# Synthesis and Structure of Neutral and Cationic Gallium Complexes Incorporating Bis(oxazolinato) Ligands

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The bis(oxazolinato)dimethylgallium complexes [{BOX-$Me_2$}$GaMe_2$] (**2a**) and [{BOX-(*S*)-*i*Pr}$GaMe_2$] (**2b**) are easily obtained in nearly quantitative yield by a methane elimination reaction between $GaMe_3$ and the corresponding bis(oxazoline) ligands {BOX-$Me_2$}H (**1a**) and {BOX-(*S*)-*i*Pr}H (**1b**). Compound **2a** was also synthesized by a salt metathesis involving the formation of the dichloro complex [{BOX-$Me_2$}$GaCl_2$] by reaction of [(BOX-$Me_2$)Li] with $GaCl_3$, followed by its in situ methylation with MeMgBr. The neutral complexes **2a** and **2b** are rapidly ionized by $B(C_6F_5)_3$ to cations **3a**$^+$ and **3b**$^+$, respectively, which are either three-coordinate methylgallium cations or four-coordinate Ga solvent adducts, as their $MeB(C_6F_5)_3^-$ salts. These cationic species exhibit a limited stability and decompose in solution within several hours at room temperature. However, stable four-coordinate Ga-$NMe_2Ph$ cations (**4a**$^+$ and **4b**$^+$) are isolated in good yield when these ionization reactions are performed in the presence of a Lewis base such as $NMe_2Ph$. Unlike that of $B(C_6F_5)_3$, the reaction of [{BOX-$Me_2$}$GaMe_2$] with $[Ph_3C][B(C_6F_5)_4]$ quantitatively affords an unusual bis(imine)-dimethylgallium cation {$H_2C$=C(OX-$Me_2$)$_2$}$GaMe_2^+$ (**5a**$^+$) in a reaction that proceeds via a hydride abstraction occurring at the Me group located at the back of the bis(oxazolinato) ligand chelated to the Ga center in **2a**. Overall, the reactivity and structural trends observed for the Ga derivatives are closely related to those of the Al analogs, with the Ga compounds being more stable.



## Introduction

Cationic group 13 complexes have been the subject of several studies over the past few years since the enhanced Lewis acidity at the metal center, which is a result of its cationic charge, renders these species potentially interesting as Lewis acid catalysts.[1] As such, they have already found applications in isobutene,[2] ethylene,[3] alkene oxide,[4] and D,L-lactide[5] polymerization catalysis. In this regard, three- and four-coordinate cationic group 13 complexes of the general type $[(LX)MR]^+$ and $[(LX)M(R)(L)]^+$ (L labile), readily accessible by reaction of neutral precursors $[(LX)MR_2]$ with strong Lewis acids such as $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$, have appeared as appealing targets because they incorporate a cationic and low-coordinate metal center; accordingly, these cations behave like potent Lewis acids.[6,7] Thus far, most of the investigations in this area have concerned aluminum derivatives, where it has been found that the structure and the stability of the formed Al cations are greatly dependent upon the steric properties of the ancillary $LX^-$ bidentate ligand and the nature of the counterion.[7] More specifically, the presence of an extremely bulky $LX^-$ ligand and the use of an inert counterion $[B(C_6F_5)_4^-$ or $MeB(C_6F_5)_3^-]$ are required to obtain, in some cases, reasonably stable Al cations. However, the frequent poor stability of these highly reactive alkylaluminum species may limit the scope of their applications in catalysis.

Although much less studied than their Al counterparts, low-coordinate cationic alkylgallium complexes are expected to exhibit an increased stability as a result of the less polar character of the Ga–C vs. Al–C bond,[8] while still remaining reactive due to the presence of an electron-deficient metal center. Thus, cationic Ga derivatives may well represent a reasonable balance of reactivity and stability, which is a required feature for catalysis involving polar substrates and/or media.

We are interested in the design and synthesis of stable low-coordinate cationic group 13 complexes of the type $[(LX)MR]^+$ and $[(LX)M(R)(L)]^+$ for applications in catalysis. To this purpose, we have recently focused our attention toward the synthesis of $[(LX)AlR]^+$ and $[(LX)Al(R)(L)]^+$

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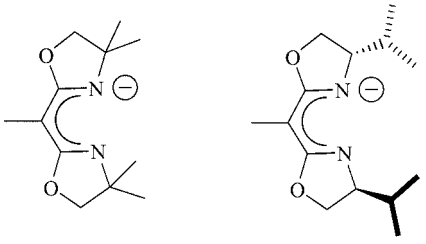
cations bearing either an *N*,O-aminophenolate or an *N*,*N*-bis(oxazolinato) bidentate ligand (**A** and **B**, Scheme 1).[9,10] In particular, the use of a chiral $C_2$-symmetric *N*,*N*-bis(oxazolinato) ligand has provided access to chiral cationic alkylaluminum complexes, which are of potential interest in asymmetric catalysis.[10] However, the instability of the Al cations incorporating **B**, especially in catalytic conditions, prompted us toward the synthesis of the Ga analogs, which are expected to be more stable. Thus, as part of our continuous studies of cationic and chiral group 13 alkyl complexes, we here report the synthesis and structure of neutral and cationic bis(oxazolinato)methylgallium complexes.



**A** **B**

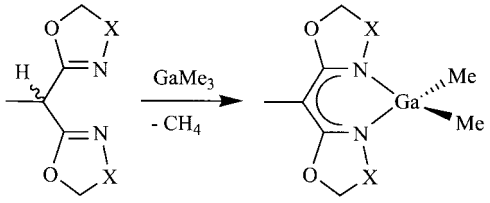
Scheme 1.

## Results and Discussion

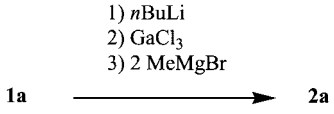
Bis(oxazolinato)dimethylgallium compounds were synthesized by the classical alkane elimination route involving a reaction between the appropriate bis(oxazoline) ligand and $GaMe_3$. This pathway was found to be the most straightforward and efficient method to access such compounds.

Thus, the reaction of the bis(oxazoline) ligands (BOX-$Me_2$)H (**1a**) and {BOX-(*S*)-*i*Pr}H (**1b**; Scheme 2) with an equimolar amount of $GaMe_3$ in pentane at –35 °C yields the bis(oxazolinato)dimethylgallium compounds [(BOX-$Me_2$)$GaMe_2$] (**2a**) and [{BOX-(*S*)-*i*Pr}$GaMe_2$] (**2b**; Scheme 2), respectively, which were isolated in nearly quantitative yields (>95% yield) as air-stable colorless solids. Alternatively, the achiral Ga derivative **2a** was also obtained by a salt metathesis pathway, although this approach was less efficient. Thus, the reaction of the bis(oxazolinato)lithium salt [(BOX-$Me_2$)Li], generated by deprotonation of bisoxazoline **1a** with *t*BuLi at –78 °C, with an equimolar amount of $GaCl_3$ (18 h, room temp.) yields [(BOX-$Me_2$)-$GaCl_2$], as observed by $^1$H NMR spectroscopy. The in situ methylation of the dichlorogallium derivative with two equivalents of MeMgBr affords [(BOX-$Me_2$)$GaMe_2$] (**2a**) in moderate yield (48%).

The molecular structures of the Ga complexes **2a** and **2b** were determined by X-ray crystallography analysis, thus establishing their monomeric nature as well as the effective chelation of one bis(oxazolinato) ligand (Figures 1 and 2 and Table 1). As expected, both Ga species exhibit very similar structural features in the solid state and these will only discussed for the chiral derivative **2b**.




**1a**: X = $CMe_2$ **2a**: X = $CMe_2$
**1b**: X = (*S*)-CH*i*Pr **2b**: X = (*S*)-CH*i*Pr




Scheme 2.

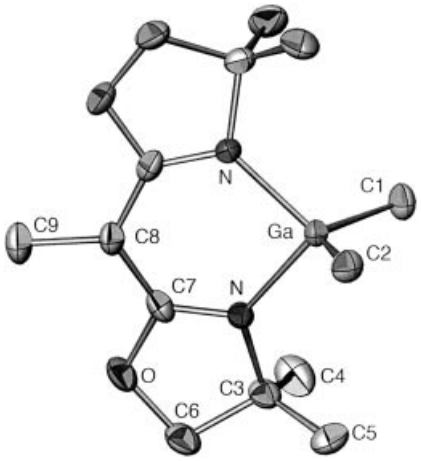



Figure 1. Molecular structure of complex **2a**. The H atoms have been omitted for clarity.

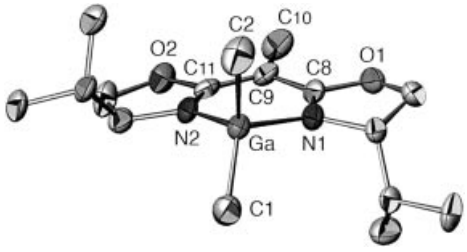



Figure 2. Molecular structure of chiral complex **2b**. The H atoms have been omitted for clarity. Selected torsion angles [°]: N(1)–C(8)–C(9)–C(11) = 5.8(15), Ga–N(2)–C(11)–C(10) = 3.2(4), Ga–N(2)–C(11)–C(9) = 2.5(11).

The Ga metal center in **2b** adopts a slightly distorted tetrahedral geometry with a chelate bite angle [N(1)–Ga–N(2) = 91.1(2)°] similar to that in the related β-diketiminatodimethylgallium complex [HC{C(Me)N($C_6H_3$-2,6-*i*$Pr_2$)}-$GaMe_2$] [93.92(7)°], which also contains a six-membered $C_3N_2Ga$ metallacycle.[11] The Ga–N and Ga–C bond lengths in **2b** [1.966(9) Å and 1.98(1) Å average, respectively] are similar to those observed in related {LX}$GaMe_2$

Table 1. Selected bond lengths [Å] and angles [°] for **2a** and **2b**.

| **2a** | | **2b** | |
|---|---|---|---|
| Ga–N | 1.9677(17) | Ga–N(1) | 1.967(6) |
| Ga–C(1) | 1.970(3) | Ga–N(2) | 1.966(6) |
| Ga–C(2) | 1.970(3) | Ga–C(1) | 1.963(9) |
| N–C(7) | 1.320(3) | Ga–C(2) | 2.004(10) |
| C(7)–C(8) | 1.395(3) | N(1)–C(8) | 1.333(8) |
| | | N(2)–C(11) | 1.306(9) |
| | | C(8)–C(9) | 1.384(11) |
| | | C(9)–C(11) | 1.386(10) |
| N–Ga–N | 91.33(10) | N(1)–Ga–N(2) | 91.1(2) |
| N–Ga–C(2) | 109.38(8) | C(1)–Ga–N(2) | 111.8(4) |
| N–Ga–C(1) | 111.85(8) | C(1)–Ga–N(1) | 113.5(3) |
| C(1)–Ga–C(2) | 119.47(14) | C(1)–Ga–C(2) | 119.9(4) |

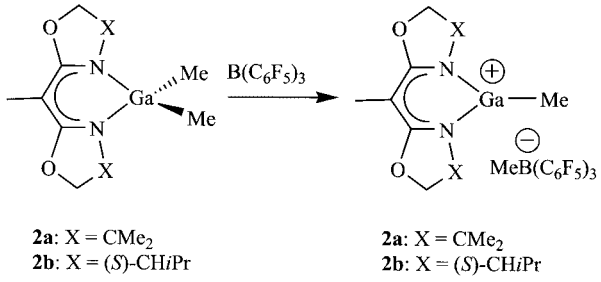
species such as [HC{C(Me)N($C_6H_3$-2,6-*i*$Pr_2$)}$GaMe_2$],[11] [{PhC($NPh)_2$}$GaMe_2$],[12] and [{*t*BuC($NCy)_2$}$GaMe_2$].[13]

The six-membered $C_3N_2Ga$ metallacycle in [{BOX-(*S*)-*i*Pr}$GaMe_2$] (**2b**) is nearly planar (C–C–Ga–N < 6°) with the carbon and nitrogen atoms adopting a trigonal-planar geometry (sum of angles ca. 360°). The planarity of the six-membered $C_3N_2Ga$ backbone in **2b** contrasts with the folding of the $C_3N_2Ga$ ring observed in [HC{C(Me)N($C_6H_3$-2,6-*i*$Pr_2$)}$GaMe_2$], in which the Ga metal center lies significantly out of the $C_3N_2$ plane (0.76 Å). This structural difference presumably results from much weaker steric interactions between the Ga metal center and the chelating ligand in **2b** compared to [HC{C(Me)N($C_6H_3$-2,6-*i*$Pr_2$)}-$GaMe_2$].[11] The C–C bond lengths within the $C_3N_2$ moiety [1.38(1) Å average] in **2b** are close to the C–C bond length in aromatic systems (1.395 Å), while the C–N bond lengths [1.32(1) Å average] lie between the C=N double-bond length in imines (1.28 Å) and the C($sp^2$)–N single-bond length (1.47 Å). Altogether, these structural data are consistent with significant π-delocalization of the bis(oxazolinato) ligand backbone, resulting in a nearly $C_2$ symmetry for **2b** in the solid state. Similar structural features have been observed for the Al analogs.[10]

The NMR spectroscopic data for the Ga complexes **2a** and **2b** at room temperature are consistent with these species adopting overall $C_{2v}$ and $C_2$ symmetry, respectively, in solution. These NMR spectroscopic data are therefore in agreement with the solid-state structures of **2a** and **2b** being retained in solution under the conditions studied here. For example, the $^1$H NMR spectrum of **2b** ($C_6D_6$, room temp.) exhibits one Ga*Me*$_2$ resonance, one N-C*H* resonance and two Me-*i*Pr resonances, which is in agreement with a $C_2$-symmetric complex.

### Reaction of Bis(oxazolinato)dimethylgallium Complexes 2a and 2b with $B(C_6F_5)_3$

Cationic alkylgallium complexes could be obtained by reaction of the neutral dimethylgallium derivatives with the strong Lewis acid $B(C_6F_5)_3$, which is known to readily abstract a methyl anion from the metal center of group 13 [{LX}$MMe_2$] species. Thus, the reaction of [{BOX}$GaMe_2$] (**2a**,**b**) with one equivalent of $B(C_6F_5)_3$ ($C_6D_5Br$, room temp., 10 min) results in the nearly quantitative formation of the cations [{BOX-$Me_2$}GaMe]$^+$ (**3a**$^+$) and [BOX-(*S*)-*i*Pr}GaMe]$^+$ (**3b**$^+$), respectively, as their $MeB(C_6F_5)_3^-$ salts, as observed by $^1$H, $^{13}$C, and $^{19}$F NMR spectroscopy (Scheme 3). As expected, the Ga cations **3a**,**b**$^+$ are more stable than their Al counterparts; however, they slowly decompose at room temp. in $C_6D_5Br$ ($t_{1/2} \approx 10$ h) to yield unidentified species, which precluded their isolation in a pure form. Initial attempts (by $^1$H NMR) to observe cations **3a**,**b**$^+$ by carrying out the reaction on an NMR-tube scale in $CD_2Cl_2$ were unsuccessful, presumably due to fast decomposition of the desired cations in $CD_2Cl_2$.




Scheme 3.

The $^1$H, $^{13}$C and $^{19}$F NMR spectroscopic data for the [**3a**,**b**][$MeB(C_6F_5)_3$] salt species are consistent with weak interactions between the cation and the anion down to –30 °C in $C_6D_5Br$ solution. In particular, the *Me*$B(C_6F_5)_3^-$ resonance ($\delta$ = 0.97 ppm) in the $^1$H NMR spectra of [**3a**,**b**]-[$MeB(C_6F_5)_3$] is characteristic of a free $MeB(C_6F_5)_3^-$ anion in solution at room temp. (Figure 3).[14] The NMR spectroscopic data for the Ga cations **3a**$^+$ and **3b**$^+$ are essentially unchanged between –30 °C and room temp. and agree with effective $C_{2v}$- and $C_2$-symmetric species for **3a**$^+$ and **3b**$^+$, respectively, under these conditions. For instance, as illustrated in Figure 3, the $^1$H NMR spectrum of [**3a**][$MeB(C_6F_5)_3$] only exhibits four resonances for cation **3a**$^+$ (Ga*Me*$^+$, C*Me*$_2$, O-C*H*$_2$, and C*Me*), which is in agreement with a $C_{2v}$-symmetric complex. In addition, the Ga*Me*$^+$ resonance in **3a**$^+$ ($\delta$ = 0.40 ppm) is shifted dramatically downfield relative to the Ga*Me*$_2$ resonance of the neutral precursor **2a** ($\delta$ = –0.17 ppm) as a result of the cationic charge on Ga. Overall, on the basis of NMR spectroscopic data, the Ga cations **3a**,**b**$^+$ are most likely either three-coordinate "base-free" cationic species or four-coordinate cationic Ga solvent adducts (i.e. $C_6D_5Br$ adducts) with a fast coordination/decoordination process on the NMR scale down to –30 °C. The latter proposal is based on the fact that a solid-state structure of a four-coordinate cationic Ga-ClPh adduct has been reported recently.[15]

The Lewis acidic Ga cation **3a**$^+$ reacts rapidly with an excess of propylene oxide (PO; 200 equiv., –20 °C, 5 min) to yield atactic oligomers with a broad polydispersity (40% conversion, $M_n$ = 448, $M_w/M_n$ = 2.38). A longer reaction time did not yield higher conversion, which strongly suggests a fast decomposition of cation **3a**$^+$ (within 5 min at –20 °C) to inactive species in the presence of excess PO.

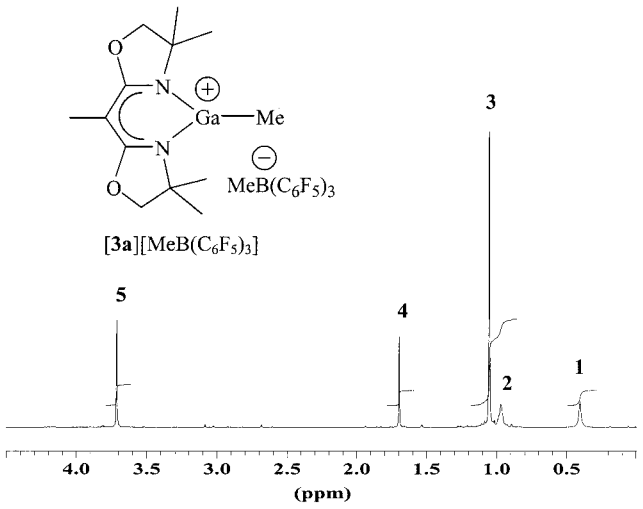
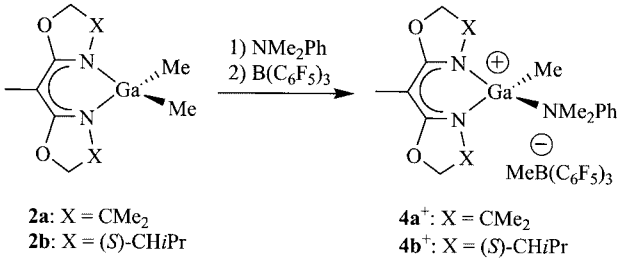



Figure 3. $^1$H NMR spectrum of [**3a**][MeB($C_6F_5$)$_3$] ($C_6D_5Br$, room temp.): $\delta$ = 0.40 (**1**, Ga*Me*), 0.97 (**2**, *Me*B), 1.05 (**3**, C*Me*$_2$), 1.70 (**4**, *Me*CCN), 3.71 (**5**, OC$H_2$) ppm.

### Synthesis and Structure of Four-Coordinate Methylgallium Cations (4a,b$^+$)

The lack of stability of cations **3a**,**b**$^+$ prompted us to generate them in the presence of a Lewis base such as $NMe_2Ph$, which is expected to trap the Ga cations to yield stable four-coordinate Ga–$NMe_2Ph$ cationic adducts. Thus, the reaction of the bis(oxazolinato)dimethylgallium complexes (**2a**,**b**) with one equivalent of B($C_6F_5$)$_3$ in the presence of one equivalent of $NMe_2Ph$ ($CH_2Cl_2$, room temp., 10 min) yields the quantitative formation of the four-coordinate cations [{BOX-$Me_2$}Ga(Me)($NMe_2Ph$)]$^+$ (**4a**$^+$) and [{BOX-(*S*)-*i*Pr}Ga(Me)($NMe_2Ph$)]$^+$ (**4b**$^+$), respectively, as their MeB($C_6F_5$)$_3^-$ salts (Scheme 4). The salt compounds [**4a**,**b**][MeB($C_6F_5$)$_3$] are stable for days at room temperature in $CH_2Cl_2$ and could thus be isolated in a pure form as colorless solids in good yields. To the best of our knowledge, cation **4b**$^+$ in [**4b**][MeB($C_6F_5$)$_3$] is the first example of a chiral cationic alkylgallium complex.




Scheme 4.

Compounds [**4a**,**b**][MeB($C_6F_5$)$_3$] are dissociated species down to –30 °C in $CD_2Cl_2$ with weakly interacting **4a**,**b**$^+$ cations and MeB($C_6F_5$)$_3^-$. The $^1$H NMR spectra of the cationic $NMe_2Ph$ adducts **4a**,**b**$^+$ both contain a Ga*Me*$^+$ resonance that is significantly downfield shifted as compared to the Ga*Me*$_2$ resonances in the neutral precursors **2a**,**b**, which is indicative of a cationic Ga center. Likewise, the $^1$H and $^{13}$C NMR resonances of **4a**,**b**$^+$ assigned to the coordinated $NMe_2Ph$ are strongly downfield shifted relative to those in free $NMe_2Ph$, which is consistent with an effective coordination of $NMe_2Ph$ to the Ga center. Overall, the NMR spectroscopic data at room temp. agree with effective $C_{2v}$- and $C_2$-symmetric solution structures for cations **4a** and **4b**$^+$, respectively, thereby indicating a fast face-exchange of $NMe_2Ph$ on the NMR timescale. To probe this issue further, low temperature $^1$H and $^{13}$C NMR experiments were carried out to reach a slow $NMe_2Ph$ exchange process. Thus, the NMR spectroscopic data for cations **4a**$^+$ and **4b**$^+$ recorded at –25 °C and –35 °C in $CD_2Cl_2$, respectively, exhibit an overall $C_s$ symmetry for **4a**$^+$ and a $C_1$ symmetry for chiral **4b**$^+$. These data are consistent with a slow face-exchange of $NMe_2Ph$ on the NMR timescale for both cations (see Exp. Sect.). For comparison, the labile coordination of $NMe_2Ph$ to Ga observed here for **4a**,**b**$^+$ at room temperature contrasts with the nonlabile coordination of this amine to Al in the cationic Al analogs under identical conditions, which may reflect a more Lewis acidic cationic Al vs. Ga center.[10]

The Lewis acid character of the Ga–$NMe_2Ph$ adduct **4a**$^+$ was also tested with PO. Like **3a**$^+$, cation **4a**$^+$ oligomerizes PO (200 equiv. of PO, room temp., 15 min) to afford low molecular weight oligomers in high conversion (85% conversion, $M_n$ = 339, $M_w/M_n$ = 1.25). The oligomerization process is clearly multimodal, as deducted from size exclusion chromatographic data, thus suggesting the presence of several active species.

### Solid-State Structure of the Cationic Adduct 4a$^+$

While a few examples of X-ray characterized low-coordinate Al cations are known, solid-state structures of Ga analogs are rather scarce,[1,7a,16] and, to date, none of the type [{LX}Ga(R)(L)]$^+$ have been reported.

The molecular structure of the salt species [**4a**][MeB($C_6F_5$)$_3$] was confirmed by X-ray crystallography analysis (Tables 2 and 3). It crystallizes as discrete **4a**$^+$ cations and MeB($C_6F_5$)$_3^-$ anions, with no cation–anion interaction. As shown in Figure 4, cation **4a**$^+$ is an $NMe_2Ph$-stabilized four-coordinate methylgallium cation in which the Ga center adopts a distorted tetrahedral structure with a chelate bite angle N(1)–Ga–N(2) [96.98(7)°] similar to that in the neutral precursor **2a**. Unlike the nearly planar six-membered $C_3N_2Ga$ metallacycle in complexes **2a**,**b**, that in **4a**$^+$ is significantly distorted from planarity, with the Ga center being displaced by 0.33(2) Å from the N(2)–C(6)–N(1)–C(9) average plane toward the coordinated $NMe_2Ph$. This distortion may well be to minimize steric interactions between the Ga-$NMe_2Ph$ moiety and the bis(oxazolinato) ligand. The Ga–N bond lengths within the chelate-Ga entity [1.9018(19) and 1.9100(16) Å] are rather short as compared to those in **2a** [1.966(9) Å], due to the stronger ionic character of these bonds in **4a**$^+$ vs. **2a**, a result of the cationic charge, whereas the Ga–$N_{amine}$ bond length [Ga–N(3) = 2.124(3) Å] is considerably longer and is comparable to those observed in neutral bulky gallium amine adducts such

as $[Me_3Ga(tBuNH_2)]$ [2.12(1) Å].[17] Due to the enhanced Lewis acidity of Ga in **4a**$^+$ vs. $[Me_3Ga(tBuNH_2)]$, a shorter Ga–N(3) bond length in **4a**$^+$ vs. $Me_3Ga(tBuNH_2)$ would be expected from an electronic point of view; this rather long Ga–N distance for **4a**$^+$ may be to minimize steric interactions between the aniline and the chelating ligand.

Table 2. Selected bond lengths [Å] and angles [°] for [**4a**][$MeB(C_6F_5)_3$] and [**5a**][$B(C_6F_5)_4$].

| **4a**$^+$ | | **5a**$^+$ | |
|---|---|---|---|
| Ga–N(1) | 1.9018(19) | Ga–C(2) | 1.953(2) |
| Ga–N(2) | 1.9100(16) | Ga–C(1) | 1.956(2) |
| Ga–C(1) | 1.944(3) | Ga–N(1) | 2.0171(17) |
| Ga–N(3) | 2.124(2) | Ga–N(2) | 2.0191(17) |
| N(1)–C(9) | 1.331(2) | N(2)–C(10) | 1.282(3) |
| N(2)–C(6) | 1.339(3) | N(1)–C(3) | 1.285(3) |
| C(7)–C(9) | 1.395(3) | C(8)–C(9) | 1.329(3) |
| C(7)–C(6) | 1.383(3) | C(8)–C(3) | 1.466(3) |
| | | C(8)–C(10) | 1.470(3) |
| N(1)–Ga–N(2) | 96.98(7) | C(1)–Ga–C(2) | 122.76(11) |
| N(1)–Ga–N(3) | 103.06(8) | N(1)–Ga–N(2) | 90.18(8) |
| C(1)–Ga–N(3) | 108.60(11) | C(1)–Ga–N(1) | 107.28(10) |
| N(2)–Ga–C(1) | 123.12(12) | C(1)–Ga–N(2) | 110.12(10) |

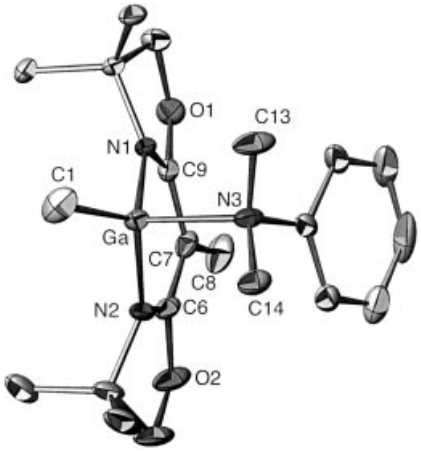
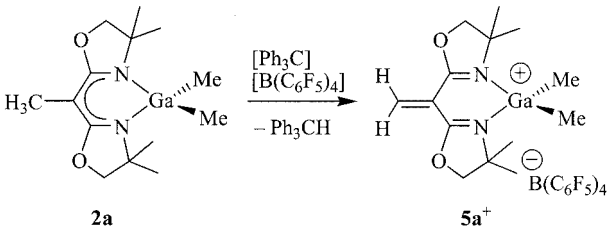



Figure 4. Molecular structure of the Ga cation **4a**$^+$. The H atoms have been omitted for clarity. Selected torsion angles [°]: N(2)–Ga–N(1)–C(9) = 13.54(14),; N(1)–Ga–N(2)–C(6) = 15.36(15), N(1)–C(9)–C(7)–C(6) = 13.0(3).

### Reaction of [{BOX-$Me_2$}$GaMe_2$] (2a) with [$Ph_3C$][$B(C_6F_5)_4$]

As stated in the introduction, the trityl salt [$Ph_3C$][$B(C_6F_5)_4$] is the other landmark reagent, along with $B(C_6F_5)_3$, that is used to generate group-13 alkyl cations of the type [{LX}MMe]$^+$ from [{LX}$MMe_2$] by a $Me^-$ abstraction at the metal center. We thus decided to study the reaction between [{BOX-$Me_2$}$GaMe_2$] (**2a**) and [$Ph_3C$][$B(C_6F_5)_4$].

The reaction of [{BOX-$Me_2$}$GaMe_2$] (**2a**) with one equivalent of [$Ph_3C$][$B(C_6F_5)_4$] ($CH_2Cl_2$, room temp., 10 min) yields the quantitative formation of the bis(imine)-dimethylgallium cation [{$H_2C$=C(OX-$Me_2$)$_2$}$GaMe_2$]$^+$ (**5a**$^+$) as a $B(C_6F_5)_4^-$ salt, along with one equivalent of $Ph_3CH$ (Scheme 5). Thus, instead of abstracting a $Me^-$ from the Ga center of **2a**, $Ph_3C^+$ abstracts a hydride from the Me group located at the back of the bis(oxazolinato) ligand in compound **2a** to afford cation **5a**$^+$. The outcome of this reaction confirms a reactivity already observed with the Al analog [{BOX-$Me_2$}$AlMe_2$], which has been found to yield a similar bis-imine cation when treated with [$Ph_3C$][$B(C_6F_5)_4$].[10] Nevertheless, the observed reactivity, i.e. a hydride abstraction at a group rather far away from the metal center, contrasts with the usual reactivity of $Ph_3C^+$ with alkyl metal complexes. Typically, hydride abstractions by $Ph_3C^+$ at such dialkyl species occur either at the $C_\alpha$ of the metal-bonded alkyl group or at the $C_\beta$, both of which, in any case, are in the vicinity of the metal center.[18]




Scheme 5.

The salt compound [**5a**][$B(C_6F_5)_4$], which is stable for days at room temp. in $CH_2Cl_2$, was obtained as an analytically pure colorless solid in good yield (see Exp. Sect.). Its molecular structure, as determined by X-ray crystallography, shows that [**5a**][$B(C_6F_5)_4$] crystallizes as **5a**$^+$ cations and $B(C_6F_5)_4^-$ anions with no cation–anion interaction in the solid state. The cationic species **5a**$^+$can be seen as a dimethylgallium cation in which the $GaMe_2^+$ moiety is chelated by the neutral bisoxaline $H_2C$=C(OX-$Me_2$)$_2$ (Figure 5). Accordingly, the bonding parameters within the $C_3N_2$ ligand backbone in **5a**$^+$ are consistent with a π-localized structure: the C(3)–N(1) and C(10)–N(2) bond lengths [1.285(3) and 1.282(3) Å] compare with the typical value for C(sp$^2$)=N double bonds (1.30 Å) while the C(8)–C(9) bond length [1.329(3) Å] is consistent with that of a C=C double

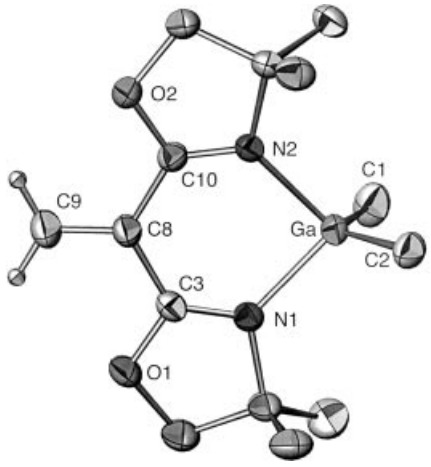



Figure 5. Molecular structure of the Ga cation **5a**$^+$. The H atoms have been omitted for clarity. Selected torsion angles [°]: N(1)–Ga–N(2)–C(10) = 12.53(19), N(2)–C(10)–C(8)–C(3) = 3.7(3), N(2)–C(10)–C(8)–C(9) = 3.0(3).

bond (1.337 Å). In addition, the Ga–N bond lengths in **5a**$^+$ [2.018(1) Å average] are comparable to those observed in neutral Ga imine complexes, e.g. in dimethyl-(*N*-methylsalicylaldiminato)gallium, Ga–N = 2.019 Å,[19] as expected for a bis-imine gallium complex such as **5a**$^+$. All other structural parameters are very similar to those in the neutral precursor **2a**.

As for the solution structure of **5a**$^+$, the NMR spectroscopic data agree with the solid-state structure being retained in solution and with no association between **5a**$^+$ and its counterion in $CD_2Cl_2$ solution at room temp. In particular, the $^1H$ and $^{13}C$ NMR spectra of **5a**$^+$ both contain one characteristic resonance at $\delta$ = 7.30 and 143.7 ppm, respectively, which can be assigned to the $H_2C$=C group of the chelating bis(oxazoline).

## Summary and Conclusions

Bis(oxazolinato)dimethylgallium complexes of the type [{BOX}$GaMe_2$] (**2a**,**b**) can be obtained in high yield by reaction of $GaMe_3$ with the desired neutral bis(oxazoline) via methane elimination. These neutral dimethylgallium precursors react rapidly with $B(C_6F_5)_3$, via a $Me^-$ abstraction, to yield the Ga cations **3a**,**b**$^+$, which are either three-coordinate methylgallium cations of the type [{BOX}GaMe]$^+$ or four-coordinate cationic Ga-solvent adducts. Although more stable than their Al counterparts, cations **3a**,**b**$^+$ decompose over the course of several hours to give unidentified species. The lack of stability of the [{BOX}GaMe]$^+$ methyl cations reported here contrasts with the stability of the three-coordinate Al cation [HC{C(Me)N($C_6H_3$-2,6-*i*$Pr_2$)}AlMe]$^+$, which also incorporates a six-membered Al metallacycle. The greater steric crowding provided at the metal center by HC{C(Me)N($C_6H_3$-2,6-*i*$Pr_2$)}$^-$ vs. {BOX-$Me_2$}$^-$ or {BOX-(*S*)-*i*Pr}$^-$ may be responsible for this difference of stability.

When the ionization of [{BOX}$GaMe_2$] (**2a**,**b**) with $B(C_6F_5)_3$ is performed in the presence of an external Lewis base such as $NMe_2Ph$, the corresponding four-coordinate cationic Ga adducts [{BOX}Ga(Me)($NMe_2Ph$)]$^+$ (**4a**,**b**$^+$) are isolated in good yield, the cation **4b**$^+$ being of particular interest as a chiral cationic derivative. Finally, [{BOX-$Me_2$}$GaMe_2$] (**2a**) reacts with [$Ph_3C$][$B(C_6F_5)_4$] to yield an unusual cationic bis(imino)gallium adduct [{$H_2C$=C(OX-$Me_2$)$_2$}$GaMe_2$]$^+$ (**5a**$^+$) via a hydride abstraction at the back of the bis(oxazolinato) ligand.

Cations **3a**$^+$ and **4a**$^+$ were found to rapidly olygomerize PO at low temperature, thereby illustrating the Lewis acid character of these species. However, the broad polydispersity of the obtained oligomers suggests a poor stability of these species in catalytic conditions.

Further studies will focus on the synthesis and use of bulkier and chiral $LX^-$ ligands for coordination to group 13 metals.

## Experimental Section

**General Procedures:** All experiments were carried out under $N_2$ using standard Schlenk techniques or in an Mbraun Unilab glovebox. Toluene, pentane, and THF were distilled from Na/benzophenone and stored over activated molecular sieves (4 Å) in a glovebox prior to use. $CH_2Cl_2$ and $CD_2Cl_2$, were distilled from $CaH_2$ and stored over activated molecular sieves (4 Å) in a glovebox prior to use. $C_6D_6$ was degassed under an $N_2$ flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. $B(C_6F_5)_3$ was purchased from Strem Chemicals and was extracted with dry pentane prior to use. [$Ph_3C$][$B(C_6F_5)_4$] was purchased from Asahi Glass Europe and used as received. $CD_2Cl_2$, $C_6D_6$, and $C_6D_5Br$ were purchased from Eurisotop. All other chemicals were purchased from Aldrich and were used as received. The bisoxazoline ligands **1a**,**b** were synthesized according to a literature procedure.[10] All NMR spectra were recorded at room temperature (unless otherwise indicated) on a Bruker Avance 300 MHz or 400 MHz spectrometer. $^1H$ and $^{13}C$ chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual $^1H$ and $^{13}C$ solvent peaks. $^{11}B$ and $^{19}F$ chemical shifts are reported relative to $BF_3{\cdot}Et_2O$ in $CD_2Cl_2$ and $CFCl_3/CDCl_3$, respectively. SEC analysis was carried out on a system equipped with 4 PL Gel columns (250 mm length × 7.5 mm inner diameter) in series and with THF as solvent. A Shimadzu SPD10Avp UV detector coupled with a Shimadzu RID6A refractometer was employed. The apparatus was calibrated using a POE standard from Polymer Laboratories. Elemental analyses for [**4a**,**b**][$MeB(C_6F_5)_3$] and [**5a**][$B(C_6F_5)_4$] were performed by the Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany, while those for compounds **2a**,**b** were performed by the microanalysis laboratory of the Université Pierre et Marie Curie, Paris, France.

For the compounds listed below, the assignment of all $^1H$ and $^{13}C\{^1H\}$ NMR resonances was possible using DEPT experiments combined, when necessary, with HMQC experiments.

**[{BOX-$Me_2$}$GaMe_2$] (2a) by Methane Elimination:** In a glovebox, a pentane solution (3 mL) of $GaMe_3$ (285 mg, 2.48 mmol), previously cooled to –35 °C in a freezer, was slowly added with a Pasteur pipette to a pentane solution (7 mL) of bisoxazoline **1a** (557 mg, 2.48 mmol), also precooled to –35 °C. The resulting colorless solution was then allowed to warm to room temperature. Upon warming to room temperature, a slight bubbling was observed, as expected for methane formation. After stirring the solution for 2 h at room temperature, it was then evaporated to dryness under vacuum to yield pure **2a** as a colorless solid in nearly quantitative yield (785 mg, 98% yield). $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ = 0.03 (s, 6 H, Ga*Me*$_2$), 1.02 (s, 12 H, C*Me*$_2$), 2.26 (s, 3 H, *Me*CCN), 3.41 (s, 4 H, OC*H*$_2$) ppm. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ = –0.38 (s, 6 H, Ga*Me*$_2$), 1.29 (s, 12 H, C*Me*$_2$), 1.70 (s, 3 H, *Me*CCN), 3.95 (s, 4 H, OC*H*$_2$) ppm. $^1H$ NMR (400 MHz, $C_6D_5Br$): $\delta$ = –0.17 (s, 6 H, Ga*Me*$_2$), 1.11 (s, 12 H, CMe$_2$), 1.99 (s, 3 H, *Me*CCN), 3.64 (s, 4 H, OC*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): $\delta$ = –2.8 (Ga*Me*$_2$), 10.3 (*Me*CCN), 27.7 (C*Me*$_2$), 62.3 (Me*C*CN), 63.7 (*C*Me$_2$), 78.7 (O*C*H$_2$), 170.2 (O*C*N) ppm. $C_{14}H_{25}GaN_2O_2$ (323.08): calcd. C 52.05, H 7.80; found C 52.14, H 7.72.

**[{BOX-$Me_2$}$GaMe_2$] (2a) by Salt Metathesis:** On a nitrogen-filled vacuum line, *t*BuLi (0.550 mL of a 1.7 M pentane solution, 0.934 mmol) was added dropwise, from a syringe, to a THF solution (10 mL) of bisoxazoline **1a** (209 mg, 0.934 mmol) that had been cooled to –78 °C in an acetone/dry ice bath. Upon addition of *t*BuLi, the initial colorless solution turned bright yellow. After the addition, the resulting yellow solution was allowed to warm to room temperature and was stirred for 3 h. Evaporation of the volatiles under reduced pressure yielded a yellow sticky residue which was washed twice with cold pentane (2 × 10 mL cooled to –35 °C) to afford a colorless solid. In a glovebox, this solid was dissolved

in toluene (10 mL) in a small Schlenk flask and cooled to –35 °C in a freezer for 1 h. After this time, the cold colorless solution was taken out of the freezer and stirred vigorously. A toluene solution (5 mL) of $GaCl_3$ (164 mg, 0.934 mmol), also precooled to –35 °C, was then quickly added to this solution and the resulting mixture was allowed to warm to room temperature. Upon warming to room temperature, the initial solution turned into a colorless suspension (indicating the formation of LiCl), which was left stirring overnight at room temperature. The reaction mixture was then filtered through a glass frit and the resulting filtrate evaporated under vacuum to yield crude **2a** as a sticky colorless solid. Recrystallization of this crude product from a 1:1 $Et_2O$/pentane solution cooled to –35 °C afforded pure **2a** as colorless crystals (145 mg, 48% yield).

**[{BOX-(*S*)-*i*Pr}$GaMe_2$] (2b):** The chiral dimethylgallium compound **2b** was synthesized by methane elimination using the same procedure as for **2a**, using an equimolar amount of {BOX-(*S*)-*i*Pr}H (300 mg, 1.19 mmol) and $GaMe_3$ (136 mg, 1.19 mmol) to afford pure **2b** as a colorless solid in high yield (401 mg, 96% yield). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 0.00 (s, 6 H, Ga*Me*$_2$), 0.49 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, *Me*-*i*Pr), 0.74 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, *Me*-*i*Pr), 1.91 (d of septet, $^3J_{H,H\ doublet}$ = 3.3, $^3J_{H,H\ septet}$ = 6.9 Hz, 2 H, C*H*-*i*Pr), 2.21 (s, 3 H, *Me*CCN), 3.56–3.66 (m, 4 H, OC$H_2$), 3.68–3.75 (m, 2 H, C*H*N) ppm. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = –0.45 (s, 6 H, Ga*Me*$_2$), 0.80 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, *Me*-*i*Pr), 0.89 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, *Me*-*i*Pr), 1.68 (s, 3 H, *Me*CCN), 1.96 (d of septet, $^3J_{H,H\ doublet}$ = 3.4, $^3J_{H,H\ septet}$ = 6.9 Hz, 2 H, C*H*-*i*Pr), 3.96–4.01 (m, 2 H, C*H*N), 4.06–4.11 (dd, $^2J_{H,H}$ = 8.4, $^3J_{H,H}$ = 8.4 Hz, 2 H, OC$H_2$), 4.17–4.23 (dd, $^2J_{H,H}$ = 8.4, $^3J_{H,H}$ = 9.2 Hz, 2 H, OC$H_2$) ppm. $^1$H NMR (300 MHz, $C_6D_5Br$): $\delta$ = –0.19 (s, 6 H, Ga*Me*$_2$), 0.66 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, *Me*-*i*Pr), 0.73 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, *Me*-*i*Pr), 1.90 (d of septet, $^3J_{H,H\ doublet}$ = 3.3, $^3J_{H,H\ septet}$ = 6.9 Hz, 2 H, C*H*-*i*Pr), 1.96 (s, 3 H, *Me*CCN), 3.84–3.92 (m, 6 H, OC$H_2$ and C*H*N) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$): $\delta$ = –6.4 (Ga*Me*$_2$), 10.4 (*Me*CCN), 14.5 (*Me*-*i*Pr), 18.9 (*Me*-*i*Pr), 30.0 (*C*H-*i*Pr), 61.4 (Me*C*CN), 66.5 (*C*HN), 66.9 (O*C*H$_2$), 171.1 (O*C*N) ppm. $C_{16}H_{29}GaN_2O_2$ (351.14): calcd. C 54.73, H 8.32; found C 54.42, H 8.17.

**[{BOX-$Me_2$}GaMe][MeB($C_6F_5$)$_3$] ([3a][MeB($C_6F_5$)$_3$]):** In a glovebox, an equimolar amount of **2a** (30.0 mg, 0.093 mmol) and B($C_6F_5$)$_3$ (47.5 mg, 0.093 mmol) were charged in a J-Young NMR tube and 0.75 mL of $C_6D_5Br$ was added. The NMR tube was vigorously shaken to yield a colorless solution and a $^1$H NMR spectrum was immediately recorded, showing the nearly quantitative formation of [**3a**][MeB($C_6F_5$)$_3$] as a fully dissociated salt species, along with minor impurities. Due to the relatively poor stability of [**3a**][MeB($C_6F_5$)$_3$], the $^{13}$C{$^1$H} NMR spectrum was recorded at –25 °C to ensure good data. $^1$H NMR (400 MHz, $C_6D_5Br$): $\delta$ = 0.40 (s,3 H, Ga*Me*), 0.97 (br. s, 3 H, *Me*B), 1.05 (s, 12 H, C*Me*$_2$), 1.70 (s, 3 H, *Me*CCN), 3.71 (s, 4 H, OC$H_2$) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_5Br$, 248 K): $\delta$ = –4.6 (Ga*Me*), 9.3 (*Me*CCN), 11.7 (br., *Me*B), 28.2 (C*Me*$_2$), 64.4 (*C*Me$_2$), 71.3 (Me*C*CN), 79.4 (O*C*H$_2$), 137.2 (dm, $^2J_{C,F}$ = 256 Hz, *o*- or *m*-$C_6F_5$), 137.9 (dm, $^2J_{C,F}$ = 243 Hz, *p*-$C_6F_5$), 148.8 (dm, $^2J_{C,F}$ = 237 Hz, *o*- or *m*-$C_6F_5$), 171.0 (O*C*N) ppm.

**[{BOX-(*S*)-*i*Pr}GaMe][Me(B$C_6F_5$)$_3$] ([3b][MeB($C_6F_5$)$_3$]):** The chiral salt compound [**3b**][MeB($C_6F_5$)$_3$] was generated on an NMR scale using the same procedure as that for [**3a**][MeB($C_6F_5$)$_3$], with an equimolar amount of **2b** (15 mg, 0.043 mmol) and B($C_6F_5$)$_3$ (21.9 mg, 0.043 mmol). $^1$H NMR (400 MHz, $C_6D_5Br$, 298 K): $\delta$ = 0.36 (s,3 H, Ga*Me*), 0.57 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, Me-*i*Pr), 0.63 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, Me-*i*Pr), 0.97 (br. s, 3 H, *Me*B), 1.57 (d of septet, $^3J_{H,H\ doublet}$ = 3.1, $^3J_{H,H\ septet}$ = 6.6 Hz, 2 H, C*H*-*i*Pr), 1.74 (s, 3 H, *Me*CCN), 3.77–3.83 (m, 4 H, OC$H_2$), 3.90–3.95 (m, 2 H, NC*H*) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_5Br$, 248 K): $\delta$ = –4.1 (Ga*Me*), 9.9 (*Me*CCN), 11.7 (br., *Me*B), 15.2 (*Me*-*i*Pr), 18.7 (*Me*-*i*Pr), 33.1 (*C*H-*i*Pr), 65.9 (*C*HN), 69.7 (*C*H$_2$O), 71.9 (Me*C*CN), 137.2 (dm, $^2J_{C,F}$ = 256 Hz, *o*- or *m*-$C_6F_5$), 137.9 (dm, $^2J_{C,F}$ = 243 Hz, *p*-$C_6F_5$), 148.8 (dm, $^2J_{C,F}$ = 237 Hz, *o*- or *m*-$C_6F_5$), 172.3 (O*C*N) ppm.

**[{BOX-$Me_2$}Ga(Me)(N$Me_2$Ph)][MeB($C_6F_5$)$_3$] ([4a][MeB($C_6F_5$)$_3$]):** In a glovebox, the dimethylgallium derivative **2a** (200 mg, 0.619 mmol) was charged in a Schlenk flask and dissolved in $CH_2Cl_2$ (5 mL). N$Me_2$Ph (78.5 µL, 0.620 mmol) was then first added from a syringe to the colorless solution, followed by the addition of B($C_6F_5$)$_3$ (317 mg, 0.619 mmol) all at once. The resulting mixture was stirred for 1 h at room temperature and, after this time, evaporated to dryness under vacuum to yield a colorless foamy residue. Trituration of this residue with cold pentane (precooled to –35 °C) caused the precipitation of a colorless solid, which, after passing the solution through a glass frit nd further drying in vacuo, was found to be the salt species [**4a**][MeB($C_6F_5$)$_3$] in a pure form (479 mg, 81% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 0.39 (s, 3 H, Ga*Me*), 0.48 (*Me*B), 1.13 (br., 12 H, C*Me*$_2$), 1.73 (s, 3 H, *Me*CCN), 2.96 (s, 6 H, N*Me*$_2$Ph), 4.05 (br., 4 H, OC$H_2$), 7.00–7.41 (br., 5 H, NMe$_2$*Ph*) ppm. $^1$H NMR (400 MHz, $CD_2Cl_2$, 253 K): $\delta$ = 0.36 (s, 3 H, Ga*Me*), 0.42 (*Me*B), 0.92 (s, 6 H, C*Me*$_2$), 1.11 (s, 6 H, C*Me*$_2$), 1.67 (s, 3 H, *Me*CCN), 2.93 (s, 6 H, N*Me*$_2$Ph), 3.81 (br. d, $^2J_{H,H}$ = 8.2 Hz, 2 H, OC$H_2$), 4.16 (br. d, $^2J_{H,H}$ = 8.2 Hz, 2 H, OC$H_2$), 7.20 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, NMe$_2$*Ph*), 7.33 (br., 1 H, NMe$_2$*Ph*), 7.44 (br., 2 H, NMe$_2$*Ph*) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = –10.2 (Ga*Me*), 8.3 (*Me*CCN), 9.1 (br., *Me*B), 26.8 (br., C*Me*$_2$), 45.2 (br., N*Me*$_2$Ph), 63.6 (*C*Me$_2$), 67.4 (Me*C*CN), 78.4 (O*C*H$_2$), 118.5 (br., NMe$_2$*Ph*), 129.0 (br., NMe$_2$*Ph*), 129.5 (NMe$_2$*Ph*), 136.7 (d, $^1J_{C,F}$ = 233 Hz, *m*-$C_6F_5$), 137.9 (d, $^1J_{C,F}$ = 238 Hz, *p*-$C_6F_5$), 148.6 (d, $^1J_{C,F}$ = 233 Hz, *o*-$C_6F_5$), 171.7 (O*C*N) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$, 263 K): $\delta$ = –10.7 (Ga*Me*), 8.1 (*Me*CCN), 9.4 (br., *Me*B), 23.8 (C*Me*$_2$), 27.6 (C*Me*$_2$), 45.8 (br., N*Me*$_2$Ph), 63.2 (*C*Me$_2$), 69.0 (Me*C*CN), 77.9 (O*C*H$_2$), 119.6 (*o*-*Ph*NMe$_2$), 127.2 (*p*-*Ph*NMe$_2$), 129.4 (*m*-*Ph*NMe$_2$), 136.7 (d, $^1J_{C,F}$ = 233 Hz, *m*-$C_6F_5$), 137.9 (d, $^1J_{C,F}$ = 238 Hz, *p*-$C_6F_5$), 145.1 ($C_{ipso}$-*Ph*NMe$_2$), 148.6 (d, $^1J_{C,F}$ = 233 Hz, *o*-$C_6F_5$), 171.2 (O*C*N) ppm. $C_{40}H_{36}BF_{15}GaN_3O_2$ (956.24): calcd. C 50.24, H 3.79; found C 49.91, H 3.47.

**[{BOX-(*S*)-*i*Pr}Ga(Me)(N$Me_2$Ph)][MeB($C_6F_5$)$_3$] ([4b][MeB($C_6F_5$)$_3$]):** The chiral salt species [**4b**][MeB($C_6F_5$)$_3$] was generated following the same procedure as that for [**4a**][MeB($C_6F_5$)$_3$], using equimolar amounts of compound **2b** (72.0 mg, 0.205 mmol), N$Me_2$Ph (26 µL, 0.205 mmol), and B($C_6F_5$)$_3$ (105 mg, 0.205 mmol). It was isolated as an analytically pure colorless solid in a similar yield (151 mg, 75% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 0.37 (s,3 H, Ga*Me*), 0.48 (br. s, 3 H, *Me*B), 0.60–0.98 (br., 12 H, *Me*-*i*Pr), 1.65 (br., 2 H), 1.72 (s, 3 H, *Me*CCN), 1.78 (br., 1 H), 3.00 (s, 3 H, N*Me*$_2$Ph), 3.80–4.40 (6 H, C$H_2$O and C*H*N), 7.24 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *o*-*Ph*NMe$_2$), 7.31 (br., 1 H, *p*-*Ph*NMe$_2$), 7.51 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, *m*-*Ph*NMe$_2$) ppm. $^1$H NMR (400 MHz, $CD_2Cl_2$, 243 K): $\delta$ = 0.33 (s,3 H, Ga*Me*), 0.40 (br. s, 3 H, *Me*B), 0.44 (br. d, 3 H, Me-*i*Pr), 0.46 (br. d, 3 H, Me-*i*Pr), 0.99 (br. d, 3 H, Me-*i*Pr), 1.02 (br. d, 3 H, Me-*i*Pr), 1.29 (br., 1 H, C*H*-*i*Pr), 1.65 (s, 3 H, *Me*CCN), 1.70 (br., 1 H, C*H*-*i*Pr), 1.81 (br., 1 H, C*H*N), 2.88 (s, 3 H, N*Me*$_2$Ph), 3.00 (s, 3 H, N*Me*$_2$Ph), 3.81 (t, $J_{H,H}$ = 8.7 Hz, 1 H, C$H_2$O), 4.02 (br., 1 H, C*H*N), 4.12 (t, $J_{H,H}$ = 8.6 Hz, 1 H, C$H_2$O), 4.30 (t, $J_{H,H}$ = 8.7 Hz, 1 H, C$H_2$O), 4.41 (t, $J_{H,H}$ = 8.6 Hz, 1 H, C$H_2$O), 7.30 (br., 2 H, *o*-*Ph*NMe$_2$), 7.42 (br., 1 H, *p*-*Ph*NMe$_2$), 7.52 (br., 2 H, *m*-*Ph*NMe$_2$) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$, 243 K): $\delta$ = –11.3 (Ga*Me*), 8.6 (*Me*CCN), 9.5 (br., *Me*B), 12.8 (*Me*-*i*Pr), 14.5

Table 3. Crystal data and refinements details for compounds **2a**, **2b**, [**4a**][$MeB(C_6F_5)_3$], and [**5a**][$B(C_6F_5)_4$].

| | **2a** | **2b** | [**4a**][$MeB(C_6F_5)_3$] | [**5a**][$B(C_6F_5)_4$] |
|---|---|---|---|---|
| Formula | $C_{14}H_{25}GaN_2O_2$ | $C_{16}H_{29}GaN_2O_2$ | $C_{21}H_{33}GaN_3O_2$, $C_{19}H_3BF_{15}$ | $C_{14}H_{24}GaN_2O_2$, $C_{24}BF_{20}$ |
| Formula mass | 323.08 | 351.13 | 956.25 | 1001.12 |
| Crystal system | orthorhombic | monoclinic | triclinic | monoclinic |
| Space group | *Pnma* | $P2_1$ | $P\bar{1}$ | $P2_1/c$ |
| *a* [Å] | 11.7380(10) | 9.3270(4) | 10.397(5) | 12.843(2) |
| *b* [Å] | 11.0420(10) | 11.5310(6) | 13.441(5) | 19.380(3) |
| *c* [Å] | 12.249(2) | 9.5600(7) | 15.762(5) | 15.829(2) |
| *α* [°] | 90.00 | 90.00 | 73.66(5) | 90.00 |
| *β* [°] | 90.00 | 116.8500(19) | 80.66(5) | 97.85(5) |
| *γ* [°] | 90.00 | 90.00 | 73.90(5) | 90.00 |
| *V* [Å$^3$] | 1587.6(3) | 917.33(9) | 2022.3(14) | 3902.9(10) |
| *Z* | 4 | 2 | 2 | 4 |
| Density [g cm$^{-3}$] | 1.352 | 1.271 | 1.570 | 1.704 |
| $\mu$ (Mo-$K_\alpha$) [mm$^{-1}$] | 1.734 | 1.506 | 0.790 | 0.840 |
| *F*(000) | 680 | 372 | 968 | 1992 |
| *Data collection* | | | | |
| Temperature [K] | 173(2) | 173(2) | 173(2) | 173(2) |
| $\theta$ min./max. | 2.40/30.03 | 2.39/30.00 | 1.35/30.01 | 1.60/30.04 |
| Data set [*h*,*k*,*l*] | –16/14, –15/14, –16/17 | –13/11, 0/16, 0/13 | –14/14, –17/18, 0/22 | –18/17, 0/27, 0/22 |
| Total, unique data, *R*(int) | 2445, 1898, 0.0615 | 2780, 1699, 0.0000 | 11773, 8935, 0.0000 | 11395, 7624, 0.0000 |
| Observed data | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| *Refinement* | | | | |
| No. of reflections, parameters | 2445, 94 | 2780, 190 | 11773, 559 | 11395, 577 |
| $R_2$, $R_1$, w$R_2$, w$R_1$, Goof | 0.0715, 0.0456, 0.0856, 0.0800, 1.074 | 0.0961, 0.0457, 0.1525, 0.1026, 0.951 | 0.0617, 0.0417, 0.1184, 0.1089, 1.063 | 0.0728, 0.0404, 0.1188, 0.1000, 0.929 |
| Flack *x* | – | 0.04(3) | – | – |
| Min., max. residual electron density [e Å$^{-3}$] | –0.477, 0.378 | –0.855, 0.691 | –0.607, 0.365 | 0.002, 0.000 |

(*Me*-*i*Pr), 17.3 (*Me*-*i*Pr), 19.7 (*Me*-*i*Pr), 31.0 (*C*H-*i*Pr), 31.2 (*C*H-*i*Pr), 43.1 (N*Me*$_2$Ph), 47.0 (N*Me*$_2$Ph), 64.2 (N*C*H), 65.2 (N*C*H), 65.9 (Me*C*CN), 67.0 (*C*H$_2$O), 67.5 (*C*H$_2$O), 119.2 (*o*-*Ph*NMe$_2$), 127.3 (*p*-*Ph*NMe$_2$), 129.8 (*m*-*Ph*NMe$_2$), 136.7 (d, $^1J_{C,F}$ = 233 Hz, *m*-$C_6F_5$), 137.9 (d, $^1J_{C,F}$ = 238 Hz, *p*-$C_6F_5$), 145.3 ($C_{ipso}$-*Ph*NMe$_2$), 148.6 (d, $^1J_{C,F}$ = 233 Hz, *o*-$C_6F_5$), 170.9 (O*C*N), 172.0 (O*C*N) ppm. $C_{42}H_{40}BF_{15}GaN_3O_2$ (984.29): calcd. C 51.25, H 4.10; found C 51.03, H 3.88.

**[{H$_2$C=C(OX-Me$_2$)$_2$}GaMe$_2$][B(C$_6$F$_5$)$_4$] ([5a][B(C$_6$F$_5$)$_4$]):** In a glovebox, stoichiometric amounts of [{BOX-Me$_2$}GaMe$_2$] (50 mg, 0.155 mmol) and [$Ph_3C$][$B(C_6F_5)_4$] (143 mg, 0.155 mmol) were charged in a 25-mL round-bottomed flask and dissolved in $CH_2Cl_2$ (2 mL). While under vigorous stirring at room temperature, the initial bright-red solution turned pale yellow within seconds, indicating the total consumption of the trityl salt. The mixture was stirred for 1 h at room temperature, after which it was evaporated to dryness under vacuum. Addition of cold pentane (precooled to –35 °C) provoked the precipitation of a colorless solid. The mixture was then filtered through a glass frit and the obtained colorless residue washed three times with cold pentane to remove any remaining $Ph_3CH$. Further drying of the residue in vacuo afforded the salt species [**5a**][$B(C_6F_5)_4$] as an analytically pure colorless solid (136 mg, 88% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = –0.01 (s, 6 H, Ga*Me*$_2$), 1.53 (s, 12 H, C*Me*$_2$), 4.44 (s, 4 H, OC*H*$_2$), 7.30 (s, 2 H, C*H*$_2$=C) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = –4.3 (Ga*Me*$_2$), 26.8 (C*Me*$_2$), 69.3 (*C*Me$_2$), 80.6 (O*C*H$_2$), 118.4 (H$_2$C=*C*), 136.7 (dm, $^1J_{C,F}$ = 243 Hz, *C*$_6$F$_5$), 138.6 (dm, $^1J_{C,F}$ = 243 Hz, *C*$_6$F$_5$), 143.7 (H$_2$*C*=C), 148.5 (dm, $^1J_{C,F}$ = 239 Hz, *C*$_6$F$_5$), 162.6 (O*C*=N) ppm. $C_{38}H_{24}BF_{20}GaN_2O_2$ (1001.11): calcd. C 45.59, H 2.42; found C 45.95, H 2.37.

**X-ray Structure Analysis of Complexes 2a,b, [4a][MeB(C$_6$F$_5$)$_3$] and [5a][B(C$_6$F$_5$)$_4$]:** Single crystal of **2a**, **2b**, [**4a**][$MeB(C_6F_5)_3$], and [**5a**][$B(C_6F_5)_4$] were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo-$K_\alpha$ radiation; $\lambda$ = 0.71073 Å). The complete conditions of data collection (Denzo software)[20] and structure refinements are given in Table 3. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by direct methods (SHELXS97) and refined against $F^2$ using the SHELXL97 software.[21] The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

CCDC-273080 (for **2a**), -273081 (for **2b**), -273082 (for [**4a**][$MeB(C_6F_5)_3$]), and -273083 (for [**5a**][$MeB(C_6F_5)_3$]) contains 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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[1] D. A. Atwood, *Coord. Chem. Rev.* **1998**, *176*, 407–430.
[2] M. Bochmann, D. M. Dawson, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2226–2228.

  

[3] a) M. P. Coles, R. F. Jordan, *J. Am. Chem. Soc.* **1997**, *119*, 8125–8126; b) M. Bruce, V. C. Gibson, C. Redshaw, G. A. Solan, A. J. P. White, *Chem. Commun.* **1998**, 2523–2524.
[4] a) D. A. Atwood, J. A. Jegier, D. Rutherford, *J. Am. Chem. Soc.* **1995**, *117*, 6779–67780; b) J. A. Jegier, D. A. Atwood, *Inorg. Chem.* **1997**, *36*, 2034–2039.
[5] N. Emig, H. Nguyen, H. Krautscheid, R. Réau, J.-B. Cazaux, G. Bertrand, *Organometallics* **1998**, *17*, 3599–3608.
[6] For two structurally characterized "base-free" three-coordinate group 13 alkyls, see: a) C. E. Radzewich, M. P. Coles, R. F. Jordan, *J. Am. Chem. Soc.* **1999**, *121*, 8673–8674; b) A. H. Cowley, Z. Lu, J. N. Jones, J. A. More, *J. Organomet. Chem.* **2004**, *689*, 2562–2564.
[7] a) S. Dagorne, I. A. Guzei, M. P. Coles, *J. Am. Chem. Soc.* **2000**, *122*, 274–289; b) A. V. Korolev, E. Ihara, I. A. Guzei, V. G. Young, Jr., R. F. Jordan, *J. Am. Chem. Soc.* **2001**, *123*, 8291–8309; c) P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, G. A. Solan, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **2001**, 1472–1476; d) P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **2002**, 415–422; e) D. Pappalardo, C. Tedesco, C. Pellechia, *Eur. J. Inorg. Chem.* **2002**, 621–628; f) J. A. R. Schmidt, J. Arnold, *Organometallics* **2002**, *21*, 2306–2313; g) D. Pappalardo, M. Mazzeo, P. Montefusco, C. Tedesco, C. Pellechia, *Eur. J. Inorg. Chem.* **2004**, 1292–1298.
[8] Several cationic methylgallium complexes are stable in water due to the high stability of the $GaMe^{2+}$ moiety. For examples, see: a) D. F. Shriver, R. W. Parry, *Inorg. Chem.* **1962**, *1*, 835–838; b) R. S. Tobias, M. J. Sprague, G. E. Glass, *Inorg. Chem.* **1968**, *7*, 1714–1721.
[9] a) S. Dagorne, L. Lavanant, R. Welter, C. Chassenieux, P. Haquette, G. Jaouen, *Organometallics* **2003**, *22*, 3732–3741; b) S. Dagorne, I. Janowska, R. Welter, J. Zakrzewski, G. Jaouen, *Organometallics* **2004**, *23*, 4706–4710.
[10] S. Dagorne, S. Bellemin-Laponnaz, R. Welter, *Organometallics* **2004**, *23*, 3053–3061.
[11] M. Stender, B. E. Eichler, N. J. Hardman, P. P. Power, J. Prust, M. Noltemeyer, H. W. Roesky, *Inorg. Chem.* **2001**, *40*, 2794–2799.
[12] J. Barker, N. C. Blacker, P. R. Phillips, N. W. Alcock, W. Errington, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.* **1996**, 431–437.
[13] S. Dagorne, R. F. Jordan, V. J. Young, *Organometallics* **1999**, *18*, 4619–4623.
[14] The $^1H$ NMR resonance of the $MeB(C_6F_5)_3^-$ anion ($\delta$ = 0.97 ppm) at room temp. in $C_6D_5Br$ is close to that of the ammonium salt $[NBu_3(CH_2Ph)][MeB(C_6F_5)_3]$ ($\delta$ = 1.01 ppm).
[15] A. V. Korolev, F. Delpech, S. Dagorne, I. A. Guzei, R. F. Jordan, *Organometallics* **2001**, *20*, 3367–3369.
[16] D. A. Atwood, R. A. Jones, A. H. Cowley, S. G. Bott, J. L. Atwood, *J. Organomet. Chem.* **1992**, *425*, C1–C3.
[17] D. A. Atwood, R. A. Jones, A. H. Cowley, S. G. Bott, J. L. Atwood, *J. Organomet. Chem.* **1992**, *434*, 143–150.
[18] For a $H^-$ abstraction by $Ph_3C^+$ at a $C_\alpha$ metal-bonded alkyl group, see, for example: P. Jernakoff, N. J. Cooper, *Organometallics* **1986**, *5*, 747–751. For a recent example of an abstraction at a $C_\beta$ metal-bonded alkyl group, see: P. Mehrkhodavanti, R. R. Schrock, *J. Am. Chem. Soc.* **2001**, *123*, 10746–10747.
[19] V. I. Bregadze, N. G. Furmanova, L. M. Golubiskaya, O. Y. Kompan, Y. T. Struchkov, *J. Organomet. Chem.* **1980**, *192*, 1–15.
[20] *Kappa CCD Operation Manual*; Nonius B. V.: Delft, The Netherlands, **1997**.
[21] G. M. Sheldrick, *SHELXL97*, *Program for the refinement of crystal structures*, University of Göttingen, Germany, **1997**.

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