Twofold Insertion of Isocyanides into the Ga–Ga Bond of Tetrakis[bis(trimethylsilyl)methyl]digallane(4)

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Tetrakis[bis(trimethylsilyl)methyl]digallane(4) (**1**) reacts with *tert*-butyl or aryl isocyanides (aryl = phenyl, *o*-methylphenyl, *o*-methoxyphenyl, *p*-methoxyphenyl) by a twofold insertion of the central carbon atoms into the Ga–Ga bond and formation of C–C single bonds. 1,4-Diazabutadiene derivatives bound to two R_2Ga groups are formed (**2**–**6**), which in contrast to an aluminium analog exhibit only weak interactions between the imine nitrogen atoms and the coordinatively unsaturated gallium atoms as indicated by NMR spectroscopy and the long Ga–N distances in the molecular structures of three products: **2** ($R = C_6H_5$), **4** ($R = o\text{-}MeOC_6H_4$), and **6** ($R = CMe_3$).

Tetrakis[bis(trimethylsilyl)methyl]digallane(4) (**1**) with a Ga–Ga bond[1] shows a remarkable chemical reactivity similar to the dialuminium(4)[2] or diindium(4) analogs[3]. Up to now we published insertion reactions with the chalcogens sulfur[4], selenium[4], and tellurium[5] and a metathesis reaction with $(Me_3Si)_3SiTe{-}TeSi(SiMe_3)_3$[6], which all gave monomeric organogallium chalcogenides with coordinatively unsaturated gallium atoms. A digallane(4) radical anion exhibiting a 1e-Ga–Ga π bond[7] was obtained by the reaction of **1** with ethyllithium. The dialane(4) derivative reacts with *tert*-butyl or phenyl isothiocyanates to yield a tetraalkyldialuminium sulfide and the product of the insertion of an isocyanide fragment into the Al–Al bond by the cleavage of the C=S bond[8]. The latter product could also be directly obtained by the reaction of the dialane(4) with isocyanides[8]. Imine derivatives with a C–N double bond are formed, in which the imine carbon atom is bound to two Al atoms, and three-membered AlCN heterocycles with a very short Al–N bond result by the interaction of the nitrogen atom with one aluminium atom. Compounds with similar structures were recently synthesized by the reaction of isocyanides with heterodinuclear transition metal complexes[9]. An excess of phenyl isocyanide yields another product, in which two isocyanide molecules are inserted into the Al–Al bond with the formation of a C–C single bond and two four-membered AlC_2N heterocycles anellated across the C–C bond with normal "dative" Al–N bond lengths[8]. In contrast, an excess of *tert*-butyl isocyanide gives by cleavage of the N–*tert*-butyl bond a dialkylaluminium cyanide, which is a trimer in the solid state[10]. As shown by systematic investigations the digallane(4) derivative **1** is less reactive than the aluminium analog, and it was of interest, whether or not a reaction with isocyanides or isothiocyanates occur. Additionally, alkylgallium derivatives are known to be weaker Lewis acids[11] than alkylaluminium compounds. Thus, the formation of heterocycles by the interaction between Ga and N could not be expected.

