The Reaction of Diazomethane Derivatives with the Dielement Compounds R$_2$Al–AlR$_2$ and R$_2$Ga–GaR$_2$ [R = CH(SiMe$_3$)$_2$] – Insertion versus Fragmentation

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Tetrakis[bis(trimethylsilyl)methyl]dialane(4) **1** reacted with trimethylsilyldiazomethane and bis(trimethylsilyl)diazomethane at room temperature by the insertion of the terminal nitrogen atoms into its aluminium–aluminium bond. As shown by a crystal structure determination, one of the aluminium atoms of each product enhanced its coordination number to four by the interaction with the central nitrogen atom of the C=N–N group, which results in the formation of a three-membered AlN$_2$ heterocycle bearing an exocyclic N=C double bond. The reactions of the corresponding gallium compound (**2**) containing a gallium–gallium single bond needed more drastic conditions. Mixtures of many unknown products were formed, and only on treatment with

trimethylsilyldiazomethane two compounds could be isolated after repeated recrystallization in yields below 10%, which were characterized by crystal structure determinations. One was identified as the trimeric dialkylgallium cyanide (**8**) with a nine-membered Ga$_3$C$_3$N$_3$ heterocycle, and the other one (**9**) has a dialkylgallium fragment coordinated by both terminal nitrogen atoms of the chelating ligand NH$_2$–N=C(SiMe$_3$)–NH$^-$. Due to the NMR spectroscopic characterization, **8** seems to be tetrameric in solution with an asymmetric structure containing four different gallium atoms. With this unusual structure, the IR spectrum of tetrameric dimethylgallium cyanide could now completely be interpreted, which was published more than 20 years ago.

Tetrakis[bis(trimethylsilyl)methyl]dielement(4) compounds with aluminium−aluminium (**1**)[1], gallium−gallium (**2**)[2], and indium−indium bonds (**3**)[3] were isolated and completely characterized for the first time about ten years ago in our group. They showed a remarkable and unprecedented chemical reactivity, and up to now we observed six different types of reaction[4]. Among these, the insertions of atoms, molecules, and molecular fragments are quite outstanding owing to the number and the structural variety of the isolated products. At present, we are much interested in the insertion of carbenes into the element−element bonds, which may lead to the formation of methylene-bridged dielement compounds with two coordinatively unsaturated aluminium, gallium, or indium atoms. Such compounds are of particular interest in current organoelement chemistry, because they are potentially useful as chelating Lewis acids[5]. However, only once before we unexpectedly succeeded in inserting a carbene, when we treated the dialuminium derivative **1** with LiCH$_2$SMe[6]. In the course of this reaction, the thiomethyl compound was cleaved to yield CH$_2$, which was inserted into the Al−Al bond by the formation of an Al−CH$_2$−Al group, and the remaining thiomethanolate was coordinated in a chelating manner by both aluminium atoms to give compound **4** (Scheme 1). A similar reaction was not observed for the gallium (**2**) or indium analogues (**3**), which on similar conditions gave a complete fragmentation[6]. In order to obtain the uncoordinated methylene bridged dielement compounds by the insertion of


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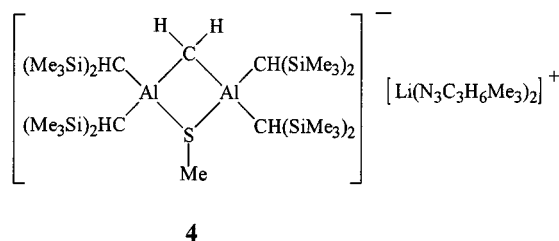
Scheme 1

carbenes, we treated **1** to **3** with diazomethane derivatives.

Reactions of the Dialuminium(4) Compound 1 with Trimethylsilyl and Bis(trimethylsilyl) Diazomethane

One equivalent of each of the diazomethane derivatives was added to solutions of **1** in hexane at room temperature, and **1** was completely consumed after stirring for about one day in both cases. Trimethylsilyldiazomethane gave only a highly viscous fluid (**5**), which could not be purified by recrystallization. Its purity was, however, high enough to allow the complete NMR spectroscopic characterization. In contrast, product (**6**) obtained by the reaction of **1** with bis(trimethylsilyl)diazomethane was isolated as a yellow crystalline solid by recrystallization from *n*-hexane. Both products have a similar constitution, as was easily derived from some very characteristic NMR data. In **5**, the resonance of one proton was observed at very low field (δ = 7.95) indicative for a N=C(H)R group, and the protons of the trimethylsilyl groups attached to the diazomethane carbon atom of compound **6** gave two resonances in accord-

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ance with the differing chemical vicinity at each side of a C=N double bond. The corresponding central carbon atoms revealed ^{13}C-NMR shifts of $\delta = 152.9$ (**5**) and $\delta = 179.0$ (**6**) characteristic of imines[7]. Thus, the diazomethane derivatives did not react as a carbene donor, but they were completely inserted into the Al−Al bond of the starting compound **1** by the formation of energetically favored Al−N bonds (Eq. 1).

