Investigations into the Reactivity of Organoelement Gallium and Indium Subhalides – Syntheses of Digallium and Diindium Acetylacetonates

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The organoelement subhalides $R_2Ga_2I_2$ (**1**) and $[R_2In_2Cl_2]_2$ (**2**) [R = $C(SiMe_3)_3$] react with silver acetylacetonate Ag(acac) (acac = $[OC(CH_3)]_2CH$) and lithium acetylacetonate Li(acac), respectively, to yield the di(acetylacetonato)dielement compounds $R_2E_2(acac)_2$ (**3**: E = Ga; **4**: E = In). Both products possess E–E single bonds with relatively long E–E distances of 251.1 (Ga–Ga) and 278.0 pm (In–In). The gallium or indium atoms are terminally coordinated by an alkyl and a bidentate acetylacetonato group. Similar reactions of the subhalides **1** and $[R_2In_2Br_2]_2$ with lithium diphenyltriazenide $LiN_3(C_6H_5)_2$ did not result in the formation of dielement compounds analogous with **3** and **4** but in the cleavage of the E–E bonds with formation of element(III) compounds of the type R–$E(X)[N_3(C_6H_5)_2]$ (E = Ga, In; X = Br, I).

Introduction

Organoelement subhalides of the heavier elements of the third main-group, i.e. aluminum, gallium, indium and thallium form an interesting class of compounds. They possess the elements in unusually low oxidation states with direct E–E interactions and are valuable starting materials for the generation of secondary products by salt elimination reactions. Their synthesis can be accomplished by several different methods such as (i) the treatment of tetrahalogenosubhalides of the type $X_2(L)E–E(L)X_2$ with aryl or silyl alkali-metal compounds in molar ratios of 1:1 or 1:2[1–4] (ii) the reduction of organogallium(III) compounds by alkali metals[5] (iii) the treatment of GaBr or "GaI" with organo lithium or sodium compounds accompanied by disproportionation of the third main-group element[1,6,7] (iv) the reduction of an indium(III) compound with an aminoborole[8] (v) the insertion of AlCp* into Al–I bonds of the aluminum triiodide dimer[9] and (vi) the careful oxidation of tetragallium or tetraindium clusters $E_4[C(SiMe_3)_3]_4$ with halogens or halogen donors.[10–13] The last method was introduced by our group and affords subhalides possessing different structures in reasonable yields. The transfer of one bromine molecule to the tetrahedral tetraindium cluster affords the compound $In_4Br_2[C(SiMe_3)_3]_4$ in which the tetrahedral arrangement of the indium atoms is retained but one triangular face of the In_4 tetrahedron and one edge of that face are bridged by bromine atoms.[11] The oxidation of all element(I) atoms of the starting clusters to an oxidation state of +II yields the element(II) halides R(X)E–E(X)R (E = Ga, In; X = Cl, Br, I) which possess E–E single bonds.[11–13] They remain monomeric even in the solid state for gallium whereas they form dimers with all halogen atoms in bridging positions for the indium derivatives. A chain of three indium atoms connected by two In–In single bonds was observed for the subhalide $In_3I_2[C(SiMe_3)_3]_3$[10] which resulted from the oxidation of the tetraindium cluster with elemental iodine in the presence of AlI_3.

These subhalides proved to be very effective starting compounds for the synthesis of secondary products by salt elimination reactions. For instance, several transition-metal gallium or indium compounds possessing quite different and interesting structures can be obtained by such a route on treatment with transition-metal carbonylate anions such as $[Fe(CO)_4]^{2-}$ or $[Fe_2(CO)_8]^{2-}$.[14–17] Silver or lithium carboxylates give dialkyldicarboxylatodielement compounds in which the carboxylato ligands occupy bridging positions across the relatively short E–E bonds.[18] Whereas the corresponding digallium compounds are easily available by the direct treatment of a tetraalkyldigallium(4) derivative $R_2Ga–GaR_2$ [R = $CH(SiMe_3)_2$] with carboxylic acids,[19–24] the In–In bonds of the diindium analogue $R_2In–InR_2$ are completely cleaved by oxidation of the indium atoms under similar conditions.[25] Thus, the reactions of these organoelement subhalides of gallium and, in particular, indium seem to offer a valuable route for the syntheses of new compounds which contain the elements in unusually low oxidation states and are not accessible by other methods. The behaviour of the dielement compounds $R_2E–ER_2$ towards acetylacetones is similar to that described for carboxylic acids. While substituent exchange with retention of the Ga–Ga bonds was observed for the digallium derivative, oxidation and cleavage of the In–In bond occurred with the diindium compound.[26,27] Diindium acetylacetonates containing an In–In bond may, however, be accessible by use

