THE UTILIZATION OF STERICALLY DEMANDING LIGANDS IN THE STABILIZATION OF MAIN GROUP METAL COMPLEXES

by

JASON KENNETT VOHS

(Under the direction of Gregory H. Robinson)

ABSTRACT

The syntheses and molecular structures of group 13 and 15 organometallic complexes are presented herein. Five different ligand systems were employed in this work: (1) tetraphenylbutadienyl; (2) pentamethylphenyl; (3) adamantyl; (4) ferrocenyl; and (5) triphenylmethyl. The tetraphenylbutadienyl ligand has previously been used to isolate the first spirogallane as well as a number of interesting group 14 organometallic complexes. Utilizing 1,4-dilithiotetraphenylbutadiene with MX_3 (M = P or B; X = Br) yields a novel diphosphine, $[(Ph_4C_4)P—P(C_4Ph_4)]$ **I**, and the fused-ring borane $[(Ph_4C_4)_2(C_2H_5)]B$ **II**. Using both organolithium and organomagnesium derivatives of the pentamethylphenyl ligand, various aluminum and gallium complexes have been isolated (**III-V**). These complexes possess dihedral angles which distinguish them from previous complexes which have employed phenyl-based ligands. The reaction of adamantylmagnesium bromide with $AlCl_3$, $GaCl_3$, Me_2GaCl, and Me_2AlCl gives complexes which are the first examples of adamantyl-based group 13 organometallic compounds (**VI-IX**). These ionic main group complexes possess not only main group adamantyl anions, but also unusual trimetallic magnesium cluster cations. The use of the ferrocenyl and triphenylmethyl moieties as ligands is also explored in this work. These molecules, although not traditionally thought of or used as ligands, are potentially useful due to their interesting structural features.

INDEX WORDS: Adamantyl, Alanes, Aluminum, Bonding, Boranes, Ferrocenyl, Gallanes, Gallium, Gallyne, Group 13, Magnesium Cluster, Main Group, Metalloaromaticity, Organometallic, Pentamethylphenyl, Phosphine, Sterically Demanding Ligands, Tetraphenylbutadienyl, Triphenylmethyl.

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DEDICATION

I would like to dedicate this dissertation to Charlie Franklin. Mr. Franklin was by far the best teacher I ever had. It was not only the enthusiasm he brought to the subject of chemistry, but the way he carried himself. He tried to connect with every student that sat before him. He was perhaps most influential in the way that he shared his faith. Mr. Franklin stressed the importance of doing the right thing and living a clean life even though it may not be popular. I have encountered very few teachers who could command the same amount of respect and admiration that Mr. Franklin enjoyed. Mr. Franklin could not possibly know how he's touched the lives of each of his students, but I want him to know that I am forever indebted to him for the guidance he gave me. Some teachers and professors taught me many courses, but I never learned more than I did in the one course I had with Mr. Franklin, and for that I am eternally grateful. Thank you so much Mr. Franklin.

God Bless,
Jason Vohs

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INTRODUCTION

1.1 ORGANOMETALLIC CHEMISTRY

Organometallic chemistry has often been viewed as a hybrid subset of traditional inorganic and organic chemistry. Initially it was slow to develop and encompassed little more than a handful of curious compounds. However, in the last half-century the field has grown tremendously and many areas of applied chemical research routinely deal with the metal-carbon bond. From biochemistry to polymer science, materials science to theoretical chemistry, one would be hard pressed to find an area of study that does not have an organometallic component.

The first organometallic compound reported was that of Ziese in 1872 (Fig. 1), who isolated yellow needle-like crystals from the reaction of $PtCl_4$ and $PtCl_2$ in ethanol, followed by the addition of KCl solution.[1]

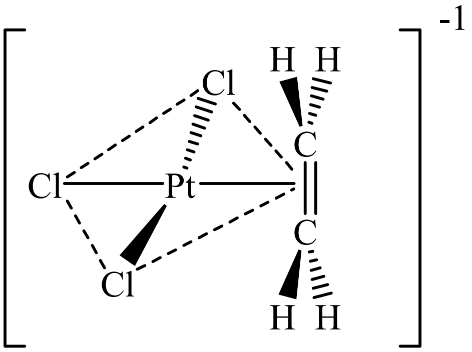
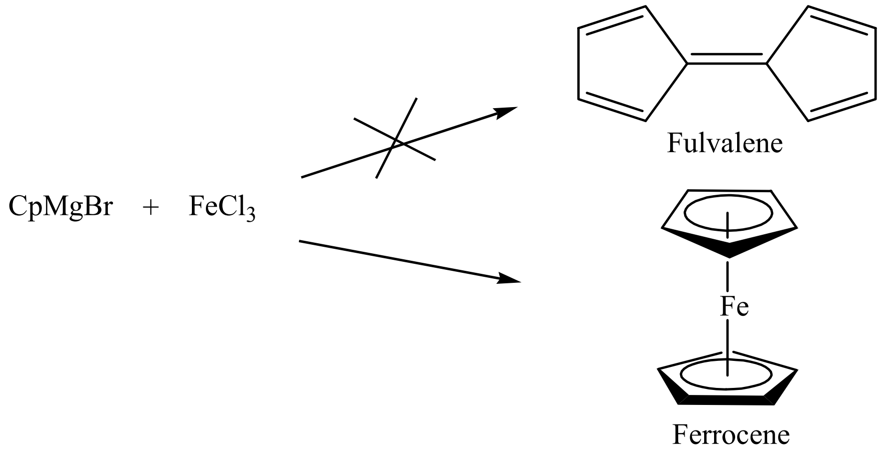


Figure 1. Anion of Zeise's salt.

The resulting product, later dubbed “Zeise’s Salt,” has the formula $K[Pt(C_2H_4)Cl_3]{\bullet}H_2O$ and was the first documented example of an organic molecule moiety bonding to a metal through the π system of electrons. A recent article by Seyferth details much of the history of this seminal compound and Zeise’s early investigations.[2] In the year’s following the discovery of Zeise’s Salt, little work would be done in the area of organometallic chemistry. Although in the early part of the 20th century organolithium[3] and Grignard[4] reagents began to find utility in organic synthesis, it would not be until the early 1950’s that organometallic chemistry would begin to flourish. In 1951 Kealy and Pauson, while attempting to synthesize fulvalene, happened upon an orange, air stable, relatively inert, iron compound (Eq. 1).[5] Ferrocene was the first compound containing a metal atom “sandwiched” between two cyclopentadienyl rings.



(1)

In 1956 a single crystal X-ray diffraction study confirmed the structure as having the rings in an eclipsed conformation.[6] Further studies have shown that ferrocene possesses multiple ring conformations which are temperature dependent.[7] In 2001, in order to commemorate the discovery of ferrocene, a number of articles were written detailing much of the early explorations of this groundbreaking compound.[8]

Since ferrocene's discovery many other sandwich compounds containing other metals have been reported. Recent pursuits in organometallic chemistry involve the design and synthesis of catalysts for use in polymer production, cancer fighting agents in medicine, inorganic polymers, and semiconductor precursors.

1.2 THE GROUP 13 ELEMENTS

The elements of Group 1 on the Periodic Table, the Alkali Metals, exhibit very similar chemical behavior. Furthermore, with the exception of beryllium, the elements of Group 2, the Alkaline Earth Metals, also exhibit very similar chemistry. However, the elements of Group 13 have chemistries and physical properties which can vary quite a bit (Table 1). The chemistry of boron, for example, is often discussed separately from the chemistry of the heavier members in most textbooks.

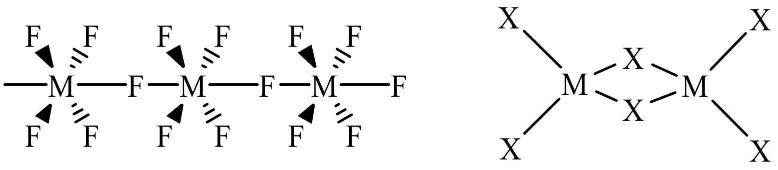
Table 1. Selected properties of the Group 13 elements and their ions.[9]

Property	B	Al	Ga	In	Tl
Atomic Number	5	13	31	49	81
Atomic Weight	10.81	26.98	69.72	114.82	204.38
Covalent Radii, Å	0.88	1.30	1.22	1.50	1.55
Electronic Configuration	$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10} 4s^2 4p^1$	$[Kr]4d^{10} 5s^2 5p^1$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
Ionization Energy, kJ/mol					
I	800.6	577.5	578.8	558.3	589.4
II	2427	1817	1979	1821	1971
III	3660	2745	2963	2704	2878
IV	25030	11580	6200	5200	4900

Most of an element's chemical properties are determined by its valence electrons; however, some of the differences in the chemistry of the Group 13 elements can be attributed to the different inner electron configurations of each. These inner core electrons, although not directly involved in bonding, contribute to valence electron shielding. For example, boron and aluminum have an ns^2np^1 configuration while gallium, indium, and thallium possess a full complement of d^{10} electrons between the valence electrons and the nucleus. Furthermore, thallium also has 14 electrons in the $4f$ shell. These differences along with effective nuclear charge changes and size contraction prohibit a simple extrapolation of ionization energies from boron and aluminum.[10] There is also a tendency for the heavier members of the group to exist in lower oxidation states. The phenomenon has been referred to as the inert pair effect. This theory states that the filled s^2 subshell is inert resulting in a complex having an oxidation number 2 less than what is expected for the group. The actual explanation is more complex and can be attributed to the decreasing bond strengths and certain relativistic effects present in the heavier atoms.[11]

1.3 HALIDES OF THE GROUP 13 ELEMENTS

The halides of the Group 13 metals are of particular interest due to their utility in catalyzing organic reactions and because they are frequently used as starting materials in organometallic syntheses. All of the metal trihalides of the Group 13 elements are known except for Tl(III) iodide which exists as Tl(I) tri-iodide $[I\text{-}I\text{-}I]^-$, where I_3^- has almost a linear geometry. With the exception of the boron trihalides, all of the Group 13 trihalides exist as dimers or in infinite lattices with the metal centers having an octahedral geometry (Fig. 2).



M = Al, Ga, In, Tl

M = Al, Ga
X = Br, I

Figure 2. Diagrams of the geometries of some of the Group 13 halides.

The boron trihalides exist as monomers with planar geometries. This phenomenon can be attributed to the existence of π bonds formed from the donation of electron density from the filled *p* orbital of the halide atom into the empty 2*p* orbital on the boron. This has been experimentally observed by the shorter than expected bond distances in the boron trihalides. Another result of having π-bonding in the molecule would be the reversed trend in Lewis acidity of the boron trihalides. Electronegativity would dictate that the BF_3 complex would be the most Lewis acidic; however, BI_3 is actually more so. The loss of π-character contributes to the highly disfavored geometric conversion from a trigonal planar geometry to a tetrahedral one. Moreover, with the amount of π-character in the B-X bonds following the trend $BF_3 > BCl_3 > BBr_3 > BI_3$, the trend of Lewis acidity strength would be reversed.

The divalent derivatives of the Group 13 elements have been isolated *via* reductions of the trihalides. These mixed valence salts have the general formulae $M^+[M(III)X_4]^-$. When electron donating ligands are added to these systems, M-M bonded species result with each metal having a 2^+ oxidation state. An example would be Ga_2Br_4•(1,4-dioxane)$_2$, in which one dioxane molecule is coordinated to each gallium atom.

The univalent species of the group are much less common. The stability of such species decrease down the group with In(I) and Tl(I) being more common, owing their stability to factors discussed earlier such as decreasing bond strength and the inert pair effect. Al(I) and Ga(I) species are much less stable and are likely to form disproportionate salts. Furthermore, these low valent species are seen mainly at high temperatures or in the gas phase.

1.4 METHODS OF ORGANOMETALLIC SYNTHESIS

1.4.1 General Considerations

Many of the reagents and products involved in organometallic syntheses are air- and/or moisture-sensitive and require that manipulations to be performed under an inert atmosphere. These manipulations also include the use of Schlenk techniques[12] and rigorously dried solvents. In addition, the glassware involved must also be free of moisture, oxygen, and any other impurities.

Generally Group 13 organometallic compounds are prepared *via* one of the following classes of reactions:

1. Direct reaction of the metal with an organic reagent;
2. Oxidation-Reduction reactions; or
3. Metathesis reactions between a metal alkyl and a Group 13 metal compound.

1.4.2 Organomercury Reagents

In the formative days of organometallic chemistry, organomercury reagents were widely used. These simple oxidation-reduction reactions are generally straightforward, with product separation proceeding with little difficulty. Much of the early organoaluminum chemistry was accomplished *via* such reactions (Eq. 2).

$$2Al + 3R_2Hg \longrightarrow 2R_3Al + 3Hg \qquad (2)$$

Although the organomercury compounds are for the most part easy to prepare, they are not currently the reagents of choice due to significant health and environmental concerns.

1.4.3 Grignard Reagents

Since their discovery, Grignard reagents have found great utility in the major areas of synthetic chemistry. Such reagents actually consist of a series of species in equilibria and have complex reaction mechanisms. The particular reaction conditions required vary somewhat with the nature of the R group, but typically the preparation involves the reaction of an alkyl or aryl halide with magnesium metal in an ethereal solvent. In many cases the effectiveness of the reagent can be improved by heating the magnesium to "activate" it, or by adding a small amount of I_2 or Br_2 to the reaction to generate MgX_2 *in situ*. The presence of additional MgX_2 drives the Schlenk equilibrium in a favorable direction (Fig. 3).[13]

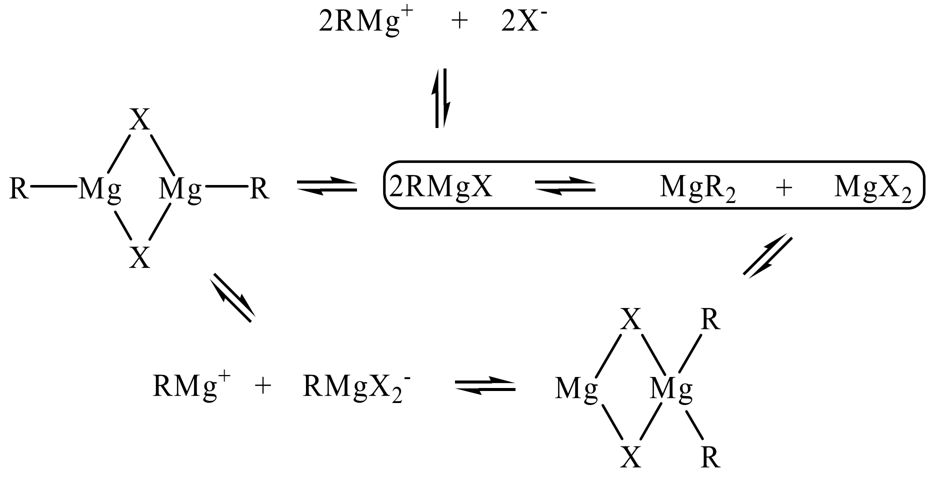


Figure 3. Grignard reagent equilibria. The highlighted region is the most often referred to portion of the overall Schlenk equilibrium.

1.4.4. Organolithium Reagents

Organolithium reagents, like Grignard reagents, are very useful in a variety of synthetic situations, yet they are typically more reactive. They can be prepared by reacting an alkyl or aryl halide with lithium metal (Eq. 3), or by the metallation of an organic species by *n*-butyllithium (Eq. 4). These species often exist in solution as aggregates forming dimers, tetramers, and hexamers. The commercial availability of these reagents also contributes to their utility.

$$\mathrm{RX} + 2\mathrm{Li} \xrightarrow{\text{hydrocarbon solvent}} \mathrm{RLi} + \mathrm{LiX} \qquad (3)$$

$$n\mathrm{BuLi} + \mathrm{RH} \xrightarrow{\text{hydrocarbon solvent}} n\mathrm{BuH} + \mathrm{RLi} \qquad (4)$$

1.5 ORGANOALUMINUM AND ORGANOGALLIUM CHEMISTRY

1.5.1 Organoaluminum Chemistry

Organoaluminum chemistry has a rich and varied history. The dominant feature is the Lewis acidity of the aluminum alkyls and aryls. This property has made this class of compounds an important component of numerous industrial applications, more specifically Ziegler-Natta heterogeneous catalysis.

These compounds can generally be prepared by reacting aluminum halides with the appropriate organolithium or Grignard reagents. In large scale or industrial settings, aluminum metal can be combined with the appropriate alkene in the presence of hydrogen gas at elevated temperatures and pressures (Eq. 5).

$$2\mathrm{Al} + 3\mathrm{H_2} + 6\,\mathrm{RHC{=}CH_2} \xrightarrow[\text{100-200 atm}]{\text{60-110}^\circ\text{C}} \mathrm{Al_2(CH_2CH_2R)_6} \qquad (5)$$

Because the Al-C bond is highly susceptible to protolysis, the simple aluminum alkyls are highly pyrophoric in nature. Moreover, this susceptibility allows for the simple preparation of aluminum alkoxides and amides.[14] These compounds exist as dimers with the aluminum atoms in a four-coordinate tetrahedral environment. The bridging carbon atoms engage in electron deficient, three center-two electron bonding (3c-2e$^-$). This bonding model was first proposed in order to describe the bonding in the boron compound, B_2H_6. Although it was initially controversial, further studies indicated that this was indeed the correct description of the bonding (Fig 4.)

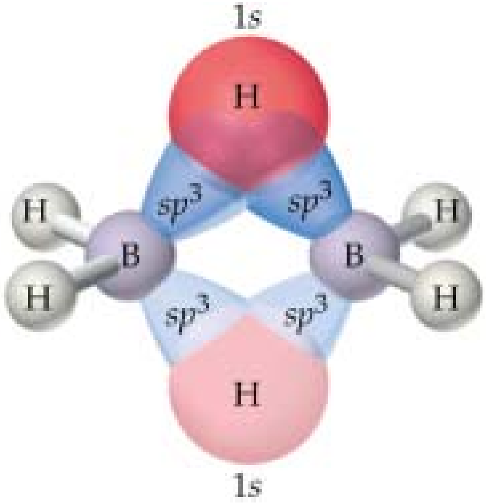


Figure 4. Depiction of the three center-two electron bonding in B_2H_6.

X-ray crystallographic data from both Me_6Al_2[15] and Ph_6Al_2[16,17] show that the bridging Al-C bond distances are 9-11% longer than the terminal Al-C bonds (Fig. 5). These bonds are also generally weak as they readily cleave symmetrically across the bridging bonds upon reaction. Although aluminum has been shown to engage in these electron deficient bonding schemes, the size of the ligand attached to the metal has a profound effect on the geometry of the complex.

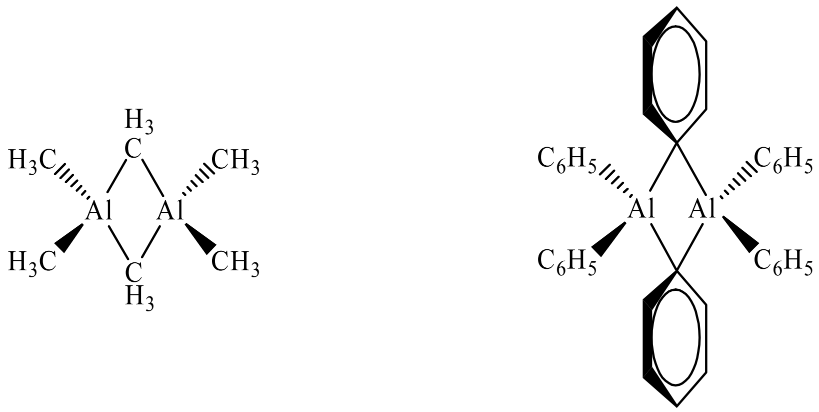


Figure 5. The structures of Me_6Al_2 and Ph_6Al_2 showing the bridging nature of the carbon ligands.

Trimesitylaluminum, Mes_3Al[18] (Mes = 1,3,5-trimethylphenyl), prepared by the reaction of aluminum metal with dimesitylmercury exists as a monomer with the aluminum center assuming a three-coordinate trigonal planar geometry. The Al-C bond distance is 1.995(8) Å with bond angles of 120° (Fig. 6).

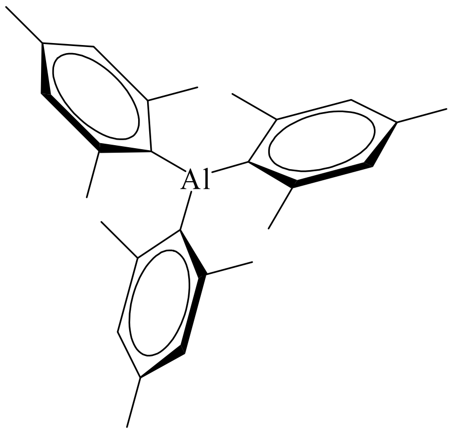


Figure 6. Structure of trimesitylaluminum.

The mesityl ligands are arranged around the aluminum center in a propeller-like fashion with dihedral angles of 55°. The design and use of other types of sterically demanding ligands have been the focus of a number of workers, as such ligands allow for interesting geometries and the stabilization of metal-metal bonds.

1.5.2 Organogallium Chemistry

The organometallic chemistry of gallium is generally similar to that of aluminum. However, there are notable differences. The first organogallium complex, triethylgallium monoetherate, $Et_3Ga{\bullet}OEt_2$, was reported in 1932. The synthesis involved the reaction of ethylmagnesium bromide with gallium bromide in diethyl ether (Eq. 6).[19]

$$3\ EtMgBr + GaBr_3 \xrightarrow[Et_2O]{} 3\ MgBr_2 + Et_3Ga(Et_2O) \tag{6}$$

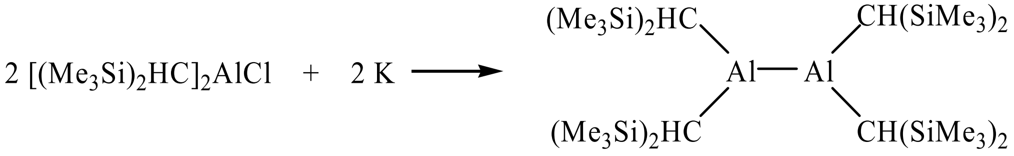
Unlike the simple aluminum alkyls which form dimers, the analogous gallium complexes form monomers. Triphenylgallium, $(C_6H_5)_3Ga$,[20] exists as a monomer in contrast to its aluminum analog. Trimesitylgallium, Mes_3Ga (Mes = 1,3,5-trimethylphenyl), is isostructural with trimesitylaluminum.[21]

Much of the organogallium chemistry that has developed over the last decade has involved the use of sterically demanding ligands on gallium. One of the most sterically demanding ligand systems is the aryl based *ortho*-substituted phenyl derivatives known as *m*-terphenyls. In particular, the *m*-terphenyl based ligands have led to the isolation of $(Mes_2C_6H_3)_2GaCl$, the first example of a main group metal possessing a highly distorted three-coordinate T-shaped geometry.[22] A similar compound, $(Mes_2C_6H_3)GaMes_2$,[23] contains the most sterically hindered gallium center on record. Furthermore, these very bulky ligands have also resulted in metal-metal bonding schemes which are unprecedented in main group organometallic chemistry.

1.6 METAL-METAL BONDING

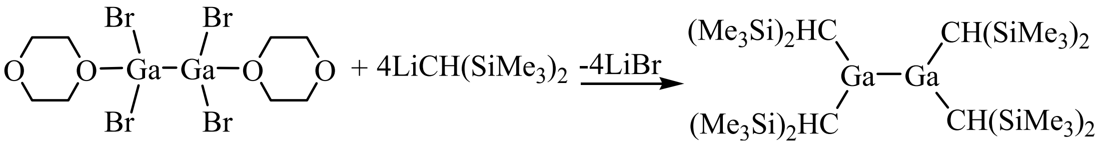
1.6.1 Group 13 Metal-Metal Single Bonding

There are numerous examples of organometallic complexes containing both single[24-26] and multiple[27,28] homonuclear boron-boron bonds. Boron is the lightest member of the group and is classified as a nonmetal. Furthermore, it was not until 1988 when the first organometallic complex containing an unambiguous metal-metal bond was reported. The aluminum complex, tetrakis[bis(trimethylsilyl)methyl]dialane, $[\{(Me_3Si)_2HC\}_2]Al\text{-}Al[CH\{(SiMe_3)_2\}_2]$, was prepared by the potassium metal reduction of chlorobis{bis(trimethylsilyl)methyl}aluminum (Eq. 7).[29] The use of these very bulky silyl ligands is credited with the kinetic stabilization of the metal-metal bond.



$$2\,[(Me_3Si)_2HC]_2AlCl \quad + \quad 2\,K \longrightarrow [(Me_3Si)_2HC]_2Al\text{—}Al[CH(SiMe_3)_2]_2 \qquad (7)$$

The gallium analog, tetrakis[bis(trimethylsilyl)methyl]digallane, $[\{(Me_3Si)_2HC\}_2]Ga\text{-}Ga[CH\{(SiMe_3)_2\}_2]$, was subsequently prepared by the same workers *via* the reaction of [bis(trimethylsily)methyl]lithium, $LiCH(SiMe_3)_2$, with Ga_2Br_4•2dioxane (Eq. 8).[30] With the isolation of these two important compounds began one of the more fascinating areas of Group 13 chemistry. The central factor in the stabilization of the compounds is the nature of the ligand. The steric bulk prevents the metal center from forming dimers or oligomers. The nature of the ligand can also have significant effects on the electronics of the molecule.


(8)

1.6.2 π-Bonding in Group 13 Organometallic Complexes

Having already prepared Group 13 organometallic complexes possessing metal-metal single bonds, the next endeavor for chemists was to isolate multiple bonded species. Such compounds were already realized in boron chemistry. The empty *p*-orbital of boron was ideal for accepting electron density from a lone pair of electrons of a substituent or by a metal reduction. However, π-bonding among heaver main group elements was an elusive phenomenon. Such was the difficulty in isolating main group multiple bonds that the so-called “double bond rule” was established. This rule stated that elements having principle quantum numbers greater than two were precluded from engaging in π-bonding with themselves or other elements. This theory has since been discarded as a number of main group organometallic compounds possessing multiple bonds have been prepared.

Regarding aluminum and gallium, the first π-bonded species reported were the radical anions $[i\text{-Pr}_3\text{C}_6\text{H}_2]_2\text{Al-Al}[i\text{-Pr}_3\text{C}_6\text{H}_2]_2^{-}$,[31] and $[i\text{-Pr}_3\text{C}_6\text{H}_2]_2\text{Ga-Ga}[i\text{-Pr}_3\text{C}_6\text{H}_2]_2^{-}$.[32] The Al-Al bond distance shortened from 2.647(3) Å to 2.470(2) Å, and the Ga-Ga bond distance was reduced to 2.343(2) Å from 2.515(3) Å in the neutral species. Both of these compounds were prepared *via* lithium metal reductions of the neutral species. The results are one-electron π-bonds generated by the overlap of *p*-orbitals of Al and Ga. The effective bond orders of the compounds are 1.5.

1.6.3 Metal-Metal Multiple Bonding in Group 13 Complexes

The report of a tin-tin double bond by Lappert in 1976,[33] and the subsequent reports of silicon,[34] germanium,[35] and lead[36] also engaging in multiple bond formation, began a new area of interest in organometallic chemistry. Furthermore, with the reports of so many new compounds came a renewed discussion of the nature of the metal-metal multiple bond. The traditional depiction of π-bonding involved a side-on overlap of *p*-orbitals. A second depiction was put forth by Lappert in the characterization of $[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_2]_2$. This new model depicts a donor-acceptor arrangement of orbitals with the tin atoms assuming a non-planar geometry (Fig. 7).

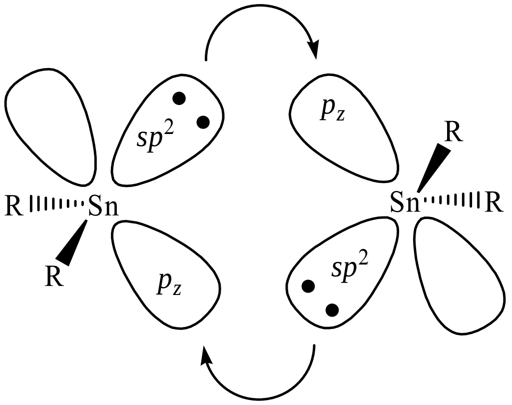


Figure 7. Donor-acceptor bonding model for $[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_2]_2$.

Specifically, a pair of electrons is donated from a hybridized sp^2 orbital on the first tin atom into an empty p_z orbital on the second.

In classical organic chemistry, there are fundamental criteria that are used to describe the nature of a chemical bond. For bonds involving carbon, as the bond order is increased the bond length is shortened. Moreover, as the bond order is increased, so is the bond strength. These criteria hold well for organic systems; however, they do not hold well for organometallic bonding systems.

In 1997, the Robinson group reported the synthesis of $Na_2[Mes^*{}_2C_6H_3Ga{\equiv}GaC_6H_3Mes^*{}_2]$ ($Mes^*{=}2,4,6\text{-}i\text{-}Pr_3C_6H_2$), the first gallyne, an organometallic complex possessing a gallium-gallium triple bond.[37] This report was highly provocative and generated much discussion as to the nature of the metal-metal bond.[38,39] The chief disputes concerned the length of the Ga-Ga bond. At 2.319(3) Å, it represents the shortest Ga-Ga bond distance on record; however, opponents claim that it is not short enough to warrant classification as a triple bond. Over the next few years a number of computational studies were reported using a number of different models and methods.[40,41] The bonding model in the gallyne is similar to that of the distannene (Fig. 8). The only difference is that the two donor-acceptor bonds are augmented by an additional π-bond. The geometry of the gallyne is also trans-bent, as predicted by this bonding model. Contrary to the behavior of carbon systems, doubly-bonded organometallic species could be expected to have only marginally shorter or even longer bond lengths than singly-bonded complexes. Furthermore, the bond strengths of the model compounds were found to be weaker than single bonds. The key findings and observations are best summarized in a quote from Klinkhammer: "neither the bond length, nor the bond strength or the topology are reliable criteria for determining the bond order of bonds between heavy main group elements."[42]

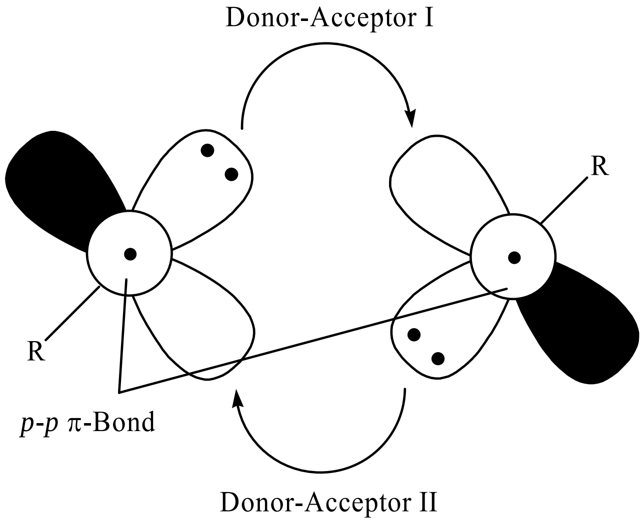


Figure 8. Bonding in the gallyne consists of two donor-acceptor bonds augmented by an additional π-bond.

1.7 METALLOAROMATICITY

The concept of aromaticity has been almost exclusively confined to organic chemistry. Moreover, benzene is the iconic model used to illustrate this concept. Relative to inorganic chemistry, the closest analog is the boron-nitrogen compound borazine.[43] The two compounds share very similar physical properties; however they have very different chemical behaviors.

In 1995, Robinson and coworkers reported $Na_2[(Mes_2C_6H_3)Ga]_3$, the first cyclogallene.[44] This complex consisted of a planar, three-membered, gallium ring, with sodium atoms centered above and below the plane. The bond distance of 2.441(1) Å represented a rather short Ga-Ga bond with an effective bond order of 1.3. The gallium atoms have a sp^2 hybridization leaving an empty p orbital to accept electron density from the sodium atoms. Each sodium atom donates one electron into the π electron cloud. These two electrons, which are delocalized over all three gallium atoms, fulfill Hückel's

(4n + 2) definition of aromaticity. The potassium analog, $K_2[(Mes_2C_6H_3)Ga]_3$ was reported a short time later,[45] as was a theoretical study detailing the electronic properties of these compounds (Fig. 9).[46]

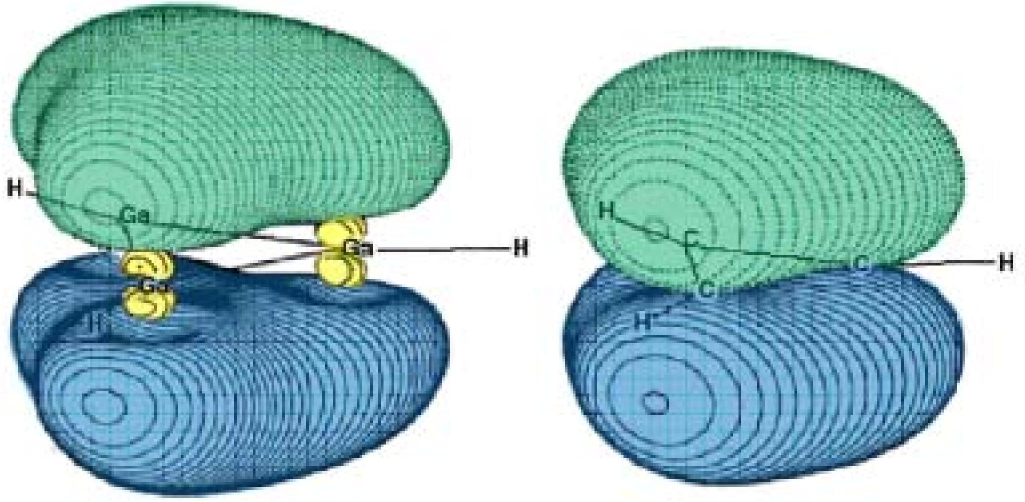


Figure 9. Depiction of the π-electron clouds of $[Ga_3H_3]^{2-}$ and $[C_3H_3]^{+}$.

The key to isolating organometallic compounds containing metal-metal bonds is through kinetic stabilization *via* sterically demanding ligands. Furthermore, the nature of the ligand is very important in that small changes in the ligand design can bring about substantial changes in the final product. The ultimate goal of this research is to isolate compounds containing metal-metal bonds and to study their molecular and electronic structure. This information will further the discussion and aid in an accurate description of the nature of the organometallic metal-metal bond. Herein are described different ligand systems and their utilization in the stabilization of novel main group metal complexes. Although none of the compounds presented here possess metal-metal bonds, their syntheses and structures have provided valuable insight into the utility of the chosen ligand systems. The complexes themselves are interesting in their own right in that most of them are the first examples of Group 13 complexes that contain a certain type of ligand. Moreover, they may contain some structural feature that is unique to main group complexes. Furthermore, studies are ongoing into reacting these compounds further so as to form metal-metal bonds, as well as to incorporate these moieties into larger ligands.

CHAPTER 2

RESULTS AND DICUSSION

Our laboratory is interested in the Group 13 organometallic chemistry of a variety of sterically demanding ligand systems. The main focus was on the *m*-terphenyl type of ligands. These are monodentate ligands which sterically crowd the metal center and enable the kinetic stabilization of metal-metal bonding and strained molecular geometries. A number of relevant compounds were isolated by this laboratory using such ligands. Recent aims have involved the exploration of new ligand systems which continue to explore the concept of steric crowding. These ligands include: the bidentate tetraphenylbutadienyl ligand, pentamethylphenyl, adamantyl, ferrocenyl, and triphenylmethyl (Fig. 10).

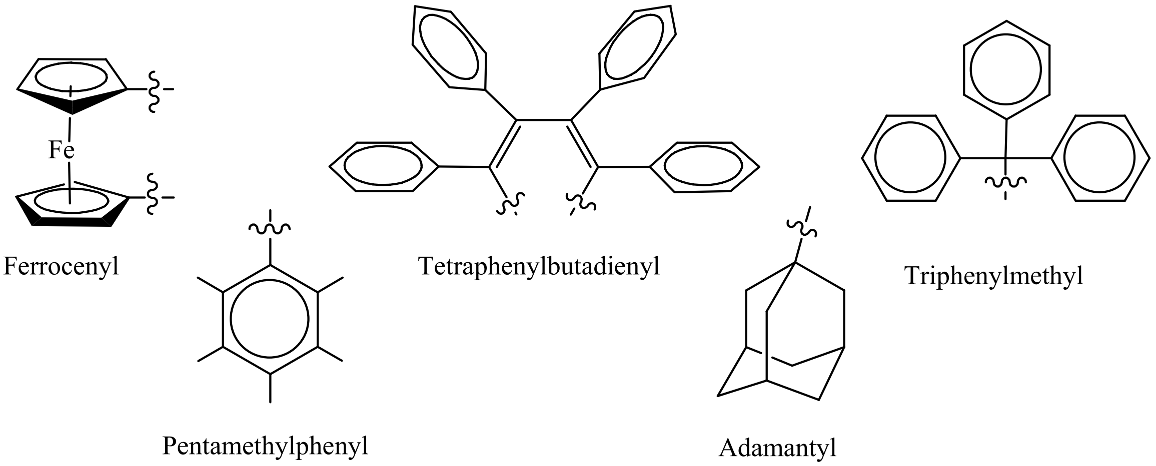


Figure 10. Ligand systems employed in the stabilization of main group metal complexes.

We have also continued to explore previous systems by trying to employ the pentamethylphenyl and adamantyl moieties in the *ortho*-positions of the *m*-terphenyl ligands. This work will highlight the compounds that have been isolated using these ligands, their relevance to organometallic chemistry, and some difficulties faced in their preparation.