(1)

5: R = H
6: R = SiMe₃
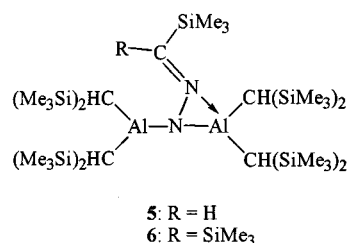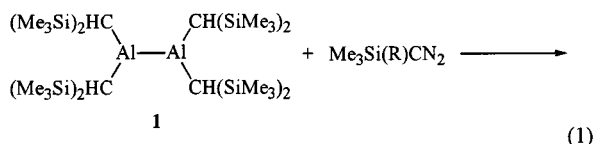
The constitution of **5** and **6** given in Equation (1) was verified also by a crystal structure determination of compound **6** (Figure 1). Bis(trimethylsilyl)diazomethane inserted into the Al−Al bond of **1** with its terminal nitrogen atom N1, and by the interaction of the nitrogen lone pair at N2 with the aluminium atom Al1 a three-membered AlN₂ heterocycle results. The compound may be described as a hydrazone derivative with both N−H hydrogen atoms replaced by dialkylaluminium groups. The shortest Al−N bond is observed to the coordinatively unsaturated exocyclic atom Al2 [183.5(2) pm], while the bond Al1−N1 in the ring is little lengthened to 189.6(2) pm. Both are within the characteristic range of Al−N single bonds[8]. As expected, the dative bond[8] between the imine nitrogen atom N2 and Al1 is much elongated to 198.9(2) pm. The N1−N2 bond [141.7(2) pm] is shorter than in hydrazine or derivatives of hydrazine[9], but similar to some N−N distances observed in hydrazones with a more comparable bonding situation[10]. The length of the C=N double bond (131.5 pm) corresponds to the standard value of 128 pm[11]. The angle Al1−N1−Al2 is 141.5°, an even closer approach to linearity is observed for the group Al1−N2−C including the C=N double bond (159.3°).

The structures of **5** and **6** have two chemically different dialkylaluminium groups, one with a tricoordinated, coordinatively unsaturated and one with a tetracoordinated, saturated aluminium atom. Thus, two different types of bis(trimethylsilyl)methyl groups should be detectable in the NMR spectra. But at room temperature only one singlet was observed for the SiMe₃ or methine protons indicating a fast exchange process of the imine nitrogen atom (N2) between both aluminium atoms. The chemical shifts of the methine resonances, which are very indicative for the coordination number at the aluminium atoms[12], are intermediate [$\delta =$
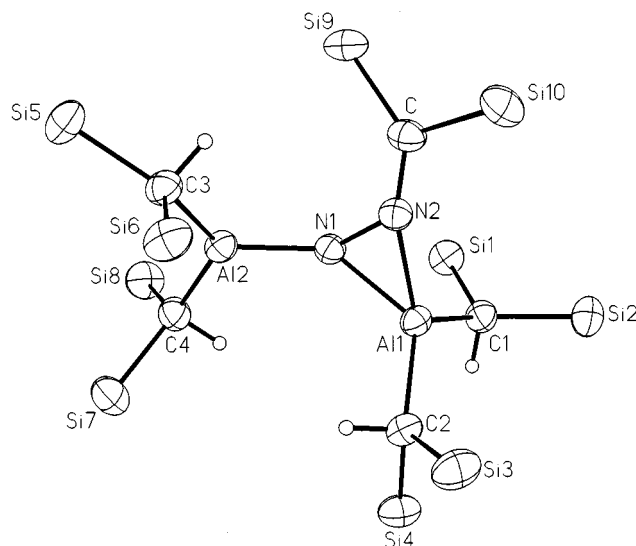
Figure 1. Molecular structure and numbering scheme of compound **6**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; selected bond lengths [pm] and angles [°]: N1−N2 141.7(2), N2−C 131.5(3), Al1−N1 189.6(2), Al1−N2 198.9(2), Al1−C1 199.3(3), Al1−C2 199.1(2), Al2−N1 183.5(2), Al2−C3 198.2(3), Al2−C4 197.6(2), Al1−N1−Al2 141.5(1), Al1−N1−N2 72.2(1), Al1−N2−N1 65.1(1), Al1−N2−C 159.3(2), N1−Al1−N2 42.70(7), Al2−N1−N2 132.9(2), N1−N2−C 127.6(2)

−0.51 (**5**) and −0.44 (**6**)] between the range of tetracoordinated ($\delta < -0.7$) and tricoordinated ($\delta > -0.2$) bis(trimethylsilyl)methyl aluminium compounds. On cooling to −70°C a complicated splitting of all resonances was observed indicating, that all bis(trimethylsilyl)methyl groups became different. The signals of the methine protons splitted into four resonances of equal intensity at $\delta = -0.26, -0.45, -0.47,$ and −0.78, from which only the last one was in that region characteristic for tetracoordinated aluminium atoms. For the trimethylsilyl groups a multiplet with nine maxima in the range between $\delta = 0.16$ and 0.43 was observed. The behavior of the diazomethane insertion products is thus quite different from that of the related products (**7**) obtained by the insertion of isonitriles into the Al−Al bond of **1**[13]. The structure of **7** in the solid state is quite similar to that of compound **6** with one tricoordinated and one tetracoordinated aluminium atom and a three-membered heterocycle; but a C=N double bond is included in the ring (Scheme 2). This structure was retained in solution, and we observed the resonances of the different CH(SiMe₃)₂ groups even at +100°C. The much faster exchange process detected for **5** and **6** is favored by the easy rotation around the N−N single bond of the heterocycle after opening of the Al−N2 bond, while an exchange with the isonitrile products requires the energetically unfavorable inversion of the nitrogen atom, which is part of the C=N double bond. Furthermore, it seems, that the dative nitrogen−aluminium interaction in **5** or **6** is weaker than that in the isonitrile insertion products. The Al−N2 distance is much lengthened to 198.9 pm in the hydrazone derivative **6** compared to 186.4 pm of the isonitrile product **7**.

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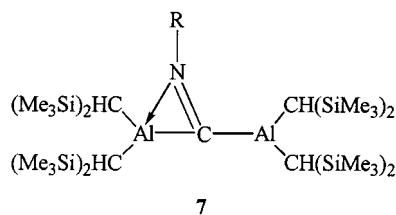
Scheme 2

Compound **6** melts at 110 °C without decomposition. UV irradiation in *n*-pentane gave no reaction after five minutes. After 60 minutes, complete decomposition occurred with the formation of a mixture of many unknown products, from which no one could be isolated in a pure form.

