

Di(μ -acetato)dialkyldigallium as starting compound for the facile syntheses of digallium derivatives containing bridged or terminally co-ordinated Ga–Ga single bonds

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Di(μ -acetato)dialkyldigallium $\text{Ga}_2\text{R}_2(\mu\text{-O}_2\text{CCH}_3\text{-O},\text{O}')_2$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] **2** was easily obtained in an almost quantitative yield by the reaction of $\text{R}_2\text{Ga-GaR}_2$ **1** with acetic acid. As shown by a crystal structure determination, the short Ga–Ga bond of **2** [237.85(3) pm] is bridged by two acetato groups. This compound appeared to be a very suitable starting material for the facile syntheses of further derivatives containing Ga–Ga bonds, when treated with appropriate lithium compounds. Thus **1** was re-formed in a high yield by the reaction of **2** with two equivalents of $\text{LiCH}(\text{SiMe}_3)_2$ and the precipitation of lithium acetate. Treatment with two equivalents of lithium diphenyltriazenide yielded the bis(triazenido)digallium derivative **3**, which before was obtained in our group only in an inseparable mixture with a monogallium product. The reaction with lithium diphenyltriazenide in an equimolar ratio gave a product **4** in which the Ga–Ga bond [236.75(4) pm] was unsymmetrically bridged by one triazenido and one acetato group and in which the gallium atoms adopted a chiral co-ordination sphere. A similar compound **5** was obtained with lithiated diphenylbenzamidine. Furthermore, the reaction of **1** with pentafluorophenol was reinvestigated, which did not yield the dimeric dialkylgallium fluoride, as recently reported by our group, but a dialkylgallium phenolato derivative. The latter is monomeric even in the solid state and has short Ga–O bonds (184.3 pm on average). The dialkylgallium fluoride was obtained by treatment of **1** with the hydrogen fluoride–pyridine complex.

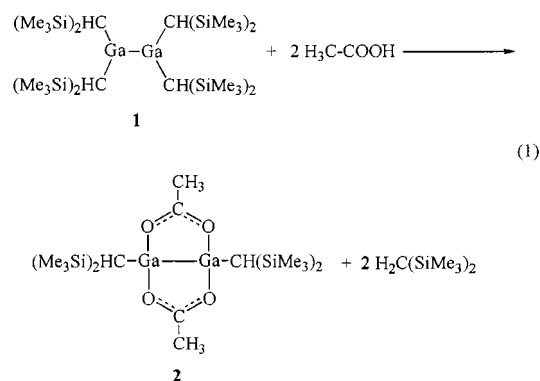
The dielement compounds $\text{R}_2\text{E-ER}_2$ with $\text{E} = \text{Al}, \text{Ga}, \text{In}$ and $\text{R} = \text{CH}(\text{SiMe}_3)_2$ were obtained by our group about ten years ago.^{1–3} They were the first completely characterized organoelement compounds reported,⁴ which contained Al–Al, Ga–Ga, and In–In single bonds, and showed a remarkable thermal stability in solution and in the solid state. Our systematic investigations into the reactivity of this new class of compounds revealed fascinating chemical properties, and up to now we have observed six different types of reaction.⁵ One of these is the substituent exchange reaction, which by the treatment of the dielement compounds with protonic acids and the release of bis(trimethylsilyl)methane gives novel dielement species. These reactions succeeded, however, only when the digallium derivative was employed.^{6–8} In contrast, cleavage of the Al–Al or In–In bonds was observed whenever we treated the dialuminium or diindium compounds with a proton donor.^{8,9} Also the successful reactions of the digallium compound are subjected to some important restrictions. A chelating group must be introduced into the product to stabilize the Ga–Ga bond, and very weak acids reacted by an at least partial cleavage of the Ga–Ga bonds. The best results with the formation of the digallium products in almost quantitative yield were obtained by the reaction of **1** with two equivalents of carboxylic acids,⁶ and even macrocyclic compounds with up to 22 atoms in their heterocycles were isolated in high yields by the application of bifunctional dicarboxylic acids.¹⁰ All these derivatives have the Ga–Ga bonds bridged by two carboxylato ligands, which causes very short Ga–Ga distances below 240 pm. Beside formation of the quite interesting macrocycles we hoped to use those dicarboxylato compounds as starting materials for the syntheses of further bridged or terminally co-ordinated digallium derivatives. Reactions with appropriate lithium alkyls or amides should proceed by the precipitation of lithium carboxylates, which are almost insoluble in non-polar solvents like *n*-pentane. Novel products containing Ga–Ga bonds may be formed by this method in high and reproducible yields, which due to the cleavage reaction described above were not accessible by the treat-

ment of **1** with very weak or non-chelating proton donors. These compounds should give a better insight into the reasons which determine the terminal or bridging co-ordination of the Ga–Ga bonds by systematically changing the bite of the chelating ligands. The diacetato compound seemed to be the most suitable derivative, because of its low steric shielding and the formation of the almost insoluble lithium acetate upon reaction with lithium reagents. Its synthesis and some of its reactions are described here. Furthermore, we report on a reinvestigation of the reaction of **1** with pentafluorophenol.⁸

Results

Synthesis and crystal structure of di(μ -acetato)dialkyldigallium **2**

Compound **2** was synthesized according to the previously published method⁶ by treatment of digallane(**1**) with two equivalents of pure acetic acid, eqn. (1). The reaction started at low



temperature (–25 °C), and by the release of bis(trimethylsilyl)methane, **2** was formed and isolated after recrystallization in a yield of 81%. All groups gave singlets in the ¹H and ¹³C NMR spectra. The resonances of the hydrogen and carbon atoms of

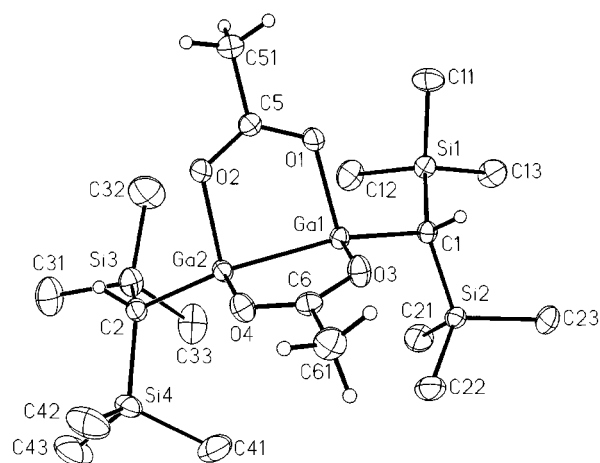


Fig. 1 Molecular structure and numbering scheme of compound **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity.