1. Reactions of Digallane(4) 1 with Alkyl and Aryl Isocyanides

The digallium(4) derivative **1** did not react with methyl, *tert*-butyl or phenyl isothiocyanates, although we systematically changed the solvent (pentane, hexane, toluene, pure isothiocyanates) and the reaction temperature. Phenyl isocyanide reacted independently of the stoichiometric ratio of the starting compounds within one day at room temperature to yield dark red crystals of **2**, which were the product of a twofold insertion of isocyanide into the Ga–Ga bond as easily detected by the integration of the corresponding signals in the ^{1}H-NMR spectrum (eq. 1). Compound **2** was isolated in almost 90% yield, when **1** and phenyl isocyanide were allowed to react in the correct stoichiometric ratio of 1 to 2. The product of the insertion of only one isocyano group, which was formed with the corresponding dialane(4) derivative as the main component[8], could not be detected by NMR spectroscopy even when an excess of the digallane(4) **1** was employed. In order to realize a monoinsertion we used sterically more shielded aryl isocyanides, like *o*- and *p*-methoxyphenyl or *o*-methylphenyl isocyanide, which should sterically prevent the attack of a second isocyanide molecule, but we always exclusively isolated the orange-red products (**3** to **5**) of the twofold insertion (eq. 1). 2,6-Diisopropylphenyl and 2,6-dimethylphenyl isocyanide did not react with **1** at all. Stoichiometric amounts of *tert*-butyl isocyanide and **1** could be stored in solution at room temperature for several weeks without any detectable reaction. But when **1** was dissolved in a large excess of the isocyanide, it was completely consumed within 30 hours, and a yellow crystalline product (**6**) could be isolated, which once again had

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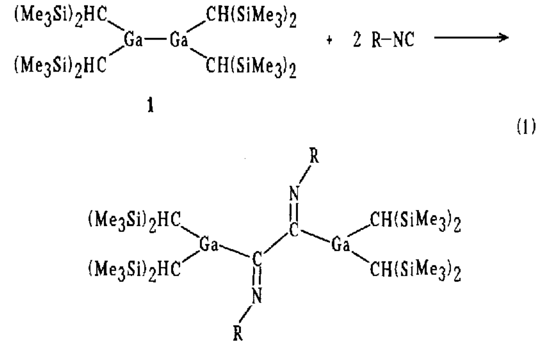
two isocyanide molecules inserted into the Ga–Ga bond as shown by NMR spectroscopy and a crystal structure analysis (see below).



	R		R
2	C_6H_5	5	$(o\text{-Me})C_6H_4$
3	$(p\text{-MeO})C_6H_4$	6	CMe_3
4	$(o\text{-MeO})C_6H_4$		

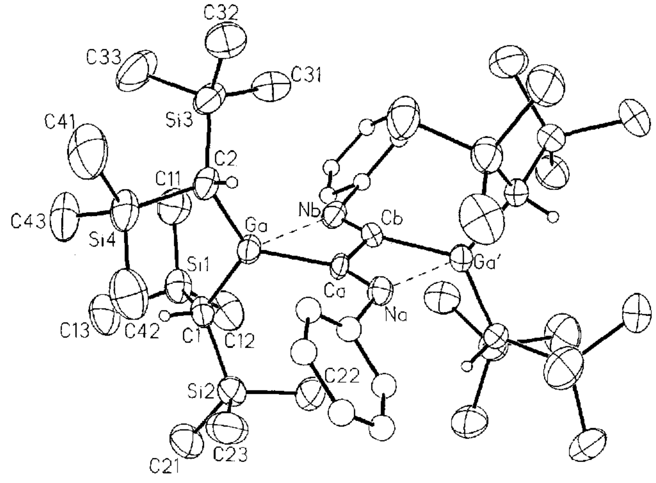
As schematically shown in equation (1) 1,4-diazabutadiene derivatives are formed by the insertion of two isocyanide molecules[12]. As mentioned above, a four-membered heterocycle was detected in the aluminium analog[8] with a strong Al–N interaction, which results in diastereotopic $SiMe_3$ groups with two separate resonances in the ^1H-NMR spectrum. The aryl isocyanide insertion products **2** to **5** show, however, only one singlet for the $SiMe_3$ protons at room temperature, and a splitting into two resonances is observed with the phenyl derivative **2** only on cooling a solution in [D$_8$]toluene to −40°C. The spectrum of the *tert*-butyl derivative **6** shows two broad resonances of the trimethylsilyl protons at room temperature, which coalesce by a slight warming of the solution to 40°C and give one sharp singlet on further heating. As crystal structure analyses revealed, the interaction between nitrogen and gallium is weakest in **6** (R = *tert*-butyl). We therefore believe, that the splitting of these resonances is not caused by a strong Ga–N bond, but by a steric hindrance of the free rotation around the Ga–C bonds, which should be strongest with the bulky *tert*-butyl group. The resonances of the carbon atoms of the C_2 bridge [δ = 211 (**6**) and 218 to 224 (**2** to **5**)] are shifted to low field compared to those of the C=N bonds in organic molecules (δ = 150 to 180)[13] and are similar to that found in the aluminium analog (δ = 236.5)[8].