Reaction of the Digallium(4) Compound 2 with Trimethylsilyldiazomethane

In contrast to the easy reactions of the Al–Al bond, the insertion into the Ga–Ga bond of **2** usually needs more drastic reaction conditions with longer reaction times or does not occur at all[14]. In accordance with these observations, **2** did not react with trimethylsilyl or bis(trimethylsilyl) diazomethane at room temperature. Even in boiling solvents no reaction was observed with the last one, but on UV irradiation in a quartz apparatus **2** was completely consumed within 35 minutes. The main product of the obtained mixture was, however, formed by the disproportionation reaction of **2** and was spectroscopically identified as the trialkylgallium compound Ga[CH(SiMe₃)₂]₃[2]. Sterically less shielded trimethylsilyldiazomethane reacted in boiling *n*-hexane with **2**, but the reaction time was 24 h. A complicated mixture of products was formed, from which after repeated recrystallization from toluene two components (**8** and **9**) could reproducibly be isolated in a pure form and in a very low yield below 10% (Eq. 2). They were identified by crystal structure determinations.
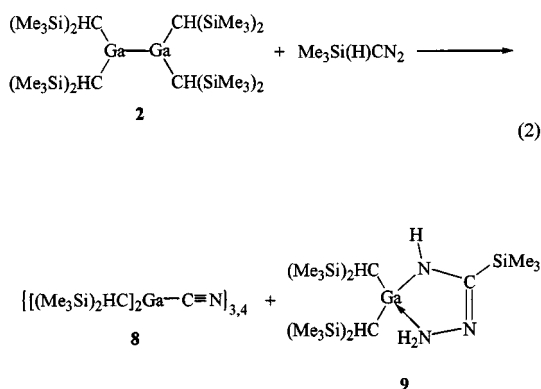
Compound **8** was isolated in a yield of 6% and identified as the trimeric dialkylgalliumcyanide (Figure 2). The isotypic aluminium compound was recently obtained in our group[15]. **8** has a nine-membered $Ga_3C_3N_3$ heterocycle, in which three gallium atoms are bridged by three cyanide groups. This is an unusual structure for alkyl metal cyan-

ides, which often polymerize like Me_2In-CN[16] or Me_3Sn-CN[17]. A tetrameric structure was reported for a dialkylgold compound[18]. Some other dialkylelement cyanides with the heavier elements of the third main group are known in literature, their degree of association between four and eight was, however, detected only by mass spectroscopy or molecular weight determinations[19]. The heterocycle of **8** deviates from planarity and adopts almost a boat conformation with the atom Ga1 furthest above the mean plane (34.3 pm). The GaC_2 planes with the central atoms of the $CH(SiMe_3)_2$ groups are not exactly perpendicular to the heterocycle, the angles between their normals are 102.6° (Ga1), 71.7° (Ga2), and 105.2° (Ga3). The bond lengths of the C–N triple bonds is 115.2 pm on average, they lie within the range observed for covalent or ionic cyanides[11][16–18][20]. The cyanide groups are not exactly linear coordinated by the gallium atoms, and angles of 164° on average are detected at the carbon or nitrogen atoms. The bonds Ga–N and Ga–C (208.8 pm on average) are much lengthened compared with the corresponding aluminium compound (202.2 pm)[15], which may be caused by a lower ionic contribution to the Ga–C or Ga–N bonds.
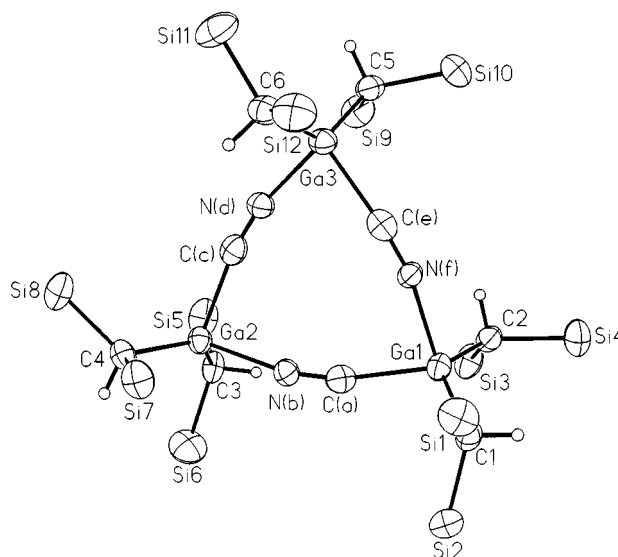

Figure 2. Molecular structure and numbering scheme of compound **8**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; the atoms of the cyanide groups are statistically disordered, the labels of the atoms are idealized; selected bond lengths [pm] and angles [°]: Ga1–C1 197.0(4), Ga1–C2 198.3(3), Ga2–C3 197.4(4), Ga2–C4 197.5(4), Ga3–C5 197.7(4), Ga3–C6 198.2(4), Ga1–(C,N)(a) 208.1(4), Ga1–(C,N)(f) 209.3(4), Ga2–(C,N)(b) 209.5(4), Ga2–(C,N)(c) 207.7(4), Ga3–(C,N)(d) 208.7(4), Ga3–(C,N)(e) 209.2(4), (C,N)(a)–(C,N)(b) 115.0(5), (C,N)(c)–(C,N)(d) 115.7(5), (C,N)(e)–(C,N)(f) 114.9(4), Ga–(C,N)–(C,N) 164.4 (average), (C,N)–Ga–(C,N) 85.1 (average)