2.1 SYNTHESIS OF TETRAPHENYLBUTADIENE COMPLEXES

The synthetic reports of 1,4-dilithiotetraphenylbutadiene date back decades;[47-49] however, the crystal structure of this moiety was only recently reported.[50] The tetraphenylbutadiene ligand has a rich chemistry with transition metals.[51-53] Our group has also employed this ligand to isolate silicon and germanium halide complexes,[54] a very interesting In_2C_8 ten-membered ring,[55] $(Et_2O)_2Li(Br)_2In\{(C_4Ph_4)\}_2In(Br)_2Li(OEt_2)_2$, and a spirogallane anion, $[(Ph_4C_4)Ga(C_4Ph_4)]^-$ (Fig. 11).[56]

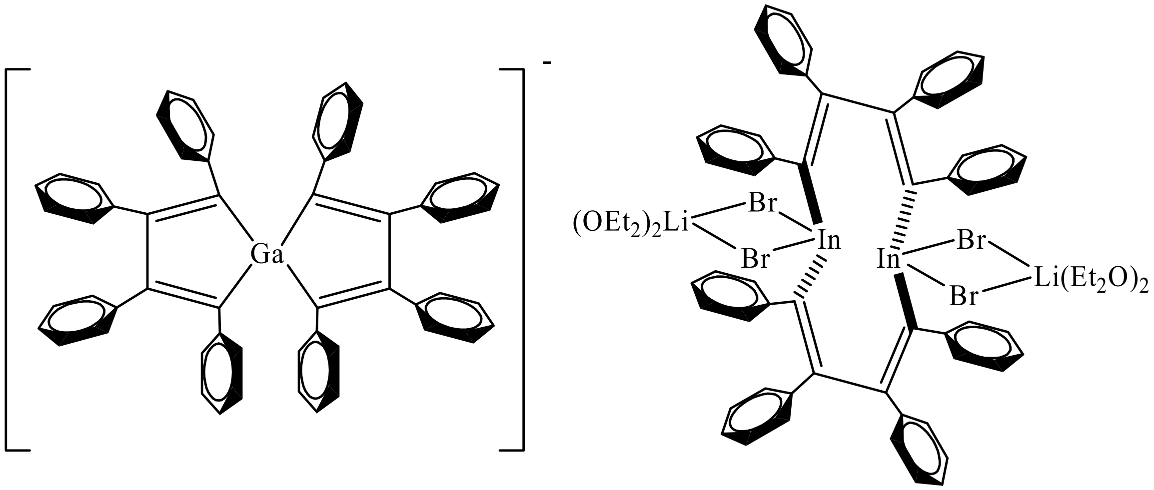
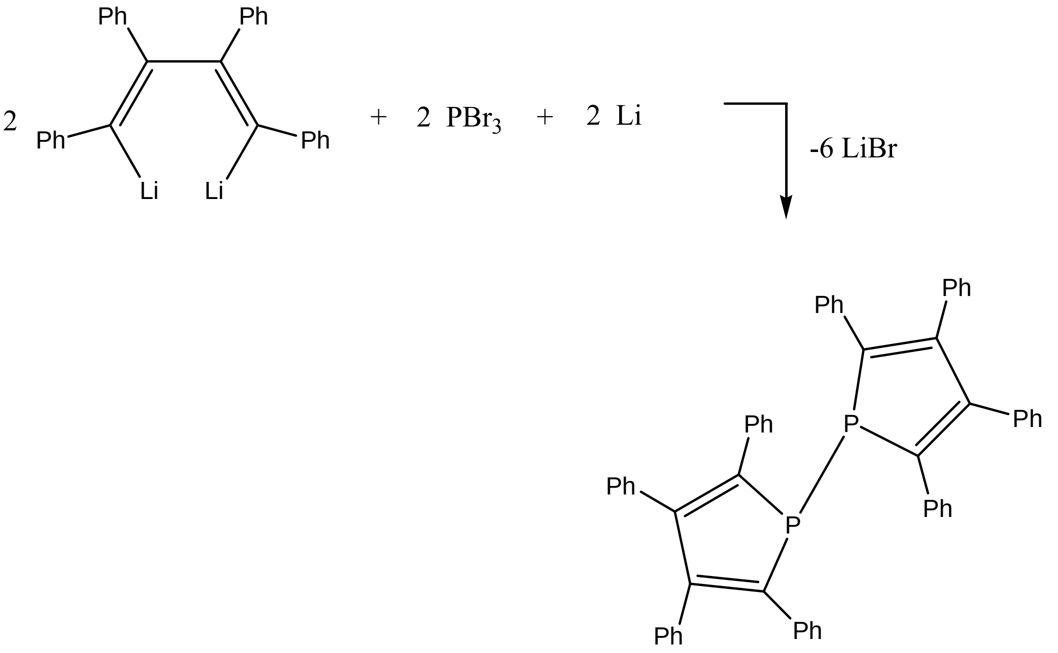


Figure 11. Structures of the spirogallane anion and the In_2C_8 ten-membered ring complex.

2.1.1 Synthesis and Molecular Structure of $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I**

The synthesis of bis(tetraphenylbutadienyl)diphosphine, $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I**, was achieved by the action of excess metallic lithium on diphenylacetylene, with phosphorus(III) bromide (Eq. 9).[57] This compound, characterized by ^1H, ^{13}C and ^{31}P

NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction, is significant as it represents an interestingly facile, if unexpected, one-pot route to a diphosphine.



(9)

The past two decades have witnessed a number of studies concerning compounds containing phosphorus-phosphorus bonds.[58-61] Indeed, this laboratory has had an interest in the preparation of diphosphines having previously reported the synthesis and molecular structure of $[(Me_3Si)_2P\{Me_2Ga\}_2PMe]_2$,[62] isolated from the reaction of Me_3P-$GaMe_3$ with $P(SiMe_3)_3$, having a P-P single bond length of 2.25(3) Å. Relative to diphosphines it is important to note the previously reported σ-bonded disphosphene, bis(pentamethylcyclopentadienyl)diphosphene, $(\sigma\text{-}C_5Me_5)P{=}P(\sigma\text{-}C_5Me_5)$.[63] The phosphorus atoms in $(\sigma\text{-}C_5Me_5)P{=}P(\sigma\text{-}C_5Me_5)$ are two-coordinate (σ-bonding to one of the carbon atoms of the ring and to the other phosphorus atom) with a P-P double bond length of 2.031(3) Å.

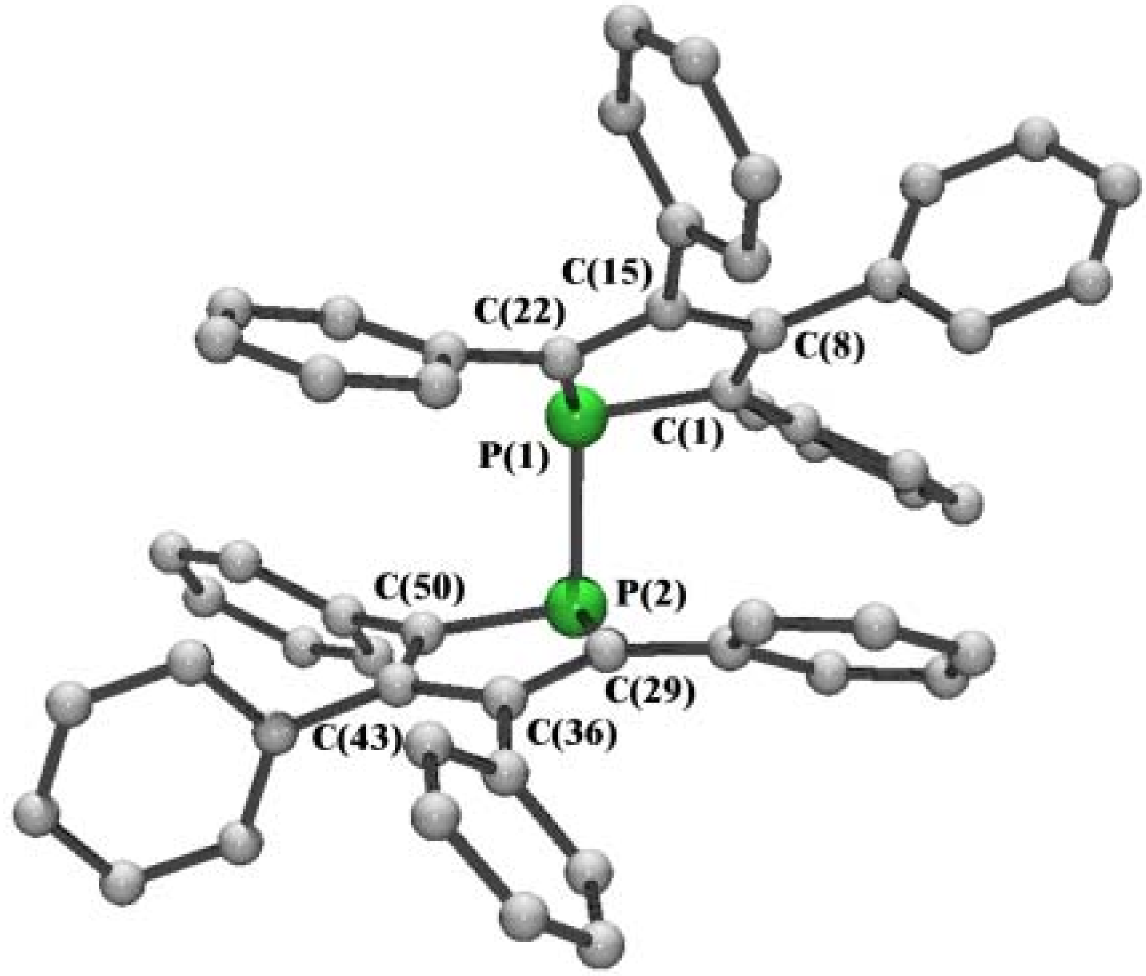


Figure 12. Molecular diagram of $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I** showing the atom-labeling scheme.

Table 2. Selected bond lengths [Å] and angles [º] for $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I**

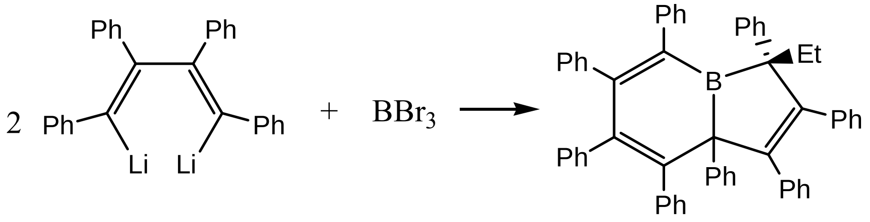
P(1)-P(2)	2.2051(11)	C(1)-P(1)-P(2)	100.16(9)
P(1)-C(1)	1.799(3)	C(22)-P(1)-P(2)	108.13(9)
P(1)-C(22)	1.797(3)	C(50)-P(2)-P(1)	99.92(10)
P(2)-C(29)	1.796(3)	C(29)-P(2)-P(1)	106.14(10)
P(2)-C(50)	1.799(3)	C(50)-P(2)-C(29)	91.26(14)

A number of points regarding the structure and bonding in $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ are relevant (Fig. 12). As expected, the five-membered butadienyl rings are planar about the phosphorus atoms with the phenyl rings arranged in a propeller-like fashion. Indeed, the molecule resides in a *trans* configuration. The environment about the phosphorus atoms must be considered distorted pyramidal thereby precluding significant interaction of the phosphorus lone electron pairs with the conjugated system of tetraphenylbutadienyl moieties. The P-C bond lengths are generally unremarkable. Clearly, the phosphorus-phosphorus bond of 2.2051(11) Å in $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ must be considered a single bond. Moreover, the ^{31}P NMR resonance of δ -15.98 in $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ is also consistent with a P-P single bond. The ^{31}P resonance of $(\sigma\text{-}C_5Me_5)P{=}P(\sigma\text{-}C_5Me_5)$ was reported to be δ 504 (121 MHz, C_6D_6), while that for the diphosphene $[trans\{[Fe(CO)_4)]_2[PCH(SiMe_3)_2]_2\}]$ was reported at δ 384.55 (external 85% H_3PO_4). The reported P-P bond length was 2.039(1) Å.[59]

2.1.2 Synthesis and Molecular Structure of $[(Ph_4C_4)_2(C_2H_5)]B$ **II**

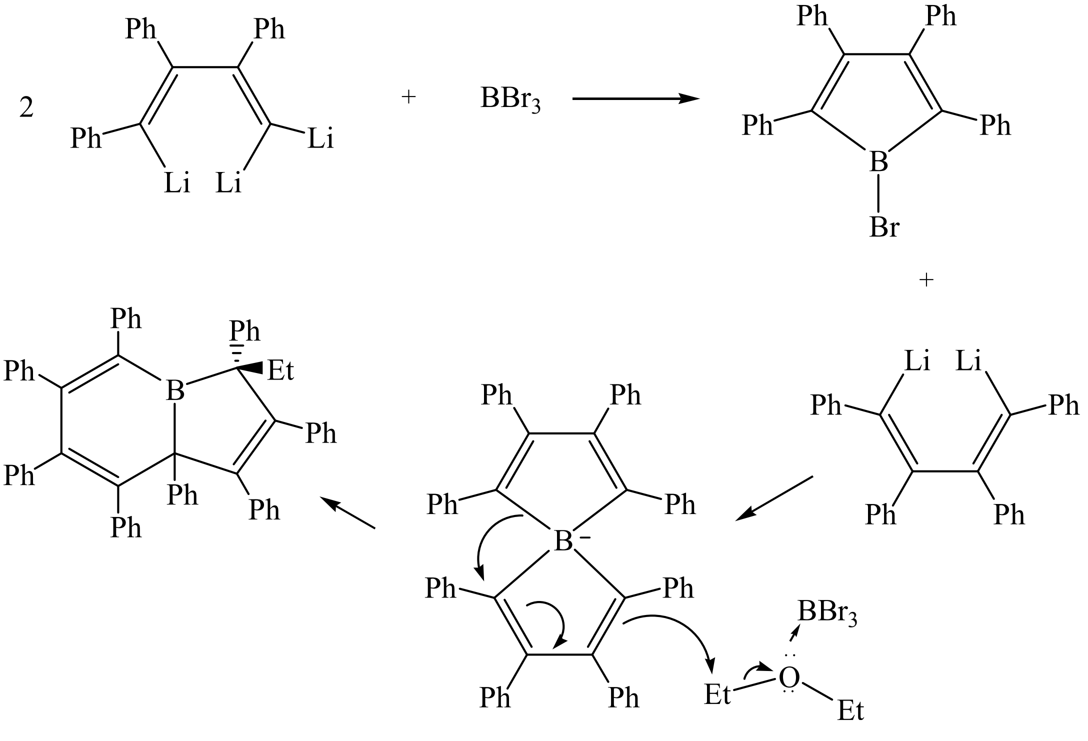
Boron, the lightest Group 13 element, is not typically explored by this research group as extensively as the heavier members. However, as we have explored the chemistry of tetraphenylbutadienyl with regard to many of the other main group elements, its experimentation seemed warranted. The reaction of 1,4-dilithiotetraphenylbutadiene with boron(III) bromide affords the novel organoborane derivative $[(Ph_4C_4)_2(C_2H_5)]B$ **II**, as yellow crystals characterized by ^1H, ^{13}C NMR, elemental analyses and single crystal X-ray diffraction (Eq. 10).[64]

Compound **II** contains one boron atom, two combined tetraphenylbutadienyl moieties, and one ethyl group fragment. The addition of the ethyl group to one of the butadienyl groups and the C-C bond, which combines two butadienyl units, warrants special attention. The proposed mechanism involves the cleavage of an ethyl group from diethyl ether, this cleavage is most likely due to the high Lewis acidity of boron bromide (Eq. 11).



(10)

Several points are noteworthy regarding the structure and bonding in compound **II** (Fig. 13). The coordination of the boron atom is distorted trigonal planar with bond angles around the boron atom of 128.9(5)º, 118.8(5)º, and 110.8(5)º for C(1)-B(1)-C(50), C(1)-B(1)-C(29), and C(50)-B(1)-C(29), respectively.



(11)

The relatively large difference in C-B-C angles is due to the constrained environment around the boron atom. The average B-C bond distance of 1.559 Å compares well to that reported for triphenylborane [1.570 Å].[65]

Although diethyl ether is inert in the reaction of 1,4-dilithiotetraphenylbutadiene with other Group 13 halides, the formation of **II** indicates that, under appropriate conditions, facile O-C_2H_5 bond cleavage can occur.

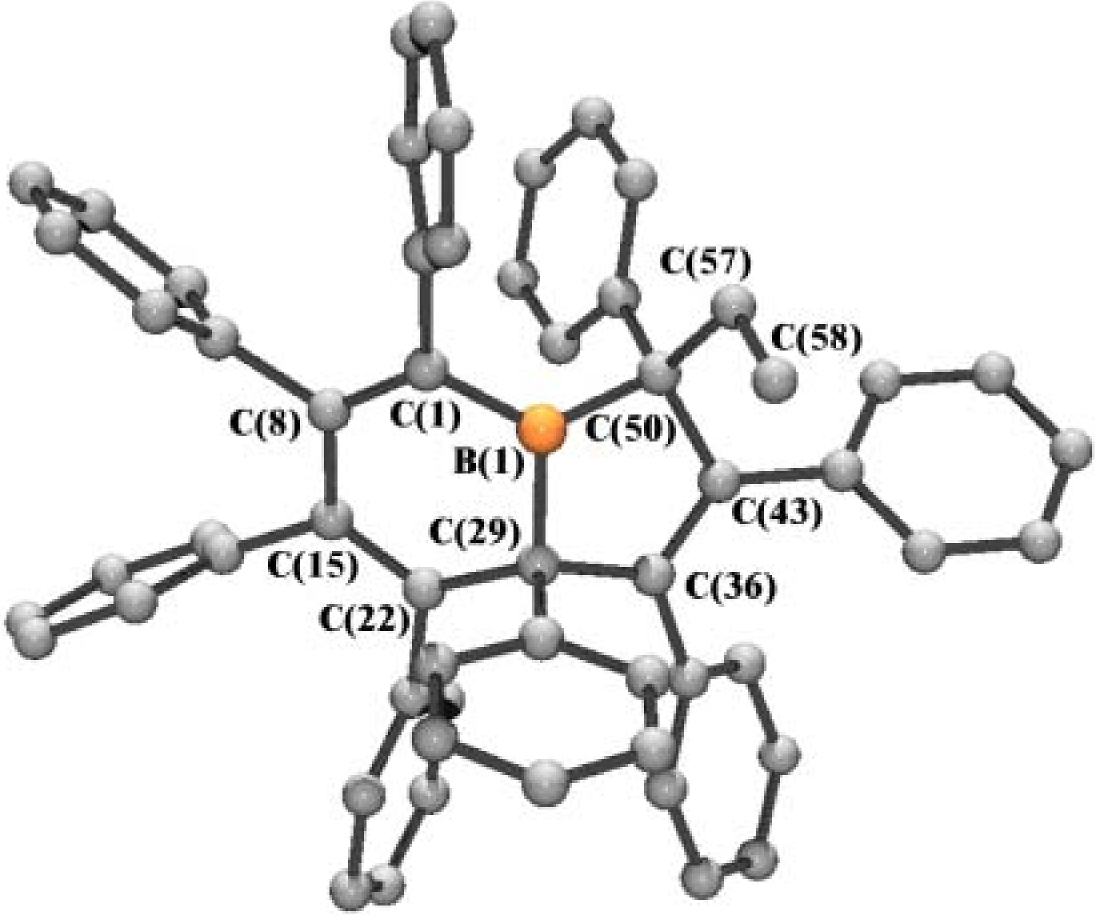


Figure 13. Molecular diagram of $[(Ph_4C_4)_2(C_2H_5)]B$ **II** showing the atom-labeling scheme.

Table 3. Selected bond lengths [Å] and angles [°] for $[(Ph_4C_4)_2(C_2H_5)]B$ **II**

B(1)-C(29)	1.592(5)	C(1)-B(1)-C(50)	129.1(4)
B(1)-C(1)	1.527(5)	C(50)-B(1)-C(29)	110.8(4)
B(1)-C(50)	1.559(5)	C(1)-B(1)-C(29)	118.7(4)
C(50)-C(57)	1.522(5)	B(1)-C(29)-C(22)	108.8(3)
C(57)-C(58)	1.506(5)	C(22)-C(29)-C(36)	118.8(3)

2.2 SYNTHESIS OF PENTAMETHYLPHENYL COMPLEXES

Although the phenyl ligand, C_6H_5, is not generally considered to possess significant steric bulk, it has served as the template upon which some notable sterically demanding ligands have been derived.[66] It is interesting that the methyl-saturated phenyl derivative, pentamethylphenyl, Me_5C_6, has not been examined in the organometallic chemistry of gallium or aluminum (*vide infra*).

2.2.1 Synthesis and Molecular Structure of $(C_6Me_5)_3Ga$ **III**

The compound $(C_6Me_5)_3Ga$ **III** was isolated from reaction of the pentamethylphenylmagnesium bromide Grignard reagent with gallium(III) chloride (Eq. 12).[67] The product was isolated as colorless, needle crystals and was characterized by ^1H and ^{13}C NMR, elemental analyses, and single crystal X-ray diffraction.

$$3(C_6Me_5)MgBr \; + \; GaCl_3 \longrightarrow (C_6Me_5)_3Ga \; + \; 3MgBrCl \qquad (12)$$

The crystal structure of triphenylgallium, Ph_3Ga reveals a monomeric gallium center residing in a virtually idealized trigonal planar environment and a mean Ga-C bond distance of 1.957 Å. A closer examination of the structure reveals subtle factors at work contributing to the observed orientation. In particular, one of the phenyl rings of Ph_3Ga is co-planar with the GaC_3 basal plane while the remaining two phenyl rings were observed with dihedral angles of 13.2 and 31.6º. Moreover, while the immediate coordination about the gallium center in Ph_3Ga is certainly trigonal planar, an examination of the unit cell packing reveals weak inter-molecular interactions (3.42 Å) between a gallium atom of one Ph_3Ga molecule and the phenyl π-electrons of a neighboring Ph_3Ga molecule. Thus, when taken in a larger context, the coordination of the gallium center in triphenylgallium approaches five-coordinate trigonal bipyramidal.

For a further comparison, the sterically demanding Mes_3Ga molecule resides about a three-fold crystallographic axis with approximate D_3 symmetry. While the Ga-C bond distance of 1.968 Å and the trigonal planar coordination about the gallium center in Mes_3Ga compares with the values obtained for Ph_3Ga (Ga-C: 1.957 Å), the dihedral angle of the mesityl rings relative to the GaC_3 plane is noteworthy. Each of the aromatic rings of the mesityl ligands reside in a propeller arrangement about the gallium atom at an angle of 55.9º. The gallium center is sufficiently protected to prevent diethyl ether coordination. Indeed, the orientation of the three mesityl ligands of trimesitylgallium preclude the weak secondary interactions present in triphenylgallium and the associated secondary trigonal bipyramidal coordination of the metal center.

The pentamethylphenyl ligand has received considerably less attention than the mesityl derivative in Group 13 chemistry. This is due to the fact that it is not immediately obvious that adding steric bulk (in the form of methyl groups) in the *meta* positions of the phenyl-based ligand (compared with the mesityl ligand) would effect significant changes at the metal center. In an effort to ascertain what effects, if any, would result from this ligand (compared with other $(aryl)_3Ga$ compounds) we prepared compound **III** (Fig. 14).

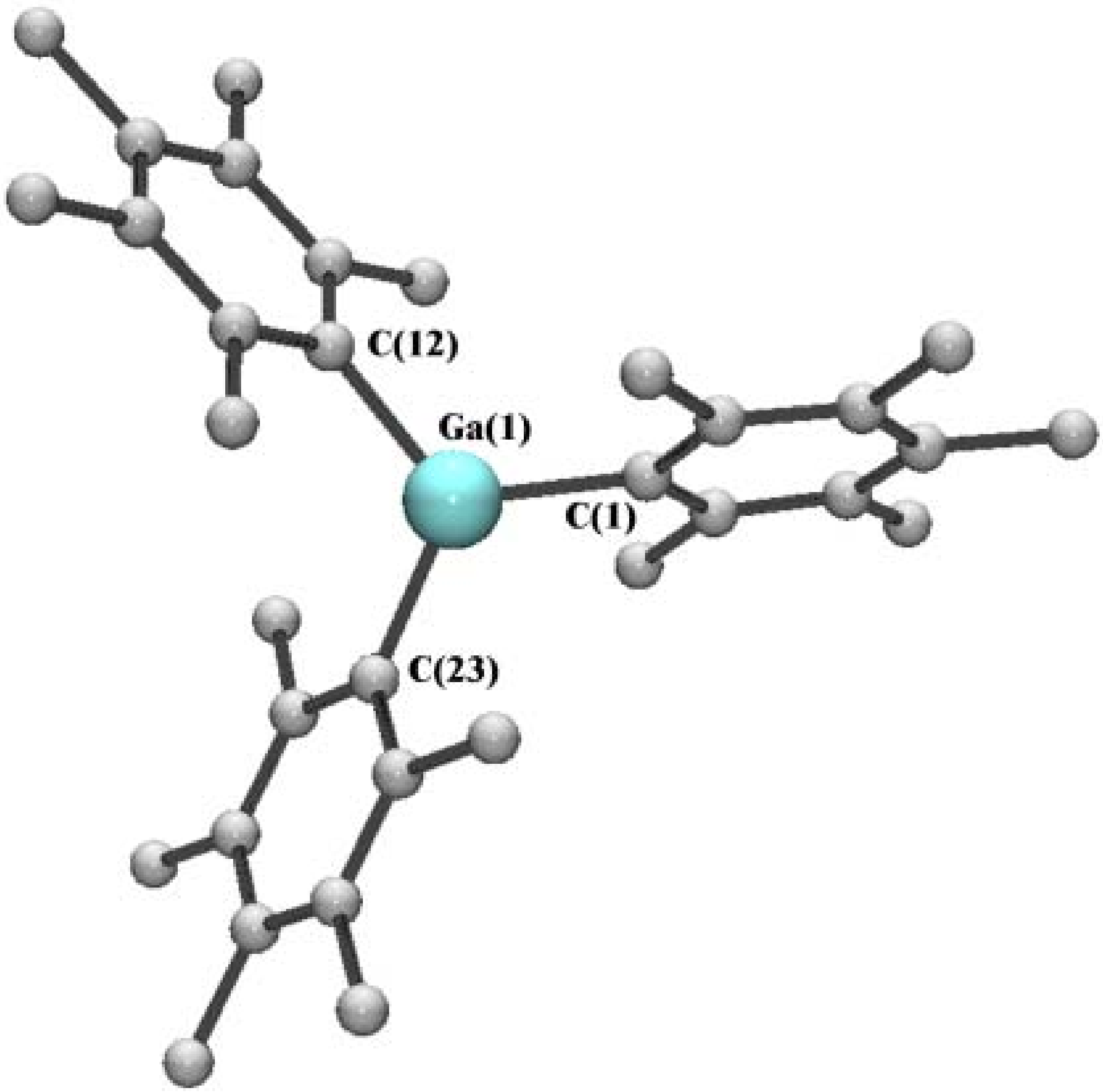


Figure 14. Molecular diagram of $(C_6Me_5)_3Ga$ **III** showing the atom-labeling scheme.

Table 4. Selected bond lengths [Å] and angles [°] for $(C_6Me_5)_3Ga$ **III**

Ga(1)-C(1)	1.974(3)	C(1)-Ga(1)-C(12)	121.91(11)
Ga(1)-C(12)	1.986(3)	C(1)-Ga(1)-C(23)	120.36(11)
Ga(1)-C(23)	1.984(3)	C(12)-Ga(1)-C(23)	117.73(11)

The coordination of the gallium atom is almost idealized trigonal planar with a mean C-Ga-C bond angle of 120.0(1)º. Similar to Mes_3Ga, $(Me_5C_6)_3Ga$ has approximate D_3 symmetry. The mean Ga-C bond distance of 1.981(5) Å in $(Me_5C_6)_3Ga$ is considerably longer than that observed for either Ph_3Ga (1.957 Å) or Mes_3Ga (1.968 Å). This is somewhat surprising considering that the additional two methyl groups on each ligand are not in close proximity to the metal bonding site (compared with the mesityl ligand). A factor contributing to the elongated Ga-C bond distance in compound **III** perhaps involves an electronic component. It is plausible that the pentamethylphenyl ligand donates more electron density (as compared with the phenyl or mesityl ligands) into a Ga-C anti-bonding orbital (thereby resulting in a longer Ga-C bond).

Also surprising about $(Me_5C_6)_3Ga$ are the dihedral angles of the pentamethylphenyl ligands with the GaC_3 basal plane. The dihedral planes were found to be 67.3º, 62.3º, and 60.9º, for the C(1), C(12), and C(23) pentamethylphenyl planes, respectively. These angles are considerably greater than values obtained for Ph_3Ga (0º, 13.2º, and 31.6º). Indeed, the dihedral angles observed in the title compound are significantly greater than the values obtained for Mes_3Ga (55.9º). As for possible causes for the dihedral plane angles observed in the title compound, one is drawn to the unit cell. In the unit cell of $(Me_5C_6)_3Ga$ it is shown that there is an aromatic-aromatic interaction, albeit a weak one at 4.1 Å, between parallel rings between two $(Me_5C_6)_3Ga$ molecules (Fig. 15). The only $(aryl)_3Ga$ derivative with dihedral bond angles greater than those observed for $(Me_5C_6)_3Ga$ is 2,6-dimesitylphenyldimesitylgallium, $(Mes_2C_6H_2)Mes_2Ga$,[23] wherein the rings approach orthogonality values of 82.4º, 82.4º, and 86.3º.

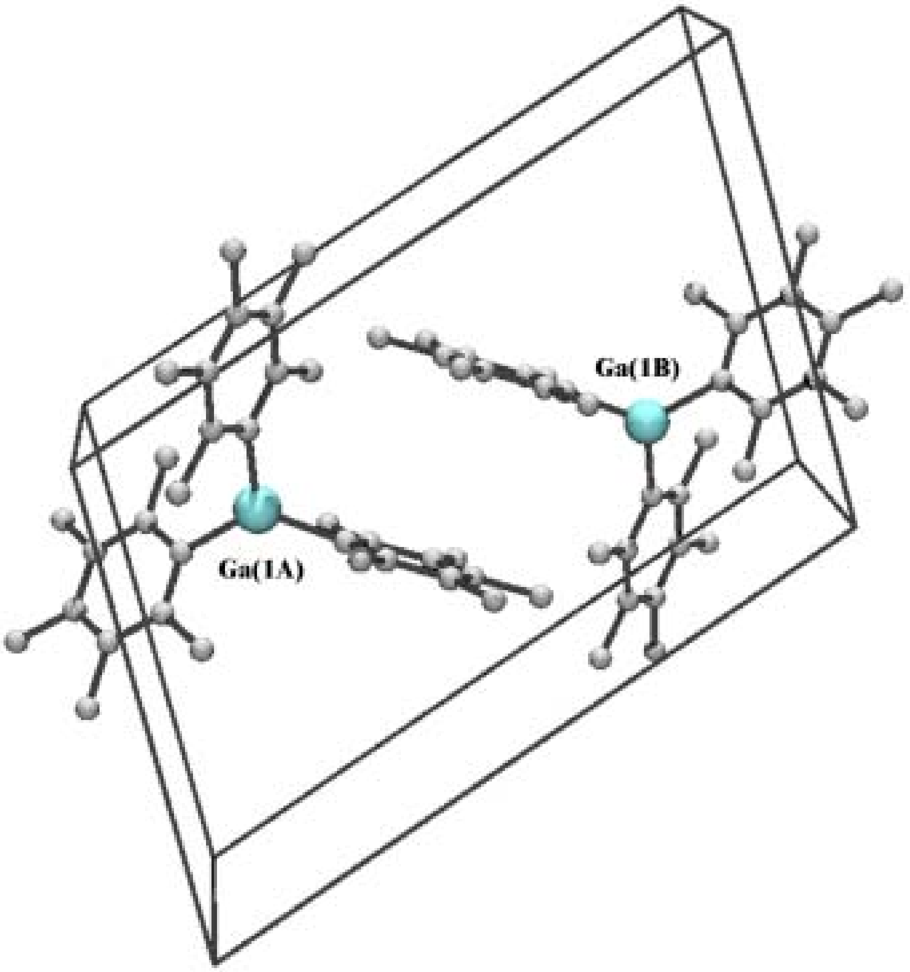


Figure 15. A view of the unit cell of $(Me_5C_6)_3Ga$ showing the parallel nature of two pentamethylphenyl ligands (4.1 Å).

2.2.2 Synthesis and Molecular Structure of $(C_6Me_5)_3Al$ **IV**

Compound **IV** was prepared *via* the reaction of the pentamethylphenylmagnesium bromide Grignard reagent with aluminum(III) chloride (Eq. 13).[68] The product was isolated as colorless crystals and was characterized by ^1H and ^{13}C NMR, elemental analyses, and single crystal X-ray diffraction.

$$3(C_6Me_5)MgBr \quad + \quad AlCl_3 \xrightarrow{\qquad\qquad} (C_6Me_5)_3Al \quad + \quad 3MgBrCl \qquad (13)$$

The structure of $(C_6Me_5)_3Al$ **IV** is most conveniently compared to trimesistylaluminum, Mes_3Al, prepared by reaction of dimesitylmercury with aluminum metal. While the mean Al-C bond distance in Mes_3Al is 1.995 Å, the most interesting feature of this compound is the dihedral angle of the mesityl rings relative to the central AlC_3 ring. Each of the mesityl rings in Mes_3Al was canted at angles of 54.5°. The trigonal planar-based monomeric nature of trimesitylaluminum is easily contrasted with the dimeric structure of di-μ-phenyl-bis(diphenylaluminum), Ph_6Al_2 (i.e. the triphenylaluminum dimer), with tetrahedral aluminum centers and electron deficient three center-two electron $Al\text{-}C_{Ph}\text{-}Al$ bridges. The coordination of the aluminum center in **IV** is almost idealized trigonal planar with a mean C-Al-C bond angle of 120.0(2)° while the molecule possesses approximate D_3 symmetry. The mean Al-C bond distance of 1.984(3) Å in $(C_6Me_5)_3Al$ compares closely to that for Mes_3Al (1.995 Å). Just as its gallium analog, compound **IV** exhibits subtle yet noteworthy features (Fig 16). The dihedral planes were found to be 67.2, 62.4, and 61.2° for the C(1), C(12), and C(23) pentamethylphenyl planes respectively. These angles are significantly greater than the values obtained for Mes_3Al (54.5°). These values are possibly due to a weak interaction between parallel rings between two $(C_6Me_5)_3Al$ molecules (Fig. 17).

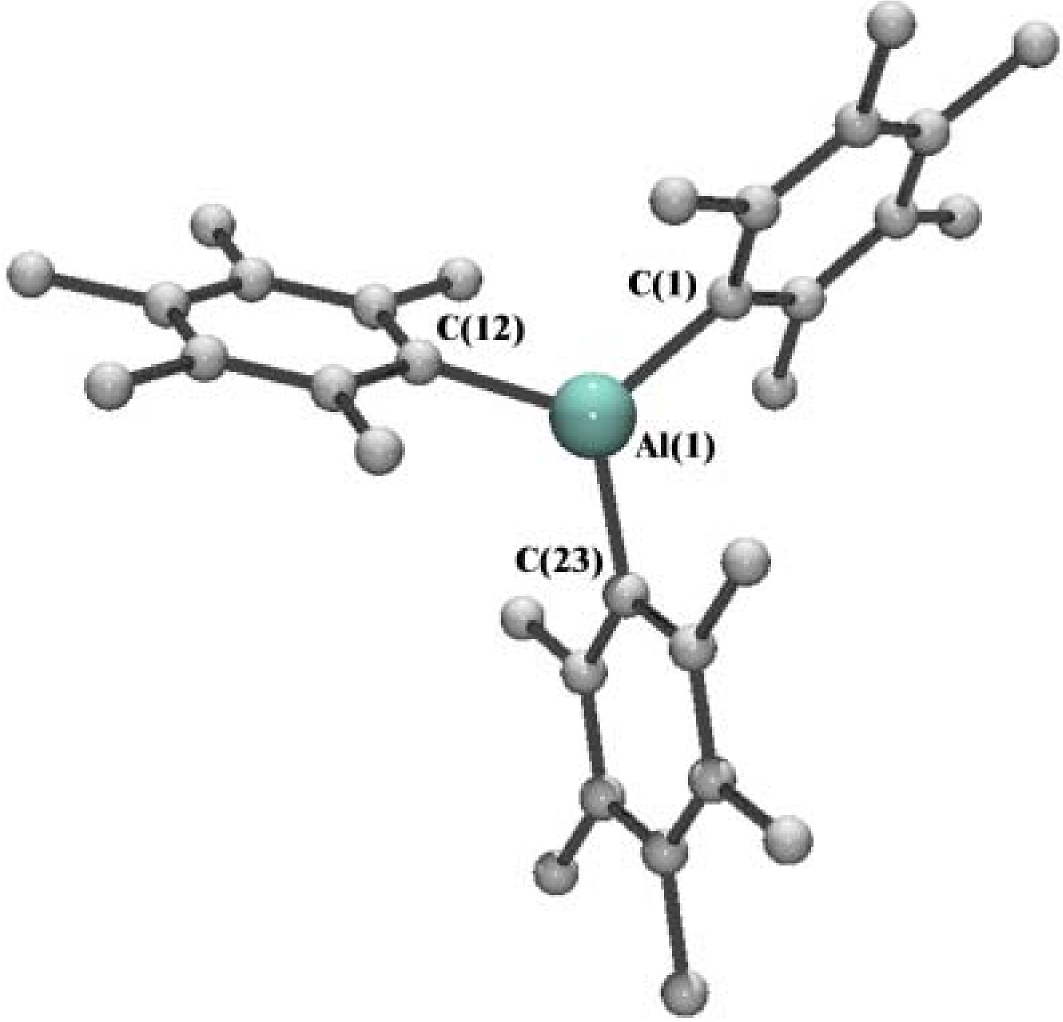


Figure 16. Molecular diagram of $(C_6Me_5)_3Al$ **IV** showing the atom-labeling scheme.

Table 5. Selected bond lengths [Å] and angles [°] for $(C_6Me_5)_3Al$ **IV**

Al(1)-C(1)	1.9819(16)	C(1)-Al(1)-C(12)	121.71(6)
Al(1)-C(12)	1.9833(15)	C(1)-Al(1)-C(23)	120.49(6)
Al(1)-C(23)	1.9865(16)	C(12)-Al(1)-C(23)	117.80(6)

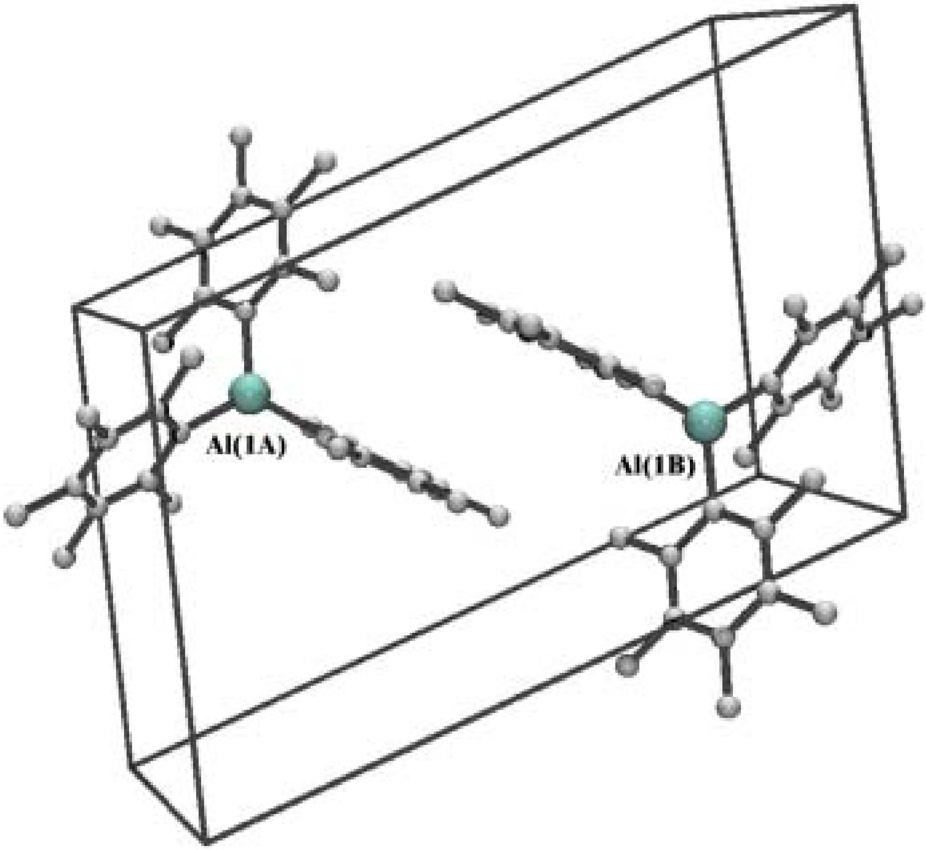


Figure 17. A view of the unit cell of $(Me_5C_6)_3Al$ showing the parallel nature of two pentamethylphenyl ligands (4.19 Å).