the methine groups attached to gallium were shifted to high field (δ -0.29 and 4.4 , respectively), which is in accordance with the enhancement of the co-ordination number at the gallium atoms from three to four.^{6–8,10,11}

The molecular structure of compound **2** is depicted in Fig. 1. It possesses a Ga–Ga single bond bridged by two acetato groups. Owing to the small bite of the co-ordinating oxygen atoms of 224.2 pm, the Ga–Ga distance [$237.85(3)$ pm, Table 1] is shortened in comparison to that of the starting compound **1** (254.0 pm).² Similar short distances have been observed in other bridged digallium derivatives.^{6,8,10} The C–Ga–Ga–C group is almost linear and has Ga–Ga–C angles of 156.9° on average. The Ga–O bonds are approximately perpendicular to the Ga–Ga bond, as indicated by Ga–Ga–O angles of 88.0° , and the angle between the normals to the $\text{Ga}_2\text{O}_2\text{C}$ planes including the chelating ligands and the Ga–Ga bond is 85.5° , similarly to those observed before for other digallium compounds with bridging chelating ligands. Thus, the bonding situation may simply be described by the classic picture of sp -hybridized gallium atoms, and both p orbitals perpendicular to the Ga–Ga bond interact with the oxygen atoms of the bridging groups. Quantum-chemical calculations[†] on a formate bridged derivative verify this simple model, and that orbitals of the gallium atoms, which are used for the formation of the Ga–O bonds, have a strong p character ($sp^{6.1}$). The largest contribution of the gallium s orbital was calculated for the Ga–C molecular orbital ($sp^{1.4}$), while the orbitals of the Ga–Ga bond have a higher p character ($sp^{2.4}$). For comparison, also a molecule with terminally co-ordinated carboxylato groups was calculated by quantum chemical methods.[†] As the most remarkable result, this configuration was found to be 117 kJ mol⁻¹ more unfavorable than the molecule with bridging carboxylato groups. An important contribution to this higher energy is made by the deformation of the OCO angle from 124.7° in the bridged molecule to 116.7° for the molecule with terminally co-ordinated gallium atoms (calculated for free HCO_2^- : 129.9°). Accordingly, even the carboxylates of the trivalent elements aluminium, gallium, and indium often form dinuclear, bridged compounds, instead of mononuclear derivatives with the central atom co-ordinated by both oxygen atoms of only one ligand.^{9,13}

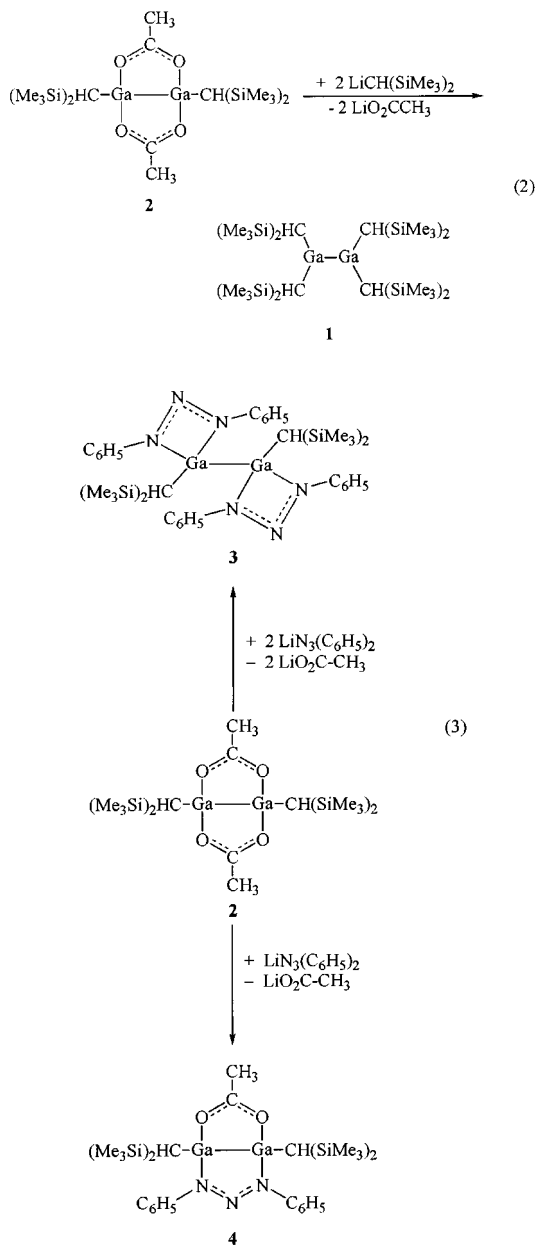
[†] Selected bond lengths (pm) and angles ($^\circ$) calculated by quantum chemical methods¹² for the digallium compounds $\text{R}_2\text{Ga}_2(\text{O}_2\text{CH})_2$ with bridging and terminally co-ordinating (in brackets) formate ligands (R = methyl): Ga–Ga 251.4 (252.7), Ga–O 202.1 (209.5) and Ga–C 195.9 (196.5); Ga–Ga–C 158.5 (134.3), O–Ga–O 94.3 (58.0), Ga–Ga–O 86.9 (109.4) and O–C–O 124.7 (116.7). Geometry optimizations at the B3LYP/LANL2DZ level of theory; NBO population analysis performed with the GAUSSIAN94 program system.