The aluminium analogue of **8** was a dimer in solution and showed three resonances in the ¹H-NMR spectrum in the ratio of 1 to 2 to 1 for the SiMe₃ and methine protons. These observations were interpreted in terms of a different coordination of the aluminium atoms, one by two carbon and one by two nitrogen atoms of the cyanide ligands. Both bis(trimethylsilyl)methyl groups of one aluminium atom

gave two separate resonances possibly owing to a hindered rotation and the usually observed molecular conformation with the methine hydrogen atom of one substituent pointing between both trimethylsilyl groups of the second one[15]. The NMR spectra of **8** are much more complicated. The ¹H-NMR spectrum shows four different methine protons of equal intensity at $\delta = -0.23, -0.33, -0.34$, and -0.50 in a range characteristic of tetracoordinated gallium atoms [6][21]. Furthermore, six different SiMe₃ groups with the integration ratio of 1 to 1 to 2 to 2 to 1 to 1 are observed; one of the more intensive signals has a shoulder possibly indicating a poorly resolved further splitting. A similar ¹³C-NMR spectrum is observed with six resonances of the SiMe₃ groups and four resonances of the methine carbon atoms. Most striking is the occurrence of four different ¹³C resonances of the cyanide groups in the characteristic range of about $\delta = 143$; these resonances were difficult to detect due to the low solubility of these dialkyl cyanides. The appearance of the NMR spectra clearly cannot be explained by the formation of a single dimer in solution. For two isomeric dimers in an equilibrium with four different cyanide groups, an even more complicated pattern of resonances of the methine and trimethylsilyl protons has to be expected, and despite their different structures and energy those two isomers must be present in absolutely identical concentrations to account for the observed NMR spectra, which seems to be quite unlikely. A tetrameric structure was formulated for dimethylgallium cyanide owing to molecular mass determinations[19], and a similar structure may be adopted by compound **6** in solution. A complete interpretation of the NMR spectra succeeds, however, only by the assumption of a asymmetric constitution with one gallium atom coordinated by two carbon atoms of cyanide, one by two nitrogen atoms, and the remaining two by one carbon and one nitrogen atom, as shown in Scheme 3. This structure has four different cyanide carbon atoms and four different methine groups. Furthermore, two resonances are expected for those bis(trimethylsilyl)methyl groups, which have diastereotopic trimethylsilyl groups owing to the asymmetric coordination of the gallium atoms by one carbon and one nitrogen atom of the ring. In contrast, only one singlet should be observed for the CH(SiMe₃)₂ groups attached to the gallium atoms, which are symmetrically coordinated by two carbon or two nitrogen atoms of the ring with a local mirror plane bisecting the C−Ga−C or N−Ga−N as well as the Si−C−Si angles. All these expectations are in accordance with the experimental ¹H- and ¹³C-NMR spectra described above. The question arose, whether this asymmetry was observed in the IR spectra of dimethylgallium cyanide, too, which was intensively investigated by the group of Dehnicke 23 years ago[19]. Six absorptions were observed for the Ga-(C,N) stretching vibrations of the ring between 316 and 365 cm⁻¹, this number was too high for a symmetric structure. They originally were explained by the intermolecular coupling of vibrations. A calculation now done by Dehnicke with the asymmetric structure proposed by us for compound **6** gave, however, an excellent agreement with the experimental spectrum. It was

based on a local C_{2v} symmetry of those gallium atoms coordinated by two carbon or two nitrogen atoms of the heterocycle (Ga¹ and Ga²), which result in two IR active stretching vibrations (A₁, B₂) for each of the groups Ga¹−(CN)₂ and Ga²−(NC)₂. The local C_s symmetry at both gallium atoms asymmetrically coordinated by one carbon and one nitrogen atom of the heterocycle (Ga³ and Ga⁴) leads to two indistinguishable stretching vibrations for Ga−(CN) and Ga−(NC) of the symmetry type A′, which gives a total of six IR active stretching vibrations for the (GaCN)₄ group. This result impressively confirms our interpretation of compound **6** as a tetramer in solution and the asymmetric structure of the tetramers.
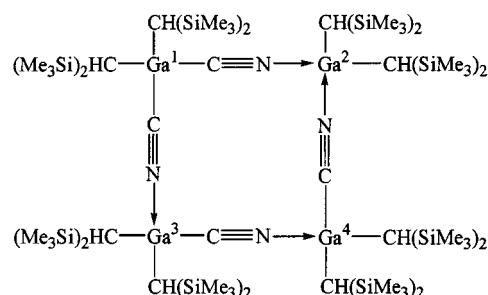
Scheme 3

Upon heating solutions of **8**, the splitting of the SiMe₃ resonances disappeared and only one singulet was observed at $\delta = 0.31$. The methine protons gave three resonances with an intensity ratio of 1 to 2 to 1 with similar chemical shifts as observed at room temperature. The temperature of coalescence was at about 40°C. Probably, the resonances of different SiMe₃ groups coincided, and there is not enough information for a sensible interpretation. In the IR spectra, the CN stretching vibration was observed in an expected range[22] at 2172 cm⁻¹ similar to the aluminium analogue (2185 cm⁻¹)[15].