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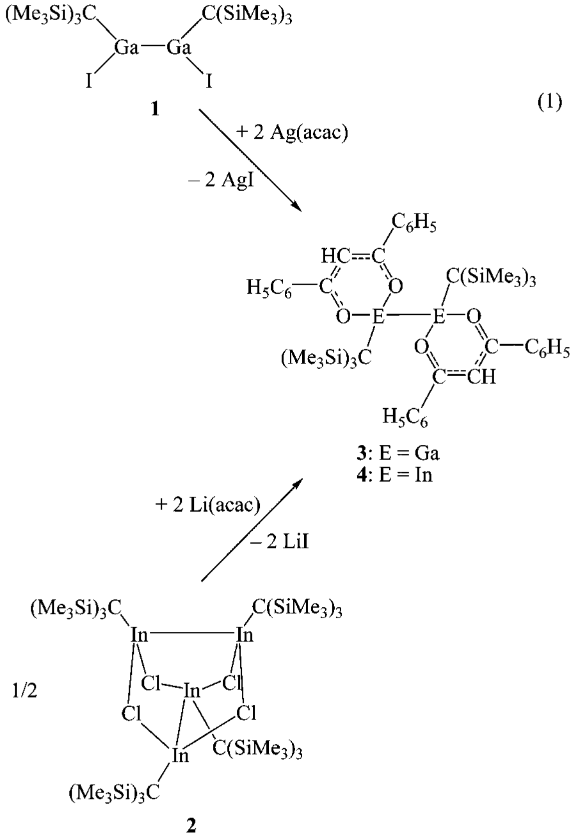
of the corresponding subhalides. We report here on the continuation of our systematic investigations into the reactivities of these subhalides and on their reactions with acetylacetonate and diphenyltriazenide anions.

Results and Discussion

Syntheses and Molecular Structures of the Di(acetylacetonato)digallium and-diindium Compounds 3 and 4

Treatment of the monomeric dialkyldigallium subiodide $R_2Ga_2I_2$ (**1**) [R = $C(SiMe_3)_3$] with lithium acetylacetonate gave a mixture of unknown products, none of which could be isolated in a pure form. We therefore employed silver acetylacetonate in order to enhance the driving force of the reaction with the formation of silver iodide. A suspension of the silver salt was treated with **1** at low temperature (–90 °C) and it appeared that the reaction was complete upon warming to –70 °C. Filtration was carried out at that temperature and subsequent workup yielded yellow crystals of the product **3** in 67% yield [Equation (1)]. In contrast, the corresponding reaction of the dimeric diindium subchloride $(R_2In_2Cl_2)_2$**2** with silver acetylacetonate gave decomposition only. Probably, the In–In bond was cleaved by oxidation of the indium atoms with the formation of unknown products. A silver mirror formed at the glass wall of the Schlenk tube. Lithium acetylacetonate now gave a clean reaction although reproducible yields after reasonable reaction times were obtained only upon warming of the mixtures in toluene to 50 °C. Pale yellow crystals of the product **4** were isolated in 66% yield after recrystallisation from *n*-hexane. The chemical shifts of the trimethylsilyl protons of both products **3** and **4** (δ = 0.44 and 0.42 ppm, respectively) are in the characteristic range for $C(SiMe_3)_3$ groups attached to Ga–Ga or In–In single bonds possessing coordinatively saturated Ga or In atoms (about δ = 0.4 to 0.5 ppm).[11,18] The integration ratios in the ^1H NMR spectra, too, were in accordance with the formulae given schematically in Equation (1) with intact Ga–Ga or In–In bonds and the replacement of both halogen atoms of the starting dielementdihalides by chelating acetylacetonato groups. We were not able to detect the resonance of the inner carbon atoms of the $C(SiMe_3)_3$ groups attached to the In–In bond, probably as a result of the quadrupole moment of indium. The corresponding ^{13}C NMR signal of the gallium compound appeared at δ = 5.0 ppm which is characteristic of compounds possessing coordination numbers of four at their gallium atoms. Usually, tetraalkyl- or tetraaryldielement compounds of the type $R_2E–ER_2$ (E = Ga, In) containing Ga–Ga or In–In single bonds and an empty p-orbital at each Ga or In atom are deeply coloured.[28] However, upon coordinative saturation of the central gallium atoms by introduction of chelating ligands such as a carboxylato[19–24] or imidotetraphenyldiphosphinato groups,[29] colourless digallium products were isolated. Colours observed for those compounds in some cases are caused by transitions within ligands which possess electronically delocalised bonding systems such as diphenyltriazenide.[30,31] Similar to the acetylacetonato digallium derivatives[26,27] cited in the introduction, compounds **3** and **4** are yellow. The longest wavelengths were observed at 345 and 355 nm, respectively, the absorption of the gallium compound **3** is broader than that of the diindium diacetylacetonate **4**. The mononuclear E(III) compounds $E(acac)_3$ (E = Al, Ga, In) were reported to be colourless to orange.[32–34] Absorptions in the UV/Vis spectra were assigned to π-π transitions within the ligands.[35]



