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Investigations into the Reactivity of Organoelement Gallium Subhalides – Syntheses of Bifunctional Digallium Carboxylate Iodides Possessing Bridged Ga–Ga Bonds and Terminal Iodine Atoms

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Dedicated to Prof. Dr. H. Schnöckel on the occasion of his 65th birthday

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The organoelement subhalide $R_2Ga_2I_2$ (**1**) [R = $C(SiMe_3)_3$] reacted with one equivalent of different lithium carboxylates LiO_2CR [R = $-C_6H_5$, $-4-Me_3C–C_6H_4$, $-4-BrC_6H_4$, $-3,5-Me_2C_6H_3$, $-CMe_3$] by the selective replacement of only one iodine atom. Bifunctional digallium compounds were formed, in which one chelating carboxylato group bridges the Ga–Ga bonds. Thus, both gallium atoms are coordinated to one carbon atom of the tris(trimethylsilyl)methyl groups and one oxygen atom of the chelating ligand, while only one is further attached to a terminal iodine atom. This asymmetric substitution pattern results in different coordination numbers of three and four for the gallium atoms.

Introduction

The tetrahedral cluster compounds $E_4[C(SiMe_3)_3]_4$ (E = Ga, In) are easily available by the reduction of the corresponding alkyltrichlorogallate with magnesium[1] or by the treatment of indium(I) bromide with $LiC(SiMe_3)_3$.[2] These compounds possess the gallium or indium atoms in an unusual low oxidation state of +1. Careful oxidation reactions employing the halogens or appropriate halogen donors open the facile access to organoelement subhalides, which proved to be very effective starting compounds for the generation of secondary products still containing the elements in low oxidation states. Different kinds of subhalides were obtained depending on the halogen source or the stoichiometric ratio of the starting compounds. Transfer of one bromine molecule to the tetraindium cluster gave the remarkable compound $Br_2In_4[C(SiMe_3)_3]_4$, in which the overall tetrahedral arrangement of the indium atoms is retained with some distortion.[3] The bromine atoms occupy one face of the tetrahedron and one edge of that particular face. The average oxidation state of the metal atoms is +1.5. Such a derivative could not be isolated with gallium atoms, which may be caused by the ready dissociation of the tetrahedral tetragallium cluster owing to the relatively strong steric interaction between the bulky substituents.[1] An oxidation state of +2 occurs in the compounds R(X)E–E(X)R (X = Cl, Br, I), which have E–E single bonds. They are monomeric for gallium with coordinatively unsaturated central atoms,[4,5] while In_4X_4 cages with all of the halogen atoms in a bridging position are formed with the larger indium atoms.[3] A further structural motif of these subhalides was observed for the compounds $I_2E_3[C(SiMe_3)_3]_3$, which contain chains of three gallium or indium atoms and iodine bridges between both terminal metal atoms.[5,6] A halogen adduct of the triindium compound with all indium atoms possessing a coordination number of four was obtained as a by-product of the cluster synthesis.[7] Organoelement subhalides that are not derived from clusters are also known in the literature.[8,9]

The organoelement subhalides of the type $X_2E_2R_2$ have been employed in several secondary reactions, which impressively showed their importance for the generation of new compounds. Treatment with two equivalents of lithium or silver acetylacetonates yielded the corresponding diacetylacetonato derivatives by the replacement of both halogen atoms and retainment of the E–E bonds.[10] The chelating ligands occupy terminal positions at each gallium or indium atom. In contrast, the bridging of the E–E bonds was observed for dicarboxylato compounds.[11] A very short E–E distance resulted in particular for the indium derivative owing to the small bite of the carboxylato group. Lithium diphenylphosphanide and the subhalide $I_2Ga_2R_2$ (**1**) gave an interesting reaction course with the formation of a gallium phosphanide possessing a Ga_2P_2 heterocycle.[12] Oxidation of the gallium atoms occurred and Ga–H bonds were probably formed by the reaction of radical intermediates with

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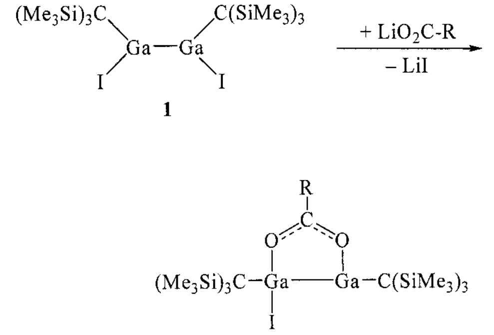
the solvent. The reduction of some subhalides substituted by aryl groups afforded products containing E–E multiple bonds.[9] Several transition metal gallium or indium compounds could be synthesized by treatment of these subhalides with transition metal carbonylate anions.[13] In general, the introduction of monodentate ligands such as alkyl or alkoxy groups proved to be rather difficult, and in most cases secondary reactions were induced with the cleavage of the E–E bonds. This instability is probably caused by the coordinative unsaturation of the central gallium or indium atoms, which favors intramolecular substituent exchange processes as the starting step for disproportionation reactions. This behavior is similar to that of the solvent-free subhalides of these elements, E_2X_4, which do not possess E–E bonds, but are mixed valent with the formulae $E^I[E^{III}X_4]$.[14] Therefore, we tried to synthesize digallium compounds bearing a protecting chelating group at one gallium atom, while the second one still bears its halogen atom. These bifunctional compounds are valuable starting compounds for the generation of a broad variety of secondary products.