The second product of the reaction of **2** with trimethylsilyldiazomethane was identified as compound **9**, which was isolated in a yield of 4%. A dialkylgallium fragment is coordinated by the ligand H₂N−N=C(SiMe₃)−NH− (Figure 3), which to the best of our knowledge has never been used before in coordination chemistry. However, few derivatives of the neutral compound with two terminal NH₂ groups (amidrazones) are reported in literature[23]. The gallium atom in **9** has a distorted tetrahedral coordination sphere with normal Ga−C bond lengths of 200.0 pm on average. The Ga−N distances differ with 204.8(2) pm to the nitrogen atom N1 of the NH₂ group and 192.7(2) pm to the amide nitrogen atom N3. The N1−N2 single bond length [149.5(2) pm] is longer than in the diazomethane insertion product **6** discussed above, in which both nitrogen atoms were part of a three-membered heterocycle and coordinated by aluminium. The carbon−nitrogen double bond C3−N2 has a length of 130.9(3) pm in the normal range similar to that observed in compound **6**. Also, the C−N bond between C3 and the NH group (N3) is short [134.0(2) pm] and has some π character due to the delocalization of elec-

tron density. A five-membered heterocycle is formed by the coordination of the gallium atom by both terminal nitrogen atoms of the ligand (N1 and N3), which is almost ideally planar. The atom N1 deviates furthest from the average plane by only 4.9 pm. Also, the silicon atom Si5 bound to the carbon atom C3 and the hydrogen atom at N3 lie within this plane with small deviations of 9.1 and 3.5 pm, respectively.
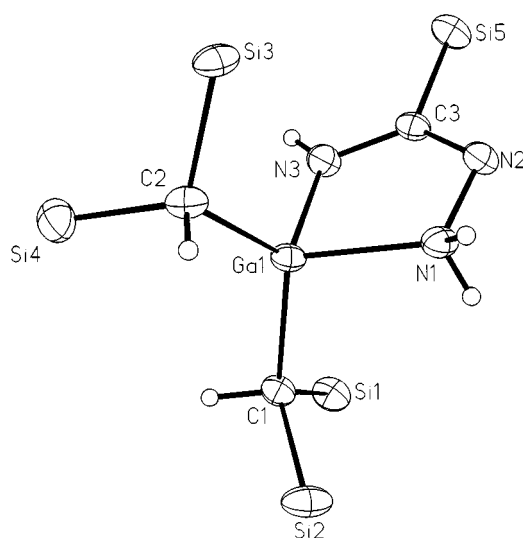

Figure 3. Molecular structure and numbering scheme of compound **9**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; selected bond lengths [pm] and angles [°]: Ga1−N1 204.8(2), Ga1−N3 192.7(2), N1−N2 149.5(2), N2−C3 130.9(3), N3−C3 134.0(2), C3−Si5 190.1(2), Ga1−C1 199.9(2), Ga1−C2 200.0(2), N1−Ga1−N3 80.11(8), Ga1−N1−N2 111.3(1), N1−N2−C3 110.1(2), N2−C3−N3 122.6(2), C3−N3−Ga1 115.3(2)

The trimethylsilyl groups of the $CH(SiMe_3)_2$ substituents are diastereotopic due to the molecular symmetry and give two resonances in the ^1H- and ^{13}C-NMR spectra. The methine protons show a resonance at very high field ($\delta = -0.75$), which is characteristic for a coordination number of four at the gallium atom[21], and the N−H protons give two broad signals in the intensity ratio of 1 to 2 at $\delta = 4.51$ and 4.20. The carbon atom of the chelating ligand has, as expected, a resonance at low field ($\delta = 176.7$) similar to the bis(trimethylsilyl)diazomethane product **6** discussed above. In the IR spectrum, two absorptions are observed at 1584 and 1501 cm^{-1}, which can be attributed to the N−C−N moiety with a delocalized π bond in the chelate ligand.

The diindium compound **3** with an In−In single bond did not react with the diazomethane derivatives at room temperature. Complete disproportionation by the formation of elemental indium and the corresponding InR_3 compound occurred upon heating in boiling n-hexane or under irradiation with UV light, and no product of a reaction with the diazomethanes could be detected by NMR spectroscopy.

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene with Na/benzophenone, n-hexane with Li-AlH$_4$). Compounds **1**, **2**, and **3** were synthesized as described in ref.[1−3]. A commercially available solution of trimethylsilyldiazomethane in n-hexane was used without further purification; bis(trimethylsilyl)diazomethane was synthesized according to ref.[24].

Reaction of 1 with Trimethylsilyldiazomethane. − Synthesis of 5: A solution of trimethylsilyldiazomethane in n-hexane (2 M, 0.77 ml, 1.53 mmol) was added to a solution of dialane(4) **1** (0.960 g; 1.39 mmol) in 50 ml of n-hexane at room temperature. The mixture was stirred for 24 h. The color changed from pale-yellow to orange. The solvent was removed in vacuo, and the residue was thoroughly dried in vacuo. The product (**5**) could not be purified by recrystallization. − ^1H NMR (C$_6$D$_6$, 300 MHz): δ = 7.95 (1 H, CH of azomethane), 0.32 [72 H, SiMe$_3$ of bis(trimethylsilyl)methyl], 0.26 (9 H, SiMe$_3$ of diazomethane), −0.51 (4 H, AlCHSi$_2$). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 152.9 (C=N), 6.0 (SiMe$_3$ of diazomethane), 5.2 [SiMe$_3$ of bis(trimethylsilyl)methyl], −0.6 (AlCSi$_2$).