The molecular structures of **3** and **4** determined by single-crystal X-ray diffraction studies are depicted in Figure 1 and Figure 2. The compounds are not isostructural. While the molecules of **3** are in general positions, the molecules of **4** reside on crystallographic twofold rotation axes. The chelating acetylacetonato ligands of both compounds are terminally coordinated to the gallium or indium atoms of the unsupported Ga–Ga or In–In single bonds. Each central atom is further attached to an alkyl group so that coordination numbers of four result. Although an approach to the *trans* arrangement of the ligands is observed for both structures, the molecules deviate more or less significantly from an ideal centrosymmetric conformation. The torsion angles across the E–E bonds (C–E–E–C) are 151.4(3)° and 146.4(1)°, respectively. The Ga–Ga and In–In bond lengths (251.1 and 278.0 pm) are relatively long and similar to those of tetraalkyldielement derivatives $R_2E–ER_2$ [R = $CH(SiMe_3)_2$].[28,36,37] Thus, the shortening usually detected upon coordination of electronegative atoms to the E–E bonds[28] is not observed in these cases. Two dialkyldigallium compounds containing terminal acetylacetonato groups attached to their Ga–Ga bonds have been reported in the literature.[26,27,38] They show shorter Ga–Ga bond lengths of 244.3 pm on average. Owing to the smaller alkyl groups employed in these compounds [$CH(SiMe_3)_2$ compared with $C(SiMe_3)_3$ in **3** and **4**], we suppose that the long E–E distances of **3** and **4** may be caused by some steric interactions between their very bulky substituents. Accordingly, the Ga–C distances are longer in the tris(trimethylsilyl)methyl compounds described here (199 versus 204 pm). In contrast, the Ga–O distances are unaffected by the different alkyl groups and, at 195 pm,are almost indistinguishable between the compounds. An analogous dialkyldiindium compound was not obtained before so that a sound comparison of bond distances is difficult. However, the In–C bonds appear to be relatively long (221.2 pm).[37]

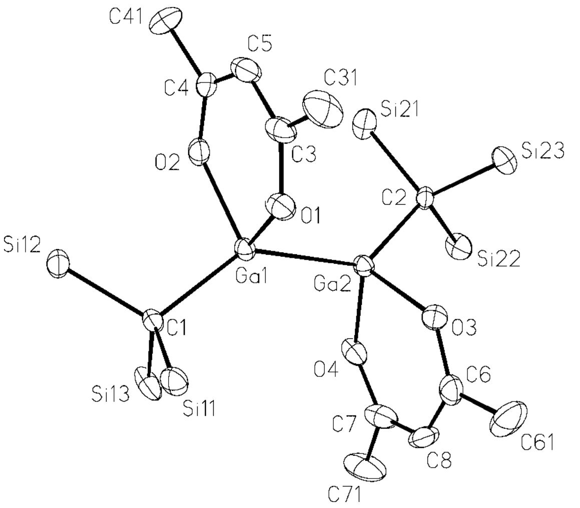


Figure 1. Molecular structure and numbering scheme of compound **3**. Thermal ellipsoids are drawn at the 40% probability level. Methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1–Ga2 251.12(8), Ga1–C1 204.0(5), Ga2–C2 204.5(6), Ga1–O1 195.1(3), Ga1–O2 195.7(4), Ga2–O3 195.1(3), Ga2–O4 195.1(4), Ga1–Ga2–C2 134.1(1), Ga2–Ga1–C1 133.8(1), O1–Ga1–O2 91.3(2), O3–Ga2–O4 91.3(2).

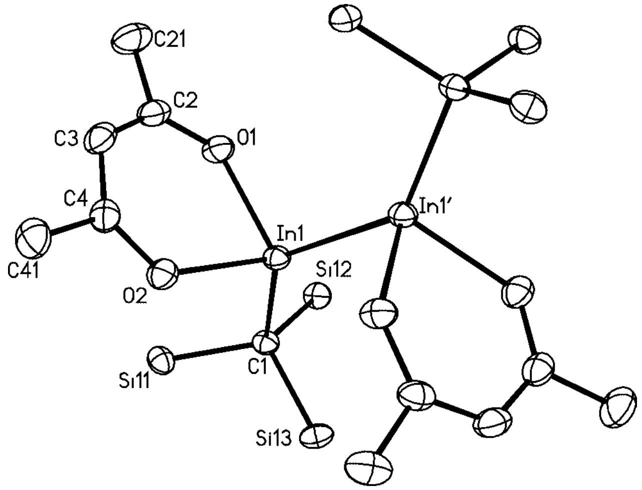
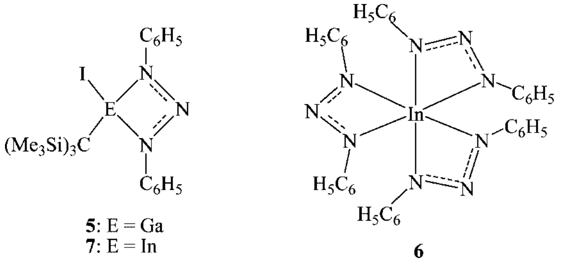


Figure 2. Molecular structure and numbering scheme of compound **4**. Thermal ellipsoids are drawn at the 40% probability level. Methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: In1–In1′ 278.04(7), In1–C1 221.3(2), In1–O1 216.3(1), In1–O2 216.0(1), In1′–In1–C1 136.73(5), O1–In1–O2 85.31(5); In1′ generated by –*x*, *y*, –*z* + 1/2.

Reactions of the Subhalides with Lithium Diphenyltriazenide

As was shown before, the subhalides of gallium and indium are excellent starting compounds for the generation of secondary products containing Ga–Ga or In–In bonds. Carboxylato and acetylacetonato ligands could be introduced by such a route and the products were generally isolated in reasonable yields. Another ligand which is able to stabilise the Ga–Ga bond of bis(trimethylsilyl)methyl compounds is diphenyltriazenide. However, the direct reaction of $R_2Ga–GaR_2$ [R = $CH(SiMe_3)_2$] with diphenyltriazene by release of two equivalents of bis(trimethylsilyl)methane gave partial cleavage of the Ga–Ga bond as an undesired side-reaction and the separation of both products by recrystallisation did not succeed.[30] Owing to their different colours, the crystalline products could be separated in very small quantities under a microscope only. Later, the bis(triazenido)digallium compound containing a Ga–Ga bond was isolated in an almost quantitative yield by the reaction of an acetato derivative, $R_2Ga_2(\mu\text{-}O_2C\text{-}CH_3)_2$ [R = $CH(SiMe_3)_2$], with lithium diphenyltriazenide.[31] The driving force was the precipitation of lithium acetate. Such a procedure is similar to the method described here. Diindium compounds bearing triazenido ligands are unknown and so we tried to introduce triazenido groups into digallium or diindium compounds starting with our subhalides. Treatment of the digallium subhalide $R_2Ga_2I_2$**1** with lithium diphenyltriazenide (easily obtained by deprotonation of diphenyltriazene with *n*-butyllithium) in *n*-hexane afforded a mixture of products. Recrystallisation from diisopropyl ether yielded a small quantity of orange crystals of compound **5** which was identified from a crystal structure determination (see below) as the mononuclear compound $IGa[C(SiMe_3)_3][N_3(C_6H_5)_2]$ (Scheme 1) possessing gallium atoms in the +III oxidation state. Compound **5** was formed by the cleavage of the Ga–Ga bond. Although the ^1H NMR spectrum of the crude product of the reaction showed that **5** (δ = 0.31 ppm, $SiMe_3$) had formed in a considerable amount, no second fraction could be isolated after concentration and cooling of the mother liquor. Furthermore, a second main product was detected (δ = 0.25 ppm) which could not be isolated in a pure form at all. Its constitution remains unknown and we do not have any suitable information to allow a sound discussion of the reaction course. A similar situation holds for the reactions of the diindium subhalides $(R_2In_2X_2)_2$ [X = Cl: **2**; X = Br] with lithium diphenyltriazenide. Mixtures were formed in which $HC(SiMe_3)_3$ and the protonated triazenide $N_3(C_6H_5)_2H$

could be detected by NMR spectroscopy. Both compounds may indicate the occurrence of radical intermediates. Another product formed was indium tris(diphenyltriazenide) **6** (Scheme 1) which could be isolated as yellow crystals in a low yield from the reaction of the dibromide but was also clearly identified in the NMR spectrum of the crude product from the reaction of **2**. The mother liquor remaining after the separation of **6** showed one resonance of relatively high intensity in the trimethylsilyl range of the ^1H NMR spectrum at $\delta = 0.22$ ppm which is characteristic of $C(SiMe_3)_3$ groups attached to gallium or indium in the +III oxidation state. It may result from the cleavage of the In–In bond and, in accordance with the integration ratio, may be described as $BrIn[C(SiMe_3)_3][N_3(C_6H_5)_2]$ similar to the gallium compound **5** described before. We did not succeed in isolating this compound in a pure form. However, a few crystals of a similar indium compound were isolated from the reaction of lithium diphenyltriazenide with the triindium subiodide $In_3I_2[C(SiMe_3)_3]_3$. This product, $InI[C(SiMe_3)_3][N_3(C_6H_5)_2]$ **7**, was identified by a crystal structure determination (see below) and by ^1H NMR spectroscopy ($\delta = 0.28$ pm for the trimethylsilyl groups). It was obtained as well as $HC(SiMe_3)_3$ and several other compounds. The main resonances in the ^1H NMR spectrum of the crude product were observed at $\delta = 0.22$, 0.50 and 0.68 ppm. We did not succeed in isolating any of these components in a pure form.



Scheme 1.

Three triazenido compounds (**5**, **6** and **7**) were characterised by single-crystal X-ray diffraction studies. The structure of the tris(triazenido)indium compound **6**, containing an indium atom coordinated by six nitrogen atoms in a distorted octahedral coordination sphere, was determined before.[39] We observed the occurrence of another space group and crystal system (monoclinic instead of orthorhombic). Therefore, we include some details of the structure determination in Table 1 but omit a pictorial presentation of the molecular structure. The bond parameters (In–N 224.1 pm on average; N–In–N within the chelate 56.4° on average; N–N–N 108.6° on average) are almost identical to those reported in the literature and do not need a further discussion. The structures of compounds **5** and **7** (Figures 3 and 4) are quite similar but they do not crystallise isotypically. They possess central gallium or indium atoms with oxidation numbers of +III which are coordinated by an iodine atom, a tris(trimethylsilyl)methyl group and a chelating triazenido ligand. The E–I distances (Ga–I 252.7 pm; In–I 269.5 pm) are in the expected ranges for terminal Ga–I or In–I bonds (some examples are given in refs.[12,40–54]). The same holds for the E–C (197.7 and 217.3 pm, respectively) and E–N distances (203.9 and 223.7 pm, respectively).[30,31,39,55,56] The N–N bond lengths of the triazenido groups are almost indistinguishable in both compounds (130.4 pm on average) while the N–N–N angle is slightly enlarged in the indium derivative **7** (107.5 compared with 109.6°) which may be caused by the larger covalent radius of indium.

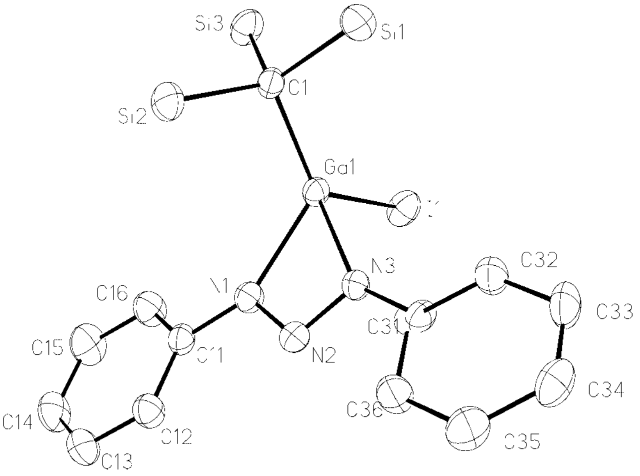


Figure 3. Molecular structure and numbering scheme of compound **5**. Thermal ellipsoids are drawn at the 40% probability level. Methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1–I1 252.7(1), Ga1–C1 197.7(4), Ga1–N1 203.6(3), Ga1–N3 204.2(3), N1–N2 130.7(5), N2–N3 130.0(4), N1–Ga1–N3 62.1(1), N1–N2–N3 107.5(3).

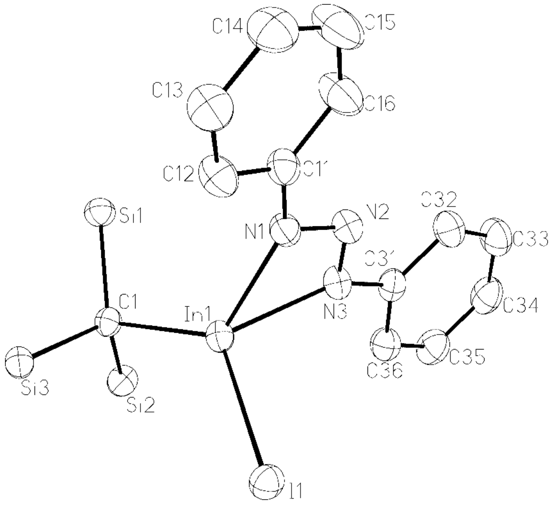


Figure 4. Molecular structure and numbering scheme of compound **7**. Thermal ellipsoids are drawn at the 40% probability level. Methyl groups of $SiMe_3$ substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: In1–I1 269.49(3), In1–C1 217.3(2), In1–N1 223.8(2), In1–N3 223.6(2), N1–N2 130.5(3), N2–N3 130.2(3), N1–In1–N3 56.85(9), N1–N2–N3 109.6(2).

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene and diisopropyl ether over Na/benzophenone; *n*-hexane and cyclopentane over $LiAlH_4$; 1,2-difluorobenzene over molecular sieves). The compounds $R_2Ga_2I_2$ (**1**),[12] $(R_2In_2Cl_2)_2$ (**2**),[11] $(R_2In_2Br_2)_2$[11] and $R_3In_3I_2$[10] were synthesised according to literature procedures. Commercially available silver acetylacetonate Ag(acac) (STREM), acetylacetone acacH (Aldrich) and diphenyltriazene (Aldrich) were employed without further purification. Lithium diphenyltriazenide was prepared by treatment of diphenyltriazene with an equimolar quantity of *n*-butyllithium in *n*-hexane. The insoluble product was filtered off and dried in vacuo.

Synthesis of $R_2Ga_2(acac)_2$ (3) [R = $C(SiMe_3)_3$]: A suspension of silver acetylacetonate (68 mg, 0.328 mmol) in toluene (25 mL) was cooled to –90 °C and treated with the diiodide **1** (141 mg, 0.165 mmol) dissolved in toluene (10 mL). The mixture was stirred and warmed to –70 °C (20 min). The precipitate was filtered off at –70 °C and the solvent was subsequently removed in vacuo at room temperature. The yellowish solid residue was recrystallised from cyclopentane (temp. range +20 to +8 °C). Yield: 89 mg of yellow crystals, 67%. M.p. (argon, sealed capillary): 194 °C (dec.). ^1H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.44 (s, 27 H, $SiMe_3$), 1.64 (s, 6 H, acac-Me), 5.03 (s, 1 H,acac-CH) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 5.0 (GaC), 6.2 ($SiMe_3$), 27.7 (acac-Me), 103.1 (acac-C, inner), 192.2 (CO) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1644 (vw), 1580 (w), 1555 (vw), 1525 (w, νCO, νCC), 1461 (vs), 1377 (vs, paraffin), 1304 (vw), 1260 (s, νCO, δCH_3), 1125 (s), 1095 (s), 1026 (s, δCH, νCC), 934 (vw), 843 (s), 804 [s, $\rho CH_3(Si)$], 720 (w, paraffin), 699 (w), 677 (w), 659 (vw, ν_{as}SiC), 618 (vw, ν_sSiC), 514 (w), 464 (vw), 404 (vw), 390 (vw, νGaC, νGaO) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} (log ε) = 250 (4.0), 275 (sh, 3.7), 345 (sh, 3.0) nm.

Synthesis of $R_2In_2(acac)_2$ (4) [R = $C(SiMe_3)_3$]: Acetylacetone (27.5 mg, 0.275 mmol) was dissolved in toluene (10 mL), cooled to –30 °C and treated with a solution of *n*-butyllithium (1.6 M, 17.2 µL) in *n*-hexane. After warming to room temperature the mixture was stirred for 30 min. A solution of the diindium dichloride (**2**) (105 mg, 0.138 mmol) in toluene (15 mL) was then added at room temperature. After stirring for 1 h the mixture was heated in a prewarmed oil-bath at 50 °C for a further hour. The solvent was removed in vacuo and the residue was treated with *n*-hexane. After filtration, the solution was cooled to –15 °C to give the solid, yellowish product **4**. Yield: 81 mg of yellowish crystals, 66%. M.p. (argon, sealed capillary): 178–182 °C. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.42 (s, 27 H, $SiMe_3$), 1.71 (s, 6 H, acac-Me), 5.09 (s, 1 H, acac-CH) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 6.3 ($SiMe_3$), 29.0 (acac-Me), 102.7 (acac-C, inner), 193.0 (CO) ppm, InC not detected. IR (CsBr, paraffin): $\tilde{\nu}$ = 1577 (s), 1543 (m), 1517 (s, νCO, νCC), 1459 (vs), 1375 (vs, paraffin), 1260 (s), 1248 (s, νCO, δCH_3), 1019 (ν_{as}Me-CO), 927 (ν_sMe-CO), 858 (vs), 777 [s, $\rho CH_3(Si)$], 724 (w, paraffin), 676 (m), 653 (m, ν_{as}SiC), 615 (w), 600 (m, ν_sSiC), 555 (w), 417 (w), 399 (w, νInC, νInO) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} (log ε) = 250 (3.4), 300 (sh, 3.6), 355 (3.7) nm.

Reaction of $R_2Ga_2I_2$ 1 with Lithium Diphenyltriazenide: A cooled (–80 °C) mixture of lithium diphenyltriazenide (57 mg, 0.281 mmol) and *n*-hexane (20 mL) was treated with a solution of **1** (117 mg, 0.137 mmol) in *n*-hexane (10 mL). The suspension was warmed to room temperature and stirred overnight. After filtration and evaporation of the solvent, the red residue was recrystallised twice from diisopropyl ether (temp. range +20 to –45 °C) to afford a small quantity of the pure compound $IGa[C(SiMe_3)_3][N_3(C_6H_5)_2]$ (**5**) as orange crystals. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.31 (s, 27 H, $SiMe_3$), 6.92 (pseudo-t, 2 H, *para*-PhH), 7.09 (pseudo-t, 4 H, *meta*-PhH), 7.52 (pseudo-d, 4 H, *ortho*-PhH) ppm.

Table 1. Crystal data, data collection parameters and structure refinement of compounds **4** to **8**.[a]

	3	**4**	**5**	**6**	**7**
Formula	$C_{30}H_{68}Ga_2O_4Si_{16}$	$C_{30}H_{68}In_2O_4Si_6$	$C_{22}H_{37}GaIN_3Si_3$	$C_{42}H_{30}F_2InN_9$	$C_{22}H_{37}IIn_2N_3Si_3$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$ (No. 4)[57]	$C2/c$ (No. 15)[57]	$P2_1/n$ (No. 14)[57]	$P2_1/c$ (No. 14)[57]	$P2_1/c$ (No. 14)[57]
Z	2	4	4	4	4
T [K]	193(2)	193(2)	193(2)	193(2)	193(2)
$d_{calcd.}$ [$g\,cm^{-3}$]	1.248	1.360	1.468	1.422	1.538
a [pm]	901.02(9)	2117.3(4)	1322.7(3)	929.10(9)	900.24(4)
b [pm]	1437.22(9)	899.0(2)	1322.2(3)	1182.77(8)	1829.60(7)
c [pm]	1646.0(2)	2286.5(5)	1717.4(3)	3467.5(4)	1758.50(8)
β [°]	90.24(1)	91.75(3)	109.87(3)	94.36(1)	93.197(4)
V [$10^{-30}\,m^3$]	2131.5(3)	4350(2)	2824(1)	3799.4(6)	2891.9(2)
µ [mm^{-1}]	1.462	1.254	2.209	0.675	2.023
Crystal size [mm]	0.26 × 0.07 × 0.15	0.45 × 0.35 × 0.30	0.30 × 0.24 × 0.09	0.80 × 0.60 × 0.40	0.21 × 0.12 × 0.09
Diffractometer	STOE IPDS				
Radiation	Mo-K_α radiation; graphite monochromator				
θ range [°]	1.88 to 25.95	2.46 to 26.16	1.99 to 26.03	2.09 to 26.01	1.61 to 26.26
Index ranges	$-11 \le h \le 10$	$-26 \le h \le 26$	$-16 \le h \le 16$	$-11 \le h \le 11$	$-11 \le h \le 11$
	$-17 \le k \le 16$	$-11 \le k \le 11$	$-16 \le k \le 16$	$-14 \le k \le 14$	$-22 \le k \le 22$
	$-20 \le l \le 20$	$-28 \le l \le 28$	$-21 \le l \le 21$	$-42 \le l \le 42$	$-21 \le l \le 21$
Independent reflections	7709 [R(int) = 0.0492]	4271 [R(int) = 0.0856]	5523 [R(int) = 0.0677]	7312 [R(int) = 0.0751]	5814 [R(int) = 0.0351]
Reflections $I > 2\sigma(I)$	5758	4035	4371	4524	5080
Parameters	402	201	280	459	280
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$ [$I > 2\sigma(I)$]	0.0429	0.0201	0.0407	0.0635	0.0284
$wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.0965	0.0579	0.1236	0.1764	0.0840
Max./min. residual [10^{30} e/m^3]	0.497/–0.599	0.547/–0.819	2.051/–0.776	1.936/–1.289	0.425/–0.941

[a]Programs: SHELXTL-Plus and SHELXL-97.[58] Solutions by direct methods. Full-matrix refinement with all independent structure factors.

^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 5.2 ($SiMe_3$), 6.0 (GaC?), 120.0, 126.4, 129.6 and 144.0 (phenyl) ppm.

Reaction of $(R_2In_2Br_2)_2$ with Lithium Diphenyltriazenide: Diphenyltriazene (69 mg, 0.35 mmol) was dissolved in *n*-hexane (20 mL), cooled to –30 °C and treated with a solution of *n*-butyllithium (0.2 mL, 1.6 M, 0.32 mmol) in *n*-hexane. The resultant suspension was stirred for 30 min at room temperature, cooled again to –30 °C and treated with a solution of the dibromide (130 mg, 1.53 mmol based on the monomeric formula) in *n*-hexane (25 mL). The mixture was warmed to room temperature and stirred for 30 min. A black precipitate formed which probably contained elemental indium. After filtration, the yellow-orange solution was concentrated and cooled to –30 °C. Only a few crystals of $In[N_3(C_6H_5)_2]_3$ (**6**) sufficient for a crystal structure determination could be isolated. All attempts to crystallise a second component from the reaction mixture failed.

Reaction of $R_3In_3I_2$ with Lithium Diphenyltriazenide: A cooled (–80 °C) suspension of lithium diphenyltriazenide (35 mg, 0.172 mmol) in *n*-hexane (25 mL) was treated with a solution of the triindiumdiiodide (101 mg, 0.078 mmol) in *n*-hexane (10 mL). The mixture was stirred for 1 h at room temperature. After filtration, the red solution was concentrated and cooled to –15 °C. Only a few crystals of $InI[C(SiMe_3)_3][N_3(C_6H_5)_2]$ (**7**) could be isolated. ^{1}H NMR (C_6D_6, 200 MHz, 298 K): δ = 0.28 (s, 27 H, $SiMe_3$), 6.92 (pseudo-t, 2 H, *para*-PhH), 7.10 (pseudo-t, 4 H, *meta*-PhH), 7.46 (pseudo-d, 4 H, *ortho*-PhH) ppm.

Crystal Structure Determinations: Single crystals of the compounds **3** to **7** were obtained by cooling solutions in cyclopentane (temp. range from +20 to +8 °C, **3**), *n*-hexane (temp. range from +20 to +8 °C, **4**), diisopropyl ether (temp. range from +20 to –45 °C, **5**), 1,2-difluorobenzene (temp. range from +20 to –30 °C, **6**) or *n*-hexane (temp. range +20 to 0 °C, **7**). Crystal data and structure refinement parameters are given in Table 1.[59] The molecules of compound **4** reside on a crystallographic twofold rotation axis. The crystals of **6** contain one molecule of 1,2-difluorobenzene per formula unit of **6**. These solvent molecules are strongly disordered.

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