Compound **2** (R = phenyl) is dark red both in the solid state and in solution, while the aryl compounds **3**, **4**, and **5** crystallize as orange-red solids, which give yellow solutions in pentane and benzene. The UV/Vis spectra of **3**, **4**, and **5** exhibit broad maxima at 385 (**3**), 370 (**4**), and 325 (**5**) nm as the most bathochromically shifted absorptions, which are probably caused by the conjugated double bonds of the diazabutadiene moiety. Only a weak absorption is observed in the same region (400 nm) for the yellow compound **6** (R = *tert*-butyl). Besides bands at 210 and 355 nm the phenyl derivative **2** shows a further absorption at 523 nm similar to the corresponding phenylaluminium derivative[8]. The reason for the additional band is not well understood. The phenyl group is the sterically less bulky group of the substituents employed, and the unsubstituted phenyl ring lies closest to the C_2N_2 plane of the diazabutadiene moiety as shown by crystal structure analyses. Thus, the aromatic system might interact to a larger extent with the delocalized diazabutadiene π bond. However, the conformations of the aryl compounds in the solid state differ only slightly, as will be discussed below, and do not strongly verify such a hypothesis.

2. Crystal Structures of 2, 4, and 6

Figures 1 to 3 show the molecular structures of compounds **2** (R = phenyl), **4** (R = *o*-methoxyphenyl) and **6** (R = *tert*-butyl). In all cases two isocyanide molecules are inserted into the Ga–Ga bond with the formation of a C–C single bond. The compounds can be described as 1,4-diazabutadiene derivatives, which bear two dialkylgallium groups in positions 2 and 3. All molecules are situated on special positions. The C_2N_2 center in **2** is statistically disordered across a crystallographic twofold rotational axis, which lies within the C_2N_2 plane. **4** is located perpendicularly to a twofold rotational axis, and an inversion center bisects the inner C–C bond in **6**. The $Ga_2C_2N_2$ molecular core is almost planar in all structures, and the gallium atoms deviate from the C_2N_2 planes with 6.4 (**2**), 13.4 (**4**), and 2.5 (**6**) pm. The bond lengths of the inner C–C bond amount to 147.2(8) (**2**), 152.1 (6) (**4**), and 149.1(4) (**6**) pm and are in that region, in which bonds between sp^2 C atoms are to be expected[14]. Also, the C=N distances [129.1(5) and 128.2(6) in **2**, 127.4(4) in **4** and 129.2(3) in **6**] correspond to the normal value of a C=N double bond[14].

Figure 1. Molecular structure of **2**; the ellipsoids are drawn at the 40% probability level; only one position is drawn from the statistically disordered C_2N_2 group. – Selected bond lengths [pm] and angles [°]: Ga–C(a) 205.6(4), Ga–C(b)′ 212.2(5), Ga–N(b) 244.7(5), Ga–N(a)′ 222.4(4), C(a)–N(a) 129.1(5), C(b)–N(b) 128.2(6), C(a)–C(b) 147.2(8), C(a)–Ga–N(b) 59.4(2), C(b)′–Ga–N(a)′ 62.5(2), C(b)–C(a)–Ga 101.2(3), C(a)–C(b)–Ga′ 93.6(3), Ga–C(a)–N(a) 149.4(4), Ga′–C(b)–N(b) 156.5(4), N(a)–C(a)–C(b) 109.4(4), N(b)–C(b)–C(a) 109.8(4)



A remarkable difference to the Al derivative (R = phenyl)[8] results from the element-nitrogen distances. A normal