Reaction of 1 with Bis(trimethylsilyl)diazomethane. − Synthesis of 6: A solution of 0.796 g (1.15 mmol) dialane(4) **1** in 60 ml of n-hexane was added to 0.294 g (1.58 mmol) bis(trimethylsilyl)diazomethane at room temperature. The mixture was stirred for 18 h. The solvent was removed in vacuo. The residue was recrystallized from n-hexane. Yield: 0.761 g (75%), yellow crystals. − M. p. (argon, sealed capillary): 110°C. − ^1H NMR (C$_6$D$_6$, 300 MHz, 300 K): δ = 0.43 (9 H, SiMe$_3$ of diazomethane), 0.36 [72 H, SiMe$_3$ of bis(trimethylsilyl)methyl], 0.32 (9 H, SiMe$_3$ of diazomethane), −0.44 (4 H, AlCHSi$_2$). − ^1H NMR ([D$_8$]toluene, 300 MHz, 203 K): δ = 0.43, 0.40, 0.39, 0.36, 0.34, 0.30, 0.24, 0.19, 0.16 (SiMe$_3$), −0.26, −0.45, −0.47, −0.78 (each 1 H, AlCHSi$_2$). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 179.0 (C=N), 5.9 [SiMe$_3$ of bis(trimethylsilyl)methyl], 5.1 (SiMe$_3$ of diazomethane), 4.0 (AlCSi$_2$), 2.1 (SiMe$_3$ of diazomethane). − IR (CsBr, paraffin): ṽ = 1289 vw cm^{-1}, 1248 vs δCH$_3$; 1187 vw, 1154 vw, 1071 w, 1045 m νNN; 1007 m δCH; 951 m, 922 m, 845 vs, 777 m, 752 m, 723 m ρCH$_3$(Si); 675 s ν$_{as}$SiC; 646 w, 631 w ν$_s$SiC; 594 vw, 557 w, 527 w, 515 m, 502 w, 465 w, 451 w νAlC, νAlN; 401 vw, 378 vw, 339 vw δSiC. − UV (n-hexane): λmax (lg ε) = 260 nm (br., 3.5), 360 (3.5), 370 (sh, 3.3). − C$_{35}$H$_{94}$N$_2$Si$_{10}$Al$_2$ (878.0): calcd. Al 6.1, found Al 6.0. − Mol. mass: 825 (cryoscopically measured in benzene).

Reaction of 2 with Trimethylsilyldiazomethane − Synthesis of 8 and 9: A solution of trimethylsilyldiazomethane (2 ml; 2 M; 4.00 mmol) was added to a solution of 0.953 g (1.23 mmol) digallane(4) **2** in 50 ml of n-hexane. The mixture was refluxed for 24 h. After cooling to room temperature, the solvent was removed in vacuo, and the brown residue was dissolved in 1.5 ml of toluene. An amorphous solid crystallized on storing the solution at −50°C for 14 d, which was isolated and recrystallized from 2 ml of toluene at −50°C for seven days. Three compounds were detected in the solid by NMR spectroscopy, one could not be isolated in a pure form and was not identified. Compound **8** [(R$_2$GaCN)$_3$] was isolated after dissolution of the solid in 2.5 ml of toluene and slow cooling to 0°C. The mother liquor was cooled to −50°C to obtain a colorless solid, which was dissolved in n-hexane and gave product **9** upon slow cooling to −20°C.

Characterization of 8: Yield: 0.06 g (6%, based on **2**), colorless crystals. − M. p. (argon, sealed capillary): 224−226°C (dec.). − ^1H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ = 0.369 (9 H), 0.362 (9 H), 0.353 (18 H), 0.346 (sh) and 0.342 (18 H), 0.335 (9 H), 0.325 (9 H, all SiMe$_3$), −0.225, −0.332, −0.339, −0.504 (each 1 H, GaCHSi$_2$).

Table 1. Crystal data, data collection parameters and structure refinement for **6**, **8**, and **9**[a]

	6	**8**	**9**
Formula	$C_{35}H_{94}N_2Al_2Si_{10}$	$C_{45}H_{114}N_3Si_{12}Ga_3$	$C_{18}H_{50}N_3Si_5Ga$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$; No.14 [25]	$P2_1/n$; No.14 [25]	$P2_1/n$; No.14 [25]
Z	4	4	4
Temperature [K]	293(2)	293(2)	213(2)
$d_{calc.}$ [g/cm^3]	1.019	1.105	1.110
a [pm]	1916.0(2)	1234.2(2)	1229.7(1)
b [pm]	1506.7(1)	2323.4(5)	1735.1(1)
c [pm]	1997.2(2)	2610.5(5)	1476.8(1)
β [°]	97.01(2)	93.36(2)	99.914(9)
V [10^{-30} m^3]	5722.5(9)	7473(3)	3103.9(4)
μ [mm^{-1}]	0.284	1.294	1.089
Crystal size [mm]	0.8 × 0.8 × 0.9	0.3 × 0.4 × 0.4	0.4 × 0.5 × 0.5
Diffractometer	AED-2	AED-2	Stoe-IPDS
Radiation	Mo-K_α; graphite monochromator		
2Θ range [°]	$3.1 \leq 2\Theta \leq 50.0$	$3.1 \leq 2\Theta \leq 45.0$	$4.0 \leq 2\Theta \leq 51.8$
Index ranges	$-22 \leq h \leq 22$	$-13 \leq h \leq 13$	$-14 \leq h \leq 15$
	$0 \leq k \leq 17$	$0 \leq k \leq 25$	$-21 \leq k \leq 21$
	$0 \leq l \leq 23$	$0 \leq l \leq 28$	$-17 \leq l \leq 16$
Independent reflections	10025	10339	5841
Reflections $F > 4\ \sigma(F)$	7940	7710	4585
Parameters	472	604	270
$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($F > 4\ \sigma(F)$)	0.0519	0.0478	0.0300
$wR^2 = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.0934	0.0903	0.0562
Max./min. residual [10^{30} e/m^3]	0.296/−0.204	0.336/−0.255	0.353/−0.300

[a] Programmes SHELXL-93; SHELXTL[26]; solutions by direct methods, full matrix refinement with all independent structure factors.

