

## Synthesis, Characterization, and Applications of Group 13 Cationic Compounds

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## Synthesis, Characterization, and Applications of Group 13 Cationic Compounds

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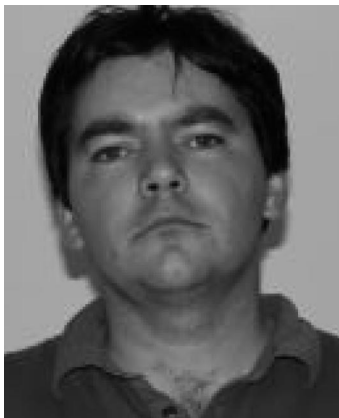
### Contents

1. Introduction	4037	3.4.3. Reactivity of {LX}AlR <sup>+</sup> Aluminum Cations toward Alkynes	4051
2. Monocoordinate and Two-Coordinate Group 13 Cations	4039	3.4.4. Summary	4052
2.1. Monocoordinate Group 13 Cations	4039	3.5. Highlight on Low-Coordinate Group 13 Cations	4052
2.2. Two-Coordinate Trivalent Group 13 Cations	4039	4. Four-Coordinate Group 13 Cations	4052
2.2.1. Metallocenium Cations	4039	4.1. Overview	4052
2.2.2. Two-Coordinate Group 13 Cations of the Type MR <sub>2</sub> <sup>+</sup> (M = Al, Ga; R = alkyl, aryl, silyl)	4041	4.2. Al Species	4053
2.2.3. Two-Coordinate Heteronuclear Group 13 Cations	4044	4.2.1. Type <b>A–D</b> Al Cations	4053
2.3. Univalent Two-Coordinate Indium and Thallium Cations	4044	4.2.2. Type <b>E–F</b> Al Cations	4055
2.3.1. Univalent Two-Coordinate Indium Cations	4044	4.2.3. Four-Coordinate Al Dinuclear Cations	4058
2.3.2. Univalent Two-Coordinate Thallium Cations	4045	4.3. Gallium Species	4060
3. Three-Coordinate Group 13 Cations	4045	4.3.1. Synthesis and Structure	4060
3.1. Three-Coordinate Group 13 Alkyl and Hydrido Cations Supported by a LX <sup>–</sup> Bidentate Ligand: Synthesis, Structure, and Stability	4046	4.4. Indium and Thallium Species	4062
3.1.1. Bidentate Aminotroponimate, β-Diketimate, Amidinate, and Bis(oxazolinato) Group 13 Cations	4046	4.5. Summary	4063
3.1.2. Bidentate Amidophosphinimine, N-Imidoylamidine, and N,O-Aminophenolate Group 13 Cations	4047	5. Five-Coordinate Group 13 Cations	4063
3.2. Three-Coordinate Al Cations Only Incorporating Monodentate Ligands	4048	5.1. Background	4063
3.3. Three-Coordinate Thallium Cations	4049	5.2. Aluminum Cations	4063
3.4. Reactivity Trends and Catalytic Applications of Three-Coordinate Group 13 Alkyl Cationic Derivatives	4049	5.3. Gallium and Indium Cations	4065
3.4.1. Reactivity of {LX}MR <sup>+</sup> Group 13 Metal Cations toward Lewis Bases, Ketones, and Propylene Oxide	4049	5.4. Applications	4065
3.4.2. Reactivity of {LX}MR <sup>+</sup> Aluminum Cations toward Olefins	4050	5.5. Summary	4065
		6. Six-Coordinate Group 13 Cations	4065
		6.1. Background	4065
		6.2. Aluminum Cations	4066
		6.3. Aluminum Dication	4067
		6.4. Gallium, Indium, and Thallium Species	4067
		6.5. Applications	4067
		6.6. Summary	4068
		7. Higher Coordination Numbers and Unique Compounds	4068
		8. Conclusions—Perspectives	4069
		9. Acknowledgments	4069
		10. References	4069

### 1. Introduction

Group 13 cations have been known for a surprisingly long time. Although initiated in the 1930s, work in this area really started to be developed in the 1960s when it was shown that

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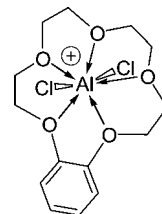


Samuel Dagorne obtained his undergraduate degree in chemistry at the Université de Rennes I (Rennes, France) in 1994. In 1995, he joined the group of Professor Richard F. Jordan at the University of Iowa (Iowa City, IA, U.S.A.) and graduated with a Ph.D in 1999 on the chemistry of chiral zirconocenes and group 13 compounds. In 1999, he became a member of the group of Professor Richard R. Schrock (Massachusetts Institute of Technology, Cambridge, MA, U.S.A.) as a postdoctoral fellow working on molybdenum alkylidene chemistry. Back in France, he joined the C.N.R.S. in 2000 as an associate researcher and is currently at The Université Louis Pasteur (Strasbourg, France). His research interests mainly concern the synthesis and reactivity studies of highly electrophilic and electron-deficient organometallic species.

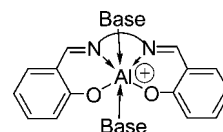


David Allan Atwood was born in 1965 in Urbana, Illinois. At an early age, David moved to Tuscaloosa, Alabama, where he grew up and ultimately attended college. After graduation from the University of Alabama, he moved to Austin, Texas, to attend graduate school at the University of Texas with Richard Jones as his advisor. He graduated with his Ph.D (in Inorganic Chemistry) in the Spring of 1992 but stayed in Austin as a postdoctoral associate with Alan Cowley until his wife, Vicki Ossink Atwood, finished her Ph.D (also in Inorganic Chemistry). From UT, he moved as an Assistant Professor to North Dakota State University as part of their new Center for Main Group Chemistry (of which he was co-director). In 1998, David Atwood joined the chemistry department at the University of Kentucky faculty as an Associate Professor. He now has over 160 publications, 10 patents, and serves on numerous editorial boards, including the Encyclopedia of Inorganic Chemistry, a 15 volume set published in Fall 2005. He is the founding editor and Editor-in-Chief of Main Group Chemistry. His research interests include detection and removal of inorganic contaminants from the environment, preparation of nanoparticulate metal oxides, prevention of aluminum alloy oxidation, and synthesis of new Lewis acid chelates to effect new reactions, such as the breaking of phosphate esters bonds like those found in nerve gas agents and pesticides.

$\text{Me}_2\text{TlOH}$  readily ionizes in water to yield the weak aquo-acid  $\text{Me}_2\text{Tl}^+$  cation, isoelectronic with  $\text{Me}_2\text{Hg}$ .<sup>1</sup> A few years later, the X-ray-determined molecular structure of the Tl(III)–phenanthroline cationic adduct  $(\text{phen})\text{TlMe}_2^+$  (as a  $\text{ClO}_4^-$  salt) unambiguously established the possibility of



**Figure 1.** Structure of the seven-coordinate Al cation  $\{\text{benzo-15-crown-5}\}\text{AlCl}_2^+$ .



**Figure 2.** General structure of Salen-based Al cations  $\text{SalenAl}(\text{base})_2^+$ .

synthesizing well-defined and discrete group 13 cationic species.<sup>2</sup> Through the 1960s and 1970s,  $\text{Me}_2\text{GaOH}$  was also found to form cationic species in aqueous acid to yield  $[\text{Me}_2\text{Ga}(\text{H}_2\text{O})_2]^+$ .<sup>3,4</sup> Subsequent studies found that indium behaved similarly.<sup>5</sup> Ga(I) cations were well-developed in the 1980s and were typically of the form  $[\text{Ga}(\text{arene})_2][\text{GaX}_4]$ .<sup>6</sup> Tl(I) cations of the type  $\text{Tl}(\text{arene})_2^+$ , associated with various weakly coordinating counterions, have been the subject of a few reports from the 1980s up to the mid-1990s.<sup>7</sup> Little additional work with low-valent Ga, In, and Tl cations has appeared since then.

With the exception of extensive investigations of the aqueous chemistry of aluminum,<sup>8</sup> group 13 cations were rarely treated as a separate subject and have long been viewed as structural curiosities. This can be attributed to the fact that distinct and well-defined cationic compounds of aluminum were only prepared in 1984 in combinations of crown ethers and alkylaluminum dichlorides to produce solution species that formed “liquid clathrates”.<sup>9,10</sup> One such example from the combination of benzo-15-crown-5 with  $\text{EtAlCl}_2$  is shown in Figure 1 (the anion is  $\text{Cl}_2\text{AlEt}_2^-$ ).<sup>11</sup>

The discovery that chelates, particularly those of the Salen class of ligands, allowed the straightforward formation of a wide variety of well-defined group 13 cations opened the way to new possibilities in this research both from an academic and an applied point of view.<sup>12</sup> The general structure of these new Salen-based group 13 cations  $[\text{SalenAl}(\text{base})_2]^+\text{X}^-$  (where base =  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ ,<sup>13,14</sup>  $\text{HMPA}$ ,<sup>15</sup> etc. and  $\text{X}^-$  = halide,  $\text{BPh}_4^-$ , etc.) is shown in Figure 2. Importantly, the *enhanced* Lewis acidity of such cations versus that of neutral analogues was shown to be beneficial in Lewis acid-type catalysis, which may account for the increased interest this class of compounds has received.

The first review on group 13 cations in 1998 described Al, Ga, and In cations according to the types of reactions that were used in their formation.<sup>16</sup> There were also sections comparing and contrasting the structural and spectroscopic trends of these elements. A review of aluminum organometallics published as recently as 2007 did not contain references to cationic derivatives.<sup>17</sup> Thus, there is a need for a comprehensive review of group 13 cations. The present review will cover the new cationic compounds for Al, Ga, In, and Tl produced since 1998.

The concluding sentence in one of the first review chapters on aluminum cations reads: “Although the chemistry of cationic organoaluminum complexes is not well developed, the reports in the literature indicate that this is a rich area

for future development".<sup>10</sup> This statement was prescient as group 13 cations, particularly the lower- and higher-coordinate derivatives of aluminum, have been the subject of intense interest in recent years because of their increased Lewis acidity and ligand lability. The anticipation is that such species may outperform their neutral analogs in various Lewis acid-catalyzed reactions. As a result of this strong interest, straightforward and widely applicable synthetic methods have become available, providing ready access to different types of cationic group 13 compounds. This has led to a growing number of applications in organic synthesis and catalysis, which will be described herein.

This review will not cover aqueous group 13 chemistry unless the group 13 fragment is organometallic and cationic clusters in which a group 13 atom may appear unless the cluster is comprised entirely of group 13 metals. Thus, aluminum binding by ion-exchange resins and environmental binding agents such as humic matter, etc. will not be covered. "Classical" thallium salts such as in amido-Tl species, for example, in which the Tl atom(s) exhibits a significant degree of association with its counterion will not be covered because the rich structural and applied chemistry of such molecular entities sharply differs from that of the majority of group 13 cationic species and constitutes a subject on its own. Additionally, thallium cations in which the Tl(I) "cationic center" exhibits any metal-metal interaction (Tl(I)-M or Tl(I)-Tl(I)) are not included in the present work. Solid state materials containing group 13 cations are also beyond the scope of this work.

Finally, compared with the 1998 review on the subject, a special emphasis will be given to low-coordinate trivalent aluminum and gallium cations (two- and three-coordinate), as such species were unknown ten years ago and have been the subject of numerous research efforts since then to better understand their trends in structure, reactivity, and potential applications in catalysis. A general review of these cations was published in 2005.<sup>18</sup> Thus, the present review includes Al, Ga, In, and Tl cations and all of the varieties in coordination number, from low-coordinate to higher-coordinate.

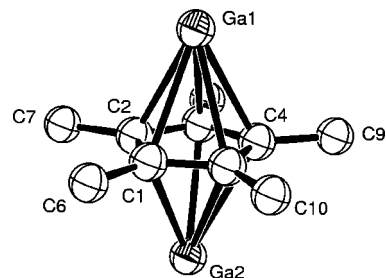
## 2. Monocoordinate and Two-Coordinate Group 13 Cations

### 2.1. Monocoordinate Group 13 Cations

In a recent contribution, Fischer et al. reported the synthesis of the dinuclear gallium(I) cation  $\text{Ga}_2(\text{Cp}^*)^+$  ( $\mathbf{1}^+$ ) as a fully dissociated  $\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4^-$  salt, which was generated by protonolysis of  $\text{Cp}^*\text{Ga}$  with  $[\text{H}(\text{OEt}_2)_2]\text{-}[\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$  along with formation of  $\text{Cp}^*\text{H}$  (Scheme 1).<sup>19</sup>

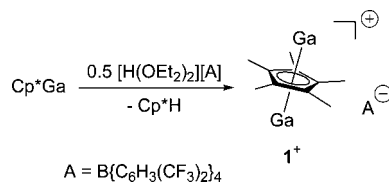
As illustrated in Figure 3, the molecular structure of  $\mathbf{1}^+$  in the solid state shows an unusual, highly symmetric bipyramidal double-cone structure, in which both Ga atoms (above and below) are coordinated to the  $\text{Cp}^*$  ring. The Ga-Cp\*<sub>centr.</sub> distances in  $\mathbf{1}^+$  (~ 2.23 Å) are significantly longer than that in  $\text{Cp}^*\text{Ga}$  (2.081 Å). Thus, as supported by density functional theory (DFT) calculations, the  $\text{Ga}_2(\text{Cp}^*)^+$  cation is best considered as a stabilized and almost "naked"  $\text{Ga}^+$  ion, not known in solution under ordinary conditions.

Unprecedented mono(arene)-Tl(I) cationic complexes supported by a weakly coordinating anion have very recently been shown to be accessible by Bochmann et al. with the synthesis and solid-state structure determination of the Tl(I)

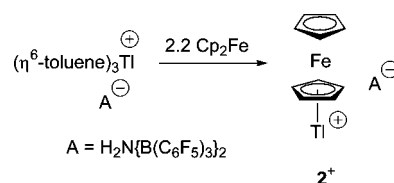


**Figure 3.** Solid-state structure of the dinuclear Ga(I) cation  $\mathbf{1}^+$  with partial atom labeling for clarity.

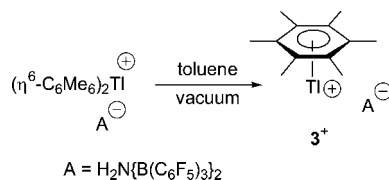
#### Scheme 1



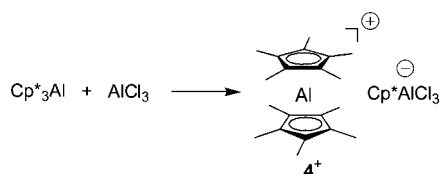
#### Scheme 2



#### Scheme 3



#### Scheme 4



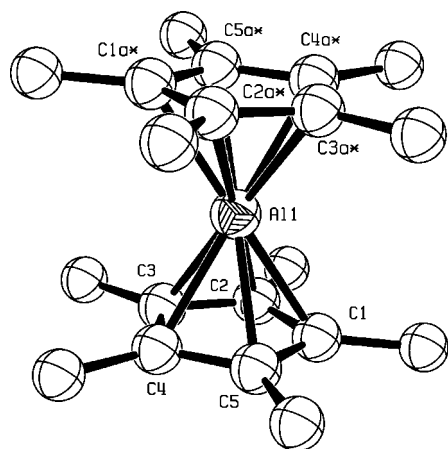
cations  $\text{Tl}(\text{Cp}_2\text{Fe})^+$  ( $\mathbf{2}^+$ ) and  $\text{Tl}(\text{C}_6\text{Me}_6)^+$  ( $\mathbf{3}^+$ ) as weakly associated  $\text{NH}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$  salts (Schemes 2 and 3).<sup>20</sup>

In the solid state of  $\mathbf{2}^+$ , one Cp ring of the ferrocene moiety is  $\eta^5$ -coordinated to the Tl atom, while  $\mathbf{3}^+$  exhibits a Tl atom that is  $\eta^6$ -bound to the aromatic ring of  $\text{C}_6\text{Me}_6$ . The Tl-arene interaction in  $\mathbf{3}^+$  (Tl-centroid distance = 2.723 Å) is the shortest reported to date. Overall, these two cations represent unique examples of discrete thallium half-sandwich structures, with minimal interactions with the anion.

## 2.2. Two-Coordinate Trivalent Group 13 Cations

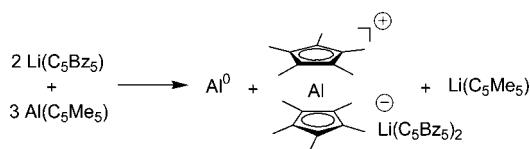
### 2.2.1. Metallocenium Cations

**Aluminocenium Cations.** In the early 1990s, Schnöckel et al. first reported the synthesis and structure of a well-defined two-coordinate aluminocenium cation  $\text{Cp}^*_2\text{Al}^+$  ( $\mathbf{4}^+$ ,  $\text{Cp}^* = \text{C}_5\text{Me}_5$ , Scheme 4) as a  $\text{Cp}^*\text{AlCl}_3^-$  salt by disproportionation of  $\text{Cp}^*_3\text{Al}$  in the presence of  $\text{AlCl}_3$ , thereby showing that two-coordinate organoaluminum species could



**Figure 4.** Solid-state structure of the aluminocenium cation  $\text{Cp}^*{}_{2}\text{Al}^+$  ( $4^+$ ) with partial atom labeling for clarity.

### Scheme 5



be readily obtained.<sup>21</sup> The solid-state structure of  $\text{Cp}^*{}_{2}\text{Al}^+$  confirmed the metallocene-type structure with two  $\eta^5$ -bound  $\text{Cp}^*$  ligands to the Al center (Figure 4), and this sandwich structure appears to be retained in solution.

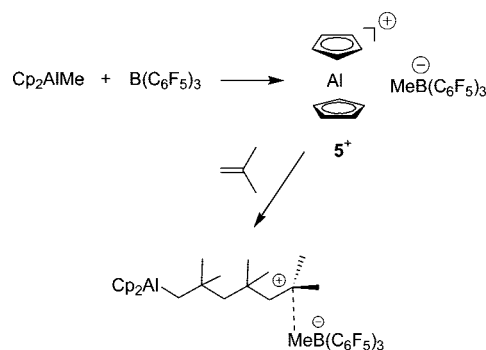
Subsequently, these authors also reported the synthesis of  $\text{Cp}^*{}_{2}\text{Al}^+$  as a bis-pentabenzylcyclopentadienide Li salt, which was obtained as a side product of the reaction between  $\text{Li}[\text{C}_5\text{Bz}_5]$  and the Al(I) compound  $\text{Cp}^*\text{Al}$  (Scheme 5).<sup>22</sup> The synthesis of the aluminocenium salt  $[\text{Cp}^*{}_{2}\text{Al}][\text{AlCl}_4]$ , through the reaction of  $\text{Al}_2\text{Cl}_6$  with  $\text{Cp}^*{}_{2}\text{AlCl}$ , has been reported; solid-state NMR experiments of the latter salt were carried out to study the Al chemical shielding and electric field gradient tensors of  $\text{Cp}^*{}_{2}\text{Al}^+$ .<sup>23</sup>

This seminal work on  $\text{Cp}^*{}_{2}\text{Al}^+$  has prompted further studies on aluminocenium cations with the aim of exploring their reactivity and potential usefulness in catalysis. Bochmann showed that the aluminocenium cation  $\text{Cp}_2\text{Al}^+$  ( $5^+$ , Scheme 6) could be readily accessible as a  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  salt by reaction of the neutral alkyl precursor  $\text{Cp}_2\text{AlMe}$  with  $\text{B}(\text{C}_6\text{F}_5)_3$ . This reaction proceeds through  $\text{Me}^-$  abstraction at the Al center of  $\text{Cp}_2\text{AlMe}$ .<sup>24</sup> The Lewis acidic  $\text{Cp}_2\text{Al}^+$  cation exhibits limited stability in solution at room temperature but was nevertheless found to be an effective initiator of the cationic polymerization of isobutene at low temperature, affording polymers with molecular weights ranging from  $3 \times 10^5$  to  $1.8 \times 10^6$ , with low polydispersities.

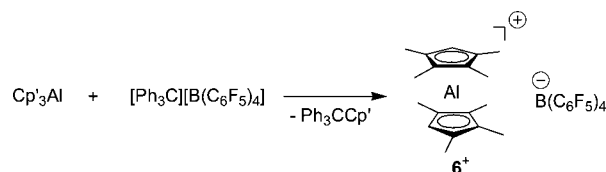
As depicted in Scheme 6, it is likely that weak interactions with the counterion stabilize the propagating carbocationic species. In addition, the aluminocenium cation also initiates the copolymerization of isobutene with 2–5 vol % of isoprene at low temperature to yield a polymer containing about 2.7% isoprene with a 1,4-*trans* structure.

Similarly, the  $\text{Cp}^*{}_{2}\text{Al}^+$  cation  $4^+$  may be accessible through a  $\text{Me}^-$  abstraction reaction between  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{Cp}^*{}_{2}\text{AlMe}$  (eq 1).<sup>25</sup> The increased stability of  $4^+$ , stable at room temperature in solution, versus that of  $\text{Cp}_2\text{Al}^+$  and its decreased effectiveness at activating cationic isobutene polymerization is not surprising. It highlights the importance of steric hindrance around the metal center to stabilize such

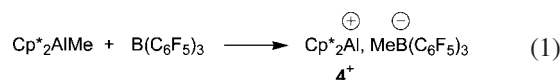
### Scheme 6



### Scheme 7



low-coordinate cations as well as the possibility of varying the Cp ring substituents of the aluminocenium cation to tune its activity in Lewis acid catalysis.



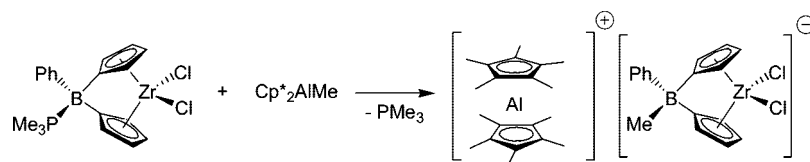
Shapiro et al. recently reported the synthesis of  $\text{Cp}'_{2}\text{Al}^+$  ( $6^+$ ,  $\text{Cp}' =$  tetramethylcyclopentadienyl anion, Scheme 7) as a  $\text{B}(\text{C}_6\text{F}_5)_4^-$  salt through abstraction of a cyclopentadienyl anion from  $\text{Cp}'_3\text{Al}$  by  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .<sup>26</sup> As can be expected on the basis of steric factors, the  $\text{Cp}'_{2}\text{Al}^+$  cation is less stable thermally than  $\text{Cp}^*{}_{2}\text{Al}^+$ , while being more active in isobutene polymerization.

X-ray crystallography analysis of  $[\mathbf{6}][\text{B}(\text{C}_6\text{F}_5)_4]$  reveals no significant cation–anion interactions and confirms that both  $\text{Cp}'$  ligands are  $\eta^5$ -bonded to the Al center. The crystallographic disorder observed for the  $\text{Cp}'$  ligands in  $\text{Cp}'_{2}\text{Al}^+$  prompted the authors to suggest that the  $\text{Cp}'$  rings may be “wagging” back and forth as a result of the inadequate steric shielding of the low-coordinate and electrophilic aluminum center. This study emphasizes the importance of the methyl substituents on the Cp rings to create stable aluminocenium cations, although this may be detrimental to their catalytic activity.

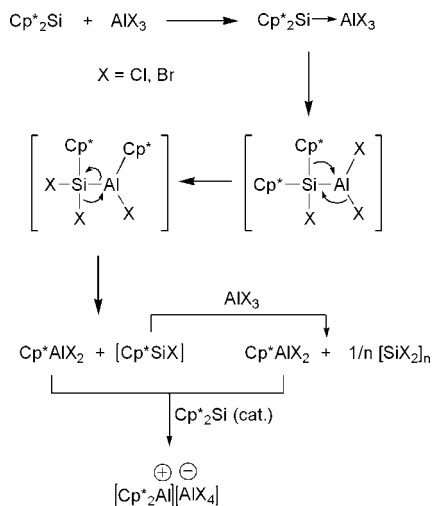
Two rather unusual and unrelated synthetic pathways to access the  $\text{Cp}^*{}_{2}\text{Al}^+$  cation have been reported over the past few years. The borate-bridged *ansa*-zirconocene complex  $\{\text{Ph}(\text{PMe}_3)\text{B}-(\eta^5\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2$  readily abstracts a  $\text{Me}^-$  group from  $\text{Cp}^*\text{AlMe}$  to afford  $\text{Cp}^*{}_{2}\text{Al}^+$  as a  $\{\text{Ph}(\text{Me})\text{B}-(\eta^5\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2^-$  salt, along with the release of  $\text{PMe}_3$ , illustrating the effective Lewis acidity of the boron bridge in base-free  $\{\text{PhB}-(\eta^5\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2$  (Scheme 8).<sup>27</sup> The reactivity of the phenyl boron bridge may be seen as comparable to that of  $\text{B}(\text{C}_6\text{F}_5)_3$ .

As part of their reactivity studies of the silicocene derivative  $\text{Cp}^*{}_{2}\text{Si}$  with group 13 halide complexes, Jutzi et al. reported the high yield synthesis of  $\text{Cp}^*{}_{2}\text{Al}^+$  with  $\text{AlX}_4^-$  as the counteranion ( $\text{X} = \text{Cl}, \text{Br}$ ) by combining  $\text{Cp}^*{}_{2}\text{Si}$  with 2 equiv of  $\text{AlCl}_3$  or  $\text{AlBr}_3$ .<sup>28</sup> This surprising outcome was rationalized by the authors through a process best described as a  $\text{Cp}^*{}_{2}\text{Si}$ -catalyzed dismutation of  $\text{Cp}^*\text{AlCl}_2$  (presumably

## Scheme 8

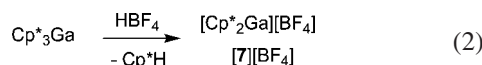


## Scheme 9



formed during the reaction), in which  $\text{Cp}^*_2\text{Si}$  would act as a Lewis base inducing the dismutation reaction (Scheme 9).

**Galocenium Cations.** In 2000, Cowley et al. reported the synthesis of the Ga metallocenium  $\text{Cp}^*_2\text{Ga}^+$  ( $7^+$ , eq 2) as a  $\text{BF}_4^-$  salt through protonolysis of  $\text{Cp}^*_3\text{Ga}$  with  $\text{HBF}_4$ .<sup>29</sup> Cation  $7^+$  constitutes the first and only galocenium cation reported to date. As illustrated in Figure 5, the solid-state structure of  $[7][\text{BF}_4]$  consists of pairs of  $\text{Cp}^*_2\text{Ga}^+$  cations connected by two bridging  $\text{BF}_4^-$  anions such that the symmetry of each dimeric unit is  $\text{C}_2$ . Interestingly, the molecular structure of  $7^+$  is quite different to that of its Al analog  $\text{Cp}^*_2\text{Al}^+$ . Thus, instead of two  $\eta^5$ -bound  $\text{Cp}^*$  ligands on the metal center, one  $\text{Cp}^*$  ring in  $7^+$  is attached to gallium in an  $\eta^1$  fashion while the other ring is attached in an  $\eta^3$  fashion, as evidenced by the fact that three of the Ga–C distances [to C(1), C(13), and C(15); see Figure 5] are considerably shorter than the other two [to C(12) and C(14)]. The Ga cation  $7^+$  is clearly fluxional in solution as deduced from the singlet NMR resonances down to  $-70^\circ\text{C}$ . The authors rationalized the unique bonding in  $7^+$  by means of DFT calculations.<sup>29</sup>

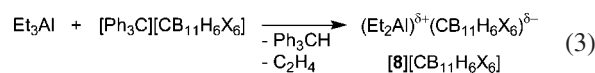


### 2.2.2. Two-Coordinate Group 13 Cations of the Type $\text{MR}_2^+$ ( $M = \text{Al}, \text{Ga}; R = \text{alkyl}, \text{aryl}, \text{silyl}$ )

While two-coordinate trivalent indium and thallium cations of the type  $\text{MR}_2^+$  ( $R = \text{alkyl}, \text{aryl}$ ) have been known for decades and structurally well-characterized,<sup>3,4,16</sup> access to Al and Ga analogues has only been recently reported. The preparation of such highly electrophilic complexes was driven by both fundamental and applied considerations, with the expectations that such group 13 derivatives might mediate unusual and unprecedented transformations.

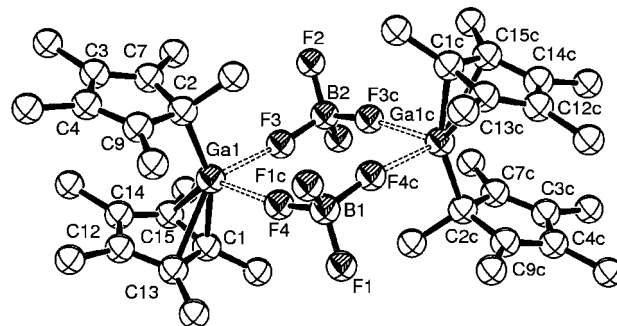
**Dialkyl Aluminum Cations.** In 2002, Reed and co-workers treated  $\text{AlEt}_3$  with a carborane trityl salt

$[\text{Ph}_3\text{C}][\text{CB}_{11}\text{H}_6\text{X}_6]$  ( $X = \text{Cl}, \text{Br}$ ) to afford the aluminum species  $\text{Et}_2\text{Al}^{\delta+}(\text{CB}_{11}\text{H}_6\text{X}_6)^{\delta-}$  ( $[8][\text{CB}_{11}\text{H}_6\text{X}_6]$ , eq 3) as a tight ion pair in benzene solution.<sup>30</sup>

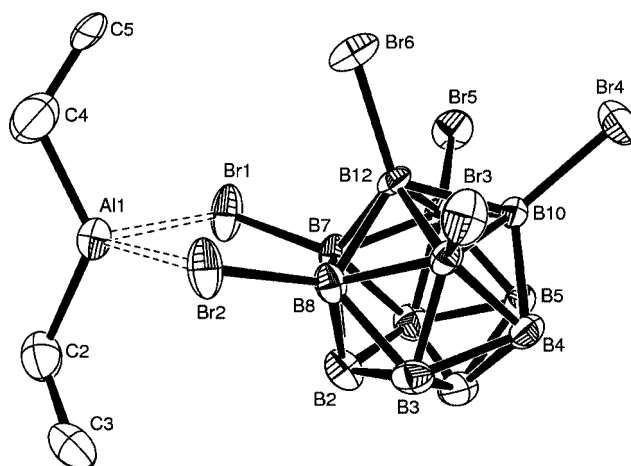


This reaction, which proceeds through a  $\beta$ -hydrogen abstraction reaction at an Al–Et group of  $\text{AlEt}_3$  along with release of ethylene, provides access to the first salt species formally incorporating an  $\text{AlR}_2^+$  moiety. This illustrates the suitability of carborane anions of the type  $\text{CB}_{11}\text{H}_6\text{X}_6^-$ , which are among the most inert and least coordinating anions known, for the generation and stabilization of  $\text{AlR}_2^+$  cations.

The inertness of the counterion for the stability of  $\text{AlR}_2^+$  appears to be crucial. Earlier attempts to generate free  $\text{AlR}_2^+$  cations by reacting  $\text{AlR}_3$  with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  afforded a mixture of the neutral species  $\text{AlR}_{3-x}(\text{C}_6\text{F}_5)_x$  and  $\text{R}_x\text{B}(\text{C}_6\text{F}_5)_{3-x}$ , whose formation most likely arose from the decomposition of the putative transient species  $[\text{AlR}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  through  $\text{C}_6\text{F}_5^-$  ligand transfer from the boron center to the  $\text{AlR}_2^+$  fragment.<sup>31</sup> Such an outcome illustrates the apparent unsuitability of  $\text{B}(\text{C}_6\text{F}_5)_4^-$  as a spectator anion for the generation of dialkyl aluminum cations,  $\text{AlR}_2^+$ .

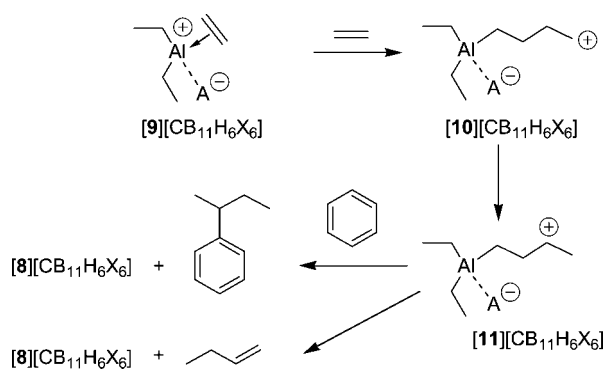


**Figure 5.** Solid-state structure of the galocenium salt  $[\text{Cp}^*_2\text{Ga}][\text{BF}_4]$  ( $7$ )[ $\text{BF}_4$ ] with partial atom labeling for clarity.



**Figure 6.** Solid-state structure of the aluminum species  $\text{Et}_2\text{Al}^{\delta+}(\text{CB}_{11}\text{H}_6\text{Br}_6)^{\delta-}$  ( $[8][\text{CB}_{11}\text{H}_6\text{Br}_6]$ ) with partial atom labeling for clarity.

Scheme 10



The molecular structure of  $[8][CB_{11}H_6X_6]$ , as illustrated in Figure 6, clearly shows a weak bidentate coordination of the  $CB_{11}H_6Br_6^-$  anion to the  $Et_2Al^+$  fragment, with the two Al–Br bond distances (2.58, 2.54 Å) being ca. 0.3 Å longer than typical Al–Br bond distances (2.25–2.30 Å). The C–Al–C bond angle (130.0°) of the  $AlEt_2^+$  moiety is considerably larger than expected for a tetrahedral ( $sp^3$ ) or trigonal ( $sp^2$ ) geometry, further suggesting the presence of alumenium ion character ( $sp$ ). The  $Et_2Al^{\delta+}(CB_{11}H_6X_6)^{\delta-}$  designation for the alumenium species  $[8][CB_{11}H_6X_6]$  appears appropriate from the structural data. Although “ion-like” species are not free ions, they can behave like free ions in solution; reactivity studies on  $Et_2Al^{\delta+}(CB_{11}H_6X_6)^{\delta-}$  support this view. Subsequent theoretical calculations on the nature of the interaction between Al and X in  $[8][CB_{11}H_6X_6]$  provided support for designating their structures as ion-like.<sup>32</sup> These calculations found that bonding between the  $Et_2Al^+$  moiety and the  $CB_{11}H_6X_6^-$  anion is more than half electrostatic (ionic bonding of 59.8% and 57.9% for the Al–Cl and Al–Br bonds, respectively).

The reactivity of  $[8][CB_{11}H_6X_6]$  is dominated by the potent Lewis acidity of the Al center. In the presence of ethylene, a benzene solution of  $[8][CB_{11}H_6X_6]$  yields a mixture of butenes and alkylated benzenes. As illustrated in Scheme 10, the likely chemistry giving rise to these products involves the Lewis acid activation of ethylene to form  $Et_2Al(\eta^2-C_2H_4)^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$  ( $[9][CB_{11}H_6X_6]$ ), which may then further react with either benzene or ethylene.

Reaction of  $[9][CB_{11}H_6X_6]$  with benzene would lead to ethylbenzene through a straightforward electrophilic substitution, while that with ethylene may yield the primary butyl carbocation  $10^+$ . Rapid rearrangement of  $10^+$  to the secondary cation  $11^+$ , by 1,2-H shifts, followed by an elimination of butene or an electrophilic attack on benzene, would rationalize the formation of the observed products. The alumenium species  $8^+$  was also found to oligomerize ethylene (700 psi ethylene, 60 °C, 24 h), albeit with low activity. It is also an extremely efficient catalyst for the controlled polymerization of cyclohexene oxide with im-

mediate and quantitative formation of poly(cyclohexene) oxide ( $M_w = 7600$ , PDI = 1.5) under mild conditions. Interestingly, throughout the course of these reactions, there is apparently no “Aufbau” insertion of ethylene into the Al–Et bond, strongly suggesting that the Lewis acidity of the aluminum center is largely responsible for the observed reactivity of two-coordinate cationic Al alkyls. The domination of Lewis acid type reactivity over insertion chemistry will also be noted in higher-coordinated group 13 cationic alkyls.

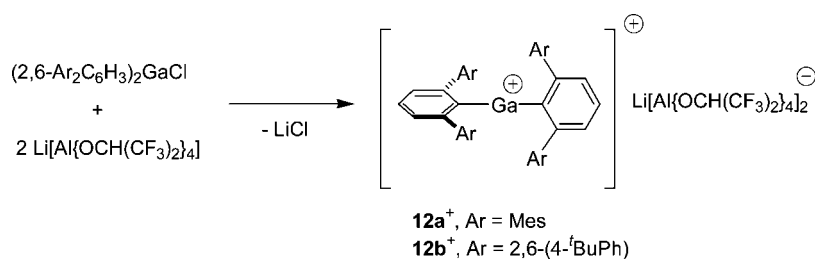
#### Diaryl Two-Coordinate Aluminum and Gallium Cations.

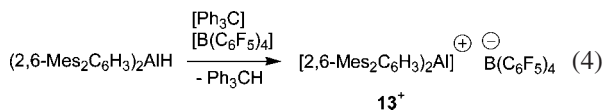
Two-coordinate diaryl gallium cations have been recently prepared by Wehmschulte et al. by using bulky *o*-terphenyl substituents on the coordinated aryl ligands.<sup>33,34</sup> On the basis of simple modeling, the authors reasoned that two of these large bowl-shaped aryl groups might be able to shield the central cationic Ga center and prevent it from interacting with the counterion and/or the solvent.

The metathesis reaction of the gallium chloro derivative  $(2,6-Ar_2C_6H_3)_2GaCl$  with 2 equiv of  $Li[Al\{OCH(CF_3)_2\}_4]$  affords the two-coordinate diaryl cation  $(2,6-Ar_2C_6H_3)_2Ga^+$  ( $12a^+$ , Ar = Mes;  $12b^+$ , Ar = 2,6-(4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>); Scheme 11) as a  $Li[Al\{OCH(CF_3)_2\}_4]_2^-$  salt, along with formation of  $LiCl$ .<sup>33,34</sup> Unlike  $Et_2Al^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$ , the solution data for the salts  $[12a-12b][Li[Al\{OCH(CF_3)_2\}_4]_2]$  are consistent with no interaction between the cation and the anion; these data are supported by the solid-state structure of  $[12a][Li[Al\{OCH(CF_3)_2\}_4]_2]$ . As a consequence, these two Ga cations may be seen as truly “free” two-coordinate gallium cations. Accordingly and as shown in Figure 7, the molecular structure of  $12a^+$  displays a two-coordinate gallium center with an essentially linear array  $C(15)-Ga(1)-C(39) = 175.69(7)^\circ$  similar to that observed in the isoelectronic  $HgR_2$  species. This agrees with  $sp$  character for the metal center. The bowl-shaped terphenyl substituents are arranged in a staggered conformation that almost completely envelopes the gallium center, which rationalizes the observed stability of this species. This dramatic steric shielding clearly reduces the reactivity that may be expected for such an electrophilic group 13 cation. Thus,  $(2,6-Mes_2C_6H_3)_2Ga^+$  does not coordinate tetrahydrofuran (thf), while its reactions with other Lewis bases such as pyridine or DMAP remain unclear. Unlike  $[8][CB_{11}H_6X_6]$ , it does not react with olefins or aromatics but exhibits an excellent ability to polymerize cyclohexene oxide.

The use of bulky *o*-terphenyl substituents as supporting aryl ligands also allowed the synthesis and structural characterization of the almost linear and quasi-two-coordinate aluminum cation  $(2,6-Mes_2C_6H_3)_2Al^+$  ( $13^+$ , eq 4), prepared as a fully dissociated  $B(C_6F_5)_4^-$  salt by ionization of the hydrido aluminum derivative  $(2,6-Mes_2C_6H_3)_2AlH$  with  $[Ph_3C][B(C_6F_5)_4]$ .<sup>35</sup>

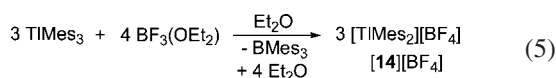
Scheme 11





The solid-state structure of cation **13<sup>+</sup>** exhibits a quasi-two-coordinate metal center. However, unlike its Ga analog, the strong Lewis acidity of the cationic aluminum center in **13<sup>+</sup>** is manifested in short Al<sup>+</sup>–C contacts, at least in the solid state, involving the mesityl groups. This Al cation appears to be more reactive than its Ga analogue and oligomerizes 1-octene to yield mainly hexamers, heptamers, and octamers, but it does not react with ethylene. Overall, both the structural and reactivity features of the Al cation versus that of the Ga analogue reflect the more Lewis acidic nature of Al versus Ga.

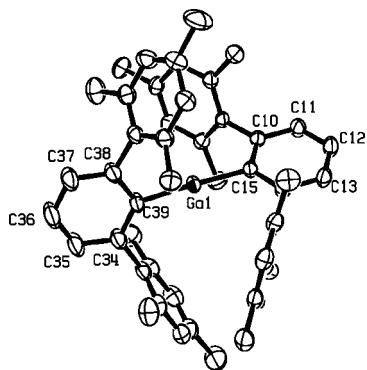
**Diaryl Two-Coordinate Thallium(III) Cations.** Although diaryl thallium(III) cations of the type Ar<sub>2</sub>Tl<sup>+</sup> have been known for quite some time, the discrete Tl(III) cation (Mes)<sub>2</sub>Tl<sup>+</sup> (**14<sup>+</sup>**) has recently been synthesized and characterized by X-ray crystallography as a BF<sub>4</sub><sup>−</sup> salt (eq 5 and Figure 8).<sup>36</sup> The two-coordinate cation adopts a classical linear geometry and exhibits some interactions with the BF<sub>4</sub><sup>−</sup> anion.



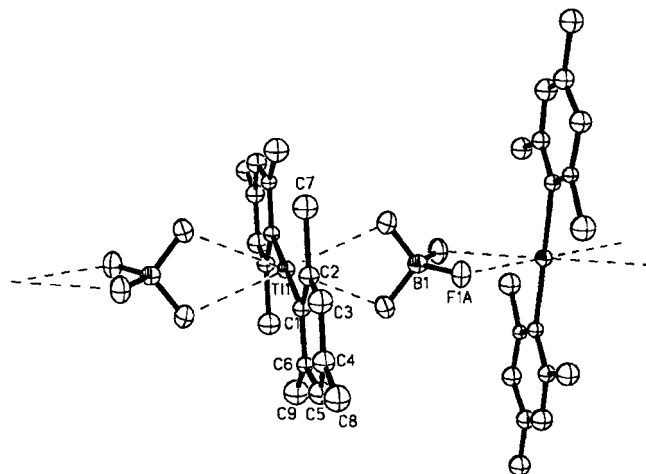
**Aryl–Alkyl Two-Coordinate Gallium Cations.** In an effort to increase the reactivity of two-coordinate Ga cations, the syntheses of less sterically hindered two-coordinate aryl alkyl Ga cations [(terph)GaR]<sup>+</sup> (**15a–15b<sup>+</sup>**, Scheme 12) has been reported by treatment of neutral precursors of the type (terph)GaR<sub>2</sub> with trityl salts of weakly coordinating anions.<sup>34</sup> Cations **15a–15b<sup>+</sup>** are remarkably stable in solution (for days at room temperature) and, unlike their diaryl cationic analogues, are quite reactive with olefins such 1-octene. Preliminary reactivity studies of the salt [**15b**][CHB<sub>11</sub>Cl<sub>11</sub>] with 1-octene found facile alkyl/olefin exchange at the cationic gallium center as well as slow octene isomerization and benzene (solvent) alkylation.

**Disilyl Two-Coordinate Aluminum and Gallium Cations.** The Al and Ga disilyl cations (**16a–16b<sup>+</sup>**, Scheme 13) have been shown to be readily accessible as B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> salts by reaction of [Et<sub>3</sub>Si(C<sub>6</sub>H<sub>6</sub>)] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with the trisilyl group 13 precursors (<sup>t</sup>Bu<sub>2</sub>MeSi)<sub>3</sub>M (M = Al, Ga).<sup>37</sup>

This reaction was proposed to proceed by an initial Me<sup>−</sup> abstraction by Et<sub>3</sub>Si<sup>+</sup> from (<sup>t</sup>Bu<sub>2</sub>MeSi)<sub>3</sub>M to form a transient

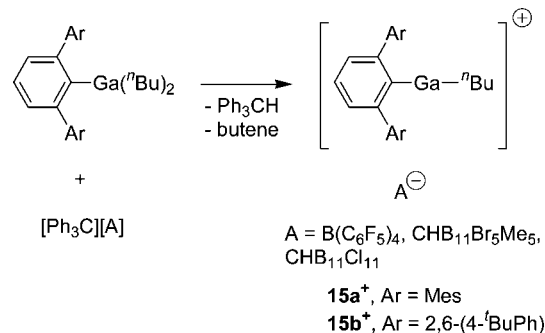


**Figure 7.** Solid-state structure of the two-coordinate diaryl Ga cation (2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>Ga<sup>+</sup> (**12a<sup>+</sup>**) with partial atom labeling for clarity.

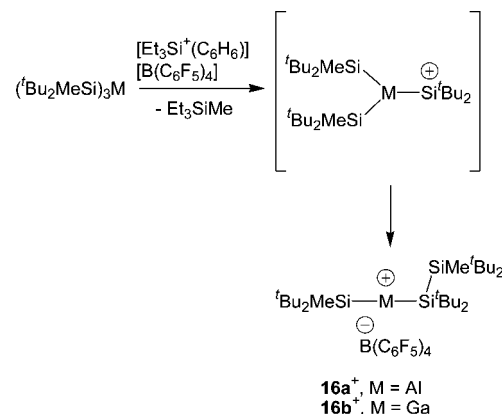


**Figure 8.** Solid-state structure of the thallium species [(Mes)<sub>2</sub>Tl][BF<sub>4</sub>] (**[14][BF<sub>4</sub>]**) ([TlMes<sub>2</sub>][BF<sub>4</sub>], a salt with the linear cation (Mes-Tl-Mes)<sup>+</sup>). Reprinted with permission from Neumüller et al. *Z. Anorg. Allg. Chem.* **2007**, 633, 941. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

#### Scheme 12

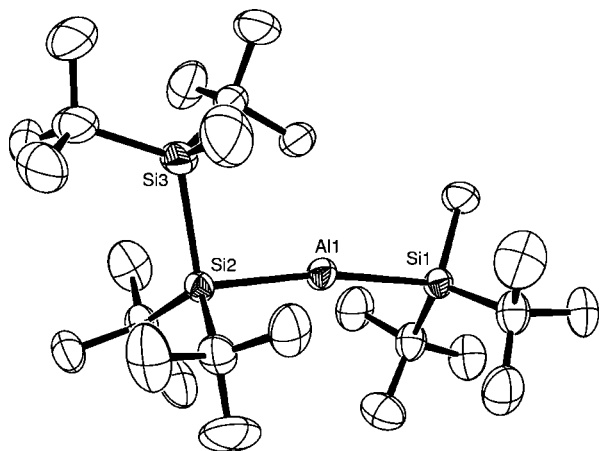


#### Scheme 13



silyl cation (Scheme 13), which may then rearrange through migration of a <sup>t</sup>Bu<sub>2</sub>MeSiM group to the cationic silicon center to yield cation **16a–16b<sup>+</sup>**. The solid-state structure of [**16a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] contains no close cation–anion interactions, and the molecular structure of **16a<sup>+</sup>** is illustrated in Figure 9. Notably, the rather short Al(1)–Si(2) bond distance (2.4581(9) versus 2.4969(9) Å for Al(1)–Si(1)) combined with a relatively small Al(1)–Si(2)–Si(3) angle (97.79(3) Å) was ascribed to a hyperconjugative interaction of the Si(2)–Si(3) σ-bond with the cationic Al center. Also supported by theoretical calculations, the latter interaction most likely accounts for the stability of cations **16a–16b<sup>+</sup>** and their absence of interaction, even in the solid state, with B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup>. As expected, cations **16a–16b<sup>+</sup>** were found to





**Figure 9.** Solid-state structure of the two-coordinate disilyl cation  $16a^+$  with partial atom labeling for clarity.

react with excess  $\text{CH}_3\text{CN}$  to form the corresponding tetra-coordinate cationic adducts.

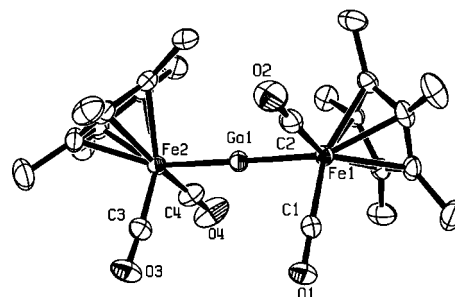
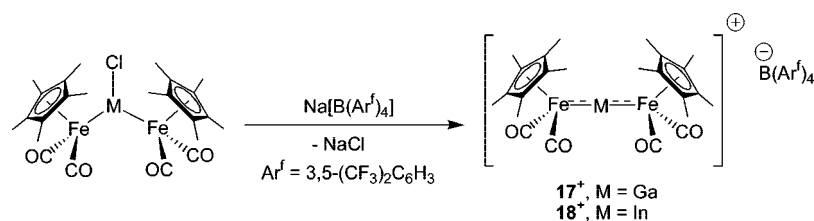
### 2.2.3. Two-Coordinate Heteronuclear Group 13 Cations

The possibility of using relatively bulky and appropriate transition metal moieties as supporting ligands for the preparation of stable two-coordinate group 13 cationic species has been discovered by Aldridge et al., opening the way to low-coordinate cationic heteronuclear complexes containing metal–group 13 element bonds.<sup>38,39</sup> The heteronuclear two-coordinate gallium and indium cationic derivatives  $\{(\eta^5\text{-Cp}^*)\text{Fe}(\text{CO})_2\}_2\text{M}^+$  ( $17^+$ ,  $\text{M} = \text{Ga}$ ;  $18^+$ ,  $\text{M} = \text{In}$ ) were easily prepared as  $\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4^-$  salts through a straightforward halide abstraction involving the reaction of the neutral group 13 halide precursor  $\{(\eta^5\text{-Cp}^*)\text{Fe}(\text{CO})_2\}_2\text{MCl}$  ( $\text{M} = \text{Ga}, \text{In}$ ) with  $\text{Na}[\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$  (Scheme 14).

As can be expected, the bulkyness of the starting transition metal moieties strongly influences structural and reaction chemistry. Hence, the use of a Cp–iron–dicarbonyl  $\{(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2\}$  fragment (in place of  $\{(\eta^5\text{-Cp}^*)\text{Fe}(\text{CO})_2\}$ ) yields oligomerization products through the formation of Ga–Cl–Ga bridges.

The molecular structures of the heteronuclear cations  $17^+$  and  $18^+$ , as determined by X-ray crystallography, exhibit overall similar bonding features, and the structure of the gallium derivative  $17^+$  is illustrated in Figure 10. The linear Fe–Ga–Fe (Fe(1)–Ga(1)–Fe(2)) angle is consistent with a two-coordinate gallium center engaging no interaction with the counterion, while the Fe–Ga bond lengths (2.266(1) and 2.272(1) Å) are significantly shorter than those in compounds typically thought to possess one single Fe–Ga bond (2.36–2.46 Å). The Ga and In cations reversibly coordinate one molecule of thf, thus indicating a surprisingly weak Lewis acidic behavior for such low-coordinate group 13 cations.<sup>39</sup> In contrast, the Ga cation  $17^+$  readily coordinates 4-picoline to yield a robust three-coordinate Ga cation

#### Scheme 14



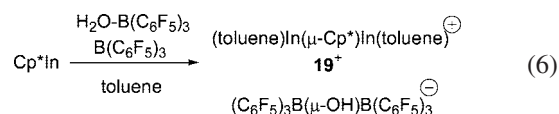
**Figure 10.** Solid-state structure of the heteronuclear two-coordinate Ga cation  $17^+$  with partial atom labeling for clarity.

showing no sign of dissociation in solution.<sup>40</sup> As for the nature of bonding interactions within the Fe–Ga–Fe backbone, structural, spectroscopic, and computational studies performed on  $17^+$  are consistent with a substantial Fe–Ga  $\pi$ -bonding character, arising from Fe→Ga back-bonding, which may rationalize the moderate Lewis acidity of the incorporated Ga center. In contrast, the Fe–In  $\pi$ -component appears to be much smaller in  $18^+$ .<sup>38,41</sup>

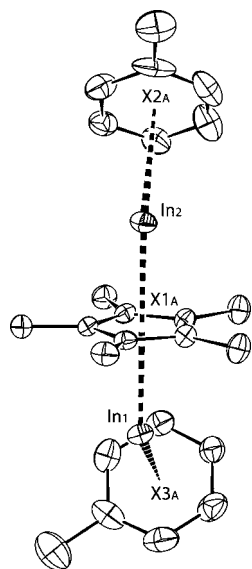
## 2.3. Univalent Two-Coordinate Indium and Thallium Cations

### 2.3.1. Univalent Two-Coordinate Indium Cations

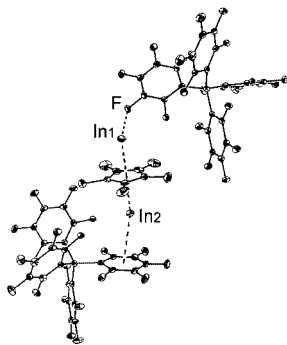
As noted in the Introduction, little has been done over the past 10 years in the area of low-valent cationic indium species. The synthesis and structural characterization of novel indium(I) cations by Cowley et al. constitutes the only advance in this domain and has been the subject of a recent review.<sup>42</sup> In an attempt to generate  $\text{In}(\text{arene})^+$  cations, these authors reported the synthesis and solid-state structure of the dinuclear sandwich cation  $[(\text{toluene})\text{In}(\mu\text{-Cp}^*)\text{In}(\text{toluene})]^+$  ( $19^+$ , eq 6) as a  $[(\text{C}_6\text{F}_5)_3\text{BO}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3]^-$  anion, formed through the protolytic cleavage of  $\text{Cp}^*\text{In}$  with the Brønsted acid  $\text{H}_2\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$  in the presence of 1 equiv of  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene.<sup>43</sup>



As illustrated in Figure 11, the molecular structure of  $19^+$  features an  $\eta^5$ -bound In atom on each face of the  $\mu\text{-Cp}^*$  group and each In atom is capped with an  $\eta^6$ -bound toluene molecule. The In–toluene ring centroid distances (3.407(4) Å average) are considerably longer than the In–Cp\* centroids (2.481(4) Å average), which is consistent with extremely weak In–toluene bonding in  $19^+$ . In fact, the use of a smaller anion such as  $\text{B}(\text{C}_6\text{F}_5)_4^-$  for association with the  $[\text{In}(\mu\text{-Cp}^*)\text{In}]^+$  cation expels toluene from the In coordination sphere to afford cation  $20^+$ , as determined by X-ray crystallography (Figure 12).<sup>44</sup> Remarkably, one of the



**Figure 11.** Solid-state structure of the dinuclear In sandwich cation  $19^+$  with partial atom labeling for clarity.

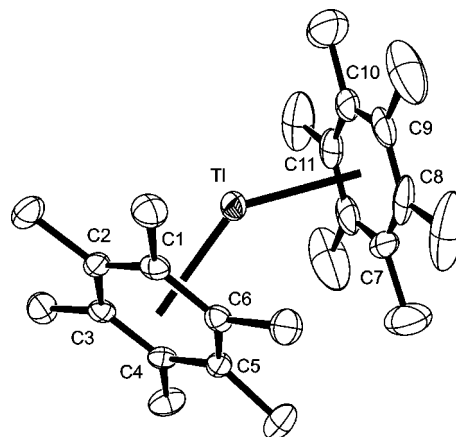


**Figure 12.** Solid-state interactions between the  $\text{In}(\mu\text{-Cp}^*)\text{In}^+$  cation ( $20^+$ ) and its counterion  $\text{B}(\text{C}_6\text{F}_5)_4^-$  (with partial atom labeling for clarity).

In atoms in  $20^+$  undergoes a weak  $\eta^6$ -interaction with one of the  $\text{C}_6\text{F}_5$  groups of  $\text{B}(\text{C}_6\text{F}_5)_4^-$ , which constitutes an unprecedented mode of interaction for this borate anion. Finally, as for Ga(I) cationic derivatives, one should note the synthesis and structural characterization of a polymeric multidecker sandwich cation featuring an array of alternating Ga(I) and Fe(II) ions bridged by Cp moieties.<sup>45</sup> The multidecker polynuclear cation was generated by the combination of ferrocene and  $\text{GaCl}_3$  and involves a redox process with the system  $\text{GaCl}_3/\text{ferrocene}$ .

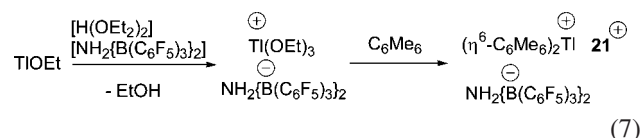
### 2.3.2. Univalent Two-Coordinate Thallium Cations

Bis( $\eta^6$ -arene) $\text{Tl}(\text{I})^+$  cations have been known since the 1980s with the pioneering work of Schmidbaur et al. Such low-valent cations have been associated with various counterions with the aim of minimizing cation–anion interactions. To date, the great majority of characterized  $\text{Tl}(\text{I})$ –arene cations feature some degree of anion coordination. It was, however, shown that the use of the inert and noncoordinating counterion  $\text{NH}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$  may be suitable for the generation of discrete bis( $\eta^6$ -arene) $\text{Tl}(\text{I})^+$  cations with no close contact with the anion.<sup>46</sup> Thus, the reaction of  $\text{TlOEt}$  with  $[\text{H}(\text{OEt}_2)_2][\text{NH}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  was found to yield the three-coordinate  $\text{Tl}$  cation  $\text{Tl}(\text{OEt}_2)_3^+$ , which, upon exposure to



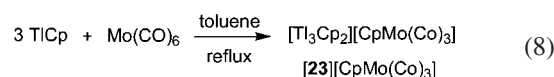
**Figure 13.** Solid-state structure of the two-coordinate cation ( $\eta^6\text{-C}_6\text{Me}_6$ ) $_2\text{Tl}^+$  ( $21^+$ ).

$\text{C}_6\text{Me}_6$ , can be quantitatively converted to the two-coordinate cation ( $\eta^6\text{-C}_6\text{Me}_6$ ) $_2\text{Tl}^+$  ( $21^+$ , eq 7 and Figure 13) as a fully dissociated  $\text{NH}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$  salt.



The solid-state structure of  $[21][\text{NH}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  is remarkable in that there is no interaction between the metal and the counterion. Another structural feature of interest is the  $\text{Tl}$ –centroid distances in ( $\eta^6\text{-C}_6\text{Me}_6$ ) $_2\text{Tl}^+$  (2.789 and 2.855 Å), which are the shortest to date for this type of cationic species. In a similar manner, the bis-toluene  $\text{Tl}$  cation ( $\eta^6\text{-tol}$ ) $_2\text{Tl}^+$  ( $22^+$ ) was also synthesized as a  $\text{NH}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$  salt and was formulated as a two-coordinate cation on the basis of its  $^{205}\text{Tl}$  NMR chemical shift and elemental analysis. Cation  $22^+$  readily reacts with dimethoxyethane (DME) to form the 1:1 adduct  $(\text{DME})\text{Tl}^+$  along with release of toluene. Cation  $22^+$  was also combined with ferrocene (Fc) to form stable multidecker cations of the type  $(\text{Tl}\text{--Fc})^+$  and  $(\text{Fc}\text{--Tl}\text{--Fc})^+$ . The bonding in the above  $\text{Tl}$ –arene cations was explored by DFT calculations and found to be predominantly due to polarization effects, without geometric preferences other than those provided by ligand repulsion.

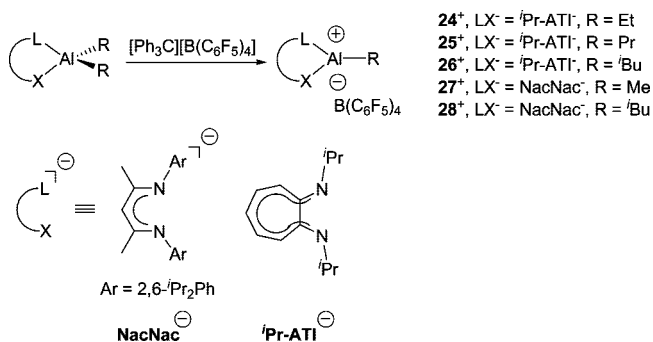
The synthesis and X-ray characterization of the salt species  $[\text{Tl}_3\text{Cp}_2][\text{CpMo}(\text{CO})_3]$  incorporates the new cation  $\text{Tl}_3\text{Cp}_2^+$  ( $23^+$ ) as a  $\text{CpMo}(\text{CO})_3^-$  salt (eq 8).<sup>47</sup> In the solid state, there are cation–anion interactions as evidenced by contacts between the Cp ring of  $\text{CpMo}(\text{CO})_3^-$  and one of the  $\text{Tl}$  atoms in  $\text{Tl}_3\text{Cp}_2^+$ .



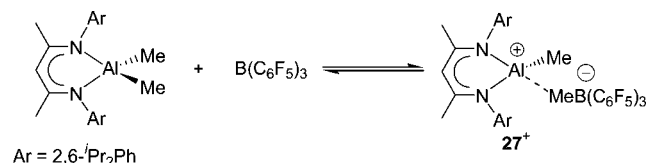
## 3. Three-Coordinate Group 13 Cations

Unknown 10 years ago, with the exception of a few indium and thallium derivatives, three-coordinate cationic group 13 species have appeared as attractive targets for investigation since then. In this regard, most research has been focused on the generation of stable group 13 alkyl cations of the type  $\{\text{LX}\}\text{MR}^+$  through an alkyl or hydride abstraction reaction from neutral precursors of the type  $\{\text{LX}\}\text{MR}_2$  by a strong Lewis acid such as  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ . When

## Scheme 15



## Scheme 16



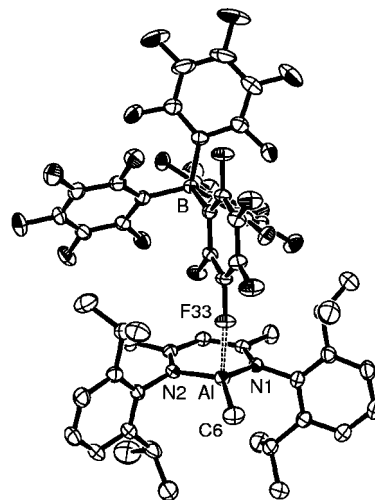
compared to two-coordinate group 13 cations, which require an extremely subtle balance of stability versus reactivity, three-coordinate cations  $\{LX\}MR^+$  may exhibit a broader range of electrophilicity and stability. In such species, the use of bulky bidentate  $LX^-$  ligands for incorporation in  $\{LX\}MR^+$  may alleviate complications from ligand redistribution reactions and may limit aggregation phenomena by protecting the metal center, thus favoring the stability of these low-coordinate cations.

### 3.1. Three-Coordinate Group 13 Alkyl and Hydrido Cations Supported by a $LX^-$ Bidentate Ligand: Synthesis, Structure, and Stability

#### 3.1.1. Bidentate Aminotroponimate, $\beta$ -Diketiminato, Amidinate, and Bis(oxazolinato) Group 13 Cations

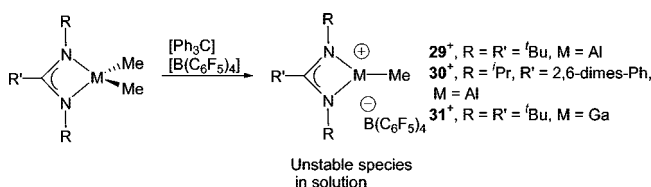
In the late 1990s, Jordan et al. first reported the synthesis of stable three-coordinate aluminum cations of the type  $\{LX\}AIR^+$  ( $R = \text{alkyl}$ ), where  $LX^-$  is a bulky monoanionic  $\pi$ -delocalized  $N,N$ -bidentate ligand of the type aminotroponimate or  $\beta$ -diketiminato ( ${}^i\text{Pr-ATI}^-$  and  $\text{NacNac}^-$ ; Scheme 15). Thus, following an alkyl/hydride abstraction approach, the neutral dialkyl precursors  $\{ATI\}AlR_2$  ( $R = \text{Et, Pr, }^i\text{Bu}$ ) were found to readily react with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  through a  $\beta$ -hydride abstraction at the  $\text{Al}-\text{C}\beta$  of  $\{ATI\}AlR_2$  to afford the corresponding three-coordinate cations  $\{{}^i\text{Pr-ATI}\}AlR^+$  ( $24^+$ ,  $R = \text{Et}$ ;  $25^+$ ,  $R = \text{Pr}$ ;  $26^+$ ,  $R = {}^i\text{Bu}$ ; Scheme 15) as  $\text{B}(\text{C}_6\text{F}_5)_4^-$  salts along with ethylene, propene, or poly(isobutene), respectively.<sup>48,49</sup> In a similar manner, the  $\beta$ -diketiminato Al dialkyl species  $\{\text{NacNac}\}AlR_2$  ( $R = \text{Me, }^i\text{Bu}$ ) may be ionized by  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  through a  $\text{Me}^-$  or  $\beta$ -hydride abstraction to afford the corresponding Al cations  $\{\text{NacNac}\}AlR^+$  ( $27^+$ ,  $R = \text{Me}$ ;  $28^+$ ,  $R = {}^i\text{Bu}$ ; Scheme 15) as fully dissociated  $\text{B}(\text{C}_6\text{F}_5)_4^-$  salts in solution.<sup>50</sup>

It is noteworthy that cation  $27^+$  could also be generated as a  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  salt by reaction of  $\{\text{NacNac}\}Al\text{Me}_2$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 16); this  $\text{Me}^-$  abstraction reaction proceeds, however, in a reversible manner. The stability of the salt species  $[27][\text{MeB}(\text{C}_6\text{F}_5)_3]$  and the observation of a  $\text{Me}^-$  rather than  $\text{C}_6\text{F}_5^-$  transfer from  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  to  $\{\text{NacNac}\}Al\text{Me}^+$  are unusual features in three-coordinate group 13 chemistry. Such alkyl cations associated with the  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  anion may be unstable and decompose by



**Figure 14.** Solid-state structure of  $[27][\text{B}(\text{C}_6\text{F}_5)_4]$ : A three-coordinate Al alkyl cation supported by a  $\beta$ -diketiminato ligand ( $27^+$ ) associated with  $\text{B}(\text{C}_6\text{F}_5)_4^-$ .

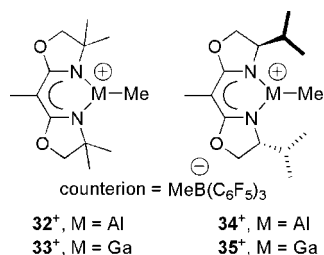
## Scheme 17



irreversible  $\text{C}_6\text{F}_5^-$  transfer (*vide infra*). Crystallization of  $[27][\text{B}(\text{C}_6\text{F}_5)_4]$  allowed the first X-ray crystallography determination of a quasi-three-coordinate Al cation, as illustrated in Figure 14.<sup>50</sup>

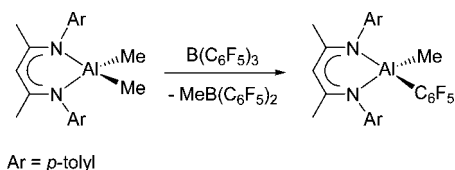
In the solid state, the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  counterion binds weakly to the cationic Al center in  $27^+$ , as evidenced by the  $\text{Al}-\text{F}_{\text{meta}}$  distance ( $\text{Al}-\text{F}(33) = 2.151(1) \text{ \AA}$ ). Although significantly longer than typical terminal  $\text{Al}-\text{F}$  bond distances ( $\sim 1.65 \text{ \AA}$ ), this  $\text{Al}-\text{F}$  contact illustrates the potent Lewis acidity of the Al center in such low-coordinate species. Accordingly, the salt species  $[24][\text{B}(\text{C}_6\text{F}_5)_4]$ , crystallized from a more coordinating solvent such as  $\text{PhCl}$ , afforded the four-coordinate  $\text{Al}-\text{ClPh}$  cationic adduct  $\{\text{ATI}\}Al(\text{Et})(\text{PhCl})^+$  as a  $\text{B}(\text{C}_6\text{F}_5)_4^-$  salt.<sup>51</sup> As deduced from X-ray crystallographic studies, the extreme Lewis acidity of the Al center in cations  $24^+ - 27^+$  results in a significant shortening of the  $\text{Al}-\text{N}$  bond distances versus those in neutral analogues, which may be ascribed to increased ionic interactions (and, thus, ionic contraction) or  $\text{N}-\text{Al}$   $\pi$ -bonding in these cationic species. When associated with the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion, cations  $24^+ - 28^+$  were all found to be stable for days in  $\text{PhCl}$ ,  $\text{PhBr}$ , or toluene solution at ambient temperature under inert atmosphere. In solution, these cations behave like “base-free” three-coordinate Al cations (*vide infra* for their reactivity). However, it is very likely that these cations form solvent adducts (at least with  $\text{PhCl}$  or  $\text{PhBr}$ ) that undergo rapid face exchange in solution.

Unlike the Al cations  $24^+ - 28^+$ , three-coordinate Al cations supported by a  $\pi$ -delocalized bulky amidinate ligand  $\{R'C(\text{NR})_2\}Al\text{Me}^+$  ( $29^+$ ,  $R = R' = {}^i\text{Bu}$ ;  $30^+$ ,  $R = {}^i\text{Pr}$ ,  $R' = 2,6\text{-dimesitylphenyl}$ ; Scheme 17) generated by reaction of  $\{R'C(\text{NR})_2\}Al\text{Me}_2$  with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  are unstable in solution and could only be observed by NMR.<sup>52,53</sup> The amidinate gallium methyl cationic analog  $\{^i\text{BuC}(\text{CN}^i\text{-Bu})_2\}Ga\text{Me}^+$  ( $31^+$ , Scheme 17), generated following the



**Figure 15.** Three-coordinate group 13 alkyl cations incorporating a bisoxazolinato ligand.

### Scheme 18



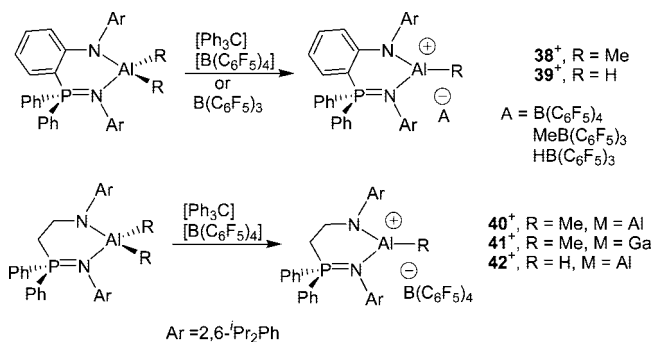
same ionization procedure, was also found to be poorly stable in solution and to decompose to unidentified species.<sup>52</sup> Similarly, the three-coordinate Al methyl cations  $32^+–35^+$  (Figure 15), supported by a chiral or an achiral bisoxazolinato bidentate ligand, are thermally unstable and readily degrade to unknown species;<sup>54,55</sup> in the present case, the counterion  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  is not involved in the decomposition process.

The instability of the Al cations  $29^+$  and  $30^+$  versus that of  $24^+–28^+$  was ascribed to the nature of the ancillary ligand; in the amidinate Al cations, the more strained four-membered Al–metallacycle relative to that in  $24^+–28^+$  may partially rationalize the lack of stability of the derived Al complexes. In addition, the more acute N–Al–N bite angle in cations  $29^+$  and  $30^+$  versus that in  $24^+–28^+$  combined with the compact size of the  $\{\text{R}'\text{C}(\text{NR})_2\}\text{Al}$  unit may result in a more open sphere of coordination for the metal center in  $29^+$  and  $30^+$ , thereby favoring decomposition and/or aggregation reactions.

The nature of the counterion associated with the electrophilic  $\{\text{LX}\}\text{AlR}^+\text{Al}$  cation as well as the nature of the  $\text{Al–R}^+$  moiety may be crucial for the stability of such cations. According to studies carried out thus far, the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion seems to be suitable to yield stable  $\{\text{LX}\}\text{AlR}^+$  cations, while the more reactive  $\text{RB}(\text{C}_6\text{F}_5)_3^-$  anion may irreversibly react with  $\{\text{LX}\}\text{AlR}^+$  through a  $\text{C}_6\text{F}_5^-$  ligand transfer to generate  $\{\text{LX}\}\text{Al}(\text{R})(\text{C}_6\text{F}_5)$  along with the  $\text{RB}(\text{C}_6\text{F}_5)_2$ . In this regard, initial studies by Smith et al. concluded that the  $\text{Me}^-$  abstraction reaction between  $\text{B}(\text{C}_6\text{F}_5)_3$  and the Al dimethyl derivative  $\{\text{HC}(\text{CMeNAr})_2\}\text{AlMe}_2$  (Ar = *p*-tolyl) afforded a 1/1 mixture of  $\{\text{HC}(\text{CMeNAr})_2\}\text{Al}(\text{Me})(\text{C}_6\text{F}_5)$  and  $\text{Me}(\text{C}_6\text{F}_5)_2$  (Scheme 18).<sup>56</sup>

Similar decomposition products have been subsequently observed with other supporting *N,N*-ligand systems such as the amidinate and aminotroponimate ligands.<sup>49,52</sup> As for the nature of the  $\text{Al–R}$  moiety, its steric properties may significantly influence the stability of the formed cations; this feature has been remarkably demonstrated in the case of  $\{\text{Pr-ATI}\}\text{Al}$  alkyl cationic systems.<sup>49</sup> Thus, while the Al alkyl cations  $\{\text{Pr-ATI}\}\text{AlR}^+$  ( $24^+–26^+$ , R = Et, Pr, *i*Bu) are stable as  $\text{B}(\text{C}_6\text{F}_5)_4^-$  salts, the ionization of the benzyl and cyclohexyl  $\{\text{Pr-ATI}\}\text{AlR}_2$  derivatives (R = Bz, Cy) with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  apparently yields the corresponding three-coordinate cations  $\{\text{Pr-ATI}\}\text{AlR}^+$  (R = Bz, Cy), that do, however, rapidly decompose to  $\{\text{Pr-ATI}\}\text{Al}(\text{R})(\text{C}_6\text{F}_5)$  spe-

### Scheme 19



cies. This difference of stability shows that sterics of the  $\text{Al–R}^+$  moiety may greatly influence the stability of  $\{\text{LX}\}\text{AlR}^+$  cations.

Finally, one should add that stable three-coordinate gallium and indium methyl cations supported by the  $\text{Pr-ATI}^-$  ligand have been described.<sup>51,57</sup> Thus, the reaction of  $\{\text{Pr-ATI}\}\text{MMe}_2$  (M = Ga, In) with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  cleanly affords the corresponding group 13 cation  $\{\text{Pr-ATI}\}\text{MMe}^+$  ( $36^+$ , M = Ga;  $37^+$ , M = In) as fully dissociated  $\text{B}(\text{C}_6\text{F}_5)_4^-$  salts in solution. Although cations  $36^+$  and  $37^+$  behave as base-free species in solution, interactions between the group 13 metal center and the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion or the solvent are observed in the solid state, as with the Al analogues. The In methyl cation of  $\{\text{Pr-ATI}\}\text{InMe}^+$  ( $37^+$ ) can also be generated as a  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  salt through ionization of  $\{\text{Pr-ATI}\}\text{InMe}_2$  with  $\text{B}(\text{C}_6\text{F}_5)_3$ . However, as observed with some Al analogues, the salt species  $[\text{37}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  is unstable and decomposes through  $\text{C}_6\text{F}_5^-$  ligand transfer from boron to indium to yield the neutral derivatives  $\{\text{Pr-ATI}\}\text{In}(\text{Me})(\text{C}_6\text{F}_5)$  and  $\{\text{Pr-ATI}\}\text{In}(\text{C}_6\text{F}_5)_2$ .<sup>57</sup>

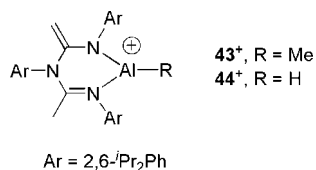
### 3.1.2. Bidentate Amidophosphinimine, *N*-Imidoilamidine, and *N,O*-Aminophenolate Group 13 Cations

The suitability of  $\pi$ -delocalized *N,N*-type  $\text{LX}^-$  bidentate ligands for the generation of stable three-coordinate group 13 cations has encouraged research efforts in this area, with the aim of increasing the stability and the robustness of such cations through fine-tuning of the chelate ligand. In this regard, bidentate amidophosphinimine and *N*-imidoilamidine *N,N*- $\text{LX}^-$  ligand, which may combine a significant steric bulk with an increased donor ability versus more classical *N,N*- $\text{LX}^-$  ligands, have been used for the generation of stable group 13 alkyl cations of the type  $\{\text{LX}\}\text{MR}^+$  (M = Al, Ga; R = alkyl, H).

The groups of Piers and Stephan concurrently reported on the synthesis of stable bidentate amidophosphinimine group 13 methyl and hydrido cations  $38^+–42^+$  (Scheme 19), through ionization of the corresponding group 13 dialkyl or dihydrido neutral precursors with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>58,59</sup> To date, cations  $39^+$  and  $42^+$  constitute the only examples of stable and well-defined three-coordinate Al hydrido cations.

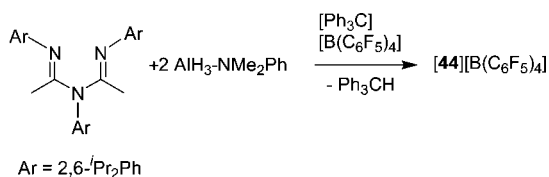
The stability of the salt species  $[\text{39}][\text{HB}(\text{C}_6\text{F}_5)_3]$ , which associates a highly electrophilic three-coordinate Al cation with the  $\text{HB}(\text{C}_6\text{F}_5)_3^-$  anion, a formal hydride source, is rather remarkable and clearly demonstrates the stabilizing properties of the chosen chelate ligand.

Similarly, the three-coordinate Al methyl and hydrido cations  $43^+$  and  $44^+$  (Figure 16) supported by a disymmetric amidoimine ligand derived from a sterically bulky *N*-



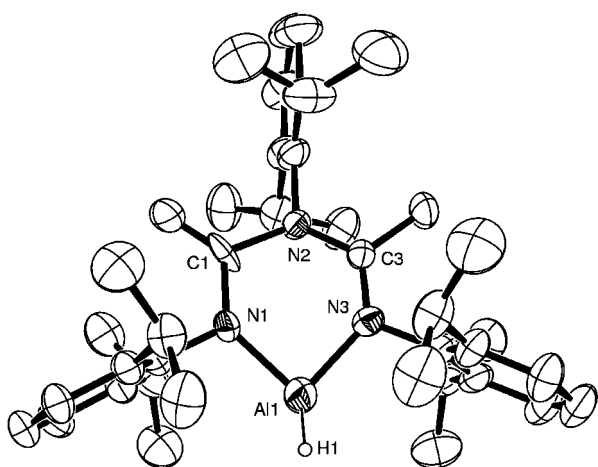
**Figure 16.** Three-coordinate Al cations supported a *N*-imidoylamidinate bidentate ligand.

#### Scheme 20



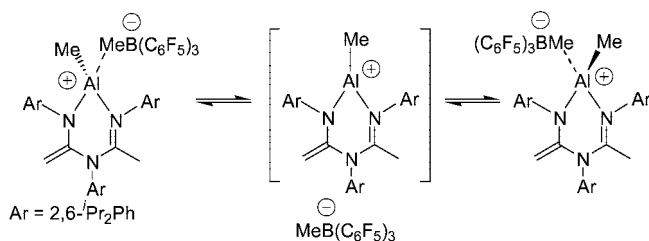
imidoylamidinate and were recently synthesized and shown to be quite robust and stable.<sup>60</sup> While the Al methyl cation **43**<sup>+</sup> was generated through a classical Me<sup>−</sup> abstraction by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at a neutral Al dimethyl precursor, the three-coordinate Al hydrido cation **44**<sup>+</sup> was produced by reacting the appropriate neutral *N*-imidoylamidinate, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], and 2 equiv of the amine Al adduct AlH<sub>3</sub>–NMe<sub>2</sub>Et to afford in high yield cation **44**<sup>+</sup> as a stable and fully dissociated B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> salt in solution (Scheme 20).

The molecular structure of **44**<sup>+</sup>, as determined by X-ray crystallography, constitutes the first three-coordinate Al hydrido cation to be structurally characterized (Figure 17). The overall solid-state structure of cation **44**<sup>+</sup> is reminiscent of that of the three-coordinate {NacNac}AlMe<sup>+</sup> (**27**<sup>+</sup>) mentioned earlier. The Al–H hydride in **44**<sup>+</sup>, which was located and refined to give an Al–H distance of 1.22 Å, is symmetrically located below the AlN<sub>2</sub> plane with N–Al–H averaging 123.6(2)°. Interestingly and unlike the cationic methyl Al analogues **24**<sup>+</sup> and **27**<sup>+</sup>, no interaction between the Al cation **44**<sup>+</sup> and the B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> anion (or any solvent molecule) are observed in the solid state, which may reflect an increased donor ability of the chelating ligand versus other *N,N*-ligand systems. As for the Al methyl cation **43**<sup>+</sup>, although formally formulated as a three-coordinate species, it clearly interacts with the MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> anion in solution: an exchange process involving the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> group was observed by <sup>1</sup>H NMR between the two Al-bound methyl groups, and its activation parameters were determined (ΔH<sup>‡</sup>



**Figure 17.** Solid-state structure of a three-coordinate Al hydrido cation bearing a *N*-imidoylamidinate bidentate ligand (with partial atom labeling for clarity).

#### Scheme 21



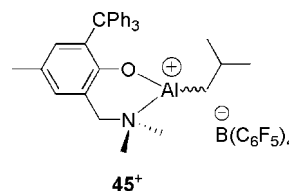
= 49(1) kJ mol<sup>−1</sup> and ΔS<sup>‡</sup> = −54(6) J mol<sup>−1</sup> K<sup>−1</sup>). While the entropy term suggests a bimolecular process and, thus, favors the proposition of a dissociative exchange pathway (Scheme 21), an intramolecular exchange process cannot be entirely excluded.

Although group 13 metal ions(III) are notoriously oxophilic, the use of *N,O*-type bidentate ligand as a supporting ligand for three-coordinate Al cations has been much less studied than that of π-delocalized *N,N*-ligands described above. The recent synthesis and characterization of a quasi-three-coordinate Al cation bearing a sterically demanding aminophenolate ligand constitute the only example in this area.<sup>61</sup> The aminophenolate isobutyl cation {2-CPh<sub>3</sub>-4-Me-C<sub>6</sub>H<sub>2</sub>O}Al<sup>+</sup> (**45**<sup>+</sup>, Figure 18) was readily prepared in bromobenzene by ionization of the corresponding dialkyl precursor with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. The weak coordinating properties of bromobenzene toward Al in {LX}AlR<sup>+</sup> systems, as previously observed with some *N,N*-ligand systems, most likely play a key role in the stability of **45**<sup>+</sup> through the formation of weak Al–BrPh adducts in solution. Nevertheless, cation **45**<sup>+</sup> clearly behaves as a three-coordinate species in solution.

### 3.2. Three-Coordinate Al Cations Only Incorporating Monodentate Ligands

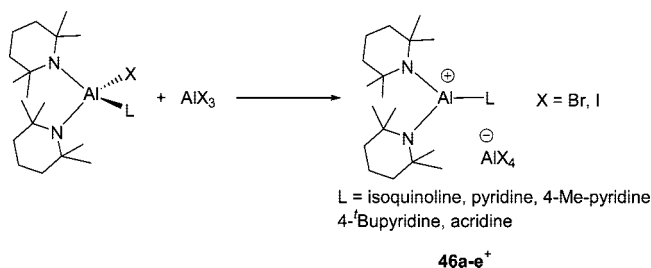
While the use of bulky bidentate ligands LX<sup>−</sup> has clearly appeared as a “privileged” method for the generation of stable three-coordinate group 13 species, cationic aluminum 13 species of the type LAIX<sub>2</sub><sup>+</sup>, which only incorporate simple monodentate ligands, have been much less studied. On that matter, a series of three-coordinate dipiperidinoaluminum cations (tmp)<sub>2</sub>AlL<sup>+</sup> (tmp = 2,2,6,6-tetramethylpiperidino, **46a**<sup>+</sup>–**46e**<sup>+</sup>) as AlX<sub>4</sub><sup>−</sup> salts have been reported by Nöth et al. and prepared through halide abstraction at the corresponding neutral precursors (tmp)<sub>2</sub>Al(X)L by AlX<sub>3</sub> (X = Br, I; Scheme 22).<sup>62</sup>

The formation of cations of type **46a**–**46e**<sup>+</sup>, the structures of which were deduced on the basis of <sup>27</sup>Al NMR data, conductivity, and computational results, shows that sterically demanding monodentate X-type ligands such as tmp may yield stable low-coordinate Al cations. Attempts to prepare cations **46a**–**46e**<sup>+</sup> as BPh<sub>4</sub><sup>−</sup>, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup>, or Otos<sup>−</sup> salts through halide abstraction led to either decomposition products or the formation of molecular adducts. Additionally,



**Figure 18.** Three-coordinate Al alkyl cation supported by a bidentate aminophenolate ligand.

Scheme 22



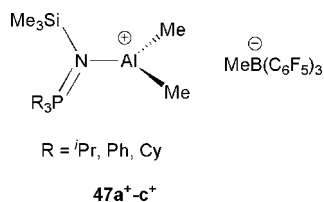
the ionization of the Al–pyridine halide precursor  $(\text{tmp})_2\text{Al}(\text{X})(\text{py})$  with  $\text{Ag}[\text{BF}_4]$  yields the salt compound  $[(\text{tmp})_2\text{Al}(\text{X})(\text{py})][\text{BF}_4]$ , which fully dissociates into the Al cation  $(\text{tmp})_2\text{Al}(\text{py})^+$  and the anion  $\text{BF}_4^-$  in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  solution.

Sterically bulky monodentate phosphinimine ligands may also be suitable for the stabilization of tricoordinated alkyl group 13 complexes. Thus, stable three-coordinate phosphinimine Al dimethyl cations ( $\text{R}_3\text{P} = \text{NSiMe}_3$ ) $\text{AlMe}_2^+$  (**47a<sup>+</sup>**–**47c<sup>+</sup>**; R = <sup>t</sup>Pr, Ph, Cy; Figure 19) were found to be readily accessible through a  $\text{Me}^-$  abstraction by  $\text{B}(\text{C}_6\text{F}_5)_3$  at the corresponding neutral precursors ( $\text{R}_3\text{P}=\text{NSiMe}_3$ )- $\text{AlMe}_3$ .<sup>63</sup>

### 3.3. Three-Coordinate Thallium Cations

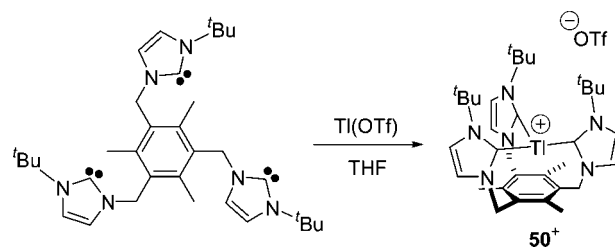
Since 1998, very few reports mentioned the synthesis and characterization of three-coordinate thallium cations weakly interacting with their counterions. These include the obtainment of the  $\text{Tl}(\text{I})$ – $\text{Et}_2\text{O}$  cation  $\text{Tl}(\text{Et}_2\text{O})_3^+$  (**48<sup>+</sup>**) as a  $(\text{NH}_2)\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$  salt, which was generated by reaction of  $[\text{H}(\text{OEt})_2][(\text{NH}_2)\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  with  $\text{TlOEt}$ . The latter salt was used as a precursor for the synthesis of the new  $\text{Tl}(\text{I})$ –arene complex  $[\text{Tl}(\text{toluene})_3][(\text{NH}_2)\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  (**49**) $[(\text{NH}_2)\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ . Remarkably, its solid-state structure displays discrete  $\text{Tl}(\text{toluene})_3^+$  cations (**49<sup>+</sup>**) free of bonding contacts to the counterion.<sup>46</sup> The environment around the thallium atom consists of three toluene rings, all of which are  $\eta^6$ -coordinated to the metal. The  $\text{Tl}$ – $\text{C}_{\text{centroid}}$  distances (from 2.942 to 3.010 Å) are indicative of very substantial interactions between  $\text{Tl}$  and the coordinated toluene molecules.

The synthesis and characterization of the triscarbene cationic complex of  $\text{Tl}(\text{I})$  (**50<sup>+</sup>**) has also been reported.<sup>64</sup> Thus, the reaction of the tripodal carbene 1,3,5-{tris(3-tert-butylimidazol-2-ylidene)methyl}-2,4,6-trimethylbenzene with  $\text{Tl}(\text{OTf})$  yields the three-coordinate  $\text{Tl}(\text{I})$  cation **50<sup>+</sup>** as a fully dissociated  $\text{TfO}^-$  salt as determined by X-ray crystallographic studies (Scheme 23). As illustrated in Figure 20, in the solid state, the tripodal carbene in cation **50<sup>+</sup>** coordinates the thallium atom in the expected tridentate conformation, but the three carbene centers are not symmetrically bound to the  $\text{Tl}(\text{I})$  atom, which was ascribed to the sterically demanding <sup>t</sup>Bu groups.



**Figure 19.** Three-coordinate Al alkyl cations incorporating a monodentate phosphinimine ligand.

Scheme 23



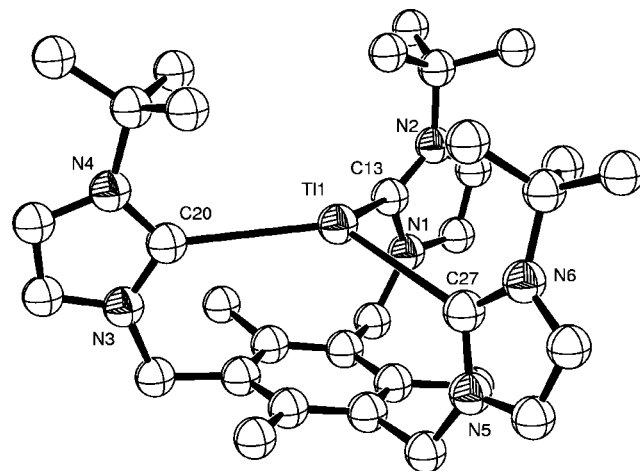
### 3.4. Reactivity Trends and Catalytic Applications of Three-Coordinate Group 13 Alkyl Cationic Derivatives

This section aims at providing insight into the type of reactivity exhibited thus far by  $\{\text{LX}\}\text{MR}^+$  group 13 metal alkyl cations, which have attracted the strongest interest over the past few years among three-coordinate group 13 cations. Rather than an exhaustive listing of compounds derived from reactivity studies, we wish to present the key reactivity trends of these cations toward small unsaturated organic substrates as well as the catalytic applications of the compounds. As can be expected, the reactivity of  $\{\text{LX}\}\text{MR}^+$  cations toward most substrates generally yields the formation of much more stable four-coordinate group 13 cations, some of which are structurally unique and unprecedented; while the reactions of some of these cations are mentioned in the present section, most of them are included in the Four-Coordinate Group 13 Cations section (*vide infra*). Comparison of the reactivity of  $\{\text{LX}\}\text{MR}^+$  group 13 cations relative to that of their neutral analogues is also briefly discussed here as this is of particular interest, both from a fundamental and an applied point of view, to gain insight on the influence of the cationic charge in these systems.

#### 3.4.1. Reactivity of $\{\text{LX}\}\text{MR}^+$ Group 13 Metal Cations toward Lewis Bases, Ketones, and Propylene Oxide

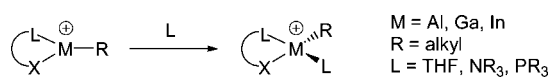
The reactivity of  $\{\text{LX}\}\text{MR}^+$  cations is dominated by their potent Lewis acid character; accordingly, these three-coordinate cations readily form robust four-coordinate cationic adducts  $\{\text{LX}\}\text{M}(\text{R})(\text{L})^+$  in the presence of common Lewis bases (L) such as thf, tertiary amines, and  $\text{PMe}_3$  (Scheme 24).

Unlike that of neutral group 13 alkyls such as  $\text{MR}_3$  (M = Al, Ga), the reactivity of  $\{\text{LX}\}\text{MR}^+$  cations remains

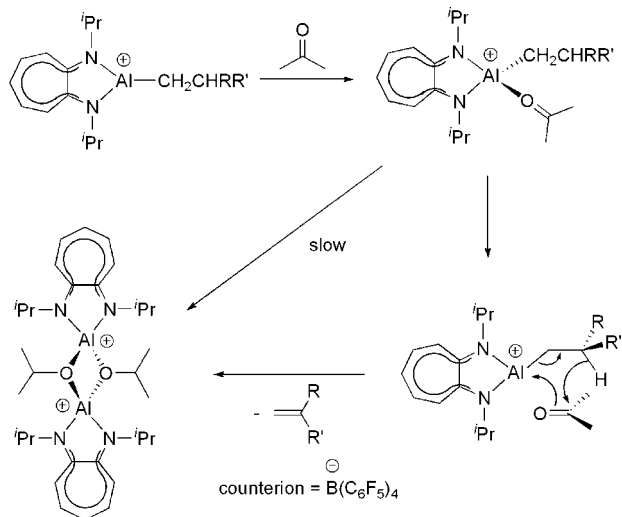


**Figure 20.** Solid-state structure of the tripodal carbene  $\text{Tl}(\text{I})$  cation **50<sup>+</sup>** with partial atom labeling for clarity.

Scheme 24



Scheme 25



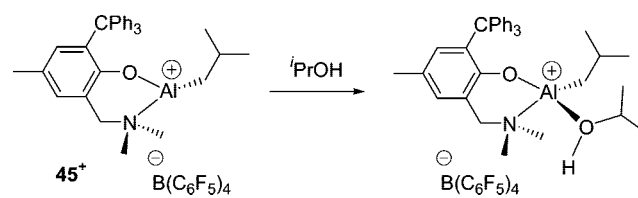
dominated by their potent Lewis acidity even with unsaturated substrates, as thoroughly demonstrated by reactivity studies with the  $\{i\text{Pr-ATI}\}AlR^+$  cations.<sup>49</sup> For instance, simple Al–acetonitrile cationic adducts  $\{i\text{Pr-ATI}\}Al(R)(\text{MeCN})^+$  ( $R = \text{Et, Pr, } i\text{Bu}$ ), generated upon reaction of  $\{i\text{Pr-ATI}\}AlR^+$  with MeCN, are remarkably stable and show no sign of reaction after 16 h at 180 °C in  $C_6H_5Cl$  solution. In contrast, neutral alkylaluminum compounds generally react with nitriles by insertion, C–H activation, or  $\beta$ -H transfer under similar conditions.<sup>65</sup>

When acetone is added to the  $\{i\text{Pr-ATI}\}AlR^+$  ( $R = \text{Et, Pr, } i\text{Bu}$ ) cations, the corresponding cationic Al–ketone Lewis base adducts  $\{i\text{Pr-ATI}\}Al(R)(O=CMe_2)^+$  readily form, but slowly and selectively  $\beta$ -H transfer to an isopropoxide Al dication (Scheme 25).<sup>66</sup> For comparison,  $AlEt_3$  reacts quickly with diethyl ketone by competitive ketone insertion into the Al–Et bond,  $\beta$ -H transfer, and enolization.<sup>67</sup>

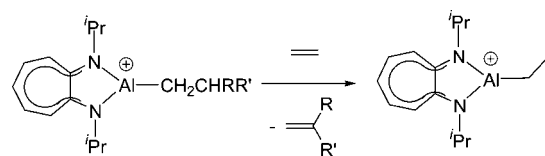
In agreement with the high Lewis acidity of  $\{LX\}MR^+$  cations, the three-coordinate  $\{i\text{PrATI}\}Al^i\text{Bu}^+$  cation ( $26^+$ ) is a very efficient initiator of propylene oxide (500 equiv of PO, 240 t.o./h) to yield atactic poly(propylene oxide).<sup>49</sup> Although the mechanism of this polymerization reaction has not been studied, a cationic Lewis acid assisted mechanism appears to be very likely, with an initial coordination of the monomer to the Al cationic center. Six-coordinate Al cations of the type  $(\text{Salen})Al(L)_2^+$  ( $L$  labile) have been reported to polymerize PO in a cationic manner (*vide infra*).<sup>68</sup>

Overall, these studies on the reactivity of  $\{ATI\}AlR^+$  species revealed a poor insertion reactivity in the Al–C bond toward unsaturated Lewis bases. In fact, these cations appear to be less reactive than neutral  $AlR_3$  species; this feature may be related to the strong Lewis acidity of such cations, which favors the stability of four-coordinate cationic species once formed and limits further reaction. Interestingly, three-coordinate Al alkyl cations may form stable four-coordinate adducts when reacted with protic Lewis bases such as  $i\text{PrOH}$ , without undergoing spontaneous protonolysis of the Al– $R^+$  bond, as usually observed when analogous neutral Al alkyl complexes are reacted with an alcohol derivative. Thus, the quantitative forma-

Scheme 26



Scheme 27



tion of  $\{2\text{-CPh}_3\text{-4-Me-C}_6\text{H}_2\text{O}\}Al(i\text{Bu})(i\text{PrOH})^+$  is observed upon reaction of the Al cation  $45^+$  with  $i\text{PrOH}$  (Scheme 26).<sup>61</sup> The Lewis acidity of the Al center along with steric factors rationalizes the stability of the Al–HO $i\text{Pr}$  adduct.

### 3.4.2. Reactivity of $\{LX\}MR^+$ Aluminum Cations toward Olefins

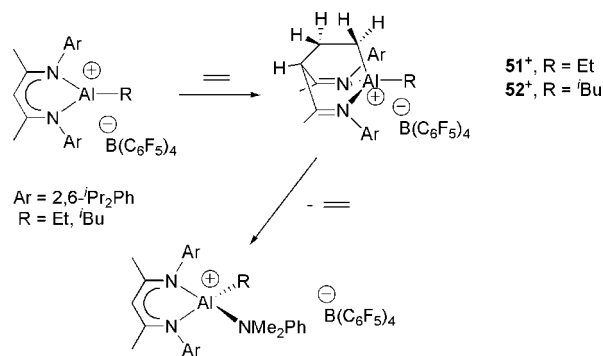
The promising possibility to use low-coordinate Al cations as catalysts for the polymerization of olefins such as ethylene is largely responsible for the interest in such species over the last 10 years, with the aim of designing inexpensive and transition-metal-free catalysts. In this area, three-coordinate Al cations of the type  $\{LX\}MR^+$  have appeared as good candidates as they contain an electron-deficient metal center able to coordinate an olefin, combined with a quite polar Al– $R^+$  bond that may insert the coordinated olefin. Alternatively, in view of their potent electrophilic character, a cationic polymerization of some olefins by  $\{LX\}MR^+$  cations may also be envisaged.

Although the  $\{i\text{Pr-ATI}\}AlR^+$  ( $R = \text{Et, } i\text{Bu}$ ) Al cations ( $24^+$  and  $26^+$ ) were originally thought to be active in ethylene polymerization, thorough studies on these cationic systems have clearly shown that  $\{i\text{Pr-ATI}\}AlR^+$  cations just undergo a fast and selective chain-transfer reaction through a  $\beta$ -hydrogen transfer process when combined with ethylene (Scheme 27).<sup>49</sup>

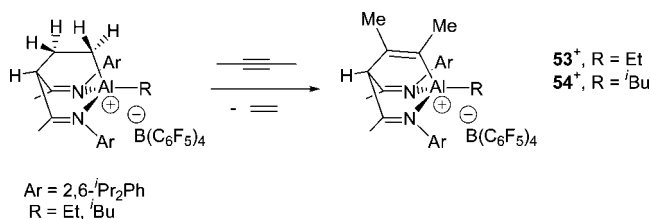
In a similar manner, the aminophenolate Al cation  $45^+$  (Figure 18) reacts fast with 1-hexene to yield the corresponding Al–hexyl cation along with isobutene, through a  $\beta$ -hydrogen transfer reaction.<sup>61</sup> Thus, as with ketone derivatives, three-coordinate Al cations exhibit a poor reactivity toward insertion into the Al–C bond with olefins. These experimental results matched theoretical studies performed on the putative ethylene polymerization activity of three-coordinate Al–amidinate and  $\{i\text{Pr-ATI}\}Al$  alkyl cationic systems.<sup>69</sup> All calculation methods agree that the energy barrier for chain transfer, through a bimolecular  $\beta$ -hydrogen transfer reaction to the monomer, is substantially easier than that for propagation, i.e., insertion of the monomer into the Al–C bond. In fact, the propagation/chain transfer balance for the modeled three-coordinate Al cations appears to be worse (higher preference for chain transfer) than that for  $Me_2AlEt$ , which is an ethylene oligomerization catalyst (Aufbau reaction).<sup>70</sup>

As for their reactivity with isobutene, it is noteworthy that the  $\{LX\}M^i\text{Bu}^+$  ( $LX^- = \text{ATI}^-, \beta\text{-diketiminato}, \text{CPh}_3\text{-aminophenolate}$ ) monoalkyl cations  $26^+$  and  $45^+$ , generated

Scheme 28



Scheme 29



through a  $\beta$ -hydride abstraction from  $\{LX\}M^iBu_2$ , readily polymerize isobutene, generated as a side product, to afford atactic poly(isobutene).<sup>49,61</sup> In view of the potent electrophilic character of such low-coordinate Al cations and of precedent with two-coordinate Cp-based Al cations,<sup>24</sup> these polymerization reactions presumably proceed by a cationic mechanism.

Unlike that of the aforementioned  $\{LX\}AlR^+$ , the reactivity of the  $\beta$ -diketiminate Al-alkyl cations  $\{NacNac\}AlR^+$  (R = Et, *t*Bu) toward ethylene is rather peculiar and represents a spectacular illustration of the key role that may be played by the so-called supporting ligand in the reactivity of  $\{LX\}AlR^+$ . Thus, cations  $\{NacNac\}AlR^+$  (R = Et, *t*Bu) react fast with ethylene to yield the bicyclic  $\beta$ -diimine complexes (**51**<sup>+</sup>, R = Et; **52**<sup>+</sup>, R = *t*Bu; Scheme 28), through a cycloaddition process.<sup>71</sup> Remarkably, cations **51**<sup>+</sup> and **52**<sup>+</sup> also undergo cycloreversion and ethylene loss upon reaction of nucleophiles such as NMe<sub>2</sub>Ph under mild conditions (Scheme 28).

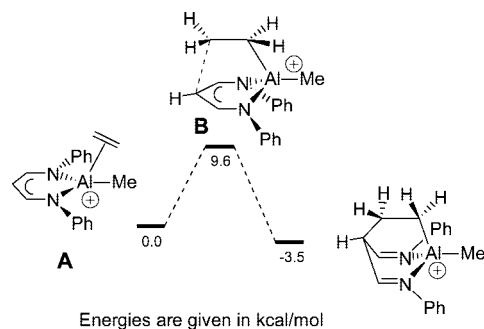
The ethylene cycloadducts **51**<sup>+</sup> and **52**<sup>+</sup> react with an alkyne such as 2-butyne to yield the newly alkyne cycloadducts **53**<sup>+</sup> and **54**<sup>+</sup> (Scheme 29), presumably by initial extrusion of ethylene followed by trapping of the generated  $\{NacNac\}AlR^+$  (R = Et, *t*Bu) by 2-butyne cycloaddition.

Recent DFT calculations on these cycloadditions of ethylene to  $\{NacNac\}AlMe^+$  systems suggest that these reactions proceed through the initial formation of an Al-ethylene adduct (**A**, Scheme 30). Adduct **A** would then cycloadd the coordinated alkene through a concerted asynchronous process through an unsymmetrical transition state (**B**), in which the new Al-C bond is almost fully formed, with the C=C bond length intermediate between the reactant and product distances, while the new C-C distance is long, to eventually afford the more stable cycloadduct.<sup>72</sup> The calculated energy profile for the cycloaddition of ethylene of  $\{NacNac\}AlMe^+$  is depicted in Scheme 30.

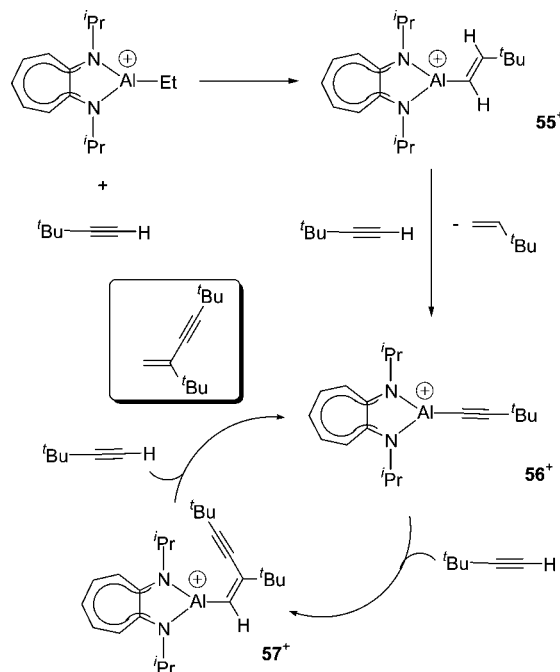
### 3.4.3. Reactivity of $\{LX\}AlR^+$ Aluminum Cations toward Alkynes

The reactivity of the Al cations  $\{iPr-ATI\}AlR^+$  (R = Et, *t*Bu) toward terminal alkynes has also been studied. These

Scheme 30



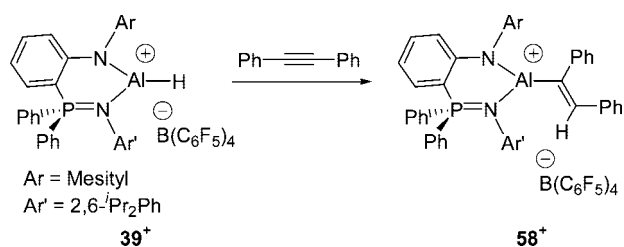
Scheme 31



cations were found to catalytically dimerize *t*BuC'CH to the head-to-tail dimer 2-*t*Bu-5,5-dimethyl-1-hexen-3-yne (RT, 4 t.o/h, >90% selectivity) through an insertion/ $\sigma$ -bond metathesis mechanism illustrated in Scheme 31.<sup>49,66</sup> According to this mechanism, the cationic vinyl Al cation **55**<sup>+</sup>, generated by an initial  $\beta$ -hydrogen reaction between  $\{ATI\}AlEt^+$  and *t*BuC'CH, reacts with additional *t*BuC'CH by  $\sigma$ -bond metathesis to yield the alkyne complex  $\{ATI\}Al-(C'CBu)^+$  (**56**<sup>+</sup>) and *t*BuC'CH; the Al alkyne cation **56**<sup>+</sup> appears to be the actual catalyst of the dimerization process. Thus, cation **56**<sup>+</sup> readily inserts *t*BuC'CH to yield cation **57**<sup>+</sup>, which upon a  $\sigma$ -bond metathesis reaction with *t*BuC'CH regenerates **56**<sup>+</sup> along with the dimeric product 2-*t*Bu-5,5-dimethyl-1-hexen-3-yne. The reactivity of the Al-alkyne complex **56**<sup>+</sup> with *t*BuC'CH thus represents the first example of an Al-C insertion reactivity toward unsaturated substrates of a  $\{LX\}MR^+$ -type species; in the present case, the absence of  $\beta$ -hydrogens on the Al-R<sup>+</sup> moiety in **56**<sup>+</sup> prevents any  $\beta$ -hydrogen transfer, which may play an important role in the observed reactivity toward *t*BuC'CH. Similarly, the three-coordinate Al hydride cation **39**<sup>+</sup>, which is supported by an anilido-phosphinimine bidentate ligand, was also found to slowly react with an alkyne such as diphenylacetylene to yield the hydroalumination product **58**<sup>+</sup>, through insertion into the Al-H bond (Scheme 32).<sup>58</sup> Notably, for comparison, AlR<sub>3</sub> compounds normally react with terminal alkynes R'C'CH predominantly



## Scheme 32



by  $\sigma$ -bond metathesis to give  $R_2Al-C'CR'$  and  $RH$ , while insertion and  $\beta$ -hydrogen transfer reactions are less common.<sup>73</sup>

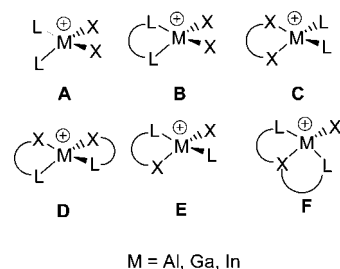
Finally, although the reactivity of three-coordinate gallium and indium cations has not been much studied, one should nevertheless mention that the three-coordinate indium  $\{ATI\}InMe^+$  was reported not to react with the alkyne  $HC'CBu$  and to show only trace activity for isobutene polymerization.<sup>57</sup> This decreased reactivity relative to the Al cationic analogs is certainly related to the less Lewis acidic character of In vs Al.

## 3.4.4. Summary

The reactivity of three-coordinate group 13 cations of the type  $\{LX\}AlR^+$  ( $R = \text{alkyl}$ ) is clearly dominated by their potent Lewis acidity as they form robust adducts with saturated Lewis bases such as tertiary amines, with thf, and even with protic Lewis bases such as *i*PrOH. The extreme Lewis acidity of  $\{LX\}AlR^+$  cations is most likely responsible for their excellent activity in isobutene and oxirane polymerizations. Their reactivity toward unsaturated substrates such as ketones and  $\alpha$ -olefins predominantly involves  $\beta$ -hydrogen transfer reactions with no  $M-C$  insertion reactivity, while that toward acetonitrile simply yields the corresponding Lewis base–acid cationic adduct. The preference for  $\beta$ -hydrogen transfer over insertion in the reactions with unsaturated substrates such as ketones and  $\alpha$ -olefins is more pronounced for  $\{LX\}AlR^+$  species than for neutral  $AlR_3$  compounds, which may reflect, at least in part, increased  $Al-R$  bond strengths due to the charge at Al. Notably, the ancillary ligand may greatly influence the outcome of the reaction between  $\{LX\}AlR^+$  and ethylene, as observed in the case of  $\{NacNac\}AlR^+$  derivatives, which, upon exposure to ethylene, afford unprecedented and unusual ethylene cycloadducts. The  $\{^iPr-ATI\}AlR^+$  cations were found to efficiently catalyze the dimerization of terminal alkynes. The insertion reactivity toward alkynes observed for the three-coordinate Al alkenyl cation  $\{ATI\}Al(C'CBu)^+$  and an anilido–phosphinimino Al hydrido cation contrasts with the reactivity of  $\{LX\}AlR^+$  toward most unsaturated substrates.

## 3.5. Highlight on Low-Coordinate Group 13 Cations

As described above, two- and three-coordinate group 13 cationic species, which combine a cationic metal center with a low coordination number, are highly electrophilic and Lewis acidic entities and, as such, have found applications in catalysis (isobutene and propylene oxide polymerization, dimerization of terminal alkynes) as well as in the mediation of other reactions ( $\beta$ -hydrogen transfer reactions to olefins or ketones). In addition to their potential usefulness, low-coordinate group 13 cationic species have also attracted



**Figure 21.** Different coordination modes for four-coordinate group 13 cations.

significant interest for a better understanding of the fundamental issues concerning their structures, bonding, and reactivity relative to their neutral analogues. This has opened the way to new fundamental and applied perspectives in group 13 chemistry.

From a synthetic point of view, the alkyl/hydride and, to a lesser extent, halide abstraction routes involving the ionization of neutral group 13 alkyl or halide precursors through abstraction of a  $X^-$  group ( $X = \text{alkyl, hydride, halide}$ ) at the metal center have dominated recent attempts to prepare low-coordinate group 13 cations. These approaches may allow the preparation of base-free (or coordinated by labile ligands) and, thus, low-coordinate group 13 cations. However, because of the high reactivity of the metal center in such cations, the isolation of stable and well-defined species requires two key features: (i) the use of an inert and weakly coordinating anion such as  $B(C_6F_5)_4^-$ ,  $B\{3,5-(CF_3)_2C_6H_3\}_4^-$ , or a  $CB_{11}H_6X_6^-$  carborane anion to limit interactions and possible decomposition reactions that may take place between the cation and the anion and (ii) the use of supporting ligands with a significant steric bulk to fill the sphere of coordination of the metal center in order to avoid decomposition reactions as well as the formation of aggregates.

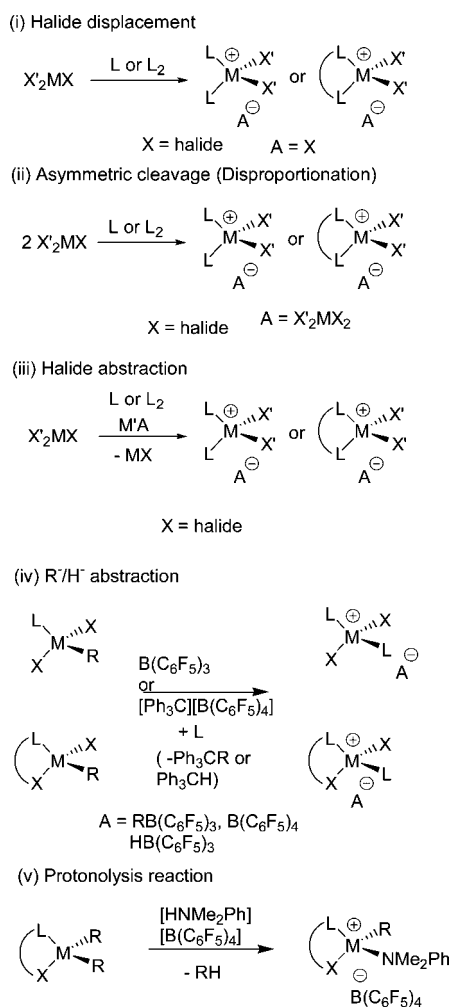
## 4. Four-Coordinate Group 13 Cations

## 4.1. Overview

Four-coordinate cations are the most common among group 13 cations as they incorporate an electronically saturated metal center, adopting its preferred tetrahedral geometry; features that greatly favor their formation and their stability. As a result, a wide structural variety of group 13 four-coordinate cations has been reported. For ease of description and clarity, this section will present the different classes of mononuclear cations according to six structural types **A–F** (Figure 21), reflecting the principal coordination modes observed thus far for these species. As for the dinuclear group 13 cations reported herein, their principal structural and reactivity features will also be discussed.

As illustrated in Figure 21, the modes **A–F** contain various combinations of neutral L and anionic X ligands with separate Lewis basic groups and those with ligands that are singly or doubly charged and contain internal basic donors. An early example of the first of these modes (type **A**),  $[Me_2Ga(H_2O)_2]^+$ , was prepared in 1968. It was formed through the reaction of  $Me_2GaOH$  with aqueous acid.<sup>3,4</sup> Shortly thereafter, the In derivatives were also accessed through this route. It was not until 1996 that the related Al derivatives,  $[Me_2Al(\text{base})_2]^+$ , were prepared through the displacement of Br or I from  $Me_2AlX$  with amines and  $Ph_3P$

Scheme 33



= O.<sup>74,75</sup> In the case of X = Cl, only adducts were obtained (Me<sub>2</sub>AlCl(amine)).

A detailed description of the remaining structural types with compounds published before 1998 is not appropriate here. However, it can be noted that all of the structural types, except type **E**, have been prepared (**B**,<sup>76</sup> **C**, **D**,<sup>77</sup> and **F**<sup>78</sup>) prior to 1997. As will be seen, type **E** group 13 cations have received the strongest interest over the past few years. It is noteworthy that the few compounds referenced for type **F** include the first (and only) chiral tetracoordinated Al cation.<sup>78</sup> Very few examples of types **C**, **D**, and **F** group 13 cations have been reported since 1998. It thus appears that four-coordinate group 13 cations with the coordination modes **A**, **B**, and **E** have been the most studied recently.

From a general synthetic point of view, four-coordinate group 13 cations were prepared, for the most part, according to the synthetic pathways depicted in Scheme 33: (i) a *halide displacement* route from X<sub>2</sub>MX (X = halide) and an external Lewis base L or L<sub>2</sub> (amines or phosphines, in general) causing the generation of a tetracoordinate cation of the type X<sub>2</sub>ML<sub>n</sub><sup>+</sup> as a X<sup>-</sup> salt; (ii) an *asymmetric cleavage* (or disproportionation reaction) involving the reaction of 2 equiv of a halido group 13 compound in the presence of a monodentate (L) or a bidentate (L<sub>2</sub>) Lewis base to yield a four-coordinate group 13 cation and an anion resulting from the addition of the generated halide to 1 equiv of the starting halido neutral group 13 compound; (iii) a *halide abstraction* reaction through salt metathesis from a neutral halido group

13 species by salts such as Na[BPh<sub>4</sub>], Na[B{C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>-3,5<sub>4</sub>], or Na[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] resulting in the formation of a tetracoordinate group 13 cation along with formation of NaX, with the latter reaction usually promoted by the presence of a monodentate (L) or bidentate (L<sub>2</sub>) Lewis base, which then coordinates to the newly formed cationic center; (iv) an *R<sup>-</sup>/H<sup>-</sup> abstraction* by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] from a four-coordinate dialkyl group 13 neutral species in the presence of a Lewis base L to afford tetracoordinate M–L cationic adducts as a MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> or B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> salts; and (v) a M–C protolysis reaction by the ammonium HNMe<sub>2</sub>Ph<sup>+</sup> at a four-coordinate dialkyl group 13 neutral species to yield the corresponding M–NMe<sub>2</sub>Ph cation.

## 4.2. Al Species

### 4.2.1. Type A–D Al Cations

Aluminum cations comprised within these four types of coordination have been the subject of several studies yielding the synthesis and characterization of the cationic compounds 59<sup>+</sup>–72<sup>+</sup>. These are depicted in Table 1 with references to the corresponding work.

**Synthesis of Type A Cations.** The type **A** cations 59<sup>+</sup>–64<sup>+</sup> essentially incorporate nitrogen-based ligands and, for the most part, are accessible either through the R<sup>-</sup> abstraction or protonolysis methods (Scheme 33).<sup>63,79,80</sup> The Al–thf methyl cation 64e<sup>+</sup> associated with the dinuclear zirconium anion [{Me<sub>2</sub>Si(NAr)<sub>2</sub>]<sub>2</sub>Zr<sub>2</sub>Cl<sub>5</sub>]<sup>-</sup> (Ar = 2,6-<sup>i</sup>PrPh) was prepared from reaction of {Me<sub>2</sub>Si(NAr)<sub>2</sub>}Zr(Cl)<sub>2</sub>(thf)<sub>2</sub> with 2 equiv of AlMe<sub>3</sub>.<sup>81</sup> The cation 61<sup>+</sup> is classically derived from AlMe<sub>2</sub>I and (*S*)-phenylethylamine through iodine displacement,<sup>82</sup> while the aniline cation 62<sup>+</sup> is derived from a dismutation reaction of a siloxaluminum alkyl compound with [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], as illustrated in Scheme 34.<sup>83</sup> We also note the generation and structural characterization of the dihydro Al cation H<sub>2</sub>Al(NMe<sub>3</sub>)<sup>+</sup> (63<sup>+</sup>).<sup>84</sup>

**Synthesis of Type B, C, and D Cations.** A few group 13 cations of the type {L<sub>2</sub>}AlX<sub>2</sub><sup>+</sup> (where L<sub>2</sub> is a bidentate neutral chelate, type **B** cations) have appeared in the literature since 1998 (65<sup>+</sup>–69<sup>+</sup>, Table 1). As shown below, the formation of these species may arise from unexpected reactivity. Thus, several unusual pathways allowing access to such cations have been recently reported, revealing new aspects of the reactivity of group 13 chelates and affording structurally interesting Al cationic species.

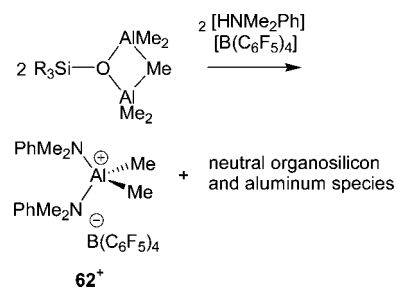
Eaborn et al. reported the synthesis of a peculiar zwitterionic species containing a four-coordinate Al cation and a planar carbanion (**65**) by reaction of the Li reagent [C(SiMe<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub>]Li with AlEt<sub>2</sub>Cl (Scheme 35).<sup>85</sup> The appearance of the AlEt<sub>3</sub> entity in 65<sup>+</sup> was rationalized in terms of the ready redistribution of AlR<sub>x</sub>Cl<sub>3-x</sub> species in the presence of alkali–metal halides. Interestingly, the outcome of the reaction is different when performed with AlCl<sub>3</sub>, in which case the formation of the “expected” salt metathesis product [C(SiMe<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub>]AlCl<sub>2</sub> is observed.

The unexpected formation of {L<sub>2</sub>}AlR<sub>2</sub><sup>+</sup> species was also observed in attempts to ionize {LX}AlR<sub>2</sub> aluminum derivatives with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in view of generating {LX}AlR<sup>+</sup> cations. Thus, Jordan et al. observed that {<sup>i</sup>Pr-ATI}AlR<sub>2</sub> (R = Me, Et) react with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at low temperature through electrophilic attack of Ph<sub>3</sub>C<sup>+</sup> at the <sup>i</sup>Pr-ATI C5 carbon to yield the thermally unstable Al diimine intermediates 66a<sup>+</sup>–66b<sup>+</sup>, which decompose to the corresponding

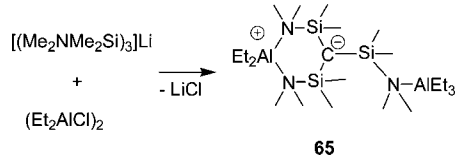
Table 1. Four-Coordinate Al Cations Referenced Adopting the Coordination Modes A–D

<p><b>59*</b> (ref. 79)</p>	<p><b>60*</b> (ref. 63)</p>	<p>[Me<sub>2</sub>Al{NH<sub>2</sub>-(S)-C(H)(Me)(Ph)}][I]<sup>-</sup></p> <p><b>[61][I]</b> (ref. 82)</p>	<p>[Me<sub>2</sub>Al(NMe<sub>2</sub>Ph)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup></p> <p><b>[62][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]</b> (ref. 83)</p>
<p>[H<sub>2</sub>Al(NMe<sub>3</sub>)<sub>2</sub>].0.5[(AlH)<sub>8</sub>(CCH<sub>2</sub><sup>t</sup>Bu)<sub>6</sub>]</p> <p><b>[63][0.5(AlH)<sub>8</sub>(CCH<sub>2</sub><sup>t</sup>Bu)<sub>6</sub>]</b> (ref. 84)</p>	<p>[Me<sub>2</sub>Al(OEt<sub>2</sub>)<sub>2</sub>][A]<sup>+</sup></p> <p><b>[64a-c][A]</b>: R = Me, Et, octyl; A = MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>  <b>[64d][A]</b>: R = Me; A = MeB(C<sub>12</sub>F<sub>9</sub>)<sub>3</sub>  <b>[64e][A]</b>: R = Me; A = {Me<sub>2</sub>Si(NAr)<sub>2</sub>Zr<sub>2</sub>Cl<sub>5</sub>}</p> <p>(refs. 80, 81)</p>	<p><b>65</b> (ref. 85)</p>	<p><b>66a-b*</b> (ref. 49)</p>
<p><b>67*</b> (ref. 54)</p>	<p><b>[68a-c][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]</b>: X = Me, H, D  <b>[68d][AlMe<sub>4</sub>][AlMe<sub>3</sub>]</b>: X = Me  <b>[68e][AlI<sub>4</sub>]</b>: X = I</p> <p>(ref. 60)</p>	<p><b>69*</b> (ref. 86)</p>	<p><b>70a-b*</b>: L = Ph<sub>3</sub>P=O, HMPA</p> <p>(ref. 82)</p>

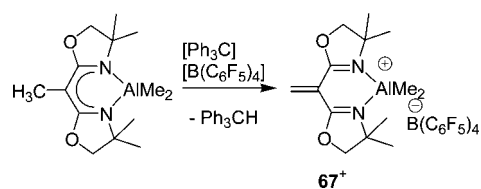
## Scheme 34



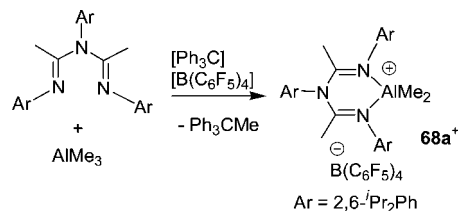
## Scheme 35



## Scheme 36



## Scheme 37

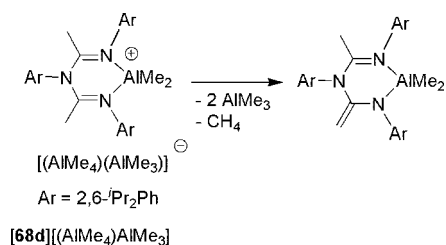


three-coordinate Al cations {<sup>*i*</sup>Pr-ATI}AlR<sup>+</sup>.<sup>49</sup> More recently, a bis(oxazolinato)aluminum dimethyl compound {BOX-Me<sub>2</sub>}AlMe<sub>2</sub> was found to react with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to quantitatively form the stable dimine Al cation **67\*** (Scheme 36).<sup>54</sup> The formation of cation **67\*** proceeds through hydride abstraction by Ph<sub>3</sub>C<sup>+</sup> at the Me group located at the back of the BOX ligand in the neutral compound {BOX-Me<sub>2</sub>}AlMe<sub>2</sub>. Hydride abstraction, i.e., at a bidentate LX<sup>-</sup> ligand chelating the metal center and rather far away from this metal center, further illustrates the rich reactivity group 13 chelates might exhibit when reacted with a strong Lewis acid such as Ph<sub>3</sub>C<sup>+</sup>.

The {L<sub>2</sub>}AlX<sub>2</sub><sup>+</sup>-type *N*-imidoylamidine Al cations **68a\***–**68e\*** were also very recently shown to be readily accessible.<sup>60</sup> While the diido cationic analogue **68e\*** was generated as an AlI<sub>4</sub><sup>-</sup> salt from the neutral diimine ligand and excess AlI<sub>3</sub> through an asymmetric cleavage pathway, the cationic derivatives **68a\***–**68c\*** may be formed as B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> salts in a straightforward manner by simply reacting a stoichiometric amount of the neutral ligand, AlX<sub>3</sub> (X = Me, H, D, respectively) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], as illustrated in Scheme 37 in the case of **68a\***.

Notably, the compound **[68d][AlMe<sub>4</sub>AlMe<sub>3</sub>]**, also synthesized by reaction of the neutral diimine ligand and excess AlMe<sub>3</sub>, was formulated as an Al cation associated with the

## Scheme 38



$[\text{AlMe}_4]^- \cdot \text{AlMe}_3$  anionic moiety on the basis of elemental analysis. This salt species is apparently unstable and readily decomposes to a neutral Al chelate along with  $\text{AlMe}_3$  and  $\text{CH}_4$  (Scheme 38). A likely mechanism for this unusual transformation was proposed by the authors on the basis of kinetic data and various NMR control experiments.<sup>60</sup>

One should finally mention that cation **69**<sup>+</sup> incorporating a bicyclic guanidine ligand was prepared by reaction of the corresponding *N*-protonated guanidinium cation (as a  $\text{BPh}_4^-$  salt) with  $\text{AlMe}_3$ , thus illustrating an alternative route for the clean generation of Al cations of the type  $\{\text{L}_2\}\text{AlR}_2^+$ .<sup>86</sup>

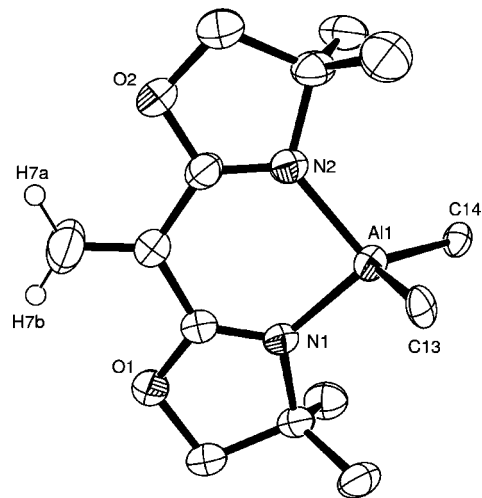
The Al cations **70a**<sup>+</sup>–**70b**<sup>+</sup>, the only examples of type C cations reported since 1998, were prepared through  $\text{I}^-$  displacement from a neutral biphenolate iodo Al compound in the presence of the Lewis bases  $\text{P}(\text{=O})\text{Ph}_3$  and HMPA, respectively.<sup>82</sup> As for the type D Al lactate cations **71**<sup>+</sup> and **72**<sup>+</sup>, these were prepared by reaction of  $\text{Me}_2\text{AlI}$  with (*S*)-(–)-ethyl lactate and (*R*)-(–)-pantolone, respectively.<sup>82</sup>

**Structure and Reactivity of Type A–D Al Cations.** The reactivity and potential catalytic applications of Al cations of the type A–D remain to be studied and evaluated. The lack of interest for such entities may be due to the fact that they incorporate an electronically saturated Al center and, at least in the case of  $\{\text{L}_2\}\text{AlX}_2^+$  (type B cations), with no labile L ligand susceptible to generate a vacant coordination site in catalytic conditions. Accordingly, such derivatives are often remarkably stable.

Although a few molecular structures of type A Al cations have been reported, these exhibit rather classical features comparable to those observed, for instance, with the Al cations  $[\text{Me}_2\text{Al}(\text{base})_2]^+$  (base = amine) reported in 1996.<sup>74,75</sup> Three new  $\{\text{L}_2\}\text{AlX}_2^+$  (type B cations **67**<sup>+</sup>, **68d**<sup>+</sup>, and **69**<sup>+</sup>) have recently been X-ray characterized, and they all do incorporate a bidentate bisimine-type chelate forming a six-membered ring Al metallacycle,<sup>54,60,85</sup> as an example, the molecular structure of cation **67**<sup>+</sup> is illustrated in Figure 22. The Al center in these three cations adopts a distorted tetrahedral structure with the N–Al–N bite angle (96.2° average) resulting in an opening of the X–Al–X bond angles. One can also note that the Al–N<sub>imine</sub> bond distances (1.92 Å average) are shorter than those in neutral Al imine complexes (1.97 Å average), as a result of the increased ionic character of the Al–N bonds when going from neutral to cationic derivatives.

## 4.2.2. Type E–F Al Cations

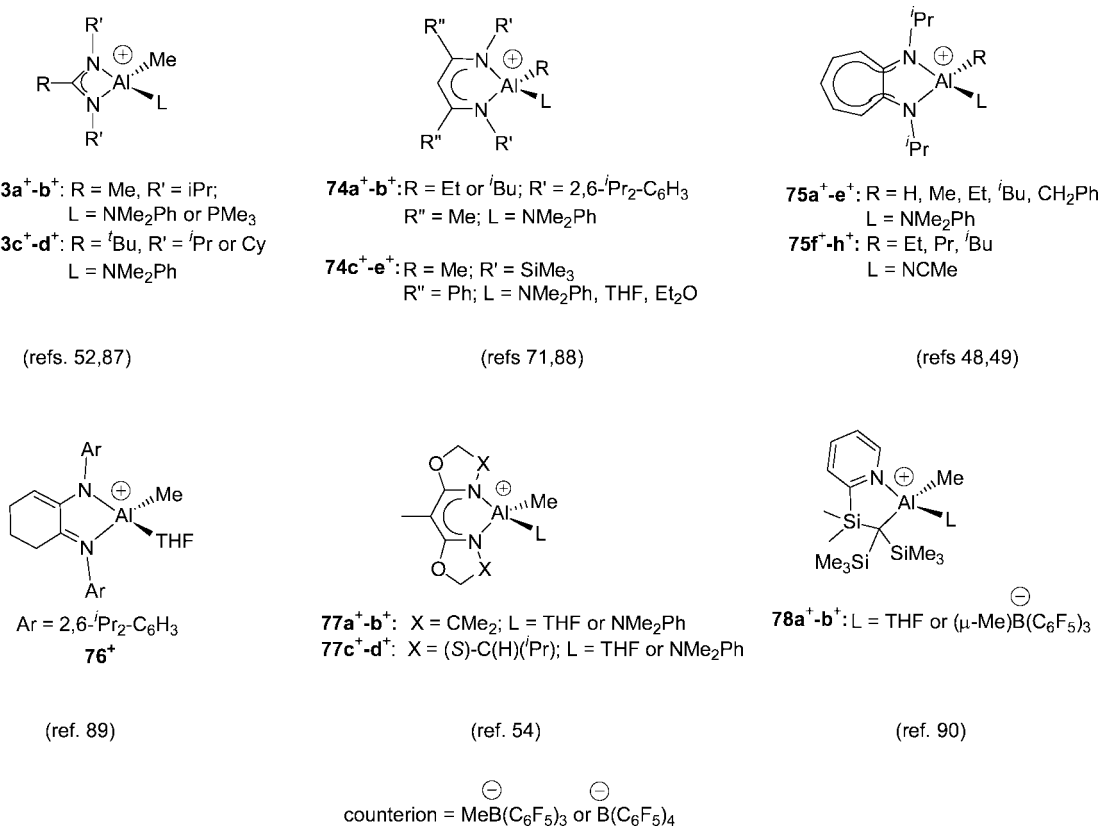
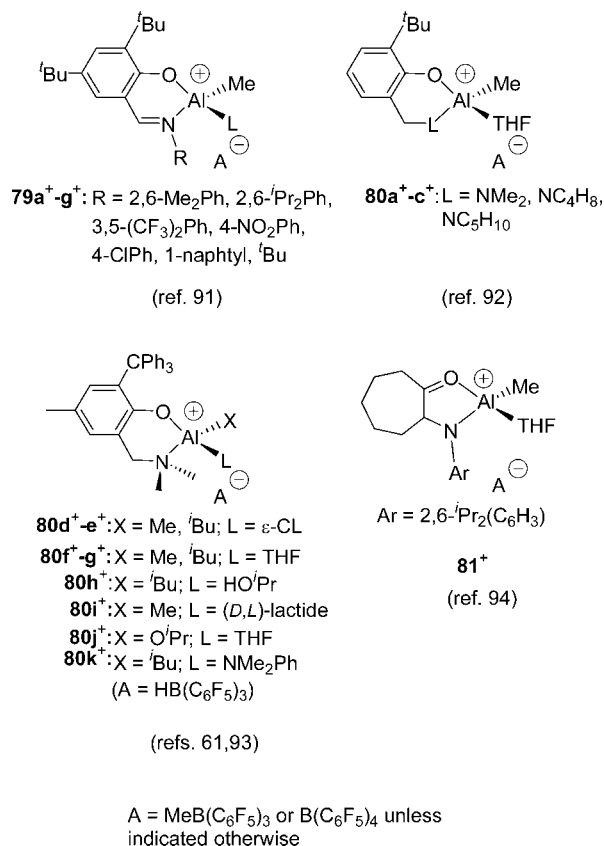
Aluminum cations of the types  $\{\text{LX}\}\text{Al}(\text{X})(\text{L})^+$  and, to a lesser extent,  $\{\text{L}_2\text{X}\}\text{Al}(\text{X})^+$  (X = alkyl, alkoxide) have recently been the subject of numerous research efforts. Interest in this class of species undoubtedly stems from the fact that the potential lability of L renders such species a formal source of highly reactive, yet more stable, three-coordinate  $\{\text{LX}\}\text{AlX}^+$ .



**Figure 22.** Solid-state structure (with partial atom labeling for clarity) of the bioxazoline–Al dimethyl cation **67**<sup>+</sup> (type B Al cation).

**Synthesis.** Numerous reports have appeared in the literature dealing with the generation of  $\{\text{LX}\}\text{Al}(\text{X})(\text{L})^+$  (type E) or  $\{\text{L}_2\text{X}\}\text{AlX}^+$  (type F) Al cations supported by various chelating ligands, and these are listed in Tables 2–4. From these tables, it clearly appears that *N,N*- and *O,N*-type bidentate chelating ligands as well as *N,N,N*- and *O,N,N*-monoanionic tridentates have been the most studied owing to the ready accessibility and tunability of these ligands and the excellent coordination properties of N and O toward group 13 metals. Nearly all  $\{\text{LX}\}\text{Al}(\text{R})(\text{L})^+$  (type E) Al alkyl cations were prepared through a  $\text{R}^-/\text{H}^-$  abstraction reaction by  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  from  $\{\text{LX}\}\text{AlR}_2$  in the presence of a Lewis base L.<sup>48,49,52,54,61,71,87–94</sup> Alternatively, protonolysis reaction between  $\{\text{LX}\}\text{AlR}_2$  and  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  may also be used. With the exception of compounds **82a**<sup>+</sup>–**82c**<sup>+</sup> and **85a**<sup>+</sup>–**85e**<sup>+</sup>,<sup>95,96</sup> the type F Al cations  $\{\text{LL}'\text{X}\}\text{AlR}^+$  were also prepared following the “ $\text{R}^-/\text{H}^-$  abstraction” ionization pathway but in the absence of an external Lewis base because the ancillary ligand  $\text{LL}'\text{X}^-$  incorporates an extra Lewis base L' that stabilizes the generated cationic center.<sup>97–100</sup> Four-coordinate Al cationic alkyl and aryl species may also be accessible in a straightforward manner through chloride abstraction as recently demonstrated by the preparation of cations **85a**<sup>+</sup>–**85c**<sup>+</sup> from reaction of a neutral precursor  $\{\text{LL}'\text{X}\}\text{Al}(\text{Me})(\text{Cl})$  with  $\text{NaBPh}_4$  or  $\text{AlCl}_3$ .<sup>96</sup> While this method is obviously attractive because it involves relatively cheap ionizing agents ( $\text{NaBPh}_4$  or  $\text{AlCl}_3$  versus  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ), the solution structure of these species may be complicated by ligand exchange reaction between the Al cation and the counterion  $\text{BPh}_4^-$ , yielding a mixture of cations **85b**<sup>+</sup> and **85c**<sup>+</sup>. This illustrates the fact that the use of an inert counterion is often a key requirement for the generation of well-defined four-coordinate Al alkyl cations. A simple protonation reaction may also yield Al cations of type F provided the appropriate chelating ligand is used. Thus, neutral aminobisamido complexes of the type  $\{\eta^3\text{-R}'\text{N}(\text{CH}_2)_2\text{N}(\text{R}')(\text{CH}_2)_2\text{NR}'\}\text{AlCl}$  readily react with HCl and  $\text{AlCl}_3$  to afford the bisaminoamide cations **82a**<sup>+</sup>–**82c**<sup>+</sup>, through protonation of an amido nitrogen atom.<sup>95</sup>

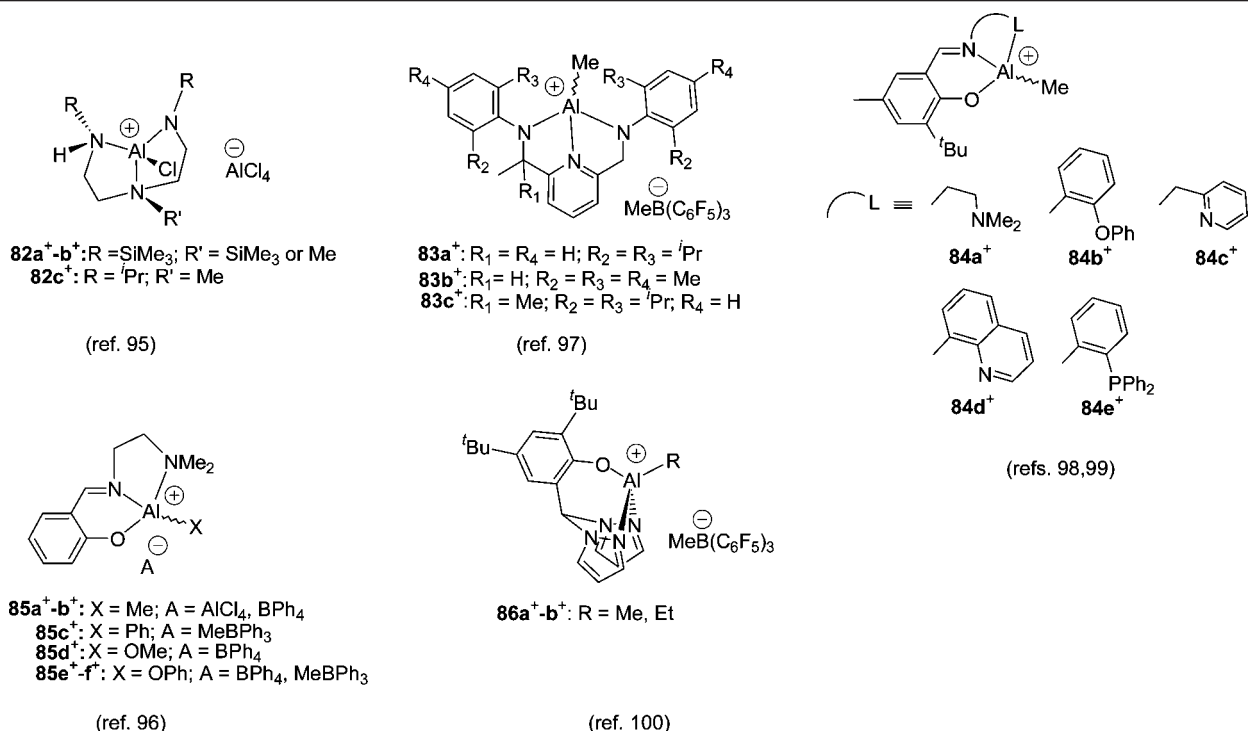
While the literature is largely dominated by the synthesis of four-coordinate cationic Al alkyls, a couple of recent studies have shown that these cations may be easily converted into alkoxide cationic derivatives, which are

**Table 2. Four-Coordinate *N,N'*- and *C,N'*-Chelate Al Cations Referenced As Type E****Table 3. Four-Coordinate *O,N*- and *N,O*-Chelate Al Cations Referenced As Type E**

**85a<sup>+</sup>–85c<sup>+</sup>** were found to readily react with excess O<sub>2</sub> to afford the clean formation of the corresponding alkoxides compounds **85d<sup>+</sup>–85f<sup>+</sup>**.<sup>96</sup> Alternatively, a clean Al–R<sup>+</sup> alcoholysis occurred when the {NO}Al chelates **80f<sup>+</sup>–80g<sup>+</sup>** were reacted with *t*PrOH, thus yielding the Al alkoxide derivative **80j<sup>+</sup>**.<sup>61</sup>

**Solid-State and Solution Structures.** The solid-state structures of several {LX}Al(X)(L)<sup>+</sup> (type E) Al cations have been determined, providing insight into the bonding trends that might be expected for this class of Al chelates. Structurally characterized {LX}Al(X)(L)<sup>+</sup> cations bearing a *N,N*- and *N,O*-type chelating ligand are by far the most common, and their key bonding parameters are listed in Table 5, which also lists the corresponding parameters for the neutral analogues {LX}AlR<sub>2</sub> as a comparison. As representative examples, the molecular structures of **74c<sup>+</sup>** and **75f<sup>+</sup>** are depicted in Figures 23 and 24, respectively. The Al center in all these cations adopts a distorted tetrahedral geometry with X–Al–L angles ranging from ca. 83° to 103°. The Al–X and Al–L chelate bond distances are in general significantly shorter in cationic {LX}Al(X')(L')<sup>+</sup> than in neutral {LX}AlR<sub>2</sub> species, which reflects stronger bonding of the {LX}Al chelate in the former systems and arises from an increased ionic character. The extent of this shortening appears to be dependent upon the nature of X' and L', as deduced from comparing data for the *O,N*-based cations **80d<sup>+</sup>**, **80h<sup>+</sup>**, **80j<sup>+</sup>**, and **80k<sup>+</sup>**, all of which were supported by the same NO<sup>−</sup> ligand.<sup>61,93</sup> Thus, for example, the Al–N<sub>chelate</sub> and Al–O<sub>chelate</sub> bond distances of the alkoxide cation **80j** are dramatically shorter (~0.1 and ~0.05 Å, respectively) than those in the neutral analogue, while those of the Al–NMe<sub>2</sub>Ph cation **80k<sup>+</sup>** exhibit a smaller deviation (~0.04 and ~0.02 Å, respectively). This may reflect the more

of interest in catalysis, through a controlled oxygenation or alcoholysis process. Thus, the alkyl compounds

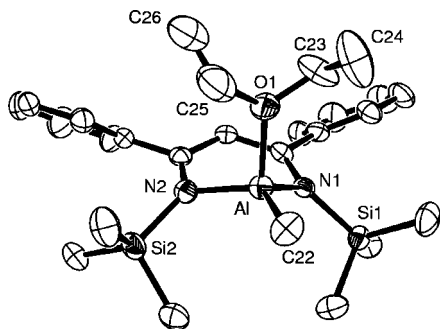
**Table 4. Four-Coordinate Al Cations Referenced as Type F****Table 5. Key Structural Parameters for X-ray Characterized N<sub>2</sub>N- and N<sub>2</sub>O-{LX}Al(X)(L)<sup>+</sup> Cations**

compound	Al-N <sub>chelate</sub> (average)	Al-C	N-Al-N <sub>chelate</sub>
<b>74c<sup>+</sup></b>	1.872(4)	1.951(5)	102.6(2)
<b>74d<sup>+</sup></b>	1.868(4)	1.941(5)	100.8(2)
neutral precursor	1.921(4)	1.959(5)	97.1(2)
<b>75f<sup>+</sup></b>	1.855(1)	1.942(2)	87.04(5)
neutral precursor	1.915(1)	1.967(2)	83.3(1)
<b>77b<sup>+</sup></b>	1.942(6)	1.854(2)	95.8(2)
neutral precursor	1.903(1)	1.967(2)	93.13(7)

compound	Al-N <sub>chelate</sub>	Al-O <sub>chelate</sub>	Al-C	O-Al-N
<b>80d<sup>+</sup></b>	1.935(3)	1.719(2)	1.919(5)	99.88(13)
<b>80h<sup>+</sup></b>	1.961(7)	1.713(5)	1.917(10)	97.5(3)
<b>80j<sup>+</sup></b>	1.928(3)	1.710(3)	1.946(4)	102.05(12)
<b>80k<sup>+</sup></b>	1.985(4)	1.735(3)	1.946(4)	97.8(1)
neutral precursor	2.023(2)	1.764(2)	1.974(3)	93.98(8)

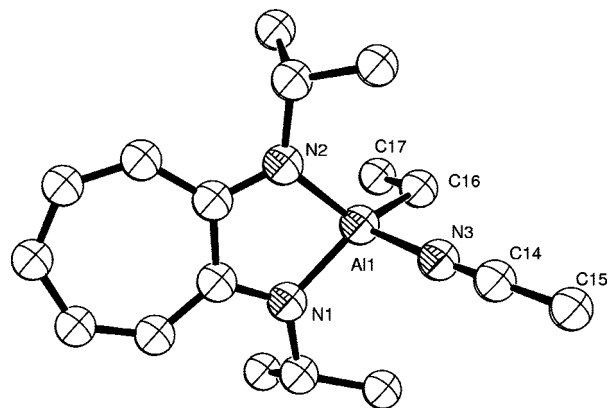
electrodeficient Al center in **80j<sup>+</sup>** versus **80k<sup>+</sup>**, a result of the more electronegative X group in **80j<sup>+</sup>** (X' = O<sup>i</sup>Pr) versus **80k<sup>+</sup>** (X' = Me) combined with the more donating properties of NMe<sub>2</sub>Ph versus thf. For a given LX<sup>-</sup> ligand, key bonding distances may constitute a useful probe to estimate the electron deficiency of these cationic compounds.

**Figure 23.** Solid-state structure of a four-coordinate Al-Et<sub>2</sub>O alkyl cation supported by a β-diketiminato ligand (**74e<sup>+</sup>**) with partial atom labeling for clarity.

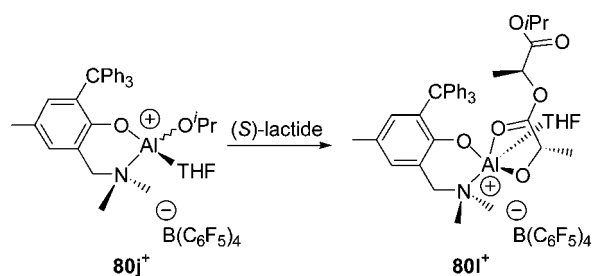
In {LX}Al(X')(L')<sup>+</sup> species, the L' ligand (L' = thf, NMe<sub>2</sub>Ph) has been observed, in most cases, to be labile (room temperature, chlorinated solvents) when it is used in excess, which suggests that this dynamic process proceeds through an associative mechanism.<sup>49</sup> Evidence for the lability of L' in {LL'X}Al(X')<sup>+</sup> cations has also been reported for compounds **84a<sup>+</sup>-84b<sup>+</sup>** and **85a<sup>+</sup>-85b<sup>+</sup>**.<sup>87,89</sup> On the basis of their solution behavior, these cations may, thus, effectively be seen as potential {LX}Al(X')<sup>+</sup> sources.

**Stability, Reactivity, and Applications in Catalysis.** When compared to their lower coordinate chelate analogues, {LX}Al(X)(L)<sup>+</sup> (type E) or {L<sub>2</sub>X}AlX<sup>+</sup> (type F) are remarkably stable when generated as Me(BC<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> or B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> salts. More reactive counterions such as AlCl<sub>4</sub><sup>-</sup> may even be used without loss of stability (with cations **82a<sup>+</sup>-82c<sup>+</sup>** and **85a<sup>+</sup>**).

Often seen as a potential source of three-coordinate Al cations but yet stable, these highly Lewis acidic cations have attracted much attention for their applications in polymeri-

**Figure 24.** Solid-state structure of the four-coordinate Al cation {<sup>i</sup>Pr-ATI}Al(Et)(NCMe)<sup>+</sup> (**75f<sup>+</sup>**) with partial atom labeling for clarity.

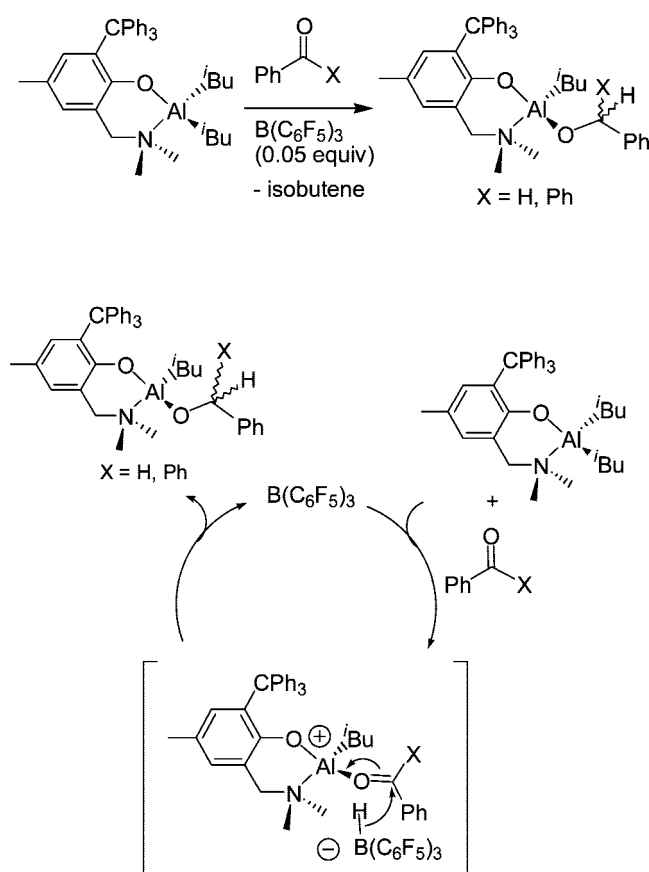
Scheme 39



zation catalysis of various substrates. While several initial and independent studies in this area reported that Al alkyl cations {LX}Al(R)(L)<sup>+</sup> (type E) or {L<sub>2</sub>X}AlR<sup>+</sup> (type F) may polymerize ethylene,<sup>87,89,97</sup> subsequent experimental and theoretical studies have ruled out this proposal.<sup>49,69,70</sup> Type E and F Al alkyl cations appear to be much more reactive with polar monomers such as methylmethacrylate (MMA), propylene oxide, and cyclic esters like (D,L)-lactide and  $\epsilon$ -caprolactone. In this regard, preliminary studies by Lappert et al. showed that the Al cation **74c**<sup>+</sup> catalyzes the conversion of MMA to syndiotactic PMMA of low dispersity.<sup>88</sup> Bertrand et al. reported that the polymerization of (D,L)-lactide may be initiated by the Al complex **82b**<sup>+</sup> in the presence of propylene oxide (PO) to afford atactic polylactic acid, albeit with low activity (best run: 50 equiv of monomer, toluene, 50 °C, 5 d, 46% yield,  $M_w/M_n = 1.23$ ).<sup>95</sup> In the latter system, the role of PO appears to be crucial as it inserts into the Al–Cl<sup>+</sup> bond of **82b**<sup>+</sup> to generate an Al–OR<sup>+</sup> species susceptible to undergo ring-opening polymerization (ROP) of (D,L)-lactide. Notably, the Al cation **82a**<sup>+</sup> was also shown to oligomerize propylene oxide ( $M_n = 1416$ ,  $M_n/M_w = 1.18$ ) with low activity: this catalysis was proposed to proceed through successive insertions into an Al–O bond (formed in situ) rather than through a Lewis acid-assisted cationic mechanism. More recently, the Al cations **80j**<sup>+</sup> and **85d**<sup>+</sup>–**85f**<sup>+</sup>, which both incorporate a terminal alkoxide Al–OR<sup>+</sup> moiety, were demonstrated to be highly active in the ROP of  $\epsilon$ -caprolactone (from 50 to 120 equiv of  $\epsilon$ -CL) to quantitatively yield poly( $\epsilon$ -CL) of low dispersity (ranging from 1.24 to 1.53).<sup>61,96</sup> The catalytic activity of both cations in  $\epsilon$ -CL polymerization compares to that of the best neutral Al catalysts developed thus far. Different control experiments are consistent with this polymerization proceeding selectively through successive ring-opening/insertion reactions into the terminal Al–OR<sup>+</sup> bond. As demonstrated recently with the Al alkyl cations **86a**<sup>+</sup>–**86b**<sup>+</sup>, it is noteworthy that the ROP of  $\epsilon$ -CL may also proceed through initial insertion into the Al–O<sub>phenolate</sub> bond of a cationic {O,N,N}Al chelate moiety, albeit the observed activity is lower than those of the terminal alkoxide cations **80j**<sup>+</sup> and **85d**<sup>+</sup>–**85f**<sup>+</sup>. As for the reactivity of Al alkoxide cations with lactides, the alkoxide cation **80j**<sup>+</sup> was found to be inactive in lactides polymerization: instead, **80j**<sup>+</sup> readily reacts with (S)-lactide through fast monoinsertion into the Al–O<sup>i</sup>Pr<sup>+</sup> bond to yield a five-coordinate Al lactate adduct cation (**80l**<sup>+</sup>, Scheme 39) that does not react further.<sup>62</sup> The presence of a chelating lactate moiety in **80l**<sup>+</sup> (vs none in **80j**<sup>+</sup>) most likely accounts for the remarkable stability of this cation with regard to subsequent (S)-lactide insertions.

Apart from polymerization catalysis, one should also note that four-coordinate Al alkyl cation/HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> salt systems (of the type [**80k**][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]) have been implicated in a B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed hydroalumination reaction of benzophe-

Scheme 40



none and benzaldehyde, whose overall equations along with the presumed mechanism are depicted in Scheme 40.<sup>93</sup> In this salt system, the use of the more reactive and more Lewis basic HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup>, a formal hydride source, in combination with a Lewis acidic Al cation susceptible to activate unsaturated substrates (such as carbonyl derivatives), allows this catalysis to proceed.

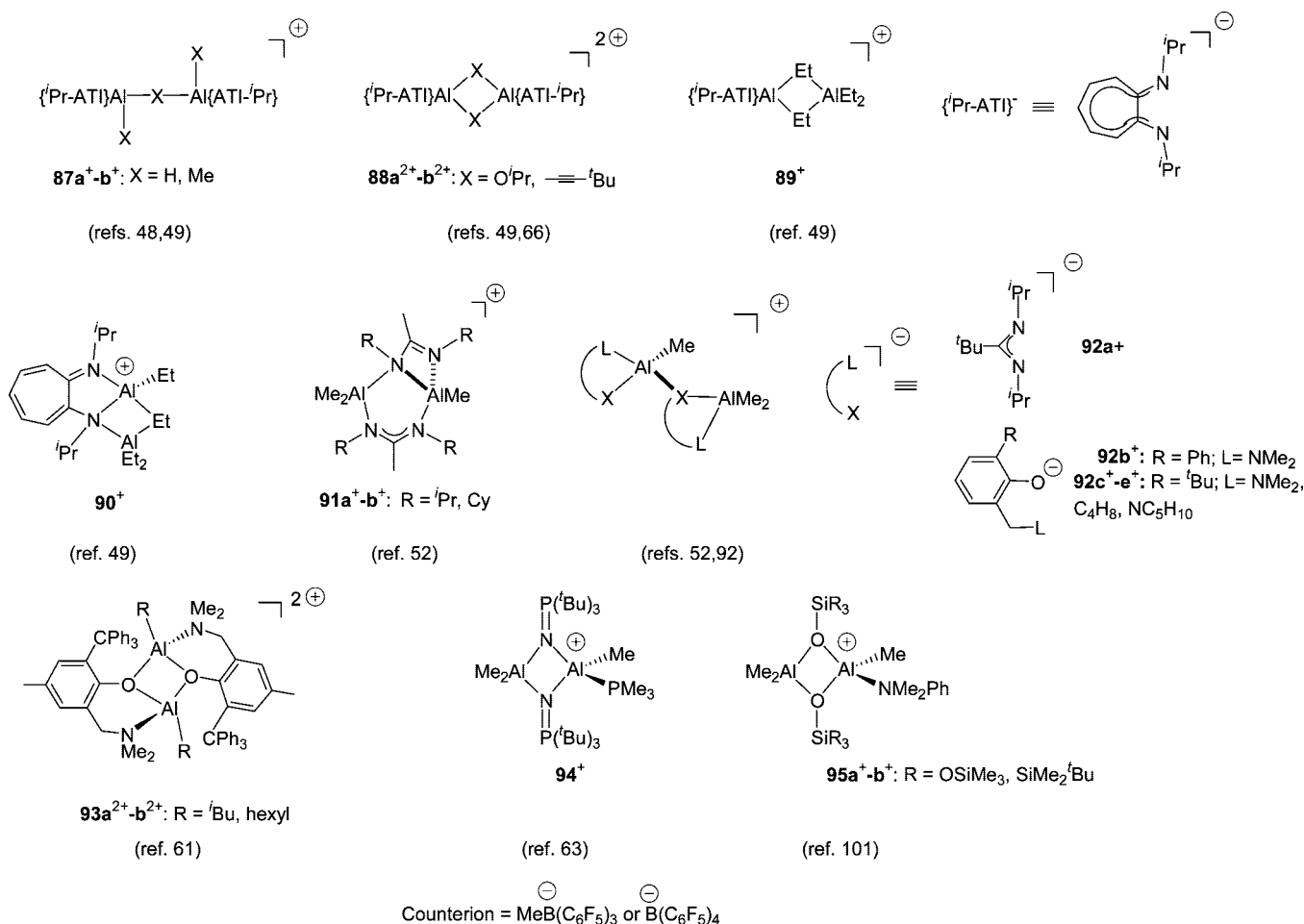
As a final remark in this catalysis part, chiral bisoxazolinato Al cations **77c**<sup>+</sup>–**77d**<sup>+</sup> were used as chiral Lewis acids in hetero Diels–Alder catalysis; while excellent conversions were obtained, the ee's of the product are very low.<sup>54</sup>

#### 4.2.3. Four-Coordinate Al Dinuclear Cations

The high propensity of neutral group 13 metal compounds for aggregation has long been known and has yielded a rich and diversified structural chemistry of neutral polynuclear group 13 species. The enhanced Lewis acidity of the metal center in cationic versus neutral analogues further favors aggregation phenomena, as a result of the increased ionic character of the coordination bonds. It is, thus, not surprising that the ionization of mononuclear group 13 derivatives may often yield the formation of dinuclear cationic species. The vast majority of four-coordinate dinuclear Al cations that have been reported are Al alkyl cations, and these are depicted in Table 6.

**Synthesis and Structure.** The dinuclear compounds **87**<sup>+</sup>–**95**<sup>+</sup> were all derived, as a first step at least, from R<sup>-</sup>/H<sup>-</sup> abstraction from a neutral precursor of the type {LX}AlR<sub>2</sub> or {LX}AlH<sub>2</sub> by [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and were, thus, prepared as B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> or R(BC<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> salts.<sup>48,49,52,61,63,66,92,101</sup> While this type of ionization is expected to yield three-coordinate cations of the type

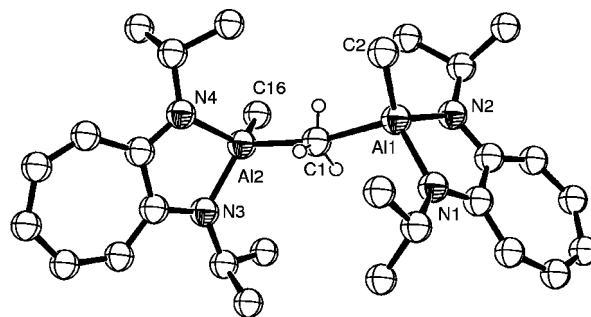
Table 6. Four-Coordinate Dinuclear Al Cations



{LX}AlR<sup>+</sup> as those described above, aggregation between the formed cationic center and its neutral precursor may occur if the cationic metal center is sterically open. Dinuclear cations **87a<sup>+</sup>–87b<sup>+</sup>** and **92a<sup>+</sup>–92e<sup>+</sup>** were prepared directly from the reaction of the corresponding {LX}AlR<sub>2</sub> with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; this reaction proceeds through initial formation of the transient {LX}AlR<sup>+</sup> (not observed in these cases) and subsequent coordination of unreacted {LX}AlR<sub>2</sub> to yield formal adducts of the type {LX}AlR·{LX}AlR<sub>2</sub><sup>+</sup>. The amidinate cations **91a<sup>+</sup>–91b<sup>+</sup>** were synthesized following the same ionization procedure but are structurally different as both amidinate ligands coordinate in a bridging mode to the two Al centers, which is indicative of a poor steric protection of the Al center by the chelate ligand in these systems.<sup>52</sup> The cations **89<sup>+</sup>** and **90<sup>+</sup>** were prepared as a 1/2 mixture, respectively, by reaction of AlEt<sub>3</sub> with the three-coordinate Al cation {*i*Pr-ATI}AlEt<sup>+</sup>.<sup>49</sup> The dications **88a<sup>2+</sup>–88b<sup>2+</sup>** and **93a<sup>2+</sup>–93b<sup>2+</sup>** are dimers derived from the association of two pregenerated {LX}AlR<sup>+</sup> cations.<sup>61,66</sup> Thus, in the latter systems, the driving force to achieve an 8-electron configuration at Al overcomes the Coulombic repulsion between the two cationic centers. Finally, unlike the other dinuclear cations, which all results from aggregation, **94<sup>+</sup>** and **95a<sup>+</sup>–95b<sup>+</sup>** arise from the ionization of a neutral dinuclear tetraalkyl precursor with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (in the presence of PMe<sub>3</sub>) and [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], respectively.

The molecular structures of most reported dinuclear Al cations have been confirmed by crystallographic studies.

Given the structural diversity of the few dinuclear Al cations reported so far, it is difficult to establish structural trends. Thus, various interesting features of these compounds will be highlighted. For instance, as illustrated in Figure 25, the dinuclear trimethyl cation {(*i*Pr-ATI)AlMe}<sub>2</sub>(μ-Me)<sup>+</sup> (**87b<sup>+</sup>**) is of interest as it contains an unusual, nearly linear Al–Me–Al bridge (Al(1)–C(1)–Al(2) = 167.8(2)°) linking the two (*i*Pr-ATI)AlMe units. The μ-Me hydrogens were located in the equatorial plane of the nearly trigonal bipyramidal (tbp) carbon center. Notably, the molecular structures of the dinuclear cations **91a<sup>+</sup>–91b<sup>+</sup>** are also unusual as the two Al centers are linked by two different amidinate bridges (μ-η<sup>1</sup>,η<sup>2</sup>- and μ-η<sup>1</sup>,η<sup>1</sup>-). The μ-η<sup>1</sup>,η<sup>2</sup>-aminophenolate units incorporated in dinuclear species **92b<sup>+</sup>–92e<sup>+</sup>** and **93a<sup>2+</sup>–93b<sup>2+</sup>**, the {μ-η<sup>1</sup>,η<sup>2</sup>-(*i*Pr-ATI)} unit



**Figure 25.** Solid-state structure of the dinuclear Al cation {*i*Pr-ATI}Al(Me)(μ-Me)(Me)Al{*i*Pr-ATI}<sup>+</sup> (**87b<sup>+</sup>**) with partial atom labeling for clarity.



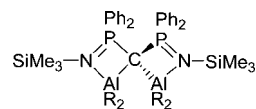
in  $90^+$ , and the  $\mu\text{-}\eta^1, \eta^2$ -amidinate in  $91a^+$  illustrate the high tendency of cationic Al species to coordinate *N,N*- and *N,O*-bidentate ligands in a bridging mode. Overall, the structure of the Al dinuclear cations appears to be strongly dependent upon the steric and electronic properties of the bidentate ligands.

As can be anticipated from their structural variety in the solid state, the solution behavior of these dinuclear cationic species is not uniform. For instance, while the doubly bridged amidinate cations  $91a^+ - 91b^+$  are fluxional at room temperature, the amidinate and aminophenolate dinuclear cations  $92a^+ - 92e^+$  are robust under identical conditions, which illustrates the importance of the bridging mode(s) on the lability of these species in solution.<sup>52</sup> For the Al cations  $87a^+ - 87b^+$ , a bridge/terminal Al-X group (X = Me, H) exchange process has been determined by NMR studies. While this exchange occurs too fast on the NMR time scale at  $-90^\circ\text{C}$  for the hydrido cation  $87a^+$ , the Al-Me exchange is slower for  $87b^+$ , allowing the determination of the free energy barrier of the process ( $\Delta G = 9.5(3)$  kcal/mol).<sup>48</sup>

**Stability, Reactivity, and Catalytic Applications.** With the exception of the thermally unstable salt species  $[92a][B(C_6F_5)_4]$ , the dinuclear species  $87^+ - 95^+$  are stable whether in the solid state or in aromatic solvents such as benzene and PhCl when these cations are associated with the  $B(C_6F_5)_4^-$  or  $MeB(C_6F_5)_3^-$  anion.

In terms of reactivity, the adduct cations  $92a^+ - 92e^+$ , which are of the type  $\{LX\}AlR \cdot \{LX\}AlR_2^+$ , were shown to readily dissociate when reacted with Lewis bases such as  $NMe_2Ph$  or  $thf$  to afford a 1/1 mixture of the corresponding Al-L cationic adduct  $\{LX\}Al(R)(L)^+$  and the neutral precursor  $\{LX\}AlR_2$ , thus showing the potential suitability of these dinuclear species as Lewis acid catalysts.<sup>52,92</sup> Albeit structurally different, cations  $91a^+ - 91b^+$  dissociate in a similar manner in the presence of Lewis bases.

Although dinuclear cationic Al species are usually less "desired" than the "base-free" mononuclear three-coordinate cations because they are anticipated to be less reactive and more complicated to fully characterize, their ready dissociation by Lewis bases has prompted studies on their potential usefulness as polymerization catalysts of various polar monomers. The hydrido Al cation  $87a^+$  was found to efficiently polymerize methylmethacrylate (MMA) at RT to afford moderately syndiotactic poly(MMA) (450 equiv of MMA; *mm/mr/rr* = 1:22:77).<sup>49</sup> Remarkably, the Al methyl cation  $87b^+$  as well as three-coordinate  $\{^iPr-(ATI)\}AlR^+$  Al alkyl cations do not polymerize MMA. On this basis, the MMA polymerization by  $87a^+$  was proposed to occur by a group transfer mechanism, similar to that established for MMA polymerization catalyzed by transition metal complexes. The amidinate cations  $91a^+$  and  $92a^+$  were also reported to be good initiators of the polymerization of MMA; however, in these studies, a Lewis acid-assisted cationic mechanism has been invoked because both cations were apparently also found to polymerize  $thf$ .<sup>102</sup> The latter investigations also concluded that the amidinate cation  $91a^+$  may efficiently act as an initiator of the polymerization of  $\epsilon\text{-CL}$  in a fairly well-controlled manner (100 equiv of  $\epsilon\text{-CL}$ ; 93% yield;  $M_n = 6330$ ;  $M_w/M_n = 1.57$ ), albeit no mechanism was proposed and the nature of the active species remains unclear. The dinuclear cations  $91a^+$ ,  $92a^+$ , and  $92c^+ - 92e^+$  also catalyze the polymerization of PO at room temperature or  $0^\circ\text{C}$  to yield atactic PPO with a low to moderate activity (10–70% conversion).<sup>92,102</sup> At best, the aminophenolate



**Figure 26.** Neutral and dinuclear alkyl aluminum bis(iminophosphorano) methandiide precursors.

systems  $92c^+ - 92e^+$  do polymerize 200 equiv of PO with 70% conversion at  $0^\circ\text{C}$  within 1 h ( $M_n = 9022$ ,  $M_w/M_n = 1.73$ ), thus showing the high reactivity of these dinuclear cations toward PO.<sup>92</sup> While the mechanism remains to be studied, this catalysis is likely to proceed through initial dissociation of the dinuclear species to yield an Al-PO mononuclear cationic adduct of the type  $\{LX\}Al(R)(L)^+$  that may undergo subsequent cationic polymerization in the presence of excess PO.

**Overview of Dinuclear Al Cations.** The potential reactivity and catalytic applications of dinuclear Al cationic species have just emerged in the literature and remain at a preliminary stage. Although further studies are needed to fully evaluate the scope of applications of these species, these early results do already point out that, in some cases, the use of dinuclear versus mononuclear species may be beneficial to catalytic activity (e.g., MMA polymerization by Al cations). In this regard, while mononuclear Al alkyl cations can be definitely ruled out as ethylene polymerization catalysts, dinuclear Al alkyl cations cannot. In fact, Cavell et al. found that a 1/1 mixture of a neutral dinuclear Al alkyl species (Figure 26) and  $[Ph_3C][B(C_6F_5)_4]$  exhibited an ethylene polymerization activity (up to  $\sim 2.9$  kg of PE/mmol of Al/h) that rules out trace contamination of transition metals.<sup>103</sup> As yet unidentified dinuclear and/or polynuclear Al cationic species may well be the active species in this catalysis. Future work in this area may, thus, be concerned with the ionization of neutral dinuclear and/or polynuclear Al alkyls and subsequent reactivity studies of the formed cations. The use of various and tunable bidentate ligands combined with the now available synthetic methodologies should allow the rational design and synthesis of well-defined dinuclear and/or polynuclear Al alkyl cations.

## 4.3. Gallium Species

### 4.3.1. Synthesis and Structure

Although four-coordinate Ga cations such as  $(H_2O)_2\text{-GaMe}_2^+$  have been known since the 1960s, the first X-ray characterized four-coordinate organogallium cation was only reported in 1992.<sup>104</sup> Over the past 10 years, various new four-coordinate gallium cations have been synthesized and structurally characterized, and these are listed in Tables 7 and 8 according to the **A–F** modes of coordination previously defined. In general, analogous synthetic pathways are used to access Al and Ga cations, and the cations are structurally very similar. Thus, the present section does not go into great detail concerning the synthesis and structures of Ga cations.

The synthesis of four-coordinate Ga cations of the types **A** and **B** (Table 7) remains quite popular as such species may be easily accessible through synthetic pathways outlined in the Overview section. For the most part, their synthesis involved either an *asymmetric cleavage* reaction (or disproportionation reaction; see the formation of cations  $98a^+ - 98b^+$ ,  $99^+$ ,  $100a^+$ ,  $101a^+$ ,  $101f^+$ ,  $103a^+ - 103b^+$ , and  $104^+$ )<sup>105–109</sup> or a *halide abstraction* reaction (see the formation of cations  $100b^+ - 100e^+$ ,  $101b^+ - 101e^+$ , and  $101g^+ - 101j^+$ ).<sup>106,107</sup> In

Table 7. Four-Coordinate Ga Cations of the Types A–C

<p><b>96<sup>+</sup></b> (ref. 80)</p>	<p><b>97a<sup>+</sup>-b<sup>+</sup></b>: L = <sup>t</sup>BuNH<sub>2</sub>, <sup>s</sup>BuNH<sub>2</sub> (ref. 110)</p>	<p><b>98a<sup>+</sup>-b<sup>+</sup></b>: X = Br, I (ref. 105)</p>	<p><b>99<sup>+</sup></b> (ref. 105)</p>	<p><b>100a<sup>+</sup></b>: A = (Fp)<sub>2</sub>GaCl<sub>2</sub>; L-L = 2,2'-bipy <b>100b<sup>+</sup>-e<sup>+</sup></b>: A = BPh<sub>4</sub>; L-L = 2,2'-bipy, 1,10-phenanthroline, tmeda, dmap (ref. 106)</p>
<p><b>101a<sup>+</sup></b>: X = Fp; A = (Fp)GaCl<sub>3</sub>; L-L = 2,2'-bipy <b>101b<sup>+</sup>-e<sup>+</sup></b>: X = Fp; A = BPh<sub>4</sub>; L-L = 2,2'-bipy, 1,10-phenanthroline, tmeda, dmap <b>101f<sup>+</sup></b>: X = Fp*; A = (Fp*)GaCl<sub>3</sub>; L-L = 2,2'-bipy <b>101g<sup>+</sup>-j<sup>+</sup></b>: X = Fp*; A = BPh<sub>4</sub>; L-L = 2,2'-bipy, 1,10-phenanthroline, tmeda, dmap (ref. 107)</p>	<p><b>102<sup>+</sup></b> (ref. 107)</p>	<p><b>103a<sup>+</sup>-b<sup>+</sup></b>: R = H, <sup>n</sup>Pr (ref. 108)</p>	<p><b>104<sup>+</sup></b> (ref. 109)</p>	<p><b>105<sup>+</sup></b> (ref. 55)</p>

contrast, the Ga dimethyl cation **96<sup>+</sup>** was prepared by reaction of GaMe<sub>3</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in the presence of Et<sub>2</sub>O through a Me<sup>-</sup> abstraction reaction and, thus, isolated as a MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> salt.<sup>80</sup> The dihydro Ga cations **97a<sup>+</sup>–97b<sup>+</sup>** were generated by an H<sub>2</sub> elimination reaction between LiGaH<sub>4</sub> with 2 equiv of the corresponding ammonium salts.<sup>110</sup> The bis(oxazoline) Ga dimethyl cation **105<sup>+</sup>** is isostructural to the Al analog **67<sup>+</sup>** and was prepared following the same procedure.<sup>55</sup> Finally, as shown in Scheme 41, it is noteworthy that the sulfido Ga cation **102<sup>+</sup>** was generated by reaction of the Ga chloro cation **101g<sup>+</sup>** with Me<sub>3</sub>Si(*p*-Tol), thus showing that derivatization chemistry of preformed Ga cations may allow access to new families of cationic species.<sup>107</sup> No type C Ga cation has been reported since 1998.

Type D–E Ga cations are listed in Table 8. As the only example of type D Ga cation, the rather exotic spirogallium cation **106<sup>+</sup>** may be generated through disproportionation of the monochelate Ga dichloro precursor (Scheme 42).<sup>111</sup>

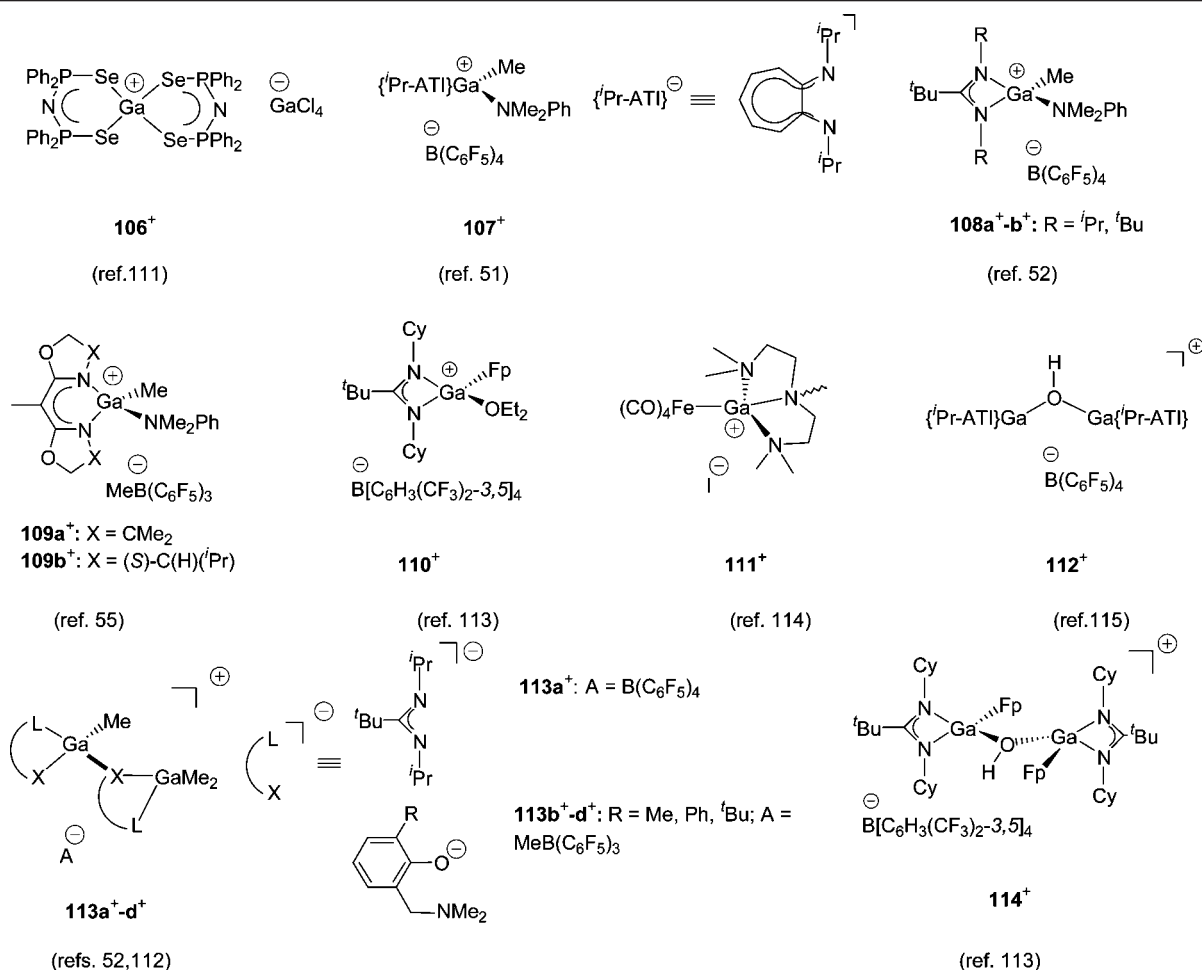
{LX}Ga(Me)(L)<sup>+</sup> Ga cations were unknown 10 years ago but may now be readily available through Me<sup>-</sup> abstraction from a {LX}GaMe<sub>2</sub> precursor with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of a Lewis base to stabilize the cationic Ga center (see **107<sup>+</sup>**, **108<sup>+</sup>**, and **109<sup>+</sup>**, Table 8).<sup>52,55</sup> Notably, the anilinium Ga cation **107<sup>+</sup>** may also be prepared by reaction of (<sup>t</sup>Pr-ATI)GaMe<sub>2</sub> with [HNMe<sub>2</sub>-Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] through a protonolysis reaction. The dinuclear Ga cationic adduct species **113a<sup>+</sup>–113d<sup>+</sup>** also arise from a Me<sup>-</sup> abstraction reaction but in the absence of an external Lewis base.<sup>52,112</sup> As observed for the Al dinuclear analogs

**92a<sup>+</sup>–92e<sup>+</sup>**, the {LX}GaMe<sub>2</sub> precursor acts as a Lewis base to stabilize the generated cationic center. The halide abstraction and displacement approaches may be also suitable for the generation of type E Ga cations,<sup>113,114</sup> for instance, the formation of the Ga–[Fe(Cp)(CO)<sub>2</sub>] amidinate cation **110<sup>+</sup>** by reaction of the corresponding monohalido neutral precursor with Na[B{C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>-3,5}4] in the presence of Et<sub>2</sub>O.<sup>113</sup> One should also mention that the dinuclear hydroxide Ga cations **112<sup>+</sup>** and **114<sup>+</sup>** are derived from a controlled hydrolysis reaction of the anilinium Ga cation **107<sup>+</sup>** and the organocation **110<sup>+</sup>**, respectively.<sup>113,115</sup>

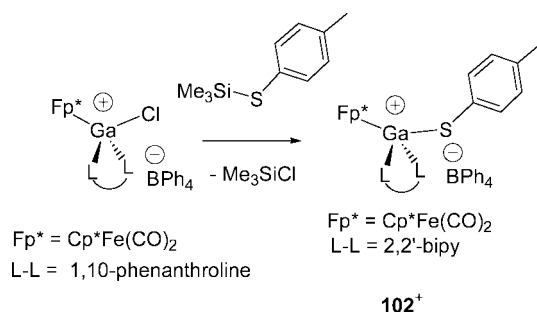
The vast majority of the four-coordinate Ga cations have been X-ray characterized, allowing the unambiguous determination of their molecular structures. In all cases, the Ga cationic center adopts a distorted tetrahedral geometry with a degree of distortion being obviously dependent upon the nature of the surrounding ligands. Overall, these Ga species are structurally similar to their Al analogues, and thus, trends established and discussed above for the Al cations also apply for Ga derivatives. As for their structure solution, these cations appear to be robust species and no remarkable dynamic behavior has been reported. We should however note that the coordinated NMe<sub>2</sub>Ph was shown to be labile in solution at room temperature in cations **107a<sup>+</sup>–107b<sup>+</sup>** and **108a<sup>+</sup>–108b<sup>+</sup>** in the presence of free NMe<sub>2</sub>Ph, showing that cations of the type {LX}Ga(Me)(L)<sup>+</sup> may readily react in the presence of coordinative substrates.

**Stability, Reactivity, and Catalytic Applications.** As can be expected, four-coordinate Ga cations are extremely stable

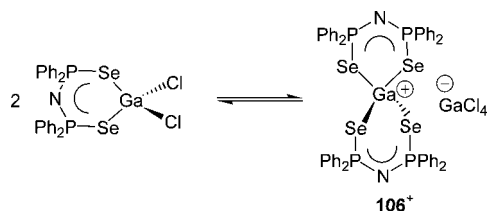
Table 8. Four-Coordinate Ga Cations of the Types D–F



Scheme 41



Scheme 42



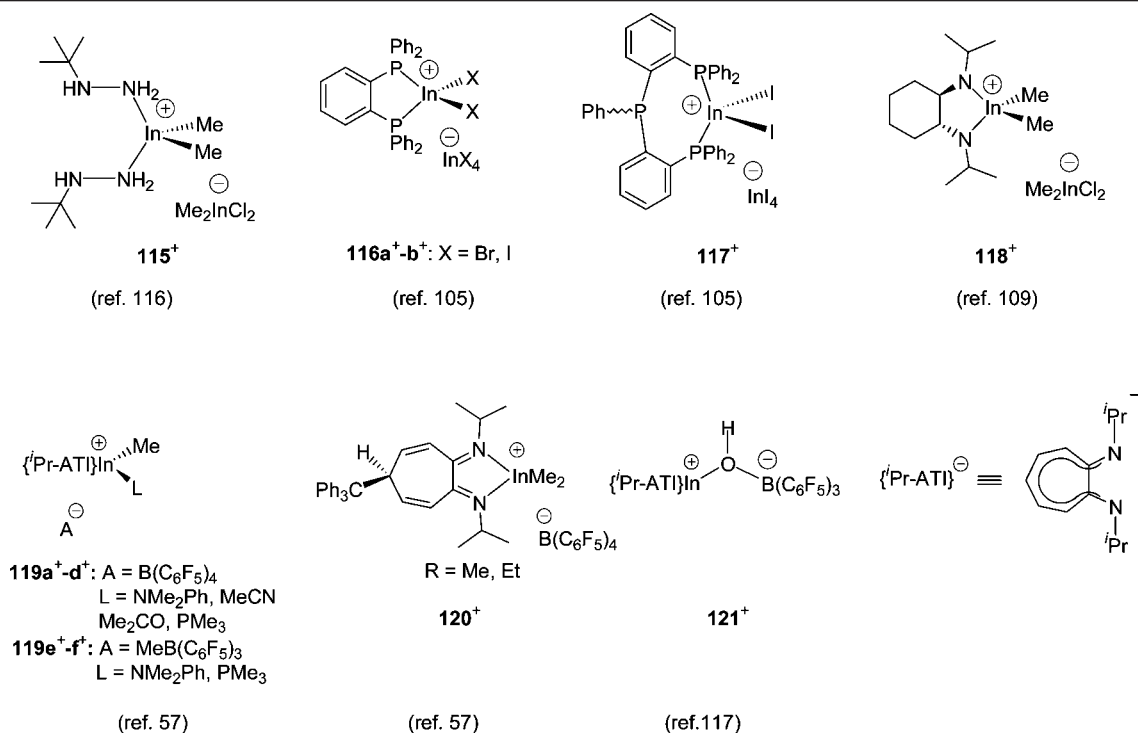
whether in the solid state or in solution and may exhibit an increased thermal stability versus Al analogues. For instance, while the Al dinuclear methyl cation **92<sup>+</sup>** is thermally unstable in solution, the isostructural Ga cation **113a<sup>+</sup>** is very stable and could be X-ray characterized. The less polar character of the M–C bond, combined with a lower Lewis acidity of the metal center when going from Al to Ga, most likely rationalizes this difference of stability.

Despite the growing number of tetracoordinate Ga cations, reactivity studies and the use in catalysis of such Lewis acidic species remain rare. Studies in this area have been restricted to the Ga methyl cations **113a<sup>+</sup>** and **109a<sup>+</sup>**. Like its Al analogue, the dinuclear Ga cation **113a<sup>+</sup>** readily dissociates in the presence of Lewis bases such as thf or NMe<sub>2</sub>Ph to yield a 1/1 mixture of the mononuclear cation {<sup>t</sup>BuC(N<sup>i</sup>Pr)<sub>2</sub>}Ga(Me)(L)<sup>+</sup> (L = thf, NMe<sub>2</sub>Ph) and the neutral precursor {<sup>t</sup>BuC(N<sup>i</sup>Pr)<sub>2</sub>}GaMe<sub>2</sub>. This dinuclear species does not react, however, with ethylene or 2-butyne. Interestingly, the bisoxazolinato Ga–NMe<sub>2</sub>Ph cation **109a<sup>+</sup>** was found to react rapidly with an excess of propylene oxide (200 equiv, –20 °C, 5 min) to yield atactic oligomers with a broad polydispersity (40% conversion, *M<sub>n</sub>* = 448, *M<sub>w</sub>*/*M<sub>n</sub>* = 2.38), thereby showing that this class of Ga cations may act as Lewis acid catalysts.<sup>55</sup>

#### 4.4. Indium and Thallium Species

Four-coordinate indium cations have just been the subject of a few reports since 1998 (Table 9). The In methyl cations **119a<sup>+</sup>**–**119f<sup>+</sup>** were prepared through a Me<sup>–</sup> abstraction reaction between B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with the neutral precursor {<sup>i</sup>Pr-ATI}InMe<sub>2</sub> in the presence of the appropriate Lewis base L, which subsequently coordinates to the formed In cationic center (type E cations).<sup>57</sup> The anilinium In cation **119a<sup>+</sup>** can also be prepared through protonolysis of {<sup>i</sup>Pr-ATI}InMe<sub>2</sub> with [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Compounds **115<sup>+</sup>**–**118<sup>+</sup>** were all synthesized through an

Table 9. Four-Coordinate In Cations



asymmetric cleavage pathway involving the reaction of the dimer [Me<sub>2</sub>In(μ-Cl)]<sub>2</sub> or [I<sub>2</sub>In(μ-I)]<sub>2</sub> with a chelating L<sub>2</sub> ligand or, in the case of **115<sup>+</sup>**, with two L ligands.<sup>104,108,116</sup> As for the hydroxo In cation **121<sup>+</sup>**, it appears to derive from a controlled hydrolysis of the salt species [{<sup>i</sup>Pr-ATI]InMe]-[Me B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>].<sup>117</sup> The solid-state structures of the In cations **119a<sup>+</sup>**, **115<sup>+</sup>**–**118<sup>+</sup>**, **120<sup>+</sup>**, and **121<sup>+</sup>** were confirmed by X-ray crystallographic analysis, and their structural features and trends parallel those of Al and Ga analogues. A recent report has described the synthesis and structural characterization of the first example of a Tl(I)–Et<sub>2</sub>O cation Tl(Et<sub>2</sub>O)<sub>4</sub><sup>+</sup> (**122<sup>+</sup>**) as a fully dissociated H<sub>2</sub>N{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub><sup>−</sup> salt species.<sup>46</sup> Despite the increasing use of In(III) species as Lewis acid catalysts for organic transformations, no catalytic application have been thus far reported for well-defined four-coordinate indium cations.

## 4.5. Summary

Four-coordinate group 13 cationic species have received increased attention over the last 10 years because such Lewis acidic entities are of interest in catalysis. As detailed above, the Al cations may exhibit a rich structural chemistry and undoubtedly have an enhanced tendency to aggregate when compared to their neutral analogues, as illustrated by the frequent formation of dinuclear cations from mononuclear neutral precursors.

The Al derivatives have been the most studied thus far and have already found applications as polymerization catalysts of polar monomers such as propylene oxide, ε-caprolactone, (D,L)-lactide, and methylmethacrylate. Compared with their Al analogues, Ga and In cations have been much less investigated in terms of reactivity and use in catalysis, although such Lewis acid cations should be suitable for catalysis involving polar substrates and/or media.

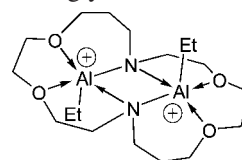
## 5. Five-Coordinate Group 13 Cations

### 5.1. Background

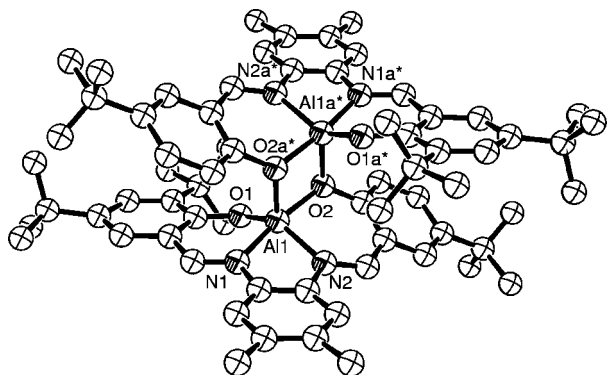
Six-coordinate cations exist with six separate ligands [AlCl<sub>2</sub>(L)<sub>4</sub><sup>+</sup>] (where L = NH<sub>3</sub>, thf, pyridine) (see section 6 below), and it might be assumed that similar five-coordinate compounds with five separate ligands could also be accessed using ligands having slightly more steric encumbrance than pyridine. However, five-coordinate cations remain somewhat rare and typically require the use of chelate ligands to provide the appropriate number of coordination sites. It appears that little systematic work has focused specifically on five-coordinate cations. While some work has appeared, as described below, most of the results originate from studies of six-coordinate cations or from a fundamental exploration of group 13–ligand combinations.

### 5.2. Aluminum Cations

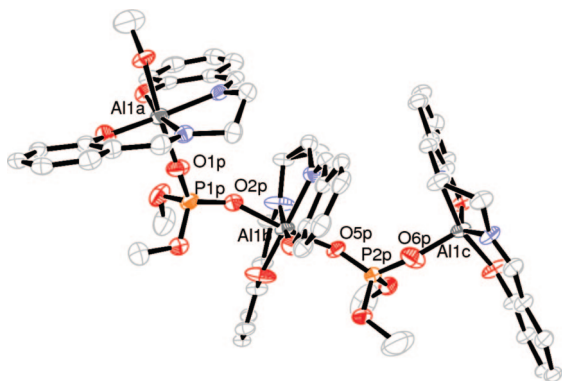
One of the first five-coordinate aluminum compounds reported employed diaza-18-crown-6 to create a compound of formula (AlEt)<sub>2</sub>(diaza-18-crown-6)<sup>2+</sup> with EtAlCl<sub>3</sub><sup>−</sup> as the counteranions (Figure 27).<sup>118</sup> The crown is a dinegative ligand after deprotonation of the two amine groups. The Al atoms in the compound are in square-pyramidal geometries with the Al atoms 0.732 Å from the N<sub>2</sub>O<sub>2</sub> plane. The Al atoms are bridged by the nitrogens of the ligand forming a central planar N<sub>2</sub>Al<sub>2</sub> unit. This compound is structurally reminiscent of the singly cationic dinuclear compound,



**Figure 27.** Structure of the dinuclear Al dication [Al(Et)<sub>2</sub>(diaza-18-crown-6)]<sup>2+</sup>.



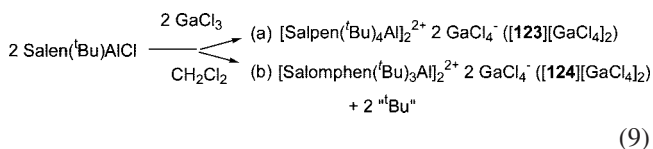
**Figure 28.** Solid-state structure of the dinuclear dication [Salomphen(<sup>t</sup>Bu)<sub>3</sub>Al]<sub>2</sub><sup>2+</sup> (in compound **124**) with partial atom labeling for clarity.



**Figure 29.** Solid-state structure of the trinuclear Salen–Al cation in the salt species **125** with partial atom labeling for clarity.

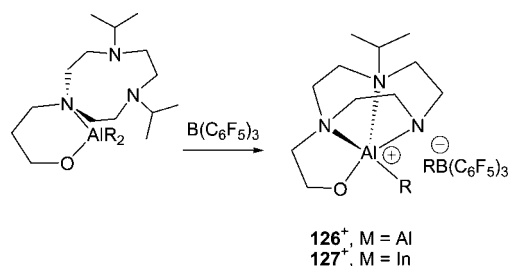
(*acac*)<sub>3</sub>(AlCl)<sub>2</sub><sup>+</sup>·AlCl<sub>4</sub><sup>−</sup>, which contains an Al<sub>2</sub>O<sub>2</sub> rather than an Al<sub>2</sub>N<sub>2</sub> core.<sup>119</sup>

When the compound Salpen(<sup>t</sup>Bu)AlCl (Salpen(<sup>t</sup>Bu)<sub>2</sub> = *N,N'*-propylene-bis(3,5-di-*tert*-butylsalicylideneimine)) is combined with GaCl<sub>3</sub> in either toluene or CH<sub>2</sub>Cl<sub>2</sub>, the unique dicationic dimeric compound, [Salpen(<sup>t</sup>Bu)Al]<sub>2</sub><sup>2+</sup> (**123**<sup>2+</sup>), forms as GaCl<sub>4</sub><sup>−</sup> salts from abstraction of the chloride on aluminum followed by dimerization (eq 9).<sup>120</sup> The propylene backbones of the ligand allow the Al atoms to adopt trigonal-bipyramidal geometries.



In an attempt to create a potentially planar cation, the more rigid Salomphen ligand (4,5-dimethyl, *N,N'*-*o*-phenylene-bis(3,5-di-*tert*-butylsalicylideneimine)) was also employed in this reaction. It was thought that the combination of a rigid phenylene backbone with the *tert*-butyl groups would prevent dimerization. However, the product was also found to be dimeric with the Al atoms in a distorted square-pyramidal geometry with bridging oxygens (Figure 28). In dimerizing, the Salomphen(<sup>t</sup>Bu) ligands underwent a rare, single, Friedel–Crafts dealkylation<sup>121</sup> to form a compound with the formula [Salomphen(<sup>t</sup>Bu)<sub>3</sub>Al]<sub>2</sub><sup>2+</sup>·2GaCl<sub>4</sub><sup>−</sup> ([**124**]-[GaCl<sub>4</sub>]<sub>2</sub>). Thus, it appears that the desired cation formed but was of sufficient Lewis acidity to force the dealkylation to occur in order to ameliorate the undesirable charge on a coordinatively unsaturated Al cation.

**Scheme 43**



A great deal of work has been conducted on the use of chelated SalenAlBr (SalenH<sub>2</sub> = *N,N'*-ethylene-bis(salicylideneimine)) compounds to dealkylate phosphate esters (described in more detail in the six-coordinate section below). In an attempt to isolate intermediates in this reaction, an adventitious product was isolated containing possibly the first example of five-coordinate SalenAl cation.<sup>122</sup> The compound, [Salen(<sup>t</sup>Bu)Al(MeOH){μ-O(MeO)<sub>2</sub>P(O)}Salen(<sup>t</sup>Bu)Al{μ-O(MeO)<sub>2</sub>P(O)}Salen(<sup>t</sup>Bu)Al]Br ([**125**]Br) (Figure 29), may have formed by having Salen(<sup>t</sup>Bu)AlBr dedimerize the known compound [Salen(<sup>t</sup>Bu)Al{O(MeO)<sub>2</sub>P(O)}]<sub>2</sub>.

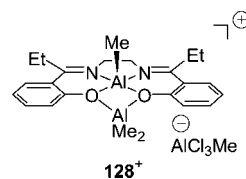
Compounds of general formula LAlMe<sub>2</sub> (where L = 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclonane) and L(AlMe<sub>3</sub>)AlMe<sub>2</sub> (where L = 1-(2-hydroxy-2-methylethyl)-4,7-diisopropyl-1,4,7-triazacyclonane) can be combined with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to produce the five-coordinate chelated cation [LAlMe]<sub>2</sub>[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] ([**126**][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]) and the indium derivative [**127**]-[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] in high yield (>80%) (Scheme 43).<sup>123</sup>

These methide abstraction reactions are similar to those used in preparing three- and four-coordinate cations described above. The only difference is that the ligands have the capability of higher coordination numbers.

Various unique bimetallic aluminum cations have been isolated adventitiously. When SalenTiCl<sub>2</sub> is combined with AlMe<sub>3</sub>, a low yield (~5%) transmetalation occurs where the Salen ligand is displaced from titanium and [Salen(AlMe)(AlMe<sub>2</sub>)] [AlCl<sub>3</sub>Me] ([**128**][AlCl<sub>3</sub>Me]) results (Figure 30).<sup>124</sup> In the structure, the central Al atom is in a highly distorted geometry that is hard to classify as either *tbp* or *sqpy*.

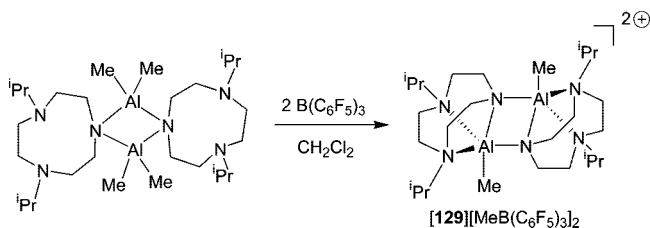
The combination of [tacnAlMe<sub>2</sub>]<sub>2</sub> (tacn = 1,4-diisopropyl-1,4,7-triazacyclonane) held together with nitrogens bridging the two Al atoms and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> produced the compound (tacnAlMe)<sub>2</sub><sup>2+</sup>·2MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> ([**129**][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub>), which contains a nitrogen bridged bimetallic Al dication, with an Al<sub>2</sub>N<sub>2</sub> core (Scheme 44).<sup>125</sup> The product contains the same bridging nitrogens that supported the original dimeric compound, but the displacement of the methide group leads to coordination by the remaining two nitrogens of the ligand producing a distorted *tbp* geometry.

Interestingly, this and other compounds appear to indicate that reactions of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with dimeric starting materials containing AlMe<sub>2</sub> groups bridged by nitrogen atoms readily produce cations while those having



**Figure 30.** Structure of the salt [Salen(AlMe)(AlMe<sub>2</sub>)] [AlCl<sub>3</sub>Me] (**128**) with partial atom labeling for clarity.

## Scheme 44



an  $\text{Al}_2\text{O}_2$  four-membered ring in the starting material do not. This is an important finding, and it should guide future efforts at cation formation, particularly those seeking catalytically active compounds.

In another example of how the Salen ligands support a variety of neutral and cationic aluminum compounds, the bimetallic neutral compound,  $\text{Salpen}(\text{tBu})(\text{AlMeCl})_2$ , was combined with  $\text{GaCl}_3$  to produce, in 97% yield, the trimetallic dication ( $\text{Salpen}(\text{tBu})_2(\text{AlCl})_3^{2+} \cdot \text{GaCl}_4^- \cdot \text{GaMe}_2\text{Cl}_2^-$ ) ( $[\mathbf{130}][\text{GaCl}_4][\text{GaMe}_2\text{Cl}_2]$ ) (Figure 31).<sup>126</sup> In the structure, the three Al atoms are in distorted tbp geometries with the Al–Cl groups occupying axial positions with bond lengths of  $\sim 2.1 \text{ \AA}$ .

## 5.3. Gallium and Indium Cations

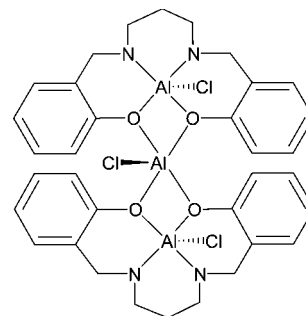
Organogallium and indium cations are exceedingly rare, and it has been demonstrated that cation formation reactions that work for aluminum do not, or rarely, work for creating analogous gallium and indium cations. The exception to this general observation is the formation of the indium cation  $\mathbf{127}^+$  in  $\sim 70\%$  yield following the procedure shown in Scheme 43.

## 5.4. Applications

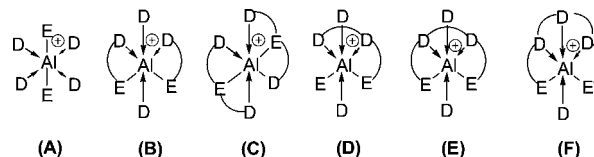
The unsolvated salts,  $[\text{Salpen}(\text{tBu})\text{Al}]_2^{2+} \cdot 2\text{GaCl}_4^-$  ( $[\mathbf{123}][\text{GaCl}_4]_2$ ) and  $[\text{Salomphen}(\text{tBu})_3\text{Al}]_2^{2+} \cdot 2\text{GaCl}_4^-$  ( $[\mathbf{124}][\text{GaCl}_4]_2$ ), effect the polymerization (or oligomerization) of propylene oxide (PO), isobutyl vinyl ether (IBVE) and styrene. For PO, oligomers with molecular weights of 2000–3000 were obtained with a PDI of 1.6. For IBVE, polymers of 9 000–29 000  $M_w$  and PDI of  $\sim 2$  were produced. Styrene was polymerized to  $\sim 24\,000 M_w$  and PDI of  $\sim 2$ . However, no products were obtained with ethylene and propylene under the same conditions. At lower temperature ( $-78 \text{ }^\circ\text{C}$ ), the  $M_w$  of IBVE increased to  $\sim 30\,000$  and that of styrene increased to  $\sim 110\,000$ . These results were interpreted in terms of Lewis acid activation and a cationic polymerization mechanism.

## 5.5. Summary

Even before 1998, five-coordinate cationic group 13 compounds were rare and appeared to result from adventitious isolation during the pursuit of other compounds. The exception to this observation was a series of compounds supported by a ligand containing a triazacyclonane functionality. This created an environment where abstraction of an Al or In alkyl group would lead to either mononuclear or dinuclear five-coordinate cations. A key observation was made in this study that dimeric compounds containing an  $\text{Al}_2\text{O}_2$  four-membered ring would not undergo alkyl abstraction by either  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . This appears to be the first instance that a discrete class of readily prepared



**Figure 31.** Structure of the Al trinuclear dication  $[\text{Salpen}(\text{tBu})_2(\text{AlCl})_3]^{2+}$  in compound  $\mathbf{130}$ .



**Figure 32.** Different coordination modes in six-coordinate group 13 cations.

five-coordinate cations could be prepared in high yields and used in further studies.

## 6. Six-Coordinate Group 13 Cations

## 6.1. Background

Aluminum cations with six ligands can be readily prepared by base-assisted heterogeneous cleavage of the  $[\text{AlCl}_3]_2$  dimer. This produces cations of the formula  $\text{AlCl}_2(\text{L})_4^+$  as  $\text{AlCl}_4^-$  salts with  $\text{L} = \text{thf}$ ,<sup>127</sup>  $\text{thf}$  (with  $\text{EtAlCl}_3^-$  as the anion),<sup>128</sup> pyridine,<sup>129</sup>  $\text{NH}_3$ ,<sup>130</sup> etc. These cations would correspond to the type **A** class of cations (Figure 32). There are also a couple of interesting  $\text{AlX}_2(\text{L})_4^+$  cations reported including the following: (i) an Al dihydride compound,  $\text{AlH}_2(\text{thf})_4^+$ , with the anion  $\{\text{Cp}_3\text{Yb}\}(\text{Na})^-$  produced through autoionization of aluminum hydride<sup>131</sup> and (ii) the Al difluoro cations  $\text{AlF}_2(\text{py})_4^+$  (as a  $\text{Cl}^-$  salt) and  $\text{AlF}_2(\text{py})_4^+ \cdot 2\text{pyH}^+ \cdot 3\text{Cl}^-$  ( $\text{py} = \text{pyridine}$ ), which may be formed through a F/Cl exchange reaction between  $\text{AlCl}_3 \cdot 3\text{py}$  and  $\text{Me}_3\text{SiF}$  in pyridine.<sup>132</sup> Bidentate ligands, such as 2,2'-bipyridine, can also be used in this cation formation reaction.<sup>133</sup> This appears to be a technique that can be employed with a virtually limitless choice of base ligands. These simple cations would correspond to the type **B** coordination environment (Figure 32). In systematic work with  $(\text{acac})\text{AlCl}_2$ , it was found that addition of bases ( $\text{Et}_2\text{O}$ ,  $\text{thf}$ ,  $\text{Py}$ ,  $\text{DMF}$ ) readily forms cations of formula  $(\text{acac})_2\text{Al}(\text{base})_2^+$ .<sup>134</sup>

The halide displacement reaction has not been demonstrated as extensively with gallium, but salt elimination reactions with pyrazolylborate ligands (tris(3,5-dimethyl-1-pyrazolyl)hydridoborate) can create six-coordinate gallium cations of formula  $\text{GaL}_2^+ \cdot \text{GaCl}_4^-$ .<sup>135</sup> Al cations with two pyrazolylborate ligands can be prepared in a similar manner.<sup>136</sup> These compounds are classified as type **C** cations (Figure 32).

Tetradentate chelates such as porphyrins and the Salen ligands have been extremely useful in forming very stable six-coordinate cations. Cationic Al and Ga derivatives of TPP (tetraphenylporphyrin) were prepared by combining the salts  $[\text{M}(\text{TPP})(\text{OH}_2)\text{X}]$  ( $\text{M} = \text{Al}$ ,<sup>137</sup>  $\text{Ga}$ ;  $\text{X} = \text{Cl}$ ,  $\text{O}_3\text{SCF}_3$ ) with various  $\text{Fe}(\text{TPP})$  and  $\text{Cu}(\text{TPP})$  salts.<sup>138</sup> The products are the

**Table 10.** Six-Coordinate Aluminum Cations with the Salen Ligands

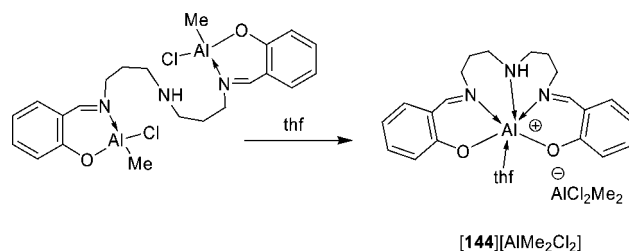
compound	reference
[Salen( <sup>t</sup> Bu)Al(MeOH) <sub>2</sub> ]Cl [ <b>120</b> ] (X-ray)	144
[Salen( <sup>t</sup> Bu)Al(MeOH) <sub>2</sub> ]OTs [ <b>121</b> ] (X-ray)	144
[Salen( <sup>t</sup> Bu)Al(H <sub>2</sub> O) <sub>2</sub> ]Cl [ <b>122</b> ] (X-ray)	144
[Salcen( <sup>t</sup> Bu)Al(thf) <sub>2</sub> ]BPh <sub>4</sub> [ <b>123</b> ] (X-ray)	143
[Salen( <sup>t</sup> Bu)Al(thf) <sub>2</sub> ]BPh <sub>4</sub> [ <b>124</b> ]	68
[Salpen( <sup>t</sup> Bu)Al(thf) <sub>2</sub> ]BPh <sub>4</sub> [ <b>125</b> ] (X-ray)	146
[Salben( <sup>t</sup> Bu)Al(thf) <sub>2</sub> ]BPh <sub>4</sub> [ <b>126</b> ]	68
[Salophen( <sup>t</sup> Bu)Al(thf) <sub>2</sub> ]BPh <sub>4</sub> [ <b>127</b> ]	68
[Salomphen( <sup>t</sup> Bu)Al(thf) <sub>2</sub> ]Ph <sub>4</sub> [ <b>128</b> ]	68
[Salen( <sup>t</sup> Bu)Al(Ph <sub>3</sub> P=O) <sub>2</sub> ]Br [ <b>129</b> ]	141
[Salpen( <sup>t</sup> Bu)Al(Ph <sub>3</sub> P=O) <sub>2</sub> ]Br [ <b>130</b> ] (X-ray)	141
[Salophen( <sup>t</sup> Bu)Al(Ph <sub>3</sub> P=O) <sub>2</sub> ]Br [ <b>131</b> ] (X-ray)	141
[Salophen( <sup>t</sup> Bu)Al{(PhO) <sub>3</sub> P=O} <sub>2</sub> ]Br [ <b>132</b> ] (X-ray)	141

six-coordinate cations Al(TPP)(H<sub>2</sub>O)(thf)<sup>+</sup> and Ga(TPP)(thf)<sub>2</sub><sup>+</sup> where the central metal is in an octahedral geometry.

The Salen ligands support a wide range of six-coordinate cations.<sup>12</sup> The cation precursors are formed by combination of the SalenH<sub>2</sub> ligand with the dialkyl group 13 halide to yield the SalenMX species. In the case of Al, the addition of base (H<sub>2</sub>O, thf, etc.) produces the cation [SalenAl(base)<sub>2</sub>]<sup>+</sup>.<sup>13–15</sup> In all cases, the Al atoms are octahedrally coordinated with the bases in the apical sites and the ligand is coordinated equatorially. It is interesting to note that the formation of the Ga and In analogues through similar synthetic procedures has not been achieved even though the starting materials, SalenMX, are known (with M = Ga,<sup>139</sup> X = Cl and M = In,<sup>140</sup> X = Cl, Br). This appears to indicate that the M–X bonds for Ga and In are not ionic enough to allow displacement of the halide by base. However, it probably also indicates that the coordination of a single base to the complex must take place to help release the halide. Thus, in the Al reactions, the putative intermediate SalenAlX(base) precedes the release of halide. The coordination by base for the Ga and In derivatives would be impeded by the distance the metals are located above the N<sub>2</sub>O<sub>2</sub> plane (~0.6 Å). This distance for the Al derivatives is ~0.4 Å. The use of tetradentate dianionic ligands creates the type **E** class of cations.

## 6.2. Aluminum Cations

The majority of the work that has occurred since 1998 has resulted in type **E** cations with the Salen ligands. The Salen ligands employed were as follows: Salen(<sup>t</sup>Bu)H<sub>2</sub> (*N,N'*-ethylene-bis(3,5-di-*tert*-butylsalicylideneimine), Salpen(<sup>t</sup>Bu)H<sub>2</sub> (*N,N'*-propylene-bis(3,5-di-*tert*-butylsalicylideneimine), Salben(<sup>t</sup>Bu)H<sub>2</sub> (*N,N'*-butylene-bis(3,5-di-*tert*-butylsalicylideneimine), Salophen(<sup>t</sup>Bu)H<sub>2</sub> (*N,N'*-*o*-phenylene-bis(3,5-di-*tert*-butylsalicylideneimine), and Salomphen(<sup>t</sup>Bu)H<sub>2</sub> (*N,N'*-*o*-(4,5-dimethyl)phenylene-bis(3,5-di-*tert*-butylsalicylideneimine). The Salen-supported six coordinate cations that have been obtained since 1998 are listed in Table 10. They are solvated by thf<sup>68</sup> and by phosphine oxides.<sup>141</sup> This adds to the list of known bases that solvate the cation SalenAl(base)<sub>2</sub><sup>+</sup>, which previously included H<sub>2</sub>O, MeOH, hmpa, and thf.<sup>12</sup> The synthetic procedure for accessing these cations generally involved either salt elimination or halide displacement by two base molecules.<sup>142</sup> The X-ray structure of the chiral derivative, [Salcen(<sup>t</sup>Bu)Al(thf)<sub>2</sub>][BPh<sub>4</sub>], has been determined.<sup>143</sup> In two of the cations, the base coordinating Al was found to participate in hydrogen bonding.<sup>144</sup> For example, the salt [Salen(<sup>t</sup>Bu)Al(MeOH)<sub>2</sub>][OTs] has an additional MeOH molecule bridging the coordinated MeOH

**Scheme 45**

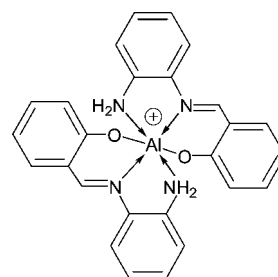
and the counteranion. For [Salen(<sup>t</sup>Bu)Al(H<sub>2</sub>O)<sub>2</sub>]Cl, an acetophenone molecule hydrogen bonds to each of the coordinated waters. The Cl<sup>−</sup> counteranion is also hydrogen bonded to one of the waters. These hydrated cations are unique in that they are soluble in organic solvents.

Some typical features in the structures include ligand O–Al–O angles (~89–96°) that are more obtuse than the ligand N–Al–N angles (~80–90°). This provides a more “open front” to the compound that may be of utility in further applications. The axial O–Al–O angles are nearly linear (~178°). The Al–O(axial) distances (~2.0 Å) are longer than the Al–O(ligand) distances (~1.8 Å). The Al–N(ligand) distances are ~2.0 Å.

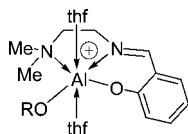
The Salen(<sup>t</sup>Bu)AlBr compounds dealkylate trialkylphosphates (see Applications section below). In one reaction with trimethylphosphate, a unique trimetallic cation with three Salen(<sup>t</sup>Bu)Al groups bridged by two singly dealkylated phosphate groups ((MeO)<sub>2</sub>PO<sub>2</sub>) (**125**<sup>+</sup>, *vide supra*) was isolated.<sup>122</sup> The structure of this compound is shown in Figure 29. The presence of the MeOH group was attributed to hydrolysis of the MeBr produced during the dealkylation.

Two different cationic compounds supported by Salen-like ligands have been prepared and structurally characterized. The ligand, aminobis(*N*-propylenesalicylideneimine) (SalpenN<sub>3</sub>H<sub>3</sub>) can be viewed as a Salen ligand with an amido group in the connection between the two salicylidene constituents. The compound, SalpenN<sub>3</sub>HAl(thf)<sup>+</sup>·AlMe<sub>2</sub>Cl<sub>2</sub><sup>−</sup> (**144**)[AlMe<sub>2</sub>Cl<sub>2</sub>], the only example of a type **F** cation, was prepared by dissolution of the bimetallic (SalpenN<sub>3</sub>H{AlMeCl<sub>2</sub>})<sub>2</sub> in thf followed by redistribution (Scheme 45).<sup>145</sup>

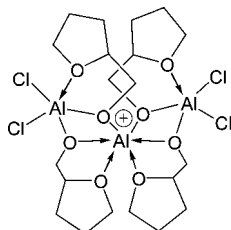
In the structure, the Al–O(thf) bond distance (2.046(3) Å) is longer than the Al–O(ligand) bonds (~1.8 Å). In contrast, the partial Salen ligand, phensal(<sup>t</sup>Bu)H<sub>2</sub> (*N*-phenyleneaminesalicylidene), can be used to prepare the six-coordinate cations [phensal(<sup>t</sup>Bu)H<sub>2</sub>Al]<sup>+</sup> as X<sup>−</sup> salts (X<sup>−</sup> = Cl<sup>−</sup>, GaCl<sub>4</sub><sup>−</sup>, Me<sub>2</sub>AlCl<sub>2</sub><sup>−</sup>) in MeOH, CH<sub>2</sub>Cl<sub>2</sub>, and toluene, respectively.<sup>146</sup> In the crystal structures of **145** and **146**, the two cations are similar (Figure 33), with the amine group and the oxygen atoms *trans* to one another and, likewise, the imine groups being *trans*. Both compounds feature



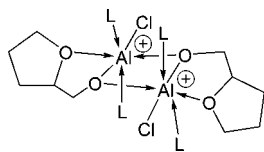
**Figure 33.** Structure of the six-coordinate Al cation [(phensal(<sup>t</sup>Bu)H<sub>2</sub>)Al]<sup>+</sup> in compounds **145**–**147** (the <sup>t</sup>Bu are omitted for clarity).



**Figure 34.** Structure of a six-coordinate Al alkoxide cation derived from crystallization of four-coordinate cation **85e**<sup>+</sup> (see Table 4) from thf.



**Figure 35.** Structure of the trinuclear Al cation [(thffo)<sub>4</sub>-(Al)(AlCl<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> in compound (**148**<sup>+</sup>).



**Figure 36.** Structure of the dinuclear Al dication [(thffo)<sub>2</sub>-(AlCl<sub>2</sub>)<sub>2</sub>(EtOH)<sub>4</sub>]<sup>2+</sup> in compound (**149**<sup>2+</sup>).

hydrogen bonding between the amine group and the halides in the anions.

A new six-coordinate structural type (six-coordinate type **D**, Figure 32) was created in a series of reactions designed to prepare the four-coordinate cation **85e**<sup>+</sup> in solution (see Four-Coordinate section, Table 4),<sup>96</sup> which was crystallized from thf as a six-coordinate thf solvate (Figure 34).

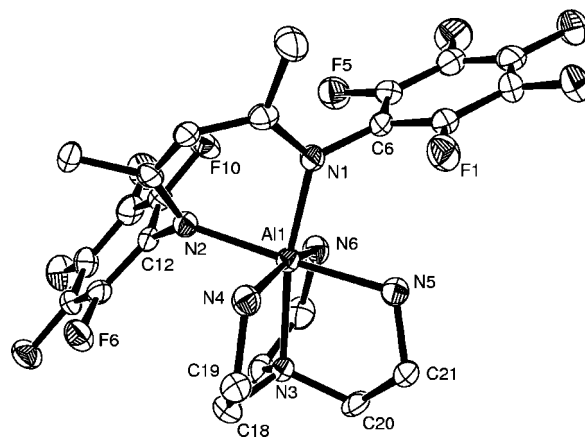
The relatively simple ligand thffo (2-tetrahydrofuryloxo) was used to prepare an interesting six-coordinate cation with peripheral AlCl<sub>2</sub> groups, [(thffo)<sub>4</sub>(Al)(AlCl<sub>2</sub>)<sub>2</sub>][AlEtCl<sub>3</sub>] (**148**)[AlEtCl<sub>3</sub>], Figure 35) in addition to the bimetallic dication [(thffo)<sub>2</sub>(AlCl<sub>2</sub>)<sub>2</sub>(EtOH)<sub>4</sub>]Cl<sub>2</sub> (**149**)Cl<sub>2</sub>, Figure 36).<sup>147</sup> Despite the remarkable difference in the structures, the two compounds were prepared by similar synthetic routes by the combination of Nathffo with AlCl<sub>3</sub>(thf)<sub>3</sub> in EtOH/toluene for **149**<sup>+</sup> and AlEtCl<sub>2</sub> in benzene for **148**<sup>+</sup>.

### 6.3. Aluminum Dication

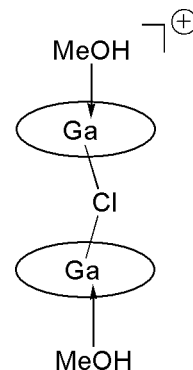
In a remarkable series of reactions, the unique  $\beta$ -diketiminate-supported starting material, LAl(OTf)<sub>2</sub> (L = HC{CMeN(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>})<sub>2</sub><sup>-</sup>), was used to prepare a six-coordinate cation [LAl(terpy)][OTf] (**150**)[OTf] and the first example of a chelated dicationic aluminum compound LAl(tren)<sup>2+</sup>·2OTf<sup>-</sup> (**151**)[OTf]<sub>2</sub>.<sup>148</sup> The crystal structure of **151**<sup>2+</sup> (Figure 37) reveals a moderately distorted octahedral geometry around the aluminum with an axial (N–Al–N) bond angle of 164° and equatorial angles ranging from 81–102°. Perhaps due to the crowded coordination environment, the Al–O and Al–N bond distances are similar to that observed for **150**<sup>+</sup>.

### 6.4. Gallium, Indium, and Thallium Species

Higher-coordinate cationic Ga and In compounds remain rare, and the only example reported since 1998 occurred adventitiously in the attempt to prepare, as had been successfully accomplished numerous times for aluminum,



**Figure 37.** Solid-state structure of the mononuclear Al dication [(HC{CMeN(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>})<sub>2</sub>Al(tren)]<sup>2+</sup> in compound (**151**<sup>2+</sup>) with partial atom labeling for clarity.



**Figure 38.** Structure of the Ga chloro-bridged cation **152**<sup>+</sup>.

the cation [Salen(<sup>t</sup>Bu)Ga(MeOH)<sub>2</sub>]BPh<sub>4</sub>. What resulted from this reaction was the chloro-bridged Ga cationic compound **152**<sup>+</sup> (Figure 38).<sup>149</sup> The full refinement of this structure was complicated by the presence of five disordered MeOH groups in the unit cell. Nevertheless, the structure revealed that the Ga–Cl–Ga angle was 149°.

Two six-coordinate thallium cations have been prepared and fully characterized over the past 10 years. The reaction of Tl(S<sub>3</sub>) (S<sub>3</sub><sup>-</sup> = hydrotris(3-methyl-1-imidazolyl-2-thione)-borate) with excess iodine was found to afford the efficient formation of the six-coordinate Tl(III) cation Tl(S<sub>3</sub>)<sub>2</sub><sup>+</sup> (**153**<sup>+</sup>) as a dissociated TlI<sub>4</sub><sup>-</sup> salt in the solid state.<sup>150</sup> In this reaction, iodine is believed to provide the oxidative drive of the reaction (to go from Tl(I) to Tl(III)) and is reduced to I<sub>3</sub><sup>-</sup>. The six-coordinate Tl(III) cations Tl(phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> (phen = 1,10-phenanthroline) and Tl(en)<sub>3</sub><sup>+</sup> (en = ethylenediamine), which were both obtained as dissociated ClO<sub>4</sub><sup>-</sup> salts, were characterized by X-ray crystallography.<sup>151,152</sup>

### 6.5. Applications

In previous work, it was shown that [SalenAl(MeOH)<sub>2</sub>]-[BPh<sub>4</sub>] polymerized propylene oxide while the compounds coordinated by water or with Cl<sup>-</sup> as the counteranion did not.<sup>13</sup> However, Salen(<sup>t</sup>Bu)Al(MeOH)<sub>2</sub> was found to oligomerize propylene oxide to produce low *M<sub>w</sub>* oligomers with *M<sub>n</sub>* = 427 and PDI = 1.5.<sup>144</sup> Since it is known that Brønsted acids can oligomerize oxiranes, a further study for 48 h was conducted on propylene oxide with the thf supported cations, [LAl(thf)<sub>2</sub>][BPh<sub>4</sub>] (with L = Salen(<sup>t</sup>Bu) and Salpen(<sup>t</sup>Bu)). The *M<sub>w</sub>* of the polymers were 400 000 and 180 000, with PDIs of 1.32 and 1.16, respectively. A theoretical analysis



indicated that the likely mechanism was one where the polymerization proceeded through a carbocation terminal end. The aluminum served to ring-open the original oxirane. Binding of the cation to the monomer releases  $9 \text{ kcal mol}^{-1}$  of energy. The energy required to form the first carbocation was calculated to be  $11.2 \text{ kcal mol}^{-1}$ .<sup>68</sup> In a related study, the six-coordinate Schiff base cation shown in Figure 34 was found to be an excellent initiator of the polymerization of  $\epsilon$ -caprolactone with 95% conversion in 1 h with a PDI of 1.3.<sup>96</sup>

The relative binding of PO to a series of LM(III)<sup>+</sup> cations was studied by electrospray tandem mass spectrometry (where M = Al, Ga, Cr, Co and L = tetraphenylporphyrin (TPP) and (*R,R-N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine ("Salcen"))).<sup>153</sup> Through collision-induced dissociation experiments, it was shown that the Cr and Al cations bind PO more strongly than Co (which has the lowest Lewis acidity) and TPP provided a stronger binding environment than Salcen. For the five-coordinate cations LM(PO)<sup>+</sup>, the PO–Al bond strength is greater than that for PO–Cr. For the six-coordinate cations LM(PO)<sub>2</sub><sup>+</sup>, Al loses the first PO more easily than Cr. The TTPAl cations can be classified as "closed" type E compounds where the ligand completely encircles the Al atom and the donor nitrogens are *trans* to one another.

Binuclear boron halide chelate compounds can dealkylate a wide range of phosphates at ambient temperature.<sup>154–156</sup> For example, salpen(<sup>t</sup>Bu)[BBr<sub>2</sub>]<sub>2</sub> dealkylates (MeO)<sub>3</sub>P(O) by 89% and (<sup>t</sup>BuO)<sub>3</sub>P(O) by 99% in only 30 min. This is significant considering the fact that BCl<sub>3</sub> or BBr<sub>3</sub> alone are ineffective for phosphate dealkylation. It was also shown that mononuclear Schiff base aluminum compounds such as Salen(<sup>t</sup>Bu)AlBr could dealkylate organophosphate esters under mild conditions.<sup>141</sup> Triethylphosphate and tributylphosphate were dealkylated 100% over 2 h by three Salen(<sup>t</sup>Bu)AlBr compounds. The mechanism is thought to be one in which the phosphate displaces the Br<sup>−</sup> to form a six-coordinate compound. The free Br<sup>−</sup> then attacks the alkyl carbon of the phosphate to effect the dealkylation. As partial confirmation of this mechanism, MeOP(O)Ph<sub>2</sub> was demonstrated to be dealkylated to produce a Salen(<sup>t</sup>Bu)Al(OP(O)Ph<sub>2</sub>) compound by reaction of Salen(<sup>t</sup>Bu)AlBr with (MeO)P(O)Ph<sub>2</sub>.<sup>122</sup> In the dealkylation reaction, MeBr is produced along with several potential phosphate containing chelate compounds. The reaction can be monitored by comparing the <sup>1</sup>H NMR peak integration of methyl halide to that of the original phosphate.

The regioselective ring-expansion carbonylation of aziridines to form lactams was achieved with the catalyst, [Salophen(<sup>t</sup>Bu)Al(thf)<sub>2</sub>][Co(CO)<sub>4</sub>] (Salophen = (*N,N'*-*o*-phenylene-bis(3,5-di-*tert*-butylsalicylideneimine))).<sup>157</sup> In the best-case example, 1-tosyl-2-methylaziridine was converted to lactam in 99% yield at 90 °C over 6 h. The mechanism is thought to be one where the Al cation coordinates the aziridine nitrogen, causing ring opening and formation of a C–Co bond, which then undergoes carbonylation.

The same cationic catalyst was also used in the carbonylation of epoxides.<sup>158,159</sup> The resting state for the reaction was the neutral compound Salophen(<sup>t</sup>Bu)AlOCH(R)CH(R)C(O)–Co(CO)<sub>4</sub> (where R = H or alkyl). The rate of lactone formation depended on the type of solvent used. Lewis basic solvents were found to assist the catalysis by supporting the Al cation formed when the lactone was created in the rate-determining step. In related work, the first double-

carbonylation of epoxides to succinic anhydrides with [CITPPAl(thf)<sub>2</sub>][Co(CO)<sub>4</sub>] was achieved.<sup>160</sup> In this catalytic reaction, a lactone is carbonylated to lactone, followed by carbonylation of the lactone to the anhydride. 1,4-dioxane is essential as the solvent in this system.

SalophenAl(NO<sub>3</sub>), which would exist as the six-coordinate diaquo cation in solution, was used in creating new coated graphite electrodes for the detection of salicylate, a metabolite of aspirin.<sup>161</sup> The electrode had the composition 32% PVC, 65.8% plasticizer, and 2.2% of the Salen compound. The sensors are easy to prepare; have high sensitivity, high selectivity, very low detection limits, and rapid response times; and operate over the pH range of 3–8. The mode of action was suggested to be one where the SalophenAl(H<sub>2</sub>O)<sub>2</sub><sup>+</sup> cation undergoes deprotonation to form neutral SalophenAl(H<sub>2</sub>O)OH. This compound then binds directly to the salicylate anion, forming the salt [SalenAl(sal)(OH)]Na.

## 6.6. Summary

Six-coordinate aluminum cations (and related neutral derivatives) supported by Salen and porphyrin ligands have now become widely used for catalytic applications including propylene oxide polymerization and a wide range of carbonylation reactions. These applications rely on the stable environment provided by the ligands and the Lewis acidity of the cations. In the carbonylation reactions, added Lewis basic ligands are needed to mitigate the cationic charge on the aluminum atom.

## 7. Higher Coordination Numbers and Unique Compounds

Aqueous aluminum chemistry is important in many industrial processes, including aluminum production and water treatment, and knowledge of this area is important in geochemistry and soil science. However, little is known about the multitude of aqueous aluminum compounds beyond the simple species Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> and Al(OH)<sub>4</sub><sup>−</sup>. The exception is the structural elucidation of the Keggin polycation ( $\epsilon$ -Al<sub>13</sub>), Al<sub>12</sub>(AlO<sub>4</sub>)(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub><sup>7+</sup>, achieved over 40 years ago.<sup>162,163</sup> More recently, however, a remarkable new structure, Al<sub>30</sub>-O<sub>8</sub>(OH)<sub>56</sub>(H<sub>2</sub>O)<sub>24</sub><sup>18+</sup>, has been prepared and characterized by Al<sup>27</sup> NMR.<sup>164</sup> The structure consists of two  $\delta$ -Al<sub>13</sub> units bridged by four AlO<sub>6</sub> octahedra. It is the largest Al polycation ever observed and the first instance where the  $\delta$ -Al<sub>13</sub> was unequivocally characterized.

Because of the high toxicity of the monovalent cation Tl<sup>+</sup>, neutral carriers able to selectively complex the Tl(I)<sup>+</sup> cation are of great importance for the design of Tl<sup>+</sup>-selective electrodes. Such an electrode may significantly improve the current instrumentation for the Tl(I)<sup>+</sup> assay in human body fluids. Tl<sup>+</sup>-selective neutral carriers such as crown ethers have been developed in the 1980s, and these typically yield complexes in which the Tl atom has a high coordination number (>6). Little more work has appeared over the past few years with the exception of a couple of reports on the selective complexation of Tl<sup>+</sup> cations by calix[4]arene derivatives.<sup>165</sup> In the latter systems, whether in the solid state or in solution, two thallium cations are incorporated within the calix[4]arene cavities, and each is bonded through  $\pi$ -cation interactions to 12 carbon atoms of the two vertical phenyl rings.

## 8. Conclusions—Perspectives

The synthesis, structure, and catalytic applications of cationic group 13 species have undoubtedly witnessed an unprecedented growth over the last 10 years, which is largely due to the now widespread use of synthetic methodologies that allow access, in a selective and well-defined manner, to lower- and higher-coordinate group 13 cations. As a consequence, various mononuclear and polynuclear group 13 cations have been characterized, providing insight into the rich structural trends that might be expected for this class of species.

For the most part, group 13 cations have been shown to be very effective in Lewis acid catalysis with transformations involving the activation of an unsaturated substrate through coordination to the Lewis acidic cationic group 13 metal center (PO,  $\epsilon$ -CL, and isobutene polymerization and dealkylation of alkylphosphates). The insertion chemistry of group 13 cations remains surprisingly unexplored with the exception of reactivity studies toward some three-coordinate Al alkyl cations, which were shown to be less reactive in this regard than their neutral counterparts. However, studies on four-coordinate Al alkoxide cations showed that such species may readily insert polar monomers such as lactides and  $\epsilon$ -CL, which shows the potential use of group 13 cations for insertion.

Thus, more extensive reactivity studies of lower- to four-coordinate group 13 cations other than group 13 alkyl cations clearly remain to be explored. Such cationic derivatives may mediate interesting transformations through Lewis acid/insertion chemistry. Further developments in the area of four-coordinate group 13 cations may also occur with the preparation and systematic reactivity studies of dinuclear/polynuclear group 13 cations. Although the formation of such species is typically thought to be detrimental to reactivity, a couple of reports in this domain have shown that such species may well be of interest in catalysis.

Higher-coordinate group 13 cations have now become widely used for catalytic applications including propylene oxide polymerization and a wide range of carbonylation reactions. When compared to their lower-coordinate analogues, six-coordinate cations such as the  $[(\text{Salen})\text{Al}(\text{L})_2]^+$  cations are less Lewis acidic but exhibit an increased stability, which renders them suitable for chemical transformations involving polar media and/or substrates. Accordingly, future developments in this area may be concerned with an extension of the scope of applications of such stable and Lewis acidic cationic species.

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