Figure 2. Molecular structure of **4**; the ellipsoids are drawn at the 40% probability level. – Selected bond lengths [pm] and angles [°]: Ga–C' 209.1(3), Ga–N 226.7(3), C–N 127.4(4), C–C' 152.1(6); C'–Ga–N 62.4(1), N–C–C' 107.8(3), C–C'–Ga 94.9(3), Ga–C'–N' 157.0(3), Ga–N–C 94.7(2)

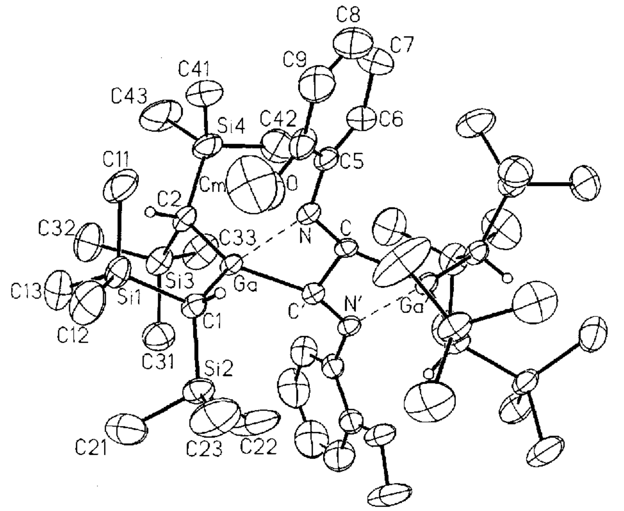
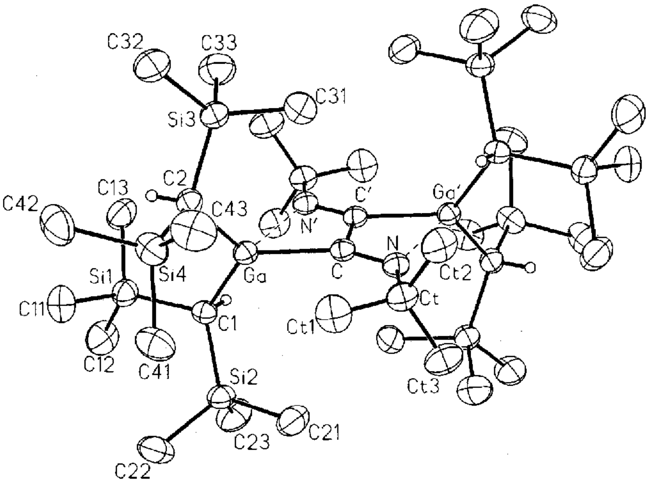


Figure 3. Molecular structure of **6**; the ellipsoids are drawn at the 40% probability level. – Selected bond lengths [pm] and angles [°]: Ga–C 206.0(2), Ga–N' 248.0(2), C–N 129.2(3), C–C' 149.1(4); C–Ga–N' 59.5(1), N–C–C' 110.1(3), C'–C–Ga 101.5(2), Ga–C–N 148.4(2), Ga–N'–C' 88.8(2)



Al–N "dative" bond[15] (204.0(2) pm) is consistent with strong Al–N interactions and the formation of two AlC$_2$N heterocycles in the Al compound. While the Ga–C bond lengths to the inner C atoms are, as expected, similar to the Al–C distances [208.9 (average, **2**), 209.1(3) (**4**) and 206.0(2) (**6**) pm compared to 207.5(2) pm in the Al derivative], the Ga–N distances are significantly lengthened [222.4(4) and 244.7(5) in **2**, 226.7(3) in **4**, and 248.0(3) pm in **6**]. Thus, the gallium derivatives exhibit only very weak interactions between the coordinatively unsaturated gallium atoms and the nitrogen atom. The very long Ga–N distance with R = *tert*-butyl might have solely geometrical causes, and probably no Ga–N interaction exists at all. These results are in accordance with the weak Lewis acidity of gallium compared to aluminium compounds[11]. The oxygen atom of the methoxy group in **4** has no significant contact to the Ga atoms.