Table 1 Selected bond lengths (pm) and angles ($^\circ$)

Compound 2			
Ga(1)–C(1)	195.5(2)	C(1)–Ga(1)–Ga(2)	158.37(5)
Ga(1)–O(1)	201.5(1)	C(2)–Ga(2)–Ga(1)	155.52(5)
Ga(1)–O(3)	201.4(1)	C(5)–O(1)–Ga(1)	119.7(1)
Ga(1)–Ga(2)	237.85(3)	C(5)–O(2)–Ga(2)	119.6(1)
Ga(2)–C(2)	196.3(2)	C(6)–O(3)–Ga(1)	120.0(1)
Ga(2)–O(2)	200.9(1)	C(6)–O(4)–Ga(2)	118.9(1)
Ga(2)–O(4)	201.6(1)	O(1)–Ga(1)–Ga(2)	87.89(3)
O(1)–C(5)	126.3(2)	O(1)–C(5)–O(2)	124.5(2)
O(2)–C(5)	126.7(2)	O(2)–Ga(2)–Ga(1)	88.12(3)
O(3)–C(6)	126.5(2)	O(2)–Ga(2)–O(4)	93.76(6)
O(4)–C(6)	127.3(2)	O(3)–Ga(1)–Ga(2)	87.61(3)
		O(1)–Ga(1)–O(3)	92.50(6)
		O(3)–C(6)–O(4)	124.4(2)
		O(4)–Ga(2)–Ga(1)	88.59(3)
Compound 4			
Ga(1)–C(1)	196.4(2)	C(1)–Ga(1)–Ga(2)	151.82(7)
Ga(1)–O(1)	202.5(2)	C(2)–Ga(2)–Ga(1)	153.44(7)
Ga(1)–N(1)	206.4(2)	C(5)–O(1)–Ga(1)	120.2(2)
Ga(1)–Ga(2)	236.75(4)	C(5)–O(2)–Ga(2)	117.5(2)
Ga(2)–C(2)	197.2(2)	O(1)–Ga(1)–N(1)	90.89(7)
Ga(2)–O(2)	202.4(2)	O(1)–Ga(1)–Ga(2)	87.12(5)
Ga(2)–N(3)	206.0(2)	O(1)–C(5)–O(2)	124.9(2)
O(1)–C(5)	126.2(3)	O(2)–Ga(2)–N(3)	91.19(7)
O(2)–C(5)	126.9(3)	O(2)–Ga(2)–Ga(1)	89.25(5)
N(1)–N(2)	129.7(3)	N(1)–Ga(1)–Ga(2)	88.59(5)
N(2)–N(3)	130.4(3)	N(3)–Ga(2)–Ga(1)	87.06(6)
		N(1)–N(2)–N(3)	116.8(2)
		N(2)–N(1)–Ga(1)	122.7(1)
		N(2)–N(3)–Ga(2)	124.0(2)
Compound 5			
Ga(1)–C(1)	196.9(2)	C(1)–Ga(1)–Ga(2)	155.34(7)
Ga(1)–N(1)	201.4(2)	C(2)–Ga(2)–Ga(1)	152.50(7)
Ga(1)–O(1)	204.9(2)	C(5)–O(1)–Ga(1)	119.7(2)
Ga(1)–Ga(2)	236.67(4)	C(5)–O(2)–Ga(2)	119.0(1)
Ga(2)–C(2)	196.0(2)	C(6)–N(1)–Ga(1)	120.2(1)
Ga(2)–N(2)	202.0(2)	C(6)–N(2)–Ga(2)	120.6(1)
Ga(2)–O(2)	202.5(2)	O(1)–Ga(1)–Ga(2)	87.10(5)
C(5)–O(1)	126.6(3)	O(2)–Ga(2)–Ga(1)	89.18(5)
C(5)–O(2)	125.7(3)	O(2)–C(5)–O(1)	124.9(2)
C(6)–N(1)	132.8(3)	N(1)–Ga(1)–Ga(2)	89.50(5)
C(6)–N(2)	132.7(3)	N(1)–Ga(1)–O(1)	92.68(7)
		N(2)–Ga(2)–Ga(1)	88.83(5)
		N(2)–Ga(2)–O(2)	93.44(7)
		N(2)–C(6)–N(1)	120.8(2)
Compound 8			
Molecule 1			
Ga(1)–O(1)	184.4(2)	O(1)–Ga(1)–C(1)	105.0(1)
Ga(1)–C(1)	193.3(3)	O(1)–Ga(1)–C(2)	114.6(1)
Ga(1)–C(2)	194.6(3)	C(1)–Ga(1)–C(2)	140.2(1)
O(1)–C(14)	132.0(4)	C(14)–O(1)–Ga(1)	130.8(2)
Molecule 2			
Ga(1)–O(2)	184.1(2)	O(2)–Ga(2)–C(3)	113.9(1)
Ga(2)–C(4)	193.7(3)	O(2)–Ga(2)–C(4)	105.3(1)
Ga(2)–C(3)	194.6(3)	C(3)–Ga(2)–C(4)	140.7(1)
O(2)–C(24)	131.8(4)	C(24)–O(2)–Ga(2)	132.4(2)

Reactions of compound **2** with lithium compounds

First of all we carried out two reactions, which led to the formation of known compounds. In these and most of the following reactions, **2** was not isolated and purified by recrystallization, but treated *in situ* with the corresponding lithium reagent. Treatment of **2** with two equivalents of bis(trimethylsilyl)methylolithium¹⁴ gave, upon precipitation of lithium acetate, the tetraalkyldigallane(**4**) **1** in an overall yield of 51% based on the starting amount of **1**, eqn. (2). Although a trivial reaction, it showed that compound **2** may be suitable for the synthesis of unknown tetraalkyldigallanes(**4**), containing different alkyl substituents attached to their gallium atoms. In a second reaction, **2** was treated with lithium diphenyltriazene in the molar



ratio of 1 to 2, eqn. (3), which gave the corresponding orange bis(diphenyltriazenido) derivative **3** under mild conditions at room temperature in a yield of 86% based on **1**. Compound **3** has been obtained before by the reaction of **1** with the weak acid diphenyltriazene.⁷ However, a mixture of products was formed, which contained the mononuclear dialkyltriazenido gallium compound beside **3** and could not be separated by repeated recrystallization. Single crystals were isolated by manual sorting under a microscope, and the crystal structure of **3**⁷ showed, that, in contrast to the carboxylato derivatives, the chelating triazenido ligands occupied terminal positions at the Ga–Ga bond. We supposed that the smaller bite of the triazenido groups (209 pm) in comparison with that of the carboxylato ligand (224 pm) prevented the occupation of a bridging position. Furthermore, the different co-ordination behavior may be caused by the approach of the phenyl groups of the nitrogen atoms co-ordinated to one gallium atom, which should occur in the typical perpendicular arrangement of the bridging ligands and should result in a steric repulsion. Quantum-chemical calculations showed that the triazenido ligand is more suitable for a terminal co-ordination.¹² The angle calculated for the free triazenido anion is 114.6°, which is intermediate between that observed for the bridging (116.8°, see below) and terminally co-ordinated triazenido group (105.9°). The energy

