The Reactions of $R_2Ga-GaR_2$ and $R_2In-InR_2$ [R = CH(SiMe$_3$)$_2$] with Protic Reagents: Substituent Exchange versus Cleavage of the Element−Element Bond

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Tetrakis[bis(trimethylsilyl)methyl]digallane(4) (**1**) with a Ga−Ga single bond and the corresponding diindane(4) **2** with an In−In single bond were treated with different protic reagents: *tert*-Butyl alcohol did not react with **1** at all, while phenol gave a mixture of unknown products, which could not be separated. The more acidic pentafluorophenol did not react as an acid, but C−F bonds were cleaved to form almost quantitatively the dimer (R$_2$GaF)$_2$ **5**, which was characterized by a crystal-structure determination. Water and **1** yielded the dimeric dialkylgallium hydroxide **6**. The Ga−Ga bond was also cleaved by the reaction of **1** with durylthiophenol (duryl = 2,3,5,6-tetramethylphenyl), which gave two main products: R$_2$Ga(SDuryl) **7** and RGa(SDuryl)$_2$ **8**. In contrast, the chelating acid dibenzoylmethane reacted by means of a substituent exchange, with the release of two equiv. of bis(trimethylsilyl)methane for each formula unit of **1**, to form **9**, in which the Ga−Ga bond is retained and each chelating 1,3-diphenyl-1,3-propanedionato ligand is in a terminal position bonded to only one Ga atom, in more than 80 % yield. The Ga−Ga bond is shortened [244.1(1) pm] compared to that in the starting compound tetraalkyldigallane(4) **1**. The In−In bond of diindane(4) **2** is, however, cleaved in a similar reaction with dibenzoylmethane, and only the fragmentation product dialkyl(1,3-diphenyl-1,3-propanedionato)indium **10** could be isolated.

Tetrakis[bis(trimethylsilyl)methyl]dielement(4) compounds with the elements aluminium[1], gallium (**1**)[2], and indium (**2**)[3] in an unusually low oxidation state of +II and an element−element single bond, showed a remarkable reactivity towards carboxylic acids: Dialane(4) reacted on treatment with benzoic acid by the insertion of the Al atoms into the O−H bond, the cleavage of the Al−Al bond and the reduction of the proton by two electrons to give a hydride anion[4]. Both dialkylaluminium fragments of the product are unsymmetrically bridged by an O,O'-benzoato group and an hydride ion to form the six-membered heterocycle **3**. A similar product could not be obtained with diindane(4) **2**, which may be due to the inherently low thermal stability of In−H bonds. Instead, two monoindium compounds, monomeric R$_2$InO$_2$CR and dimeric RIn(O$_2$CR)$_2$, were formed[4], probably by fragmentation, the precipitation of indium metal and the release of elemental hydrogen. The most interesting products, **4**, were isolated from the reactions of digallane(4) **1** with aromatic and aliphatic carboxylic acids[5]. Two bis(trimethylsilyl)methyl groups are replaced by carboxylato groups, which occupy a bridging position above the considerably shortened Ga−Ga bond. Remarkably, the C−Ga−Ga−C group is almost linear and the angle between the normals of the planes of the car-

boxylato ligands approaches 90°. The reaction of **1** with less acidic diphenyltriazene led to a partial fragmentation and oxidation of digallane(4) **1**. Two main products are formed: by cleavage of the Ga−Ga bond the monogallane R$_2$Ga(N$_3$Ph$_2$) and by substituent exchange, the digallane R$_2$Ga$_2$(N$_3$Ph$_2$)$_2$, in which, in contrast to **4**, the chelating substituents are terminally bonded[6]. The substituent exchange thus opened up an easy route for the synthesis of novel organodigallium compounds, and we systematically employed further protic reagents like alcohol or acetylacetone derivatives.

Reactions of Digallane(4) 1 with Alcohols and Water

tert-Butyl alcohol did not react with **1** at all, even when a large molar excess of 4 equiv. of the alcohol for each formula unit of **1** was used, and the mixture was refluxed in hexane for several days. The reaction of the more acidic phenol in a molar ratio of 2 to 1 in boiling hexane resulted in the complete consumption of **1** after a period of four days, but a mixture of unknown products was formed, which could not be separated by recrystallization; only trace amounts of a colorless solid, which was not further characterized, crystallized out of solution in pentane. Pentafluorophenol reacted with **1** not as an acid, but by the cleavage of

