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m-Terphenylaluminum and -gallium Compounds: Synthesis and Conversion into Low-Coordinate Organogallium Cations

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The reaction of two or 3 equiv. of *m*-terphenyllithium with MCl_3 or $AlH_3·NMe_3$ (M = Al, Ga) affords the bis(terphenyl)-aluminum and -gallium chloride compounds [{2,6-(4-tBuC_6H_4)$_2$$C_6H_3$}$_2$GaCl] (**1**), [{2,6-(3,5-$Me_2C_6H_3$)$_2$$C_6H_3$}$_2$GaCl] (**2**), [{2,6-(4-$tBuC_6H_4$)$_2$$C_6H_3$}$_3$Ga] (**3**), [(2,6-$Mes_2C_6H_3$)$_2$AlCl] (**5**), and [(2,6-$Mes_2C_6H_3$)$_2$AlH] (**7**; Mes = 2,4,6-$Me_3C_6H_2$). While the gallium compounds can be obtained at room temperature, heating is required for the aluminum derivatives. The dibutyl compounds [(2,6-$Mes_2C_6H_3$)$GaBu_2$] (**8**) and [(2,6-$Dipp_2C_6H_3$)$GaBu_2$] (**9**; Dipp = 2,6-$i$$Pr_2C_6H_3$) have also been synthesized by the reaction of *m*-terphenyllithium with $ClGaBu_2$. A metathesis reaction of **2** with Li[Al{OCH$(CF_3)_2$}$_4$] gives the ionic species $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$[Li{Al-[OCH$(CF_3)_2$]$_4$}$_2$]$^-$ (**11**). The cationic butyl(terphenyl)gallium compounds $[(2,6\text{-}Mes_2C_6H_3)GaBu]^+$ ([**13**]$^+$) and $[(2,6\text{-}Dipp_2C_6H_3)GaBu]^+$ ([**14**]$^+$) have been prepared by butanide abstraction with the trityl salts of the weakly coordinating anions $[B(C_6F_5)_4]^-$, $[CHB_{11}Br_6Me_5]^-$, and $[CHB_{11}Cl_{11}]^-$. These ionic species are stable at room temperature for days or weeks, although their combinations with the borate anion $[B(C_6F_5)_4]^-$ suffer from C_6F_5 migration, which is slow at room temperature and faster at elevated temperatures. The compound [**14**]$^+$$[CHB_{11}Cl_{11}]^-$ is stable at 70 °C for at least 23 h. Addition of 1-octene to a solution of [**14**]$^+$$[CHB_{11}Cl_{11}]^-$ in C_6D_6 results in olefin exchange and formation of the octyl species [(2,6-$Dipp_2C_6H_3$)Ga(octyl)]$^+$ ([**17**]$^+$), and a slow alkylation of the solvent to afford various octylbenzenes. Hydrolysis of **8** and [**13**]$^+$$[CHB_{11}Br_6Me_5]^-$ gives the compounds [{(2,6-$Mes_2C_6H_3$)GaBu(μ-OH)}$_2$] (**10**) and [(BuGa)$_4$(μ-OH)$_6$]$^{2+}$$[CHB_{11}Br_6Me_5]^-_2$ (**16**). All compounds have been characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry, and compounds **3**, **5**, **7**, **10**, and **16**·4.5C_6H_6 have also been characterized by single-crystal X-ray crystallography.

Introduction

The enormous progress in the development of weakly coordinating anions during the past 10–15 years has invigorated the research of previously inaccessible, often highly reactive, cationic species.[1–4] Some recent examples in main group chemistry include a three-coordinate stannylium cation $[(Trip)_3Sn]^+$ (Trip = 2,4,6-$i$$Pr_3C_6H_2$),[5] two-coordinate gallium and aluminum cations $[(2,6\text{-}Mes_2C_6H_3)_2M]^+$ (M = Ga,[6] Al;[7] Mes = 2,4,6-$Me_3C_6H_2$), monosubstituted group 14 cations $[Cp^*Si]^+$[8] and $[(2,6\text{-}Trip_2C_6H_3)Pb]^+$,[9] or the interesting phosphorus-based cations $[P_2X_5]^+$ and $[P_5X_2]^+$.[10] On the more applied side, there have been several studies of the potential of low-coordinate cationic organoaluminum compounds as catalysts for olefin oligomerization and polymerization.[11–14] Three-coordinate species have been obtained using monoanionic bidentate ligands,[15,16] and quasi-two-coordination has been achieved by employing two large *m*-terphenyl substituents at a single cationic aluminum center.[7] In an effort to increase the reactivity of the cationic species, we have begun to investigate methods to achieve two-coordination that do not rely on excessive steric protection, which tends to decrease and change reactivity patterns. Based on the observed close secondary Al···C contacts in $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+$ involving the *ipso*- and *ortho*-carbon atoms of the flanking mesityl groups,[7] we speculate that a single *m*-terphenyl substituent in conjunction with the least-coordinating anions should be sufficient for the stabilization of a low-coordinate cationic center. The bulky substituents are expected to prevent close anion···cation contacts such as those observed in $[Et_2Al]$-$[CB_{11}H_6X_6]$ (X = Cl, Br)[13] and to stabilize the electron-poor center through secondary M···C contacts. Ideally, the internal stabilization would be sufficiently labile to allow facile cation···substrate interactions (Scheme 1).

Here, we report the synthesis of a series of terphenylaluminum and -gallium precursor molecules and the conversion of a selection of these into cationic species.

Results and Discussion

A series of mono- and diterphenylgallium halides and alkyl derivatives has been prepared from standard organo-

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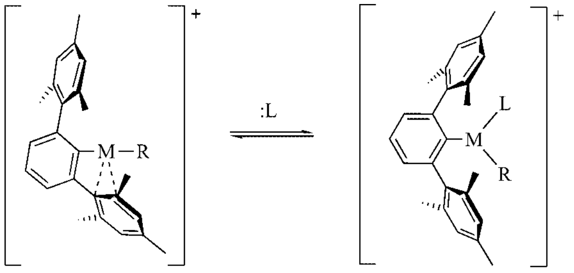


M = Al, Ga; R = alkyl; L = Lewis base, olefin

Scheme 1.

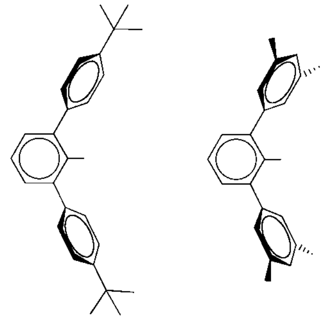
metallic procedures.[17] Selected examples have been converted into cationic species either by salt elimination or alkanide abstraction. Most of the latter reactions were performed on a small (ca. 50 µmol) scale, and the products were characterized by multinuclear NMR spectroscopy and mass spectrometry.

Diterphenylgallium Compounds

The diterphenylgallium chloride species [{2,6-(4-tBuC$_6$H$_4$)$_2$C$_6$H$_3$}$_2$GaCl] (**1**) and [{2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$-C$_6$H$_3$}$_2$GaCl] (**2**) were obtained in moderate yields by the metathesis reaction of 2 equiv. of the coresponding terphenyllithium compound with GaCl$_3$ at room temperature in hexane solution according to Equation (1). Compounds **1** and **2** were isolated as colorless microcrystalline solids that are readily soluble in aromatic solvents or CH$_2$Cl$_2$ but practically insoluble in hexanes. The synthesis of **1** under slightly different conditions and its X-ray crystal structure have been reported independently.[18] Crystals of **1** obtained from toluene solution are essentially identical to those crystallized from Et$_2$O solution described by Robinson et al. after taking low-temperature effects in the present data set into consideration.[18]

$$2\ 2,6\text{-}Ar_2C_6H_3Li + GaCl_3 \longrightarrow [(2,6\text{-}Ar_2C_6H_3)_2GaCl] + LiCl$$

2,6-Ar$_2$C$_6$H$_3$ =



1 **2** (1)

Triterphenylgallium

The very crowded compound [{2,6-(4-tBuC$_6$H$_4$)$_2$-C$_6$H$_3$}$_3$Ga] (**3**) was initially obtained in small amounts during an attempt to prepare the methyl derivative [{2,6-(4-tBuC$_6$H$_4$)$_2$C$_6$H$_3$}$_2$GaMe] by methylation of **1** with methyllithium. Ligand migration in arylgallium compounds is not uncommon and has been described previously.[17] The systematic reaction involving 3 equiv. of 2,6-(4-tBuC$_6$H$_4$)$_2$-C$_6$H$_3$Li gave **3** in 34% yield as a colorless, high-melting (m.p. 281 °C), crystalline solid. Its structure (Figure 1) features a slightly distorted trigonal-planar gallium center [Σ(C–Ga–C) = 359.3°] that is efficiently protected by three m-terphenyl substituents. The Ga–C bond lengths [1.989(2)–2.010(2) Å] fall within the upper range observed previously for diterphenylgallanes.[18–21] The slightly elongated Ga(1)–C(16) bond [2.010(2) Å] and the corresponding widening of the C(38)–Ga(1)–C(68) angle to 122.57(10)° may be attributed to the steric demands of the m-terphenyl substituents. The substituents are arranged in the typical propeller fashion,[18,22,23] and the planes of the central arene rings are rotated out of the GaC$_3$ plane by 39° [C(38) ring], 47° [C(16) ring], and 64° [C(68) ring]. Some minor distortions are found for the C(38) substituent. The central C(38) ring is bent away from the normal linear arrangement by 18.6°, as judged from the angle between the Ga(1)–C(38) and C(38)–C(41) vectors. Similarly, there is a 6.6° angle between the C(39)–C(43) and C(43)–C(46) vectors of the flanking C(43) ring. The shortest C···C contacts between neighboring arene rings are 3.22 Å for C(38)···C(18) and 3.24 Å for C(16)···C(70). Overall, the structure of **3** bears close resemblance to that of the indium analogue [{2,6-(4-tBuC$_6$H$_4$)$_2$C$_6$H$_3$}$_3$In].[18]

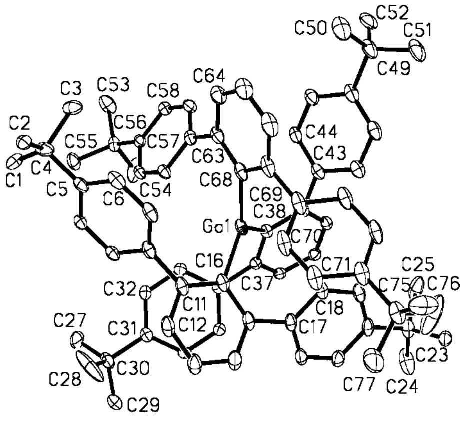


Figure 1. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **3**. Hydrogen atoms have been omitted for clarity.

Diterphenylaluminum Compounds

Whereas the synthesis of the di- and triterphenylgallium compounds **1**–**3** as well as the more crowded species [(2,6-Mes$_2$C$_6$H$_3$)$_2$GaCl][24] (**4**) proceeds at room temperature, the preparation of the aluminum analogue [(2,6-Mes$_2$C$_6$H$_3$)$_2$-AlCl] (**5**) was complicated by the formation of a stable intermediate tentatively characterized as the alanate [(2,6-Mes$_2$C$_6$H$_3$)AlCl$_3$]Li. A closely related compound has been previously observed in the reaction of 2,6-Mes$_2$C$_6$H$_3$Li with AlBr$_3$.[25] The reaction of 2 equiv. of 2,6-Mes$_2$C$_6$H$_3$-

Li with $AlCl_3$ at room temperature for 20 h resulted in the formation of a new *m*-terphenyl compound (the alanate) and unreacted 2,6-$Mes_2C_6H_3Li$ in an approximately 1:1 ratio according to ^1H NMR spectroscopy. The introduction of the second terphenyl substituent requires refluxing in benzene solution. Inadvertent Al–C bond hydrolysis during reflux reduced the yield significantly, and it was difficult to isolate pure **5**. Its crystal structure (Figure 2) is isostructural with that of the gallium congener,[24] but features a significantly shorter Al–Cl bond with a value of 2.1098(12) Å [2.177(5) Å for **4**], which indicates the higher Lewis acidity of aluminum. The Al–C bond lengths, with average values of 1.978 Å, are identical with the Ga–C distances observed for **4**. The shorter Al–Cl distance results in a slight decrease of the C–M–C angle from 153.5(5)° in **4** to 147.52(13)°. Evidence for the steric crowding brought about by two large *m*-terphenyl substituents is apparent in some distortions. For example, as in **3**, the central rings of the substituents are bent away from the ideal linear alignment by 16.2° [C(15) ring] and 12.9° [C(39) ring]. Furthermore, the flanking mesityl groups are pushed out of the plane of the C(15) ring by 12.8° [C(9) mesityl] and 10.4° [C(16) mesityl].

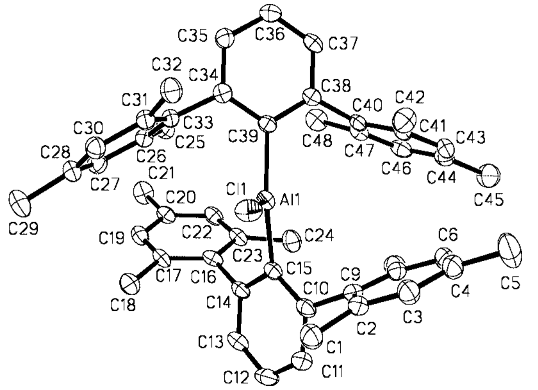


Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **5**. Hydrogen atoms have been omitted for clarity.

The hydride derivative [(2,6-$Mes_2C_6H_3)_2GaH$] (**6**) has been prepared by the reaction of the chloride **4** with $LiHBEt_3$.[21] Because **5** could only be isolated in moderate yields, a different route was selected for the preparation of the aluminum hydride [(2,6-$Mes_2C_6H_3)_2AlH$] (**7**). Thus, reaction of 2,6-$Mes_2C_6H_3Li$ with [(2,6-$Mes_2C_6H_3)AlH_2$]·OEt_2[26] [Equation (2)] at 70 °C for 30 min afforded **7** in moderate to good yields in the form of well-shaped colorless crystals.[7]

$$\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{Li} + [(\text{2,6-Mes}_2\text{C}_6\text{H}_3)\text{AlH}_2]\cdot\text{OEt}_2 \longrightarrow \underset{\mathbf{7}}{[(\text{2,6-Mes}_2\text{C}_6\text{H}_3)_2\text{AlH}]} + \text{LiH} \quad (2)$$

Compound **7** is only the second example of an aluminum hydride that is three-coordinate in the solid state.[27] Similar to [$Mes^*{}_2AlH$][27] (Mes* = 2,4,6-$tBu_3C_6H_2$), the monomeric character of **7** is also due to steric protection, as can clearly be seen in the crystal structure (Figure 3). The overall structural features are similar to those of **5** and **6**, although the distortions are less pronounced than in the structure of **5**. The Al–H distance is 1.436(18) Å and the Al–C distances average 1.990 Å. As was found for the corresponding gallium compounds **4** and **6**, the C–Al–C angle in **7**, with a value of 137.62(5)°, is also significantly smaller than in the chloride **5** [147.52(13)°, see above]. The terphenyl substituents display a staggered arrangement with respect to each other to minimize steric repulsion. The angles between the Al(1)–C(15) and C(15)–C(12) vectors and the Al(1)–C(39) and C(39)–C(36) vectors are 11.7° and 12.8°, respectively, and there are only minor distortions within the terphenyl substituents, thus indicating less steric crowding than for **5**.

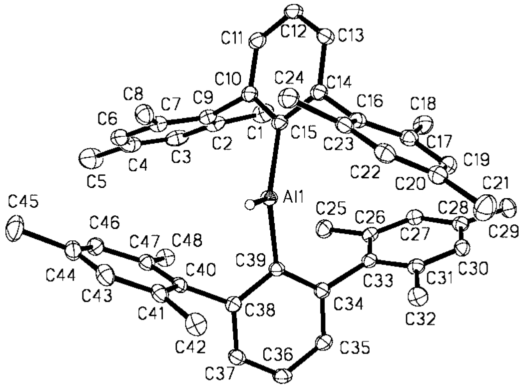


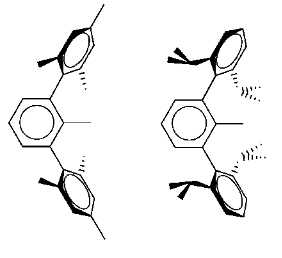
Figure 3. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **7**. Hydrogen atoms, with the exception of the hydrogen atom bound to the aluminum atom, have been omitted for clarity.

Dibutylgallium Compounds

The dibutyl(terphenyl)gallanes [(2,6-$Mes_2C_6H_3)GaBu_2$] (**8**) and [(2,6-$Dipp_2C_6H_3)GaBu_2$] (**9**) (Dipp = 2,6-$iPr_2C_6H_3$) were synthesized by the reaction of terphLi with $ClGaBu_2$ [Equation (3)].

$$\text{2,6-Ar}_2\text{C}_6\text{H}_3\text{Li} + \text{ClGaBu}_2 \longrightarrow [(\text{2,6-Ar}_2\text{C}_6\text{H}_3)\text{GaBu}_2] + \text{LiCl}$$

2,6-$Ar_2C_6H_3$ =



8 **9** (3)

The presence of the flexible *n*-butyl groups apparently prevents the formation of crystals of sufficient quality for X-ray diffraction. In fact, **8** could only be obtained as fine colorless needles, and **9** was initially isolated as a colorless oil, which eventually solidified after a month at room temperature. Despite several attempts, compounds **8** and **9** could not be obtained analytically pure. Both compounds are readily soluble in aliphatic and aromatic solvents. Their composition was confirmed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy as well as the isolation of a hydrolysis product of **8**, namely $[\{(2,6\text{-}Mes_2C_6H_3)GaBu(\mu\text{-}OH)\}_2]$ (**10**). The latter compound was isolated during an attempt to grow X-ray quality crystals by slow concentration of a 1-octene solution of **8** inside a dry box. Its structure (Figure 4) closely resembles those of the related dimeric hydroxy-bridged compounds $[\{(2,6\text{-}Mes_2C_6H_3)GaMe(\mu\text{-}OH)\}_2]$ and $[\{(2,6\text{-}Mes_2C_6H_3)GaCl(\mu\text{-}OH)\}_2]$.[21] The terphenyl substituents in the centrosymmetric molecule are positioned in a mutual *trans* orientation. The Ga–O bond lengths are essentially identical [1.947(5) and 1.952(5) Å] and are close to those found in the above-mentioned methyl derivatives and chlorides.[21]

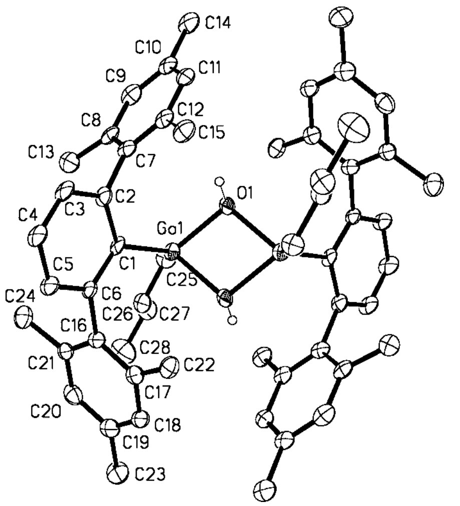
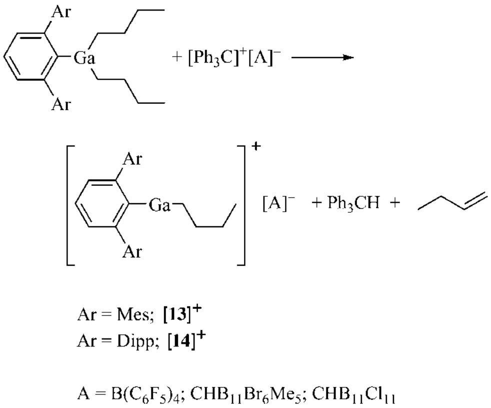


Figure 4. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **10**. Hydrogen atoms, with the exception of those bound to oxygen atoms, have been omitted for clarity.

Cation Formation

We have shown previously that the two-coordinate cationic species $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ and $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+$ can be prepared by chloride abstraction[6] with the lithium alanate $Li[Al\{OCH(CF_3)_2\}_4]$ or by alkanide or hydride abstraction with the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$.[7,21] Chloride abstraction with 2 equiv. of $Li[Al\{OCH(CF_3)_2\}_4]$ also converted the sterically less encumbered diterphenylgallium chloride **2** cleanly into the cationic species $[(2,6\text{-}Ar_2C_6H_3)_2Ga]^+[Li(Al\{OCH(CF_3)_2\}_4)_2]^-$ (**11**; Ar = 3,5-$Me_2C_6H_3$). Interestingly, the analogous reaction with compound **1** to afford **12** (Ar = 4-*t*BuC_6H_4) did not proceed. Monitoring of the reaction in C_6D_5Cl by ^{1}H NMR spectroscopy showed broadening of some of the aromatic signals (δ = 7.4–7.0 ppm), but no further reaction was observed even after prolonged heating at 70 °C. Although attempts to isolate crystals of **11** have not yet been successful, the stoichiometry of the products is supported by the presence of the methine hydrogen signal of the anion in a relative intensity corresponding to eight hydrogen atoms in the ^{1}H NMR spectra. In addition, mass spectrometric analysis of the solution showed the presence of the cation $[\{2,6\text{-}(3,5\text{-}Me_2C_6H_3)_2C_6H_3\}_2Ga]^+$. Chlorobenzene solutions of **11** remain unchanged at room temperature for days, which suggests a surprising stability of this cationic species considering that the related electron-deficient diterphenylboranes $(2,6\text{-}Ar_2C_6H_3)_2BH$ undergo C–H activation below room temperature to give 9-borafluorenes and H_2.[28]

Conversion of the dibutyl(terphenyl)gallanes **8** and **9** into the cationic species $[(2,6\text{-}Mes_2C_6H_3)GaBu]^+$ ($[\mathbf{13}]^+$) and $[(2,6\text{-}Dipp_2C_6H_3)GaBu]^+$ ($[\mathbf{14}]^+$), was accomplished by treatment with the trityl salts $[CPh_3]^+[A]^-$ [A = $B(C_6F_5)_4$,[29] $CHB_{11}Br_6Me_5$,[30] $CHB_{11}Cl_{11}$[31]] according to Equation (4).



(4)

These reactions were performed in NMR tubes sealed with J. Young valves or in small Schlenk flasks. The progress of the reactions was monitored by recording the signals due to C*H*Ph_3 and C*H*$_2$C*H*CH_2CH_3 in the ^{1}H NMR spectrum. The reactions are relatively fast: they are complete within a few hours when both reactants are soluble in the chosen solvent. Otherwise, the reaction rate is dependent on the solubility of the trityl salt, with $[CPh_3]^+[CHB_{11}Cl_{11}]^-$ being the least soluble. Despite the small scale, all reactions are readily reproducible. It has not been possible to isolate any of the products in pure or crystalline form so far due to their tendency to form oils. Nevertheless, the identities of the products have been established by multinuclear NMR spectroscopy and ESI mass spectrometry. The best general strategy for obtaining the highest-purity samples involves performing the reaction in benzene solution followed by phase separation and washing of the dense phase containing the product with benzene. All ionic products are soluble in chlorobenzene, bromobenzene, or their mixtures with benzene. Only $[\mathbf{13}]^+[CHB_{11}Br_6Me_5]^-$ is readily soluble in benzene. The other combinations of $[\mathbf{13}]^+[A]^-$ and $[\mathbf{14}]^+[A]^-$ form dense liquid phases, so-called liquid clathrates.[32] The solubility of $[\mathbf{13}]^+[CHB_{11}Cl_{11}]^-$ lies between these extremes: a liquid clathrate separates at high concentrations (ca. 0.08 M) which can be redissolved upon dilution with C_6D_6. Clathrate formation has been observed previously in our laboratory for the compounds $[(2,6\text{-}Mes_2C_6H_3)_2M]^+$-

$[B(C_6F_5)_4]^-$ (M = Al, Ga), which exist as separate ions.[7,21] Hence, we propose clathrate formation as supporting evidence for anion/cation separation in $[\mathbf{13}]^+[A]^-$ and $[\mathbf{14}]^+[A]^-$. Additional evidence is found in the ^{19}F NMR chemical shifts of $[\mathbf{13}]^+[B(C_6F_5)_4]^-$ and $[\mathbf{14}]^+[B(C_6F_5)_4]^-$, which are close to the values reported for the "free" anion.[16] However, a weak cation···XC_6H_5 (solvent) contact (X = Cl, Br) cannot be ruled out. Such interactions have been described for $[(i\mathrm{Pr}_2\text{-ATI})MR][B(C_6F_5)_4](ClPh)$ (M = Al, Ga, In; $i\mathrm{Pr}_2$-ATI = *N,N′*-diisopropylaminotroponiminate).[33]

The ^1H NMR spectrum of a C_6D_6 solution of $[\mathbf{13}]^+[CHB_{11}Br_6Me_5]^-$ shows two sets of signals for the *o*- and *o′′*-methyl groups and the *m*- and *m′′*-hydrogen atoms of the flanking mesityl groups of the *m*-terphenyl ligand due to a loss of symmetry. This, together with the fact that $[\mathbf{13}]^+[CHB_{11}Br_6Me_5]^-$ is soluble in benzene, may be viewed as good evidence for its existence as a tight ion-pair with close Ga···Br contacts similar to those observed for $[Et_2Al]^+[CB_{11}H_6X_6]^-$ (X = Cl, Br).[13] In keeping with an intermediate behavior, the ^1H NMR spectrum of $[\mathbf{13}]^+[CHB_{11}Cl_{11}]^-$ in C_6D_6 solution does not display an analogous broadening.

All ionic compounds described here are stable in solution at room temperature for days if not weeks. The $[B(C_6F_5)_4]^-$ salts are susceptible to C_6F_5 migration at elevated temperatures, a common occurrence for this anion in combination with strong Lewis acids.[34] For example, heating of a solution of $[\mathbf{14}]^+[B(C_6F_5)_4]^-$ at 60 °C for 16 h results in the clean formation of a 1:1 mixture of $[(2,6\text{-Dipp}_2C_6H_3)GaBu(C_6F_5)]$ (**15**) and $B(C_6F_5)_3$. These compounds were identified by ^1H and ^{19}F NMR spectroscopy, the latter by comparison with an authentic sample and published data[35] and the former by the similarity of its ^{19}F NMR signals with those of the related (pentafluorophenyl)aluminum species $[Me_nAl(C_6F_5)_{3-n}]$.[34] On the other hand, no change of the NMR spectra of the carborane salt $[\mathbf{14}]^+[CHB_{11}Cl_{11}]^-$ was observed after heating at 68–70 °C for 23 h, thereby indicating a surprisingly high stability of this compound.

The difficulty of obtaining pure samples of any of the new ionic compounds may be illustrated by the fact that repeated attempts to crystallize $[\mathbf{13}]^+[CHB_{11}Br_6Me_5]^-$ only afforded a few crystals of the hydrolysis product $[(BuGa)_4(\mu\text{-}OH)_6]^{2+}[CHB_{11}Br_6Me_5]^-_2$ (**16**), whose structure consists of layers of $[(BuGa)_4(\mu\text{-}OH)_6]^{2+}$ dications and $[CHB_{11}Br_6Me_5]^-$ anions separated by benzene molecules. The cations and anions are well separated, but are kept in contact through hydrogen bonding between the hydroxy hydrogen atoms of the cations and bromine atoms of the anions. These contacts can be as close as 2.44 Å for H(3)···Br(3A). The dications are cage molecules with a distorted adamantane Ga_4O_6 framework (Figure 5). The neutral analogue $[\{(Me_3Si)_3Ga\}_4(\mu\text{-}OH)_4(\mu\text{-}O)_2]$ has been reported previously.[36] The metric parameters of both compounds are comparable, with average Ga–O and Ga–C bond lengths of 1.897(6) and 1.933(1) Å and O–Ga–O and Ga–O–Ga angles of 96.9(1.8)° and 130.8(1.0)° in **16** (Table 3) vs. 1.895 and 1.998 Å and 100.46 and 125.42°, respectively, in $[\{(Me_3Si)_3Ga\}_4(\mu\text{-}OH)_4(\mu\text{-}O)_2]$.

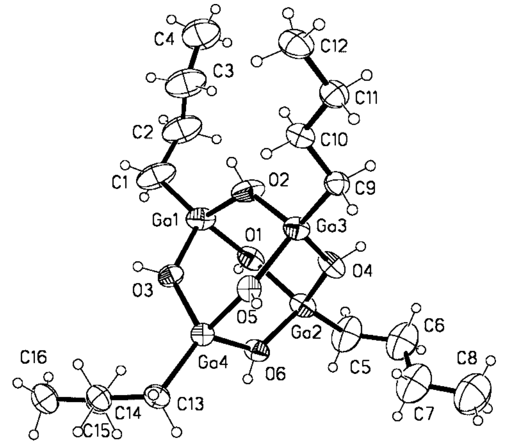
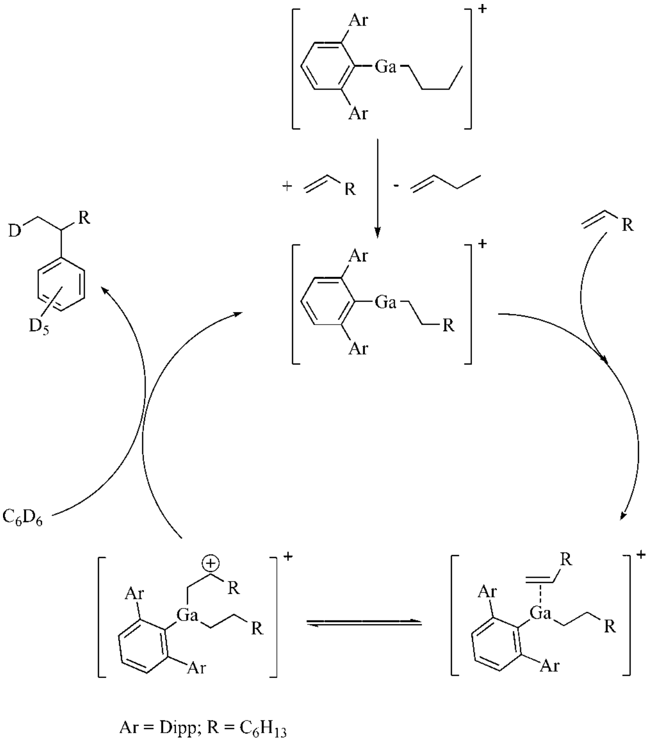


Figure 5. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of the dication in **16**.

Reaction of $[\mathbf{14}]^+$ with 1-Octene

One of the goals of the preparation of low-coordinate aluminum and gallium cations was the investigation of their interactions with olefins. The NMR spectra obtained during the monitoring of the syntheses of the various cation/anion combinations $[\mathbf{13}]^+[A]^-$ and $[\mathbf{14}]^+[A]^-$ indicated a rather slow reaction with 1-butene. Since $[\mathbf{14}]^+[CHB_{11}Cl_{11}]^-$ is thermally stable, its interaction with 1-octene was investigated more closely. Approximately 1.2 equiv. of 1-octene was added to a solution of $[\mathbf{14}]^+[CHB_{11}Cl_{11}]^-$ in a 6:1 mixture of C_6D_6 and C_6D_5Cl, and the progress of the reaction was monitored by ^1H NMR spectroscopy. About 15 min after the 1-octene addition, the ^1H NMR spectrum showed a broadening of the $\alpha\text{-}C\mathit{H_2}$ signal, and signals of free 1-octene and 1-butene in an approximately 2:1 ratio were discernible. After 48 h at room temperature, the olefinic signals had almost completely disappeared, and an additional 2.4 equiv. of 1-octene was added after a reaction time of 54 h. This time, only a small amount of free 1-butene was generated, and most of the signals due to the butyl compound $[\mathbf{14}]^+$ were replaced by similar signals that were slightly shifted from their previous positions. Two more additions of 1-octene were undertaken after the olefin had been almost completely consumed. After a total reaction time of 21 d at room temperature, no more olefin signals were present, and the spectrum was dominated by octyl signals, although a slightly broadened multiplet at δ = 0.21 ppm indicated the presence of a Ga-C$\mathit{H_2}$ group. Analysis of the mixture by ESI mass spectrometry and GC-MS showed the presence of the octyl species $[(2,6\text{-Dipp}_2C_6H_3)Ga(octyl)]^+$ ($[\mathbf{17}]^+$) and various octylbenzenes. These preliminary results suggest a facile olefin/alkyl exchange followed by octene isomerization and benzene alkylation. Scheme 2 shows a proposed reaction mechanism. Further work in this area is in progress.



Scheme 2.

Conclusion

Diterphenylaluminum and -gallium compounds have been prepared by the treatment of 2 equiv. of terphenyllithium with MCl_3 or $H_3Al·NMe_3$; the synthesis of the aluminum species requires more forcing conditions. Dibutyl(terphenyl)gallanes have also been obtained by treating terphenyllithium with $ClGaBu_2$. The best method for the preparation of cationic gallium species [(terph)GaR]$^+$ is treatment with trityl salts of weakly coordinating anions, although chloride abstraction with a fluorinated lithium tetraalkoxidoalanate can also be used for selected gallium chloride precursors. The ionic compounds are at least moderately stable in aromatic solvents at room temperature, with the compound [**14**]$^+$[$CHB_{11}Cl_{11}$]$^-$ being thermally stable up to 70 °C. All ionic compounds, with the exception of [**13**]$^+$[$CHB_{11}Br_6Me_5$]$^-$, form clathrates in benzene solution, which suggests the presence of only weak ion-pairing or even "free" ions. A preliminary study on the interaction of [**14**]$^+$[$CHB_{11}Cl_{11}$]$^-$ with 1-octene has found facile alkyl/olefin exchange at the cationic gallium center and slow octene isomerization and benzene alkylation.

Experimental Section

General Procedures: All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies or Vacuum Atmospheres drybox. Solvents were freshly distilled under N_2 from sodium, potassium, sodium/potassium alloy, or calcium hydride and degassed twice prior to use, or they were dispensed from an MBraun Solvent Purification System. $AlCl_3$, $GaCl_3$, *n*-butyllithium (1.6 M in hexanes), and MeLi (1.6 M in Et_2O) were obtained from commercial suppliers. Compounds 2,6-(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$Br,[37] 2,6-(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$Li,[38] 2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$Li,[28] [(2,6-Mes$_2$C$_6$H$_3$)$_2$AlH] (**7**),[7] ClGaBu$_2$,[39] 2,6-Mes$_2$C$_6$H$_3$Li,[40] 2,6-Dipp$_2$C$_6$H$_3$Li,[41] and [Ph$_3$C][B(C$_6$F$_5$)$_4$][29] were synthesized according to literature methods. The carborane compounds [Ph$_3$C][CHB$_{11}$Br$_6$Me$_5$] and [Ph$_3$C][CHB$_{11}$Cl$_{11}$] were supplied by Prof. Christopher A. Reed and Dr. Kee-Chan Kim from the University of California, Riverside. NMR spectra were recorded with a Varian Mercury 300 MHz, a Varian Unity Plus 400 MHz, a Bruker AMX 360, or a Bruker Avance 400 MHz spectrometer. ^{1}H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as internal reference (δ = 7.15 or 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent signal (δ = 128.0 or 77.0 ppm). ^{19}F NMR spectra were referenced to an external solution of $C_6H_5CF_3$ in C_6D_6 (δ = –63.72 ppm). IR spectra were recorded in the range 4000–400 cm^{-1} with a Nicolet Nexus 470 FTIR spectrometer. Electron impact mass spectra were recorded with a Finnigan MAT Polaris spectrometer and electrospray mass spectra with a Micromass Q-ToF or a JEOL AccuTOF DART spectrometer. Melting points were determined in Pyrex capillary tubes sealed under nitrogen with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics in Tucson, AZ.

[{(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$}$_2$GaCl] (1): A solution of (4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$Br (1.00 g, 2.4 mmol) in hexanes (60 mL) was treated with a hexane solution of *n*-butyllithium (0.97 mL, 2.78 M) at –78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The volatile material was removed from the cloudy suspension under reduced pressure. $GaCl_3$ (0.21 g, 1.2 mmol) was added to a suspension of the resulting colorless to beige solid in hexanes (50 mL) at –78 °C. Warming to room temperature and stirring overnight afforded a suspension of **1** and LiCl. Decanting of the mother liquor, washing with hexanes and extraction with benzene gave **1** as a fine colorless solid after removal of the solvent in vacuo. Yield: 0.54 g (57%). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at –24 °C. M.p. 202–208 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.32 (d, *J* = 7.5 Hz, *m*-H, 4 H), 7.28 (s, 4-*t*BuC$_6$*H*$_4$, 16 H), 7.19 (t, *J* = 7.5 Hz, *p*-H, 2 H), 1.16 (s, C*H*$_3$, 36 H) ppm. ^{13}C{^{1}H} NMR (90.567 MHz, C_6D_6, 25 °C): δ = 150.89, 149.51, 147.05 (*i*-C), 142.96; 129.75 (*p*-C), 128.65 [*o*-C(4-*t*BuC$_6$H$_4$)], 127.93 (*m*-C), 126.30 [*p*-C(4-*t*BuC$_6$H$_4$)], 34.45 [*C*(CH$_3$)$_3$], 31.29 [C(*C*H$_3$)$_3$] ppm. MS (DART, C_6D_6 solution): calcd. for [M$^+$ – Cl] 751.3794, found 751.3595.

[{(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$}$_2$GaCl] (2): $GaCl_3$ (0.39 g, 2.2 mmol) was added through an addition funnel for solids to a suspension of 2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$Li (1.37 g, 4.7 mmol) in hexanes at –78 °C. After 15 min, the reaction mixture was allowed to slowly warm to room temperature to give a cream-colored suspension and a dark grey solid on the bottom of the flask. After 3 d at room temperature, the dark solid was consumed. The insoluble material (1.09 g), which is a mixture of **2** and LiCl, was collected on a glass frit. Redissolution in CH_2Cl_2 (20 mL), followed by separation of LiCl by decantation, concentration of the clear yellow solution to ca. 2 mL and cooling at 4 °C for 2 d afforded a fine crystalline solid (0.2 g). A second batch (0.05 g) was obtained from the concentrated mother liquor at 4 °C after 3 d. Yield: 0.25 g (17%). M.p. softens at 178 °C, melts at 188–192 °C. ^{1}H NMR (400 MHz C_6D_6, 25 °C): δ = 7.43 (d, *J* = 7.6 Hz, *m*-H, 4 H), 7.31(s, *J* = 7.6 Hz, *p*-H, 2 H), 7.00 [s, *o*-H(3,5-Me$_2$C$_6$H$_3$), 8 H], 6.66 [s, *p*-H(3,5-Me$_2$C$_6$H$_3$), 4 H], 1.93 (s, C*H*$_3$, 24 H) ppm. ^{13}C{^{1}H} NMR (100.13 MHz, C_6D_6, 25 °C): δ = 149.00, 148.22, 145.82, 139.26, 129.82, 129.80, 128.31, 126.85, 21.14 (*C*H$_3$) ppm.

[{(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$}$_3$Ga] (3): GaCl$_3$ (0.18 g, 1.0 mmol) was added to a suspension of 4-(*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$Li (1.07 g, 3.1 mmol) in hexanes (50 mL) at –78 °C through an addition funnel for solids. The mixture was warmed to room temperature and stirred for 20 h. The resulting fine, colorless precipitate was separated by filtration, and the product was obtained by crystallization of the colorless supernatant liquid at –24 °C for several days. Yield: 0.64 g (58%). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at –24 °C. M.p. 281–283 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.19 [d, *J* = 8.4 Hz, 12 H, *o*- or *p*-(4-*t*BuC$_6$H$_4$)], 6.97 [d, *J* = 8.1 Hz, 12 H, *o*- or *p*-(4-*t*BuC$_6$H$_4$)], 6.97 (s, 9 H, *m*- and *p*-H), 1.22 (s, 54 H, C*H$_3$*) ppm. ^{13}C{^{1}H} NMR (75.45 MHz, C$_6$D$_6$, 25 °C): δ = 151.06 (*i*-C), 148.86, 148.60, 142.71, 129.80 [*o*-(4-*t*BuC$_6$H$_4$)], 127.93 (*m*- or *p*-C), 124.85 [*p*-(4-*t*BuC$_6$H$_4$)], 34.49 [*C*(CH$_3$)$_3$], 31.53 [C(*C*H$_3$)$_3$] ppm. C$_{78}$H$_{87}$Ga (1094.3): calcd. C 85.61, H 8.01; found C 84.35, H 8.21.

[(2,6-Mes$_2$C$_6$H$_3$)$_2$AlCl] (5): AlCl$_3$ (0.25 g, 1.9 mmol) was added to a solution of 2,6-Mes$_2$C$_6$H$_3$Li (1.28 g, 4.0 mmol) in benzene (10 mL) through an addition funnel for solids with cooling in an ice bath. After warming to room temperature, the mixture was stirred for 14 h and heated to reflux for another 2 h. After cooling to room temperature, the clear yellow solution was decanted off the fine colorless precipitate, and the volatile material was distilled off under reduced pressure to give a pale-yellow foamy solid. Addition of hexanes (5–6 mL) afforded the precipitation of **5** as a fine pale-yellow powder (0.32 g) which was found to be contaminated with 22% 2,6-Mes$_2$C$_6$H$_4$. Crystals of a quality suitable for X-ray diffraction were obtained by crystallization from a saturated toluene solution at –20 °C for 7 d, although an analytically pure bulk sample could not be isolated. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.05 (t, *J* = 7.6 Hz, 2 H, *p*-H), 6.85 [s, 8 H, *m*-H(Mes)], 6.63 (d, *J* = 7.6 Hz, 4 H, *m*-H), 2.25 (s, 12 H, *p*-C*H$_3$*), 1.83 (s, 24 H, *o*-C*H$_3$*) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 25 °C): δ = 150.68, 143.73 (*i*-C), 141.78, 137.58 [*o*-C(Mes)], 136.99, 130.21 (*p*-C), 129.13 [*m*-C(Mes)], 128.43 (*m*-C), 21.91 (*o*-*C*H$_3$), 21.29 (*p*-*C*H$_3$) ppm. MS (DART, solid): calcd. for [M + H$^+$] 689.3495, found 689.3583.

[(2,6-Mes$_2$C$_6$H$_3$)GaBu$_2$] (8): A suspension of a 9:1 mixture of 2,6-Mes$_2$C$_6$H$_3$Li/2,6-Mes$_2$C$_6$H$_4$ (2.27 g, 6.4 mmol 2,6-Mes$_2$C$_6$H$_3$Li) in hexanes (30 mL) was added slowly to a solution of ClGaBu$_2$ (1.40 g, 6.4 mmol) in hexanes (20 mL) at –78 °C. The mixture was kept at –78 °C for 30 min, then warmed to room temperature and stirred overnight. The pale-yellow solution was decanted off the fine colorless precipitate, concentrated to 5 mL, and cooled to –40 °C for 2 d. As no crystals had formed, the solution was further concentrated to about 1 mL and cooled to –40 °C for 5 d to afford fine, colorless needles (1.21 g). A second batch was obtained from the concentrated mother liquor after cooling at –40 °C for 4 d (0.81 g). Yield: 2.02 g (58%). The needles were contaminated with approximately 13% 2,6-Mes$_2$C$_6$H$_4$. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.31 (t, *J* = 7.5 Hz, 1 H, *p*-H), 7.02 (d, *J* = 7.5 Hz, 2 H, *m*-H), 6.81 [s, 4 H, *m*-H(Mes)], 2.16 (s, 12 H, *o*-Me), 2.13 (s, 6 H, *p*-Me), 1.23 (m, 4 H, β-C*H$_2$*), 1.04 (m, 4 H, γ-C*H$_2$*), 0.83 (t, *J* = 6.9 Hz, 6 H, δ-C*H$_3$*), 0.54 ("t", *J* = 7.8 Hz, 4 H, α-C*H$_2$*) ppm. ^{13}C{^{1}H} NMR (75.45 MHz, C$_6$D$_6$, 25 °C): δ = 155.61, 147.00, 140.98, 137.01, 136.17, 128.88 [*m*-C(Mes)], 128.45 (*p*-C), 126.04 (*m*-C), 28.32 (β- or γ-*C*H$_2$), 28.13 (β- or γ-*C*H$_2$), 21.11 (*o*-*C*H$_3$), 21.05 (*p*-*C*H$_3$), 19.33 (α-*C*H$_2$), 14.24 (δ-*C*H$_3$) ppm.

[(2,6-Dipp$_2$C$_6$H$_3$)GaBu$_2$] (9): A suspension of 2,6-Dipp$_2$C$_6$H$_3$Li (2.51 g, 6.2 mmol) in hexanes (30 mL) was added slowly to a solution of ClGaBu$_2$ (1.30 g, 5.9 mmol) in hexanes (20 mL) at –78 °C. The mixture was kept at –78 °C for 30 min, warmed to room temperature and stirred overnight. The cloudy, pale-yellow solution was filtered through a sintered glass frit, and the pale-yellow filtrate was concentrated to 5 mL and cooled to –40 °C for 4 d. As no crystals had formed, the volatile material was removed under reduced pressure to give crude **9** as a pale-yellow oil, which solidified after a month at room temperature. The main impurity was identified as the arene 2,6-Dipp$_2$C$_6$H$_3$I in amounts of approximately 5%. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.25 (m, 5 H), 7.16 (m, 4 H), 3.09 [sept, *J* = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.27 [d, *J* = 6.9 Hz, 12 H, CH(C*H$_3$*)$_2$], 1.14 (m, 8 H, β-, γ-CH$_2$), 1.07 [d, *J* = 6.9 Hz, 12 H, CH(C*H$_3$*)$_2$], 0.84 (t, *J* = 7.2 Hz, 6 H, δ-CH$_3$), 0.45 (m, 4 H, α-CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.45 MHz, C$_6$D$_6$, 25 °C): δ = 156.31, 147.10, 145.64, 141.89, 128.72, 127.80, 126.98, 123.36, 30.54 [*C*H(CH$_3$)$_2$], 28.24 (β- or γ-*C*H$_2$), 27.46 (β- or γ-*C*H$_2$), 26.22 [CH(*C*H$_3$)$_2$], 22.66 [CH(*C*H$_3$)$_2$], 19.93 (α-*C*H$_2$), 14.00 (δ-*C*H$_3$) ppm.

[{(2,6-Mes$_2$C$_6$H$_3$)GaBu(μ-OH)}$_2$] (10): A solution of crude **8** (30 mg) in C$_6$D$_6$ (1 mL) was placed in a small vial inside a glovebox, and the solvent was allowed to slowly evaporate through the partially tightened lid over a period of two weeks to afford a pale-yellow glass. Redissolution in 1-octene (1 mL) and subsequent slow concentration over a period of six weeks gave fine colorless needles of **10** of sufficient quality for X-ray diffraction. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.21 (t, *J* = 7.2 Hz, 2 H, *p*-H), 6.91 (d, *J* = 7.2 Hz, 4 H, *m*-H), 6.87 [s, 8 H, *m*-H(Mes)], 2.35 (s, 12 H, *p*-Me), 2.08 (s, 24 H, *o*-Me), 1.21 (m, 4 H, β-, γ-C*H$_2$*), 0.88 (t, *J* = 6.8 Hz, 6 H, δ-C*H$_3$*), 0.13 ("t", *J* = 8.1 Hz, 4 H, α-C*H$_2$*), 0.09 (s, 2 H, O*H*) ppm. ^{13}C{^{1}H} NMR (100.75 MHz, C$_6$D$_6$, 25 °C): δ = 148.30, 141.76, 136.38, 136.14, 128.59, 128.42, 126.95, 28.38 (β-or γ-*C*H$_2$), 28.24 (β-or γ-*C*H$_2$), 21.51 (*p*-*C*H$_3$), 21.32 (*o*-*C*H$_3$), 15.82 (α-*C*H$_2$), 14.00 (δ-*C*H$_3$) ppm. FTIR (thin film between CsI plates): $\tilde{\nu}$ = 3642 [m, ν(OH)] cm^{-1}.

[{2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$}$_2$Ga]$^+$[Li(Al{OCH(CF$_3$)$_2$}$_4$)$_2$]$^-$ (11): A solution of **2** (32 mg, 47 μmol) in C$_6$D$_5$Cl (1.0 mL) was added to finely powdered LiAl[OCH(CF$_3$)$_2$]$_4$ (70 mg, 0.1 mmol) in an NMR tube fitted with a J. Young valve. The NMR tube was shaken for 1 min and then rotated for 16 h around its long axis using a standard overhead stirrer lying on its side. The fine colorless precipitate was allowed to settle, and the clear colorless supernatant liquid containing essentially pure **11** was pipetted off. ^{1}H NMR (400 MHz, C$_6$D$_5$Cl, 25 °C): δ = 7.58 (t, *J* = 8.0 Hz, 2 H, *p*-H), 7.53 (d, *J* = 8.0 Hz, 4 H, *m*-H), 6.72 [s, 4 H, *p*-H of xylyl], 6.40 [s, 8 H, *o*-H of xylyl], 4.84 [sept, $J_{H,F}$ = 5.4 Hz, 8 H, C*H*(CF$_3$)$_2$], 1.95 (s, 24 H, C*H$_3$*) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_5$Cl, 25 °C): δ = 148.23, 146.74, 144.42, 131.51, 125.68, 122.34 (q, $^1J_{C,F}$ = 285 Hz, *C*F$_3$), 121.14, 70.86 [sept, $^2J_{C,F}$ = 33 Hz, *C*H(CF$_3$)$_2$], 20.67 (*C*H$_3$) ppm. MS (DART, C$_6$D$_5$Cl solution): calcd. 639.2542, found 639.2497; (neg. ion): calcd. for [Al{OCH(CF$_3$)$_2$}$_4$]$^-$ 694.9542, found 694.9511.

[(2,6-Mes$_2$C$_6$H$_3$)GaBu]$^+$[B(C$_6$F$_5$)$_4$]$^-$ {[13]$^+$[B(C$_6$F$_5$)$_4$]$^-$}: An NMR tube equipped with a J. Young valve was charged with **8** (27 mg, 50 μmol), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (43 mg, 47 μmol), and C$_6$D$_6$ (0.7 mL), and the resulting mixture was shaken for 1 min to give a pale-yellow solution above a dense red layer (ca. 0.1 mL). The mixture was rotated at room temperature for 5 h to afford a dense, dark orange-yellow layer (0.1 mL) and a pale-yellow top layer. The top layer was pipetted off, and the bottom layer was washed with C$_6$D$_6$ (2 × 0.25 mL) and then dissolved in C$_6$D$_5$Br (0.35 mL) to give a yellow solution. The solution contained mainly [**13**]$^+$[B(C$_6$F$_5$)$_4$]$^-$, which was contaminated with 15% of an unknown 2,6-Mes$_2$C$_6$H$_3$-containing species. ^{1}H NMR [400.13 MHz, C$_6$D$_6$/C$_6$D$_5$Br (1:3), 25 °C]: δ = 7.48 (t, *J* = 7.6 Hz, 1 H, *p*-H), 7.10 (d, *J* = 7.6 Hz, 2 H, *m*-H), 6.88 [s, 4 H, *m*-H(Mes)], 2.22 (s, 6 H, *p*-C*H$_3$*), 1.96 (s, 12

H, *o*-CH_3), 0.65 (m, 2 H, β-CH_2), 0.56 (s, 5 H, γ-CH_2, δ-CH_3), 0.25 (t, *J* = 7.5 Hz, 2 H, α-CH_2) ppm. $^{13}C\{^1H\}$ NMR [100.61 MHz, C_6D_6/C_6D_5Br (1:3); signals referenced to *δ* = 122.45 ppm for *i*-$C(C_6D_5Br)$, 25 °C]: *δ* = 148.83 (br. d, $^1J_{C,F}$ = 243 Hz), 146.57, 140.47, 138.71 [br. d, $^1J_{C,F}$ = 243 Hz, *p*-$C(C_6F_5)$], 138.24, 136.82 (br. d, $^1J_{C,F}$ = 246 Hz), 135.81 [*o*-C(Mes)], 133.77 (*p*-C), 130.71 [*m*-C(Mes)], 27.28 (γ-CH_2), 25.66 (β-CH_2), 21.97 (br., α-CH_2), 20.94 (*p*-CH_3), 20.82 (*o*-CH_3), 13.32 (δ-CH_3) ppm. ^{19}F NMR (284.34 MHz, C_6D_6/C_6D_5Cl (1:1), 25 °C): *δ* = –132.15 (br. d, *J* = 9.9 Hz, 8 F, *o*-F), –162.28 (t, *J* = 20.9 Hz, 4 F, *p*-F), –166.24 (br. s, 8 F, *m*-F) ppm. MS (DART, C_6D_6/C_6D_5Br (1:3) solution): calcd. 439.1916, found 439.1919.

$[(2,6\text{-}Mes_2C_6H_3)GaBu]^+[CHB_{11}Cl_{11}]^-$ {[13]$^+$[$CHB_{11}Cl_{11}$]$^-$}: An NMR tube equipped with a J. Young valve was charged with **8** (24 mg, 45 µmol), $[Ph_3C][CHB_{11}Cl_{11}]\cdot 0.8C_7H_8$ (33 mg, 39 µmol) and C_6D_6 (0.6 mL), and the resulting mixture was shaken for 1 min to give a pale-yellow solution above a fine yellow solid. The mixture was rotated at room temperature for 26 h to afford a dense orange-yellow layer (0.06 mL) and a yellow top layer. In order to ensure complete consumption of the trityl salt, an additional 5 mg of **8** was added, and the tube was rotated for another 4 h. This resulted in a significant fading of the color of both layers. The top layer was pipetted off, and the bottom layer (ca. 0.03 mL) was dissolved in C_6D_6 (0.6 mL). The NMR spectra are in agreement with the formation of [**13**]$^+$[$CHB_{11}Cl_{11}$]$^-$, which still contained around 22% Ph_3CH. No further purification was attempted. The NMR spectroscopic data are given for [**13**]$^+$[$CHB_{11}Cl_{11}$]$^-$. ^1H NMR (400.13 MHz, C_6D_6, 25 °C): *δ* = 7.15 (obscured by C_6D_5H, *p*-H), 6.85 (d, *J* = 7.6 Hz, 2 H, *m*-H), 6.79 [s, 4 H, *m*-H(Mes)], 2.08 (s, 12 H, *o*-CH_3), 2.05 (s, 6 H, *p*-CH_3), 1.24 (m, 2 H, β-CH_2), 1.12 (br. s, 2 H, α-CH_2), 0.97 (sext, *J* = 7.2 Hz, 2 H, γ-CH_2), 0.71 (t, *J* = 7.2 H, 3 Hz, δ-CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): *δ* = 147.48, 139.39, 138.53, 136.50 [*o*-C(Mes)], 131.98, 130.16 [*m*-C(Mes)], 48.03 (br., $CHB_{11}Cl_{11}$), 26.76 (γ-CH_2), 26.47 (β-CH_2), 21.55 (*o*-CH_3), 20.92 (*p*-CH_3), 13.51 (δ-CH_3) ppm.

$[(2,6\text{-}Mes_2C_6H_3)GaBu]^+[CHB_{11}Br_6Me_5]^-$ {[13]$^+$[$CHB_{11}Br_6Me_5$]$^-$}: A small tube equipped with a Teflon valve was charged with **8** (28 mg, 52 µmol), $[Ph_3C][CHB_{11}Br_6Me_5]\cdot 2.3C_7H_8$ (60 mg, 52 µmol), and C_6D_6 (1.5 mL), and the resulting mixture was rotated at room temperature for 16 h to afford a clear, orange solution. The volatile material was distilled off in vacuo, and the resulting orange-red oil was dissolved in hexanes (1 mL). The slightly cloudy solution was cooled to –20 °C for 2 h to precipitate Ph_3CH. The yellow-orange supernatant liquid was pipetted off, and the solvent was allowed to evaporate slowly inside a drybox. The resulting yellow glass was investigated by ^1H NMR spectroscopy, and the spectra were found to be in agreement with the formulation [**13**]$^+$-[$CHB_{11}Br_6Me_5$]$^-$. Small amounts of 2,6-$Mes_2C_6H_4$, Ph_3CH and *n*-hexane were also present. ^1H NMR (400 MHz, C_6D_6, 25 °C): *δ* = 6.95 (br. s, $w_{1/2}$ = 6.9 Hz, 2 H, *m*-H of Mes), 6.73 (br. s, $w_{1/2}$ = 7.6 Hz, 2 H, *m*-H of Mes), 2.49 (br. s, $w_{1/2}$ = 6.4 Hz, 6 H, *o*-CH_3), 2.06 (s, 6 H, *p*-CH_3), 1.94 (br. s, $w_{1/2}$ = 6.4 Hz, 6 H, *o*-CH_3), 1.50 (m, 4 H, α-, β-CH_2), 1.21 [m, 2 H, γ-*CH* (obscured by hexane CH_2)], 0.80 (t, *J* = 7.5 Hz, 3 H, δ-CH_3), 0.25 (s, 15 H, B-CH_3) ppm. Further attempts at purification were unsuccessful and eventually led to the formation of **16** (vide infra).

$[(2,6\text{-}Dipp_2C_6H_3)GaBu)]^+[B(C_6F_5)_4]^-$ {[14]$^+$[$B(C_6F_5)_4$]$^-$}: A solution of **9** (39 mg, 67 µmol) in C_6D_6 (0.8 mL) was added to $[Ph_3C][B(C_6F_5)_4]$ (62 mg, 67 µmol) in an NMR tube equipped with a J. Young valve at room temperature. The mixture was shaken, and a dense red liquid phase separated after standing for a few minutes. After 2 h at room temperature, only a small amount of Ph_3CH could be detected by ^1H NMR spectroscopy. The sample was rotated slightly off axis for 18 h, after which time the ^1H NMR spectrum showed the consumption of **9**. The yellow upper phase was pipetted off, and the dense red oily phase was washed with C_6D_6 (0.6 mL and 1.2 mL). The remaining red oily liquid was dissolved in a mixture of C_6D_6/C_6D_5Cl (4.5:1.5). ^1H NMR (300 MHz, C_6D_6/C_6D_5Cl (4.5:1.5), 25 °C): *δ* = 7.26 (t, *J* = 6.9 Hz, 1 H, *p*-H), 7.24 (t, *J* = 7.8 Hz, 2 H, *p*-H of Dipp), 7.14 (d, *J* = 6.9 Hz, 2 H, *m*-H), 7.07 (d, *J* = 7.8 Hz, 4 H, *m*-H of Dipp), 2.52 [sept, *J* = 6.8 Hz, 4 H, $CH(CH_3)_2$], 0.95, [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.92, [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.41 (br. s, 7 H, β-, γ-CH_2, δ-CH_3), 0.04 ("t", *J* = 6.8 Hz, 2 H, α-CH_2) ppm. $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6/C_6D_5Cl (4.5:1.5), 25 °C): *δ* = 149.1 (br. d, $^1J_{C,F}$ = 238 Hz), 147.83, 145.81, 133.54 (*p*-C), 138.8 (br. d, $^1J_{C,F}$ = 249 Hz, *p*-CF), 138.05, 137.0 (br. d, $^1J_{C,F}$ = 249 Hz), 131.77 [*m*-C(Dipp)], 129.22 (*m*-C), 125.63 [*m*-C(Dipp)], 30.95 [$CH(CH_3)_2$], 27.44 (β- or γ-CH_2), 25.38 (β- or γ-CH_2), 24.95 [$CH(CH_3)_2$], 23.43 [$CH(CH_3)_2$], 21.58 (α-CH_2), 13.28 (δ-CH_3) ppm. ^{19}F NMR (284.34 MHz, C_6D_6/C_6D_5Cl (4.5:1.5), 25 °C): *δ* = –133.12 (br. d, *J* = 7.7 Hz, 8 F, *o*-F), –163.93 (t, *J* = 20.8 Hz, 4 F, *p*-F), –167.72 ppm (br. t, *J* = 18.9 Hz, 8 F, *m*-F).

$[(2,6\text{-}Dipp_2C_6H_3)GaBu]^+[CHB_{11}Cl_{11}]^-$ {[14]$^+$[$CHB_{11}Cl_{11}$]$^-$}: An NMR tube equipped with a J. Young valve was charged with **9** (36 mg, 62 µmol, 30% excess) and $[Ph_3C][CHB_{11}Cl_{11}]\cdot 0.8C_7H_8$ (40 mg, 47 µmol), and C_6D_6 (0.75 mL) was added. The sample was rotated horizontally slightly off axis at room temperaturefor 5 d during which time a dense orange liquid layer formed (ca. 0.1 mL). The pale-yellow upper layer was pipetted off, and the lower layer was washed twice with C_6D_6 (0.5 and 0.3 mL). C_6D_5Cl (0.45 mL) was added to the remaining liquid to give a clear yellow orange solution of [**14**]$^+$[$CHB_{11}Cl_{11}$]$^-$. ^1H NMR (400.13 MHz, C_6D_5Cl/C_6D_6 (3:1), 25 °C): *δ* = 7.55 (t, *J* = 7.6 Hz, 1 H, *p*-H), 7.48 (t, *J* = 7.8 Hz, 2 H, *p*-H of Dipp), 7.39 (d, *J* = 7.6 Hz, 2 H, *m*-H), 7.27 (d, *J* = 7.8 Hz, 4 H, *m*-H of Dipp), 2.86 (br. s, 1 H, $CHB_{11}Cl_{11}$), 2.66 [sept, *J* = 6.8 Hz, 4 H, $CH(CH_3)_2$], 1.11 [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.07 [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.69 (quint, *J* = 6.8 Hz, 2 H, β-CH_2), 0.55 (t, *J* = 7.6 Hz, 2 H, α-CH_2), 0.49 (br. s, 5 H, γ-CH_2, δ-CH_3) ppm. $^{13}C\{^1H\}$ NMR [100.61 MHz, C_6D_5Cl/C_6D_6 (3:1); signals referenced to *δ* = 133.69 ppm for *i*-$C(C_6D_5Cl)$, 25 °C]: *δ* = 149.14 (*i*-C), 147.27 [*o*-C(Dipp)], 145.40, 137.79, 133.46 (*p*-C), 131.58, 128.51, 125.49 [*m*-C(Dipp)], 46.76 (br., $CHB_{11}Cl_{11}$), 30.52 [$CH(CH_3)_2$], 24.60 [$CH(CH_3)_2$], 23.46 [$CH(CH_3)_2$], 13.20 (δ-CH_3) ppm. MS (ESI, acetonitrile solution): calcd. for [$C_{34}H_{46}Ga^+$] 523.286, found 523.3; calcd. for [$M^+ + CH_3CN$] 564.312, found 564.4.

Thermal Stability of [14]$^+$[$B(C_6F_5)_4$]$^-$: A solution of [**14**]$^+$[$B(C_6F_5)_4$]$^-$ (ca. 5 µmol) in C_6D_6/C_6D_5Cl (ca. 12:1 ratio, 0.6 mL) in an NMR tube equipped with a J. Young valve was heated at 60 °C for 16 h. During that time, the phase separation disappeared and a pale-yellow solution was obtained. The NMR spectroscopic data are in accordance with the presence of two compounds, namely $[(2,6\text{-}Dipp_2C_6H_3)GaBu(C_6F_5)]$ (**15**)[34] and $B(C_6F_5)_3$.[35] ^1H NMR (300 MHz, C_6D_6/C_6D_5Cl (12:1), 25 °C): *δ* = 7.26 (br. s, 3 H, *m*-, *p*-H), 7.00 [d, *J* = 7.5 Hz, 4 H, *m*-H of Dipp], 2.99 [sept, *J* = 6.8 Hz, 4 H, $CH(CH_3)_2$], 1.15, [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.99, [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.68 ("t", *J* = 6.0 Hz, 3 H, δ-CH_3), 0.45 ("t", *J* = 8.0 Hz, 2 H, α-CH_2) ppm. ^{19}F NMR [284.34 MHz, C_6D_6/C_6D_5Cl (12:1), 25 °C]: **15**: *δ* = –121.90 (m, *o*-F), –155.18 (t, *J* = 19.9 Hz, *p*-F), –162.18 (m, *m*-F) ppm; $B(C_6F_5)_3$: *δ* = –129.89 (m, *o*-F), –142.86 (m, *p*-F), –161.18 (m, *m*-F) ppm.

$[(BuGa)_4(\mu\text{-}OH)_6]^{2+}[CHB_{11}Br_6Me_5]^-_2$ (16): The solution of [**13**]$^+$-[$CHB_{11}Br_6Me_5$]$^-$ that was used to measure the ^1H NMR spectrum was transferred to a small vial inside the glove box, and the solvent was allowed to slowly evaporate. The resulting colorless crystals were analyzed by X-ray diffraction as $Ph_3CH{\cdot}C_6H_6$[42] and **16**$\cdot 4.5C_6D_6$.

Reaction of [14]$^+$[CHB$_{11}$Cl$_{11}$]$^-$ with 1-Octene: A solution of [**14**]$^+$[CHB$_{11}$Cl$_{11}$]$^-$ (11 mg, 12 µmol) in a 6:1 mixture of C_6D_6/C_6D_5Cl (0.6 mL) was treated with 1-octene (14 µmol, 2.4 µL) at room temperature. The reaction was monitored by ^1H NMR spectroscopy. After most of the free olefin had been consumed, additional olefin was added at various intervals starting after 54 h (5 µL), then after an additional 8 d (5 µL), and finally after further 4 d (10 µL). The last olefin added had been consumed at room temperature after 7 d. Two drops of the reaction mixture were used for ESI mass spectrometry. The rest was poured into a vial in air, the solvent was allowed to evaporate, and the remaining oil was investigated by GC/MS. MS (ESI, acetonitrile solution): calcd. for $C_{38}H_{54}Ga$ [M$^+$] 579.35; found 579.6; calcd. for $C_{40}H_{57}GaN$ [M$^+$ + MeCN] 620.37; found 620.6. GC/MS: t_R = 11.62 min (16%), calcd. for $C_{14}H_{16}D_6$ (4-octylbenzene) 196.21, found 196.1; 11.73 min (25%), calcd. for $C_{14}H_{16}D_6$ (3-octylbenzene) 196.21, found 196.1; 11.97 min (59%), calcd. for $C_{14}H_{16}D_6$ (2-octylbenzene) 196.21, found 196.1. Assignments were made based on the fragmentation patterns.

X-ray Crystallography: Crystals of **1**, **3**, and **5** were obtained by crystallization from concentrated toluene solutions at –24 °C, crystals of **7** were obtained from a concentrated benzene solution at 3–4 °C, and crystals of **10** and **16** at room temperature from a 1-octene or benzene solution of **8** or [**13**]$^+$[CHB$_{11}$Br$_6$Me$_5$]$^-$, respectively, by slow evaporation of the solvents inside a drybox. Crystals of **1**, **3**, **5**, and **7** were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil, and crystals of **10** and **16** were covered with a layer of hydrocarbon oil inside a drybox. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream. Crystals of **16** experienced a phase transition around 170 K, and the data were collected at 178 K. The data were collected with a Bruker Apex diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. Absorption corrections using a multi-scan method from equivalent reflections were applied for **1**, **3**, **5**, **7**, and **10**; a semi-empirical method was used for **16**.[43] The structures were solved by direct methods using the SHELXTL program suite (version 6.1[44]) and refined by full-matrix least squares on F^2 including all reflections. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in the refinement with idealized parameters. The OH hydrogen atoms in compounds **10** and **16** were not observed, but were placed into calculated positions using riding and distance restraints, respectively. The X-ray crystal structure of **1** at room temperature was reported recently.[18] Its parameters are very similar to the ones given here with the exception of a slightly larger unit cell. The structure of **16** displayed some serious disorder problems. The structure includes one dication, two monoanions, and four and one half benzene molecules. One of the solvent molecules was severely disordered and was best modeled using the Squeeze program.[45] Three of the *n*-butyl groups on the cation were disordered and each was modeled in two orientations. The occupancies of atoms C(1)–C(4), C(5)–C(8), and C(13)–C(16) refined to 0.689(12) and 0.311(12), 0.627(11) and 0.373(11), and 0.797(9) and 0.203(9) for the unprimed and primed atoms, respectively. Restraints were placed on the positional and displacement parameters of the disordered atoms and the solvent atoms as well as the positional parameters of the hydrogen atoms bonded to the oxygen atoms and the hydrogen atoms on C(1A) and C(1B). Some details of the crystal data and refinement are given in Table 1, and selected bond lengths and angles are listed in

Table 1. Crystal data and structural refinement details for **1**, **3**, **5**, **7**, **10**, and **16**$\cdot 4.5C_6H_6$.

	1	**3**	**5**	**7**	**10**	**16**$\cdot 4.5C_6H_6$
Empirical formula	$C_{52}H_{58}ClGa$	$C_{78}H_{87}Ga$	$C_{48}H_{50}AlCl$	$C_{48}H_{51}Al$	$C_{56}H_{70}Ga_2O_2$	$C_{55}H_{101}B_{22}Br_{12}Ga_4O_6$
Formula mass	788.15	1094.2	689.31	654.87	914.56	2333.98
T [K]	100(2)	100(2)	130(2)	120(2)	110(2)	178(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$\mathrm{P}2_12_12_1$	$P\bar{1}$	$C2/c$
a [Å]	17.1401(9)	9.9494(8)	11.9518(16)	11.9283(5)	9.010(6)	33.122(5)
b [Å]	13.7377(7)	33.470(3)	20.391(3)	15.8012(7)	12.163(7)	18.094(2)
c [Å]	19.7484(10)	18.6120(15)	16.157(2)	20.3941(9)	12.211(7)	31.434(4)
α [°]	90	90	90	90	67.407(7)	90
β [°]	110.2180(10)	94.3920(10)	100.167(2)	90	78.940(8)	112.014(5)
γ [°]	90	90	90	90	82.428(7)	90
V [Å^3]	4363.6(4)	6179.6(9)	3875.9(9)	3843.9(3)	1210.1(13)	17465(4)
Z	4	4	4	4	1	8
$D_{\mathrm{calcd.}}$ [Mg m^{-3}]	1.200	1.176	1.181	1.132	1.255	1.775
μ(Mo-K_α) [mm^{-1}]	0.725	0.489	0.154	0.085	1.153	0.71073
F(000)	1672	2344	1472	1408	484	9064
Crystal size [mm]	0.16 × 0.12 × 0.06	0.38 × 0.22 × 0.20	0.26 × 0.18 × 0.04	0.28 × 0.22 × 0.18	0.48 × 0.08 × 0.02	0.24 × 0.22 × 0.14
Crystal color and habit	colorless prism	colorless plate	colorless prism	colorless prism	colorless needle	colorless prism
$2\Theta_{\max}$ [°]	54.3	52.8	52.2	54.0	52.0	52.0
No. of obsd. recflections	9643	12644	7663	8384	4581	17168
No. of variables	499	760	463	458	271	983
R_1[a] [$I > 2\sigma(I)$]	0.0347	0.0509	0.0625	0.0332	0.0859	0.0671
wR_2[b] [$I > 2\sigma(I)$]	0.0803	0.1155	0.1081	0.0906	0.2364	0.1772
Goodness-of-fit on F^2	1.005	1.006	1.011	1.026	1.068	1.027
Largest diff. peak [e Å^{-3}]	0.418	0.648	0.301	0.280	1.842	1.804

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

Tables 2 and 3. CCDC-626538 to -626542 and 626654 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/datarequest/cif.

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **3**, **5**, and **7**.

	1 (M = Ga)	**3** (M = Ga)	**5** (M = Al; X = Cl)	**7** (M = Al; X = H)
M–C	1.9701(16)	2.010(2)	1.976(3)	1.9936(13)
	1.9816(17)	1.989(2)	1.979(3)	1.9864(13)
		1.996(3)		
M–X	2.1786(5)		2.1098(12)	1.436(18)
C–M–C	138.26(7)	117.64(10)	147.52(13)	137.62(5)
		119.05(10)		
		122.57(10)		
C–M–X	107.04(5)		105.22(10)	113.8(7)
	114.52(5)		107.26(9)	108.6(7)

Table 3. Selected bond lengths [Å] and angles [°] for **10** and **16**.

Compound **10**			
Ga(1)–O(1)	1.947(5)	O(1)–Ga(1)–O(1A)	78.4(2)
Ga(1)–O(1A)	1.952(5)	O(1)–Ga(1)–C(1)	111.0(2)
Ga(1)–C(1)	1.992(6)	O(1A)–Ga(1)–C(1)	110.8(3)
Ga(1)–C(25)	1.967(7)	O(1)–Ga(1)–C(25)	108.1(3)
		O(1A)–Ga(1)–C(25)	107.0(3)
		C(25)–Ga(1)–C(1)	129.7(3)
Compound **16**			
Ga(1)–O(1)	1.889(6)	Ga(3)–O(5)	1.890(5)
Ga(1)–O(2)	1.903(5)	Ga(4)–O(3)	1.887(5)
Ga(1)–O(3)	1.898(5)	Ga(4)–O(5)	1.901(5)
Ga(2)–O(1)	1.901(6)	Ga(4)–O(6)	1.898(5)
Ga(2)–O(4)	1.893(5)	Ga(1)–C(1)	1.932(5)
Ga(2)–O(6)	1.907(5)	Ga(2)–C(5)	1.933(5)
Ga(3)–O(2)	1.903(5)	Ga(3)–C(9)	1.932(4)
Ga(3)–O(4)	1.896(5)	Ga(4)–C(13)	1.934(5)
O(1)–Ga(1)–O(2)	97.0(3)	O(3)–Ga(4)–O(5)	95.1(2)
O(1)–Ga(1)–O(3)	97.2(2)	O(3)–Ga(4)–O(6)	97.5(2)
O(2)–Ga(1)–O(3)	96.8(3)	O(5)–Ga(4)–O(6)	96.4(2)
O(1)–Ga(2)–O(4)	98.3(2)	Ga(1)–O(1)–Ga(2)	129.5(3)
O(1)–Ga(2)–O(6)	96.0(2)	Ga(1)–O(2)–Ga(3)	130.1(3)
O(4)–Ga(2)–O(6)	97.3(2)	Ga(1)–O(3)–Ga(4)	132.5(3)
O(2)–Ga(3)–O(4)	93.1(3)	Ga(2)–O(4)–Ga(3)	130.9(3)
O(2)–Ga(3)–O(5)	100.4(3)	Ga(3)–O(5)–Ga(4)	130.6(3)
O(4)–Ga(3)–O(5)	98.1(2)	Ga(2)–O(6)–Ga(4)	131.1(3)

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