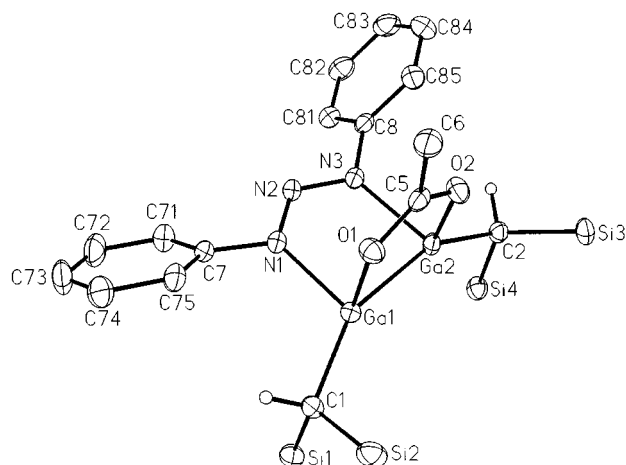


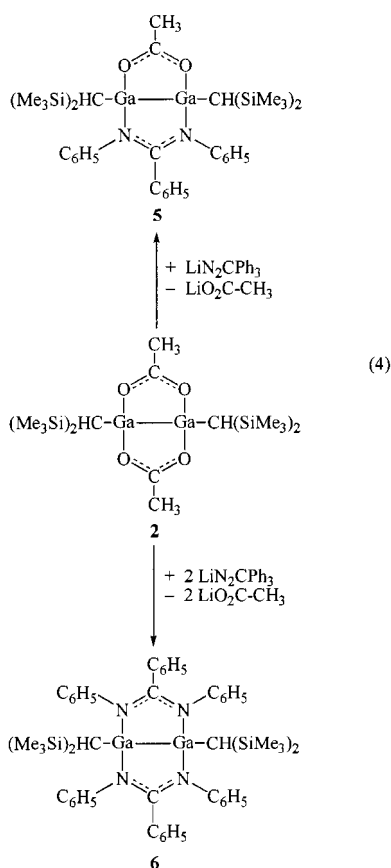
Fig. 2 Molecular structure and numbering scheme of compound **4**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups of the SiMe₃ substituents and the hydrogen atoms of the phenyl groups and the acetato ligand are omitted for clarity.

difference between terminal and bridging triazenido ligands was calculated to be only 13 kJ mol⁻¹.

It was of particular interest now whether we could succeed in replacing only one of the acetato groups, in order to obtain digallium compounds with different chelating ligands. Such derivatives are useful as starting materials for the syntheses of further products bearing different chelating groups and contain gallium atoms in a chiral environment. Therefore, we treated **2** with lithium diphenyltriazene in a stoichiometric 1 to 1 ratio at low temperature (–75 °C) and allowed the mixture to stir at room temperature for 15 h. After recrystallization of the product from *n*-pentane compound **4** was isolated in a yield of 80%, eqn. (3). The characterization by NMR spectroscopy and the crystal structure determination showed that indeed only one of the acetato groups was replaced by a triazenido ligand and a mixed (μ-acetato)dialkyl(μ-diphenyltriazenido)digallium compound was formed (Fig. 2). In contrast to the bis(triazenido) compound **3** with an exclusively terminal arrangement of the substituents, the triazenido group in **4** occupies a bridging position, which may be forced by the high preference of the carboxylato group for bridging the Ga–Ga bond, as discussed above. The Ga–Ga bond length is 236.75(4) pm (Table 1), which is similar to those usually observed in dicarboxylato bridged digallium compounds. Bond lengths and angles of the acetato part of the molecule are quite similar to those observed before, but owing to the different co-ordination modes of the triazenido ligands in compound **3** and **4** the N–N–N angle of the bridging ligand is enlarged to 116.8(2)° compared to 105.9(1)° in terminally co-ordinated **3**. The Ga–N and N–N distances differ only slightly (**3**: 205.0 and 131.2 pm; **4**: 206.2 and 130.1 pm). The enlargement of the angle at the central nitrogen atom leads to a larger bite between both co-ordinating nitrogen atoms of 221.6 pm in comparison to 209 pm in compound **3**, which is quite similar to the bite of the acetato group (224.4 pm). Both gallium atoms have a chiral co-ordination sphere, which results in a *R* (Ga1) and *S* configuration (Ga2), but the whole molecule is non-chiral due to a mirror plane perpendicular to the Ga–Ga bond and possesses a *meso* structure. Once again, the molecule adopts the typical configuration of these bridged digallium compounds. The C–Ga–Ga–C group is almost linear (angle Ga–Ga–C 152.6°), and the bridging groups are almost perpendicular to one another (angle between the normals to the planes Ga₂O₂C and Ga₂N₃: 91.0°). The chiral environment of the Ga atoms in **4** is reflected by the results of the NMR spectroscopic characterization. Only one resonance was observed in the ¹H and ¹³C NMR spectra for the methine hydrogen and methine carbon atoms, but the trimethylsilyl groups of the CH(SiMe₃)₂ substituents became

diastereotopic and gave two resonances of equal intensity in each spectrum.

The suitability of **2** as a starting compound for the synthesis of bridged or terminally co-ordinated products was further investigated by the reaction with deprotonated diphenylbenzamidine. An equimolar ratio of the components gave the mixed (acetato)(benzamidinato)digallium compound **5**, eqn. (4),



which has the Ga–Ga bond bridged by chelating acetato and benzamidinato groups. As in compound **4**, the trimethylsilyl groups become diastereotopic and gave two resonances in the ^1H and ^{13}C NMR spectra. The signal of the methine protons is shifted to high field ($\delta -0.51$), which is characteristic for bis-(trimethylsilyl)methyl compounds with four-co-ordinated Ga atoms.¹¹ The molecular structure is quite similar to that of **4** with two chiral molecular halves (Fig. 3). The Ga–Ga bond is short [236.67(4) pm, Table 1], and the angles Ga–Ga–C approach linearity (153.9°). The angle between the planes $\text{Ga}_2\text{O}_2\text{C}$ and $\text{Ga}_2\text{N}_2\text{C}$ is 93.1°, which probably due to the growing steric interaction between the bridging ligands is larger than in the diacetato compound **2** (85.5°) or, to a smaller extent, in the mixed acetato triazenido compound **4** (91.0°). While the Ga–O distances (203.7 pm) are similar to those of compound **4** (202.4 pm), the Ga–N distances are shorter (201.7 compared to 206.2 pm in **4**), which may indicate less steric stress in the heterocycle containing the chelating benzamidinato group owing to its longer bonds and the enlarged angle at its central carbon atom (**4**: NNN: 130.1 pm and 116.8°. **5**: NCN: 132.8 pm and 120.8°). The separation between the co-ordinating atoms is 223.6 (O1...O2) and 230.9 pm (N1...N2).

