCH_3; 1169 vw, 1157 w, 1127 w, 1111 w diisopropyl ether; 1017 vs δCH; 963 m, 843 vs, 775 s, 758 s, 725 m $\rho CH_3(Si)$; 671 s $\nu_{as}SiC$; 631 s ν_sSiC; 519 m, 478 vs, 405 m νGaC, νGaN; 347 vw δSiC. − $C_{18}H_{47}GaN_2Si_5$ (501.7 of the monomer): calcd. Ga 13.9, found Ga 14.1. − Mol. mass: 650 (cryoscopically in benzene).

Synthesis of the Aluminium Diazomethane Derivative 2: A cooled (−60 to −70°C) solution of *n*-butyllithium (2.07 mL, 1.6 M, 3.31 mmol) in hexane, diluted with 20 mL of same solvent, was added to a cooled (−100°C) mixture of 20 mL of hexane and 1.66 mL of a solution (2 M) of trimethylsilyldiazomethane in hexane (3.31 mmol) over a period of 40 min. The mixture was stirred at −100°C and treated with a cooled (−40 to −50°C) solution of 1.26 g (3.31 mmol) of $[(Me_3Si)_2CH]_2AlCl$ in 70 mL of hexane. The mixture was slowly warmed to room temperature and filtered. The solvent was removed in vacuo, and the residue was recrystallized from hexane (20/0°C) to isolate colorless crystals of compound **2**. Further fractions contain mixtures of **2** and the by-product **3**, which could not completely be separated even after repeated recrystallization. Yield: 0.32 g (21%). − M. p. (argon, sealed capillary): 200−204°C (dec.). − ^1H NMR (C_6D_6, 300 MHz): $\delta = 0.36$ and 0.35 [each 36 H, $SiMe_3$ of $CH(SiMe_3)_2$], 0.32 (18 H, $SiMe_3$ of diazomethane), −0.90 (4 H, $AlCHSi_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 98.0$ (C=N), 5.45 and 5.38 [$SiMe_3$ of $CH(SiMe_3)_2$], 3.0 ($AlCSi_2$), 0.7 ($SiMe_3$ of diazomethane). − IR (CsBr, paraffin): $\tilde{\nu} = 2220$ m cm^{-1}, 2184 m, 2135 s νCNN; 1462 vs, 1377 vs paraffin; 1248 vs δCH_3; 1109 m, 1086 m; 1007 vs δCH; 959 w, 937 m, 843 vs, 775 s, 750 s, 727 s $\rho CH_3(Si)$; 671 s $\nu_{as}SiC$; 638 w, 629 m, 613 w ν_sSiC; 505 s, 484 s, 455 s, 442 s νAlC, νAlN; 392 w, 382 w, 374 w, 361 w, 343 vw, 320 w δSiC. − $C_{36}H_{94}Al_2N_4Si_{10}$ (918.0): calcd. Al 5.9, found Al 5.9. − Mol. mass: 865 (cryoscopically in benzene).

Table 1. Crystal data, data-collection parameters and structure refinement for **1** and **2**[a]

	1	**2**
Formula	$C_{42}H_{95}F_5Ga_2N_4Si_{10}$	$C_{18}H_{47}AlN_2Si_5$
Crystal system	triclinic	monoclinic
Space group	$P-1$[25]	$P2_1/n$[25]
Z	4	4
T [K]	213(2)	300(2)
$d_{\mathrm{calcd.}}$ [g/cm^3]	1.191	1.009
a [pm]	1507.1(1)	1156.8(1)
b [pm]	2260.6(2)	2151.3(2)
c [pm]	2305.1(1)	1235.2(1)
α [°]	116.272(8)	90
β [°]	105.664(8)	100.67(2)
γ [°]	96.402(8)	90
V [10^{-30} m^3]	6533.2(8)	3020.8(5)
μ [mm^{-1}]	0.994[b]	0.272
Crystal size [mm]	0.45 × 0.50 × 0.53	0.72 × 0.76 × 0.34
Diffractometer	Stoe-IPDS	
Radiation	Mo-K_{α}; graphite monochromator	
2Θ range [°]	$4.0 \le 2\Theta \le 52.1$	$4.0 \le 2\Theta \le 48.0$
Scan mode (number of exposures; $\Delta\varphi$)	267; 1.2°	180; 1.0°
Index ranges	$-18 \le h \le 18$ $-27 \le k \le 27$ $-28 \le l \le 28$	$-12 \le h \le 13$ $-24 \le k \le 24$ $-14 \le l \le 14$
Independent reflections	23924	4691
Reflections $F > 4\ \sigma(F)$	16842	3041
Parameters	1178	240
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$; [$F > 4\ \sigma(F)$][b]	0.045	0.071
$wR2 = \{\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$ (all data)	0.169	0.141
Max./min. residual electron density [10^{30} e/m^3]	1.06[c]/−0.75	0.61

[a]Programs: SHELXTL, SHELXL-93;[26] solutions by direct methods; full-matrix refinement with all independent structure factors. − [b]Numerical absorption correction. − [c]Near the solvent molecules.

NMR Characterization of 3: ^{1}H NMR (C_6D_6, 300 MHz, mixture with **2**): δ = 0.40 [72 H, $SiMe_3$ of $CH(SiMe_3)_2$], 0.11 ($SiMe_3$ of diazomethane), −0.73 (4 H, $AlCHSi_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 5.7 [$SiMe_3$ of $CH(SiMe_3)_2$], 4.9 ($AlCHSi_2$), −0.8 ($SiMe_3$ of diazomethane); the carbon atom signal of the diazomethane component could not be detected.

Crystal Structure Determinations: Single crystals of the compounds **1** and **2** were obtained by recrystallization from a mixture of pentafluorobenzene and cyclopentane (**1**) and from *n*-hexane (**2**). Crystal data and structure refinement parameters are given in Table 1.[27] The crystals of **1** include one molecule of pentafluorobenzene per formula unit. Two independent molecules were observed in the asymmetric unit, which have similar bond lengths and angles, but differ in the orientation of the bis(trimethylsilyl)methyl groups. Two trimethylsilyl groups (Si6 and Si7) showed a disorder, their atoms were isotropically refined by restrictions of bond lengths and angles with occupation factors of 0.75 and 0.25. The heterocycle of **2** is located on a crystallographic inversion center. One bis(trimethylsilyl)methyl group showed a disorder caused by different orientations of the methine C−H bond with a partial overlap of the atoms (Si1 and C11). All other atoms (C1, C12, C13) were isotropically refined with restrictions of bond lengths and angles using occupation factors of 0.52 and 0.48.

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[27] The crystallographic data of **1** and **2** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103107 (**1**) and -103108 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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