The GaC1C2 planes are almost perpendicular to the Ga$_2$N$_2$C$_2$ planes in compounds **2** and **4** (angles between the normals of the planes: 83.1 and 89.7°, respectively). In compound **6** (R = *tert*-butyl) with no significant Ga–N interaction this angle is 73.5°. The phenyl rings do not lie in the Ga$_2$N$_2$C$_2$ planes, and the angles between the normals of the planes amount ot 56.9° in **4** and 43.3° in **2**. For the aluminium derivative (R = phenyl) we found an angle of 49.2°[8]. The flattening of the molecule on going to the unsubstituted phenyl derivative seems, however, not to be strong enough to account for the deep red color and the unique UV/Vis spectrum of **2** by a delocalization of the π electrons over the diazabutadiene and the aryl system.

The terminal Ga–C bonds are shorter than the bonds of the gallium atoms to the diazabutadiene carbon atoms and amount on average to 200.2 (**2**), 200.7 (**4**), and 201.1 (**6**) pm; they are in the same region like the Ga–C bond lengths in the digallane(4) starting compound **1** (199.6 pm)[1].

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Experimental

All procedures were carried out under purified argon in dried solvents (*n*-hexane and *n*-pentane with LiAlH$_4$, benzene with Na/benzophenone). Compound **1** was prepared as described in ref.[1]; *tert*-butyl isocyanide from Aldrich was dried with molecular sieves; phenyl, *o*-methoxyphenyl, *p*-methoxyphenyl, and *o*-methylphenyl isocyanide were synthesized as described in ref.[16].

Synthesis of **2** *(R = Phenyl):* 0.98 g (1.26 mmol) of **1** was dissolved in 40 ml of *n*-pentane, and the solution was cooled to –60 °C. A solution of 0.27 g (2.52 mmol) of phenyl isocyanide in 10 ml of *n*-pentane was added in 15 min. The mixture was warmed to room temp. and stirred for 24 h. The color changed from yellow to dark red. The solvent was evaporated and the residue crystallized from *n*-pentane. Yield: 1.1 g of **2** (89%); dark red, fairly air-stable crystals, m.p. (closed capillary, argon) 161 °C. – ^{1}H NMR (C$_6$D$_6$, 300 MHz, 300 K): δ = 7.40 (4H, pseudo-d, *o*-H of phenyl), 7.19 (4H, pseudo-t, *m*-H of phenyl), 7.01 (2H, pseudo-t, *p*-H of phenyl), 0.22 (72H, SiMe$_3$), 0.09 (4H, GaCH). – ^{1}H NMR ([D$_8$]toluene, 500 MHz, 203 K): δ = 0.29 and 0.25 (each 36H, SiMe$_3$), 0.11 (4H, GaCH). – ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 223.7 (GaC$_2$Ga), 150.1 (*i*-C of phenyl), 129.2 and 122.4 (*o*- and *m*-C of phenyl), *p*-C signal not detected, 12.5 (GaCSi$_2$), 4.7 (SiMe$_3$). – IR (paraffin, CsBr): $\tilde{\nu}$ = 1576 cm^{-1} m (phenyl); 1462 vs, 1377 vs (paraffin); 1304 w, 1262 s, 1248 s δCH$_3$; 1200 w, 1167 vw, 1153 vw, 1121 vw, 1072 w νCC, νNC; 1015 s, 1003 sh δCH; 968 m, 951 w, 843 vs, 766 s, 751 s, 721 vs ρCH$_3$(Si); 669 s ν_{as}SiC; 619 w ν_sSiC; 580 vw, 548 vw, 536 vw, 506 w, 490 m, 469 m νGaC; 366 w, 346 vw δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 210 nm (4.4), 255 (3.9, sh), 355 (3.7), 523 (3.5). – C$_{42}$H$_{86}$Ga$_2$N$_2$Si$_8$ (983.3): calcd. C 51.3, H 8.8, Ga 14.2; found C 51.0, H 8.8, Ga 14.3. – Mol. mass: 952 (cryoscopically in benzene).