The second acetato group was replaced by the reaction of compound **2** with lithium benzamidinate in a molar ratio of 1 to 2 in boiling *n*-hexane over a period of 15 h, eqn. (4). Although the product **6** was formed almost quantitatively, we did not succeed in purification of the oily residue by recrystallization from many different solvents. Thus the characterization was restricted to the ^1H NMR spectrum of the crude product. Owing to the molecular symmetry with a mirror plane parallel

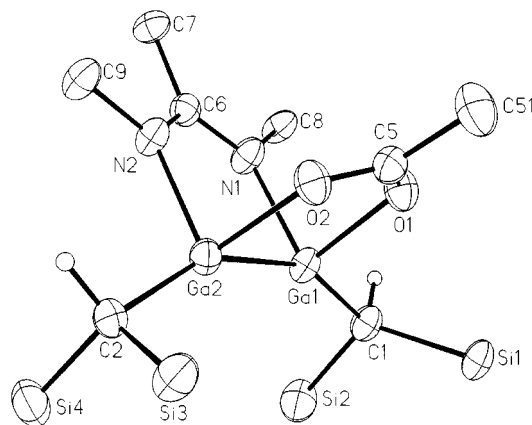


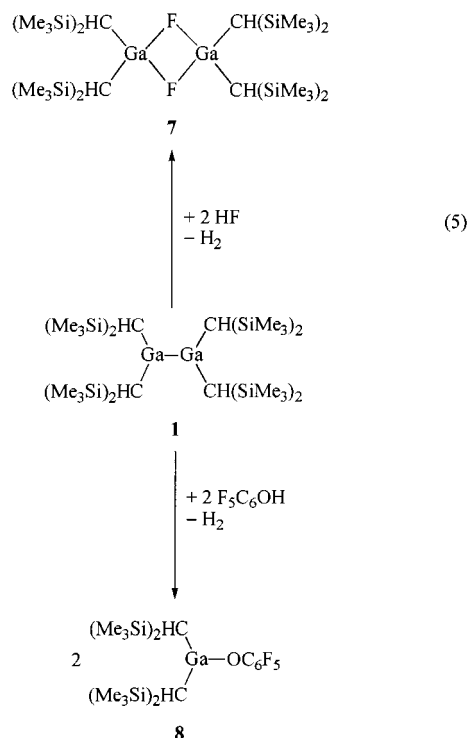
Fig. 3 Molecular structure and numbering scheme of compound **5**; the thermal ellipsoids are drawn at the 40% probability level; methyl and phenyl groups (with the exception of the acetato group and of the *ipso* carbon atoms) are omitted for clarity.

to the Ga–Ga bond, the trimethylsilyl groups are equivalent and only one singlet is observed.

Reaction of compound **1** with pentafluorophenol and hydrogen fluoride

Pentafluorophenol was one of the proton donors, employed in the course of our systematic investigations into the reactivity of digallane(**4**) **1**. As recently published by our group, we isolated almost quantitatively the corresponding cleavage product dialkylgallium fluoride **7**, a dimer containing Ga–F bridges.⁸ This fluoride is a very useful starting compound for secondary reactions, but upon employing new charges of pentafluorophenol only mixtures of two compounds were obtained with **7** as one component. A thorough reinvestigation of this reaction showed that **7** was not formed by the rather implausible cleavage of a C–F bond but by an impurity in commercially available pentafluorophenol, which was not completely removed by a single sublimation step.

The dialkylgallium fluoride **7** was obtained in a reproducible yield of 67% and in high purity when we treated the tetraalkyldigallane(**4**) **1** with the adduct of hydrogen fluoride and pyridine, eqn. (5). The yellow color of **1** disappeared after



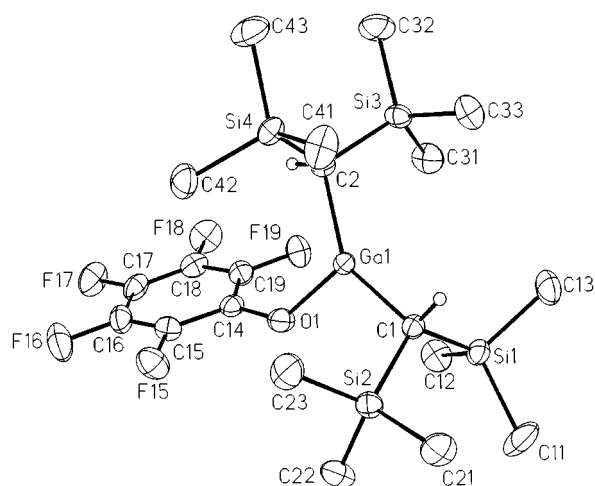


Fig. 4 Molecular structure and numbering scheme of compound **8**; only one of the two independent molecules is shown; the thermal ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity.

1.5 h of stirring at room temperature. Compound **7** is a dimer in benzene solution as found by the cryoscopic determination of its molar mass and in the solid state as shown by the crystal structure.⁸