3

4
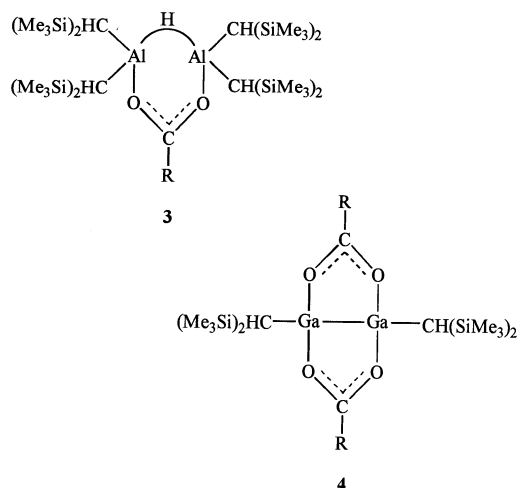
C−F bonds. The reaction required more than 48 h in boiling hexane, and only one product could be isolated after recrystallization from pentane in a yield of more than 80%. A dialkylgallium fluoride **5**, which is a dimer in the solid state (see below) and in solution, as cryoscopically determined in benzene, was formed by the cleavage of the Ga−Ga bond (eq. 1). **5** thus differs from the recently published analogous compound Br−Ga[CH(SiMe₃)₂]₂[7] and the corresponding chloroaluminium derivative Cl−AlR₂[1], which are both monomeric in solution, with coordinatively unsaturated central atoms, probably due to strong steric interactions between the bulky bis(trimethylsilyl)methyl substituents. A dimer was, however, also observed in the corresponding hydroxide[8], so that, interestingly, the smallest donor atoms are able to form the most stable dimers. Because OH and F are the most electronegative of the employed substituents, this observation may be explained as resulting from a more effective ionic interaction and a high electrostatic contribution to the bonding in these molecules. The monomeric bromide BrGaR₂ and the dimeric fluoride **5** differ significantly in their ¹³C-NMR spectra. The C atoms bonded to gallium show a chemical shift of δ = 25.6 in the bromo derivative, which is within the range usually observed with bis(trimethylsilyl)methyl compounds of tricoordinated Ga atoms[2][7]. In **5**, however, the corresponding resonance is shifted to higher field (δ = 16.6), characteristic for compounds with tetracoordinated Ga atoms. Absorptions in the IR spectra at 525 and 490 cm⁻¹ could be assigned to the stretching vibrations of the Ga₂F₂ unit[9]. Dimesityl- and diisopropylgallium fluoride, as recently published by Neumüller et al.[10], are also dimeric in solution, and the IR absorptions at 473 and 450 cm⁻¹ (R = mesityl) and 496 cm⁻¹ (R = benzyl) were assigned to the Ga₂F₂ molecular center. In comparison to these gallium fluorides (δ = −152.7 and −169.7) the ¹⁹F-NMR resonance of **5** is shifted downfield to δ = −109.5. The similar cleavage of a C−F bond of a fluorinated aromatic compound accompanied by the formation of an Al−F bond has recently been reported[11].
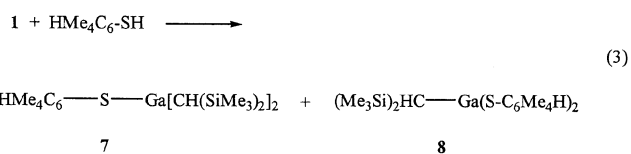
Water also does not react with **1** by the release of bis(trimethylsilyl)methane, but by the oxidation of the gallium
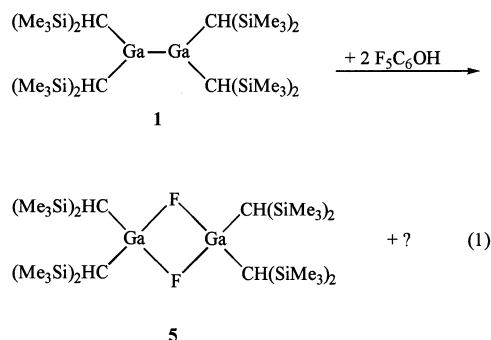
atoms and cleavage of the Ga−Ga bond. Dimeric dialkylgallium hydroxide **6** is formed (eq. 2), which is isolated after recrystallization from _n_-pentane in a yield of about 50%. Elemental hydrogen is probably formed as a byproduct, which could, however, not be detected due to its small amount. **6** has been obtained in our group before by another route and was characterized by a crystal-structure determination[8].

$$1 + H_2O \longrightarrow \qquad (2)$$

6
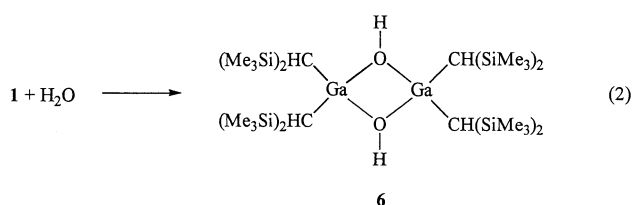
The behavior of thioalcohols was investigated in a reaction of **1** with the sterically shielded durylthiol (duryl = 2,3,5,6-tetramethylphenyl). After 72 h in boiling hexane, 70% of **1** was consumed. Two new products were formed, which could be separated with difficulty by repeated recrystallization to yield a small amount of an enriched sample of **8**, while the second component **7**, could only be detected in mixtures with **8**. Both products were identified spectroscopically as R₂GaSDuryl **7** and RGa(SDuryl)₂ **8**. The pure compounds **7** and **8** could not be obtained by the reaction of Ga[CH(SiMe₃)₂]₃[2] with one or two equiv. of durylthiol in solution or in a melt at 120°C; in all reactions, **7** was only formed as a minor component, while reactions in the molar ratio of 1:2 gave impure samples of **8**, which could not be purified by recrystallization. The spectroscopic information obtained for the impure monothiolato product is not sufficient enough to discuss the degree of oligomerization, but the dithiolato product seems to be at least a dimer with a tetracoordinated Ga atom, as can be seen from the chemical shift of the carbon atom bonded to Ga (δ = 15.5).

1

$$+ 2 F_5C_6OH \longrightarrow$$

5

$$+ ? \qquad (1)$$

$$1 + HMe_4C_6\text{-}SH \longrightarrow \qquad (3)$$

HMe₄C₆——S——Ga[CH(SiMe₃)₂]₂ + (Me₃Si)₂HC——Ga(S-C₆Me₄H)₂

7   **8**

Reaction of Digallane(4) 1 and Diindane(4) 2 with Dibenzoylmethane

As shown before, non-chelating acidic compounds such as alcohols or thioalcohols reacted exclusively by the cleavage of the Ga−Ga bond. We hoped to realize the substituent exchange by retaining the Ga−Ga bond, when we treated **1** with a chelating protic acetylacetone derivative. This reaction was of particular interest because, up to now, we had observed either a bridging or a terminal coordination by the chelating ligand in the products of both successful substituent exchange reactions. The reason for this different behavior is not well understood, but it possibly depends on the distance between the coordinating atoms (bite) with the N−N distance in the triazenido ligand too short to facilitate the bridging of the Ga−Ga bond.

When we treated a yellow solution of the digallane(4) **1** in pentane with two equiv. of dibenzoylmethane at −50 °C (eq. 4), the color changed at about −10 °C to give an orange solution, from which orange-red crystals of **9** were obtained at −50 °C in a yield of 79%. In contrast to the reactions described above, two equiv. of CH$_2$(SiMe$_3$)$_2$ are formed for each formula unit of **1**, as shown by NMR spectroscopy. Elemental analysis, mass spectrometry, the cryoscopic molar-mass determination in benzene and the integration of the ^{1}H-NMR spectrum confirm the structure of a digallium compound with two bis(trimethylsilyl)methyl and two 1,3-diphenyl-1,3-propanedionato substituents. In the NMR spectra, the resonances of the methine protons and the α-carbon atoms of the CH(SiMe$_3$)$_2$ groups are strongly shifted upfield (^{1}H: δ = −0.09; ^{13}C: δ = 10.4) compared to those of the starting compound **1** (δ = 1.09 and 25.9, respectively)[2], clearly indicating a coordination number of four at the Ga atoms. The atoms of the electronically delocalized π system of the 1,3-diphenyl-1,3-propanedionato group show the usual chemical shifts: δ = 185.7 [C(O)], 93.9 [C(H)] and δ = 6.52 (H). In contrast to the colorless triazenido or carboxylato digallium compounds mentioned above, **9** is deeply orange with absorptions at 420 and 340 nm in the UV/Vis spectrum; the color, however, is mainly a function of the chelating group and is often observed in its reaction products.

Until now, all reactions of protic reagents with diindane(4) **2** resulted in the cleavage of the In−In bond and precipitation of elemental indium. Because of the formation of the digallium compound **9** in a high yield with only minor byproducts, we treated **2** with dibenzoylmethane under similar conditions to those described above for **1** in a molar ratio of 1:2. As originally intended, the formation of bis(trimethylsilyl)methane could be detected by NMR spectroscopy, but only as a minor component, and a black precipitate of elemental indium indicated a disproportionation reaction and the fragmentation of the starting compound **2**. A crystalline product was isolated from *n*-pentane at −30 °C, which was identified by its NMR spectra and its molar mass as the dialkylindium compound **10** (eq. 5). The yield of **10** based on dibenzoylmethane amounted to only 43%, and an excess of the diketone crystallized as a second fraction. Reactions in an equimolar ratio gave **10** in a yield of 86% based on dibenzoylmethane, but a small part of the starting compound **2** was recovered. The course of these reactions may give some insight into the reaction mechanism: Similar to the reactions with carboxylic acids[4] described in the introduction, the In atoms are probably oxidized by the OH proton of the enol form of the diketone, accompanied by insertion into the O−H bond. The intermediate with an In−H bond similar to the Al compound **3** is unstable, and decomposes by the release of elemental hydrogen, which may lead to the formation of the isolated product dialkyl(1,3-diphenyl-1,3-propanedionato)indium **10** and an InR$_2$ radical, which could disproportionate via an alkylindium(I) derivative, stable only with bulkier C(SiMe$_3$)$_3$ substituents[12], to form elemental indium and the corresponding trialkylindane. The highly soluble indane[3] could indeed be identified as the main component of the mother liquor after isolation of **10** and the unreacted diindane(4) **2**. Product **10** was synthesized by the treatment of the corresponding trialkylindane with one equiv. of dibenzoylmethane in a yield of almost 90%. Due to its molar mass in benzene, **10** is monomeric in solution. The resonances of the methine groups bonded to indium are shifted upfield [^{1}H: δ = −0.18 (HCIn); ^{13}C: δ = 11.9 (CIn)], which is characteristic of a coordination number of four at the indium atom and verifies the chelating coordination by the 1,3-diphenyl-1,3-propanedionato ligand.

(4)

(5)

Crystal Structures of Compounds 5 and 9

Figure 1 shows the molecular structure of the dimeric compound $(R_2GaF)_2$ **5** [R = CH(SiMe$_3$)$_2$], which crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two dimers in each unit cell. The four CH(SiMe$_3$)$_2$ substituents are arranged in a terminal position and the dialkylgallium fragments are bridged by both fluorine atoms. A four-membered Ga$_2$F$_2$ heterocycle results; this is almost ideally planar with a maximum deviation of an atom of 2.9 pm. The GaC$_2$ planes with the methine carbon atoms of the bis-(trimethylsilyl)methyl groups are almost exactly perpendicular to this plane, and the normals of the planes include angles of 90.6° (Ga1C1C2) and 89.6° (Ga2C3C4). The bond angles in the heterocycle are most acute at the Ga atoms (76.9°) and much enlarged at the F atoms (103.0°); almost identical angles were observed in the recently published corresponding di(μ-hydroxo)digallium derivative[8]. Dialkylgallium fluorides have been known for a long time. They usually form trimers (R = Me, Et[13], iPr[10]), and it was only recently that a dimer, which was sterically highly shielded by four bulky mesityl substituents, was characterized by a crystal-structure determination[10]. A tetrameric modification was observed by Schmidbaur et al. with R = Me[13]. The Ga–F bonds in **5** and (Mes$_2$GaF)$_2$ [194.7(2) pm] are quite similar; for **5** they deviate only slightly from the average value of 196.6 pm. The CH(SiMe$_3$)$_2$ substituents of comparable dialuminium or digallium compounds usually show a conformation in which the methine hydrogen atom of one substituent points between both SiMe$_3$ groups of the second CH(SiMe$_3$)$_2$ substituent[1][2][3]. This conformation is only observed at the atom Ga1 in **5**, while at Ga2 the four trimethylsilyl groups are neighbored and can be transferred onto each other by non-crystallographic mirror planes. Thus, the molecule is not centrosymmetric in the solid state, although only one singlet of the SiMe$_3$ groups was observed in the NMR spectra in solution. The molecule shows a disorder (54–46%), and the bis(trimethylsilyl)methyl group of C2 occupies a second position, which gives the same conformation as observed at Ga2. The point group of the second molecule is thus approximately D_{2h}.

The molecular structure of **9** is depicted in Figure 2. The molecule is located on a crystallographic center of symmetry, which intersects the Ga–Ga bond. Two bis(trimethylsilyl)methyl groups are replaced by chelating 1,3-diphenyl-1,3-propanedionato ligands, which in contrast to the corresponding carboxylato derivative **4**[5], but similarly to the product obtained with diphenyltriazene[6], occupy terminal positions and are bonded to only one Ga atom. Due to its crystallographic symmetry, the molecule has an ideal *trans* conformation. The Ga–Ga bond length is 244.0 pm, which is slightly shorter than in the triazenide compound [245.79(6) pm] with a synclinal molecular conformation[6], but longer than in **4** [238.5(2) pm][5]. Compared to the starting compound **1** [254.1(1) pm][2] a significant shortening is observed; all Ga–Ga distances lie in the range characteristic of Ga–Ga bonds in organoelement or inorganic derivatives[14]. The Ga–C bond length is lengthened [199.5(5)

Figure 1. Molecular structure of **5**; the ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; only one position of the disordered CH(SiMe$_3$)$_2$ group at C2 is drawn[a]
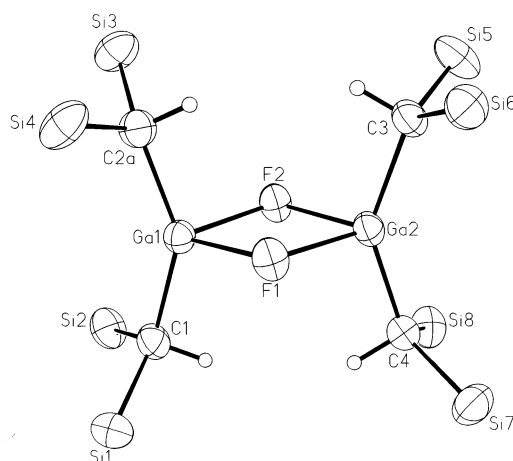
[a] Selected bond lengths [pm] and angles [°]: Ga1–F1 196.3(3), Ga1–F2 195.4(3), Ga2–F1 197.4(3), Ga2–F2 197.3(3), Ga1···Ga2 307.7, Ga1–C1 197.1(5), Ga1–C2 199.7(9), Ga1–C2A 194(1), Ga2–C3 196.5(5), Ga2–C4 196.4(5); F1–Ga1–F2 77.2(1), F1–Ga2–F2 76.5(1), Ga1–F1–Ga2 102.8(1), Ga1–F2–Ga2 103.2(1), C1–Ga1–C2 126.8(3), C1–Ga1–C2A 147.1(4), C3–Ga2–C4 143.8(2).

Figure 2. Molecular structure of **9**; the ellipsoids are drawn at the 40% probability level; methyl and phenyl groups are omitted for clarity; only one position of the disordered CH(SiMe$_3$)$_2$ group at C1 is drawn[a]
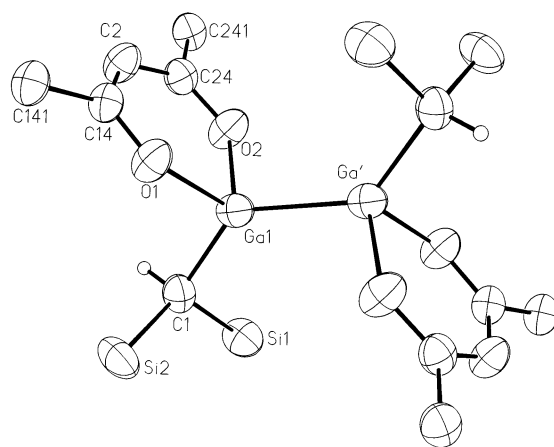
[a] Selected bond lengths [pm] and angles [°]: Ga1–Ga1′ 244.0(1), Ga1–C1 199.5(5), Ga1–O1 195.9(3), Ga1–O2 194.8(3); O1–Ga1–O2 91.1(1), O1–Ga1–C1 102.8(2), O2–Ga1–C1 103.6(2), Ga1′–Ga1–C1 133.9, Ga1′–Ga1–O1 110.0(1), Ga1′–Ga1–O2 107.2(1) (symmetry operation to generate Ga1′: –x, –y, 1 – z).

pm] compared to the carboxylato-bridged compound **4** [195.7(8) pm], but the Ga–O distances are significantly reduced [**9**: 195.9(3) pm; **4**: 201.1(6) pm], which might be caused by the bridging of the Ga–Ga bond and the resulting larger steric stress in **4**. The distance between the coordinating atoms in the chelate ring of **9** (278.9 pm) is much larger than in the carboxylato-bridged derivative **4** (224.0 pm)[5]. A shorter bite is observed with the triazenido ligand (209.2 pm)[6], which occupies a terminal position.

The kind of the coordination, terminal or bridging, seems therefore not to be determined by the magnitude of the distance between the coordinating atoms, and remains an open question, in which case a particular coordination is adopted. The (1,3-diphenyl-1,3-propanedionato)gallium heterocycle is almost planar, with the maximum deviation from the plane of 8.1 pm by the oxygen atom O1; its bond lengths and angles resemble that of comparable derivatives of gallium in an oxidation state of +III[15].

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (*n*-pentane, cyclopentane, and *n*-hexane with LiAlH$_4$, benzene with Na/benzophenone). Compounds **1** and **2** were synthesized as described in ref.[2][3], durylthiol was obtained by the reduction of ClSO$_2$−C$_6$Me$_4$H with LiAlH$_4$[16], dibenzoylmethane and pentafluorophenol (Aldrich) were sublimed in vacuo, *tert*-butyl alcohol was treated with Na and distilled, phenol (99+%, Aldrich) was used without further purification.

*Synthesis of (R$_2$GaF)$_2$ **5**:* 0.91 g (1.17 mmol) of digallane(4) **1** was dissolved in 50 ml of *n*-hexane and treated with 0.43 g (2.34 mmol) of solid pentafluorophenol. The mixture was heated under reflux for 48 h, and the color changed from yellow to colorless. The solvent was evaporated and the residue recrystallized from *n*-pentane (20/−30°C). Yield: 0.83 g (87%); colorless, slightly air-sensitive crystals; m.p. (argon; closed capillary) 157°C. − ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 0.17 (1 H, GaCH), 0.16 (18 H, SiMe$_3$). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 16.6 (GaC), 3.5 (SiMe$_3$). − ^{19}F NMR (C$_6$D$_6$, 282 MHz): δ = −109.5. − IR (CsBr, paraffin): ṽ = 1314 cm^{-1} (w), 1262 (sh), 1252 (vs, δCH$_3$), 1171 (w), 1018 (vs), 995 (sh, δCH), 843 (vs), 777 (s), 762 (s), 723 [s, ρCH$_3$(Si)], 673 (m, ν$_{as}$SiC), 646 (w), 613 (w, ν$_s$SiC), 573 (vw, νGa$_2$F$_2$), 527 (w, νGaC$_2$), 509 (w, νGa$_2$F$_2$), 490 (w, νGaC$_2$), 463 (vw, νGaC$_2$), 421 (vw), 376 (vw, δSiC). − C$_{28}$H$_{76}$F$_2$Ga$_2$Si$_8$ (815.0): calcd. F 4.7, Ga 17.1; found F 4.5, Ga 16.9. − Mol. mass: 745 (cryoscopically in benzene).

*Reaction of Digallane(4) **1** with Water:* Digallane(4) **1** (0.19 g, 0.25 mmol) was dissolved in 20 ml of *n*-hexane and treated with 8.8 μl of water. The mixture was stirred vigorously for 6 h until the water phase was completely consumed. The solvent was evaporated, and the residue recrystallized from *n*-hexane (20/−50°C). Yield: 0.103 mg (51%) colorless crystals of compound **6**; characterization see ref.[8].

*Reaction of Digallane(4) **1** with Durylthiol:* Digallane(4) **1** (0.695 g, 0.896 mmol) was dissolved in 40 ml of *n*-hexane and cooled to −30°C. 23.3 ml of a 0.077 M solution of durylthiol (1.79 mmol) in *n*-hexane was added. The mixture was warmed to room temperature and stirred for 72 h. The pale yellow solution was concentrated and the residue recrystallized from *n*-pentane. A mixture of both products **7** and **8** was obtained with the dithiol derivative **8** enriched as the less soluble component. − ^{1}H NMR of R$_2$GaSCMe$_4$H **7** (C$_6$D$_6$, 300 MHz): δ = 6.76 (1 H, phenyl), 2.55 and 2.10 (each 6 H, methyl of duryl), 0.22 (36 H, SiMe$_3$); methine proton signal not detected. − Characterization of **8**: colorless, slightly air-sensitive crystals; m.p. (argon; closed capillary) 146°C. − ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 6.71 (2 H, phenyl), 2.48 and 2.05 (each 12 H, methyl of duryl), 0.18 (18 H, SiMe$_3$); methine proton signal not detected. − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 137.3, 134.0, 132.3, 130.9 (all phenyl), 21.0 and 20.2 (methyl of duryl), 15.5 (GaC), 3.2 (SiMe$_3$). − IR (CsBr, paraffin): ṽ = 1553 cm^{-1} (w, phenyl); 1462

(vs), 1377 (vs, paraffin); 1302 (w), 1260 (m), 1250 (s, δCH$_3$), 1155 (vw), 1020 (m), 1003 (m, δCH), 964 (m), 862 (s), 839 (vs), 775 (s), 762 (s), 721 [s, ρCH$_3$(Si)], 675 (m, ν$_{as}$SiC), 629 (w), 613 (vw, ν$_s$SiC), 546 (w), 517 (w, νGaC), 461 (m), 430 (w), 397 (w), 378 (w, νGaS, δSiC). − C$_{27}$H$_{45}$GaS$_2$Si$_2$ (559.7): calcd. Ga 12.5; found Ga 12.2.

*Synthesis of Dialkylbis(μ-1,3-diphenyl-1,3-propanedionato-O,O')digallium **9**:* A solution of 0.314 g (1.40 mmol) of dibenzoylmethane in 50 ml of *n*-pentane was added dropwise to a cooled solution (−50°C) of digallane(4) **1** (0.518 g, 0.67 mmol) in 75 ml of *n*-pentane. The mixture was slowly warmed to room temperature, and the color changed at about −10°C from yellow to orange. The solvent was evaporated, the residue thoroughly dried in vacuo to completely remove bis(trimethylsilyl)methane and recrystallized from 60 ml of *n*-pentane (20/−50°C). Yield: 0.478 g (79%); orange-red, slightly air-sensitive crystals; m.p. (argon; closed capillary) 168−169°C. − ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 7.81 (4 H, pseudo-d, *o*-H of phenyl), 7.09 (2 H, pseudo-t, *p*-H of phenyl), 7.01 (4 H, pseudo-t, *m*-H of phenyl), 6.52 [1 H, s, HC(CO)$_2$], 0.40 (18 H, s, SiMe$_3$), −0.09 (1 H, s, GaCH). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 185.7 (CO), 138.3, 132.2, 128.4 (all phenyl), 93.9 [C(CO)$_2$], 10.4 (GaC), 3.8 (SiMe$_3$). − IR (CsBr, paraffin): ṽ = 1973 cm^{-1} (vw), 1954 (vw), 1912 (vw), 1892 (vw), 1852 (vw), 1804 (vw), 1765 (vw, phenyl), 1591 (m), 1535 (s), 1524 (s, chelate), 1466 (vs), 1362 (vs, paraffin), 1316 (s), 1304 (s), 1252 (sh), 1244 (s), 1229 (sh, δCH$_3$), 1182 (m), 1157 (m), 1127 (m), 1092 (m), 1063 (s, νCC, νCO), 1022 (vs), 999 (w, δCH), 970 (vw), 953 (vw), 939 (s), 914 (s), 862 (sh), 841 (vs), 787 (m), 756 (vs), 716 vr, ρCH$_3$(Si)], 694 (sh), 681 (s), 669 (sh, ν$_{as}$SiC), 629 (s), 617 (s, ν$_s$SiC), 556 (s), 527 (s), 509 (vs), 494 (m), 455 (w, νGaC, νGaO), 436 (w), 395 (w), 338 (vw, δSiC). − UV (*n*-hexane): λ$_{max}$ (lg ε) = 200 nm (5.0), 260 (4.6), 340 (4.7), 421 (3.8). − FD MS; *m/z*: 903.3, 904.7, 906.7 [all M$^+$, in agreement with a calculated isotope pattern]. − C$_{44}$H$_{60}$Ga$_2$O$_4$Si$_4$ (904.7): calcd. Ga 15.4; found Ga 15.4. − Mol. mass: 855 (cryoscopically in benzene).

*Reaction of Diindane(4) **2** with Dibenzoylmethane:* A solution of 0.086 g (0.38 mmol) of dibenzoylmethane in 20 ml of *n*-pentane was added to a cooled (−90°C) solution of 0.323 g (0.37 mmol) of diindane(4) **2** in 20 ml of *n*-pentane. The mixture was slowly warmed to room temperature, the color changed from orange to brown and elemental indium precipitated. After filtration and concentration, compound **10** crystallized as a yellow solid on cooling to −50°C. A quarter of the starting compound **2** was isolated as a second fraction. The mother liquor contained the readily soluble In[CH(SiMe$_3$)$_2$]$_3$ as a main component. Yield of **10**: 0.210 g (86% based on dibenzoylmethane); characterization of **10**: see below.

*Synthesis of Dialkyl(1,3-diphenyl-1,3-propanedionato-O,O')indium **10**:* A solution of 0.348 g (1.55 mmol) of dibenzoylmethane in 30 ml of *n*-pentane was added to a cooled (−80°C) solution of 0.943 (1.59 mmol) of In[CH(SiMe$_3$)$_2$]$_3$ in 20 ml of *n*-pentane. The mixture was slowly warmed to room temperature, filtered and concentrated in vacuo. **10** crystallized on cooling to −30°C. Yield: 0.931 g (89%); yellow, slightly air-sensitive crystals; m.p. (argon; closed capillary) 121°C. − ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 7.98 (4 H, pseudo-d, *o*-H of phenyl), 7.13 (6 H, m, phenyl), 6.83 [1 H, s, HC(CO)$_2$], 0.29 (36 H, s, SiMe$_3$), −0.18 (2 H, s, GaCH). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ = 186.6 (CO), 139.8, 132.0, 128.7, 127.8 (all phenyl), 95.2 [C(CO)$_2$]; 11.9 (GaC), 3.9 (SiMe$_3$). − IR (CsBr, paraffin): ṽ = 1971 cm^{-1} vw, 1954 (vw), 1912 (vw), 1892 (vw), 1802 (vw), 1718 (vw, phenyl), 1591 (s, phenyl), 1541 (s), 1516 (vs, νCO, νCC of the chelate), 1476 (vs), 1364 (vs, paraffin), 1312 (m), 1259 (m), 1258 (s), 1246 (s), 1227 (m, δCH$_3$), 1184 (w), 1157 (w), 1125 (w), 1092 (w), 1057 (w, νCC,νCO), 1020 (s), 1011 (s,

δCH), 968 (vw), 936 (m), 926 (m), 914 (m), 843 (vs), 785 (m), 772 (m), 754 (m), 743 (s), 708 [s, ρCH₃(Si)], 677 (s), 665 (s, ν_{as}SiC), 625 (m), 610 (w, ν_sSiC), 542 (w), 521 (w), 484 (m, νInC, νInO), 394 (vw, δSiC). − $C_{29}H_{49}InO_2Si_4$ (656.9): calcd. In 17.5; found In 17.2. − Mol. mass: 605 (cryoscopically in benzene).

Crystal-Structure Determinations: Single crystals of compounds **5** and **9** were obtained by recrystallization from hexane and cyclopentane, respectively. Crystal data and structure refinement parameters are given in Table 1[19]. Both compounds show a disorder of one bis(trimethylsilyl)methyl group, which is best described as a different orientation of the methine hydrogen atoms. Although the carbon atoms occupy different positions in each disordered group, the Si atoms coincide in compound **5**; in **9** all atoms of the CH(SiMe₃)₂ group are disordered. The disordered atoms were isotropically refined under restrictions of bond lengths and angles (exception: the higher occupied position in **9**); the occupancy factors are 0.54 and 0.46 in **5** and 0.87 and 0.13 in **9**.

Table 1. Crystal data and data-collection parameters for **5** and **9**

	5	**9**
Formula	$C_{28}H_{76}F_2Ga_2Si_8$	$C_{44}H_{60}Ga_2O_4Si_4$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$; no. 2[17]	$P\bar{1}$; no. 2[17]
Z	2	1
T [K]	293(2)	293(2)
$d_{calcd.}$ [g/cm³]	1.138	1.252
a [pm]	952.3(1)	1058.3(2)
b [pm]	1250.1(2)	1130.6(2)
c [pm]	2185.7(2)	1208.2(2)
α [°]	79.568(9)	67.93(3)
β [°]	88.652(9)	64.60(3)
γ [°]	68.54(1)	74.41(3)
V [10^{-30} m³]	2379.0(6)	1200.2(4)
μ [mm⁻¹]	1.358	1.259[a]
Crystal size [mm]	0.14 × 0.15 × 0.34	0.39 × 0.44 × 0.46
Diffractometer	Siemens P4	Siemens P4
Radiation	Mo-K_α (graphite monochromator)	
Range	3.6° ≤ 2Θ ≤ 50°	4° ≤ 2Θ ≤ 50°
Reciprocal space	−1 ≤ h ≤ 11	−1 ≤ h ≤ 12
	−14 ≤ k ≤ 14	−12 ≤ k ≤ 12
	−25 ≤ l ≤ 25	−13 ≤ l ≤ 14
Scan mode	ω	ω
Independent reflections	8241	4181
Number of reflections [with $F^2 > 2\ \sigma(F^2)$]	5133	3284
Program	SHELXTL, SHELXL-93[b][18]	
Parameters	384	292
$R = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$ [$F^2 > 2\ \sigma(F^2)$]	0.0474	0.0559
$wR^2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w(F_o^2)^2]^{1/2}$ (all data)	0.1560	0.1158
Max. residual [10^{30} e/m³]	0.469	0.863
Min. residual [10^{30} e/m³]	−0.341	−0.514

[a] Empirical absorption correction. − [b] Solutions by direct methods; full-matrix refinement with all independent structure factors.

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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−407196 (**5**) and −407197 (**9**).

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