Synthesis of **3** *(R = p-Methoxyphenyl):* 22.1 ml of a 0.078 M solution of *p*-methoxyphenyl isocyanide in *n*-hexane (1.72 mmol) was added dropwise to a solution of 0.67 g (0.86 mmol) of **1** in

40 ml of *n*-pentane at −60 °C. The mixture was warmed to room temp. and stirred for 20 h. The color changed from yellow to red. The solvent was evaporated and the residue crystallized from *n*-pentane. Yield: 0.74 g of **3** (82%); orange-red, fairly air-stable crystals, m.p. (closed capillary, argon) 133−135 °C (dec.). − ^{1}H NMR (C_6D_6, 300 MHz, 300 K): δ = 7.46 (4H, d, *J* = 8.8 Hz, *o*-H of phenyl), 6.87 (4H, d, *J* = 8.8 Hz, *m*-H of phenyl), 3.33 (6H, OMe), 0.26 (72H, $SiMe_3$), 0.09 (4H, GaCH). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 222.4 (GaC_2Ga), 160.2 (*i*-C of phenyl), 143.2 (*p*-C of phenyl), 124.0 and 114.4 (*o*- and *m*-C of phenyl), 54.9 (OMe), 11.9 ($GaCSi_2$), 4.8 ($SiMe_3$). − IR (paraffin, CsBr): $\tilde{\nu}$ = 1609 cm^{-1} w (phenyl); 1501 w νC=N; 1462 vs, 1377 vs (paraffin); 1300 w, 1248 s δCH_3; 1157 w, 1106 vw, 1074 vw νCC, νNC; 1030 m, 1017 m δCH; 964 w, 934 w, 843 vs, 774 s, 754 s, 721 s ρCH_3(Si); 669 m ν_{as}SiC; 629 w ν_sSiC; 556 vw, 519 vw, 502 vw, 475 w, 462 w νGaC; 385 vw δSiC. − UV (*n*-hexane): λ_{max} (lg ε) = 210 nm (4.4), 290 (3.8), 385 (4.0). − $C_{44}H_{90}Ga_2N_2O_2Si_8$ (1043.3): calcd. C 50.7, H 8.7, Ga 13.4; found C 50.2, H 8.8, Ga 13.3. − Mol. mass: 965 (cryoscopically in benzene).

Synthesis of **4** *(R = o-Methoxyphenyl):* 4.2 ml of a 0.34 M solution of *o*-methoxyphenyl isocyanide in *n*-hexane (1.42 mmol) was added to a solution of 0.55 g (0.71 mmol) of **1** in 30 ml of *n*-hexane at −60 °C. The mixture was warmed to room temp. and stirred for 10 h. The color changed from yellow to red. The solvent was evaporated and the residue crystallized from *n*-pentane. Yield: 0.60 g of **4** (81%); orange-red, fairly air-stable crystals, m.p. (closed capillary, argon) 138−141 °C (dec.). − ^{1}H NMR (C_6D_6, 300 MHz; 300 K): δ = 7.18 (2H, dd, *J* = 1.7 and 8.7 Hz, 6-H of phenyl), 7.04 and 6.88 (each 2H, pseudo-t, 4- and 5-H of phenyl), 6.51 (2H, dd, *J* = 1.2 and 8.1 Hz, 3-H of phenyl), 3.40 (6H, OMe), 0.34 (4H, GaCH), 0.22 (72H, $SiMe_3$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 223.9 (GaC_2Ga), 152.0 (*i*-C of phenyl), 140.0 (C-2 of phenyl), 128.6, 122.4, 120.5, and 111.0 (phenyl), 54.4 (OMe), 10.9 ($GaCSi_2$), 4.7 ($SiMe_3$). − IR (parafin, CsBr): $\tilde{\nu}$ = 1593 cm^{-1} w (phenyl); 1487 w νC=N; 1462 vs, 1377 vs (paraffin); 1302 w, 1283 w, 1256 s, 1244 s δCH_3; 1193 vw, 1175 vw, 1161 w, 1115 w, 1049 w νCC, νNC; 1034 w, 1017 m δCH; 968 m, 926 vw, 843 vs, 779 s, 745 s, 721 s ρCH_3(Si); 681 sh, 669 m ν_{as}SiC; 621 vw ν_sSiC; 577 vw, 547 vw, 520 vw, 490 m, 473 m νGaC; 407 vw, 375 vw δSiC. − UV (*n*-hexane): λ_{max} (lg ε) = 215 nm (4.8), 255 (4.6), 280 (4.2, sh), 370 (4.0). − $C_{44}H_{90}Ga_2N_2O_2Si_8$ (1043.3): calcd. C 50.7, H 8.7, Ga 13.4; found C 50.5, H 8.7, Ga 13.1.