The reaction of compound **1** with pentafluorophenol, which for purification was sublimed twice *in vacuo* prior to use, afforded a mononuclear gallium pentafluorophenolate **8** by cleavage of the Ga–Ga bond as expected for non-chelating protonic acids (see above). The product was isolated after recrystallization from *n*-pentane in a yield of 68%, eqn. (5). It is a low melting solid (78 °C), which is monomeric in benzene. In the NMR spectra, the methine carbon and hydrogen atoms show resonances at δ 16.6 and 0.15, respectively, which is in the characteristic range of bis(trimethylsilyl)methyl compounds with three-co-ordinated Ga atoms.^{11,15} Remarkably, **8** remains a monomer in the solid state (Fig. 4). The Ga atom is planar coordinated by two carbon atoms and one oxygen atom (sum of the angles 359.8 and 359.9°, Table 1). The Ga–C bond lengths (194.1 pm) are a little shorter than observed in comparable compounds with co-ordinatively unsaturated Ga atoms (>196.5 pm),^{2,11,15} and the C–Ga–C angle is enlarged to 140.5° on average. The Ga–O bonds (184.3 pm) are about 10 pm shorter than usually observed in organoelement compounds, which often have, however, higher co-ordination numbers at gallium or oxygen.¹⁶ Particularly, the co-ordination number at chalcogen atoms has a large influence on gallium–chalcogen separations.^{5,17} The Ga–O bond in **8** is 5 pm longer than in a bis(trimethylsilyl)methyl compound with a Ga–O–Ga bridge and unsaturated Ga atoms, which was recently obtained in our group.¹⁸ The angle Ga–O–C to the pentafluorophenol group is enlarged to 131.6°. Similar monomeric gallium alkoxides were published by Cleaver and Barron [(Me₃C)₂GaOCPh₃]¹⁹ and by Linti *et al.* (R₂GaOPh; R = 2,2,6,6-tetramethylpiperazinyl),²⁰ which also have short Ga–O distances of about 183 pm and large angles Ga–O–C of about 128°. Related aluminium compounds are known.²¹ The occurrence of a π interaction between oxygen lone pairs and unoccupied p orbitals of the unsaturated aluminium or gallium atoms of these monomeric aluminium or gallium alkoxides has been investigated by quantum-chemical calculations. While one paper discusses a significant π contribution,²¹ recent studies revealed that these bonds are highly ionic and at most only very weak π bonds are to be expected.²²

Experimental

All procedures were carried out under purified argon in dried solvents (*n*-pentane, *n*-hexane, cyclopentane over LiAlH₄).

Compound **1** was synthesized as described in ref. 2, LiCH(SiMe₃)₂ as in ref. 14; HF–pyridine (70% HF, Aldrich), acetic acid (99.99+%, Aldrich), diphenyltriazene (95%, Aldrich) and benzamidine (98+%, Lancaster) were used without further purification; pentafluorophenol (Aldrich) was sublimed twice *in vacuo*.

Syntheses

Di(μ -acetato-*O,O'*)bis[bis(trimethylsilyl)methyl]digallium **2.** A solution of digallane(4) **1** (0.194 g, 0.250 mmol) in 20 ml of *n*-pentane was cooled to –50 °C and treated with 29 μ l (0.500 mmol) of acetic acid. The mixture was warmed to room temperature over a period of 2 h. It changed from the yellow of **1** to colorless at –25 °C. In most cases, the obtained solutions were directly used for secondary reactions. For the isolation of **2** in a pure and crystalline form, the solvent was distilled off *in vacuo* and the residue thoroughly evacuated. Colorless crystals of **2** were obtained by cooling of a solution in *n*-pentane to –30 °C (0.117 g, 81% after recrystallization) mp (argon, sealed capillary) 68 °C (Found: Ga, 24.0. C₉H₂₂GaO₂Si₂ requires Ga, 24.2%). δ_{H} (C₆D₆, 300 MHz) 1.71 (s, 6 H, CH₃ of acetate), 0.31 (s, 36 H, SiMe₃) and –0.29 (s, 2 H, GaCHSi₂). δ_{C} (C₆D₆, 75.5 MHz) 184.1 (CO₂ of acetate), 22.7 (CH₃ of acetate) and 4.4 (GaCSi₂), 3.3 (SiMe₃). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CsBr, paraffin) 1555vs, $\nu(\text{CO}_2)$; 1464vs, 1377vs (paraffin); 1348m, 1302w, 1258s, 1248vs, $\delta(\text{CH}_3)$; 1169vw, 1155vw, 1051vw, $\nu(\text{CC})$; 1015s, $\delta(\text{CH})$; 945m, 932m, 862vs, 845vs, 785w, 775m, 758s, 721m, $\rho[\text{CH}_3(\text{Si})]$; 685s, 675s, $\nu_{\text{asym}}(\text{SiC})$; 625m, 613vw, $\nu_{\text{sym}}(\text{SiC})$; 511w, $\nu(\text{GaC})$, $\nu(\text{GaO})$; 355vw, $\delta(\text{SiC})$.

Tetrakis[bis(trimethylsilyl)methyl]digallane(4) **1 via **2**.** A solution of digallane(4) **1** (0.207 g, 0.267 mmol) in *n*-pentane was treated with acetic acid as described above. A solution of **2** was obtained, which was cooled to –50 °C and treated with a solution of LiCH(SiMe₃)₂ in diethyl ether (0.68 M, 0.79 ml, 0.534 mmol). The mixture was warmed to room temperature over a period of 2 h. The solvent was removed *in vacuo*. The residue was treated with *n*-pentane and filtered. After concentration and cooling to –30 °C, yellow crystals of **1** were obtained (0.105 g, 51% based on **1**). Characterization: see ref. 2.

Bis[bis(trimethylsilyl)methyl]bis(diphenyltriazenido-*N*¹,*N*³)-digallium **3.** A solution of compound **2** in pentane was formed by treating digallane(4) **1** (0.220 g, 0.284 mmol) with acetic acid as described above. Lithium diphenyltriazenido was prepared by treating diphenyltriazene (0.124 g, 0.629 mmol, 10% excess) with *n*-butyllithium (0.35 ml of a 1.6 M solution in *n*-hexane, 0.568 mmol) at –5 °C followed by stirring for 0.5 h at room temperature. The solution of **2** was added dropwise to the cooled (–50 °C) suspension of the lithium compound. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. The solvent was distilled off *in vacuo*. The residue was thoroughly evacuated completely to remove all volatile impurities and treated with 5 ml of *n*-pentane. Orange crystals of **3** were isolated after filtration, concentration and cooling of the solution to –30 °C (0.208 g, 86% based on **1**). Characterization: see ref. 7.

(μ -Acetato-*O,O'*)bis[bis(trimethylsilyl)methyl](μ -diphenyltriazenido-*N*¹,*N*³)digallium **4.** Compound **2** was prepared as described above (0.348 g digallane(4) **1**, 0.449 mmol). Diphenyltriazene (0.088 g, 0.449 mmol) was deprotonated by the treatment with 0.28 ml of a solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.449 mmol). The suspension was cooled to –75 °C and treated with the solution of **2**. The mixture was warmed to room temperature and stirred for 15 h. After evaporation, the residue was treated with 10 ml of *n*-pentane. Filtration, concentration and cooling to –30 °C yielded yellow crystals of compound **4** (0.257 g, 80% based on **1**), mp (argon, sealed capillary)

Table 2 Crystal data, data collection parameters and structure refinement for compounds **2**, **4**, **5** and **8**

	2	4	5	8
Formula	C ₁₈ H ₄₄ Ga ₂ O ₄ Si ₄	C ₂₈ H ₅₁ Ga ₂ N ₃ O ₂ Si ₄	C ₃₅ H ₅₆ Ga ₂ N ₂ O ₂ Si ₄	C ₂₀ H ₃₈ F ₅ GaOSi ₄
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$; no. 2	<i>P</i> 2 ₁ / <i>c</i> ; no. 14	<i>P</i> $\bar{1}$; no. 2	<i>Pbca</i> ; no. 61
<i>Z</i>	2	4	2	16
<i>TK</i>	193	193	213	213
<i>D</i> /g cm ⁻³	1.271	1.256	1.202	1.333
<i>a</i> /pm	947.67(6)	1839.2(2)	1250.32(8)	1620.9(3)
<i>b</i> /pm	1063.91(6)	1204.30(5)	1341.62(10)	1578.4(3)
<i>c</i> /pm	1555.58(9)	1823.0(2)	1462.48(13)	4454.6(9)
<i>α</i> ^o	105.588(7)		90.440(10)	
<i>β</i> ^o	93.031(7)	110.896(9)	101.676(9)	
<i>γ</i> ^o	92.251(8)		114.272(8)	
<i>U</i> /10 ⁻³⁰ m ³	1506.3(2)	3772.3(6)	2178.7(3)	11397(4)
<i>μ</i> /mm ⁻¹	1.966	1.582	1.312	1.177
Crystal size/mm	0.81 × 0.56 × 0.42	0.54 × 0.30 × 0.10	0.70 × 0.55 × 0.35	0.70 × 0.65 × 0.45
Independent reflections	5464 [<i>R</i> _{int} = 0.0280]	7256 [<i>R</i> _{int} = 0.0509]	7896 [<i>R</i> _{int} = 0.0467]	11111 [<i>R</i> _{int} = 0.1572]
Number of reflections [<i>F</i> > 4σ(<i>F</i>)]	4747	5497	6311	8876
Parameters	267	352	406	583
<i>R</i>	0.0221	0.0295	0.0306	0.0644
<i>wR</i> ₂	0.0731	0.0646	0.0798	0.1386
<i>ρ</i> /10 ³⁰ e m ⁻³	0.368/-0.292	0.413/-0.436	0.389/-0.333	0.758/-0.499

Programs SHELXL-93, SHELXTL,²³ solutions by direct methods, full matrix refinement with all independent structure factors. STOE IPDS diffractometer, graphite monochromated Mo-K α radiation.

135 °C (Found: Ga, 19.4%; *M* 702 cryoscopically in benzene. C₂₈H₅₁Ga₂N₃O₂Si₄ requires Ga, 19.5%; *M* 713.5). δ_{H} (C₆D₆, 300 MHz, 300 K) 7.52 (pseudo-d, 4 H, *ortho*-H of phenyl), 7.18 (pseudo-t, 4 H, *meta*-H of phenyl), 6.97 (pseudo-t, 2 H, *para*-H of phenyl), 1.72 (s, 3 H, CH₃ of acetate), 0.38 and 0.12 (s, 18 H, SiMe₃) and 0.13 (s, 2 H, GaCHSi₂). δ_{C} (C₆D₆, 75.5 MHz) 183.4 (CO₂ of acetate), 147.9 (*ipso*-C of phenyl), 129.1, 126.3, and 122.9 (phenyl), 22.8 (CH₃ of acetate), 3.5 and 3.0 (SiMe₃) and 2.9 (GaCSi₂). $\tilde{\nu}_{\text{max}}$ /cm⁻¹ (CsBr, paraffin) 1792vw, 1732vw, 1595w (phenyl); 1570w, ν (CO₂); 1462vs, 1377s (paraffin); 1337w, 1289w, 1246s, δ (CH₃); 1215w, 1169w, 1154w, 1074w, ν (CC), ν (CN); 1015s, δ (CH); 964w, 934m, 909w, 866(sh), 845vs, 770m, 756s, 721vs, ρ [CH₃(Si)]; 685m, 673w, ν_{asym} (SiC); 621w, ν_{sym} (SiC); 529w, 513m, 467m, ν (GaC), ν (GaO); 397w, 372vw, 347vw, δ (SiC). λ_{max} /nm (*n*-hexane) (ϵ /M⁻¹ cm⁻¹): 207 (25000), 225 (25000) and 340 (14000).

(μ -Acetato-*O,O'*)bis[bis(trimethylsilyl)methyl](μ -diphenylbenzamidinato-*N,N'*)digallium **5.** Compound **2** was synthesized as described above (0.388 g, 0.500 mmol of **1**). *N,N'*-Diphenylbenzamidine (0.143 g, 0.526 mmol) was dissolved in 25 ml of *n*-hexane and deprotonated by treatment with 0.31 ml of a solution of *n*-butyllithium in hexane (1.6 M, 0.500 mmol) at -10 °C. After stirring at room temperature for 0.5 h and cooling of the mixture to -75 °C, the solution of **2** in *n*-pentane was added. The mixture was warmed to room temperature and stirred for 15 h. The solvent was distilled off *in vacuo* and the residue treated with 10 ml of *n*-pentane and filtered. Yellow crystals of **5** precipitated from this solution upon cooling to -30 °C (0.257 g, 80%), mp (argon, sealed capillary) 135 °C (Found: Ga, 17.4%; *M* 745 cryoscopically in benzene. C₃₅H₅₆Ga₂N₂O₂Si₄ requires Ga, 17.7%; *M* 788.6). δ_{H} (C₆D₆, 300 MHz) 6.90 (m, 9 H, phenyl), 6.67 (m, 4 H, phenyl), 6.52 (m, 2 H, phenyl), 2.04 (s, 3 H, CH₃ of acetate), 0.36 and 0.30 (s, 18 H, SiMe₃) and -0.51 (s, 2 H, GaCHSi₂). δ_{C} (C₆D₆, 75.5 MHz) 183.0 (CO₂ of acetate), 171.9 (NCN), 146.4, 134.7, 130.0, 129.0, 127.8, 127.1, and 124.5 (all phenyl), 23.2 (CH₃ of acetate), 3.6 and 3.5 (SiMe₃) and 2.8 (GaCSi₂). $\tilde{\nu}_{\text{max}}$ /cm⁻¹ (CsBr, paraffin) 1792vw, 1699vw, 1643vw, 1593m, 1582w (phenyl); 1539s, ν (CO₂); 1487s, ν (NCN); 1462vs, 1377vs (paraffin); 1350m, 1308vw, 1285vw, 1271w, 1260m, 1242s, δ (CH₃); 1204w, 1169vw, 1155vw, 1132w, 1071w, 1045vw, ν (CC), ν (CN); 1018s, ν (CH); 951m, 937s, 918m, 866vs, 843vs, 791m, 777s, 756s, 723s, ρ [CH₃(Si)]; 689s, 675s, ν_{asym} (SiC); 621w, 611w, ν_{sym} (SiC); 565vw,