2.2.3 Synthesis and Molecular Structure of $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V**

The isolation of the both $(Me_5C_6)_3Ga$ and $(Me_5C_6)_3Al$ utilized the Grignard reagent pentamethylphenylmagnesium bromide. Although this reagent proved effective, its synthesis is somewhat cumbersome. Standard Grignard preparations involve reacting an alkyl or aryl halide with magnesium metal in an ethereal solvent; however, this procedure gave inconsistent and irreproducible results. A modified procedure by Garst and coworkers[69] reports yields of pentamethylphenylmagnesium bromide up to 80% when a 2.6 *M* solution of $MgBr_2$ in ether is used as the solvent. This method, although it proved to give better results, made product isolation more difficult. The solutions from which the products were isolated often contained two layers due to the concentration gradient of $MgBr_2$ solutions. The bottom layer has a $MgBr_2$ concentration greater than 2.6 *M* while that of the top layer is less than 2.6 *M*. Separation of the layers was required as side products frequently crystallized from the dense bottom layer (Fig. 18).

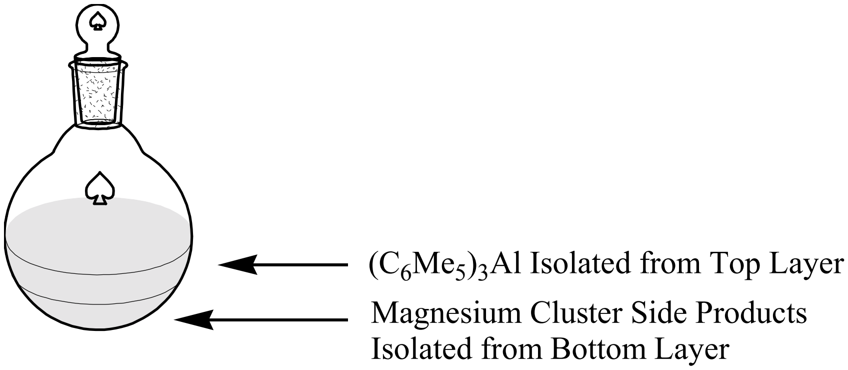
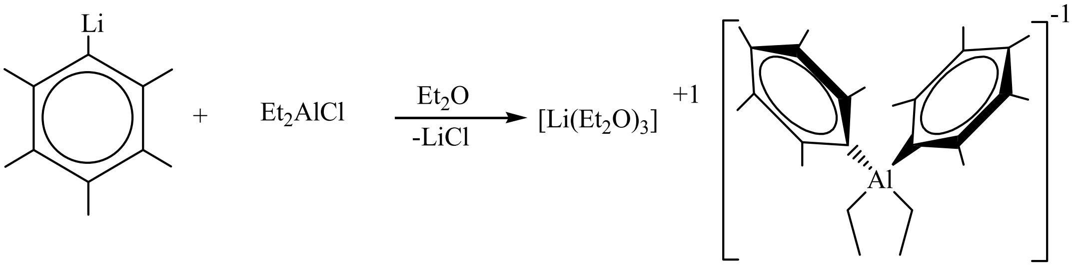


Figure 18. Diagram showing multiple layers in reaction flask.

In order to avoid the difficulties involved with the use of the Grignard reagent, we examined the possibility of using the corresponding organolithium reagent. This route would prove to be synthetically easier and preclude the formation of numerous side products. Pentamethylphenyllithium was prepared from reaction of bromopentamethylbenzene and *n*-butyllithium. This reagent reacts with diethylaluminum chloride to give the ionic complex $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V** (Eq. 14). The product was isolated as colorless crystals and was characterized by elemental analyses and single crystal X-ray diffraction (Fig. 19).



(14)

The reaction of pentamethylphenyllithium with Me_2MCl (M = Al or Ga) results in the formation of $(C_6Me_5)_3M$. Colorless crystals isolated from the respective reactions confirm this.

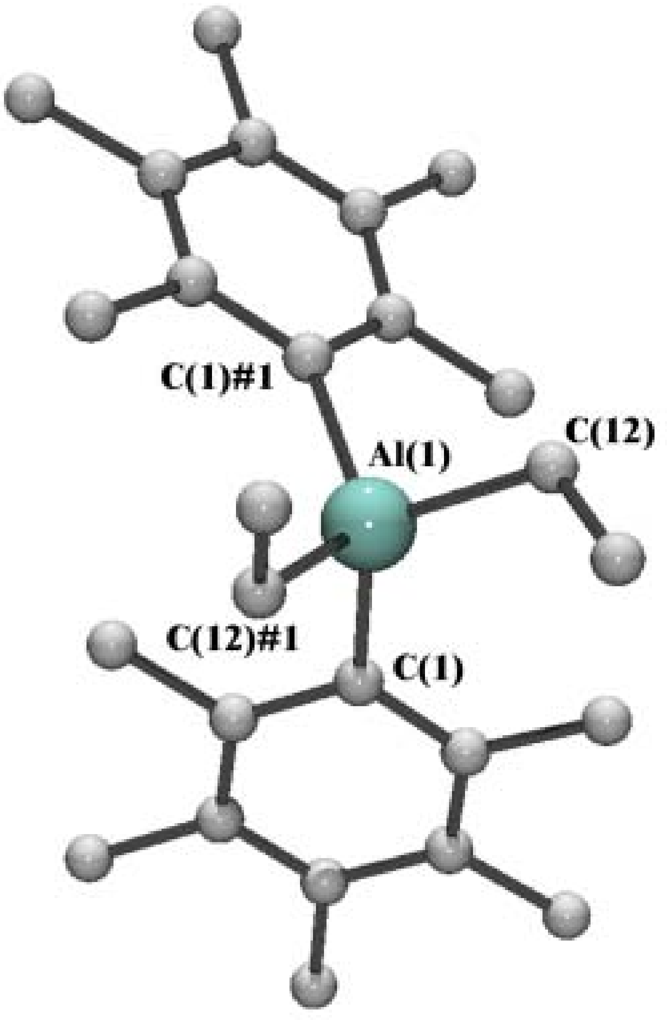


Figure 19. Molecular diagram of the anion $[(C_6Me_5)_2AlEt_2]^-$ in **V** showing the atom labeling scheme. Symmetry transformations used to generate equivalent atoms: #1 -x + 1, y, -z + ½.

Table 6. Selected bond lengths [Å] and angles [°] for the anion $[(C_6Me_5)_2AlEt_2]^-$ in **V**

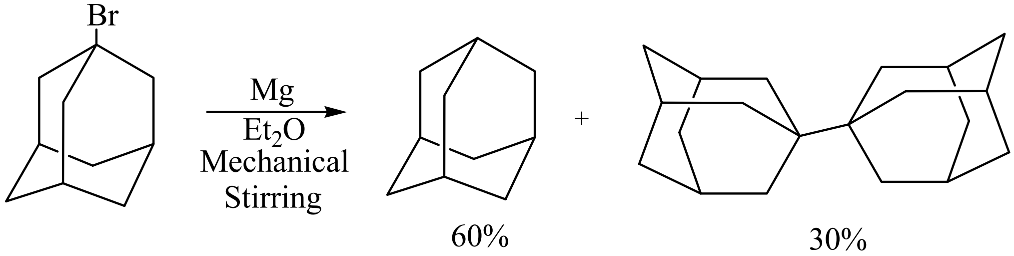
Al(1)-C(1)	2.078(4)	C(1)-Al(1)-C(12)	120.84(19)
Al(1)-C(12)	2.016(5)	C(1)#-Al(1)-C(12)	104.0(2)
Al(1)-C(1)#	2.078(4)	C(1)-Al(1)-C(1)#	106.6(2)
Al(1)-C(12)#	2.016(5)	C(12)-Al(1)-C(12)#	101.6(4)

These unexpected results reveal the potency of this reagent; furthermore, although the mechanism is not known, it apparently involves the cleavage of methyl groups from the metal so that the pentamethylphenyl ligand might coordinate to the metal center. The cleaved methyl group could then acquire an adventitious proton from the solvent to form methane.

2.3 SYNTHESIS OF ADAMANTYL COMPLEXES

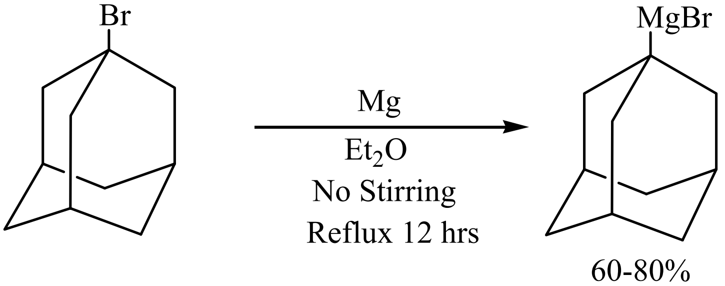
Chemists have long found both inspiration and fascination in the adamantane molecule. The symmetrical fusion of the cyclohexyl units of adamantine not only results in a virtually strain-free molecule,[70] but this configuration also affords a uniquely beautiful and conceptually pleasing structural motif. Indeed, the first convenient synthesis of adamantine by Schleyer[71] in 1957 remains a significant accomplishment. Although the adamantyl ligand has found some utility in organometallic compounds of phosophorus,[72,73] silicon, germanium, and tin,[74] it is surprising that it has not been more widely embraced as a viable ligand in the organometallic chemistry of the main group elements. Furthermore, our group sought to explore this chemistry as it relates to aluminum and gallium.

Adamantylmagnesium bromide reacts smoothly with the appropriate aluminum or gallium organometallic starting compound to give the ionic complexes $[Mg_3BrCl_3(OEt_2)_6][Ada_3AlBr]$ **VI**, $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**, $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**, and $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ **IX**.[75] The synthesis of adamantylmagnesium bromide proceeds just as other Grignard reagents; however, the reaction must take place in the absence of mechanical stirring. Molle and coworkers explain that if mechanical stirring is employed, there is no appreciable yield of the Grignard reagent (Eq. 15).



(15)

Furthermore, when the reaction proceeds in a "static" fashion, yields of 60-80% are obtained (Eq. 16).[76]



(16)

There are a couple of different explanations for this phenomenon. Molle explains that stirring causes the desorption of transient intermediates before they have a chance to form adamantylmagnesium bromide at the surface of the magnesium. A contrary opinion states that stirring may leach away $MgBr_2$ from the magnesium surface which may be required for the reaction. In the absence of stirring, this refinement of the magnesium surface would not occur.[77]

2.3.1 Synthesis and Molecular Structure of $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ **VI**

The anion of compound **VI**, $[Ada_3AlBr]^-$, is distinctive as the aluminum atom accommodates three adamantyl units at an Al-C_{ada} mean bond distance of 2.042(8) Å (Fig. 20). This value compares well to the mean Al-C bond distance of 2.091 Å observed for the *tert*-amylchloroaluminate $[(EtMe_2C)_3AlCl]^-$ anion.[78] Although there appears to be ample space to accommodate four adamantyl units about the aluminum center, to date we have only isolated the triadamantyl derivative (from numerous experiments). The Al-Br bond distance is also rather long at 2.439(3) Å. The anion approximates C_3 symmetry. The C_{ada}-Al-C_{ada} bond angles are quite consistent at values of 115.4(3), 115.4(3), and 113.7(4)°. These values compare to 102.3(3), 103.9(2), and 103.9(2)° for the C_{ada}-Al-Br bond angles. Perhaps expectedly, the steric interactions between the adamantyl moieties are manifest in the angles about the bromine atom and the Al-Br bond.

The unusual trimetallic-magnesium cations common in all four complexes warrant discussion. While the cations in all four compounds are quite similar containing a trimetallic $Mg_3(OEt_2)_6$ cluster, subtle differences exist. The cation in **VI** is distinctive as it is the only cation which contains a singular bromine atom in the cluster (Fig. 21). The central oxygen atom in the cations in **VI**, **VIII**, and **IX** is four-coordinate, bonding to the three magnesium atoms and the Et group. It is significant that the three magnesium atoms in all four cations are six-coordinate residing in (distorted) octahedral environments. A similar tri-magnesium halide cation, $[Mg_3Cl_5(OEt_2)_6]^+$, isolated from Ga_2Cl_4-$MgCp^*_2$[79] and *i*-Pr_3In-‘MgBrCl’[80] systems, has been reported.

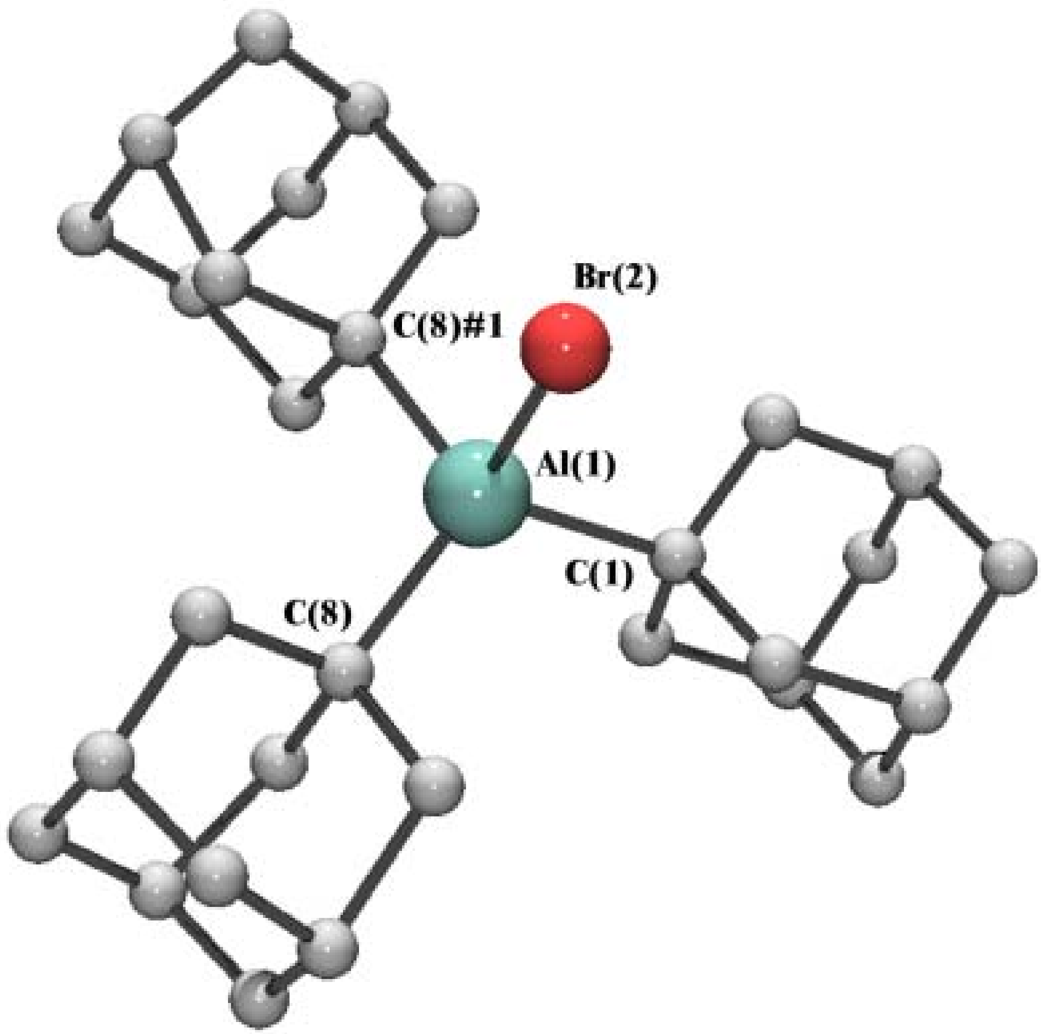


Figure 20. Molecular diagram of the anion $[Ada_3AlBr]^-$ in **VI** showing the atom-labeling scheme. Symmetry transformations used to generate equivalent atoms: #1 x, -y + ½, z.

Table 7. Selected bond lengths [Å] and angles [°] for the anion $[Ada_3AlBr]^-$ in **VI**

Al(1)-Br(2)	2.439(3)	C(1)-Al(1)-C(8)	115.4(3)
Al(1)-C(1)	2.041(10)	C(8)-Al(1)-C(8)#1	113.7(4)
Al(1)-C(8)	2.042(8)	C(1)-Al(1)-Br(2)	102.3(3)
Al(1)-C(8)#1	2.042(8)	C(8)-Al(1)-Br(2)	103.9(2)

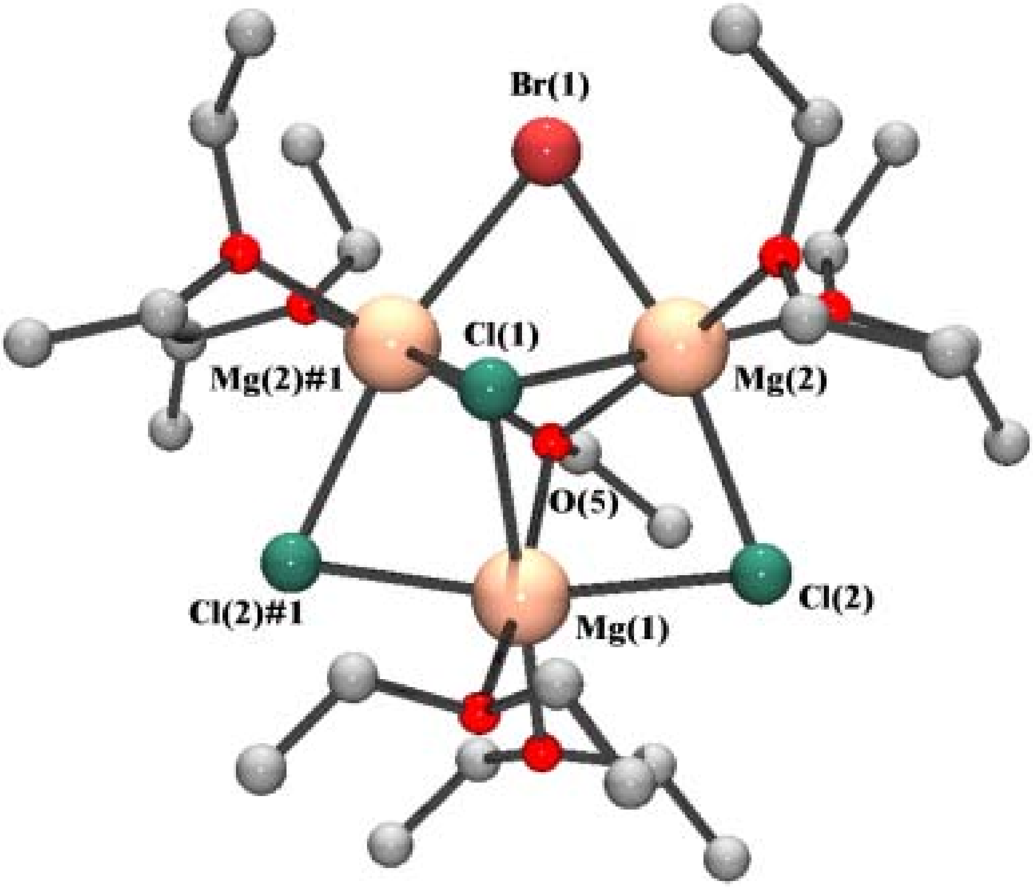


Figure 21. Molecular diagram of the cation $[Mg_3BrCl_3(OEt)(OEt_2)_6]^+$ in **VI** showing the atom-labeling scheme. Symmetry transformations used to generate equivalent atoms: #1 x, -y + ½, z.

Table 8. Selected bond lengths [Å] and angles [º] for the cation $[Mg_3BrCl_3(OEt)(OEt_2)_6]^+$ in **VI**

Mg(1)-Cl(1)	2.681(4)	Br(1)-Mg(2)-Cl(2)	165.80(10)
Mg(1)-Cl(2)	2.5733(14)	Cl(1)-Mg(1)-O(5)	75.4(2)
Mg(1)-O(5)	2.122(7)	Cl(1)-Mg(2)-O(5)	77.64(19)
Mg(2)-Cl(1)	2.595(3)	Mg(1)-Cl(2)-Mg(2)	74.62(9)
Mg(2)-O(5)	2.100(5)	Cl(2)-Mg(1)-Cl(2)#1	166.51(14)
Mg(2)-Br(1)	2.676(2)	Mg(2)-Cl(1)-Mg(1)	72.88(10)

2.3.2 Synthesis and Molecular Structure of $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**

The gallium atom in anion **VII**, $[Ada_2GaBr_2]^-$, accommodates two adamantyl units at Ga-C bond distances of 2.024(9) and 2.005(9) Å and two bromine atoms at distances of 2.4347(18) and 2.4463(16) Å (Fig. 22). Both the Ga-C (1.95(1) and 1.99(1) Å) and Ga-Br (2.402(2) and 2.402(2) Å) bond distances of the dibenzyldibromogallate anion, $[(PhCH_2)_2GaBr]^-$,[81] are comparable to those observed in **VII**. It should also be noted that the C_{ada}-Ga-C_{ada} bond angle is considerably widened from the expected four-coordinate tetrahedral value to 126.2(4)°, even as the remaining bond angles about the gallium center are slightly contracted (106.7(3), 104.6(3), and 107.3(3)°). For both of the anions in **VI** and **VII**, the reactions were initiated with aluminum chloride and gallium chloride. Yet, the halides observed in the anions are bromines with the chlorines being situated in the magnesium cluster cations. While the mechanism of formation of these ionic species remains unclear, this point is noteworthy.

The cation in **VII** is the only one of the four cations that does not have an ethoxy group at the center (apical position) of the cluster as it only contains halides (two bromine and three chlorine atoms) about the three magnesium atoms. In the remaining three cations an OEt group is opposite a halide (Br or Cl) atom (Fig. 23).

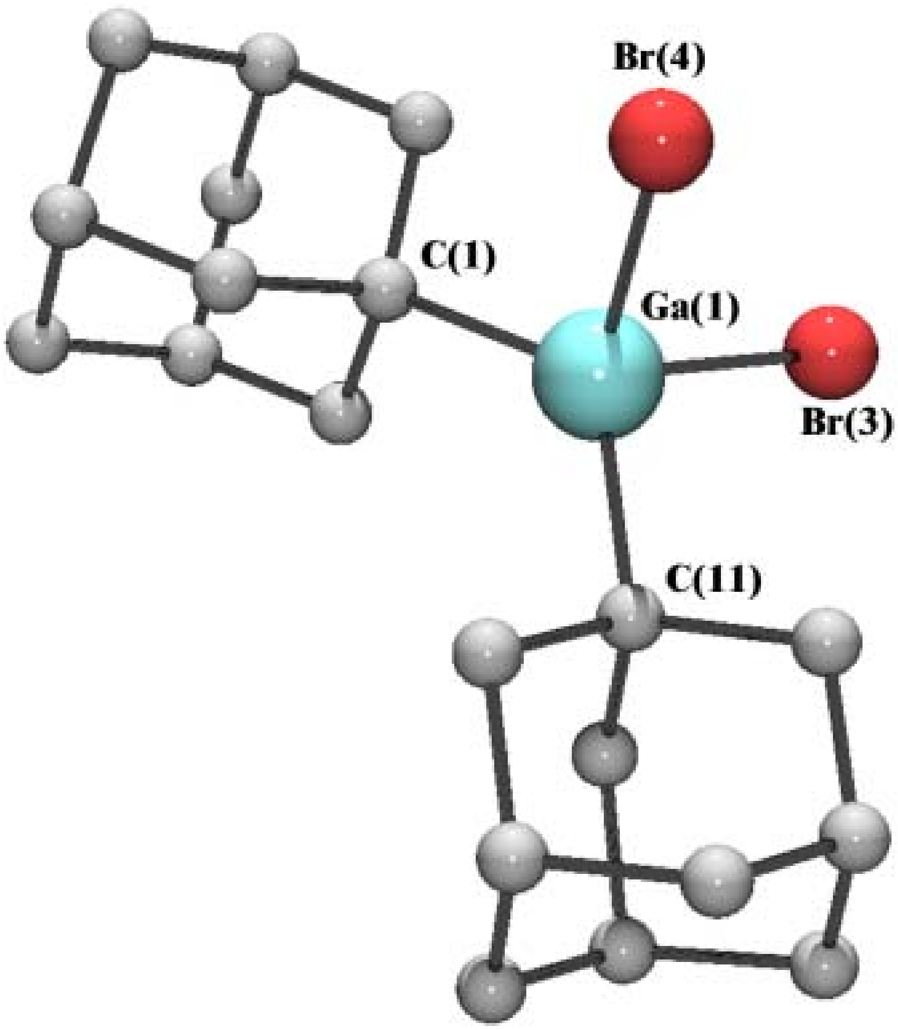


Figure 22. Molecular diagram of the anion $[Ada_2GaBr_2]^-$ in **VII** showing the atom-labeling scheme.

Table 9. Selected bond lengths [Å] and angles [º] for the anion $[Ada_2GaBr_2]^-$ in **VII**

Ga(1)-Br(3)	2.4347(18)	C(1)-Ga(1)-C(11)	126.2(4)
Ga(1)-Br(4)	2.4463(16)	C(1)-Ga(1)-Br(3)	106.7(3)
Ga(1)-C(1)	2.024(9)	C(1)-Ga(1)-Br(4)	104.6(3)
Ga(1)-C(11)	2.005(9)	C(11)-Ga(1)-Br(4)	107.3(3)

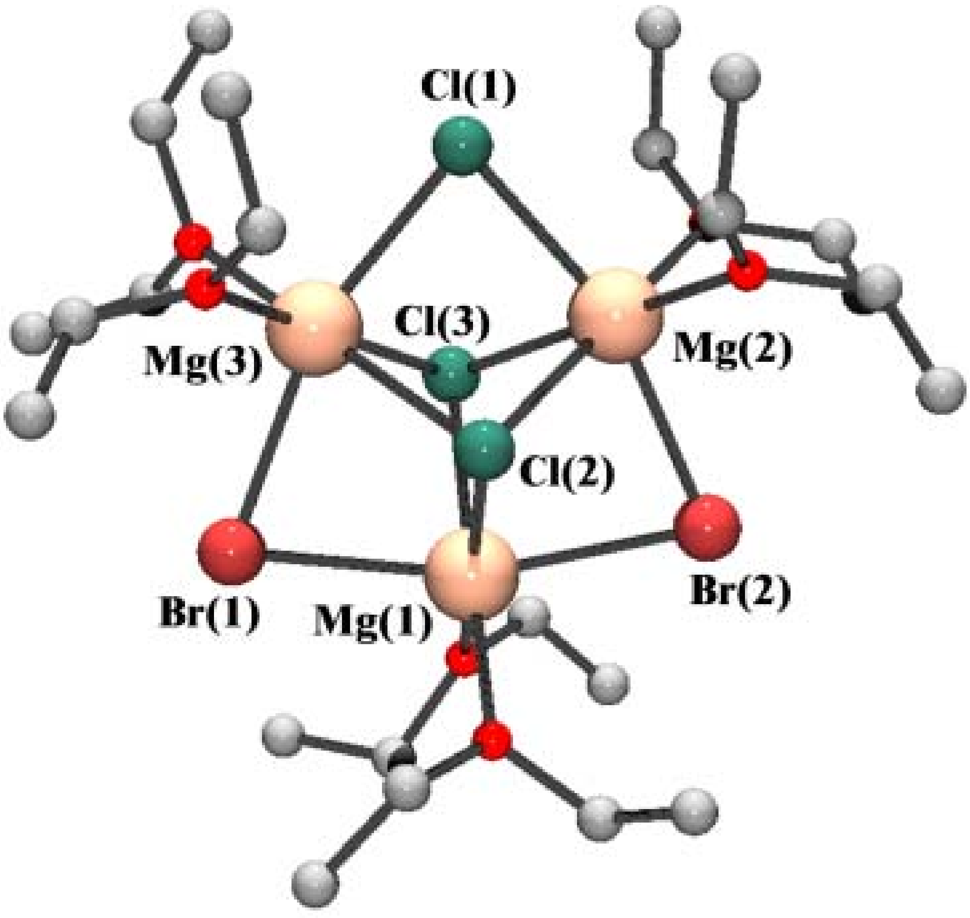


Figure 23. Molecular diagram of the cation $[Mg_3Br_2Cl_3(OEt_2)_6]^+$ in **VII** showing the atom-labeling scheme.

Table 10. Selected bond lengths [Å] and angles [º] for the cation $[Mg_3Br_2Cl_3(OEt_2)_6]^+$ in **VII**

Mg(1)-Br(1)	2.667(3)	Br(1)-Mg(1)-Br(2)	162.19(12)
Mg(3)-Cl(1)	2.561(3)	Mg(2)-Cl(1)-Mg(3)	80.29(10)
Mg(1)-Cl(2)	2.556(4)	Cl(1)-Mg(2)-Br(2)	161.90(12)
Mg(1)-Cl(3)	2.542(3)	Cl(2)-Mg(1)-Br(1)	82.94(10)
Mg(2)-Br(2)	2.657(3)	Mg(2)-Cl(2)-Mg(3)	79.09(12)
Mg(2)-Cl(2)	2.581(4)	Cl(1)-Mg(2)-Cl(2)	83.75(10)

2.3.3 Syntheses and Molecular Structures of $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII** and $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ **IX**

The anions of **VIII**, $[Ada_2GaMe_2]^-$ (Fig. 24), and **IX**, $[Ada_2AlMe_2]^-$ (Fig. 26), differ only in the Group 13 metal center. The tetrahedral coordination spheres of the gallium and aluminum atoms are saturated with carbon atoms, two adamantyl groups and two methyl groups each. The mean Ga-C bond distance in $[Ada_2GaMe_2]^-$ of 2.035 Å compares well to 2.018 Å for the corresponding Al-C bond distance in $[Ada_2AlMe_2]^-$. As evidenced by a mean M-C (M = Ga or Al) bond angle of 109.4° for both **VIII** and **IX**, the coordination about the metal atoms in these anions is virtually idealized tetrahedral. The M-C bond distances in **VIII** and **IX** are conveniently compared to other tetra-alkyl (or aryl) metallates of aluminum or gallium. For example, the Al-C bond distances in $[Et_4Al]^-$ (2.023 Å)[82] are quite comparable to those observed in **IX** while the corresponding Ga-C distances in $[(PhCH_2)_4Ga]^-$ (1.961(6) Å)[83] are shorter than observed for **VIII**. The mean M-C bond distance in the neutral Me_3M-carbene (M = Al and Ga) complexes[84] (2.053 and 2.063 Å, for gallium and aluminum, respectively) compares well with the anions of **VIII** and **IX**.

The cations in **VIII** and **IX** are identical being composed only of four bromine atoms and one OEt group about the $Mg_3(OEt_2)_6$ framework. Indeed, identical cations would be expected as compounds **VIII** (Fig. 25) and **IX** (Fig. 27) were prepared from reaction of AdaMgBr with Me_2GaCl and Me_2AlCl, respectively.

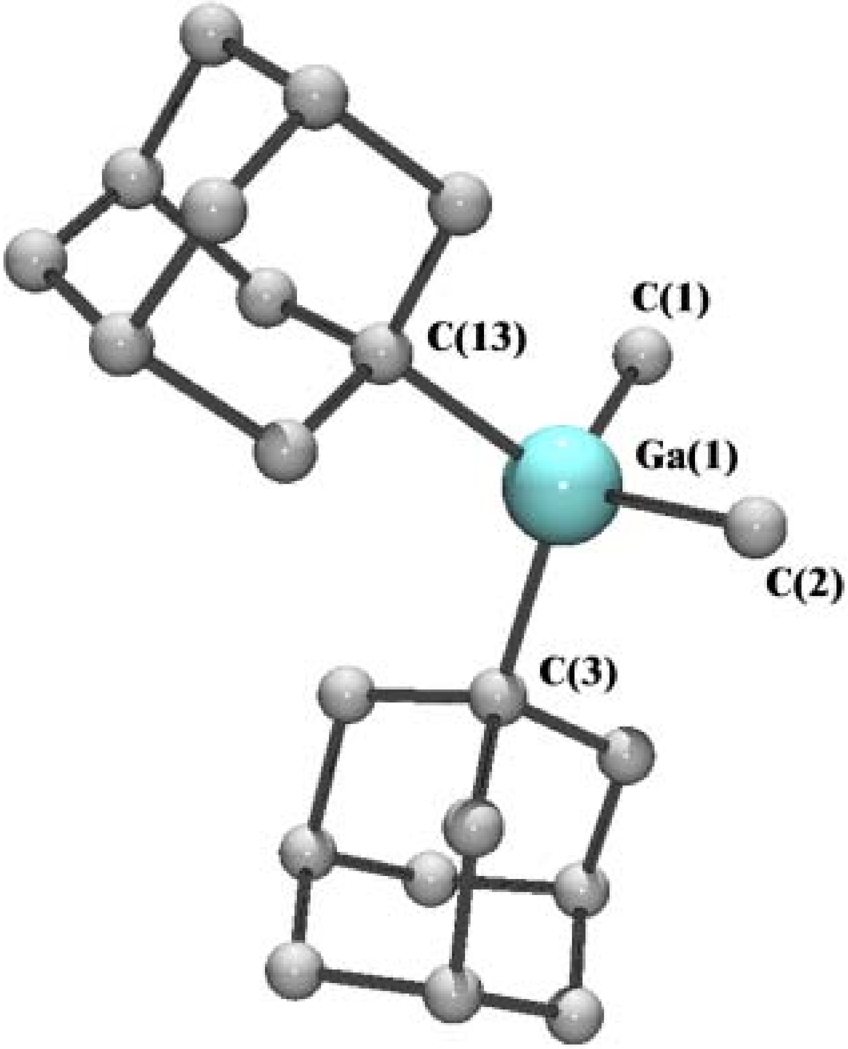


Figure 24. Molecular diagram of the anion $[Ada_2GaMe_2]^-$ in **VIII** showing the atom-labeling scheme.

Table 11. Selected bond lengths [Å] and angles [º] for the anion $[Ada_2GaMe_2]^-$ in **VIII**

Ga(1)-C(1)	2.031(7)	C(1)-Ga(1)-C(2)	107.9(4)
Ga(1)-C(2)	2.038(6)	C(1)-Ga(1)-C(13)	107.6(3)
Ga(1)-C(3)	2.058(6)	C(2)-Ga(1)-C(3)	109.6(3)
Ga(1)-C(13)	2.039(5)	C(3)-Ga(1)-C(13)	116.6(2)

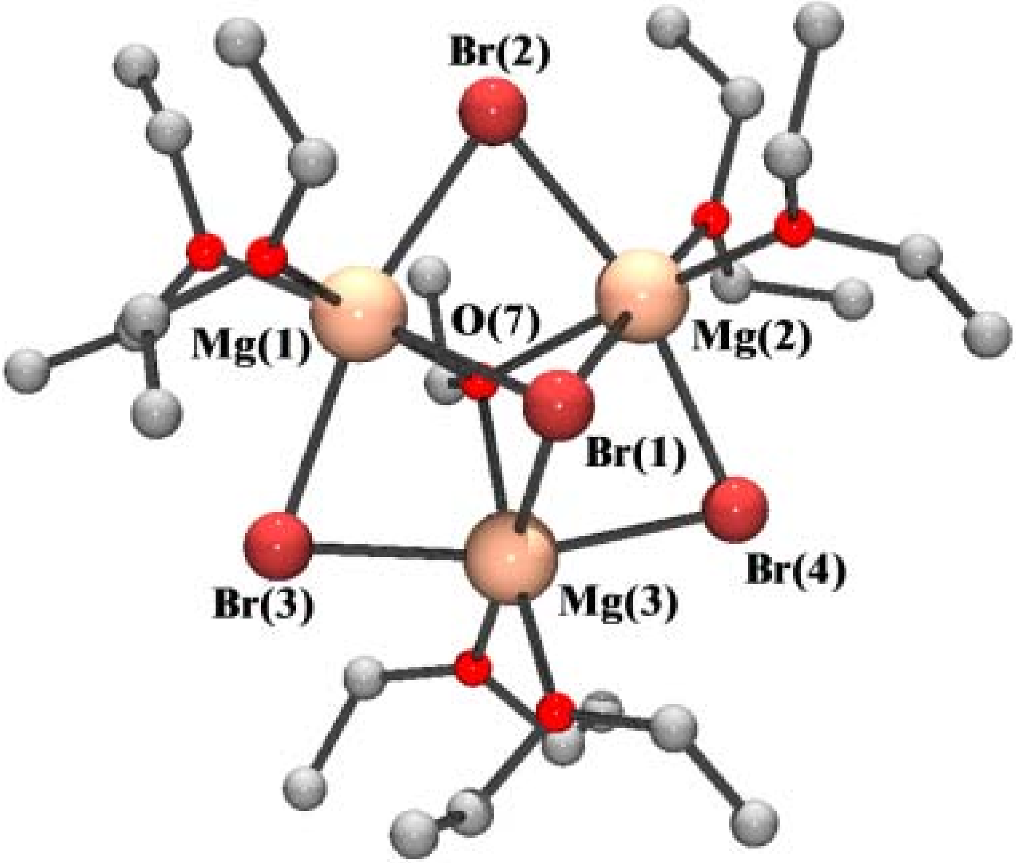


Figure 25. Molecular diagram of the cation $[Mg_3Br_4(OEt)(OEt_2)_6]^+$ in **VIII** showing the atom-labeling scheme.

Table 12. Selected bond lengths [Å] and angles [º] for the cation $[Mg_3Br_4(OEt)(OEt_2)_6]^+$ in **VIII**

Mg(1)-Br(1)	2.763(2)	Br(2)-Mg(2)-Br(4)	165.14(7)
Mg(1)-Br(2)	2.669(2)	Br(2)-Mg(2)-O(7)	83.17(11)
Mg(1)-O(7)	2.107(4)	Br(4)-Mg(3)-O(7)	83.04(10)
Mg(2)-Br(1)	2.7676(18)	Mg(1)-Br(2)-Mg(2)	74.30(6)
Mg(2)-O(7)	2.124(4)	Br(3)-Mg(3)-Br(4)	165.87(8)
Mg(2)-Br(4)	2.674(2)	Mg(3)-Br(1)-Mg(1)	71.02(6)

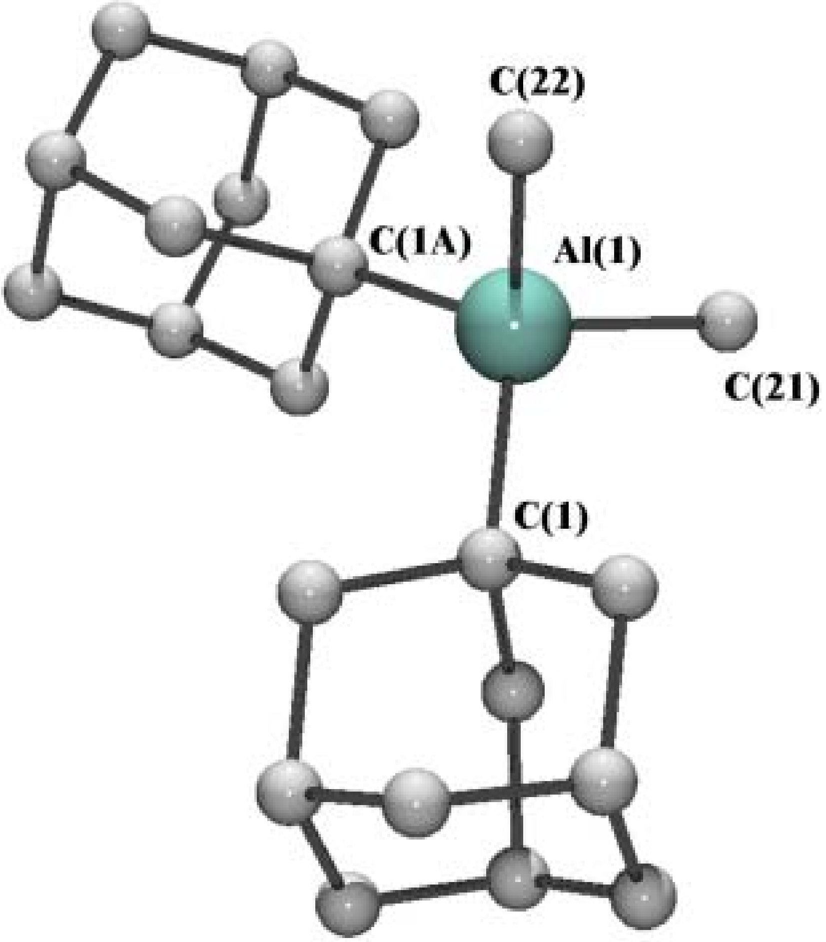


Figure 26. Molecular diagram of the anion $[Ada_2AlMe_2]^-$ in **IX** showing the atom-labeling scheme.

Table 13. Selected bond lengths [Å] and angles [º] for the anion $[Ada_2AlMe_2]^-$ in **IX**

Al(1)-C(1)	2.029(7)	C(1)-Al(1)-C(1A)	115.5(3)
Al(1)-C(1A)	2.039(7)	C(1)-Al(1)-C(21)	107.9(3)
Al(1)-C(21)	2.012(8)	C(1A)-Al(1)-C(21)	109.2(3)
Al(1)-C(22)	2.023(9)	C(21)-Al(1)-C(22)	108.5(5)

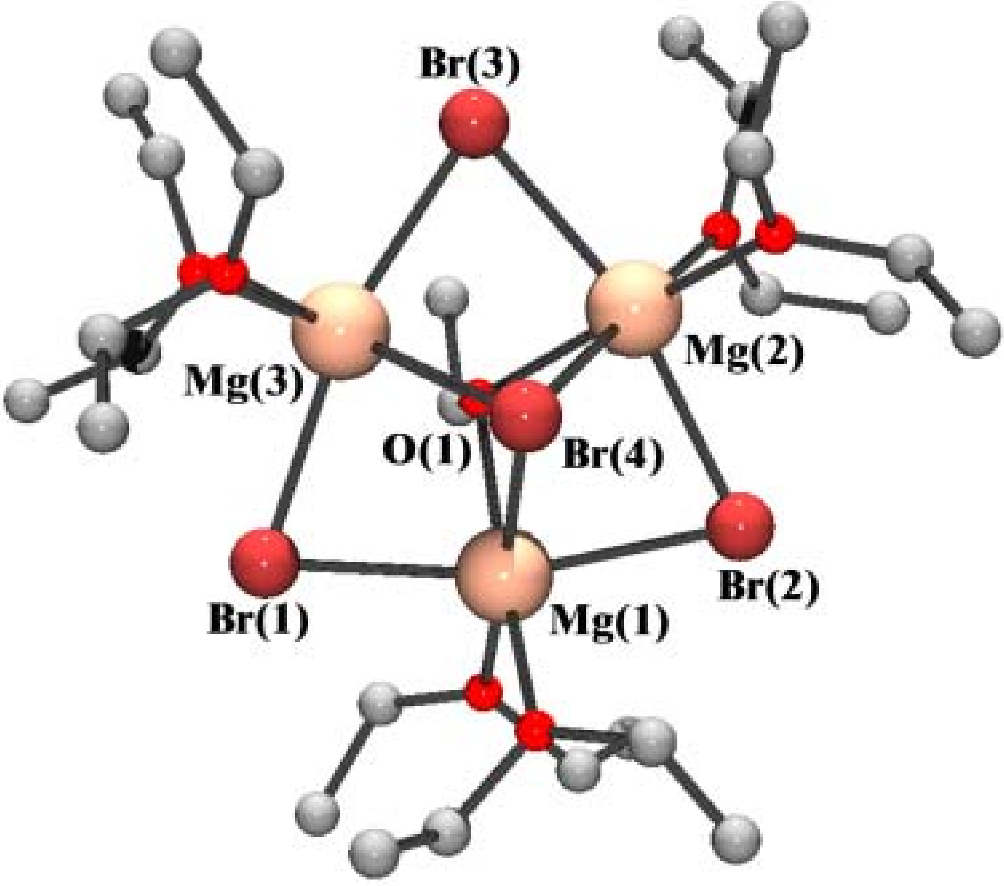


Figure 27. Molecular diagram of the cation $[Mg_3Br_4(OEt)(OEt_2)_6]^+$ in **IX** showing the atom-labeling scheme.

Table 14. Selected bond lengths [Å] and angles [º] for the cation $[Mg_3Br_4(OEt)(OEt_2)_6]^+$ in **IX**

Br(3)-Mg(2)	2.646(3)	Mg(1)-Br(4)-Mg(2)	72.51(7)
Br(4)-Mg(3)	2.710(2)	Mg(2)-Br(3)-Mg(3)	74.13(7)
Br(1)-Mg(1)	2.586(2)	Br(2)-Mg(1)-Br(4)	85.86(6)
Mg(1)-O(1)	2.141(4)	Mg(2)-O(1)-Mg(1)	97.36(18)
Mg(2)-O(1)	2.124(4)	Br(4)-Mg(3)-O(1)	77.26(13)
Mg(3)-Br(1)	2.608(2)	Br(1)-Mg(1)-Br(2)	165.58(9)

2.4 ISOLATION OF MAGNESIUM HALIDE COMPLEXES

2.4.1 Discussion of Complexes Previously Discussed in the Literature

Due to their complex equilibria and sensitivity to water and oxygen, Grignard reagent solutions frequently contain magnesium cluster side products. Two common clusters are $Mg_4Br_6O{\bullet}4C_4H_{10}O$[85] and $[Mg_6(\mu^3\text{-}OH)_2(\mu^3\text{-}Br)_8(THF)_8]$.[86] The first cluster, reported by Stucky and Rundle in 1964, was readily formed by exposing a Grignard reagent solution to small amounts of oxygen. This structure consists of four five-coordinate magnesium atoms surrounding a singular oxygen, with each magnesium atom also coordinating to three bromine atoms and a molecule of diethyl ether. The second structure, reported by Wu and coworkers, consists of two Mg_3 triangles linked together by two bridging bromide ligands. There is also one hydroxide and one bromide ligand capping both sides of the Mg_3 unit. Each six-coordinate magnesium atom has approximate octahedral symmetry and is coordinated to a THF unit. This complex is said to have resulted from the reaction of Grignard reagent with adventitious moisture.

2.4.2 Isolation of $[Mg_6(\mu^3\text{-}OH)_2(\mu^3\text{-}Br)_8(OEt_2)_8]$ **X**

Compound **X** was isolated on numerous occasions as a side product in reactions utilizing Grignard reagents (Fig. 28). This complex was most frequently isolated from reactions where a highly concentrated $MgBr_2$ solution was used in the preparation of the Grignard reagent. The crystal structure is highly analogous to the species reported by Wu *et al*. with the only difference being the coordination of diethyl ether to the magnesium centers.

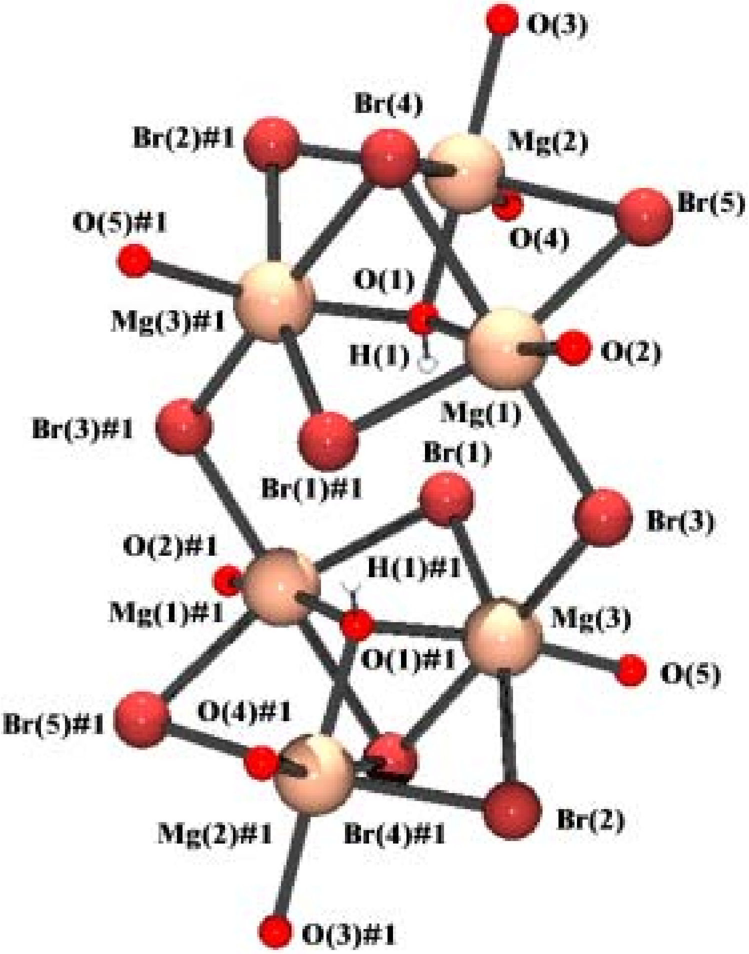


Figure 28. Molecular diagram of $[Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8]$ **X** showing the atom-labeling scheme. The ethyl groups have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 –x + 1, -y + 1, -z + 2.

Table 15. Selected bond lengths [Å] and angles [º] for $[Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8]$ **X**

Mg(1)-Br(3)	2.566(3)	Br(1)-Mg(3)-Br(2)	164.07(10)
Mg(2)-Br(5)	2.609(3)	Mg(1)-Br(4)-Mg(2)	68.58(8)
Mg(1)-Br(4)	2.774(3)	Mg(1)-Br(5)-Mg(2)	73.10(8)
Mg(3)-Br(2)	2.647(3)	Mg(1)-O(1)-Mg(2)	102.7(2)
Mg(2)-O(1)	2.019(5)	Mg(1)-Br(3)-Mg(3)	116.30(8)
Mg(2)-O(3)	2.071(7)	O(3)-Mg(2)-O(4)	91.8(3)

2.5 CURRENT INVESTIGATIONS

The following section describes work that is currently underway. Although at the time of this writing no compounds have been isolated with respect to these projects, the background and preliminary results warrant discussion.

2.5.1 The Use of the Ferrocenyl Unit as a Ligand

Ferrocene is regarded as one of the iconic molecules of organometallic chemistry. Ferrocene, as well as the other so-called "sandwich complexes," has been investigated for their use in catalysis. Ferrocene is also an attractive candidate for incorporation into polymers because of its thermal stability. There is also the potential of introducing electronic properties to the resulting materials. Moreover, there has been quite a bit of success in incorporating ferrocene into the side chain structure of organic polymers, but attempts at introducing the ferrocene moiety directly into the polymer backbone have yielded only low molecular weight oligimers.[87] By placing the ferrocenes directly into the backbone, the iron centers come in close enough proximity so that they interact.[88] It was not until the early 1990's that a new synthetic route was discovered which would allow for the incorporation of ferrocene into the main chain of a polymer with a satisfactory molecular weight. This method involved the ring-opening polymerization (ROP) of [n]metallocenophanes. [n]Metallocenophanes consist of a metallocene unit with n atoms bridging the ring functionalities. By far the most thoroughly investigated of the [n]metallocenophanes are those which have a group 14 atom in the bridge position. In 1975 Osbourne and Whitely reported the first synthesis of a [1]ferrocenophane with a silicon atom in the bridge.[89] However, since this initial species was reported, germanium, tin, phosphorus, arsenic, sulfur, selenium, and boron analogs have been prepared with a variety of substituents on the bridging atom.[90-94] These interesting compounds were typically isolated from reaction of 1,1'-dilithioferrocene with a main group halide compound.

The paucity of Group 13 ferrocenyl derivatives, i.e., those of aluminum and gallium, is noteworthy. Only the structure of the ferrocenylalane dimer $[(\eta\text{-}C_5H_3)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$ exists in the literature. With regard to gallium, a small number of ferrocenylgallanes have been reported. Many of these compounds used (trichlorostannyl)ferrocenes or (chloromercurio)ferrocenes as reagents.

Our group has recently endeavored to react a number of alkyaluminum and alkylgallium compounds with these ferrocenyl reagents in hopes of increasing the number of these highly interesting species. The reactions of 1,1'-bischloromercurioferrocene with Me_2GaCl, Me_2AlCl, $EtAlCl_2$, and Et_2AlCl were all performed in toluene and heated to reflux in an oil bath. After heating for periods ranging from 30 minutes to three hours, all four solutions turned a dark green or blue in color. In the cases of $EtAlCl_2$ and Et_2AlCl, metallic mercury was seen at the bottom of the reaction vessel. At the time of this writing, attempts are underway at isolating X-ray quality crystals from these reactions.

2.5.2 The Use of Triphenylmethyl as a Ligand

The triphenylmethyl, or trityl, ligand has found utility in a number of different areas of organic synthesis. However, there have been no reports of its use as a sterically demanding ligand on Group 13 metals. Moreover, our group is currently pursuing these compounds. By generating the organolithium derivative of triphenylmethane, triphenylmethyllithium, and reacting it in various stoichiometric ratios with aluminum and gallium halides, we hope to determine the utility of this group as a sterically demanding ligand. At the time of this writing, attempts are underway at isolating X-ray quality crystals from the reactions.

CHAPTER 3

CONCLUSIONS

3.1 CONCLUDING REMARKS

The goal of my research was to investigate a number of ligand systems and evaluate their ability to kinetically stabilize main group metal complexes. The ultimate goal was to achieve complexes possessing metal-metal bonds. During the course of my investigations I did not isolate any such complexes; however, I did isolate a number of novel organometallic compounds. These compounds not only possess interesting structural features, but they also provided insight into the synthetic utility of the ligands.

The tetraphenylbutadienyl ligand has been used by this research group previously to isolate the first spirogallane, and a number of Group 14 complexes. I sought to explore the chemistry of this ligand with regard to the lightest member of the Group 13 elements, boron, and with the Group 15 element, phosphorus. Compound **I,** $(Ph_4C_4)P\text{-}P(C_4Ph_4)$, was isolated, if unexpectedly, *via* a one-pot synthesis involving both a ring closure and alkali metal reduction. The fused-ring borane compound **II**, $[(Ph_4C_4)_2(C_2H_5)]B$, was prepared in a similar fashion, however, the mechanism involved two ring-closures, an ether cleavage, and a rearrangement.

Both the organomagnesium, C_6Me5MgBr, and organolithium, C_6Me_5Li, derivatives of the pentamethylphenyl ligand were used to isolate aluminum and gallium complexes. The Grignard reagent was prepared by two different methods, and was used to prepare compound **III**, $(C_6Me_5)_3Ga$, and compound **IV**, $(C_6Me_5)_3Al$. The first method involved the reaction of bromopentamethylbenzene with magnesium metal in ether. This method proved to give inconsistent results. A modification involving the use of a 2.6 *M* $MgBr_2$/ether solution as a solvent gave better, more consistent results. However, this route was more cumbersome and led to increased side product formation. Use of the organolithium reagent was straightforward and also resulted in the isolation of pentamethylphenyl derivatives or gallium and aluminum. The reaction of pentamethylphenyllithium with Et_2AlCl resulted in compound **V**, $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$. The reaction of pentamethylphenyllithium with Me_2MCl (M = Al or Ga) results in the formation of $(C_6Me_5)_3M$. These complexes were compared to similar compounds containing ligands based on the phenyl moiety. Although the pentamethylphenyl ligand is not much more sterically demanding than the mesityl ligand, the resulting compounds having this ligand attached were observed to have dihedral angles which distinguish it. These differences could be due to electronic or crystallographic packing factors. In any event, it would be interesting to see the pentamethylphenyl moiety placed in the *ortho*-positions of the *m*-terphenyl type ligands to see what effects, if any, it would have. Those investigations are underway.

The study of the adamantyl ligand represents a departure from phenyl based ligands to an entirely different system. Although the adamantyl ligand offers a new structural motif to work with, numerous synthetic challenges were faced. I found the organolithium derivative of adamantane to be quite elusive even after approaching it from numerous synthetic pathways. I therefore sought the Grignard reagent of adamantane, AdaMgBr, and discovered it was much easier to isolate. Adamantylmagnesium bromide reacts smoothly with the appropriate aluminum or gallium organometallic starting compound to give the ionic complexes $[Mg_3BrCl_3(OEt_2)_6][Ada_3AlBr]$ **VI**, $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**, $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**, and $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ **IX**. Neither neutral species nor metal complexes completely saturated with adamantyl groups were produced. Numerous experiments with varying stoichiometries were performed, but the results proved to be consistent. I would hypothesize that the formation of the magnesium countercation contributes to the preferred formation of ionic species over neutral species. It may even be the case that during the course of the reaction, the formation of a stable magnesium cation may influence the lability of halogen-ligand exchange at the gallium or aluminum center. Although the alkyl metal halides were also used in an attempt to form neutral complexes, the alkyl groups may have proved to be too small. Perhaps the use of a larger, more sterically demanding ligand on a metal halide would allow for the isolation of neutral Group 13 complexes containing the adamantyl ligand.

This laboratory continues to explore organometallic complexes of main group metals in order to explore and define the nature of the metal-metal bond. My investigations have helped to evaluate the utility of these ligands with regard to this pursuit. The next step will be to use these ligands to isolate main group metal complexes which could be further reacted to induce metal-metal bonding. Furthermore, these ligands could be used as building blocks to even larger sterically demanding ligands.

3.2 FUTURE PROJECTS

Among the projects in the near future for this group include the use of the previously discussed ligand systems on the lower valent aluminum and gallium halides. Also, we will continue to pursue *m*-terphenyl derivatives using the adamantyl and pentamethylphenyl groups in the *ortho*-positions of the phenyl rings. There is also the desire to form intermetallic complexes between transition metals and Group 13 metals in a very similar fashion to that of the ferrogallyne.[95]

CHAPTER 4

EXPERIMENTALS

4.1 GENERAL BACKGROUND

4.1.1 Techniques and Reagents

Most organometallic complexes of Group 13 and 15 elements are extremely air and moisture sensitive, making the exclusions of air and water during the syntheses and manipulations critical. Therefore, all manipulations were performed using standard Schlenk techniques in conjunction with an inert atmosphere drybox (M Braun Labmaster 130). Diethyl ether, hexane, and tetrahydrofuran were distilled over sodium/potassium alloy/benzophenone under a nitrogen atmosphere. Nitrogen and argon were passed through copper-based purification and molecular sieve drying columns prior to use. Melting points were measured in capillaries sealed with Apiezon H grease and are uncorrected. These were obtained on a Haake Buchler MFB 595 802 C melting point apparatus. Elemental analyses were performed by E & R Microanalytical Laboratories (Parsipanny, NJ).

Gallium(III) chloride was purchased from Strem Chemical Company (Newburyport, MA) and used without further purification. Aluminum(III) chloride, boron(III) bromide, phosphorus(III) bromide, dimethylaluminum chloride, sodium metal, potassium metal, lithium metal, diphenylacetylene, triphenylmethane, *n*-butyllithium, TMEDA, mercuric chloride, and magnesium metal were purchased from Aldrich

Chemical Company (Milwaukee, WI) and used without further purification. Bromoadamantane and ferrocene were purchased from Aldrich Chemical Company (Milwaukee, WI) and sublimed prior to use. Bromopentamethylbenzene was purchased from Lancaster Synthesis, Inc. (Windham, NH). Dimethylgallium chloride was prepared as previously noted.[96]

4.1.2 Instrumental Measurements

Nuclear Magnetic Resonance

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 FT NMR spectrometer, a Bruker AC-300 FT NMR spectrometer, or a Bruker AC-400 FT NMR spectrometer. The conventional practice of assigning positive chemical shifts downfield and negative shifts upfield with respect to a reference was employed. Chemical shifts are reported in parts per million (ppm) and are referenced to residual amounts of tetramethylsilane (TMS) in deuterated solvents. Deuterated tetrahydrofuran (THF-d_8) and chloroform ($CDCl_3$) were used as the lock solvents in NMR experiments.

X-ray Diffraction Methods

X-ray quality crystals were mounted in thin-walled glass capillaries under an inert atmosphere of nitrogen in a drybox. Glass probes with a small amount of silicon grease applied to their tips were used to retrieve the crystals from the reaction vessels. A small amount of high vacuum Apiezon H grease was used to temporarily seal the capillary for removal from the drybox to the bench top where it was flame sealed.

Single crystal X-ray data was collected on a Siemens P4/SMART CCD-based diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at

2000 watts power. The detector was placed at a distance of 4.956 cm from the crystal. A total of 1650 frames were collected with a scan width of 0.3° in ω or φ and an exposure time of 10 sec/frame. The total data collection time was 7.80 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Data were corrected for absorption effects using the empirical method (SADABS). The structures were solved and refined using the Bruker SHELXTL (Version 6.1) Software Package.[97] Non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in ideal positions riding on the attached carbon atoms without further refinement.

4.1.3 Preparation and Characterization of Starting Materials

1,4-Dilithiotetraphenylbutadiene, $Ph_4C_4Li_2$

The preparation of 1,4-dilithiotetraphenylbutadiene was carried out as reported by Schlenk and Bergmann.[98] A reaction flask was charged with diphenylacetylene (1.78 g, 10.00 mmol) and lithium powder (0.068 g, 10.00 mmol) under an inert nitrogen atmosphere. Diethyl ether (30 mL) was added and the resulting dark red solution was allowed to stir overnight. The resulting dark red slurry was then used.

Pentamethylphenylmagnessium Bromide, $(C_6Me_5)MgBr$

This Grignard reagent was prepared as previously reported. Specifically, a 2.6 *M* $MgBr_2$ ether solution was prepared from 1,2-dibromoethane (36.6 g, 0.195 mol) and magnesium metal (4.74 g, 0.195 mol). To this solution, an additional quantity of magnesium metal (0.738 g, 30.0 mmol) was added. To this flask a diethyl ether solution of bromopentamethylbenzene (3.41 g, 15.0 mmol) was slowly added *via* a dripping funnel. Upon complete addition, the solution was refluxed for 1 hour.

Pentamethylphenyllithium, $(C_6Me_5)Li$

A 1-L three-necked flask was equipped with a mechanical stirrer and addition funnel. The reaction flask was charged with bromopentamethylbenzene (56.79 g, 0.25 mol). The entire apparatus was vacuum-filled three times with argon to establish an inert atmosphere. Diethyl ether (500 mL; dry and degassed) was added to the flask *via* the addition funnel. A 1.5 *M* solution of *n*-butyllithium in hexanes (238 mL, 0.38 mol) was added slowly to the bromopentamethylbenzene slurry. A colorless precipitate began to form and the solution thickened. After the *n*-butyllithium addition was completed, the reaction mixture was stirred for an additional 2 hours. Once the reaction was complete, the slurry was filtered through a filter frit. The resulting precipitate was washed with hexanes (5 x 50 mL) to remove any unreacted *n*-butyllithium and then washed with diethyl ether (50 mL) to remove any LiBr. The product was dried *in vacuo*.

Adamantylmagnessium Bromide, AdaMgBr

This Grignard reagent was prepared as previously reported by Molle *et al.*[76] Specifically, to a three-neck round bottom flask equipped with a condenser were introduced bromoadamantane (5.37 g, 25.00 mmol), magnesium turnings (9.10 g, 375.00 mmol), and 100 mL of diethyl ether. The reaction was refluxed at 40° C overnight with no stirring.

1,1’-Dilithioferrocene, $[(\eta^5\text{-}C_5H_4Li)_2Fe][TMEDA]$

This reagent was prepared as previously reported by Rettig *et al.*[99] A stirred solution of ferrocene (14.0 g, 75.3 mmol) in diethyl ether (200 mL) maintained at 20 ˚C was treated sequentially with a 1.5 *M* solution of *n*-butyllithium (100 mL) in hexanes and TMEDA (9.6 g, 82.8 mmol). A clear orange solution resulted. Stirring was stopped and the reaction mixture was allowed to stand for 48 h. Large, red crystals of the product were deposited mainly on the vessel walls. The solution was removed *via* cannula. The remaining crystals were washed with diethyl ether (40 mL). The sample was product was then dried *in vacuo*. The yield of crystals was ~80%, however, the residual solution when placed in the freezer at -30˚C yields additional product.

1,1’-Bischloromercurioferrocene

This reagent was prepared as previously reported.[100] To a solution of 1,1’-dilithioferrocene (3.2 g, 11.8 mmol) dissolved in THF (50 mL) was added a solution of mercuric chloride (7.06 g, 26 mmol) in THF (15 mL) *via* cannula transfer. The clear orange solution immediately turned a chalky-orange upon addition of mercuric chloride. The orange suspension was stirred for 24 h under argon. The orange solid was collected by filtration and washed with THF. Removal of the solvent under vacuum afforded an insoluble orange product.

Triphenylmethyllithium

This reagent was prepared as previously reported.[101] To a stirred ether solution of triphenylmethane (7.32 g, 30 mmol) at 0˚C was added a 1.6 *M* solution of *n*-butyllithium in hexanes (18.75 mL). The solution was allowed to warm to ambient temperature and stirred for a further 12 h. A small amount of diethyl ether was removed under reduced pressure until crystallization began. Allowing the flask to stand undisturbed on the desktop overnight afforded the product as orange-red crystals. Yield 60-80%, m.p. 95-99˚C.

Determination of Grignard Reagent Concentration

The concentrations of the Grignard reagents were determined according to published methods.[102] A milligram sample of 1,10-phenanthroline added to the ether solution containing *ca.* 0.1-1.0 *M* of the Grignard reagent produced a bright violet solution. Titration of this solution with 1 *M* sec-butyl alcohol in xylene solution caused the color to fade abruptly when two mole equivalents of the titrant were added.

4.2 MAIN GROUP METAL COMPLEXES

4.2.1 Synthesis of $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I**

Inside the drybox, a 100 mL Schlenk flask was charged with phosphorus (III) bromide (1.08 g, 4.00 mmol) and diethyl ether (30 mL). At the bench top, 1,4-dilithiotetraphenylbutadiene (approx. 8.00 mmol) was slowly added to the reaction vessel at -78°C over a period of 30 minutes *via* a dripping funnel. The system was allowed to warm to room temperature and stir overnight. The solvent was removed *in vacuo*, and the solid was re-dissolved in hexane (40 mL). The resulting solution was filtered immediately and dried *in vacuo*. The solid was recrystallized in diethyl ether and resulted in yellow-orange crystals (0.56 g, 34% yield): Mp 245-246°C (dec). Calcd. (found): C, 86.60 (86.51); H, 5.80 (5.76). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.46$ (q, 3H, CH_3 (hexane)), 0.84 (m 4H, CH_2 (hexane)), 7.26-7.54 (m, 40H, Ph$\underline{H}$); ^{13}C NMR (300 MHz,

$CDCl_3$): δ = 14.0, 22.5, 31.5, 126.3, 127.1, 127.8, 129.6, 130.3, 136.5, 137.3, 143.9, 147.8, 151.8 ppm; ^{31}P NMR (300 MHz, 298K, $CDCl_3$): δ = -15.98 ppm.

4.2.2 Synthesis of $[(Ph_4C_4)_2(C_2H_5)]B$ **II**

Inside the drybox a 100 mL Schlenk flask was charged with boron bromide (0.62 g, 2.50 mmol) and diethyl ether (30 mL). At the bench top, 1,4-dilithiotetraphenylbutadiene (approx. 8.00 mmol) was slowly added to the reaction vessel at -78°C over a period of 30 minutes *via* an dripping funnel. The system was allowed to warm to room temperature and stir overnight. After filtration, the solvent was reduced and placed at -20°C to afford yellow crystals (1.22 g, 60% yield): Mp 140°C. Calcd. (found): C, 90.90 (90.04); H, 6.66 (6.34). ^1H NMR (250 MHz, THF-d_8): δ = 0.51 (m, 3H, $-CCH_2C\underline{H}_3$), 1.14 (m 6H, $-OCH_2C\underline{H}_3$), 1.60 (m, 2H, $-C\underline{C}\underline{H}_2CH_3$), 3.38 (m, 4H, $-OC\underline{H}_2CH_3$), 6.10-7.50 (m, 40H, $Ph\underline{H}$); ^{13}C NMR (250 MHz, THF-d_8): δ = 14.40 ($-CCH_2\underline{C}H_3$), 15.87 ($-OCH_2\underline{C}H_3$), 24.95 ($-C\underline{C}H_2CH_3$), 60.31 (C-29), 65.36 (C-50), 66.49 ($-O\underline{C}H_2CH_3$), 125.6, 125.9, 126.0, 126.2, 126.3, 126.7, 127.2, 127.3, 127.4, 127.6, 127.9, 128.0, 128.4, 128.8, 129.5, 129.6, 129.9, 130.6, 131.1, 131.2, 131.7, 131.8, 132.1, 133.9, 139.7, 140.4, 140.8, 141.0, 141.7, 143.3, 143.6, 144.8, 144.9, 145.3, 146.3, 148.2, 151.9, 154.8 ppm.

4.2.3 Synthesis of $(C_6Me_5)_3Ga$ **III**

To a diethyl ether solution of $GaCl_3$ (0.88 g, 5.00 mmol) was added pentamethylphenylmagnesium bromide (15.00 mmol) at 0°C. The system was allowed to warm to room temperature and stir overnight. The white precipitate was filtered resulting in a clear solution. Reduction of the solvent and cooling to -20°C afforded colorless, needlelike crystals (0.91 g, 35.6% yield): Mp 163°C. Calcd. (found): C, 77.53 (77.42); H, 8.81 (8.67). ^{1}H NMR (400 MHz, THF-d_8): δ = 2.14 (s, 18H, *m*-CH_3), 2.22 (s, 9H, *p*-CH_3), 2.33 (s, 18H, *o*-CH_3); ^{13}C NMR (400 MHz, THF-d_8): δ = 23.7, 25.4, 68.9, 131.8, 135.1, 137.6, 150.4 ppm.

4.2.4 Synthesis of $(C_6Me_5)_3Al$ **IV**

To prepare tris(pentamethylphenyl)aluminum, 150 mL of the 0.0950 *M* $(C_6Me_5)MgBr$ solution (14.3 mmol) was slowly added *via* dripping funnel to a flask containing $AlCl_3$ (0.400 g , 3.00 mmol) dissolved in 10 mL of ether at 0°C. The solution was allowed to warm to room temperature and was stirred for 12 hours. The resulting system contained two distinct layers. The layers were separated *via* cannula into separate flasks and placed in the freezer (-30°C). Crystals of **IV** were isolated from the top layer (0.506 g, 36.0% yield): Mp 291°C (dec). Calcd. (found): C, 84.57 (84.29); H, 9.68 (9.51). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 18H, *p*-CH_3), 2.23 (m, 18H, *m*-CH_3), 2.44 (s, 9H, *o*-CH_3); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 16.2, 20.5, 25.0, 128.9, 131.4, 135.7, 139.2 ppm.

4.2.5 Synthesis of $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V**

Pentamethylphenyllithium (1.2 g, 5.0 mmol) in diethyl ether was slowly added to a stirred solution of Et_2AlCl (0.63 g, 5 mmol) in diethyl ether at -78˚C. The solution was stirred for 15 hours and allowed to warm to room temperature. The solution was filtered and cooled to -30˚C and this afforded X-ray quality crystals (0.97 g, 32% yield). Anal. Calcd (found) for $C_{38}H_{70}AlLiO_3$: C, 74.96 (75.07); H, 11.59 (11.40).

4.2.6 Synthesis of $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ **VI**

Adamantylmagnesium bromide (100.00 mL, 0.10 *M*) in diethyl ether was slowly added to a stirred solution of $AlCl_3$ (0.264 g, 2.00 mmol) in diethyl ether at -78°C. The solution was stirred for 15 hours and allowed to warm to room temperature. The solution was then refluxed for 3.5 hours. After filtration, the solution was cooled to -30°C and this afforded X-ray quality crystals (0.86 g, 34% yield). Mp 257°C (dec). Anal. Calcd (found) for $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$: C, 53.30 (53.19); H, 8.80 (8.68). ^{1}H NMR (400 MHz, THF-d_8): δ 1.09 (t, 39H), $-OCH_2C\underline{H}_3$; 1.60 (m, 18H), Ada; 1.69 (m, 18H), Ada; 1.83 (m, 9H), Ada; 3.36 (q, 26H), $-OC\underline{H}_2CH_3$. ^{13}C NMR (400 MHz, THF-d_8): δ 15.8, 30.4, 38.6, 40.4, 43.4, 66.4 ppm.

4.2.7 Synthesis of $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**

Adamantylmagnesium bromide (100.00 mL, 0.127 *M*) in diethyl ether was slowly added to a stirred solution of $GaCl_3$ (0.45 g, 2.55 mmol) in diethyl ether at -78°C. The solution was stirred for 15 hours and allowed to warm to room temperature. The solution was then refluxed for 3.5 hours. After filtration, the solution was cooled to -30°C and this afforded X-ray quality crystals (1.18 g, 36% yield): Mp 257°C (dec). Anal. Calcd (found) for $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$: Mg, 5.70 (5.62); Cl ,8.30 (8.57); Br, 24.90 (24.77). ^{1}H NMR (400 MHz, THF-d_8): δ 1.08 (t, 36H), $-OCH_2C\underline{H}_3$; 1.63 (m, 12H), Ada; 1.69 (m, 12H), Ada; 1.79 (m, 6H), Ada; 3.35 (q, 24H), $-OC\underline{H}_2CH_3$. ^{13}C NMR (400 MHz, THF-d_8): δ 15.7, 30.4, 39.6, 42.4, 44.5, 66.3 ppm.

4.2.8 Synthesis of $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**

To a diethyl ether solution of Me_2GaCl (0.405 g, 3.00 mmol) was slowly added 75 mL of adamantylmagnesium bromide (0.2 *M*, 15.0 mmol) at -78°C. The solution was stirred for 15 hours and allowed to warm to room temperature. The solution was then refluxed for 3.5 hours. After filtration, the solution was cooled to -30°C and this afforded X-ray quality crystals (1.39 g, 37% yield): Mp 260°C (dec). Calcd. (found): C, 46.00 (45.96); H, 8.10 (8.21). ^1H NMR (400 MHz, THF-d_8): $\delta = 0.10$ (s, 6H, $-CH_3$), 1.11 (t, 39H, $-OCH_2C\underline{H}_3$), 1.61 (m, 12H, Ada), 1.70 (m, 12H, Ada), 1.78 (m, 6H, Ada), 3.38 (q, 26H, $-OC\underline{H}_2CH_3$); ^{13}C NMR (400 MHz, THF-d_8): $\delta = 15.8, 30.5, 36.1, 38.5, 40.0, 43.8, 66.4$ ppm.

4.2.9 Synthesis of $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ **IX**

To a diethyl ether solution of Me_2AlCl (0.277 g, 3.00 mmol) was slowly added 75 mL of adamantylmagnesium bromide (0.2 *M*, 15.0 mmol) at -78°C. The solution was stirred for fifteen hours and allowed to warm to room temperature. The solution was then refluxed for 3.5 hours. After filtration, the solution was cooled to -30°C and this afforded X-ray quality crystals (1.20 g, 33% yield): Mp 260°C (dec). ^1H NMR (400 MHz, 298K, THF-d_8): $\delta = 0.10$ (s, 6H, $-CH_3$), 1.11 (t, 39H, $-OCH_2C\underline{H}_3$), 1.60 (m, 12H, Ada), 1.70 (m, 12H, Ada), 1.83 (m, 6H, Ada), 3.38 (q, 26H, $-OC\underline{H}_2CH_3$); ^{13}C NMR (400 MHz, THF-d_8): $\delta = 15.8, 30.0, 36.2, 38.5, 39.8, 42.7, 66.5$ ppm.

4.3 MAGNESIUM COMPLEX

4.3.1 Isolation of $[Mg_6(\mu^3\text{-}OH)_2(\mu^3\text{-}Br)_2(\mu^2\text{-}Br)_8(OEt_2)_8]$ **X**

The magnesium cluster, $[Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_2(\mu_2\text{-}Br)_8(OEt_2)_8]$ **X**, was isolated numerous times as a byproduct of Grignard reactions. This compound was isolated as colorless crystals.

REFERENCES

(1) Zeise, W. C. *Ann. Phys. Chem.* **1831**, *21*, 497.

(2) Seyferth, D. *Organometallics* **2001**, *20*, 2-6.

(3) Gilman, H.; Morton, J. W., Jr. *Org. Reactions* **1954**, *8*, 258.

(4) Grignard, V. *Ann. Chim.* **1901**, *24*, 433.

(5) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039-1040.

(6) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta. Cryst.* **1956**, *9*, 373-375.

(7) Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470-476.

(8) Dagani, R. *Chem Eng News* **2001**, *79*, 37-38.

(9) Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*; 1st ed.; Prentice Hall: New York, 2001.

(10) Massey, A. G. *Main Group Chemistry*; 2nd ed.; Wiley: Chichester ; New York, 2000.

(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*; 4th ed.; Wiley: New York, 1980.

(12) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; 2nd ed.; Wiley: New York, 1986.

(13) Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*; 2nd ed.; Prentice Hall: Upper Saddle River, N.J., 1999.

(14) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; 2nd ed.; W.H. Freeman: New York, 1994.

(15) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3121.

(16) Malone, J. F.; McDonald, W. S. *Chem. Commun.* **1967**, 444-445.

(17) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. Dalton* **1972**, 2646-2648.

(18) Jerius, J. J.; Hahn, J. M.; Rahman, A. F.; Mois, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1986**, *5*, 1812-1814.

(19) Dennis, L. M.; Patnode, W. *J. Am. Chem. Soc.* **1932**, *54*, 182-188.

(20) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* **1970**, 3362-3367.

(21) Beachley, O. T., Jr. *Organometallics* **1986**, *5*, 1814-1817.

(22) Li, X. W.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 2109-2111.

(23) Crittendon, R. C.; Li, X.-W.; Su, J.; Robinson, G. H. *Organometallics* **1997**, *16*, 2443-2447.

(24) Moezzi, A.; Olmstead, M. M.; Bartlett, R. A.; Power, P. P. *Organometallics* **1992**, *11*, 2383-2388.

(25) Schluter, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 57-58.

(26) Biffar, W.; Noth, H.; Pommerening, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 56-57.

(27) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715-2717.

(28) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 870-871.

(29) Uhl, W. *Z. Naturforsch.* **1988**, *43b*, 1113-1118.

(30) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289-300.

(31) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983-2984.

(32) He, X. M.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandtsenge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717-719.

(33) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *Chem. Commun.* **1976**, 261-262.

(34) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793-800.

(35) Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 9394-9395.

(36) Sturmann, M.; Saak, W. G.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 187-189.

(37) Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471-5472.

(38) Dagani, R. *Chem. Eng. News* **1997**, *75*, 9-10.

(39) Dagani, R. *Chem. Eng. News* **1998**, *76*, 31-33.

(40) Xie, Y.; Schaefer, H. F., III; Robinson, G. H. *Chem. Phys. Lett.* **2000**, *317*, 174-180.

(41) Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F., III; Schleyer, P. v. R.; Su, J.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 3773-3780.

(42) Klinkhammer, K. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2320-2322.

(43) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59*, 2215-2223.

(44) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578-7579.

(45) Li, X.-W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaefer, H. F., III; Robinson, G. H. *Organometallics* **1996**, *15*, 3798-3803.

(46) Xie, Y.; Schreiner, P. R.; Schaefer, H. F., III; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1996**, *118*, 10635-10639.

(47) Orechoff, A. *Ber.* **1914**, *47*, 89.

(48) Bergmann, E.; Zwecker, O. *Ann.* **1931**, *487*, 155.

(49) Bergmann, E.; Schreiber, W. *Ann.* **1933**, *500*, 118.

(50) Pauer, F.; Power, P. P. *J. Organomet. Chem.* **1994**, *474*, 27-30.

(51) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454-2459.

(52) Song, J. S.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 1505-1509.

(53) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889-2894.

(54) Goodwin, S. D.; Wei, P.; Beck, B. C.; Su, J.; Robinson, G. H. *Main Group Chem.* **2000**, *3*, 137-141.

(55) Beck, B. C.; Su, J.; Wei, P.; Li, X.-W.; Robinson, G. H. *Organometallics* **2000**, *19*, 1214-1215.

(56) Su, J.; Goodwin, S. D.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 12994-12995.

(57) Vohs, J. K.; Wei, P.; Su, J.; Beck, B. C.; Goodwin, S. D.; Robinson, G. H. *Chem. Commun.* **2000**, 1037-1038.

(58) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955-3955.

(59) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085-2086.

(60) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 6887-6888.

(61) Driess, M.; Frankhauser, P.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1991**, *124*, 1497-1503.

(62) Burns, J. A.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 1533-1535.

(63) Jutzi, P.; Meyer, U.; Krebs, B.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 919-921.

(64) Brown, S. G.; Wei, P.; Beck, B. C.; Vohs, J. K.; Robinson, G. H. *J. Chem. Cryst.* **2002**, *31*, 467-470.

(65) Zettler, F.; Hausen, H. D.; Hess, H. *J. Organomet. Chem.* **1974**, *72*, 157.

(66) Robinson, G. H. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 2001; Vol. 47, pp 283-294.

(67) Vohs, J. K.; Downs, L. E.; Barfield, M. E.; Goodwin, S. D.; Robinson, G. H. *Polyhedron* **2002**, *21*, 531-534.

(68) Vohs, J. K.; Downs, L. E.; Stasalovich, J.; Barfield, M.; Robinson, G. H. *J. Clust. Sci.* **2002**, *13*, 601-608.

(69) Garst, J. F.; Lawrence, K. E.; Batlaw, R.; Boone, R.; Ungvary, F. *Inorg. Chim. Acta* **1994**, *222*, 365-375.

(70) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377-2386.

(71) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1957**, *79*, 3292.

(72) Dembowski, U.; Roesky, H. W.; Pohl, E.; Herbst-Irmer, R.; Stalke, D.; Sheldrick, G. M. *Z. Anorg. Allg. Chem.* **1992**, *611*, 92-94.

(73) Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Polyhedron* **1993**, *12*, 2279-2289.

(74) Roberts, R. M. G. *J. Organomet. Chem.* **1973**, *63*, 159-165.

(75) Vohs, J. K.; Downs, L. E.; Barfield, M.; Latibeaudiere, K.; Robinson, G. H. *J. Organomet. Chem.* **2003**, *666*, 7-13.

(76) Molle, G.; Bauer, P.; Dubois, J. E. *J. Org. Chem.* **1982**, *47*, 4120-4128.

(77) Richey, H. G. *Grignard Reagents: New Developments*; Wiley: Chichester; New York, 2000.

(78) Harlan, C. J.; Gillan, E. G.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5479-5488.

(79) Loos, D.; Eichkorn, K.; Magull, J.; Ahlrichs, R.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1582-1588.

(80) Werner, B.; Kräuter, T.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 346-358.

(81) Kopp, M. R.; Neumuller, B. *Z. Anorg. Allg. Chem.* **1997**, *623*, 796-804.

(82) Gerteis, R. L.; Dickerson, R. E.; Brown, T. L. *Inorg. Chem.* **1964**, *3*, 872-875.

(83) Kopp, M. R.; Neumuller, B. *Z. Naturforsch.* **1998**, *53b*, 545-551.

(84) Li, X.-W.; Su, J.; Robinson, G. H. *Chem. Commun.* **1996**, 2683-2684.

(85) Stucky, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 4821-4825.

(86) Wu, Q.; Zhang, Y.; Wang, S. *J. Clust. Sci.* **2000**, *11*, 253-260.

(87) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603-1621.

(88) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683-12695.

(89) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27-C28.

(90) Foucher, D. A.; Edwards, M.; Burrow, R. A.; Lough, A. J.; Manners, I. *Organometallics* **1994**, *13*, 4959-4966.

(91) Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1805-1807.

(92) Rulkens, R.; Gates, D. P.; Balaishis, D.; Pudelski, J. K.; McIntosh, D. F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1997**, *119*, 10976-10986.

(93) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275-1282.

(94) Braunschweig, H.; Dirk, R.; Muller, M.; Nguyen, P.; Resendes, R.; Gates, D. P.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2338-2340.

(95) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511-4513.

(96) Auner, N.; Klingebiel, U., Eds. *Synthetic Methods of Organometallic and Inorganic Chemistry*; Thieme Medical Publishers, Inc.: New York, 1996.

(97) Sheldrick, G. M.; Bruker Analytial X-ray Systems: Madison, WI, 2000.

(98) Schlenk, W.; Bergmann, E. *Ann.* **1928**, *463*, 71.

(99) Butler, I. R.; Cullen, W. R.; Ni, J.; Rettig, S. J. *Organometallics* **1985**, *4*, 2196-2201.

(100) Carpenter, B. E.; Piers, W. E.; McDonald, R. *Can. J. Chem.* **2001**, *79*, 291-295.

(101) Bartlett, R. A.; Dias, H. V.; Power, P. P. *J. Organomet. Chem.* **1988**, *341*, 1-9.

(102) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165-168.

APPENDIX A

CRYSTALLOGRAPHIC DATA

5.1 STRUCTURAL DATA OF $(Ph_4C_4)P\text{-}P(C_4Ph4)$ **I**

Table 16. Crystal data and structure refinement for $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I**

Empirical Formula	$C_{59}H_{47}P_2$
Formula Weight	817.91
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	C2/*c*
Unit Cell Dimensions	a = 28.092(4) Å
	b = 13.6821(16) Å
	c = 24.311(2) Å
	$\alpha = 90°$
	$\beta = 98.078(5)°$
	$\gamma = 90°$
Volume	9251.4(19) $Å^3$
Z	8
Calculated Density	1.174 Mg/m^3
Absorption Coefficient	0.132 mm^{-1}
F(000)	3448
Crystal Size	0.50 x 0.50 x 0.40 mm
Theta Range for Data Collection	1.91 to 23.30º
Limiting Indices	$-31 \leq h \leq 28$
	$-15 \leq k \leq 14$
	$-14 \leq l \leq 26$
Reflections Collected/Unique	16475 / 6568 [R(int) = 0.0730]
Completeness to Theta	98.20%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	6568 / 0 / 551
Goodness-of-fit on F^2	1.003
Final R Indices [I >2sigma(I)]	R1 = 0.0569 wR2 = 0.1165
R Indices (All Data)	R1 = 0.1026 wR2 = 0.1321
Largest Diff. Peak and Hole	0.232 and -0.212 $e^-/Å^3$

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $(Ph_4C_4)P\text{-}P(C_4Ph_4)$ **I**

Atom	X	Y	Z	U(eq)
P(1)	4037(1)	8213(1)	1026(1)	48(1)
P(2)	3322(1)	8330(1)	524(1)	53(1)
C(1)	4129(1)	6914(2)	1000(1)	44(1)
C(2)	4235(1)	6426(2)	488(1)	47(1)
C(3)	4572(1)	6823(2)	184(1)	58(1)
C(4)	4694(1)	6359(3)	-280(1)	71(1)
C(5)	4478(1)	5502(3)	-453(1)	77(1)
C(6)	4136(2)	5109(3)	-173(2)	84(1)
C(7)	4016(1)	5565(2)	297(1)	67(1)
C(8)	4154(1)	6517(2)	1514(1)	41(1)
C(9)	4290(1)	5476(2)	1639(1)	45(1)
C(10)	3941(1)	4761(2)	1630(1)	71(1)
C(11)	4068(2)	3785(3)	1705(2)	85(1)
C(12)	4534(2)	3519(3)	1779(2)	89(1)
C(13)	4883(2)	4219(3)	1798(2)	87(1)
C(14)	4763(1)	5195(2)	1727(1)	65(1)
C(15)	4068(1)	7228(2)	1944(1)	40(1)
C(16)	4143(1)	6999(2)	2549(1)	42(1)
C(17)	3892(1)	6273(2)	2777(1)	55(1)
C(18)	3948(1)	6121(2)	3345(1)	71(1)
C(19)	4254(2)	6696(3)	3687(1)	74(1)
C(20)	4517(1)	7412(2)	3473(1)	64(1)
C(21)	4461(1)	7562(2)	2907(1)	50(1)
C(22)	3956(1)	8144(2)	1745(1)	43(1)
C(23)	3843(1)	9003(2)	2070(1)	49(1)
C(24)	3559(1)	8933(2)	2491(1)	57(1)
C(25)	3478(1)	9731(3)	2811(1)	71(1)
C(26)	3664(2)	10613(3)	2717(2)	91(1)
C(27)	3942(2)	10720(3)	2301(2)	104(1)
C(28)	4030(1)	9919(2)	1974(1)	77(1)
C(29)	2897(1)	7942(2)	967(1)	50(1)
C(30)	2812(1)	6915(2)	1096(1)	54(1)
C(31)	2764(1)	6198(3)	692(2)	78(1)
C(32)	2661(1)	5240(3)	825(2)	95(1)
C(33)	2616(1)	4992(3)	1359(2)	93(1)
C(34)	2666(1)	5682(3)	1765(2)	79(1)
C(35)	2763(1)	6638(2)	1636(1)	62(1)

Atom	X	Y	Z	U(eq)
C(36)	2644(1)	8727(2)	1116(1)	51(1)
C(37)	2199(1)	8624(2)	1384(1)	53(1)
C(38)	2185(1)	8889(2)	1928(2)	71(1)
C(39)	1776(2)	8756(3)	2177(2)	83(1)
C(40)	1379(2)	8357(3)	1883(2)	88(1)
C(41)	1382(1)	8083(3)	1342(2)	94(1)
C(42)	1794(1)	8218(3)	1088(2)	81(1)
C(43)	2818(1)	9671(2)	939(1)	50(1)
C(44)	2578(1)	10606(2)	1056(1)	58(1)
C(45)	2653(2)	11033(3)	1566(2)	92(1)
C(46)	2426(2)	11916(3)	1670(2)	110(2)
C(47)	2135(2)	12359(3)	1258(3)	114(2)
C(48)	2065(2)	11953(4)	750(3)	147(2)
C(49)	2278(2)	11073(3)	652(2)	110(2)
C(50)	3192(1)	9594(2)	640(1)	52(1)
C(51)	3455(1)	10388(2)	398(1)	56(1)
C(52)	3603(1)	11232(3)	688(2)	75(1)
C(53)	3869(1)	11939(3)	458(2)	92(1)
C(54)	3977(2)	11826(4)	-64(2)	97(1)
C(55)	3826(1)	11018(4)	-369(2)	90(1)
C(56)	3568(1)	10288(3)	-139(1)	70(1)
C(57)	5020(3)	10007(11)	-355(6)	277(12)
C(58)	4797(3)	9211(9)	-606(7)	302(10)
C(59)	4840(3)	9141(9)	-1223(4)	252(5)

Table 18. Bond lengths [Å] for (Ph_4C_4)P-P(C_4Ph_4) **I***

Atoms	Distance	Atoms	Distance
P(1)-C(22)	1.797(3)	C(27)-C(28)	1.396(5)
P(1)-C(1)	1.799(3)	C(29)-C(36)	1.364(4)
P(1)-P(2)	2.2051(11)	C(29)-C(30)	1.467(4)
P(2)-C(29)	1.796(3)	C(30)-C(31)	1.382(4)
P(2)-C(50)	1.799(3)	C(30)-C(35)	1.391(4)
C(1)-C(8)	1.356(3)	C(31)-C(32)	1.391(5)
C(1)-C(2)	1.480(4)	C(32)-C(33)	1.365(5)
C(2)-C(7)	1.379(4)	C(33)-C(34)	1.359(5)

Atoms	Distance	Atoms	Distance
C(2)-C(3)	1.391(4)	C(34)-C(35)	1.383(4)
C(3)-C(4)	1.377(4)	C(36)-C(43)	1.467(4)
C(4)-C(5)	1.359(5)	C(36)-C(37)	1.495(4)
C(5)-C(6)	1.365(5)	C(37)-C(42)	1.376(4)
C(6)-C(7)	1.382(4)	C(37)-C(38)	1.378(4)
C(8)-C(15)	1.472(3)	C(38)-C(39)	1.383(4)
C(8)-C(9)	1.494(4)	C(39)-C(40)	1.353(5)
C(9)-C(14)	1.370(4)	C(40)-C(41)	1.370(5)
C(9)-C(10)	1.383(4)	C(41)-C(42)	1.397(5)
C(10)-C(11)	1.387(4)	C(43)-C(50)	1.360(4)
C(11)-C(12)	1.347(5)	C(43)-C(44)	1.492(4)
C(12)-C(13)	1.365(5)	C(44)-C(45)	1.359(4)
C(13)-C(14)	1.382(4)	C(44)-C(49)	1.361(5)
C(15)-C(22)	1.365(3)	C(45)-C(46)	1.405(5)
C(15)-C(16)	1.488(3)	C(46)-C(47)	1.344(6)
C(16)-C(17)	1.379(4)	C(47)-C(48)	1.343(6)
C(16)-C(21)	1.390(4)	C(48)-C(49)	1.380(6)
C(17)-C(18)	1.384(4)	C(50)-C(51)	1.482(4)
C(18)-C(19)	1.360(5)	C(51)-C(52)	1.385(4)
C(19)-C(20)	1.372(4)	C(51)-C(56)	1.392(4)
C(20)-C(21)	1.379(4)	C(52)-C(53)	1.386(5)
C(22)-C(23)	1.475(4)	C(53)-C(54)	1.355(5)
C(23)-C(24)	1.389(4)	C(54)-C(55)	1.363(5)
C(23)-C(28)	1.390(4)	C(55)-C(56)	1.396(5)
C(24)-C(25)	1.377(4)	C(57)-C(58)	1.359(19)
C(25)-C(26)	1.347(5)	C(57)-C(57)#1	1.75(3)
C(26)-C(27)	1.369(5)	C(58)-C(59)	1.525(15)

* Symmetry transformations used to generate equivalent atoms: #1 –x + 1, -y + 2, -z.

Table 19. Bond angles [º] for $(Ph_4C_4)P-P(C_4Ph_4)$ **I***

Atoms	Angles	Atoms	Angels
C(22)-P(1)-C(1)	91.16(12)	C(26)-C(27)-C(28)	120.2(4)
C(22)-P(1)-P(2)	108.13(9)	C(23)-C(28)-C(27)	120.7(4)
C(1)-P(1)-P(2)	100.16(9)	C(36)-C(29)-C(30)	126.2(3)
C(29)-P(2)-C(50)	91.26(14)	C(36)-C(29)-P(2)	110.0(2)

Atoms	Angles	Atoms	Angels
C(29)-P(2)-P(1)	106.14(10)	C(30)-C(29)-P(2)	123.6(2)
C(50)-P(2)-P(1)	99.92(10)	C(31)-C(30)-C(35)	117.7(3)
C(8)-C(1)-C(2)	127.2(3)	C(31)-C(30)-C(29)	122.1(3)
C(8)-C(1)-P(1)	110.7(2)	C(35)-C(30)-C(29)	120.2(3)
C(2)-C(1)-P(1)	121.4(2)	C(30)-C(31)-C(32)	120.5(4)
C(7)-C(2)-C(3)	117.3(3)	C(33)-C(32)-C(31)	120.3(4)
C(7)-C(2)-C(1)	122.5(3)	C(34)-C(33)-C(32)	120.4(4)
C(3)-C(2)-C(1)	120.2(3)	C(33)-C(34)-C(35)	119.7(4)
C(4)-C(3)-C(2)	121.4(3)	C(34)-C(35)-C(30)	121.5(3)
C(5)-C(4)-C(3)	120.0(3)	C(29)-C(36)-C(43)	114.0(3)
C(4)-C(5)-C(6)	119.9(3)	C(29)-C(36)-C(37)	122.7(3)
C(5)-C(6)-C(7)	120.3(3)	C(43)-C(36)-C(37)	123.0(3)
C(2)-C(7)-C(6)	121.0(3)	C(42)-C(37)-C(38)	118.3(3)
C(1)-C(8)-C(15)	113.4(2)	C(42)-C(37)-C(36)	119.5(3)
C(1)-C(8)-C(9)	123.3(2)	C(38)-C(37)-C(36)	122.2(3)
C(15)-C(8)-C(9)	123.2(2)	C(37)-C(38)-C(39)	121.5(3)
C(14)-C(9)-C(10)	118.3(3)	C(40)-C(39)-C(38)	119.8(4)
C(14)-C(9)-C(8)	120.8(3)	C(39)-C(40)-C(41)	120.0(4)
C(10)-C(9)-C(8)	120.7(3)	C(40)-C(41)-C(42)	120.3(4)
C(9)-C(10)-C(11)	120.6(3)	C(37)-C(42)-C(41)	120.0(4)
C(12)-C(11)-C(10)	120.4(4)	C(50)-C(43)-C(36)	113.7(3)
C(11)-C(12)-C(13)	119.6(4)	C(50)-C(43)-C(44)	124.8(3)
C(12)-C(13)-C(14)	120.8(4)	C(36)-C(43)-C(44)	121.4(3)
C(9)-C(14)-C(13)	120.3(3)	C(45)-C(44)-C(49)	117.1(3)
C(22)-C(15)-C(8)	114.1(2)	C(45)-C(44)-C(43)	121.9(3)
C(22)-C(15)-C(16)	122.4(2)	C(49)-C(44)-C(43)	121.0(3)
C(8)-C(15)-C(16)	123.2(2)	C(44)-C(45)-C(46)	121.2(4)
C(17)-C(16)-C(21)	117.8(3)	C(47)-C(46)-C(45)	119.8(5)
C(17)-C(16)-C(15)	122.7(3)	C(46)-C(47)-C(48)	119.5(5)
C(21)-C(16)-C(15)	119.5(2)	C(47)-C(48)-C(49)	120.5(5)
C(16)-C(17)-C(18)	121.2(3)	C(44)-C(49)-C(48)	121.7(4)
C(19)-C(18)-C(17)	119.8(3)	C(43)-C(50)-C(51)	128.4(3)
C(18)-C(19)-C(20)	120.6(3)	C(43)-C(50)-P(2)	110.3(2)
C(19)-C(20)-C(21)	119.5(3)	C(51)-C(50)-P(2)	121.2(2)
C(20)-C(21)-C(16)	121.1(3)	C(52)-C(51)-C(56)	117.8(3)
C(15)-C(22)-C(23)	126.7(2)	C(52)-C(51)-C(50)	122.7(3)
C(15)-C(22)-P(1)	109.80(19)	C(56)-C(51)-C(50)	119.5(3)
C(23)-C(22)-P(1)	123.1(2)	C(51)-C(52)-C(53)	121.1(4)
C(24)-C(23)-C(28)	117.1(3)	C(54)-C(53)-C(52)	120.1(4)

Atoms	Angles	Atoms	Angels
C(24)-C(23)-C(22)	121.9(3)	C(53)-C(54)-C(55)	120.5(4)
C(28)-C(23)-C(22)	120.9(3)	C(54)-C(55)-C(56)	120.2(4)
C(25)-C(24)-C(23)	121.2(3)	C(51)-C(56)-C(55)	120.2(4)
C(26)-C(25)-C(24)	121.2(4)	C(58)-C(57)-C(57)#1	110.1(11)
C(25)-C(26)-C(27)	119.6(4)	C(57)-C(58)-C(59)	113.3(12)

* Symmetry transformations used to generate equivalent atoms: #1 –x + 1, -y + 2, -z.

5.2 STRUCTURAL DATA OF [$(Ph_4C_4)_2(C_2H_5)$]B **II**

Table 20. Crystal data and structure refinement for [$(Ph_4C_4)_2(C_2H_5)$]B **II**

Empirical Formula	$C_{62}H_{55}BO$
Formula Weight	826.87
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	$P2_1/n$
Unit Cell Dimensions	a = 15.519(10) Å
	b = 12.240(6) Å
	c = 25.497(16) Å
	$\alpha = 90°$
	$\beta = 95.369(10)°$
	$\gamma = 90°$
Volume	4822(5) $Å^3$
Z	4
Calculated Density	1.139 Mg/m^3
Absorption Coefficient	0.065 mm^{-1}
F(000)	1760
Crystal Size	0.47 x 0.34 x 0.26 mm
Theta Range for Data Collection	2.59 to 23.35°
Limiting Indices	$-17 \leq h \leq 17$
	$0 \leq k \leq 13$
	$0 \leq l \leq 28$
Reflections Collected / Unique	6785 / 6785 [R(int) = 0.0000]
Completeness to Theta	96.70%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data / Restraints / Parameters	6785 / 0 / 569
Goodness-of-fit on F^2	0.84
Final R Indices [I >2sigma(I)]	R1 = 0.0590 wR2 = 0.0812
R Indices (All Data)	R1 = 0.2278 wR2 = 0.1160
Largest Diff. Peak and Hole	0.128 and -0.136 $e^-/Å^3$

Table 21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[(Ph_4C_4)_2(C_2H_5)]B$ **II***

Atom	X	Y	Z	U(eq)
B(1)	4577(3)	7118(4)	1444(2)	47(1)
C(1)	4038(2)	7431(4)	934(2)	50(1)
C(2)	3562(3)	6589(4)	595(2)	51(1)
C(3)	2689(3)	6372(4)	611(2)	63(1)
C(4)	2283(3)	5590(4)	315(2)	83(2)
C(5)	2711(4)	4974(4)	-19(2)	89(2)
C(6)	3573(4)	5146(4)	-52(2)	87(2)
C(7)	3996(3)	5939(4)	256(2)	69(1)
C(8)	3853(3)	8517(4)	881(2)	51(1)
C(9)	3137(3)	8882(3)	472(2)	55(1)
C(10)	2386(3)	9269(4)	630(2)	82(2)
C(11)	1692(4)	9490(4)	259(3)	100(2)
C(12)	1758(5)	9297(5)	-253(3)	116(3)
C(13)	2511(5)	8903(4)	-425(2)	100(2)
C(14)	3200(3)	8683(4)	-54(2)	78(2)
C(15)	4295(3)	9363(4)	1231(2)	54(1)
C(16)	4057(3)	10515(4)	1116(2)	57(1)
C(17)	3569(3)	11085(4)	1439(2)	90(2)
C(18)	3361(4)	12197(5)	1326(3)	129(3)
C(19)	3688(6)	12677(6)	890(4)	146(4)
C(20)	4183(5)	12113(6)	578(3)	121(3)
C(21)	4356(3)	11033(5)	699(2)	87(2)
C(22)	4947(3)	9130(3)	1605(2)	52(1)
C(23)	5405(3)	10058(3)	1895(2)	49(1)
C(24)	6048(3)	10649(4)	1690(2)	67(1)
C(25)	6447(3)	11518(4)	1957(2)	81(2)
C(26)	6196(4)	11825(4)	2437(2)	85(2)
C(27)	5570(3)	11271(4)	2653(2)	79(2)
C(28)	5174(3)	10380(4)	2386(2)	65(1)
C(29)	5294(3)	7951(3)	1688(2)	46(1)
C(30)	6099(3)	7795(3)	1376(2)	50(1)
C(31)	6172(3)	8347(3)	906(2)	59(1)
C(32)	6904(4)	8220(4)	629(2)	67(1)
C(33)	7555(3)	7532(4)	810(2)	65(1)
C(34)	7466(3)	6955(3)	1262(2)	66(1)
C(35)	6743(3)	7076(3)	1537(2)	54(1)
C(36)	5457(2)	7504(3)	2258(2)	46(1)

Atom	X	Y	Z	U(eq)
C(37)	6022(3)	8047(3)	2687(2)	54(1)
C(38)	5795(3)	7994(3)	3202(2)	74(1)
C(39)	6332(4)	8469(4)	3615(2)	97(2)
C(40)	7070(4)	9003(4)	3507(3)	93(2)
C(41)	7282(3)	9071(3)	3017(2)	74(2)
C(42)	6770(3)	8600(3)	2602(2)	61(1)
C(43)	5072(2)	6537(3)	2315(2)	48(1)
C(44)	5238(3)	5760(4)	2767(2)	60(1)
C(45)	6090(3)	5451(3)	2932(2)	68(1)
C(46)	6273(3)	4687(4)	3327(2)	77(2)
C(47)	5603(4)	4213(4)	3557(2)	90(2)
C(48)	4774(4)	4505(4)	3405(2)	88(2)
C(49)	4587(3)	5256(4)	3006(2)	78(2)
C(50)	4411(3)	6202(3)	1847(2)	49(1)
C(51)	3496(3)	6471(4)	1992(2)	53(1)
C(52)	2811(3)	5748(4)	1908(2)	78(2)
C(53)	1977(4)	6045(6)	2008(2)	100(2)
C(54)	1819(4)	7065(7)	2192(2)	106(2)
C(55)	2477(5)	7790(4)	2281(2)	93(2)
C(56)	3317(3)	7487(5)	2184(2)	74(1)
C(57)	4505(3)	5028(3)	1664(2)	60(1)
C(58)	5379(3)	4738(3)	1493(2)	89(2)
O(1)	4336(6)	8357(7)	4899(4)	123(3)
O(1')	4450(11)	7804(14)	5066(8)	234(7)
C(59)	3778(15)	8275(17)	3988(9)	263(9)
C(59')	3834(17)	7400(20)	4270(10)	226(13)
C(60)	4236(18)	7670(20)	4357(12)	191(11)
C(60')	4481(14)	7226(18)	4626(12)	221(11)
C(61)	5032(7)	8125(8)	5353(5)	221(4)
C(62)	4850(9)	9194(12)	5734(6)	153(7)
C(62')	5054(8)	8595(12)	5787(6)	118(5)

* The atoms of O(1), C59), C(60), C(61), C(62) were found disordered with the site occupancy of 0.31. The atoms of O(1’), C(59’), C(60’), C(61’), C(62’) were found disordered with the site occupancy of 0.69. Although some of the atoms of the phenyl rings have a somewhat high thermal factor, no disorder was found. All of the atoms except for the disordered solvent ether O(1), C(59), C(60), C(61), C(62) were anisotropically refined.

Table 22. Bond lengths [Å] for $[(Ph_4C_4)_2(C_2H_5)]B$ **II**

Atoms	Distance	Atoms	Distance
B(1)-C(1)	1.527(5)	C(33)-C(34)	1.368(5)
B(1)-C(29)	1.592(5)	C(34)-C(35)	1.387(5)
B(1)-C(50)	1.559(5)	C(36)-C(43)	1.340(4)
C(1)-C(8)	1.365(5)	C(36)-C(37)	1.494(5)
C(1)-C(2)	1.494(5)	C(37)-C(42)	1.378(5)
C(2)-C(3)	1.386(5)	C(37)-C(38)	1.393(5)
C(2)-C(7)	1.394(5)	C(38)-C(39)	1.406(6)
C(3)-C(4)	1.340(5)	C(39)-C(40)	1.369(6)
C(4)-C(5)	1.356(6)	C(40)-C(41)	1.325(6)
C(5)-C(6)	1.364(6)	C(41)-C(42)	1.387(5)
C(6)-C(7)	1.377(5)	C(43)-C(44)	1.497(5)
C(8)-C(9)	1.518(5)	C(43)-C(50)	1.552(5)
C(8)-C(15)	1.492(5)	C(44)-C(49)	1.376(5)
C(9)-C(10)	1.354(5)	C(44)-C(45)	1.402(5)
C(9)-C(14)	1.376(5)	C(45)-C(46)	1.384(5)
C(10)-C(11)	1.393(6)	C(46)-C(47)	1.369(5)
C(11)-C(12)	1.340(7)	C(47)-C(48)	1.357(6)
C(12)-C(13)	1.372(7)	C(48)-C(49)	1.381(5)
C(13)-C(14)	1.387(6)	C(50)-C(57)	1.522(5)
C(15)-C(22)	1.354(5)	C(50)-C(51)	1.536(5)
C(15)-C(16)	1.479(5)	C(51)-C(56)	1.374(5)
C(16)-C(17)	1.363(6)	C(51)-C(52)	1.384(5)
C(16)-C(21)	1.357(6)	C(52)-C(53)	1.392(6)
C(17)-C(18)	1.422(6)	C(53)-C(54)	1.364(6)
C(18)-C(19)	1.395(8)	C(54)-C(55)	1.356(6)
C(19)-C(20)	1.348(8)	C(55)-C(56)	1.400(6)
C(20)-C(21)	1.378(6)	C(57)-C(58)	1.506(5)
C(22)-C(23)	1.498(5)	O(1)-O(1')	0.809(16)
C(22)-C(29)	1.547(5)	O(1)-C(61)	1.534(16)
C(23)-C(28)	1.392(5)	O(1)-C(60)	1.61(3)
C(23)-C(24)	1.373(5)	O(1')-C(61)	1.176(17)
C(24)-C(25)	1.378(5)	O(1')-C(60')	1.33(2)
C(25)-C(26)	1.372(5)	O(1')-C(60)	1.81(4)
C(26)-C(27)	1.344(5)	C(59)-C(59')	1.29(3)
C(27)-C(28)	1.397(5)	C(59)-C(60)	1.35(3)
C(29)-C(30)	1.556(5)	C(59')-C(60)	0.72(3)
C(29)-C(36)	1.551(5)	C(59')-C(60')	1.31(3)
C(30)-C(35)	1.365(5)	C(60)-C(60')	0.93(3)

Atoms	Distance	Atoms	Distance
C(30)-C(31)	1.388(5)	C(61)-C(62')	1.245(14)
C(31)-C(32)	1.401(5)	C(61)-C(62)	1.670(16)
C(32)-C(33)	1.362(5)	C(62)-C(62')	0.806(17)

Table 23. Bond angles [º] for [$(Ph_4C_4)_2(C_2H_5)$]B **II**

Atoms	Angles	Atoms	Angels
C(1)-B(1)-C(29)	118.7(4)	C(38)-C(37)-C(36)	119.1(4)
C(1)-B(1)-C(50)	129.1(4)	C(39)-C(38)-C(37)	120.1(5)
C(29)-B(1)-C(50)	110.8(4)	C(40)-C(39)-C(38)	119.7(5)
C(8)-C(1)-C(2)	121.8(4)	C(41)-C(40)-C(39)	120.4(6)
C(8)-C(1)-B(1)	114.9(4)	C(40)-C(41)-C(42)	121.2(5)
C(2)-C(1)-B(1)	121.4(4)	C(41)-C(42)-C(37)	121.0(4)
C(3)-C(2)-C(7)	116.1(4)	C(36)-C(43)-C(44)	126.7(4)
C(3)-C(2)-C(1)	123.1(4)	C(36)-C(43)-C(50)	114.8(4)
C(7)-C(2)-C(1)	120.7(4)	C(44)-C(43)-C(50)	118.5(4)
C(4)-C(3)-C(2)	122.0(5)	C(49)-C(44)-C(45)	117.2(4)
C(5)-C(4)-C(3)	121.3(5)	C(49)-C(44)-C(43)	123.1(4)
C(4)-C(5)-C(6)	119.5(5)	C(45)-C(44)-C(43)	119.5(4)
C(5)-C(6)-C(7)	119.5(5)	C(46)-C(45)-C(44)	121.6(5)
C(2)-C(7)-C(6)	121.6(5)	C(47)-C(46)-C(45)	119.1(5)
C(1)-C(8)-C(9)	119.2(4)	C(46)-C(47)-C(48)	120.2(5)
C(1)-C(8)-C(15)	122.4(4)	C(49)-C(48)-C(47)	121.0(5)
C(9)-C(8)-C(15)	118.3(4)	C(48)-C(49)-C(44)	120.8(5)
C(10)-C(9)-C(14)	119.7(5)	C(57)-C(50)-C(51)	113.1(4)
C(10)-C(9)-C(8)	119.5(5)	C(57)-C(50)-C(43)	114.2(3)
C(14)-C(9)-C(8)	120.2(5)	C(51)-C(50)-C(43)	108.6(3)
C(9)-C(10)-C(11)	119.8(5)	C(57)-C(50)-B(1)	116.8(3)
C(12)-C(11)-C(10)	120.3(6)	C(51)-C(50)-B(1)	102.6(3)
C(11)-C(12)-C(13)	121.2(7)	C(43)-C(50)-B(1)	100.3(3)
C(12)-C(13)-C(14)	118.4(6)	C(56)-C(51)-C(52)	117.1(5)
C(9)-C(14)-C(13)	120.6(5)	C(56)-C(51)-C(50)	120.1(4)
C(22)-C(15)-C(16)	119.8(4)	C(52)-C(51)-C(50)	122.7(5)
C(22)-C(15)-C(8)	123.1(4)	C(53)-C(52)-C(51)	121.2(5)
C(16)-C(15)-C(8)	116.7(4)	C(54)-C(53)-C(52)	120.2(6)
C(17)-C(16)-C(21)	119.0(5)	C(53)-C(54)-C(55)	119.9(6)
C(17)-C(16)-C(15)	120.6(5)	C(54)-C(55)-C(56)	119.8(5)

Atoms	Angles	Atoms	Angels
C(21)-C(16)-C(15)	120.3(5)	C(51)-C(56)-C(55)	121.7(5)
C(16)-C(17)-C(18)	119.8(6)	C(50)-C(57)-C(58)	115.2(3)
C(19)-C(18)-C(17)	118.1(7)	O(1')-O(1)-C(61)	49.1(16)
C(18)-C(19)-C(20)	121.8(8)	O(1')-O(1)-C(60)	91(2)
C(19)-C(20)-C(21)	117.9(8)	C(61)-O(1)-C(60)	123.7(14)
C(16)-C(21)-C(20)	123.4(6)	O(1)-O(1')-C(61)	100(2)
C(15)-C(22)-C(23)	118.4(4)	O(1)-O(1')-C(60')	91(2)
C(15)-C(22)-C(29)	121.4(4)	C(61)-O(1')-C(60')	128(2)
C(23)-C(22)-C(29)	119.8(3)	O(1)-O(1')-C(60)	62.7(17)
C(28)-C(23)-C(24)	116.7(4)	C(61)-O(1')-C(60)	135.2(16)
C(28)-C(23)-C(22)	120.5(4)	C(60')-O(1')-C(60)	29.6(13)
C(24)-C(23)-C(22)	122.8(4)	C(59')-C(59)-C(60)	31.7(15)
C(23)-C(24)-C(25)	121.9(4)	C(60)-C(59')-C(59)	79(4)
C(26)-C(25)-C(24)	120.1(5)	C(60)-C(59')-C(60')	44(3)
C(25)-C(26)-C(27)	120.1(5)	C(59)-C(59')-C(60')	122(3)
C(26)-C(27)-C(28)	119.8(5)	C(59')-C(60)-C(60')	104(5)
C(23)-C(28)-C(27)	121.3(4)	C(59')-C(60)-C(59)	70(4)
C(22)-C(29)-C(30)	109.3(3)	C(60')-C(60)-C(59)	172(4)
C(22)-C(29)-C(36)	118.8(3)	C(59')-C(60)-O(1')	115(4)
C(30)-C(29)-C(36)	111.6(3)	C(60')-C(60)-O(1')	45(2)
C(22)-C(29)-B(1)	108.8(3)	C(59)-C(60)-O(1')	133(2)
C(30)-C(29)-B(1)	106.7(3)	C(59')-C(60)-O(1)	121(4)
C(36)-C(29)-B(1)	100.8(3)	C(60')-C(60)-O(1)	71(3)
C(35)-C(30)-C(31)	117.2(4)	C(59)-C(60)-O(1)	108(2)
C(35)-C(30)-C(29)	121.7(4)	O(1')-C(60)-O(1)	26.5(8)
C(31)-C(30)-C(29)	121.1(4)	C(60)-C(60')-O(1')	105(3)
C(32)-C(31)-C(30)	121.1(4)	C(60)-C(60')-C(59')	33(2)
C(33)-C(32)-C(31)	120.5(4)	O(1')-C(60')-C(59')	114(2)
C(32)-C(33)-C(34)	118.4(5)	O(1')-C(61)-C(62')	131.6(17)
C(33)-C(34)-C(35)	121.4(4)	O(1')-C(61)-O(1)	31.4(9)
C(30)-C(35)-C(34)	121.3(4)	C(62')-C(61)-O(1)	122.9(11)
C(43)-C(36)-C(37)	123.5(4)	O(1')-C(61)-C(62)	117.5(14)
C(43)-C(36)-C(29)	112.2(4)	C(62')-C(61)-C(62)	27.5(8)
C(37)-C(36)-C(29)	124.2(4)	O(1)-C(61)-C(62)	98.5(8)
C(42)-C(37)-C(38)	117.6(4)	C(62')-C(62)-C(61)	45.4(15)
C(42)-C(37)-C(36)	123.3(4)	C(62)-C(62')-C(61)	107(2)

5.3 STRUCTURAL DATA OF $(C_6Me_5)_3Ga$ **III**

Table 24. Crystal data and structure refinement for $(C_6Me_5)_3Ga$ **III**

Empirical Formula	$C_{33}H_{45}Ga$
Formula Weight	511.41
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 9.0026(9) Å
	b = 10.7131(10) Å
	c = 16.0657(16) Å
	$\alpha = 107.626(3)°$
	$\beta = 97.630(3)°$
	$\gamma = 90.080(3)°$
Volume	1462.2(2) $Å^3$
Z	2
Calculated Density	1.162 Mg/m^3
Absorption Coefficient	0.958 mm^{-1}
F(000)	548
Crystal Size	0.43 x 0.36 x 0.33 mm
Theta Range for Data Collection	2.00 to 28.33°
Limiting Indices	$-11 \leq h \leq 11$
	$-14 \leq k \leq 13$
	$-21 \leq l \leq 21$
Reflections Collected / Unique	10369 / 6687 [R(int) = 0.0290]
Completeness to Theta	91.80%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data / Restraints / Parameters	6687 / 0 / 322
Goodness-of-fit on F^2	0.856
Final R Indices [I >2sigma(I)]	R1 = 0.0496 wR2 = 0.1100
R Indices (All Data)	R1 = 0.0728 wR2 = 0.1145
Largest Diff. Peak and Hole	0.900 and -0.284 $e^-/Å^3$

Table 25. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $(C_6Me_5)_3Ga$ **III**

Atom	X	Y	Z	U(eq)
Ga(1)	7540(1)	3074(1)	2156(1)	43(1)
C(1)	6580(3)	3059(3)	974(2)	44(1)
C(2)	5269(3)	2274(3)	581(2)	47(1)
C(3)	4561(3)	2269(3)	-244(2)	55(1)
C(4)	5189(4)	2992(3)	-706(2)	56(1)
C(5)	6490(4)	3778(3)	-326(2)	53(1)
C(6)	7162(3)	3829(3)	522(2)	47(1)
C(7M)	4611(4)	1463(3)	1074(2)	64(1)
C(8M)	3077(4)	1505(4)	-612(2)	83(1)
C(9M)	4490(5)	2942(4)	-1628(2)	88(1)
C(10M)	7154(4)	4593(4)	-819(2)	77(1)
C(11M)	8539(4)	4700(3)	943(2)	66(1)
C(12)	7598(3)	4654(3)	3202(2)	42(1)
C(13)	6272(3)	5149(3)	3503(2)	49(1)
C(14)	6318(4)	6196(3)	4288(2)	58(1)
C(15)	7688(4)	6753(3)	4758(2)	57(1)
C(16)	9016(4)	6294(3)	4451(2)	52(1)
C(17)	8973(3)	5232(3)	3672(2)	46(1)
C(18M)	4776(3)	4543(3)	2998(2)	65(1)
C(19M)	4845(5)	6690(4)	4607(2)	96(1)
C(20M)	7714(5)	7889(3)	5603(2)	88(1)
C(21M)	10514(4)	6918(3)	4937(2)	74(1)
C(22M)	10422(3)	4716(3)	3351(2)	58(1)
C(23)	8468(3)	1479(3)	2335(2)	43(1)
C(24)	9665(3)	947(3)	1900(2)	48(1)
C(25)	10373(4)	-150(3)	2060(2)	60(1)
C(26)	9848(4)	-710(3)	2644(2)	62(1)
C(27)	8631(4)	-202(3)	3073(2)	56(1)
C(28)	7942(3)	882(3)	2915(2)	48(1)
C(29M)	10202(4)	1567(3)	1258(2)	71(1)
C(30M)	11670(5)	-709(4)	1584(3)	103(2)
C(31M)	10615(5)	-1883(4)	2825(3)	103(2)
C(32M)	8051(5)	-823(4)	3705(2)	86(1)
C(33M)	6590(4)	1405(3)	3354(2)	64(1)

Table 26. Bond lengths [Å] for $(C_6Me_5)_3Ga$ **III**

Atoms	Distance	Atoms	Distance
Ga(1)-C(1)	1.974(3)	C(25)-C(26)	1.388(5)
Ga(1)-C(23)	1.984(3)	C(25)-C(30M)	1.506(5)
Ga(1)-C(12)	1.986(3)	C(26)-C(27)	1.395(5)
C(1)-C(6)	1.394(4)	C(26)-C(31M)	1.520(5)
C(1)-C(2)	1.406(4)	C(27)-C(28)	1.390(4)
C(6)-C(5)	1.400(4)	C(27)-C(32M)	1.515(4)
C(6)-C(11M)	1.503(4)	C(28)-C(33M)	1.511(4)
C(5)-C(4)	1.396(4)	C(12)-C(13)	1.393(4)
C(5)-C(10M)	1.515(4)	C(12)-C(17)	1.397(4)
C(4)-C(3)	1.388(4)	C(17)-C(16)	1.410(4)
C(4)-C(9M)	1.516(4)	C(17)-C(22M)	1.510(4)
C(3)-C(2)	1.391(4)	C(16)-C(15)	1.388(4)
C(3)-C(8M)	1.516(4)	C(16)-C(21M)	1.509(4)
C(2)-C(7M)	1.508(4)	C(15)-C(14)	1.388(5)
C(23)-C(24)	1.390(4)	C(15)-C(20M)	1.521(4)
C(23)-C(28)	1.408(4)	C(14)-C(13)	1.407(4)
C(24)-C(25)	1.412(4)	C(14)-C(19M)	1.523(4)
C(24)-C(29M)	1.512(4)	C(13)-C(18M)	1.510(4)

Table 27. Bond angles [º] for $(C_6Me_5)_3Ga$ **III**

Atoms	Angles	Atoms	Angels
C(1)-Ga(1)-C(23)	120.36(11)	C(24)-C(25)-C(30M)	119.8(3)
C(1)-Ga(1)-C(12)	121.91(11)	C(25)-C(26)-C(27)	120.7(3)
C(23)-Ga(1)-C(12)	117.73(11)	C(25)-C(26)-C(31M)	119.6(3)
C(6)-C(1)-C(2)	118.9(3)	C(27)-C(26)-C(31M)	119.7(3)
C(6)-C(1)-Ga(1)	121.4(2)	C(28)-C(27)-C(26)	119.7(3)
C(2)-C(1)-Ga(1)	119.7(2)	C(28)-C(27)-C(32M)	119.8(3)
C(1)-C(6)-C(5)	120.6(3)	C(26)-C(27)-C(32M)	120.5(3)
C(1)-C(6)-C(11M)	119.6(3)	C(27)-C(28)-C(23)	120.7(3)
C(5)-C(6)-C(11M)	119.8(3)	C(27)-C(28)-C(33M)	119.7(3)
C(4)-C(5)-C(6)	119.6(3)	C(23)-C(28)-C(33M)	119.5(3)
C(4)-C(5)-C(10M)	120.2(3)	C(13)-C(12)-C(17)	119.4(2)
C(6)-C(5)-C(10M)	120.1(3)	C(13)-C(12)-Ga(1)	120.3(2)
C(3)-C(4)-C(5)	120.2(3)	C(17)-C(12)-Ga(1)	120.2(2)

Atoms	Angles	Atoms	Angels
C(3)-C(4)-C(9M)	121.1(3)	C(12)-C(17)-C(16)	120.2(3)
C(5)-C(4)-C(9M)	118.7(3)	C(12)-C(17)-C(22M)	120.2(2)
C(4)-C(3)-C(2)	120.0(3)	C(16)-C(17)-C(22M)	119.6(3)
C(4)-C(3)-C(8M)	120.9(3)	C(15)-C(16)-C(17)	119.8(3)
C(2)-C(3)-C(8M)	119.1(3)	C(15)-C(16)-C(21M)	121.0(3)
C(3)-C(2)-C(1)	120.6(3)	C(17)-C(16)-C(21M)	119.2(3)
C(3)-C(2)-C(7M)	120.1(3)	C(14)-C(15)-C(16)	120.2(3)
C(1)-C(2)-C(7M)	119.3(3)	C(14)-C(15)-C(20M)	119.2(3)
C(24)-C(23)-C(28)	119.0(3)	C(16)-C(15)-C(20M)	120.5(3)
C(24)-C(23)-Ga(1)	120.5(2)	C(15)-C(14)-C(13)	120.0(3)
C(28)-C(23)-Ga(1)	120.5(2)	C(15)-C(14)-C(19M)	121.2(3)
C(23)-C(24)-C(25)	120.6(3)	C(13)-C(14)-C(19M)	118.8(3)
C(23)-C(24)-C(29M)	118.9(3)	C(12)-C(13)-C(14)	120.3(3)
C(25)-C(24)-C(29M)	120.5(3)	C(12)-C(13)-C(18M)	120.1(3)
C(26)-C(25)-C(24)	119.4(3)	C(14)-C(13)-C(18M)	119.6(3)
C(26)-C(25)-C(30M)	120.8(3)		

5.4 STRUCTURAL DATA OF $(C_6Me_5)_3Al$ **IV**

Table 28. Crystal data and structural refinement for $(C_6Me_5)_3Al$ **IV**

Empirical Formula	$C_{33}H_{45}Ga$
Formula Weight	511.41
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 9.0026(9) Å
	b = 10.7131(10) Å
	c = 16.0657(16) Å
	α = 107.626(3)°
	β = 97.630(3)°
	γ = 90.080(3)°
Volume	1462.2(2) Å^3
Z	2
Calculated Density	1.162 Mg/m^3
Absorption Coefficient	0.958 mm^{-1}
F(000)	548
Crystal Size	0.43 x 0.36 x 0.33 mm
Theta Range for Data Collection	2.00 to 28.33°
Limiting Indices	$-11 \leq h \leq 11$
	$-14 \leq k \leq 13$
	$-21 \leq l \leq 21$
Reflections Collected / Unique	10369 / 6687 [R(int) = 0.0290]
Completeness to Theta	91.80%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data / Restraints / Parameters	6687 / 0 / 322
Goodness-of-fit on F^2	0.856
Final R Indices [I >2sigma(I)]	R1 = 0.0496 wR2 = 0.1100
R Indices (All Data)	R1 = 0.0728 wR2 = 0.1145
Largest Diff. Peak and Hole	0.255 and -0.202 e$^-$/Å^3

Table 29. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $(C_6Me_5)_3Al$ **IV**

Atom	X	Y	Z	U(eq)
Ga(1)	7540(1)	3074(1)	2156(1)	43(1)
C(1)	6580(3)	3059(3)	974(2)	44(1)
C(2)	5269(3)	2274(3)	581(2)	47(1)
C(3)	4561(3)	2269(3)	-244(2)	55(1)
C(4)	5189(4)	2992(3)	-706(2)	56(1)
C(5)	6490(4)	3778(3)	-326(2)	53(1)
C(6)	7162(3)	3829(3)	522(2)	47(1)
C(7M)	4611(4)	1463(3)	1074(2)	64(1)
C(8M)	3077(4)	1505(4)	-612(2)	83(1)
C(9M)	4490(5)	2942(4)	-1628(2)	88(1)
C(10M)	7154(4)	4593(4)	-819(2)	77(1)
C(11M)	8539(4)	4700(3)	943(2)	66(1)
C(12)	7598(3)	4654(3)	3202(2)	42(1)
C(13)	6272(3)	5149(3)	3503(2)	49(1)
C(14)	6318(4)	6196(3)	4288(2)	58(1)
C(15)	7688(4)	6753(3)	4758(2)	57(1)
C(16)	9016(4)	6294(3)	4451(2)	52(1)
C(17)	8973(3)	5232(3)	3672(2)	46(1)
C(18M)	4776(3)	4543(3)	2998(2)	65(1)
C(19M)	4845(5)	6690(4)	4607(2)	96(1)
C(20M)	7714(5)	7889(3)	5603(2)	88(1)
C(21M)	10514(4)	6918(3)	4937(2)	74(1)
C(22M)	10422(3)	4716(3)	3351(2)	58(1)
C(23)	8468(3)	1479(3)	2335(2)	43(1)
C(24)	9665(3)	947(3)	1900(2)	48(1)
C(25)	10373(4)	-150(3)	2060(2)	60(1)
C(26)	9848(4)	-710(3)	2644(2)	62(1)
C(27)	8631(4)	-202(3)	3073(2)	56(1)
C(28)	7942(3)	882(3)	2915(2)	48(1)
C(29M)	10202(4)	1567(3)	1258(2)	71(1)
C(30M)	11670(5)	-709(4)	1584(3)	103(2)
C(31M)	10615(5)	-1883(4)	2825(3)	103(2)
C(32M)	8051(5)	-823(4)	3705(2)	86(1)
C(33M)	6590(4)	1405(3)	3354(2)	64(1)

Table 30. Bond lengths [Å] for $(C_6Me_5)_3Al$ **IV**

Atoms	Distance	Atoms	Distance
Ga(1)-C(1)	1.974(3)	C(25)-C(26)	1.388(5)
Ga(1)-C(23)	1.984(3)	C(25)-C(30M)	1.506(5)
Ga(1)-C(12)	1.986(3)	C(26)-C(27)	1.395(5)
C(1)-C(6)	1.394(4)	C(26)-C(31M)	1.520(5)
C(1)-C(2)	1.406(4)	C(27)-C(28)	1.390(4)
C(6)-C(5)	1.400(4)	C(27)-C(32M)	1.515(4)
C(6)-C(11M)	1.503(4)	C(28)-C(33M)	1.511(4)
C(5)-C(4)	1.396(4)	C(12)-C(13)	1.393(4)
C(5)-C(10M)	1.515(4)	C(12)-C(17)	1.397(4)
C(4)-C(3)	1.388(4)	C(17)-C(16)	1.410(4)
C(4)-C(9M)	1.516(4)	C(17)-C(22M)	1.510(4)
C(3)-C(2)	1.391(4)	C(16)-C(15)	1.388(4)
C(3)-C(8M)	1.516(4)	C(16)-C(21M)	1.509(4)
C(2)-C(7M)	1.508(4)	C(15)-C(14)	1.388(5)
C(23)-C(24)	1.390(4)	C(15)-C(20M)	1.521(4)
C(23)-C(28)	1.408(4)	C(14)-C(13)	1.407(4)
C(24)-C(25)	1.412(4)	C(14)-C(19M)	1.523(4)
C(24)-C(29M)	1.512(4)	C(13)-C(18M)	1.510(4)

Table 31. Bond angles [º] for $(C_6Me_5)_3Al$ **IV**

Atoms	Angles	Atoms	Angels
C(1)-Ga(1)-C(23)	120.36(11)	C(24)-C(25)-C(30M)	119.8(3)
C(1)-Ga(1)-C(12)	121.91(11)	C(25)-C(26)-C(27)	120.7(3)
C(23)-Ga(1)-C(12)	117.73(11)	C(25)-C(26)-C(31M)	119.6(3)
C(6)-C(1)-C(2)	118.9(3)	C(27)-C(26)-C(31M)	119.7(3)
C(6)-C(1)-Ga(1)	121.4(2)	C(28)-C(27)-C(26)	119.7(3)
C(2)-C(1)-Ga(1)	119.7(2)	C(28)-C(27)-C(32M)	119.8(3)
C(1)-C(6)-C(5)	120.6(3)	C(26)-C(27)-C(32M)	120.5(3)
C(1)-C(6)-C(11M)	119.6(3)	C(27)-C(28)-C(23)	120.7(3)
C(5)-C(6)-C(11M)	119.8(3)	C(27)-C(28)-C(33M)	119.7(3)
C(4)-C(5)-C(6)	119.6(3)	C(23)-C(28)-C(33M)	119.5(3)
C(4)-C(5)-C(10M)	120.2(3)	C(13)-C(12)-C(17)	119.4(2)
C(6)-C(5)-C(10M)	120.1(3)	C(13)-C(12)-Ga(1)	120.3(2)
C(3)-C(4)-C(5)	120.2(3)	C(17)-C(12)-Ga(1)	120.2(2)

Atoms	Angles	Atoms	Angels
C(3)-C(4)-C(9M)	121.1(3)	C(12)-C(17)-C(16)	120.2(3)
C(5)-C(4)-C(9M)	118.7(3)	C(12)-C(17)-C(22M)	120.2(2)
C(4)-C(3)-C(2)	120.0(3)	C(16)-C(17)-C(22M)	119.6(3)
C(4)-C(3)-C(8M)	120.9(3)	C(15)-C(16)-C(17)	119.8(3)
C(2)-C(3)-C(8M)	119.1(3)	C(15)-C(16)-C(21M)	121.0(3)
C(3)-C(2)-C(1)	120.6(3)	C(17)-C(16)-C(21M)	119.2(3)
C(3)-C(2)-C(7M)	120.1(3)	C(14)-C(15)-C(16)	120.2(3)
C(1)-C(2)-C(7M)	119.3(3)	C(14)-C(15)-C(20M)	119.2(3)
C(24)-C(23)-C(28)	119.0(3)	C(16)-C(15)-C(20M)	120.5(3)
C(24)-C(23)-Ga(1)	120.5(2)	C(15)-C(14)-C(13)	120.0(3)
C(28)-C(23)-Ga(1)	120.5(2)	C(15)-C(14)-C(19M)	121.2(3)
C(23)-C(24)-C(25)	120.6(3)	C(13)-C(14)-C(19M)	118.8(3)
C(23)-C(24)-C(29M)	118.9(3)	C(12)-C(13)-C(14)	120.3(3)
C(25)-C(24)-C(29M)	120.5(3)	C(12)-C(13)-C(18M)	120.1(3)
C(26)-C(25)-C(24)	119.4(3)	C(14)-C(13)-C(18M)	119.6(3)
C(26)-C(25)-C(30M)	120.8(3)		

5.5 STRUCTURAL DATA OF $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V**

Table 32. Crystal data and structure refinement for $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V**

Empirical Formula	$C_{38}H_{70}AlLiO_3$
Formula Weight	608.86
Collection Temperature	293(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	C2/*c*
Unit Cell Dimensions	a = 14.1980(19) Å b = 19.537(2) Å c = 15.8996(19) Å α = 90 deg β = 109.701(2) deg γ = 90 deg
Volume	4152.2(9) $Å^3$
Z	4
Calculated Density	0.974 g/cm^3
Absorption Coefficient	0.078 mm^{-1}
F(000)	1352
Crystal Size	0.40 x 0.57 x 0.62 mm
Theta Range for Data Collection	1.85 to 28.27 deg.
Limiting Indices	$-18 \leq h \leq 18$ $-24 \leq k \leq 25$ $-21 \leq l \leq 21$
Reflections Collected/Unique	15145/4970 [R(int) = 0.0397]
Completeness to Theta	96.70%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	4970/0/213
Goodness-of-fit on F^2	0.969
Final R Indices [I >2sigma(I)]	R1 = 0.1056 wR2 = 0.2889
R Indices (All Data)	R1 = 0.2433 wR2 = 0.3763
Largest Diff. Peak and Hole	0.532 and -0.303 $e^-/Å^3$

Table 33. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V**

Atom	X	Y	Z	U(eq)
Al(1)	5000	3273(1)	2500	93(1)
C(1)	3761(3)	3909(2)	2242(3)	86(1)
C(2)	3684(4)	4311(2)	2959(3)	98(1)
C(3)	2858(5)	4725(2)	2862(4)	122(2)
C(4)	2108(5)	4782(2)	2050(5)	130(2)
C(5)	2159(4)	4407(3)	1308(4)	118(2)
C(6)	2976(3)	3970(2)	1425(3)	95(1)
C(7)	4503(4)	4293(2)	3849(3)	127(2)
C(8)	2771(5)	5118(3)	3655(5)	184(3)
C(9)	1182(5)	5253(3)	1895(6)	204(3)
C(10)	1343(4)	4468(4)	377(4)	170(2)
C(11)	2995(4)	3538(3)	629(3)	125(2)
C(12)	5127(5)	2621(3)	1562(4)	159(2)
C(13)	4475(10)	2041(6)	1351(7)	318(7)
C(14)	9112(15)	844(6)	1675(16)	480(20)
C(15)	9052(15)	3299(9)	1069(15)	349(9)
C(16)	8749(14)	1186(7)	1228(10)	344(11)
C(17)	8968(13)	2324(13)	3738(10)	388(13)
C(18)	8409(14)	3251(10)	1457(17)	403(15)
C(19)	8292(9)	2403(9)	3094(14)	427(17)
Li(1)	10000	2225(4)	2500	112(3)
O(1)	10000	1255(3)	2500	157(2)
O(2)	8822(5)	2709(3)	2296(5)	189(3)
O(3)	9942(12)	2738(6)	1485(10)	165(5)

Table 34. Bond lengths [Å] for $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V***

Atoms	Distance	Atoms	Distance
Al(1)-C(12)	2.016(5)	C(14)-C(16)	0.99(3)
Al(1)-C(12)#1	2.016(5)	C(14)-O(1)	1.69(2)
Al(1)-C(1)#1	2.078(4)	C(15)-C(18)	1.27(2)
Al(1)-C(1)	2.078(4)	C(15)-O(3)	1.64(2)
C(1)-C(6)	1.402(5)	C(17)-C(19)	1.15(2)

Atoms	Distance	Atoms	Distance
C(1)-C(2)	1.418(5)	C(17)-O(3)#2	1.88(2)
C(2)-C(3)	1.390(7)	C(18)-O(2)	1.65(2)
C(2)-C(7)	1.499(6)	C(19)-O(2)	1.78(2)
C(3)-C(4)	1.374(7)	Li(1)-O(2)#2	1.852(8)
C(3)-C(8)	1.515(7)	Li(1)-O(2)	1.852(8)
C(4)-C(5)	1.411(7)	Li(1)-O(3)#2	1.878(14)
C(4)-C(9)	1.554(8)	Li(1)-O(3)	1.878(14)
C(5)-C(6)	1.402(6)	Li(1)-O(1)	1.895(11)
C(5)-C(10)	1.546(7)	O(1)-C(14)#2	1.69(2)
C(6)-C(11)	1.528(6)	O(3)-C(17)#2	1.88(2)
C(12)-C(13)	1.430(12)		

* Symmetry transformations used to generate equivalent atoms: #1 –x + 1, y, -z + ½, #2 –x + 2, y, -z + ½

Table 35. Bond angles [º] for $[Li(Et_2O)_3][(C_6Me_5)_2AlEt_2]$ **V***

Atoms	Angles	Atoms	Angels
C(12)-Al(1)-C(12)#1	101.6(4)	C(16)-C(14)-O(1)	108.1(12)
C(12)-Al(1)-C(1)#1	104.0(2)	C(18)-C(15)-O(3)	109.8(16)
C(12)#1-Al(1)-C(1)#1	120.84(19)	C(19)-C(17)-O(3)#2	105.4(16)
C(12)-Al(1)-C(1)	120.84(19)	C(15)-C(18)-O(2)	108.9(14)
C(12)#1-Al(1)-C(1)	104.0(2)	C(17)-C(19)-O(2)	104.7(12)
C(1)#1-Al(1)-C(1)	106.6(2)	O(2)#2-Li(1)-O(2)	118.6(6)
C(6)-C(1)-C(2)	116.4(4)	O(2)#2-Li(1)-O(3)#2	78.6(6)
C(6)-C(1)-Al(1)	126.1(3)	O(2)-Li(1)-O(3)#2	69.7(5)
C(2)-C(1)-Al(1)	117.5(3)	O(2)#2-Li(1)-O(3)	69.7(5)
C(3)-C(2)-C(1)	121.6(4)	O(2)-Li(1)-O(3)	78.6(6)
C(3)-C(2)-C(7)	118.4(4)	O(3)#2-Li(1)-O(3)	115.5(9)
C(1)-C(2)-C(7)	120.0(4)	O(2)#2-Li(1)-O(1)	120.7(3)
C(4)-C(3)-C(2)	120.6(5)	O(2)-Li(1)-O(1)	120.7(3)
C(4)-C(3)-C(8)	119.1(6)	O(3)#2-Li(1)-O(1)	122.2(4)
C(2)-C(3)-C(8)	120.3(6)	O(3)-Li(1)-O(1)	122.2(4)
C(3)-C(4)-C(5)	120.1(5)	C(14)-O(1)-C(14)#2	123.1(12)
C(3)-C(4)-C(9)	122.9(6)	C(14)-O(1)-Li(1)	118.5(6)
C(5)-C(4)-C(9)	117.0(6)	C(14)#2-O(1)-Li(1)	118.5(6)
C(6)-C(5)-C(4)	118.6(5)	C(18)-O(2)-C(19)	132.2(8)
C(6)-C(5)-C(10)	119.6(5)	C(18)-O(2)-Li(1)	121.6(7)

Atoms	Angles	Atoms	Angels
C(4)-C(5)-C(10)	121.8(5)	C(19)-O(2)-Li(1)	106.1(7)
C(1)-C(6)-C(5)	122.6(4)	C(15)-O(3)-Li(1)	120.6(11)
C(1)-C(6)-C(11)	119.4(4)	C(15)-O(3)-C(17)#2	141.6(13)
C(5)-C(6)-C(11)	118.1(4)	Li(1)-O(3)-C(17)#2	97.6(9)
C(13)-C(12)-Al(1)	117.5(7)		

* Symmetry transformations used to generate equivalent atoms: #1 –x + 1, y, -z + ½, #2 –x + 2, y, -z + ½

5.6 STRUCTURAL DATA OF $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ **VI**

Table 36. Crystal data and structure refinement for $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ **VI**

Empirical Formula	$C_{56}H_{110}AlBr_2Cl_3Mg_3O_7$
Formula Weight	1261.52
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	$P2_1/m$
Unit Cell Dimensions	a = 11.528(2) Å
	b = 19.322(4) Å
	c = 15.494(3) Å
	α = 90°
	β = 101.257(4)°
	γ = 90°
Volume	3384.7(11) $Å^3$
Z	2
Calculated Density	1.238 g/cm^3
Absorption Coefficient	1.400 mm^{-1}
F(000)	1344
Crystal Size	0.36 x 0.27 x 0.12 mm
Theta Range for Data Collection	1.70 to 23.26°
Limiting Indices	$-12 \le h \le 12$
	$-21 \le k \le 20$
	$-17 \le l \le 17$
Reflections Collected/Unique	14807/5023 [R(int) = 0.0658]
Completeness to Theta	99.80%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	5023/0/370
Goodness-of-fit on F^2	1.019
Final R Indices [I >2sigma(I)]	R1 = 0.0709 wR2 = 0.1771
R Indices (All Data)	R1 = 0.1306 wR2 = 0.2088
Largest Diff. Peak and Hole	0.919 and -0.609 $e^-/Å^3$

Table 37. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ **VI***

Atom	X	Y	Z	U(eq)
Al(1)	9042(2)	2500	2889(2)	44(1)
Br(1)	9248(1)	2500	7352(1)	71(1)
Br(2)	9569(1)	2500	4492(1)	69(1)
C(1)	10659(9)	2500	2538(7)	52(3)
C(2)	11387(8)	1855(7)	2864(9)	128(5)
C(3)	12607(10)	1871(9)	2588(12)	151(8)
C(4)	12430(10)	1889(7)	1616(11)	125(5)
C(5)	11771(13)	2500	1275(11)	105(6)
C(6)	10538(11)	2500	1540(8)	83(4)
C(7)	13279(13)	2500	2963(14)	191(16)
C(8)	8075(6)	1615(4)	2600(5)	51(2)
C(9)	8768(11)	976(5)	2906(12)	177(8)
C(10)	6992(10)	1613(6)	2994(9)	130(5)
C(11)	7611(12)	1529(6)	1635(7)	117(5)
C(12)	8034(14)	270(7)	2558(13)	139(6)
C(13)	6353(14)	876(11)	2915(15)	167(9)
C(14)	6726(17)	875(7)	1454(9)	133(5)
C(15)	7220(30)	307(8)	3155(11)	198(11)
C(16)	5838(10)	884(7)	1940(16)	145(7)
C(17)	7546(12)	324(8)	1679(11)	130(5)
C(18A)	4480(40)	1962(16)	9200(30)	102(15)
C(18B)	3420(30)	1980(12)	8640(20)	130(12)
C(19)	3690(20)	1537(9)	9345(13)	196(9)
C(20A)	3250(40)	1983(16)	5700(30)	154(18)
C(20B)	2640(20)	1926(12)	6430(30)	116(18)
C(21)	2413(13)	1511(9)	5830(14)	187(9)
C(22)	9447(8)	836(6)	8507(7)	97(4)
C(23)	10230(11)	1191(9)	9228(8)	163(7)
C(24)	7670(9)	783(5)	9120(6)	80(3)
C(25)	7391(12)	41(6)	9115(7)	118(4)
C(26)	7397(9)	240(5)	6548(7)	82(3)
C(27)	6478(11)	5(7)	5829(7)	120(4)
C(28)	8321(7)	1095(5)	5783(5)	66(2)
C(29)	9413(8)	706(7)	5791(7)	112(4)
C(30)	6309(10)	2500	5788(8)	61(3)
C(31)	5553(15)	2022(9)	5257(12)	69(5)
Cl(1)	7010(2)	2500	8662(2)	46(1)

Atom	X	Y	Z	U(eq)
Cl(2)	5301(1)	1177(1)	7410(1)	57(1)
Mg(1)	5040(3)	2500	7413(3)	51(1)
Mg(2)	7391(2)	1684(1)	7417(2)	43(1)
O(1)	4103(8)	2500	8461(7)	80(3)
O(2)	3468(6)	2500	6501(7)	75(3)
O(3)	8232(4)	1014(3)	8417(3)	56(1)
O(4)	7750(4)	954(3)	6507(3)	53(1)
O(5)	6445(5)	2500	6709(5)	41(2)

* A measure of disorder was observed on the ether groups in the cation of **VI**. Carbon atom C18 was disordered over two sites with occupancies of 61% and 39%. Carbon atom C20 was disordered over two sites with occupancies of 51% and 49%. In addition, bromine atom Br1 was disorderd over both chlorine atoms (Cl2 and Cl2A) in the cluster and therefore the occupancies of these three atoms were refined to reflect this. Finally, carbon atom C31 was disorderd (over two sites) and refined with 50% occupancy.

Table 38. Bond lengths [Å] for $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ **VI***

Atoms	Distance	Atoms	Distance
Br(2)-Al(1)	2.439(3)	C(1)-C(2)	1.532(11)
Br(1)-Mg(2)	2.676(2)	C(1)-C(2)#1	1.532(11)
Br(1)-Mg(2)#1	2.676(2)	C(2)-C(3)	1.548(13)
Cl(2)-Mg(1)	2.5733(14)	C(3)-C(4)	1.479(19)
Cl(2)-Mg(2)	2.599(2)	C(3)-C(7)	1.497(19)
Cl(1)-Mg(2)	2.595(3)	C(4)-C(5)	1.446(15)
Cl(1)-Mg(2)#1	2.595(3)	C(5)-C(4)#1	1.446(15)
Cl(1)-Mg(1)	2.681(4)	C(5)-C(6)	1.555(17)
Al(1)-C(1)	2.041(10)	C(7)-C(3)#1	1.497(19)
Al(1)-C(8)	2.042(8)	C(8)-C(10)	1.494(12)
Al(1)-C(8)#1	2.042(8)	C(8)-C(11)	1.495(12)
Mg(1)-O(2)	2.069(9)	C(8)-C(9)	1.497(13)
Mg(1)-O(1)	2.118(9)	C(9)-C(12)	1.639(17)
Mg(1)-O(5)	2.122(7)	C(10)-C(13)	1.596(18)
Mg(1)-Cl(2)#1	2.5733(14)	C(11)-C(14)	1.614(16)
Mg(1)-Mg(2)#1	3.135(3)	C(12)-C(17)	1.371(18)
Mg(2)-O(4)	2.091(6)	C(12)-C(15)	1.45(2)

Atoms	Distance	Atoms	Distance
Mg(2)-O(5)	2.100(5)	C(13)-C(15)	1.48(2)
Mg(2)-O(3)	2.105(6)	C(13)-C(16)	1.51(2)
Mg(2)-Mg(2)#1	3.153(5)	C(14)-C(16)	1.385(19)
O(1)-C(18B)	1.34(2)	C(14)-C(17)	1.421(18)
O(1)-C(18B)#1	1.34(2)	C(19)-C(18A)	1.28(3)
O(1)-C(18A)	1.54(4)	C(19)-C(18B)	1.38(3)
O(1)-C(18A)#1	1.54(4)	C(20A)-C(21)	1.37(4)
O(2)-C(20B)	1.46(3)	C(20A)-C(20A)#1	2.00(6)
O(2)-C(20B)#1	1.46(3)	C(21)-C(20B)	1.22(3)
O(2)-C(20A)	1.58(4)	C(22)-C(23)	1.463(15)
O(2)-C(20A)#1	1.58(4)	C(24)-C(25)	1.470(13)
O(3)-C(22)	1.423(10)	C(26)-C(27)	1.452(13)
O(3)-C(24)	1.442(10)	C(28)-C(29)	1.464(11)
O(4)-C(28)	1.434(9)	C(30)-C(31)	1.418(18)
O(4)-C(26)	1.443(10)	C(30)-C(31)#1	1.418(18)
O(5)-C(30)	1.405(13)	C(31)-C(31)#1	1.85(4)
O(5)-Mg(2)#1	2.100(5)	C(18B)-C(18B)#1	2.01(5)
C(1)-C(6)	1.525(16)		

* Symmetry transformations used to generate equivalent atoms: #1 x, -y + ½, z.

Table 39. Bond angles [º] for [$Mg_3BrCl_3(OEt)(OEt_2)_6$][Ada_3AlBr] **VI***

Atoms	Angles	Atoms	Angels
Mg(2)-Br(1)-Mg(2)#1	72.21(10)	C(20B)#1-O(2)-Mg(1)	121.7(13)
Mg(1)-Cl(2)-Mg(2)	74.62(9)	C(20A)-O(2)-Mg(1)	121.5(16)
Mg(2)-Cl(1)-Mg(2)#1	74.82(13)	C(20A)#1-O(2)-Mg(1)	121.5(16)
Mg(2)-Cl(1)-Mg(1)	72.88(10)	C(22)-O(3)-C(24)	115.4(7)
Mg(2)#1-Cl(1)-Mg(1)	72.88(10)	C(22)-O(3)-Mg(2)	121.6(6)
C(1)-Al(1)-C(8)	115.4(3)	C(24)-O(3)-Mg(2)	122.5(5)
C(1)-Al(1)-C(8)#1	115.4(3)	C(28)-O(4)-C(26)	113.1(6)
C(8)-Al(1)-C(8)#1	113.7(4)	C(28)-O(4)-Mg(2)	125.6(5)
C(1)-Al(1)-Br(2)	102.3(3)	C(26)-O(4)-Mg(2)	121.4(5)
C(8)-Al(1)-Br(2)	103.9(2)	C(30)-O(5)-Mg(2)	118.3(3)
C(8)#1-Al(1)-Br(2)	103.9(2)	C(30)-O(5)-Mg(2)#1	118.3(3)
O(2)-Mg(1)-O(1)	90.8(4)	Mg(2)-O(5)-Mg(2)#1	97.3(3)
O(2)-Mg(1)-O(5)	107.7(4)	C(30)-O(5)-Mg(1)	125.3(6)

Atoms	Angles	Atoms	Angels
O(1)-Mg(1)-O(5)	161.5(4)	Mg(2)-O(5)-Mg(1)	95.9(2)
O(2)-Mg(1)-Cl(2)	94.94(9)	Mg(2)#1-O(5)-Mg(1)	95.9(2)
O(1)-Mg(1)-Cl(2)	94.52(9)	C(6)-C(1)-C(2)	105.7(7)
O(5)-Mg(1)-Cl(2)	84.13(8)	C(6)-C(1)-C(2)#1	105.7(7)
O(2)-Mg(1)-Cl(2)#1	94.94(9)	C(2)-C(1)-C(2)#1	108.9(12)
O(1)-Mg(1)-Cl(2)#1	94.52(9)	C(6)-C(1)-Al(1)	111.2(7)
O(5)-Mg(1)-Cl(2)#1	84.13(8)	C(2)-C(1)-Al(1)	112.4(6)
Cl(2)-Mg(1)-Cl(2)#1	166.51(14)	C(2)#1-C(1)-Al(1)	112.4(6)
O(2)-Mg(1)-Cl(1)	177.0(3)	C(1)-C(2)-C(3)	111.1(9)
O(1)-Mg(1)-Cl(1)	86.2(3)	C(4)-C(3)-C(7)	109.5(13)
O(5)-Mg(1)-Cl(1)	75.4(2)	C(4)-C(3)-C(2)	109.2(12)
Cl(2)-Mg(1)-Cl(1)	85.31(8)	C(7)-C(3)-C(2)	109.8(16)
Cl(2)#1-Mg(1)-Cl(1)	85.31(8)	C(5)-C(4)-C(3)	110.5(12)
O(2)-Mg(1)-Mg(2)#1	130.0(2)	C(4)-C(5)-C(4)#1	109.4(15)
O(1)-Mg(1)-Mg(2)#1	124.7(3)	C(4)-C(5)-C(6)	110.2(8)
O(5)-Mg(1)-Mg(2)#1	41.79(13)	C(4)#1-C(5)-C(6)	110.2(8)
Cl(2)-Mg(1)-Mg(2)#1	113.45(11)	C(1)-C(6)-C(5)	111.1(10)
Cl(2)#1-Mg(1)-Mg(2)#1	53.06(6)	C(3)-C(7)-C(3)#1	108.7(14)
Cl(1)-Mg(1)-Mg(2)#1	52.30(8)	C(10)-C(8)-C(11)	104.1(9)
O(4)-Mg(2)-O(5)	107.8(2)	C(10)-C(8)-C(9)	107.7(10)
O(4)-Mg(2)-O(3)	87.6(2)	C(11)-C(8)-C(9)	106.8(10)
O(5)-Mg(2)-O(3)	164.5(3)	C(10)-C(8)-Al(1)	112.2(6)
O(4)-Mg(2)-Cl(1)	174.44(18)	C(11)-C(8)-Al(1)	112.7(6)
O(5)-Mg(2)-Cl(1)	77.64(19)	C(9)-C(8)-Al(1)	112.7(6)
O(3)-Mg(2)-Cl(1)	86.90(17)	C(8)-C(9)-C(12)	111.9(8)
O(4)-Mg(2)-Cl(2)	92.80(16)	C(8)-C(10)-C(13)	112.4(9)
O(5)-Mg(2)-Cl(2)	83.92(16)	C(8)-C(11)-C(14)	110.6(9)
O(3)-Mg(2)-Cl(2)	93.69(17)	C(17)-C(12)-C(15)	116.0(15)
Cl(1)-Mg(2)-Cl(2)	86.57(9)	C(17)-C(12)-C(9)	110.4(12)
O(4)-Mg(2)-Br(1)	96.14(16)	C(15)-C(12)-C(9)	96.2(15)
O(5)-Mg(2)-Br(1)	82.87(15)	C(15)-C(13)-C(16)	111.9(13)
O(3)-Mg(2)-Br(1)	97.66(16)	C(15)-C(13)-C(10)	111.5(12)
Cl(1)-Mg(2)-Br(1)	85.56(9)	C(16)-C(13)-C(10)	98.8(17)
Cl(2)-Mg(2)-Br(1)	165.80(10)	C(16)-C(14)-C(17)	113.8(15)
O(4)-Mg(2)-Mg(2)#1	132.40(15)	C(16)-C(14)-C(11)	113.8(12)
O(5)-Mg(2)-Mg(2)#1	41.35(15)	C(17)-C(14)-C(11)	100.2(13)
O(3)-Mg(2)-Mg(2)#1	127.92(16)	C(12)-C(15)-C(13)	111.4(14)
Cl(1)-Mg(2)-Mg(2)#1	52.59(6)	C(14)-C(16)-C(13)	110.9(11)
Cl(2)-Mg(2)-Mg(2)#1	112.13(6)	C(12)-C(17)-C(14)	115.1(13)

Atoms	Angles	Atoms	Angels
Br(1)-Mg(2)-Mg(2)#1	53.89(5)	C(18A)-C(19)-C(18B)	61.5(19)
C(18B)-O(1)-C(18B)#1	97(2)	C(21)-C(20A)-O(2)	108(4)
C(18B)-O(1)-C(18A)	55.8(14)	C(21)-C(20A)-C(20A)#1	132(2)
C(18B)#1-O(1)-C(18A)	116.6(16)	O(2)-C(20A)-C(20A)#1	50.7(12)
C(18B)-O(1)-C(18A)#1	116.6(16)	C(20B)-C(21)-C(20A)	68(2)
C(18B)#1-O(1)-C(18A)#1	55.8(14)	O(3)-C(22)-C(23)	114.2(10)
C(18A)-O(1)-C(18A)#1	85(3)	O(3)-C(24)-C(25)	115.4(9)
C(18B)-O(1)-Mg(1)	124.5(11)	O(4)-C(26)-C(27)	115.8(9)
C(18B)#1-O(1)-Mg(1)	124.5(11)	O(4)-C(28)-C(29)	114.9(8)
C(18A)-O(1)-Mg(1)	117.0(12)	O(5)-C(30)-C(31)	121.6(10)
C(18A)#1-O(1)-Mg(1)	117.0(12)	O(5)-C(30)-C(31)#1	121.6(10)
C(20B)-O(2)-C(20B)#1	99.4(17)	C(31)-C(30)-C(31)#1	81.3(15)
C(20B)-O(2)-C(20A)	57.2(15)	C(30)-C(31)-C(31)#1	49.3(8)
C(20B)#1-O(2)-C(20A)	115.1(16)	C(19)-C(18A)-O(1)	117(3)
C(20B)-O(2)-C(20A)#1	115.1(16)	O(1)-C(18B)-C(19)	125(3)
C(20B)#1-O(2)-C(20A)#1	57.2(15)	O(1)-C(18B)-C(18B)#1	41.4(11)
C(20A)-O(2)-C(20A)#1	79(2)	C(19)-C(18B)-C(18B)#1	128.3(14)
C(20B)-O(2)-Mg(1)	121.7(13)	C(21)-C(20B)-O(2)	127(4)

* Symmetry transformations used to generate equivalent atoms: #1 x, -y + ½, z.

5.6 STRUCTURAL DATA OF $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**

Table 40. Crystal data and structural refinement for $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**

Empirical Formula	$C_{44}H_{90}Br_4Cl_3GaMg_3O_6$
Formula Weight	1283.8
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell Dimensions	a = 11.593(2) Å b = 20.546(4) Å c = 26.162(5) Å $\alpha = 90°$ $\beta = 90.69(3)°$ $\gamma = 90°$
Volume	6231(2) Å^3
Z	4
Calculated Density	1.368 g/cm^3
Absorption Coefficient	3.202 mm^{-1}
F(000)	2640
Crystal Size	0.40 x 0.34 x 0.29 mm
Theta Range for Data Collection	1.56 to 23.26°
Limiting Indices	$-12 \leq h \leq 11$ $-22 \leq k \leq 22$ $-29 \leq l \leq 29$
Reflections Collected/Unique	31827/8932 [R(int) = 0.0497]
Completeness to Theta	99.90%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	8932/471/645
Goodness-of-fit on F^2	0.99
Final R Indices [I >2sigma(I)]	R1 = 0.0747 wR2 = 0.2339
R Indices (All Data)	R1 = 0.1127 wR2 = 0.2697
Largest Diff. Peak and Hole	2.243 and -1.206 e$^-$/Å^3

Table 41. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII***

Atom	X	Y	Z	U(eq)
Ga(1)	426(1)	7763(1)	256(1)	56(1)
Br(1)	5340(1)	5966(1)	2883(1)	86(1)
Br(2)	1442(1)	5017(1)	2147(1)	79(1)
Br(3)	-485(1)	7489(1)	1061(1)	109(1)
Br(4)	466(1)	6753(1)	-239(1)	98(1)
Cl(1)	5179(1)	4858(1)	1117(1)	36(1)
Cl(2)	4289(2)	4549(1)	2336(1)	66(1)
Cl(3)	3685(2)	6024(1)	1766(1)	48(1)
Mg(1)	3217(2)	5562(2)	2641(1)	51(1)
Mg(2)	3175(2)	4839(1)	1507(1)	46(1)
Mg(3)	5613(2)	5443(2)	1961(1)	50(1)
O(1)	2334(6)	6407(3)	2839(3)	71(2)
O(2)	2872(5)	5120(3)	3338(2)	61(2)
O(3)	2265(5)	5140(3)	871(2)	55(2)
O(4)	2869(5)	3859(3)	1348(2)	60(2)
O(5)	6535(5)	6208(3)	1661(2)	64(2)
O(6)	7104(5)	4909(3)	2120(2)	62(2)
C(1)	-690(7)	8344(4)	-131(4)	53(2)
C(2)	-1867(9)	8042(6)	-154(5)	83(3)
C(3)	-2719(10)	8479(7)	-453(7)	99(3)
C(4)	-2782(9)	9136(6)	-179(6)	98(3)
C(5)	-1602(9)	9449(5)	-160(5)	71(2)
C(6)	-2285(11)	8568(7)	-977(6)	103(3)
C(7)	-1039(11)	8912(6)	-981(5)	78(3)
C(8)	-1164(9)	9561(5)	-693(4)	72(2)
C(9)	-209(9)	8471(5)	-669(4)	68(2)
C(10)	-784(8)	9002(5)	133(4)	61(2)
C(11)	2061(8)	7979(4)	448(4)	56(2)
C(12)	2669(10)	7400(6)	732(5)	89(3)
C(13)	3877(12)	7575(7)	882(6)	100(3)
C(14)	4549(11)	7705(7)	419(6)	109(4)
C(15)	4033(10)	8273(7)	119(5)	91(3)
C(16)	4052(10)	8863(6)	452(6)	95(3)
C(17)	2767(9)	8106(6)	-32(4)	77(3)
C(18)	3394(11)	8765(7)	914(6)	93(3)
C(19)	2119(9)	8578(6)	776(4)	75(3)
C(20)	3887(12)	8157(8)	1215(6)	116(4)

Atom	X	Y	Z	U(eq)
C(21)	2497(18)	6711(9)	3326(6)	160(7)
C(22)	1529(13)	6720(8)	2492(6)	138(6)
C(23)	3280(20)	7285(11)	3337(10)	225(12)
C(24)	445(14)	6720(12)	2636(9)	191(10)
C(25)	3750(11)	4886(6)	3690(4)	85(3)
C(26)	1733(11)	4927(8)	3499(5)	104(4)
C(27)	3989(13)	5323(7)	4138(5)	102(4)
C(28)	1399(15)	4304(9)	3421(6)	148(7)
C(29A)	1135(15)	4888(12)	764(13)	85(8)
C(29B)	1337(10)	5620(7)	873(5)	61(3)
C(30A)	2630(30)	5635(11)	527(8)	126(9)
C(30B)	2605(16)	4962(9)	376(5)	62(5)
C(31)	201(9)	5340(7)	793(5)	106(4)
C(32)	3141(14)	5441(8)	70(5)	130(5)
C(33A)	1741(11)	3627(8)	1236(6)	78(4)
C(33B)	2390(20)	3408(17)	1725(11)	94(9)
C(34A)	3742(14)	3351(8)	1324(6)	86(4)
C(34B)	3060(20)	3527(16)	886(9)	83(9)
C(35)	1215(11)	3237(7)	1623(6)	109(4)
C(36)	4134(13)	3192(7)	834(6)	125(5)
C(37A)	7337(14)	6158(9)	1259(6)	61(4)
C(37B)	6360(20)	6492(12)	1158(7)	98(7)
C(38A)	6354(17)	6897(9)	1800(8)	84(6)
C(38B)	7481(18)	6492(11)	1934(9)	115(8)
C(39)	7016(12)	6297(7)	746(4)	106(4)
C(40)	7239(14)	7132(8)	2127(6)	131(6)
C(41A)	8027(16)	5163(10)	2407(7)	82(6)
C(41B)	7347(18)	4602(13)	2619(7)	112(8)
C(42A)	7214(16)	4236(8)	1960(8)	75(5)
C(42B)	7980(18)	4764(11)	1761(8)	96(6)
C(43)	8296(14)	4880(10)	2886(5)	139(6)
C(44)	7992(13)	4111(8)	1555(6)	131(5)

* A measure of disorder was observed on the ether groups in the cation of **VII**. All of the ether groups were appropriately modeled to resolve this disorder.

Table 42. Bond lengths [Å] for [$Mg_3Br_2Cl_3(OEt_2)_6$][Ada_2GaBr_2] **VII**

Atoms	Distance	Atoms	Distance
Ga(1)-C(11)	2.005(9)	C(33A)-C(35)	1.434(15)
Ga(1)-C(1)	2.024(9)	C(33B)-C(35)	1.425(19)
Ga(1)-Br(3)	2.4347(18)	C(34A)-C(36)	1.405(16)
Ga(1)-Br(4)	2.4463(16)	C(34B)-C(36)	1.44(2)
Mg(1)-O(2)	2.080(7)	O(5)-C(37A)	1.415(13)
Mg(1)-O(1)	2.084(7)	O(5)-C(38B)	1.427(16)
Mg(1)-Cl(3)	2.542(3)	O(5)-C(37B)	1.452(16)
Mg(1)-Cl(2)	2.556(4)	O(5)-C(38A)	1.478(16)
Mg(1)-Br(2)	2.663(3)	C(37A)-C(39)	1.420(16)
Mg(1)-Br(1)	2.667(3)	C(37B)-C(39)	1.385(17)
Mg(1)-Mg(2)	3.316(4)	C(38A)-C(40)	1.412(17)
Mg(1)-Mg(3)	3.324(4)	C(38B)-C(40)	1.439(19)
Mg(2)-O(3)	2.053(6)	O(6)-C(41A)	1.401(15)
Mg(2)-O(4)	2.086(7)	O(6)-C(42B)	1.422(15)
Mg(2)-Cl(1)	2.550(3)	O(6)-C(42A)	1.450(15)
Mg(2)-Cl(2)	2.581(4)	O(6)-C(41B)	1.475(17)
Mg(2)-Cl(3)	2.593(4)	C(41A)-C(43)	1.412(17)
Mg(2)-Br(2)	2.657(3)	C(41B)-C(43)	1.417(18)
Mg(2)-Mg(3)	3.295(4)	C(42A)-C(44)	1.422(17)
Mg(3)-O(5)	2.062(7)	C(42B)-C(44)	1.447(19)
Mg(3)-O(6)	2.085(7)	C(1)-C(2)	1.500(13)
Mg(3)-Cl(1)	2.561(3)	C(1)-C(9)	1.542(13)
Mg(3)-Cl(3)	2.580(3)	C(1)-C(10)	1.523(13)
Mg(3)-Cl(2)	2.594(4)	C(2)-C(3)	1.542(17)
Mg(3)-Br(1)	2.663(3)	C(3)-C(6)	1.48(2)
O(2)-C(26)	1.447(12)	C(3)-C(4)	1.530(18)
O(2)-C(25)	1.447(12)	C(4)-C(5)	1.512(15)
C(25)-C(27)	1.500(15)	C(5)-C(8)	1.507(16)
C(26)-C(28)	1.351(17)	C(5)-C(10)	1.522(15)
O(1)-C(21)	1.429(14)	C(6)-C(7)	1.608(18)
O(1)-C(22)	1.445(14)	C(7)-C(9)	1.547(14)
C(21)-C(23)	1.49(2)	C(7)-C(8)	1.538(15)
C(22)-C(24)	1.316(18)	C(11)-C(17)	1.529(14)
O(3)-C(30B)	1.407(14)	C(11)-C(19)	1.501(14)
O(3)-C(30A)	1.426(17)	C(11)-C(12)	1.565(14)
O(3)-C(29A)	1.434(17)	C(12)-C(13)	1.493(17)
O(3)-C(29B)	1.459(12)	C(13)-C(20)	1.48(2)
C(29A)-C(31)	1.429(19)	C(13)-C(14)	1.47(2)

Atoms	Distance	Atoms	Distance
C(29B)-C(31)	1.450(14)	C(14)-C(15)	1.526(19)
C(30A)-C(32)	1.400(18)	C(15)-C(16)	1.492(19)
C(30B)-C(32)	1.417(17)	C(15)-C(17)	1.554(16)
O(4)-C(34B)	1.406(17)	C(16)-C(18)	1.452(19)
O(4)-C(33A)	1.420(12)	C(18)-C(20)	1.58(2)
O(4)-C(34A)	1.457(13)	C(18)-C(19)	1.565(15)
O(4)-C(33B)	1.469(18)		

Table 43. Bond angles [Å] for $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ **VII**

Atoms	Angles	Atoms	Angels
C(11)-Ga(1)-C(1)	126.2(4)	C(24)-C(22)-O(1)	115.7(17)
C(11)-Ga(1)-Br(3)	104.6(3)	C(30B)-O(3)-C(30A)	61.1(12)
C(1)-Ga(1)-Br(3)	106.7(3)	C(30B)-O(3)-C(29A)	89.5(16)
C(11)-Ga(1)-Br(4)	107.3(3)	C(30A)-O(3)-C(29A)	114.2(16)
C(1)-Ga(1)-Br(4)	104.6(3)	C(30B)-O(3)-C(29B)	113.1(9)
Br(3)-Ga(1)-Br(4)	105.83(7)	C(30A)-O(3)-C(29B)	75.0(13)
O(2)-Mg(1)-O(1)	92.5(3)	C(29A)-O(3)-C(29B)	64.7(11)
O(2)-Mg(1)-Cl(3)	176.0(2)	C(30B)-O(3)-Mg(2)	121.4(8)
O(1)-Mg(1)-Cl(3)	91.4(2)	C(30A)-O(3)-Mg(2)	125.1(13)
O(2)-Mg(1)-Cl(2)	91.0(2)	C(29A)-O(3)-Mg(2)	120.6(13)
O(1)-Mg(1)-Cl(2)	176.3(2)	C(29B)-O(3)-Mg(2)	124.9(6)
Cl(3)-Mg(1)-Cl(2)	85.08(11)	C(31)-C(29A)-O(3)	116.5(17)
O(2)-Mg(1)-Br(2)	94.9(2)	C(31)-C(29B)-O(3)	113.6(11)
O(1)-Mg(1)-Br(2)	95.3(2)	C(29B)-C(31)-C(29A)	65.1(11)
Cl(3)-Mg(1)-Br(2)	83.85(10)	C(32)-C(30A)-O(3)	117.9(17)
Cl(2)-Mg(1)-Br(2)	83.27(10)	C(32)-C(30B)-O(3)	118.0(13)
O(2)-Mg(1)-Br(1)	96.5(2)	C(30A)-C(32)-C(30B)	61.4(12)
O(1)-Mg(1)-Br(1)	97.8(2)	C(34B)-O(4)-C(33A)	79.0(14)
Cl(3)-Mg(1)-Br(1)	83.78(10)	C(34B)-O(4)-C(34A)	60.1(13)
Cl(2)-Mg(1)-Br(1)	82.94(10)	C(33A)-O(4)-C(34A)	112.9(10)
Br(2)-Mg(1)-Br(1)	162.19(12)	C(34B)-O(4)-C(33B)	109.5(18)
O(2)-Mg(1)-Mg(2)	126.0(2)	C(33A)-O(4)-C(33B)	64.5(11)
O(1)-Mg(1)-Mg(2)	126.4(2)	C(34A)-O(4)-C(33B)	81.1(16)
Cl(3)-Mg(1)-Mg(2)	50.45(9)	C(34B)-O(4)-Mg(2)	127.7(15)
Cl(2)-Mg(1)-Mg(2)	50.13(9)	C(33A)-O(4)-Mg(2)	121.3(8)

Atoms	Angles	Atoms	Angels
Br(2)-Mg(1)-Mg(2)	51.37(7)	C(34A)-O(4)-Mg(2)	125.8(8)
Br(1)-Mg(1)-Mg(2)	110.84(10)	C(33B)-O(4)-Mg(2)	122.8(16)
O(2)-Mg(1)-Mg(3)	127.4(2)	O(4)-C(33A)-C(35)	116.1(11)
O(1)-Mg(1)-Mg(3)	127.6(2)	C(35)-C(33B)-O(4)	113.6(16)
Cl(3)-Mg(1)-Mg(3)	50.04(9)	C(33B)-C(35)-C(33A)	65.3(11)
Cl(2)-Mg(1)-Mg(3)	50.30(9)	C(36)-C(34A)-O(4)	116.0(13)
Br(2)-Mg(1)-Mg(3)	110.87(11)	O(4)-C(34B)-C(36)	117.3(18)
Br(1)-Mg(1)-Mg(3)	51.35(7)	C(34A)-C(36)-C(34B)	60.6(13)
Mg(2)-Mg(1)-Mg(3)	59.50(8)	C(37A)-O(5)-C(38B)	83.9(13)
O(3)-Mg(2)-O(4)	92.5(3)	C(37A)-O(5)-C(37B)	56.1(11)
O(3)-Mg(2)-Cl(1)	97.6(2)	C(38B)-O(5)-C(37B)	112.9(15)
O(4)-Mg(2)-Cl(1)	95.0(2)	C(37A)-O(5)-C(38A)	110.4(12)
O(3)-Mg(2)-Cl(2)	175.6(2)	C(38B)-O(5)-C(38A)	66.1(12)
O(4)-Mg(2)-Cl(2)	91.5(2)	C(37B)-O(5)-C(38A)	79.6(13)
Cl(1)-Mg(2)-Cl(2)	83.75(10)	C(37A)-O(5)-Mg(3)	125.2(9)
O(3)-Mg(2)-Cl(3)	92.4(2)	C(38B)-O(5)-Mg(3)	121.3(11)
O(4)-Mg(2)-Cl(3)	175.0(2)	C(37B)-O(5)-Mg(3)	125.8(11)
Cl(1)-Mg(2)-Cl(3)	83.41(10)	C(38A)-O(5)-Mg(3)	124.1(9)
Cl(2)-Mg(2)-Cl(3)	83.55(11)	O(5)-C(37A)-C(39)	121.4(13)
O(3)-Mg(2)-Br(2)	94.83(19)	C(39)-C(37B)-O(5)	121.2(15)
O(4)-Mg(2)-Br(2)	97.5(2)	C(37B)-C(39)-C(37A)	57.4(11)
Cl(1)-Mg(2)-Br(2)	161.90(12)	C(40)-C(38A)-O(5)	111.9(14)
Cl(2)-Mg(2)-Br(2)	82.90(10)	O(5)-C(38B)-C(40)	113.4(16)
Cl(3)-Mg(2)-Br(2)	82.99(10)	C(38A)-C(40)-C(38B)	67.6(12)
O(3)-Mg(2)-Mg(3)	127.5(2)	C(41A)-O(6)-C(42B)	83.4(14)
O(4)-Mg(2)-Mg(3)	125.3(2)	C(41A)-O(6)-C(42A)	116.1(12)
Cl(1)-Mg(2)-Mg(3)	50.00(8)	C(42B)-O(6)-C(42A)	62.9(12)
Cl(2)-Mg(2)-Mg(3)	50.63(9)	C(41A)-O(6)-C(41B)	63.0(12)
Cl(3)-Mg(2)-Mg(3)	50.27(8)	C(42B)-O(6)-C(41B)	111.4(13)
Br(2)-Mg(2)-Mg(3)	111.90(10)	C(42A)-O(6)-C(41B)	80.3(14)
O(3)-Mg(2)-Mg(1)	126.3(2)	C(41A)-O(6)-Mg(3)	122.5(10)
O(4)-Mg(2)-Mg(1)	127.7(2)	C(42B)-O(6)-Mg(3)	125.2(11)
Cl(1)-Mg(2)-Mg(1)	110.38(11)	C(42A)-O(6)-Mg(3)	121.3(9)
Cl(2)-Mg(2)-Mg(1)	49.47(9)	C(41B)-O(6)-Mg(3)	123.4(10)
Cl(3)-Mg(2)-Mg(1)	49.12(8)	O(6)-C(41A)-C(43)	118.9(15)
Br(2)-Mg(2)-Mg(1)	51.52(7)	C(43)-C(41B)-O(6)	113.8(16)
Mg(3)-Mg(2)-Mg(1)	60.38(8)	C(41B)-C(43)-C(41A)	64.3(13)
O(5)-Mg(3)-O(6)	92.5(3)	C(44)-C(42A)-O(6)	116.5(14)
O(5)-Mg(3)-Cl(1)	97.2(2)	C(44)-C(42B)-O(6)	116.8(15)

Atoms	Angles	Atoms	Angels
O(6)-Mg(3)-Cl(1)	94.5(2)	C(42A)-C(44)-C(42B)	63.0(12)
O(5)-Mg(3)-Cl(3)	91.4(2)	C(2)-C(1)-C(9)	111.8(9)
O(6)-Mg(3)-Cl(3)	175.8(2)	C(2)-C(1)-C(10)	108.5(8)
Cl(1)-Mg(3)-Cl(3)	83.43(10)	C(9)-C(1)-C(10)	107.1(8)
O(5)-Mg(3)-Cl(2)	174.8(2)	C(2)-C(1)-Ga(1)	110.5(7)
O(6)-Mg(3)-Cl(2)	92.6(2)	C(9)-C(1)-Ga(1)	108.6(6)
Cl(1)-Mg(3)-Cl(2)	83.27(11)	C(10)-C(1)-Ga(1)	110.2(6)
Cl(3)-Mg(3)-Cl(2)	83.54(11)	C(1)-C(2)-C(3)	110.8(9)
O(5)-Mg(3)-Br(1)	96.1(2)	C(2)-C(3)-C(6)	108.7(11)
O(6)-Mg(3)-Br(1)	98.1(2)	C(2)-C(3)-C(4)	108.1(12)
Cl(1)-Mg(3)-Br(1)	161.27(12)	C(6)-C(3)-C(4)	110.2(12)
Cl(3)-Mg(3)-Br(1)	83.14(10)	C(5)-C(4)-C(3)	110.0(9)
Cl(2)-Mg(3)-Br(1)	82.30(10)	C(4)-C(5)-C(8)	110.4(10)
O(5)-Mg(3)-Mg(2)	126.6(2)	C(4)-C(5)-C(10)	108.5(9)
O(6)-Mg(3)-Mg(2)	125.4(2)	C(8)-C(5)-C(10)	110.1(9)
Cl(1)-Mg(3)-Mg(2)	49.71(8)	C(3)-C(6)-C(7)	112.1(10)
Cl(3)-Mg(3)-Mg(2)	50.60(8)	C(6)-C(7)-C(9)	107.0(10)
Cl(2)-Mg(3)-Mg(2)	50.28(9)	C(6)-C(7)-C(8)	106.7(10)
Br(1)-Mg(3)-Mg(2)	111.58(10)	C(9)-C(7)-C(8)	108.2(9)
O(5)-Mg(3)-Mg(1)	126.0(2)	C(5)-C(8)-C(7)	110.9(9)
O(6)-Mg(3)-Mg(1)	129.0(2)	C(1)-C(9)-C(7)	110.5(8)
Cl(1)-Mg(3)-Mg(1)	109.83(11)	C(5)-C(10)-C(1)	110.7(8)
Cl(3)-Mg(3)-Mg(1)	49.04(8)	C(17)-C(11)-C(19)	108.1(8)
Cl(2)-Mg(3)-Mg(1)	49.30(9)	C(17)-C(11)-C(12)	106.0(9)
Br(1)-Mg(3)-Mg(1)	51.46(7)	C(19)-C(11)-C(12)	109.6(9)
Mg(2)-Mg(3)-Mg(1)	60.12(8)	C(17)-C(11)-Ga(1)	110.2(7)
Mg(3)-Br(1)-Mg(1)	77.18(9)	C(19)-C(11)-Ga(1)	111.2(7)
Mg(2)-Br(2)-Mg(1)	77.11(9)	C(12)-C(11)-Ga(1)	111.7(6)
Mg(2)-Cl(1)-Mg(3)	80.29(10)	C(11)-C(12)-C(13)	111.0(9)
Mg(1)-Cl(2)-Mg(2)	80.40(12)	C(20)-C(13)-C(14)	109.7(12)
Mg(1)-Cl(2)-Mg(3)	80.40(13)	C(20)-C(13)-C(12)	110.4(13)
Mg(2)-Cl(2)-Mg(3)	79.09(12)	C(14)-C(13)-C(12)	109.3(13)
Mg(1)-Cl(3)-Mg(3)	80.93(11)	C(15)-C(14)-C(13)	110.8(11)
Mg(1)-Cl(3)-Mg(2)	80.44(11)	C(16)-C(15)-C(14)	108.5(12)
Mg(3)-Cl(3)-Mg(2)	79.13(11)	C(16)-C(15)-C(17)	109.6(10)
C(26)-O(2)-C(25)	111.1(8)	C(14)-C(15)-C(17)	108.9(11)
C(26)-O(2)-Mg(1)	124.1(6)	C(15)-C(16)-C(18)	111.7(11)
C(25)-O(2)-Mg(1)	124.2(6)	C(11)-C(17)-C(15)	110.0(9)
O(2)-C(25)-C(27)	114.9(10)	C(20)-C(18)-C(16)	109.5(12)

Atoms	Angles	Atoms	Angels
C(28)-C(26)-O(2)	118.5(13)	C(20)-C(18)-C(19)	104.8(11)
C(21)-O(1)-C(22)	116.2(11)	C(16)-C(18)-C(19)	110.2(11)
C(21)-O(1)-Mg(1)	121.8(10)	C(11)-C(19)-C(18)	111.6(9)
C(22)-O(1)-Mg(1)	122.0(7)	C(13)-C(20)-C(18)	110.2(11)
O(1)-C(21)-C(23)	116.0(16)		

5.7 STRUCTURAL DATA OF $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**

Table 44. Crystal data and structure refinement for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**

Empirical Formula	$C_{48}H_{101}Br_4GaMg_3O_7$
Formula Weight	1252.58
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 13.220(3) Å
	b = 14.270(3) Å
	c = 17.580(4) Å
	α = 80.37(3)°
	β = 79.67(3)°
	γ = 79.20(3)°
Volume	3174.1(11) $Å^3$
Z	2
Calculated Density	1.311 g/cm^3
Absorption Coefficient	3.021 mm^{-1}
F(000)	1304
Crystal Size	0.27 x 0.23 x 0.20 mm
Theta Range for Data Collection	1.59 to 26.40°
Limiting Indices	$-16 \leq h \leq 16$
	$-16 \leq k \leq 17$
	$-21 \leq l \leq 21$
Reflections Collected/Unique	21289/12898 [R(int) = 0.0326]
Completeness to Theta	99.20%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	12898/0/589
Goodness-of-fit on F^2	1.018
Final R Indices [I >2sigma(I)]	R1 = 0.0612 wR2 = 0.1667
R Indices (All Data)	R1 = 0.1091 wR2 = 0.1956
Largest Diff. Peak and Hole	1.019 and -0.293 $e^-/Å^3$

Table 45. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**

Atom	X	Y	Z	U(eq)
Ga(1)	3987(1)	6827(1)	2267(1)	79(1)
Mg(1)	9088(1)	1595(1)	1977(1)	71(1)
Mg(2)	7247(1)	448(1)	2873(1)	72(1)
Mg(3)	7955(1)	2044(1)	3683(1)	64(1)
Br(1)	9165(1)	318(1)	3341(1)	70(1)
Br(2)	8302(1)	275(1)	1455(1)	97(1)
Br(3)	9471(1)	2854(1)	2809(1)	88(1)
Br(4)	6435(1)	1017(1)	4260(1)	86(1)
C(1)	3056(7)	8105(6)	2009(6)	159(4)
C(2)	4692(6)	6933(6)	3182(4)	112(2)
C(3)	3051(5)	5782(5)	2592(4)	84(2)
C(4)	3660(7)	4790(6)	2689(7)	164(4)
C(5)	2897(12)	4013(10)	2828(14)	243(10)
C(6)	2415(14)	4163(10)	3651(13)	234(9)
C(7)	1743(13)	5061(15)	3699(7)	200(7)
C(8)	979(9)	5245(12)	3098(13)	234(7)
C(9)	1577(17)	5056(15)	2340(11)	212(8)
C(10)	2364(7)	5816(9)	2017(6)	169(4)
C(11)	2386(8)	5962(9)	3354(6)	187(5)
C(12)	2084(15)	4226(17)	2323(11)	225(11)
C(13)	5129(4)	6647(4)	1332(3)	71(1)
C(14)	6014(7)	5859(7)	1542(5)	146(3)
C(15)	6984(9)	5833(10)	869(6)	165(4)
C(16)	7254(13)	6818(15)	567(9)	222(9)
C(17)	6377(12)	7535(10)	323(10)	214(8)
C(18)	6018(13)	7149(9)	-299(6)	213(6)
C(19)	5721(7)	6197(6)	-56(4)	115(2)
C(20)	4798(6)	6349(6)	626(4)	115(2)
C(21)	5618(8)	7545(6)	1084(6)	156(4)
C(22)	6558(7)	5482(7)	229(5)	132(3)
C(23)	8914(8)	3652(7)	911(6)	166(4)
C(24)	9818(9)	4077(8)	789(7)	197(5)
C(25)	9372(14)	2273(9)	200(6)	235(7)
C(26)	9027(18)	2537(14)	-407(9)	340(13)
C(27)	11459(6)	1623(7)	1535(5)	138(3)
C(28)	12080(6)	1401(7)	2170(6)	150(3)
C(29)	11044(6)	85(6)	1487(6)	140(3)

Atom	X	Y	Z	U(eq)
C(30)	11459(13)	-69(11)	714(6)	274(10)
C(31)	8228(10)	-1723(7)	3014(6)	160(4)
C(32)	8050(13)	-2324(9)	2509(7)	234(7)
C(33)	6555(8)	-1421(7)	3832(7)	157(4)
C(34)	6886(10)	-1805(8)	4543(7)	188(5)
C(35)	5654(7)	-212(6)	2069(6)	141(3)
C(36)	5418(7)	225(6)	1280(5)	142(3)
C(37)	4816(6)	1082(7)	2848(6)	138(3)
C(38)	4090(7)	563(9)	3424(6)	184(5)
C(39)	8608(7)	967(6)	5281(5)	129(3)
C(40)	8049(7)	1051(8)	6020(5)	158(4)
C(41)	9160(9)	2501(8)	4897(6)	158(4)
C(42)	10240(8)	2233(9)	4884(8)	210(6)
C(43)	6357(6)	3415(6)	4682(5)	114(2)
C(44)	5267(6)	3678(7)	4577(5)	140(3)
C(45)	7145(7)	4329(5)	3507(5)	130(3)
C(46)	7607(8)	4964(7)	3865(7)	170(4)
C(47)	6861(5)	2630(5)	2312(4)	89(2)
C(48)	6464(7)	2614(6)	1587(5)	130(3)
O(1)	9163(4)	2568(4)	936(3)	112(2)
O(2)	10644(3)	1045(3)	1618(2)	89(1)
O(3)	7345(4)	-1031(3)	3246(3)	95(1)
O(4)	5780(3)	449(3)	2570(3)	95(1)
O(5)	8580(3)	1845(3)	4719(2)	73(1)
O(6)	7092(3)	3381(3)	3954(2)	84(1)
O(7)	7570(2)	1880(2)	2596(2)	73(2)

Table 46. Bond lengths [Å] for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**

Atoms	Distance	Atoms	Distance
Ga(1)-C(1)	2.031(7)	C(5)-C(6)	1.50(2)
Ga(1)-C(2)	2.038(6)	C(5)-C(4)	1.595(16)
Ga(1)-C(3)	2.058(6)	C(6)-C(7)	1.422(18)
Ga(1)-C(13)	2.039(5)	C(47)-C(48)	1.467(9)
Br(1)-Mg(1)	2.763(2)	C(43)-C(44)	1.456(10)
Br(1)-Mg(2)	2.7676(18)	C(45)-C(46)	1.457(12)

Atoms	Distance	Atoms	Distance
Br(1)-Mg(3)	2.768(2)	C(13)-C(21)	1.507(8)
Br(2)-Mg(2)	2.655(2)	C(13)-C(14)	1.513(9)
Br(2)-Mg(1)	2.669(2)	C(13)-C(20)	1.533(8)
Br(4)-Mg(3)	2.6632(18)	C(3)-C(10)	1.464(10)
Br(4)-Mg(2)	2.674(2)	C(3)-C(4)	1.491(11)
Br(3)-Mg(3)	2.6233(18)	C(3)-C(11)	1.497(10)
Br(3)-Mg(1)	2.667(2)	C(14)-C(15)	1.580(13)
Mg(2)-O(3)	2.090(4)	C(21)-C(17)	1.521(14)
Mg(2)-O(4)	2.101(4)	C(20)-C(19)	1.562(10)
Mg(2)-O(7)	2.124(4)	C(15)-C(16)	1.502(17)
Mg(1)-O(2)	2.083(4)	C(15)-C(22)	1.534(13)
Mg(1)-O(1)	2.102(5)	C(22)-C(19)	1.457(11)
Mg(1)-O(7)	2.107(4)	C(11)-C(7)	1.646(15)
Mg(3)-O(5)	2.088(4)	C(10)-C(9)	1.608(17)
Mg(3)-O(6)	2.113(4)	C(8)-C(9)	1.462(19)
Mg(3)-O(7)	2.123(4)	C(8)-C(7)	1.548(19)
O(7)-C(47)	1.374(7)	C(16)-C(17)	1.47(2)
O(6)-C(45)	1.453(8)	C(28)-C(27)	1.461(11)
O(6)-C(43)	1.462(8)	C(39)-C(40)	1.386(11)
O(5)-C(41)	1.420(9)	C(37)-C(38)	1.471(12)
O(5)-C(39)	1.459(9)	C(35)-C(36)	1.484(11)
O(3)-C(31)	1.426(12)	C(33)-C(34)	1.389(12)
O(3)-C(33)	1.450(10)	C(29)-C(30)	1.408(12)
O(2)-C(29)	1.414(9)	C(31)-C(32)	1.409(13)
O(2)-C(27)	1.449(9)	C(18)-C(19)	1.458(13)
O(4)-C(35)	1.442(9)	C(18)-C(17)	1.487(18)
O(4)-C(37)	1.474(10)	C(41)-C(42)	1.404(13)
O(1)-C(25)	1.393(12)	C(24)-C(23)	1.407(13)
O(1)-C(23)	1.515(11)	C(12)-C(9)	1.25(2)
C(5)-C(12)	1.47(2)	C(25)-C(26)	1.210(16)

Table 47. Bond angles [º] for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ **VIII**

Atoms	Angles	Atoms	Angels
C(1)-Ga(1)-C(2)	107.9(4)	C(45)-O(6)-Mg(3)	127.9(4)
C(1)-Ga(1)-C(13)	107.6(3)	C(43)-O(6)-Mg(3)	119.5(4)
C(2)-Ga(1)-C(13)	107.2(3)	C(41)-O(5)-C(39)	112.2(6)
C(1)-Ga(1)-C(3)	107.7(3)	C(41)-O(5)-Mg(3)	122.9(5)
C(2)-Ga(1)-C(3)	109.6(3)	C(39)-O(5)-Mg(3)	124.4(4)
C(13)-Ga(1)-C(3)	116.6(2)	C(31)-O(3)-C(33)	114.5(6)
C(12)-C(5)-C(6)	109.8(13)	C(31)-O(3)-Mg(2)	123.5(5)
C(12)-C(5)-C(4)	114.8(13)	C(33)-O(3)-Mg(2)	121.6(5)
C(6)-C(5)-C(4)	97.3(16)	C(29)-O(2)-C(27)	112.3(6)
C(7)-C(6)-C(5)	113.3(15)	C(29)-O(2)-Mg(1)	126.1(5)
Mg(1)-Br(1)-Mg(2)	71.10(6)	C(27)-O(2)-Mg(1)	121.5(4)
Mg(1)-Br(1)-Mg(3)	71.02(6)	C(35)-O(4)-C(37)	115.0(6)
Mg(2)-Br(1)-Mg(3)	71.48(6)	C(35)-O(4)-Mg(2)	120.6(5)
Mg(2)-Br(2)-Mg(1)	74.30(6)	C(37)-O(4)-Mg(2)	124.5(4)
Mg(3)-Br(4)-Mg(2)	74.57(6)	C(25)-O(1)-C(23)	113.3(7)
Mg(3)-Br(3)-Mg(1)	74.78(6)	C(25)-O(1)-Mg(1)	122.9(6)
O(3)-Mg(2)-O(4)	88.52(17)	C(23)-O(1)-Mg(1)	123.6(5)
O(3)-Mg(2)-O(7)	163.68(17)	O(7)-C(47)-C(48)	120.9(6)
O(4)-Mg(2)-O(7)	107.79(16)	C(44)-C(43)-O(6)	114.5(7)
O(3)-Mg(2)-Br(2)	95.46(17)	O(6)-C(45)-C(46)	114.7(8)
O(4)-Mg(2)-Br(2)	95.46(15)	C(21)-C(13)-C(14)	104.9(7)
O(7)-Mg(2)-Br(2)	83.17(11)	C(21)-C(13)-C(20)	109.9(6)
O(3)-Mg(2)-Br(4)	96.70(16)	C(14)-C(13)-C(20)	104.4(6)
O(4)-Mg(2)-Br(4)	93.38(16)	C(21)-C(13)-Ga(1)	110.0(4)
O(7)-Mg(2)-Br(4)	82.76(11)	C(14)-C(13)-Ga(1)	111.4(4)
Br(2)-Mg(2)-Br(4)	165.14(7)	C(20)-C(13)-Ga(1)	115.6(4)
O(3)-Mg(2)-Br(1)	87.43(13)	C(10)-C(3)-C(4)	107.5(7)
O(4)-Mg(2)-Br(1)	175.75(14)	C(10)-C(3)-C(11)	108.3(7)
O(7)-Mg(2)-Br(1)	76.26(10)	C(4)-C(3)-C(11)	108.7(8)
Br(2)-Mg(2)-Br(1)	86.23(6)	C(10)-C(3)-Ga(1)	111.5(5)
Br(4)-Mg(2)-Br(1)	85.80(6)	C(4)-C(3)-Ga(1)	112.7(5)
O(2)-Mg(1)-O(1)	87.44(19)	C(11)-C(3)-Ga(1)	108.1(5)
O(2)-Mg(1)-O(7)	165.00(17)	C(13)-C(14)-C(15)	111.7(7)
O(1)-Mg(1)-O(7)	107.55(18)	C(13)-C(21)-C(17)	114.0(6)
O(2)-Mg(1)-Br(3)	95.91(14)	C(13)-C(20)-C(19)	112.6(6)
O(1)-Mg(1)-Br(3)	93.22(18)	C(16)-C(15)-C(22)	108.5(10)
O(7)-Mg(1)-Br(3)	83.17(11)	C(16)-C(15)-C(14)	112.1(9)
O(2)-Mg(1)-Br(2)	95.73(14)	C(22)-C(15)-C(14)	101.4(10)

Atoms	Angles	Atoms	Angels
O(1)-Mg(1)-Br(2)	96.76(17)	C(19)-C(22)-C(15)	110.9(8)
O(7)-Mg(1)-Br(2)	83.12(11)	C(3)-C(11)-C(7)	109.8(7)
Br(3)-Mg(1)-Br(2)	164.98(7)	C(3)-C(4)-C(5)	110.0(8)
O(2)-Mg(1)-Br(1)	88.39(13)	C(3)-C(10)-C(9)	109.2(9)
O(1)-Mg(1)-Br(1)	175.19(15)	C(9)-C(8)-C(7)	108.2(11)
O(7)-Mg(1)-Br(1)	76.61(11)	C(17)-C(16)-C(15)	114.2(10)
Br(3)-Mg(1)-Br(1)	84.83(5)	C(6)-C(7)-C(8)	111.0(13)
Br(2)-Mg(1)-Br(1)	86.04(6)	C(6)-C(7)-C(11)	110.8(10)
O(5)-Mg(3)-O(6)	90.03(16)	C(8)-C(7)-C(11)	98.7(13)
O(5)-Mg(3)-O(7)	164.57(16)	C(40)-C(39)-O(5)	116.6(8)
O(6)-Mg(3)-O(7)	105.40(16)	C(38)-C(37)-O(4)	112.8(8)
O(5)-Mg(3)-Br(3)	95.73(11)	O(4)-C(35)-C(36)	116.0(7)
O(6)-Mg(3)-Br(3)	92.67(12)	O(2)-C(27)-C(28)	114.5(7)
O(7)-Mg(3)-Br(3)	83.96(10)	C(34)-C(33)-O(3)	114.4(8)
O(5)-Mg(3)-Br(4)	95.34(11)	C(30)-C(29)-O(2)	117.2(10)
O(6)-Mg(3)-Br(4)	96.09(12)	C(32)-C(31)-O(3)	114.3(10)
O(7)-Mg(3)-Br(4)	83.04(10)	C(19)-C(18)-C(17)	113.9(10)
Br(3)-Mg(3)-Br(4)	165.87(8)	C(42)-C(41)-O(5)	119.4(10)
O(5)-Mg(3)-Br(1)	88.32(12)	C(16)-C(17)-C(18)	106.0(12)
O(6)-Mg(3)-Br(1)	177.46(13)	C(16)-C(17)-C(21)	101.2(15)
O(7)-Mg(3)-Br(1)	76.26(11)	C(18)-C(17)-C(21)	114.4(10)
Br(3)-Mg(3)-Br(1)	85.56(6)	C(24)-C(23)-O(1)	112.2(9)
Br(4)-Mg(3)-Br(1)	86.00(5)	C(22)-C(19)-C(18)	112.8(10)
C(47)-O(7)-Mg(1)	120.2(3)	C(22)-C(19)-C(20)	109.2(7)
C(47)-O(7)-Mg(2)	121.9(3)	C(18)-C(19)-C(20)	104.1(8)
Mg(1)-O(7)-Mg(2)	98.93(16)	C(9)-C(12)-C(5)	112.4(17)
C(47)-O(7)-Mg(3)	113.5(3)	C(26)-C(25)-O(1)	135.4(17)
Mg(1)-O(7)-Mg(3)	98.83(14)	C(12)-C(9)-C(8)	115(2)
Mg(2)-O(7)-Mg(3)	99.17(15)	C(12)-C(9)-C(10)	108.3(18)
C(45)-O(6)-C(43)	112.6(5)	C(8)-C(9)-C(10)	111.2(11)

5.8 STRUCTURAL DATA OF [$Mg_3Br_4(OEt)(OEt_2)_6$][Ada_2AlMe_2] **IX**

Table 48. Crystal data and structure refinement for [$Mg_3Br_4(OEt)(OEt_2)_6$][Ada_2AlMe_2] **IX**

Empirical Formula	$C_{48}H_{101}Br_4AlMg_3O_7$
Formula Weight	1209.84
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 13.2167(19) Å
	b = 14.328(2) Å
	c = 17.472(2) Å
	α = 80.242(3)°
	β = 79.961(2)°
	γ = 79.805(2)°
Volume	3173.6(8) $Å^3$
Z	2
Calculated Density	1.266 g/cm^3
Absorption Coefficient	2.620 mm^{-1}
F(000)	1268
Crystal Size	0.32 x 0.30 x 0.27 mm
Theta Range for Data Collection	1.46 to 21.04°
Limiting Indices	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$
	$-17 \leq l \leq 17$
Reflections Collected/Unique	13320/6836 [R(int) = 0.0294]
Completeness to Theta	99.80%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	6836/252/589
Goodness-of-fit on F^2	1.012
Final R Indices [I >2sigma(I)]	R1 = 0.0649 wR2 = 0.1847
R Indices (All Data)	R1 = 0.0827 wR2 = 0.2071
Largest Diff. Peak and Hole	0.815 and -0.274 $e^-/Å^3$

Table 49. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ **IX**

Atom	X	Y	Z	U(eq)
Al(1)	6035(2)	3147(2)	7738(1)	84(1)
Br(1)	9457(1)	2832(1)	2791(1)	97(1)
Br(2)	6438(1)	1028(1)	4261(1)	95(1)
Br(3)	8290(1)	291(1)	1458(1)	105(1)
Br(4)	9112(1)	363(1)	3332(1)	84(1)
C(1)	4890(5)	3362(4)	8657(4)	75(2)
C(1A)	6966(5)	4184(5)	7413(4)	90(2)
C(2)	5188(7)	3632(7)	9381(4)	116(3)
C(2A)	7671(10)	4002(10)	6676(7)	199(6)
C(3)	4397(9)	2455(7)	8916(6)	151(4)
C(3A)	6354(8)	5184(7)	7291(8)	177(5)
C(4)	4030(7)	4156(7)	8419(5)	131(3)
C(4A)	7634(9)	4212(9)	8015(7)	170(4)
C(5)	4238(8)	3784(7)	10062(5)	116(3)
C(5A)	8361(13)	4852(12)	6339(9)	200(6)
C(6)	3477(12)	2556(10)	9615(9)	196(6)
C(6A)	7115(12)	5980(10)	7074(12)	221(7)
C(7)	3066(9)	4237(10)	9090(6)	161(4)
C(7A)	8460(13)	4931(13)	7703(9)	200(6)
C(8)	3445(8)	4524(7)	9758(6)	130(3)
C(8A)	9036(10)	4738(13)	6942(11)	229(7)
C(9)	3866(12)	2848(9)	10288(7)	194(6)
C(9A)	7685(14)	5766(12)	6287(9)	215(7)
C(10)	2681(11)	3346(14)	9328(9)	209(7)
C(10A)	7829(13)	5835(13)	7641(10)	209(7)
C(21)	5366(7)	3026(8)	6817(5)	128(3)
C(22)	6947(8)	1893(7)	8038(7)	154(4)
C(23)	6836(7)	2650(6)	2293(5)	106(3)
C(24)	6459(9)	2620(8)	1570(7)	150(4)
C(25)	9191(12)	2489(10)	4876(7)	173(5)
C(26)	10242(11)	2260(12)	4863(9)	215(7)
C(27)	8600(9)	945(9)	5279(7)	147(4)
C(28)	8100(10)	1020(12)	6003(7)	187(6)
C(29)	7196(9)	4315(7)	3482(6)	136(3)
C(30)	7646(12)	4969(8)	3811(8)	188(5)
C(31)	6386(8)	3430(7)	4657(5)	123(3)
C(32)	5295(8)	3704(8)	4543(6)	145(4)

Atom	X	Y	Z	U(eq)
C(33)	4812(9)	1033(9)	2849(8)	161(4)
C(34)	4106(9)	526(12)	3444(8)	203(7)
C(35)	5674(10)	-212(7)	2046(7)	155(4)
C(36)	5416(10)	247(8)	1262(7)	160(4)
C(37)	6567(10)	-1418(9)	3829(9)	180(5)
C(38)	6891(13)	-1828(11)	4553(8)	214(7)
C(39)	8266(13)	-1701(10)	3013(9)	189(6)
C(40)	8073(16)	-2296(11)	2547(9)	238(9)
C(41)	8920(11)	3640(9)	879(7)	171(5)
C(42)	9815(12)	4080(10)	796(9)	208(7)
C(43)	9313(19)	2302(12)	207(8)	277(11)
C(44)	9110(30)	2555(17)	-396(11)	373(15)
C(45)	11432(9)	1633(9)	1564(7)	160(4)
C(46)	12036(9)	1392(9)	2187(8)	166(5)
C(47)	11010(9)	108(9)	1495(8)	160(4)
C(48)	11479(16)	-49(14)	710(8)	297(12)
Mg(1)	7959(2)	2046(1)	3671(1)	68(1)
Mg(2)	7240(2)	467(2)	2873(1)	78(1)
Mg(3)	9075(2)	1601(2)	1977(1)	74(1)
O(1)	7536(3)	1904(3)	2573(2)	80(2)
O(2)	8604(3)	1851(3)	4702(2)	76(1)
O(3)	7121(4)	3377(3)	3942(3)	86(1)
O(4)	5781(4)	457(4)	2558(3)	104(2)
O(5)	7350(5)	-1005(4)	3257(3)	103(2)
O(6)	9160(4)	2568(5)	924(3)	115(2)
O(7)	10624(4)	1051(4)	1639(3)	92(1)

Table 50. Bond lengths [Å] for [$Mg_3Br_4(OEt)(OEt_2)_6$][Ada_2AlMe_2] **IX**

Atoms	Distance	Atoms	Distance
Al(1)-C(21)	2.012(8)	Mg(2)-O(1)	2.124(4)
Al(1)-C(22)	2.023(9)	Mg(2)-Br(3)	2.646(3)
Al(1)-C(1)	2.029(7)	Mg(2)-Br(2)	2.666(2)
Al(1)-C(1A)	2.039(7)	Mg(2)-Br(4)	2.703(2)
C(1)-C(2)	1.517(9)	Mg(3)-O(7)	2.080(5)
C(1)-C(4)	1.518(10)	Mg(3)-O(6)	2.106(5)

Atoms	Distance	Atoms	Distance
C(1)-C(3)	1.521(9)	Mg(3)-O(1)	2.125(4)
C(2)-C(5)	1.584(11)	Mg(3)-Br(1)	2.608(2)
C(3)-C(6)	1.572(13)	Mg(3)-Br(3)	2.649(2)
C(4)-C(7)	1.577(12)	Mg(3)-Br(4)	2.710(2)
C(5)-C(8)	1.454(12)	O(1)-C(23)	1.367(9)
C(5)-C(9)	1.477(13)	C(23)-C(24)	1.447(12)
C(6)-C(10)	1.487(18)	O(2)-C(25)	1.399(11)
C(6)-C(9)	1.508(16)	O(2)-C(27)	1.504(12)
C(7)-C(10)	1.428(16)	C(25)-C(26)	1.366(17)
C(7)-C(8)	1.490(13)	C(27)-C(28)	1.333(14)
C(1A)-C(2A)	1.483(10)	O(3)-C(31)	1.445(9)
C(1A)-C(4A)	1.496(11)	O(3)-C(29)	1.455(10)
C(1A)-C(3A)	1.516(11)	C(29)-C(30)	1.437(15)
C(2A)-C(5A)	1.620(14)	C(31)-C(32)	1.466(13)
C(3A)-C(6A)	1.606(14)	O(4)-C(33)	1.456(12)
C(4A)-C(7A)	1.598(14)	O(4)-C(35)	1.457(12)
C(5A)-C(9A)	1.448(16)	C(33)-C(34)	1.459(16)
C(5A)-C(8A)	1.466(16)	C(35)-C(36)	1.485(14)
C(6A)-C(10A)	1.450(18)	O(5)-C(37)	1.440(14)
C(6A)-C(9A)	1.501(18)	O(5)-C(39)	1.476(16)
C(7A)-C(10A)	1.409(17)	C(37)-C(38)	1.405(16)
C(7A)-C(8A)	1.456(15)	C(39)-C(40)	1.357(16)
Mg(1)-O(2)	2.080(5)	O(6)-C(43)	1.342(16)
Mg(1)-O(3)	2.112(5)	O(6)-C(41)	1.504(13)
Mg(1)-O(1)	2.141(4)	C(41)-C(42)	1.411(18)
Mg(1)-Br(1)	2.586(2)	C(43)-C(44)	1.117(18)
Mg(1)-Br(2)	2.654(2)	O(7)-C(47)	1.406(11)
Mg(1)-Br(4)	2.713(2)	O(7)-C(45)	1.443(13)
Mg(2)-O(5)	2.091(5)	C(45)-C(46)	1.422(15)
Mg(2)-O(4)	2.099(5)	C(47)-C(48)	1.441(16)

Table 51. Bond angles [º] for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ **IX**

Atoms	Angles	Atoms	Angels
C(21)-Al(1)-C(22)	108.5(5)	O(1)-Mg(2)-Br(3)	83.14(13)
C(21)-Al(1)-C(1)	107.9(3)	O(5)-Mg(2)-Br(2)	96.62(19)
C(22)-Al(1)-C(1)	107.8(4)	O(4)-Mg(2)-Br(2)	93.78(19)
C(21)-Al(1)-C(1A)	109.2(3)	O(1)-Mg(2)-Br(2)	83.19(13)
C(22)-Al(1)-C(1A)	107.8(4)	Br(3)-Mg(2)-Br(2)	165.31(9)
C(1)-Al(1)-C(1A)	115.5(3)	O(5)-Mg(2)-Br(4)	87.04(17)
C(2)-C(1)-C(4)	105.0(6)	O(4)-Mg(2)-Br(4)	176.21(17)
C(2)-C(1)-C(3)	107.2(7)	O(1)-Mg(2)-Br(4)	77.42(13)
C(4)-C(1)-C(3)	106.6(8)	Br(3)-Mg(2)-Br(4)	86.00(7)
C(2)-C(1)-Al(1)	117.4(5)	Br(2)-Mg(2)-Br(4)	85.83(7)
C(4)-C(1)-Al(1)	111.2(5)	O(7)-Mg(3)-O(6)	88.0(2)
C(3)-C(1)-Al(1)	108.8(5)	O(7)-Mg(3)-O(1)	165.7(2)
C(1)-C(2)-C(5)	113.3(7)	O(6)-Mg(3)-O(1)	106.3(2)
C(1)-C(3)-C(6)	112.8(7)	O(7)-Mg(3)-Br(1)	95.70(17)
C(1)-C(4)-C(7)	111.8(7)	O(6)-Mg(3)-Br(1)	93.2(2)
C(8)-C(5)-C(9)	111.8(10)	O(1)-Mg(3)-Br(1)	83.49(13)
C(8)-C(5)-C(2)	108.6(7)	O(7)-Mg(3)-Br(3)	95.76(17)
C(9)-C(5)-C(2)	105.7(8)	O(6)-Mg(3)-Br(3)	96.7(2)
C(10)-C(6)-C(9)	108.2(11)	O(1)-Mg(3)-Br(3)	83.03(13)
C(10)-C(6)-C(3)	106.5(12)	Br(1)-Mg(3)-Br(3)	165.06(9)
C(9)-C(6)-C(3)	108.9(11)	O(7)-Mg(3)-Br(4)	88.44(15)
C(10)-C(7)-C(8)	110.2(11)	O(6)-Mg(3)-Br(4)	175.87(19)
C(10)-C(7)-C(4)	111.4(10)	O(1)-Mg(3)-Br(4)	77.26(13)
C(8)-C(7)-C(4)	106.0(10)	Br(1)-Mg(3)-Br(4)	84.98(7)
C(5)-C(8)-C(7)	111.0(8)	Br(3)-Mg(3)-Br(4)	85.80(7)
C(5)-C(9)-C(6)	111.4(9)	Mg(1)-Br(1)-Mg(3)	75.56(7)
C(7)-C(10)-C(6)	112.9(11)	Mg(1)-Br(2)-Mg(2)	74.03(7)
C(2A)-C(1A)-C(4A)	107.3(9)	Mg(2)-Br(3)-Mg(3)	74.13(7)
C(2A)-C(1A)-C(3A)	109.1(9)	Mg(2)-Br(4)-Mg(3)	72.25(7)
C(4A)-C(1A)-C(3A)	105.1(8)	Mg(2)-Br(4)-Mg(1)	72.51(7)
C(2A)-C(1A)-Al(1)	109.5(5)	Mg(3)-Br(4)-Mg(1)	71.87(7)
C(4A)-C(1A)-Al(1)	112.9(6)	C(23)-O(1)-Mg(2)	123.9(4)
C(3A)-C(1A)-Al(1)	112.8(5)	C(23)-O(1)-Mg(3)	122.0(4)
C(1A)-C(2A)-C(5A)	112.2(8)	Mg(2)-O(1)-Mg(3)	97.36(19)
C(1A)-C(3A)-C(6A)	111.1(9)	C(23)-O(1)-Mg(1)	114.0(5)
C(1A)-C(4A)-C(7A)	112.0(9)	Mg(2)-O(1)-Mg(1)	97.36(18)
C(9A)-C(5A)-C(8A)	112.6(13)	Mg(3)-O(1)-Mg(1)	96.51(18)
C(9A)-C(5A)-C(2A)	109.4(12)	O(1)-C(23)-C(24)	119.2(8)

Atoms	Angles	Atoms	Angels
C(8A)-C(5A)-C(2A)	101.4(12)	C(25)-O(2)-C(27)	113.4(7)
C(10A)-C(6A)-C(9A)	110.6(14)	C(25)-O(2)-Mg(1)	123.5(5)
C(10A)-C(6A)-C(3A)	110.2(12)	C(27)-O(2)-Mg(1)	122.6(5)
C(9A)-C(6A)-C(3A)	101.7(13)	C(26)-C(25)-O(2)	121.6(15)
C(10A)-C(7A)-C(8A)	111.2(15)	C(28)-C(27)-O(2)	117.2(11)
C(10A)-C(7A)-C(4A)	102.9(13)	C(31)-O(3)-C(29)	112.3(6)
C(8A)-C(7A)-C(4A)	110.7(11)	C(31)-O(3)-Mg(1)	120.7(5)
C(7A)-C(8A)-C(5A)	112.6(11)	C(29)-O(3)-Mg(1)	127.0(5)
C(5A)-C(9A)-C(6A)	112.3(13)	C(30)-C(29)-O(3)	116.8(10)
C(7A)-C(10A)-C(6A)	114.8(14)	O(3)-C(31)-C(32)	115.0(8)
O(2)-Mg(1)-O(3)	89.99(19)	C(33)-O(4)-C(35)	114.7(8)
O(2)-Mg(1)-O(1)	165.4(2)	C(33)-O(4)-Mg(2)	125.5(6)
O(3)-Mg(1)-O(1)	104.58(19)	C(35)-O(4)-Mg(2)	119.7(6)
O(2)-Mg(1)-Br(1)	95.52(14)	O(4)-C(33)-C(34)	115.7(11)
O(3)-Mg(1)-Br(1)	92.89(14)	O(4)-C(35)-C(36)	114.4(8)
O(1)-Mg(1)-Br(1)	83.73(12)	C(37)-O(5)-C(39)	114.3(8)
O(2)-Mg(1)-Br(2)	95.64(14)	C(37)-O(5)-Mg(2)	122.5(7)
O(3)-Mg(1)-Br(2)	96.21(15)	C(39)-O(5)-Mg(2)	123.1(6)
O(1)-Mg(1)-Br(2)	83.17(12)	C(38)-C(37)-O(5)	114.8(11)
Br(1)-Mg(1)-Br(2)	165.58(9)	C(40)-C(39)-O(5)	113.4(14)
O(2)-Mg(1)-Br(4)	88.50(14)	C(43)-O(6)-C(41)	111.2(9)
O(3)-Mg(1)-Br(4)	177.55(16)	C(43)-O(6)-Mg(3)	123.9(8)
O(1)-Mg(1)-Br(4)	76.93(13)	C(41)-O(6)-Mg(3)	124.4(6)
Br(1)-Mg(1)-Br(4)	85.33(7)	C(42)-C(41)-O(6)	113.2(11)
Br(2)-Mg(1)-Br(4)	85.86(6)	C(44)-C(43)-O(6)	141(2)
O(5)-Mg(2)-O(4)	89.3(2)	C(47)-O(7)-C(45)	113.1(8)
O(5)-Mg(2)-O(1)	164.4(2)	C(47)-O(7)-Mg(3)	126.1(6)
O(4)-Mg(2)-O(1)	106.3(2)	C(45)-O(7)-Mg(3)	120.8(6)
O(5)-Mg(2)-Br(3)	95.1(2)	C(46)-C(45)-O(7)	113.5(10)
O(4)-Mg(2)-Br(3)	95.17(19)	O(7)-C(47)-C(48)	118.6(13)

5.9 STRUCTURAL DATA OF [$Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8$] **X**

Table 52. Crystal data and structural refinement for [$Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8$] **X**

Empirical Formula	$C_{32}H_{82}Br_{10}Mg_6O_{10}$
Formula Weight	1571.94
Collection Temperature	293(2)K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 11.197(2) Å b = 12.196(2) Å c = 12.879(3) Å α = 104.81(3)° β = 95.15(3)° γ = 112.35(3)°
Volume	1537.9(5) $Å^3$
Z	1
Calculated Density	1.697 g/cm^3
Absorption Coefficient	6.615 mm^{-1}
F(000)	776
Crystal Size	0.45 x 0.41 x 0.37 mm
Theta Range for Data Collection	1.90 to 28.27°
Limiting Indices	$-13 \leq h \leq 14$ $-16 \leq k \leq 16$ $-17 \leq l \leq 16$
Reflections Collected/Unique	9142/6232 [R(int) = 0.0272]
Completeness to Theta	81.70%
Absorption Correction	SADABS
Refinement Method	Full-Matrix Least-Squares on F^2
Data/Restraints/Parameters	6232/0/275
Goodness-of-fit on F^2	1.05
Final R Indices [I >2sigma(I)]	R1 = 0.0672 wR2 = 0.1973
R Indices (All Data)	R1 = 0.1233 wR2 = 0.2391
Largest Diff. Peak and Hole	1.310 and -0.558 $e^-/Å^3$

Table 53. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8]$ **X**

Atom	X	Y	Z	U(eq)
Mg(1)	6228(2)	3902(2)	8671(2)	50(1)
Mg(2)	3406(2)	1766(2)	7500(2)	53(1)
Mg(3)	6076(2)	5405(2)	12081(2)	51(1)
Br(1)	3642(1)	3888(1)	11164(1)	65(1)
Br(2)	8270(1)	7406(1)	13150(1)	74(1)
Br(3)	7128(1)	4348(1)	10710(1)	63(1)
Br(4)	5099(1)	3340(1)	6488(1)	68(1)
Br(5)	5496(1)	1430(1)	8099(1)	69(1)
O(1)	4300(4)	3452(4)	8667(4)	42(1)
O(2)	8068(5)	4321(5)	8286(4)	40(1)
O(3)	2628(7)	174(6)	6143(6)	58(2)
O(4)	2279(5)	802(5)	8475(5)	43(1)
O(5)	6223(8)	4430(6)	13120(7)	53(2)
C(1)	8427(13)	3415(12)	7654(13)	98(5)
C(2)	9144(10)	5498(11)	8786(10)	72(3)
C(3)	8951(15)	2821(17)	8174(18)	158(9)
C(4)	9529(15)	6253(13)	8088(14)	112(5)
C(5)	1330(20)	-568(18)	5857(15)	159(9)
C(6)	3340(20)	-177(18)	5362(17)	160(10)
C(7)	3100(30)	138(18)	4395(17)	190(12)
C(8)	1020(20)	-1948(13)	5731(17)	163(9)
C(9)	1273(14)	1090(15)	8894(14)	113(6)
C(10)	2610(18)	100(20)	8990(20)	182(12)
C(11)	4(16)	370(20)	8560(19)	161(9)
C(12)	3177(19)	240(30)	9868(17)	177(11)
C(13)	5890(30)	3330(50)	12790(30)	270(30)
C(14)	6793(18)	4914(14)	14242(13)	112(5)
C(15)	4900(40)	2670(30)	13010(20)	250(20)
C(16)	7988(19)	4870(18)	14543(17)	152(8)

Table 54. Bond lengths [Å] for [$Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8$] **X***

Atoms	Distance	Atoms	Distance
Mg(1)-O(1)	2.015(5)	Mg(3)-Mg(1)#1	3.153(3)
Mg(1)-O(2)	2.065(5)	Mg(3)-Mg(2)#1	3.162(3)
Mg(1)-Br(3)	2.566(3)	Br(1)-Mg(1)#1	2.596(3)
Mg(1)-Br(1)#1	2.596(3)	Br(2)-Mg(2)#1	2.614(3)
Mg(1)-Br(5)	2.679(3)	Br(4)-Mg(3)#1	2.827(3)
Mg(1)-Br(4)	2.774(3)	O(1)-Mg(3)#1	2.027(5)
Mg(1)-Mg(2)	3.150(4)	O(2)-C(1)	1.409(13)
Mg(1)-Mg(3)#1	3.153(3)	O(2)-C(2)	1.414(12)
Mg(2)-O(1)	2.019(5)	O(3)-C(5)	1.34(2)
Mg(2)-O(3)	2.071(7)	O(3)-C(6)	1.42(2)
Mg(2)-O(4)	2.112(6)	O(4)-C(10)	1.342(17)
Mg(2)-Br(5)	2.609(3)	O(4)-C(9)	1.414(17)
Mg(2)-Br(2)#1	2.614(3)	O(5)-C(13)	1.19(5)
Mg(2)-Br(4)	2.816(3)	O(5)-C(14)	1.398(17)
Mg(2)-Mg(3)#1	3.162(3)	C(1)-C(3)	1.35(2)
Mg(3)-O(1)#1	2.027(5)	C(2)-C(4)	1.425(17)
Mg(3)-O(5)	2.038(7)	C(5)-C(8)	1.54(2)
Mg(3)-Br(3)	2.556(2)	C(6)-C(7)	1.43(3)
Mg(3)-Br(1)	2.592(3)	C(9)-C(11)	1.31(2)
Mg(3)-Br(2)	2.647(3)	C(10)-C(12)	1.18(3)
Mg(3)-Br(4)#1	2.827(3)	C(13)-C(15)	1.20(4)
Mg(3)-C(13)	2.84(4)	C(14)-C(16)	1.38(2)

* Symmetry transformations used to generate equivalent atoms: #1 –x + 1, -y + 1, -z + 2.

Table 55. Bond angles [º] for [$Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_8(OEt_2)_8$] **X***

Atoms	Angles	Atoms	Angels
O(1)-Mg(1)-O(2)	166.2(2)	O(1)#1-Mg(3)-Br(2)	84.59(15)
O(1)-Mg(1)-Br(3)	100.64(16)	O(5)-Mg(3)-Br(2)	94.6(2)
O(2)-Mg(1)-Br(3)	93.07(17)	Br(3)-Mg(3)-Br(2)	96.56(9)
O(1)-Mg(1)-Br(1)#1	84.24(14)	Br(1)-Mg(3)-Br(2)	164.07(10)
O(2)-Mg(1)-Br(1)#1	93.06(18)	O(1)#1-Mg(3)-Br(4)#1	74.55(14)
Br(3)-Mg(1)-Br(1)#1	96.77(9)	O(5)-Mg(3)-Br(4)#1	90.9(2)
O(1)-Mg(1)-Br(5)	84.36(14)	Br(3)-Mg(3)-Br(4)#1	176.50(10)
O(2)-Mg(1)-Br(5)	95.50(17)	Br(1)-Mg(3)-Br(4)#1	83.11(8)

Atoms	Angles	Atoms	Angels
Br(3)-Mg(1)-Br(5)	95.76(9)	Br(2)-Mg(3)-Br(4)#1	83.09(8)
Br(1)#1-Mg(1)-Br(5)	164.40(10)	O(1)#1-Mg(3)-C(13)	164.1(8)
O(1)-Mg(1)-Br(4)	75.98(15)	O(5)-Mg(3)-C(13)	20.9(9)
O(2)-Mg(1)-Br(4)	90.34(17)	Br(3)-Mg(3)-C(13)	78.5(8)
Br(3)-Mg(1)-Br(4)	176.43(9)	Br(1)-Mg(3)-C(13)	80.0(7)
Br(1)#1-Mg(1)-Br(4)	84.09(8)	Br(2)-Mg(3)-C(13)	111.2(8)
Br(5)-Mg(1)-Br(4)	82.85(8)	Br(4)#1-Mg(3)-C(13)	104.8(8)
O(1)-Mg(1)-Mg(2)	38.70(14)	O(1)#1-Mg(3)-Mg(1)#1	38.60(13)
O(2)-Mg(1)-Mg(2)	132.97(18)	O(5)-Mg(3)-Mg(1)#1	130.9(3)
Br(3)-Mg(1)-Mg(2)	120.26(10)	Br(3)-Mg(3)-Mg(1)#1	122.29(9)
Br(1)#1-Mg(1)-Mg(2)	112.72(9)	Br(1)-Mg(3)-Mg(1)#1	52.63(7)
Br(5)-Mg(1)-Mg(2)	52.42(7)	Br(2)-Mg(3)-Mg(1)#1	112.29(9)
Br(4)-Mg(1)-Mg(2)	56.34(7)	Br(4)#1-Mg(3)-Mg(1)#1	54.96(6)
O(1)-Mg(1)-Mg(3)#1	38.88(13)	C(13)-Mg(3)-Mg(1)#1	128.0(6)
O(2)-Mg(1)-Mg(3)#1	130.92(19)	O(1)#1-Mg(3)-Mg(2)#1	38.49(14)
Br(3)-Mg(1)-Mg(3)#1	121.40(9)	O(5)-Mg(3)-Mg(2)#1	132.2(2)
Br(1)#1-Mg(1)-Mg(3)#1	52.52(7)	Br(3)-Mg(3)-Mg(2)#1	121.38(9)
Br(5)-Mg(1)-Mg(3)#1	112.57(9)	Br(1)-Mg(3)-Mg(2)#1	112.44(9)
Br(4)-Mg(1)-Mg(3)#1	56.55(7)	Br(2)-Mg(3)-Mg(2)#1	52.58(7)
Mg(2)-Mg(1)-Mg(3)#1	60.24(7)	Br(4)#1-Mg(3)-Mg(2)#1	55.75(7)
O(1)-Mg(2)-O(3)	171.4(3)	C(13)-Mg(3)-Mg(2)#1	152.9(9)
O(1)-Mg(2)-O(4)	96.8(2)	Mg(1)#1-Mg(3)-Mg(2)#1	59.84(8)
O(3)-Mg(2)-O(4)	91.8(3)	Mg(3)-Br(1)-Mg(1)#1	74.85(8)
O(1)-Mg(2)-Br(5)	86.17(15)	Mg(2)#1-Br(2)-Mg(3)	73.90(8)
O(3)-Mg(2)-Br(5)	94.0(2)	Mg(3)-Br(3)-Mg(1)	116.30(8)
O(4)-Mg(2)-Br(5)	94.84(18)	Mg(1)-Br(4)-Mg(2)	68.58(8)
O(1)-Mg(2)-Br(2)#1	85.62(14)	Mg(1)-Br(4)-Mg(3)#1	68.49(7)
O(3)-Mg(2)-Br(2)#1	92.5(2)	Mg(2)-Br(4)-Mg(3)#1	68.16(7)
O(4)-Mg(2)-Br(2)#1	97.10(17)	Mg(2)-Br(5)-Mg(1)	73.10(8)
Br(5)-Mg(2)-Br(2)#1	166.23(10)	Mg(1)-O(1)-Mg(2)	102.7(2)
O(1)-Mg(2)-Br(4)	74.92(14)	Mg(1)-O(1)-Mg(3)#1	102.5(2)
O(3)-Mg(2)-Br(4)	96.5(2)	Mg(2)-O(1)-Mg(3)#1	102.8(2)
O(4)-Mg(2)-Br(4)	171.64(19)	C(1)-O(2)-C(2)	113.5(8)
Br(5)-Mg(2)-Br(4)	83.31(7)	C(1)-O(2)-Mg(1)	123.1(6)
Br(2)#1-Mg(2)-Br(4)	83.89(8)	C(2)-O(2)-Mg(1)	122.6(5)
O(1)-Mg(2)-Mg(1)	38.61(13)	C(5)-O(3)-C(6)	112.8(11)
O(3)-Mg(2)-Mg(1)	136.4(2)	C(5)-O(3)-Mg(2)	121.6(9)
O(4)-Mg(2)-Mg(1)	117.38(19)	C(6)-O(3)-Mg(2)	125.2(8)
Br(5)-Mg(2)-Mg(1)	54.48(7)	C(10)-O(4)-C(9)	110.6(10)

Atoms	Angles	Atoms	Angels
Br(2)#1-Mg(2)-Mg(1)	113.32(9)	C(10)-O(4)-Mg(2)	125.2(7)
Br(4)-Mg(2)-Mg(1)	55.08(6)	C(9)-O(4)-Mg(2)	122.2(6)
O(1)-Mg(2)-Mg(3)#1	38.68(14)	C(13)-O(5)-C(14)	111.1(16)
O(3)-Mg(2)-Mg(3)#1	135.0(2)	C(13)-O(5)-Mg(3)	121.4(15)
O(4)-Mg(2)-Mg(3)#1	118.09(18)	C(14)-O(5)-Mg(3)	127.3(7)
Br(5)-Mg(2)-Mg(3)#1	114.32(9)	C(3)-C(1)-O(2)	118.5(14)
Br(2)#1-Mg(2)-Mg(3)#1	53.52(7)	O(2)-C(2)-C(4)	115.2(11)
Br(4)-Mg(2)-Mg(3)#1	56.08(6)	O(3)-C(5)-C(8)	113.3(17)
Mg(1)-Mg(2)-Mg(3)#1	59.93(7)	O(3)-C(6)-C(7)	111.3(18)
O(1)#1-Mg(3)-O(5)	165.5(3)	C(11)-C(9)-O(4)	124.8(18)
O(1)#1-Mg(3)-Br(3)	101.96(15)	C(12)-C(10)-O(4)	137(3)
O(5)-Mg(3)-Br(3)	92.6(2)	C(15)-C(13)-O(5)	119(5)
O(1)#1-Mg(3)-Br(1)	84.11(15)	C(15)-C(13)-Mg(3)	123(3)
O(5)-Mg(3)-Br(1)	93.6(3)	O(5)-C(13)-Mg(3)	37.7(10)
Br(3)-Mg(3)-Br(1)	96.73(9)	C(16)-C(14)-O(5)	116.5(16)

* Symmetry transformations used to generate equivalent atoms: #1 –x + 1, -y + 1, -z + 2.

APPENDIX B

RESEARCH PUBLICATIONS

Co-Authored by Jason K. Vohs

1. “Formation of a diphosphine: synthesis and molecular structure of bis(tetraphenylbutadienyl)diphosphine, $(Ph_4C_4)P\text{-}P(C_4Ph_4)$”

   Vohs, J. K.; Wei, P.; Su, J.; Beck, B. C.; Goodwin, S. D.; Robinson, G. H. *Chem. Commun.* **2000**, 1037-1038.

2. “Synthesis and molecular structure of a novel ring-fused borane derivative $[(PhC)_8C_2H_5]B$”

   Brown, S. G.; Wei, P.; Beck, B. C.; Vohs, J. K., Robinson, G. H. *J. Chem. Crystallogr.* **2002**, *31*, 467-470.

3. “Synthesis and molecular structure of tris(pentamethylphenyl)gallium”

   Vohs, J. K.; Downs, L. E.; Barfield, M. E.; Goodwin, S. D.; Robinson, G. H. *Polyhedron* **2002**, *21*, 531-534.

4. “Synthesis and molecular structure of tris(pentamethylphenyl)aluminum, $(C_6Me_5)_3Al$, and the cluster $[Mg_6(\mu_3\text{-}OH)_2(\mu_3\text{-}Br)_2(\mu_2\text{-}Br)_8(OEt_2)_8]$”

   Vohs, J. K.; Downs, L. E.; Stasalovich, J.; Barfield, M. E.; Robinson, G. H. *J. Cluster Sci.* **2002**, *13*, 601-608.

5. “The Protoadamantane Radical Cation”

   Fokin, A. A.; Tkachenko, B. A.; Shubina, T. E.; Gunchenko, P. A.; Gusev, D. V.; Vohs, J. K.; Robinson, G. H.; Yurchenko, A. G.; Schreiner, P. R. *Eur. J. Org. Chem.* **2002**, 3844-3839.

6. “Pseudotetrahedral Polyhaloadamantanes as Chirality Probes: Synthesis, Separation, and Absolute Configuration”

   Schreiner, P. R.; Fokin, A. A.; Lauenstein, O.; Okamoto, Y.; Wakita, T.; Rinderspacher, C.; Robinson, G. H.; Vohs, J. K.; Campana, C. F. *J. Am. Chem. Soc.* **2002**, *124*, 13348-13349.

7. “Unusual trimetallic magnessium cations and adamantyl anions of aluminum and gallium”

   Vohs, J. K.; Downs, L. E.; Barfield, M. E.; Latibeaudiere, K.; Robinson, G. H. *J. Organomet. Chem.* **2003**, *666*, 7-13.