Synthesis of **5** *(R = o-Methylphenyl):* These reactions must be stopped, when about 50% of the starting compound **1** is consumed. A longer reaction time leads to complete decomposition with the formation of a mixture of many unknown products. An excess of the isocyanide accelerates both the formation of **5** and the decomposition reaction. A typical reaction proceeds as follows: 2.1 ml (1.47 mmol) of a 0.71 M solution of *o*-methylphenyl isocyanide in *n*-hexane was added to a solution of 0.57 g (0.735 mmol) of **1** in 40 ml of *n*-pentane at −60 °C. The mixture was warmed to room

Table 1. Crystal data and data collection parameters for **2**, **4**, and **6**[19]

	2	**4**	**6**
Formula	$C_{42}H_{86}Ga_2N_2Si_8$	$C_{44}H_{90}Ga_2N_2O_2Si_8$	$C_{38}H_{94}Ga_2N_2Si_8$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c; No. 15 [17]	C2/c; No. 15 [17]	$P2_1/n$; No. 14 [17]
Z	4	4	2
Temperature (K)	293(2)	293(2)	293(2)
$d_{calc.}$ (g/cm^3)	1.130	1.146	1.150
a (pm)	1238.00(9)	2306.7(1)	1267.2(3)
b (pm)	1804.0(1)	2020.23(9)	1220.1(2)
c (pm)	2604.4(2)	1328.12(5)	1778.4(4)
β (°)	96.59(1)	102.248(5)	97.75(3)
V (10^{-30} m^3)	5778.1(7)	6048.3(4)	2725(1)
μ (mm^{-1})	1.125	1.081	1.190
Crystal size (mm)	0.65 x 0.53 x 0.27	0.46 x 0.55 x 0.87	1.00x0.91x0.42
Four-cycle diffractometer	AED 2	AED 2	AED 2
Radiation: Mo-K_α, graphite monochromator			
Reciprocal space	$0 \le h \le 15$	$0 \le h \le 28$	$0 \le h \le 16$
	$0 \le k \le 22$	$0 \le k \le 24$	$0 \le k \le 15$
	$-32 \le l \le 31$	$-16 \le l \le 16$	$-22 \le l \le 22$
Scan mode	ω−2Θ	ω−2Θ	ω−2Θ
Independent reflections	5687	5937	5966
Number of reflections with F > 4 σ (F)	4103	4345	4664
Program: SHELXTL, SHELXL-93 [18]; solution by direct methods; full matrix refinement with all independent structure factors			
Parameters	276	275	241
$R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$ (F > 4 σ (F))	0.049	0.053	0.0411
$wR^2 = \{\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.083	0.109	0.0845
Max. residual (10^{30} e/m^3)	0.382	1.617	0.815
Min. residual (10^{30} e/m^3)	-0.227	-0.566	-0.267

temp. and stirred for 6 h. The color changed from yellow to red. The solvent was evaporated and the residue crystallized from *n*-pentane yielding **5** as the most insoluble component. Yield: 0.30 g of **5** (81%, with respect to 50% conversion); orange-red, fairly air-stable crystals, m.p. (closed capillary, argon) 176–178 °C (dec.). – ^{1}H NMR (C_6D_6, 300 MHz, 300 K): δ = 7.11 and 7.01 (m, phenyl), 2.45 (6H, Me phenyl), 0.29 (4H, GaCH), 0.20 (72H, $SiMe_3$). – ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 218.1 (GaC_2Ga), 150.9 (*i*-C of phenyl), 131.5, 131.2 and 120.4 (phenyl), 20.3 (Me of phenyl), 13.5 ($GaCSi_2$), 4.8 ($SiMe_3$). – IR (paraffin, CsBr): ṽ = 1600 cm^{-1} w, br., 1560 vw (phenyl); 1462 vs, 1377 vs (paraffin); 1306 w, 1258 s, 1248 s δCH_3; 1185 vw, 1169 vw, 1155 vw, 1111 vw, 1047 vw, 1028 w νCC, νNC; 1003 m δCH; 937 w, 843 vs, 777 m, 752 s, 721 s $\rho CH_3(Si)$; 669 m $\nu_{as}SiC$; 621 vw $\nu_s SiC$; 577 vw, 540 vw, 520 vw, 484 m, 461 m νGaC; 395 vw, 362 vw δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 225 nm (3.7), 250 (3.8), 325 (sh, 3.3). – $C_{44}H_{90}Ga_2N_2Si_8$ (1011.3): calcd. C 52.3, H 9.0, Ga 13.8; found C 51.9, H 9.1, Ga 13.4.

Synthesis of **6** *(R = tert-Butyl):* 0.46 g (0.59 mmol) of digallane(4) **1** was dissolved in 7 ml *tert*-butyl isocyanide, and the solution was stirred at room temp. for 30 h. The solvent was evaporated and the residue recrystallized from *n*-pentane. Yield: 0.41 g of **6** (74%); yellow, fairly air-stable crystals, m.p. (closed capillary, argon) 180–182 °C. – ^{1}H NMR ([D$_8$]toluene, 300 MHz, 300 K): δ = 1.39 (18H, CMe_3), 0.35 and 0.23 (each 36H, $SiMe_3$), 0.15 (4H, GaCH). – ^{1}H NMR ([D$_8$]toluene, 500 MHz, 350 K): δ = 1.39 (18H, CMe_3), 0.27 (72H, $SiMe_3$), 0.15 (4H, GaCH). – ^{13}C NMR ([D$_8$]toluene, 75.5 MHz): δ = 211.2 (GaC_2Ga), 61.8 (*C*Me$_3$), 30.6 (C*Me*$_3$); 14.1 ($GaCSi_2$), 5.4 ($SiMe_3$). – IR (paraffin, CsBr): ṽ = 1304 cm^{-1} w, 1258 m, 1256 s δCH_3; 1196 vw, 1169 vw, 1155 vw νCC, νNC; 1013 m δCH; 964 m, 841 vs, 770 m, 754 m, 721 s $\rho CH_3(Si)$; 669 m $\nu_{as}SiC$; 638 vw, 621 vw, 611 vw $\nu_{as}SiC$; 559 vw, 511 vw, 483 w, 469 m νGaC; 384 vw δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 225 nm (4.0), 400 (1.9). – $C_{38}H_{94}Ga_2N_2Si_8$ (943.3): calcd. C 48.4, H 10.0, Ga 14.8; found C 48.0, H 9.9, Ga 14.9.

Crystal Structure Determinations: Single crystals of the compounds **2**, **4**, and **6** were grown from saturated pentane solutions by slow cooling to 0 °C. Details about the crystal structure determinations are given in Table 1[19].

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[19] Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405006 (**2**), -405007 (**4**), and -405008 (**6**).

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