548vw, 523(sh), 511m, 492m, 465w, 442vw, ν (GaC), ν (GaN), ν (Ga); 343vw, δ (SiC).

Bis[bis(trimethylsilyl)methyl]bis(μ -diphenylbenzamidinato-*N,N'*)digallium **6.** Lithium diphenylbenzamidinate was prepared from 0.210 g (0.772 mmol, excess) of benzamidine and *n*-butyllithium as described above. A solution of compound **2** in *n*-pentane prepared from 0.200 g (0.258 mmol) of digallane(**4**) **1** was added at -60 °C. The mixture was warmed to room temperature and heated under reflux for 15 h. The solvent was removed *in vacuo* and the oily residue treated with 10 ml of *n*-pentane and filtered. A solid and pure product could not be obtained by recrystallization from different solvents. δ_{H} (C₆D₆, 300 MHz) 7.32 (pseudo-d, phenyl), 6.96 (m, phenyl), 6.76 (m, phenyl), 0.30 (s, SiMe₃) and -0.20 (s, GaCHSi₂).

Bis[bis(trimethylsilyl)methyl]gallium fluoride **7.** Digallane(**4**) **1** (0.425 g, 0.548 mmol) was dissolved in 25 ml of *n*-pentane. The hydrogen fluoride-pyridine complex (60 μ l) was added at room temperature. The mixture was stirred for 1.5 h, and changed from yellow to colorless. All volatile components were removed *in vacuo*. The residue was dissolved in *n*-pentane. Colorless crystals of compound **7** were obtained upon cooling of the solution to -30 °C (0.300 g, 67%), mp (argon, sealed capillary) 262 °C (decomp.) [Found: F, 5.0; Ga, 17.4%; *M* 816 by cryoscopy in benzene. C₁₉H₃₈F₂GaSi₄ requires F, 4.7; Ga, 17.1%; *M* 815.0 (dimer)]. δ_{H} (C₆D₆, 300 MHz) 0.32 (s, 36 H, SiMe₃) and -0.02 (s, 2 H, GaCHSi₂). δ_{C} (C₆D₆, 75.5 MHz) 13.5 (GaC) and 4.9 (SiMe₃). δ_{F} (C₆D₆, 282 MHz) -109.5. $\tilde{\nu}_{\text{max}}$ /cm⁻¹ (CsBr, paraffin) 1300w, 1263m, 1248s, δ (CH₃); 1169vw, 1154vw, 1076w; 1013m, δ (CH); 974w, 953vw, 845vs, 779s, 760s, 723s, ρ [CH₃(Si)]; 675m, ν (ν_{asym} SiC); 635vw, 615vw, ν_{sym} (SiC); 513w, 500m, 482w, ν (AlC); 378s, ν (Ga₂F₂); 351w, 282w, δ (SiC). *m/z* (CI, isobutane)(%) 812.9 (50), 814.8 (100), 815.9 (60), 816.8 (95) and 817.8 (50), all M⁺ of the dimer in accordance with a calculated isotope pattern.

Bis[bis(trimethylsilyl)methyl]gallium pentafluorophenolate **8.** Digallane(**4**) **1** (0.398 g, 0.513 mmol) was dissolved in 50 ml of *n*-hexane, cooled to -50 °C and treated with 0.187 g (1.02 mmol) of freshly sublimed pentafluorophenol. The solution was heated under reflux for six days. After cooling to room temperature, all volatile components were distilled off *in vacuo*. The residue was dissolved in *n*-pentane. Colorless crystals of

compound **8** were obtained upon cooling of the solution to $-30\text{ }^{\circ}\text{C}$ (401 mg, 68%), mp (argon, sealed capillary) $78\text{ }^{\circ}\text{C}$ (Found: F, 16.6; Ga, 12.1%; M 574 by cryoscopy in benzene. $\text{C}_{20}\text{H}_{38}\text{F}_5\text{GaOSi}_4$ requires F, 16.3; Ga, 12.2%; M 571.6). δ_{H} (C_6D_6 , 300 MHz) 0.16 (s, 36 H, SiMe_3) and 0.15 (s, 2 H, GaCHSi_2). δ_{C} (C_6D_6 , 75.5 MHz) 16.6 (GaCSi_2) and 3.5 (SiMe_3). δ_{F} (C_6D_6 , 282 MHz) -160.8 and -165.7 (*ortho* and *meta* C–F of phenyl) and -172.2 (*para* C–F of phenyl). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CsBr, paraffin) 1931vw, 1805vw, 1742vw, 1705vw, 1649w, 1628vw, 1591vw, 1508vs (phenyl); 1464vs, 1377vs (paraffin); 1312m, 1252s, $\delta(\text{CH}_3)$; 1115w; 1020vs, 997vs, $\delta(\text{CH})$, $\nu(\text{CF})$; 957w, 843vs, 775m, 764m, 723m, $\rho[\text{CH}_3(\text{Si})]$; 689w, 671m, $\nu_{\text{asym}}(\text{SiC})$; 644w, 635w, 623w, 615w, 573vw, $\nu_{\text{sym}}(\text{SiC})$, $\delta(\text{CF})$; 529m, 509s, 488m, 465m, 421m, $\nu(\text{GaC})$, $\nu(\text{GaO})$, $\nu(\text{Ga})$; 345w, $\delta(\text{SiC})$.

X-Ray crystallography

Single crystals were obtained by slow cooling of solutions in *n*-pentane (compounds **2** and **5**) and cyclopentane (**4** and **8**). Crystal data and structure refinement parameters are given in Table 2.

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