− ^{1}H NMR ([D$_8$]toluene, 300 MHz, 343 K): δ = 0.31 (72 H, SiMe$_3$), −0.25 (1 H), −0.34 (2 H), −0.49 (1 H, all GaCHSi$_2$). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 144.4, 143.6, 143.5, 142.7 (cyanide), 6.98, 5.04, 5.00 (GaCSi$_2$), 4.58, 4.50, 4.42, 4.35, 4.25, 4.15 (SiMe$_3$; intensity ratio 1:2:1:1:2:1), 2.44 (GaCSi$_2$). − IR (CsBr, paraffin): $\tilde{v}$ = 2172 cm^{-1} νCN; 1462 vs, 1377 vs paraffin; 1294 w, 1260 sh, 1250 vs δCH$_3$; 1167 vw, 1115 vw; 1022 vs, 1011 vs δCH; 982 s, 970 s; 843 vs, 775 vs, 758 vs, 725 s ρCH$_3$(Si); 673 vs ν$_{as}$SiC; 625 w, 615 w ν$_s$SiC; 513 m, 486 s, 465 w, 407 m νGaC, νGaN; 361 m, 351 m, 332 m δSiC. − C$_{45}$H$_{114}$N$_3$Si$_{12}$Ga$_3$ (1243.6): calcd. Ga 16.8, found Ga 16.5.

Characterization of 9: Yield: 0.052 g (4%, based on **2**), colorless crystals. − M. p. (argon, sealed capillary): 124°C (dec.). − ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 4.51 (1 H, AlNH), 4.20 (2 H, AlNH$_2$), 0.22 (9 H, SiMe$_3$ of the chelating ligand), 0.19 and 0.10 [each 18 H, SiMe$_3$ of bis(trimethylsilyl)methyl], −0.75 (2 H, GaCHSi$_2$). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 176.7 (C=N), 4.9 (SiMe$_3$ of the chelating ligand), 4.0 and 3.8 [SiMe$_3$ of bis(trimethylsilyl)methyl], −2.4 (GaCSi$_2$). − IR (CsBr, paraffin): $\tilde{v}$ = 3428 m, 3273 m, 3185 m, 3098 m νNH; 2922 vs, 2853 vs paraffin; 1584 s cm^{-1}, 1501 s νNCN; 1462 vs, 1373 vs paraffin; 1289 w, 1256 sh, 1246 vs δCH$_3$; 1192 m, 1155 s νCN; 1017 s δCH; 936 s, 909 m, 843 vs, 785 s, 774 s, 754 s, 725 m ρCH$_3$(Si); 669 m ν$_{as}$SiC; 629 w, 619 m ν$_s$SiC; 583 m, 525 m, 517 m, 498 s νGaC, νGaN; 368 m δSiC. − C$_{18}$H$_{50}$N$_3$Si$_5$Ga (518.8): calcd. Ga 13.4, found Ga 13.3.

Crystal Structure Determinations: Single crystals of the compounds **6**, **8**, and **9** were obtained by recrystallization from *n*-hexane, toluene, and *n*-hexane, respectively. Crystal data and structure refinement parameters are given in Table 1[27]. In compound **8**, the atoms of the cyanide groups are statistically disordered as often observed before; each position was refined by the occupation with a half nitrogen and a half carbon atom. The positions of the hydrogen atoms bound to nitrogen in **9** were taken from a difference Fourier-map and isotropically refined. All other hydrogen atoms were calculated on ideal positions and refined by using the riding model.

[1] W. Uhl, *Z. Naturforsch., B. Chem. Sci.* **1988**, *43*, 1113−1118.
[2] W. Uhl, M. Layh, T. Hildenbrand, *J. Organomet. Chem.* **1989**, *364*, 289−300.
[3] W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139−154.
[4] W. Uhl, *Coord. Chem. Rev.* **1997**, *163*, 1−32.
[5] W. Uhl, F. Hannemann, W. Saak, R. Wartchow, *Eur. J. Inorg. Chem.* **1998**, 921−926. Cited literature.
[6] W. Uhl, R. Gerding, F. Hannemann, *Z. Anorg. Allg. Chem.* **1998**, *624*, 937−944.
[7] H. O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, Thieme Verlag, Stuttgart, **1984**.
[8] A. Haaland, in *Coordination Chemistry of Aluminum*, (Ed.: G. H. Robinson), VCH, Weinheim, **1993**.
[9] K. Bode, U. Klingebiel, *Adv. Organomet. Chem.* **1996**, *40*, 1−43. K. Bode, U. Klingebiel, M. Noltemeyer, H. Witte-Abel, *Z. Anorg. Allg. Chem.* **1995**, *621*, 500−505. H. Nöth, H. Sachdev, M. Schmidt, H. Schwenk, *Chem. Ber.* **1995**, *128*, 105−113. B. Gemünd, H. Nöth, H. Sachdev, M. Schmidt, *Chem. Ber.* **1996**, *129*, 1335−1344. J. Knizek, I. Krossing, H. Nöth, H. Schwenk, T. Seifert, *Chem. Ber.* **1997**, *130*, 1053−1062. S. Dielkus, C. Drost, R. Herbst-Irmer, U. Klingebiel, *Angew. Chem.* **1993**, *105*, 1689−1690; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1625−1626. C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, *J. Chem. Soc. A* **1970**, 318−323. Y. Morino, T. Iijima, Y. Murata, *Bull. Chem. Soc. Japan* **1960**, *33*, 46−48.
[10] Acyclic hydrazones, which are not coordinated by transition metal cations: D. L. Cullen, M. M. Mangion, B. V. Crist, D. A. Lightner, *Tetrahedron*, **1983**, *39*, 733−742. I. L. Knunyants, Yu. T. Struchkov, M. D. Bargamova, A. A. Espenbetov, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1985**, 1097−1099. C. R. Hauer, G. S. King, E. L. McCool, W. B. Euler, J. D. Ferrara, W. J. Youngs, *J. Am. Chem. Soc.* **1987**, *109*, 5760 −5765. A. Cousson, F. Nec-