Results and Discussion

Reactions of $I_2Ga_2R_2$ (1) [R = $C(SiMe_3)_3$] with Lithium Benzoates

The replacement of both iodine atoms of the subhalide $I_2Ga_2R_2$ (**1**) [R = $C(SiMe_3)_3$] by carboxylato groups resulted in reasonable yields and reaction times only when silver benzoate was employed as a starting compound,[11] while lithium benzoate gave complicated mixtures of products. However, it seems that only the exchange of the second iodine atom is relatively slow and unselective. Therefore, we did not employ the silver salts of the carboxylic acids, but treated **1** with one equivalent of the more easily available lithium carboxylates. The most selective reactions were observed when the components were mixed at a very low temperature (–90 °C). Slow warming to room temperature and stirring for a further 24–48 h gave almost quantitative formation of the pure monosubstitution products **2**–**6**, see Equation (1). Despite the high selectivity of all the reactions only compound **2** could be isolated by recrystallization in good yield (82%). In all other cases the high solubility in the noncoordinating solvents prevented the effective recrystallization and yields only between 20 and 60% were achieved. In one case (**5**), all attempts of crystallization failed and the characterization was done with the solid raw product of the reaction.



(1)

R = $-C_6H_5$ (**2**), $-4-Br-C_6H_4$ (**3**), $-3,5-Me_2C_6H_3$ (**4**), $-4-Me_3C-C_6H_4$ (**5**), $-CMe_3$ (**6**)

The NMR spectroscopic characterization is in complete agreement with the molecular structures of these compounds, which are schematically shown in Equation (1). The integration ratios of the resonances of the ^1H NMR spectra clearly verify that one iodine atom of the starting compound **1** is replaced by a carboxylato ligand. Interestingly, only one resonance is observed for the trimethylsilyl groups although the molecule is unsymmetrical in the solid state with coordination numbers of three and four for the gallium atoms. A splitting of these signals could not be detected even on cooling the solutions of **2** and **6** in toluene to –100 °C. Obviously a very fast exchange process occurs, probably including the migration of the iodine atoms. We suppose that this process is a key step in disproportionation reactions, which were discussed above in the Introduction chapter and have been observed often for similar digallium or diindium compounds bearing monodentate ligands.[15] In the case of compounds **2**–**6** the opening of the Ga–Ga bond is prevented by the chelating ligands, which bridge the Ga–Ga bond, since they act as a clamp and stabilize that particular arrangement. The ^{13}C NMR shift of the inner carbon atoms of the tris(trimethylsilyl)methyl group is worth mentioning. Owing to the fast exchange processes only one resonance is detected for each compound showing a chemical shift of about δ = 30 ppm. This is in the characteristic range of carbon atoms attached to tricoordinate gallium. A coordination number of four causes significant high field shifts to about δ = 5 ppm.[16] Thus, although one half of the gallium atoms are coordinatively saturated, the expected average value is not detected here, instead a low coordination number is suggested by the NMR spectroscopic data.

Two compounds (**2** and **4**) were characterized by crystal structure determinations. The molecular structures are depicted in Figure 1 (a and b) and Figure 2, respectively. Both compounds contain an intact Ga–Ga bond bridged by the chelating carboxylato ligand. One gallium atom is further attached to an iodine atom, so that different coordination numbers of three (Ga2) and four (Ga1) result for the metal atoms of one molecule. Ga2 has an almost ideal planar surrounding (sum of the angles 358.5 and 357.2° for **2** and **4**, respectively), while Ga1 has a strongly distorted tetrahedral coordination sphere. The Ga–Ga bond lengths (239.9 and 240.7 pm) are quite similar to that of the starting compound **1** (240.1 pm)[4] and to the corresponding dicarboxylato derivative, in which two chelating ligands bridge the Ga–Ga bond.[11,17] However, they are shorter than the unsupported Ga–Ga bonds of tetraalkyl or tetraaryl digallium compounds (>260 pm,[18] for a review see ref.[5]). Despite the different coordination numbers the Ga–C distances differ only slightly by about 1.5 pm, the slightly longer ones belong to the coordinatively saturated gallium atoms (CN

= 4). Also, the Ga–O distances are in a narrow range between 198.3 and 199.6 pm. In compound **2** the Ga–O bond length to the tetracoordinate gallium atom is the slightly shorter one. The Ga–I bonds are relatively long (267.8 and 263.2 pm) compared to those of the starting compound **1** (258.7 pm)[4] or other compounds bearing terminal iodine atoms.[10,19] The Ga–Ga–C groups approach linearity at the tricoordinate gallium atoms (165.2 and 162.5°) as often observed before for dicarboxylato digallium compounds.[11,17] Smaller angles were detected at the tetracoordinate atoms (147.0 and 142.7°). The Ga–O bonds are almost ideally perpendicular to the Ga–Ga bonds (angle Ga–Ga–O about 88° on average), independent of the coordination numbers of the metal atoms. The same holds for the Ga–Ga–I moieties where a relatively small angle of 81.8° was observed for compound **2**. The five-membered heterocycles obtained by the bridging of the Ga–Ga bonds are almost ideally planar, the strongest deviation was observed in both cases for the atom O2 with a value of 8.1 and 2.1 pm, respectively, for compounds **2** and **4**. The Ga–I bonds are nearly perpendicular to these planes, and the angles between their normals and the Ga–I bonds are 11.9 and 7.7°. The distances of the iodine atoms to the second gallium atoms are long (**2**: 333.1 pm; **4**: 350.1 pm) and do not indicate a significant bonding interaction. Interestingly, a disorder occurred with compound **2**, in which the iodine atom, with an occupation factor of 16%, approaches an ideal bridging position between both gallium atoms [Ga–I 278.8(9) and 306.4(12) pm, Ga–Ga 234.3(7) pm, Figure 1, b]. This arrangement reflects excellently the transition state postulated for the fast exchange process observed in solutions of these monocarboxylato compounds (**2**–**6**). Furthermore, all inner carbon atoms of the $C(SiMe_3)_3$ groups are located in the nodal planes of the gallium p orbitals, which are oriented perpendicularly to the $Ga_2C_2O_2$ plane. This particular situation may cause the shift of the ^{13}C NMR resonances to a relatively low field position at about $\delta = 30$ ppm. As discussed before these shifts are normally very characteristic of compounds possessing tricoordinate, coordinatively unsaturated gallium atoms.

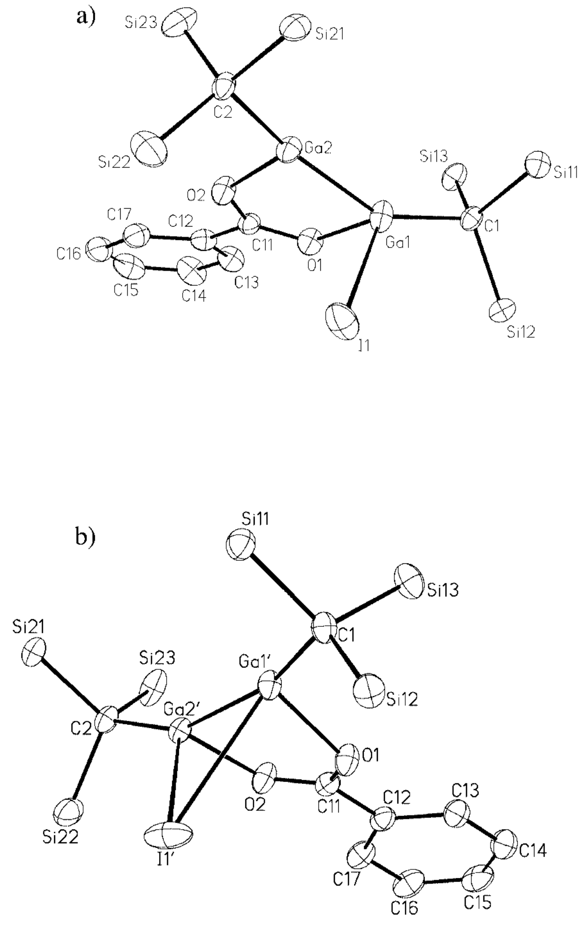


Figure 1. (a). Molecular structure and numbering scheme of compound **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted; of the disordered gallium and iodine atoms only those with the highest occupancy factors (0.84) were considered. Selected bond lengths [pm] and angles [°]: Ga1–Ga2 239.9(1), Ga1–C1 198.7(3), Ga2–C2 197.3(3), Ga1–O1 199.2(2), Ga2–O2 199.4(2), Ga1–I1 267.8(2), Ga1–Ga2–C2 165.2(1), Ga2–Ga1–C1 147.0(1), O1–Ga1–Ga2 87.69(7), O2–Ga2–Ga1 87.44(7), I1–Ga1–Ga2 81.81(9), I1–Ga1–O1 96.91(9). (b) Molecular structure and numbering scheme of the second individual of the disordered compound **2** possessing the lower occupation factors of the gallium and iodine atoms (16%); the thermal ellipsoids are drawn at the 40% probability level; methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1′–Ga2′ 234.3(7), Ga1′–I1′ 306(1), Ga2′–I1′ 278.8(8), Ga1′–C1 196.7(5), Ga2′–C2 198.5(7), Ga1′–Ga2′–I1′ 72.8(4), Ga2′–Ga1′–I1′ 60.3(4), Ga1′–I1′–Ga2′ 46.9(2).

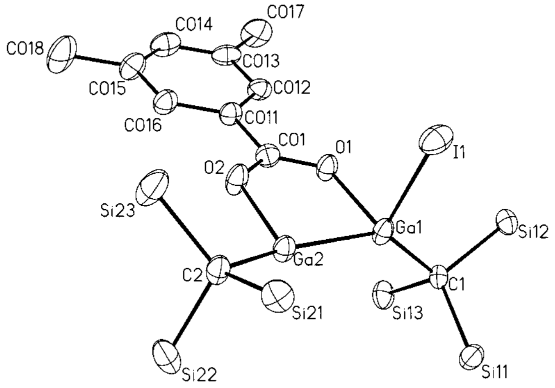
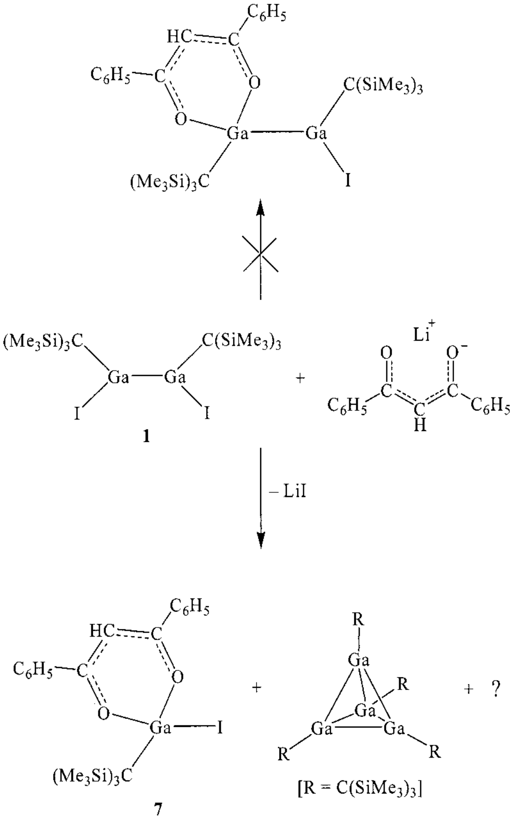


Figure 2. Molecular structure and numbering scheme of compound **4**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]:Ga1–Ga2 240.67(7), Ga1–C1 198.2(4), Ga2–C2 196.7(4), Ga1–O1 199.6(3), Ga2–O2 198.3(3), Ga1–I1 263.23(7), Ga1–Ga2–C2 162.5(1), Ga2–Ga1–C1 142.7(1), O1–Ga1–Ga2 87.43(9), O2–Ga2–Ga1 87.92(9), I1–Ga1–Ga2 87.90(2), I1–Ga1–O1 97.2(1).

Reaction of $I_2Ga_2R_2$ (1) [R = $C(SiMe_3)_3$] with Lithium Dibenzoylmethanide

Two equivalents of silver or lithium acetylacetonate reacted readily with the digallium(II) (**1**) or diindium(II) subhalides by the formation of the corresponding bis(acetylacetonato)dielement compounds.[10,15,20] In contrast to the bridging carboxylato ligands, the acetylacetonato groups occupy terminal positions at the E–E bonds. These compounds are thermally quite stable and decompose or melt only above 170 °C. We hoped to synthesize products analogous to **2**–**6** bearing one chelating acetylacetonato ligand along with one halogen atom by procedures similar to Equation (1).

However, the treatment of the subhalide **1** with one equivalent of lithium dibenzoylmethanide afforded a mixture of products. The three main components occur in an almost equimolar ratio and have chemical shifts in the ^{1}H NMR spectrum at δ = 0.55, 0.51, and 0.23 ppm. One product could be isolated by recrystallization as a bright yellow, crystalline solid. It possesses the $C(SiMe_3)_3$ group (δ = 0.55 ppm) and the chelating ligand in a 1:1 ratio, which clearly excludes the formation of the desired mixed halogeno acetylacetonato digallium species, see Equation (2). Instead, crystal structure determination revealed a gallium(III) compound (**7**) with a $C(SiMe_3)_3$ group, an iodine atom, and a chelating ligand bonded to the central gallium atom. Thus in this case disproportionation occurred, and the saturation of the coordination sphere by a terminal chelating ligand may not be sufficient to stabilize the gallium(II) compound. Elemental gallium is not formed. The chemical shift of one resonance in the ^{1}H NMR spectrum of the raw product at δ = 0.51 ppm is identical to that of the corresponding tetraalkyltetragallium(I) cluster, which has gallium atoms in an oxidation state of +1. Thus, we suppose that this cluster may be the second product of the disproportionation, however, we were unable to isolate the characteristic red crystals of that compound. Also the third main component of the reaction mixture could not be isolated in a pure form. Its constitution remains unknown. Cleavage of the Ga–Ga bond with the formation of an alkylgallium(III) iodide bearing a chelating ligand was also observed for the reaction of **1** with lithium diphenyltriazenide.[10]



(2)

The structural parameters of the molecule of **7** in the solid state (Figure 3) are as expected and do not require a detailed discussion. The gallium atom has a distorted tetrahedral coordination sphere. The Ga–I distance (254.1 pm) is shorter than that for **2** and **4** and is in the normal range for terminal Ga–I bonds.[10,19]

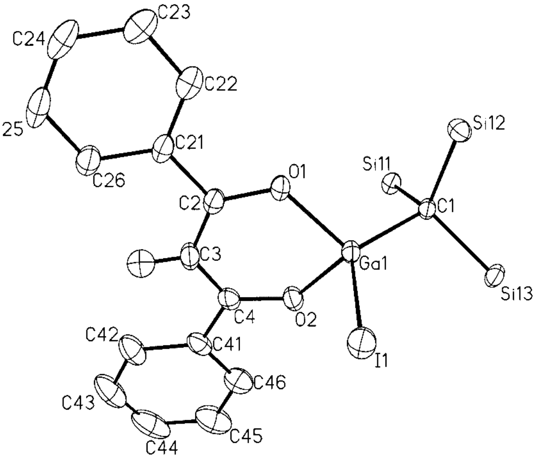


Figure 3. Molecular structure and numbering scheme of compound **7**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1–I1 254.11(4), Ga1–C1 195.9(2), Ga1–O1 189.5(2), Ga1–O2 189.3(2), O1–Ga1–O2 95.22(8), C1–Ga1–O1 114.80(9), C1–Ga1–O2 112.64(9), C1–Ga1–I1 125.53(7), O1–Ga1–I1 101.95(6), O2–Ga1–I1 101.86(6).

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene over Na/benzophenone; *n*-hexane and cyclopentane over $LiAlH_4$). The compound $R_2Ga_2I_2$ (**1**) was synthesized according to a literature procedure.[4] The commercially available carboxylic acids were sublimed in vacuo prior to use.

Synthesis of $Ga_2I(\mu$-O_2C–$C_6H_5)R_2$ (2) [R = $C(SiMe_3)_3$]: Freshly sublimed benzoic acid (17 mg, 0.141 mmol) was dissolved in toluene (20 mL) and treated with an equimolar quantity of a solution of *n*-butyllithium (0.145 M) in *n*-hexane (0.97 mL, 0.141 mmol) at room temperature. The mixture was heated to its boiling point for a minute. A suspension of lithium benzoate was obtained, which was cooled to –90 °C and treated with a solution of the subhalide **1** (121 mg, 0.141 mmol) in toluene (10 mL). The light yellow mixture was warmed slowly to room temperature und stirred for 48 h. After filtration all volatile components were removed in vacuo. The yellowish residue was dissolved in *n*-hexane and cooled to –70 °C. After a week an amorphous powder of the colorless product **2** was isolated. Yield: 97 mg (82%), m.p. (argon, sealed capillary) = 160 °C. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 0.46 (s, 54 H, $SiMe_3$), 7.04 (m, 3 H, *m*- and *p*-H of phenyl), 8.31 (2 H, *pseudo*-d, *o*-H of phenyl) ppm. ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ = 5.5 ($SiMe_3$), 30.2 (Ga–C), 128.9 (*p*-C of phenyl), 130.8 (*m*-C of phenyl), 131.0 (*i*-C of phenyl), 134.4 (*o*-C of phenyl), 178.3 (CO_2) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1600 (w, phenyl), 1503 [m, $\nu(CO_2)$], 1461 (vs, paraffin), 1409 [m, δ(CH)], 1377 (s, paraffin), 1320 (w), 1263 (m), 1251 [m, $\delta(CH_3)$], 1177 (vw), 976 (vw), 920 (vw), 857 (vs), 788 {sh, $\rho[CH_3(Si)]$}, 719 (w, paraffin), 681 (m), 662 [m, ν_{as}(SiC)], 633 (vw), 617 [vw, ν_s(SiC)], 488 (w), 474 [sh, ν(GaC), ν(GaO)] cm^{-1}. $C_{27}H_{59}Ga_2IO_2Si_6$ (850.6): calcd. C 38.1, H 7.0; found C 38.5, H 7.1.

Synthesis of $Ga_2I(\mu\text{-}O_2C\text{–}4\text{-}Br\text{–}C_6H_4)R_2$ (3) [R = $C(SiMe_3)_3$]: 4-Bromo-benzoic acid (41 mg, 0.207 mmol) was suspended in 50 mL of *n*-hexane and treated with 1.4 mL of a 0.145 M solution of *n*-butyllithium (0.207 mmol) in *n*-hexane. The mixture was stirred at room temperature for 2 h and cooled to –90 °C. A solution of the subhalide **1** (177 mg, 0.207 mmol) in 20 mL of *n*-hexane was added. The mixture was warmed to room temperature and stirred for 4 d. LiI was separated by filtration, and the solvent was removed in vacuo. The residue was dissolved in cyclopentane and cooled to –80 °C for 4 d. The product precipitated as a colorless solid. Yield: 35 mg (18%); m.p. (argon, sealed capillary) = 135 °C. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.45 (s, 54 H, $SiMe_3$), 6.99 (d, 2 H, $^3J_{HH}$ = 8 Hz, *m*-H of phenyl), 7.89 (d, 2 H, $^3J_{HH}$ = 8 Hz, *o*-H of phenyl) ppm. ^{13}C NMR (C_6D_6, 50 MHz, 298 K): δ = 5.4 ($SiMe_3$), 30.2 (Ga–C), 129.1 and 129.9 (*i*-C and *p*-C of phenyl), 132.1 and 132.3 (*o*-C and *p*-C of phenyl), 177.5 (CO_2) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1589 (m, phenyl) 1532 (m), 1505 [m, $\nu(CO_2)$], 1463 (vs, paraffin), 1407 [s, δ(CH)], 1377 (s, paraffin), 1320 (w), 1263 (m), 1252 [m, $\delta(CH_3)$], 1174 (w), 1155 (vw), 1074 (w), 1012 (w), 857 (vs), 824 (w), 770 {w, $\rho[CH_3(Si)]$}, 721 (w, paraffin), 676 (w), 663 [w, ν_{as}(SiC)], 634 (vw), 620 [vw, ν_s(SiC)], 529 (w), 471 [vw, ν(GaC), ν(GaO)] cm^{-1}.

Synthesis of $Ga_2I(\mu\text{-}O_2C\text{–}3,5\text{-}Me_2C_6H_3)R_2$ (4) [R = $C(SiMe_3)_3$]: 3,5-Dimethylbenzoic acid (47 mg, 0.313 mmol) was suspended in 50 mL of toluene and treated with 2.0 mL of a 0.145 M solution of *n*-butyllithium (0.207 mmol) in *n*-hexane. The mixture was stirred at room temperature for 15 min and cooled to –90 °C. A solution of the subhalide **1** (255 mg, 0.298 mmol) in 25 mL of toluene was added. The mixture was warmed to room temperature and stirred for 24 h. All volatiles were removed in vacuo. The residue was treated with *n*-hexane and filtered. The colorless product was obtained upon cooling the filtrate to –80 °C. Yield: 147 mg (54%); colorless crystals; m.p. (argon, sealed capillary) = 187 °C. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.49 (s, 54 H, $SiMe_3$), 2.08 (s, 6 H, Me attached to phenyl), 6.79 (s, 1 H, *p*-H of phenyl), 8.02 (s, 2 H, *o*-H of phenyl) ppm. ^{13}C NMR (C_6D_6, 50 MHz, 298 K): δ = 5.5 ($SiMe_3$), 21.1 (Me attached to phenyl), 31.9 (Ga–C), 128.3, 130.6, 136.2 and 138.6 (all phenyl), 178.7 (CO_2) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1652 (br, w, phenyl), 1494 [m, $\nu(CO)_2$] 1461 (vs, paraffin), 1392 [m, δ(CH)], 1376 (s, paraffin), 1320 (w), 1264 (m), 1251 [m, $\delta(CH_3)$], 1152 (vw), 1077 (vw), 1040 (br, w), 856 (vs), 785 (w), 768 {w, $\rho[CH_3(Si)]$}, 722 (w, paraffin), 675 (m), 661 [m, ν_{as}(SiC)], 634 (vw), 618 [vw, ν_s(SiC)], 548 (w), 488 [w, ν(GaC), ν(GaO)] cm^{-1}. UV/Vis (*n*-hexane): λ_{max} (logε) = 254 (3.54), 331 (2.84) nm. $C_{29}H_{63}Ga_2IO_2Si_6$ (878.7): calcd. C 39.6, H 7.2; found C 38.5, H 7.4.

Synthesis of $Ga_2I(\mu\text{-}O_2C\text{–}4\text{-}Me_3C\text{–}C_6H_4)R_2$ (5) [R = $C(SiMe_3)_3$]: The procedure is similar to that for the synthesis of **4** (4-*tert*-butylbenzoic acid: 48 mg, 0.269 mmol; subhalide **1**: 230 mg, 0.269 mmol). We did not succeed in recrystallizing compound **5** from different solvents. However, the compound was formed directly in high purity, and the characterization was done with the raw product of the reaction. Owing to the unsuccessful purification by recrystallization no elemental analysis was conducted. Yield: 188 mg (77%); pale yellow amorphous solid; m.p. (argon, sealed capillary) = 97 °C. ^{1}H NMR (C_6D_6, 200 MHz, 298 K): δ = 0.51 (s, 54 H, $SiMe_3$), 1.09 (s, 9 H, CMe_3), 7.16 (d, 2 H, $^3J_{HH}$ = 8 Hz, *m*-H of phenyl), 8.31 (d, 2 H, $^3J_{HH}$ = 8 Hz, *o*-H of phenyl). ^{13}C NMR (C_6D_6, 50 MHz, 298 K): δ = 5.6 ($SiMe_3$), 30.1 (Ga–C), 30.9 (Me of *tert*-butyl), 35.1 (*C*Me$_3$), 126.2, 128.3, 131.2, and 158.2 (all phenyl), 178.3 (CO_2) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1606 (m), 1579 (m, phenyl), 1515 (m), 1491 [s, $\nu(CO_2)$], 1460 (vs, paraffin), 1407 [vs, δ(CH)], 1377 (s, paraffin), 1263 (m), 1252 [m, $\delta(CH_3)$], 1193 (m), 1150 (w), 1107 (w), 1016 (m, br), 855 (vs), 800 (m), 786 (m), 749 {vw, $\rho[CH_3(Si)]$}, 728 (w, paraffin), 675 (m), 661 [m, ν_{as}(SiC)], 637 (vw), 621 [vw, ν_s(SiC)], 599 (w), 584 (vw), 541 (vw), 490 [w, ν(GaC), ν(GaO), $\delta(C_3C)$] cm^{-1}. UV/Vis (*n*-hexane): λ_{max} (logε) = 240 (3.53), 330 (2.87) nm.

Synthesis of $Ga_2I(\mu\text{-}O_2C\text{–}CMe_3)R_2$ (6) [R = $C(SiMe_3)_3$]: The procedure is similar to that for the synthesis of **4** (pivalic acid: 19 mg, 0.187 mmol, after addition of butyllithium stirred for 2 h at room temperature; subhalide **1**: 160 mg, 0.187 mmol). The colorless product was obtained upon cooling the filtrate to –80 °C. Yield: 77 mg (50%); colorless solid; m.p. (argon, sealed capillary) = 127 °C. ^{1}H NMR (C_6D_6, 200 MHz, 298 K): δ = 0.42 (s, 54 H, $SiMe_3$), 1.15 (s, 9 H, CMe_3). ^{13}C NMR (C_6D_6, 50 MHz, 298 K): δ = 5.4 ($SiMe_3$), 27.0 (Me of *tert*-butyl), 30.2 (Ga–C), 39.6 (*C*Me$_3$), 192.0 (CO_2) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1600 (m), 1502 (s), 1484 [s, $\nu(CO_2)$], 1461 (vs, paraffin), 1421 [s, δ(CH)], 1378 (s, paraffin), 1364 (sh), 1293 (w), 1263 (s), 1252 [s, $\delta(CH_3)$], 1222 (m), 1169 (w), 1000 (m, br), 855 (vs), 789 (m), 752 {vw, $\rho[CH_3(Si)]$}, 721 (m, paraffin), 675 (s), 661 [s, ν_{as}(SiC)], 632 (w), 618 [m, ν_s(SiC), 529 (vw), 443 [w, ν(GaC), ν(GaO), $\delta(C_3C)$] cm^{-1}. UV/Vis (*n*-hexane): λ_{max} (logε) = 254 (3.60) nm. $Ga_2IO_2Si_6C_{25}H_{63}$ (830.6): calcd. Ga 16.8; found Ga 16.1.

Reaction of $R_2Ga_2I_2$ 1 with Dibenzoylmethyllithium. Synthesis of 7: The procedure is similar to that for the synthesis of compound **4** (dibenzoylmethane: 76 mg, 0.341 mmol, after addition of butyllithium stirred for 2 h; subhalide **1**: 292 mg, 0.341 mmol). The intensively yellow reaction mixture was filtered, toluene was removed in vacuo, and the residue was recrystallized from cyclopentane (20/–45 °C). Product **7** was precipitated as an amorphous solid. Yield: 51 mg (23%), yellow solid; m.p. (argon, sealed capillary) = 213 °C. ^{1}H NMR (C_6D_6, 200 MHz, 298 K): δ = 0.55 (s, 27 H, $SiMe_3$), 6.80 (s, 1 H, inner H atom of the acac ligand), 7.02 (m, 6 H, *m*-H and *p*-H of phenyl), 7.84 (4 H, pseudo-d, *o*-H of phenyl) ppm. ^{13}C NMR (C_6D_6, 50 MHz, 298 K): δ = 5.1 ($SiMe_3$), 31.9 (Ga–C), 96.0 (inner C of the acac ligand), 128.9, 132.5, 133.3, and 137.0 (phenyl), 186.0 (CO) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1590 (m, phenyl), 1523 (vs), 1478 [s, $\nu(CO_2)$], 1460 (vs, paraffin), 1377 (m, paraffin), 1364 (m), 1347 (s), 1326 (m), 1303 (m), 1263 (s), 1253 [s $\delta(CH_3)$, 1229 (m), 1173 (w), 1153 (w), 1122 (w), 1096 (w), 1064 (w), 1024 (w), 997 (w), 949 (w), 852 (vs), 772 (w) 758 {w, $\rho[CH_3(Si)]$}, 719 (m, paraffin), 677 (m, ν_{as}(SiC), 643 (vw), 622 [v, ν_s(SiC)], 592 (w), 544 (w), 462 [vw, ν(GaC), ν(GaO)] cm^{-1}. UV/Vis (*n*-hexane): λ_{max} (logε) = 226 (3.98), 266 (3.81), 372 (3.85) nm. $GaIO_2Si_3C_{25}H_{38}$ (651.5): calcd. C 46.1, H 5.9; found C 47.1, H 6.6.

Crystal Structure Determinations: Single crystals of the compounds **2**, **4**, and **7** were obtained by cooling the solutions in *n*-hexane (20/–30 °C, **2**), cyclopentane (20/–45 °C, **4**), and again cyclopentane (20/+5 °C, **7**). Crystal data and structure refinement parameters are given in Table 1.[23] The crystals of **2** enclose one molecule of *n*-hexane per formula unit of **2**. Owing to their relatively large isotropic displacement parameters the solvent carbon atoms were not

Table 1. Crystal data and structure refinement for the compounds **2**, **4**, and **7**.[a]

	2	**4**	**7**
Formula	$C_{33}H_{73}Ga_2IO_2Si_6$	$C_{34}H_{73}Ga_2IO_2Si_6$	$C_{30}H_{48}GaIO_2Si_3$
Crystal system	monoclinic	monoclinic	triclinic
Space group[21]	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
Z	4	4	2
T [K]	153(2)	153(2)	153(2)
$d_{\text{calcd.}}$ [g·cm^{-3}]	1.317	1.335	1.404
a [pm]	1914.45(8)	1950.9(1)	886.64(7)
b [pm]	910.19(2)	928.04(5)	1341.6(1)
c [pm]	2837.9(1)	2676.2(1)	1609.4(1)
α [°]	90	90	65.516(1)
β [°]	107.119(3)	103.106(1)	84.529(2)
γ [°]	90	90	78.393(2)
V [10^{-30} m^3]	4726.0(3)	4719.0(4)	1706.5(2)
μ [mm^{-1}]	1.970	1.974	1.840
Crystal size [mm]	0.32 × 0.18 × 0.10	0.12 × 0.06 × 0.06	0.26 × 0.24 × 0.16
Diffractometer	STOE IPDS	Bruker Smart Apex	Bruker Smart Apex
Radiation	Mo-K_α; graphite monochromator		
θ range [°]	$1.58 \le \theta \le 27.05$	$1.17 \le \theta \le 30.07$	$1.39 \le \theta \le 31.23$
Index ranges	$-24 \le h \le 24$	$-27 \le h \le 27$	$-12 \le h \le 12$
	$-11 \le k \le 10$	$-13 \le k \le 13$	$-19 \le k \le 18$
	$-36 \le l \le 36$	$-37 \le l \le 35$	$-22 \le l \le 22$
Independent reflections	10185 [R_{int} = 0.0359]	13701 [R_{int} = 0.0887]	10067 [R_{int} = 0.0321]
Reflections $I > 2\sigma(I)$	8827	6575	7393
Parameters	388	507	343
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert / \Sigma\lvert F_o\rvert$ [$I > 2\sigma(I)$]	0.0346	0.0546	0.0421
$wR_2 = \{\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2 / \Sigma\lvert F_o\rvert^2\}^{1/2}$ (all data)	0.1036	0.1271	0.0860
Max./min. residual [10^{30} e·m^{-3}]	1.053/–0.630	1.385/–0.821	1.109/–0.848

[a] Program SHELXL-97;[22] solutions by direct methods, full-matrix refinement with all independent structure factors.

refined anisotropically. The central Ga–Ga–I group showed a disorder over two positions, see the Results and Discussion chapter for details. These atoms were refined with occupancy factors of 0.84 and 0.16. The refinement of the substituents was not affected by this disorder. The tris(trimethylsilyl)methyl group at C2 of compound **4** was disordered. Its atoms were refined with site occupation factors of 0.84 and 0.16. One molecule of cyclopentane was enclosed per formula unit of **4**. Its carbon atoms were refined only with isotropic displacement factors. Also the crystals of **7** contained one cyclopentane molecule.

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[23] CCDC-295626 (for **2**), -2956127 (for **4**), and -295628 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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