toux, B. Bachet, B. Kokel, M. Hubert-Habart, *Acta Crystallogr., Sect. C* **1994**, *50*, 1753−1756. F. Bachechi, V. M. Coiro, M. Delfini, *Acta Crystallogr., Sect. C* **1996**, *52*, 2915−2918. J. Osterodt, M. Nieger, P.-M. Windscheif, F. Vögtle, *Chem. Ber.* **1993**, *126*, 2331−2336. Hydrazones coordinated to two silicon or germanium atoms similar to **6**: K. Knipping, C. Drost, U. Klingebiel, M. Noltemeyer, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1215−1221. M. Lazraq, C. Couret, J. P. Declercq, A. Dubourg, J. Escudie, M. Riviere-Baudet, *Organometallics* **1990**, *9*, 845−848.

[11] J. March, *Advanced Organic Chemistry*, third edition, Wiley, **1985**, p. 19.

[12] W. Uhl, M. Layh, *Z. Anorg. Allg. Chem.* **1994**, *620*, 856−862. W. Uhl, M. Koch, M. Heckel, W. Hiller, H. H. Karsch, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1427−1433. W. Uhl, M. Koch, A. Vester, *Z. Anorg. Allg. Chem.* **1993**, *619*, 359−366. W. Uhl, M. Koch, J. Wagner, *Z. Anorg. Allg. Chem.* **1995**, *621*, 249−257. W. Uhl, E. Schnepf, J. Wagner, *Z. Anorg. Allg. Chem.* **1992**, *613*, 67−75. W. Uhl, A. Vester, *Chem. Ber.* **1993**, *126*, 941−945.

[13] W. Uhl, U. Schütz, W. Hiller, M. Heckel, *Chem. Ber.* **1994**, *127*, 1587−1592.

[14] W. Uhl, R. Gerding, I. Hahn, S. Pohl, W. Saak, H. Reuter, *Polyhedron* **1996**, *15*, 3987−3992. W. Uhl, I. Hahn, U. Schütz, S. Pohl, W. Saak, J. Martens, J. Manikowski, *Chem. Ber.* **1996**, *129*, 897−901.

[15] W. Uhl, U. Schütz, W. Hiller, M. Heckel, *Z. Anorg. Allg. Chem.* **1995**, *621*, 823−828.

[16] J. Blank, H.-D. Hausen, J. Weidlein, *J. Organomet. Chem.* **1993**, *444*, C4−C6.

[17] E. O. Schlemper, D. Britton, *Inorg. Chem.* **1966**, *5*, 507−510.

[18] R. F. Phillips, H. W. Powell, *Proc. Roy. Chem. Soc. London, Ser. A* **1939**, *173*, 147−148. A. F. Wells, *Structural Inorganic Chemistry*, fifth edition, Clarendon Press, Oxford, **1984**.

[19] G. E. Coates, R. N. Mukherjee, *J. Chem. Soc.* **1963**, 229−233. J. Müller, F. Schmock, A. Klopsch, K. Dehnicke, *Chem. Ber.* **1975**, *108*, 664−672. R. Ehrlich, A. R. Young, *J. Inorg. Nucl. Chem.* **1966**, *28*, 674−676.

[20] A. F. Hollemann, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, **1995**.

[21] W. Uhl, I. Hahn, H. Reuter, *Chem. Ber.* **1996**, *129*, 1425−1428. W. Uhl, I. Hahn, R. Wartchow, *Chem. Ber./Recueil* **1997**, *130*, 417−420. W. Uhl, R. Graupner, I. Hahn, T. Spies, W. Frank, *Eur. J. Inorg. Chem.* **1998**, 355−360. W. Uhl, I. Hahn, M. Koch, M. Layh, *Inorg. Chim. Acta* **1996**, *249*, 33−39. W. Uhl, R. Graupner, I. Hahn, *Z. Anorg. Allg. Chem.* **1997**, *623*, 565−572.

[22] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen I− Hauptgruppenelemente*, Thieme Verlag, Stuttgart, **1981**.

[23] T. Kauffmann, S. Spaude, D. Wolf, *Angew. Chem.* **1963**, *75*, 344. T. Kauffmann, S. Spaude, D. Wolf, *Chem. Ber.* **1964**, *97*, 3436-3443. H. Neunhoeffer, F. Weischedel, *Liebigs Ann. Chem.* **1971**, *749*, 16−23. R. O. Day, R. R. Holmes, H. Tautz, J. H. Weinmaier, A. Schmidpeter, *Inorg. Chem.* **1981**, *20*, 1222−1229. R. O. Day, A. Schmidpeter, R. R. Holmes, *ibid.* **1982**, *21*, 3916−3919 and **1983**, *22*, 3696−3699.

[24] E. Glozbach, J. Lorberth, *J. Organomet. Chem.* **1980**, *191*, 371−379.

[25] T. Hahn (Ed.), *International Tables for Crystallography, Space Group Symmetry*, Kluwer Academic Publishers, Dordrecht-Boston-London, **1989**, vol. A.

[26] *SHELXTL-Plus REL. 4.1*, Siemens Analytical X-RAY Instruments Inc., Madison, USA, **1990**; G. M. Sheldrick *SHELXL-93, Program for the Refinement of Structures*, Universität Göttingen, **1993**.

[27] The crystallographic data of **6**, **8**, and **9** (excluding structure factors) were deposited with the Cambridge Crstallographic Data Centre as supplementary publication no. CCDC-102908 (**6**), −102909 (**8**), and −102910 (**9**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ, UK [fax: Int. Code+44 (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk].