

Synthesis, Functionalization, and Coordination of  
Bulky *m*-Terphenyls and  $\beta$ -Diketiminates

by

Peter Tak Kwong Lee

A Thesis Submitted to  
Saint Mary's University, Halifax, Nova Scotia  
in Partial Fulfillment of the Requirements for  
the Degree of Master of Science in Applied Science

May, 2009, Halifax, Nova Scotia

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## Abstract

### Synthesis, Functionalization, and Coordination of Bulky *m*-Terphenyls and $\beta$ -Diketiminates

By Peter Tak Kwong Lee

The synthesis of *m*-terphenyl iodide and *m*-terphenyl carboxylic acid was performed and described. A large scale, low-cost synthesis was developed for *m*-terphenyl iodide that reduced the number of steps and time required to obtain the material. The subsequent conversion to 2,6-dimesitylbenzoic acid was performed and coordination of the carboxylate anion to cationic lithium was done and structurally characterized by X-ray crystallography.

Spartan '06 calculations of a boron ylidene at the MP2/6-31G\* level suggest that the addition of an electron-donating group to  $\beta$ -diketimate increases the singlet-triplet energy gap. The one-pot synthesis of the modified  $\beta$ -diketimate was successful using the precursor  $[\text{Me}_2\text{NC}(\text{Cl})\text{CHC}(\text{Cl})\text{NMe}_2^+][\text{HCl}_2^-]$  followed by in situ quenching with aniline. Coordination of the new ligand  $[\text{Me}_2\text{NC}(=\text{NPh})\text{CHC}(=\text{NPh})\text{NMe}_2^-]$  to  $-\text{AlMeCl}$  illustrated its capability to have similar properties to the  $\beta$ -diketimate.

May 2009

**Dedication:**

To my family, who give me the love and unconditional support each and every day in the past, today as I stand as the person I have become, and in the many days ahead. To my father, who has given me strength, morality, and discipline. To my mother, who has given me emotion, compassion, and comfort. I am here today because of your time and effort. Thank you.

**Acknowledgements:**

Though the research project bears my name, it is those who I have connected and worked with since the summer of 2006 who share in the success of this research. First and foremost is the Clyburne group. We have gone from three people sitting in a room in McNally in August 2006 to the beautifully renovated lab space we own today filled with bright, intelligent, and curious minds. I am proud to have started, watched, and now leave the group that has increased in strength, numbers, and knowledge. From the beginning to end, I would like to thank those who have started and continued the group I cherish, from Marissa Bender, Ian McIntosh, Katie Nizio, Cassandra Hawco, Craig Cooke, Cody Sherran, and Naomi Harper.

I came to Saint Mary's with the experience and knowledge of working under my previous supervisor, Dr. Charles Walsby at Simon Fraser University. During my first term of academic research, I gained the guidance, experience, autonomy, and friendship of my former group. My research presented here I consider almost a continuation of the research I began there. The group has accepted me as one of their own and continues to welcome my presence as a guest whenever I visit them. My thanks extend to Dr. Charles Walsby, and the group I worked with during the summer of 2006, Stephanie Taylor, Naniye Cetinbas, Tommy He, and Mark Strange.

For their technical assistance, the university is fortunate to have both Darlene Goucher and Elizabeth McLeod for their safety and technical assistance. Instrumentally, I have been aided by Dr. Gabriele Schatte at the Saskatchewan Structural Sciences Centre, Dr. Kathy Robertson at the Atlantic Region Magnetic Resonance Centre, and Dr. Jason Masuda here at Saint Mary's University.

I have shared wonderful experiences with my fellow graduate students, Shawna Mitchell and Christian Kyle. As a group of graduate students who have all worked and grown together, I would like to thank you for your companionship, advice, and friendship during my time here in Halifax.

I would like to especially thank my longtime lab partner, Marissa Bender. The two of us have come a long way from Vancouver, B.C. to share very memorable times. Marissa has been everything from my lab partner, friend, confidant, partner-in-crime, sidekick, and the-one-who-reminds-me-of-what-my-mother-would-say-when-I-am-not-wearing-my-jacket-on-a-cold-winter-evening. We have shared and made positive moments out of tenures. From writing my name in the dust on my desk, to laughing about door's not fitting in the doorway, and testing the wheels on our new chairs, there may have been a lot of change during my time in Halifax, but the one consistency was the companionship I shared with Marissa.

Lastly, I would like to thank my supervisor, Dr. Jason Clyburne. From the time he first gave me an uncomfortable 'double thumbs up' in the hallway at SFU to now where I have completed my work, he has given me advice, knowledge, confidence, and experience. Yet most importantly, he has shown me 'a world beyond Hope.' Thank you.

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**Table of Abbreviations:**

Abbreviation	Full Name
Ar*	2,6-bis(2,4,6-triisopropylphenyl)-1-phenyl
Ar <sup>#</sup>	2,6-bismesityl-1-phenyl
AcAc	acetylacetone
Acac/acac	acetylacetonate
d	doublet
dec	decomposed
Dipp	2,6-diisopropylphenyl
EPR	electron paramagnetic resonance
Et	ethyl
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IR	infrared
<sup>1</sup> Pr	isopropyl
KnicNac	$\beta$ -diamidine, $\text{Me}_2\text{NC}(=\text{NR}')\text{CH}_2\text{C}(=\text{NR})\text{NMe}_2$
Knicnac/knicnac	$\beta$ -amidinate, $\text{Me}_2\text{NC}(=\text{NR}')\text{CH}=\text{C}(\text{NR})\text{NMe}_2$
<i>m</i>	<i>meta</i>
m	multiplet

m	medium (infrared absorption)
Me	methyl
Mes	mesityl, 2,4,6-trimethylphenyl
m.p.	melting point
NacNac	$\beta$ -diketimine, $\text{CH}_3\text{C}(=\text{NR})\text{CH}_2\text{C}(=\text{NR}')\text{CH}_3$
Nacnac/nacnac	$\beta$ -diketimate, $\text{CH}_3\text{C}(=\text{NR})\text{CH}=\text{C}(\text{NR}')\text{CH}_3^-$
NMR	Nuclear magnetic resonance
<i>p</i>	<i>para</i>
Ph	phenyl
PI Salt	dichloro- <i>N,N</i> -dimethylammonium chloride
ppm	parts per million
py	pyridine
s	singlet
s	strong (infrared absorption)
t	triplet
THF	tetrahydrofuran
TMS	trimethylsilyl
Tripp	2,6-bis(2,4,6-triisopropylphenyl)-1-phenyl
vs	very strong (infrared absorption)
vw	very weak (infrared absorption)
w	weak (infrared absorption)

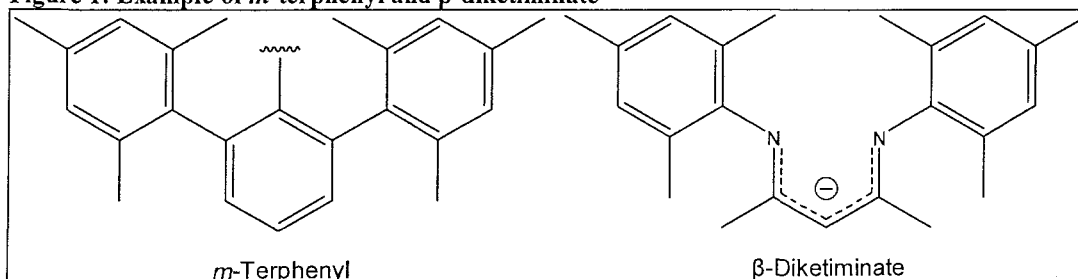
## 1 Introduction to the Chemistry of Bulky Ligands:

### 1.1 *m*-Terphenyl and $\beta$ -Diketiminato in Chemistry

Ligands in inorganic, organic, and materials chemistry bring together many chemical concepts from a wide array of different topics. Whether it is geometry, oxidation state, coordination number, reactivity, acidity,  $pK_A$ , or oligomerization, ligands play a crucial role in a compound's chemical functionality. Yet, ligands are often overlooked because of the chemist's desire for them to be 'innocent' and mere 'spectators'. While the chemistry directly at a metal center is heavily influenced by the ligand, the center is aptly named due to unique chemistry, reaction intermediate, transformation, or interaction occurring at the inorganic metal center. Though overlooked as accessories to the metal, the ligand can dictate observed chemistry as equally as a metal center. Furthermore, chemical properties are intrinsic to the system containing the metal and the ligand.

Two important ligands to be discussed are the *m*-terphenyl and the  $\beta$ -diketiminato, Figure 1, which share an important shape relationship and have found applications in the synthesis of interesting and unusual compounds.<sup>1, 2</sup> While there is a similarity in the size and geometry, differences are apparent in synthesis, functionality, denticity, and coordination.

**Figure 1: Example of *m*-terphenyl and  $\beta$ -diketiminato**



The *m*-terphenyl ligand is known for supporting many unusual transition metal and inorganic compounds.<sup>2-7</sup> As the carboxylate functionality of *m*-terphenyl, the reaction of a neutral acid with an organometallic compound containing a labile ligand has consistently produced an eight-membered dimeric rings  $[ML_nOOCAR^{\#}]_2$ .<sup>8</sup> Despite the numerous structures obtained using this method, one such structure obtained in group deviates, instead forming a four-membered ring with apparently two Sn(III) oxidation states.<sup>2</sup> To date, no further work has been published about the unusual ring structure. Thus, further studies were required to provide chemical insight into the four-membered ring in its synthesis, structure, and coordination.

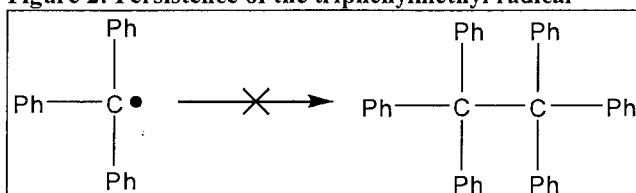
The  $\beta$ -diketiminato, also known as nacnac, relates to the established chemistry of  $\beta$ -diketonates and their well-known keto-enol chemical equilibrium.<sup>9, 10</sup> Utilizing the strength of the backbone similar to  $\beta$ -diketonates, the shape and steric hindrance of *m*-terphenyl, and the electron donating power of two adjacent nitrogen atoms, the nacnac ligand has found prominence stabilizing group 13 ylidenes including phosphorus, gallium, silicon, carbon, and aluminum.<sup>1, 11-13</sup> Though nacnac has many ideal properties as a ligand, its lack of tuneability compared to *m*-terphenyl hinders systematic modification to improve the strengths of the ligand. Changes which improve nacnac by modifying and increasing its potential as a ligand warrants research promoting unique, yet fundamental, chemistry.

## 1.2 The Chemistry of *m*-Terphenyl:

One of the earliest examples of how bulky ligands can affect low-valent chemistry was the discovery of Gomberg's radical, the triphenylmethyl radical.<sup>14, 15</sup> Originally, the

synthesis of hexaphenylethane was desired via the proposed carbon-to-carbon bond formation of triphenylmethyl fragments as shown in Figure 2. While this reaction did not work, the monomeric carbon-based radical was an early example of steric hindrance. Crowding of the hypothetical hexaphenylethane was so great that the proposed carbon-to-carbon bond did not form, resulting instead in the free radical species, the triphenylmethyl radical.

**Figure 2: Persistence of the triphenylmethyl radical**

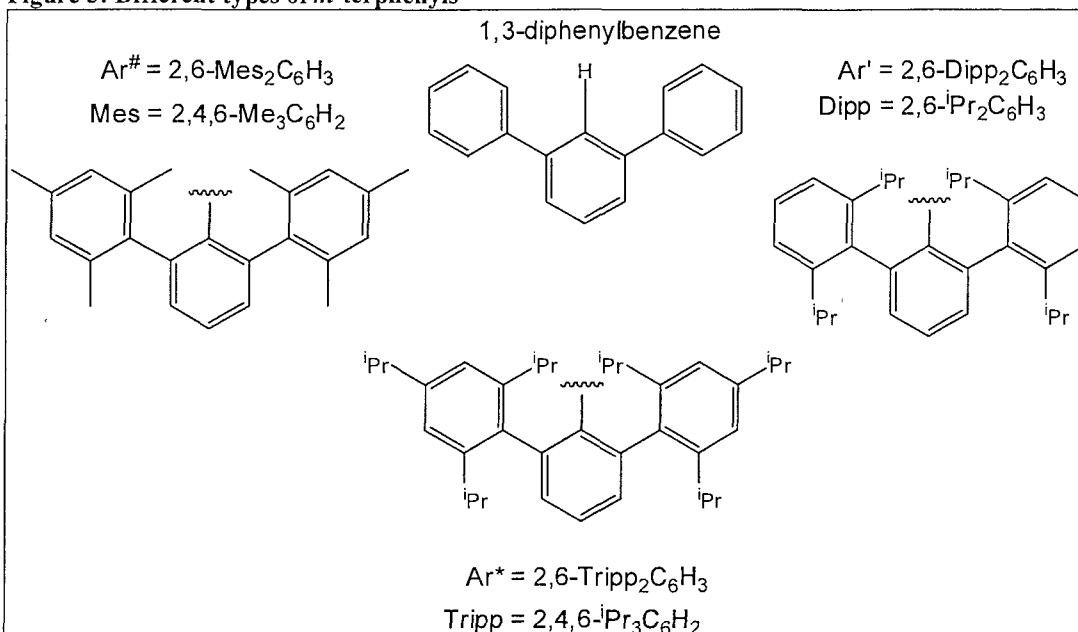


A number of ligands have been designed for new and unusual chemistry by steric control. The concept of blocking potential coordination sites by using large, bulky ligands, has been a common theme amongst many inorganic chemists to control the sterics at a metal center that influences new reactivity.<sup>16</sup>

One such bulky ligand is the *m*-terphenyl, Figure 3. The *m*-terphenyl contains two aryl groups oriented in the *meta* position on a central phenylene ring. The simplest example of a *m*-terphenyl is 2,6-diphenylbenzene.

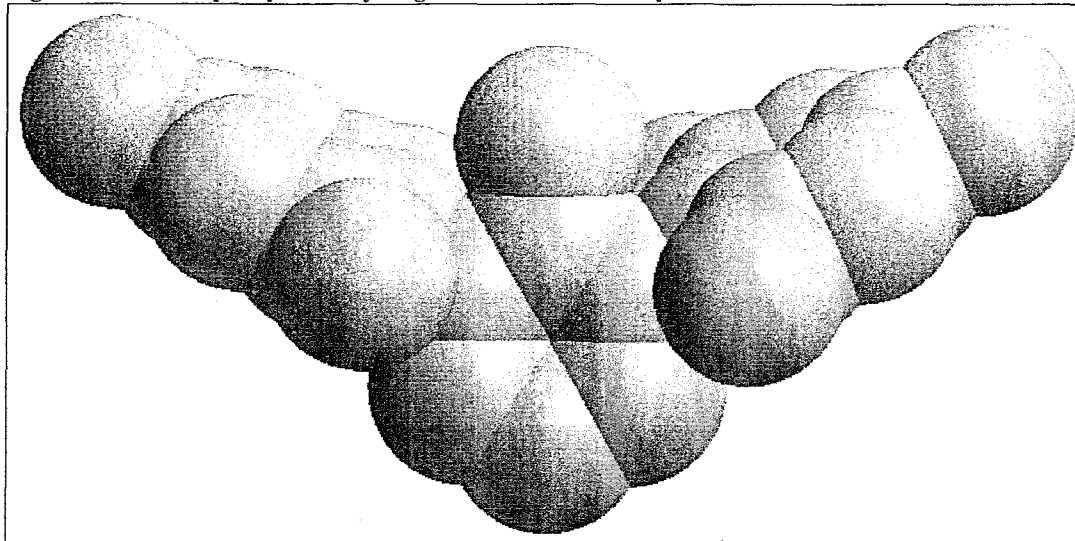


Figure 3: Different types of *m*-terphenyls



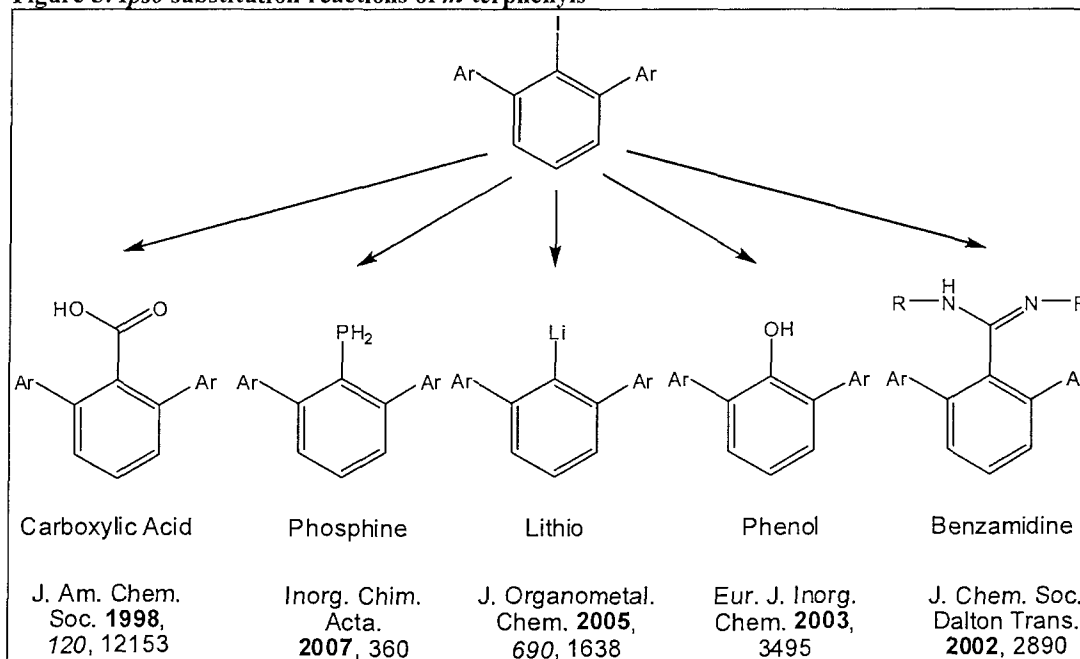
It is well-noted that biphenyls are not planar molecules as would be expected with conjugated alkenes.<sup>17</sup> Due to the steric hindrance of the 2,2'- and 6,6'- substituents, biphenyls adopt a geometry such that the phenyl rings are perpendicular to each other. For *m*-terphenyls, the ring rotation is such that the three rings together form a 'bowl-type' geometry in order to encompass an atom. Figure 4 illustrates this with a space-filling model. Effectively, molecules placed in the center of the *m*-terphenyl are sterically blocked due to the flanking aryl groups of the 'bowl' geometry.

Figure 4: 3D *m*-terphenyl with hydrogens omitted for clarity



To take advantage of the steric properties of *m*-terphenyl, the carbon between the two phenyl groups is functionalized to achieve electronic tuneability of the ligand. The functionalization of *m*-terphenyls was a highly desirable goal as novel *ipso* substitution reactions, Figure 5, have been developed to synthesize desired *m*-terphenyl functional groups, such as phenol, amine, phosphine, amidine, and carboxylic acid.<sup>18-26</sup>

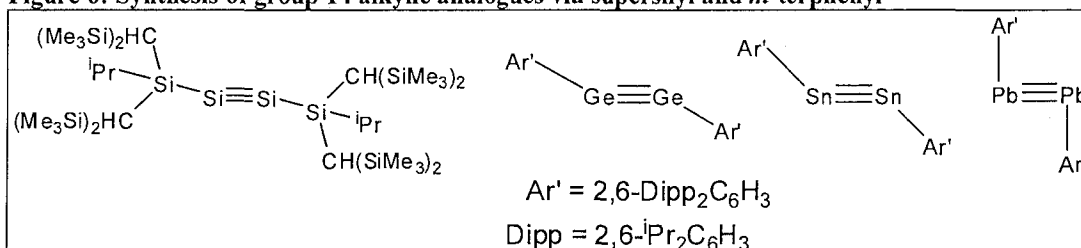
Figure 5: *Ips*o substitution reactions of *m*-terphenyls



In functionalizing *m*-terphenyl, the ligand has separation of the steric portion, the flanking aryl groups, and the electronic piece, the organic functional group. The functional group on *m*-terphenyl can be systematically changed to attain the desired metal-ligand bond strength. Thus, for *m*-terphenyl, electronic tuneability is independent of the bulky nature in *m*-terphenyl. The bonding can be modified by an *ipso* substitution of the functional group without affecting the flanking aryl groups; *m*-terphenyl can be made larger by changing the aryl groups, yet maintain the same functional group.

Using both functionalized and direct-carbon-bonding *m*-terphenyls, a variety of new and novel structures have been synthesized featuring *m*-terphenyl ligands. Of particular interest has been the reported metal-to-metal bonds synthesized by the Power group.<sup>7, 27, 28</sup> With suspected chromium, lead, tin, and germanium homo dinuclear bonding schemes, these molecules have incited a great deal of interest into these bonding schemes, Figure 6.<sup>29, 30</sup> The direct analogy of the group 14 atoms is similar to linear carbon-based alkynes, yet the observed bending of the dihedral angle as the elements become heavier seems to indicate carbon being the site of the unique triple bond.<sup>31</sup>

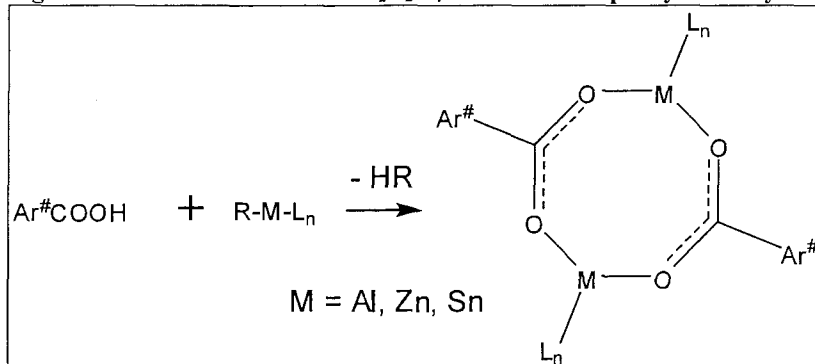
**Figure 6: Synthesis of group 14 alkyne analogues via supersilyl and *m*-terphenyl**



Similarly, functionalized *m*-terphenyls have been used to synthesize low-valent compounds of the type  $\text{M}_2\text{C}_2\text{O}_4$  wherein the compounds form an eight-membered ring.<sup>8, 32, 33</sup> The reaction of a protic functionalized *m*-terphenyl with a variety of basic metal compounds consistently produces the dimeric cyclic species. Although the monomeric

structure was desired, the persistence of the dimeric species indicates a preferred geometry of the anionic functionalized *m*-terphenyls and their coordination structures.

**Figure 7: Generic formation of  $M_2C_2O_4$  cores via *m*-terphenyl carboxylate**



### 1.3 Element Ylidenes:

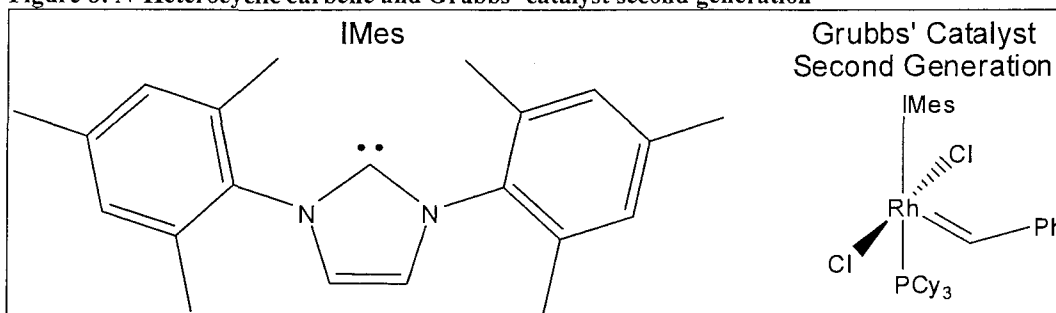
Ylidenes are elements that are formally designated two oxidation states below the highest oxidation state available.<sup>34</sup> For example, a carbon-based ylidene, commonly referred to as a carbene, is formally a carbon (II) oxidation state and can be drawn as a Lewis structure with a neutral carbon with only six electrons surrounding it.<sup>34-36</sup>

Element ylidenes are studied due to their inherent reactivity.<sup>37</sup> While they are isolable molecules, they contain a six-electron core and are particularly reactive towards even weak electrophiles. Such compounds could be used to force reactivity in typically non-reactive compounds such as molecular hydrogen, molecular nitrogen, and carbon dioxide.<sup>38-40</sup>

Carbenes, particularly as the *N*-heterocyclic carbene and derivatives similar, are heavily researched in organic and inorganic chemistry.<sup>34</sup> One of the most common *N*-heterocyclic carbenes is IMes, Figure 8. As ligands, they are heavily studied due to their

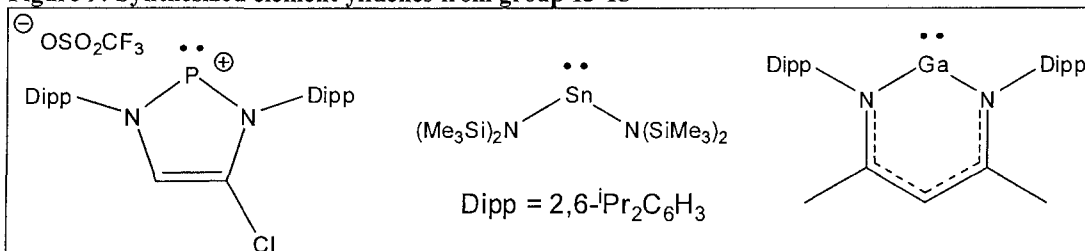
unusual bulky geometry that is similar to the *m*-terphenyl. As free compounds, particular interest has developed in their reactivity and potential as materials.<sup>39</sup>

**Figure 8: *N*-Heterocyclic carbene and Grubbs' catalyst second generation**



With heteroatoms, ylidenes are also extensively studied; their isolation, theoretical properties, and spectroscopy are common topics in the chemical literature. Looking across the main groups 13-15, many such ylidenes have been synthesized and given common names. Neutral compounds such as silylenes, germylenes, and stannylenes have been known before the discovery of *N*-heterocyclic carbenes.<sup>41-43</sup> Group 15 counterparts synthesized as a result of NHC discovery include phosphonium and arsenium cations that are prepared using the 1,4-diazabutadiene backbone.<sup>44</sup> Recently, the synthesis of neutral group 13 analogues of carbene have been synthesized using the NacNac framework using aluminum, gallium, and indium ylidenes.<sup>1, 11, 13, 45</sup>

**Figure 9: Synthesized element ylidenes from group 13-15**

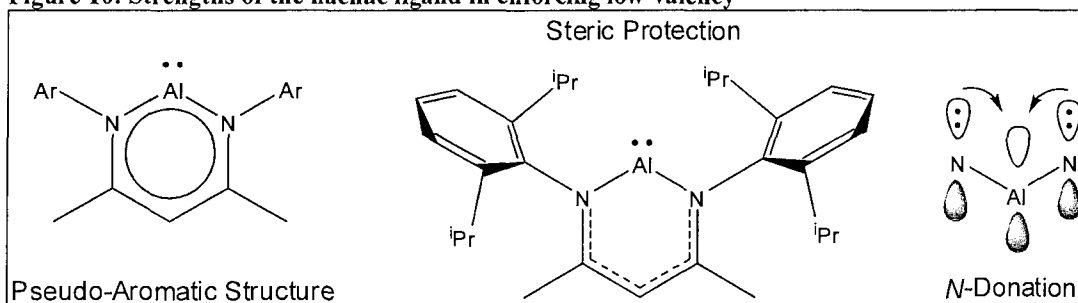


Despite extensive work in ylidenes, the one atom that is excluded from synthesized ylidenes is the boron derivative.<sup>46</sup> Boron, by periodicity, is the most electron-deficient atom of the main group elements and such a hypothetical compound, a divalent,

six-electron boron, would be even more reactive than ylidenes currently reported. Boron's inherent ability to form thermodynamically strong, yet chemically accessible B-H bonds makes low-valent boron-containing compounds a synthetic goal for inorganic chemists.

To date, the nacnac ligand has the closest framework to matching the criteria for forming a boron ylidene based on previous performance with an aluminum derivative.<sup>1</sup> Low-valent nacnac compounds achieve stabilization by several means, as illustrated in Figure 10: the steric protection afforded by the aryl groups creates a similar geometry to *m*-terphenyl which prevents self-association and oligomerization of the free ylidene; the two nitrogen atoms directly adjacent to the aluminum atom allow for electron donation towards the electron deficient aluminum; and the framework of nacnac is a six-membered ring of alternating double bonds which can be argued to be similar to an aromatic compound.

**Figure 10: Strengths of the nacnac ligand in enforcing low-valency**

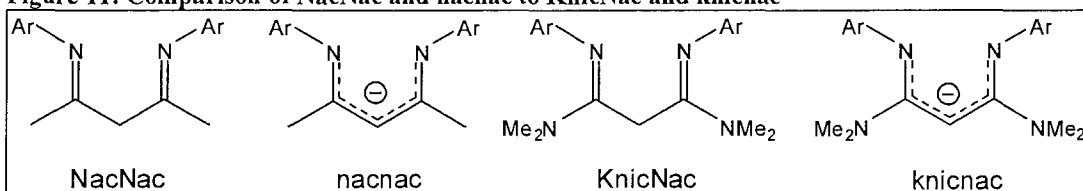


Yet despite the strengths of nacnac, the electronic optimization of the ligand is very limited. With *m*-terphenyl, electronic tuning can occur directly at the binding site by changing the functional group. Yet the functionality of nacnac is highly dependent on the nitrogen atoms, which enforce the steric 'bowl' constraint. Being directly connected, the

nitrogen atoms are a requirement for the nacnac ligand to have the flanking aryl groups which create the bulky ligand effect.

Taking these properties into consideration, an alternative design for nacnac has been established that may be considered an improvement to the properties that make nacnac attractive. This upgraded version, denoted KnicNac in its charge-neutral form and knicnac in its anionic mode, has been synthesized and characterized and an initial coordination compound illustrating its potential as a ligand has been performed with the premise that the ligand may activate new chemistry.

**Figure 11: Comparison of NacNac and nacnac to KnicNac and knicnac**



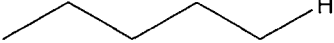
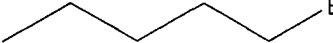
#### 1.4 The Goals of Synthetic Inorganic Chemistry:

The motivation for studying bulky ligands, low-valent elements, *m*-terphenyls, and element ylidenes has been driven by a number of factors, two of them being economics and the environment: economics, by producing highly desirable, costly chemicals in an inexpensive and efficient manner; and environmental, introducing the design of materials to store alternative and environmentally cleaner forms of energy.

Although the conversion of lead into gold has long since been abandoned by chemists, another almost alchemical goal would be the clean and efficient transformation of simple, highly abundant, non-reactive alkanes to halogenated, functionalized, transformable derivatives. Pentane, for example, with chemical formula C<sub>5</sub>H<sub>12</sub>, is a solvent and its costs to chemical research are nearly negligible. Compared to the

molecule 1-bromopentane,  $C_5H_{11}Br$ , which is sold on the gram basis by many chemical companies, they are the same molecule formula-wise except for the exchange of hydrogen, H, with bromine, Br. A non-chemist might compare the data in Table 1 and assume that chemists know of a trivial method of chemically exclusively transforming one atom.

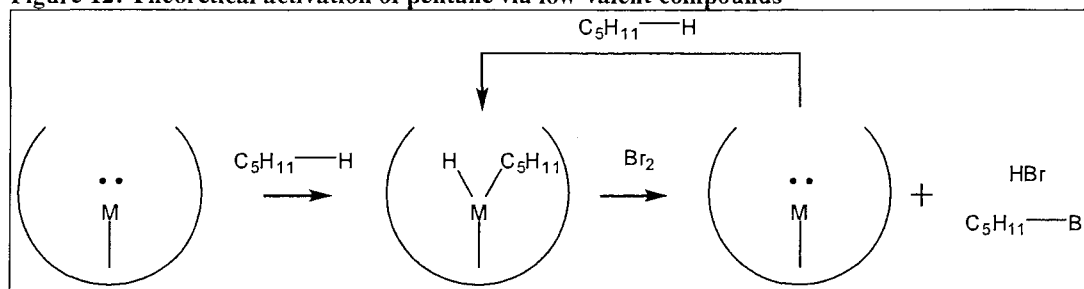
**Table 1: Comparison of pentane to 1-bromopentane**

<b>Chemical Name</b>	<b>Pentane</b>	<b>1-Bromopentane</b>
Structure		
Formula	$C_5H_{12}$	$C_5H_{11}Br$
Cost <sup>47</sup>	\$0.09/g	\$4.74/g

From basic organic chemistry, there exists no simple, clean, efficient, logical method of converting pentane into 1-bromopentane. Pentane is very non-reactive owing to mostly combustion reactions and undesirable radical reactions. Yet, in the presence of a reactive molecule, perhaps containing *m*-terphenyl-shaped sterics or a highly electron-deficient ylidene supported by  $\beta$ -diketiminates, there remains the possibility that pentane can react. Low-valent compounds preferentially react to satisfy their normal valency. The introduction of such a reactive compound to even the non-reactive pentane may result in selective C-H activation, Figure 12, which could then be used to cyclically prepare 1-bromopentane.



**Figure 12: Theoretical activation of pentane via low-valent compounds**

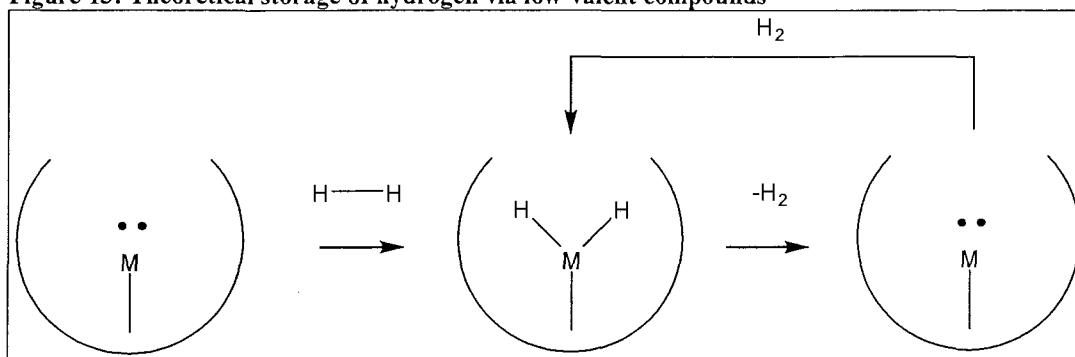


Thus, the synthesis of low-valent compounds is motivated by the potential to make very reactive, yet isolable compounds. These materials can be transported and contained while being reactive enough to activate bonds that are considered inert to most organic chemistry functional group transformations.

Low-valent compounds have also been suggested as a means of hydrogen storage.<sup>48</sup> The development of materials capable of trapping hydrogen chemically, and then releasing it has been extensively researched. Boron-containing compounds are especially favored in this development because of their ability to form strong B-H bonds, yet also be very chemically and thermally labile. For example, sodium borohydride, NaBH<sub>4</sub>, is a chemically benign source of hydride. The reduction of aldehydes and ketones can be performed using sodium borohydride in the solvent methanol. The reaction can be performed as a simple undergraduate experiment. Borohydride contains strongly hydridic B-H bonds such that they withstand the reaction in a protic solvent, methanol, yet are labile enough to react with ketones and aldehydes under mild conditions.

A low-valent boron ylidene may be the answer to a material that can contain hydrogen when introduced, yet also release the gas when mechanically required. The use of such a compound has many fuel cell and hydrogen economy considerations, thus making such a system highly desirable.

Figure 13: Theoretical storage of hydrogen via low-valent compounds



Achieving the desired goal of inorganic chemistry is beyond the scope of the thesis. This work represents some progress towards the ideal that many inorganic chemists share. The conclusions derived from this work are ones that delve to both starts and continuations, with a positive outlook at a hopeful future.

### 1.5 Thesis Report:

This work details the synthesis and chemistry of two ligands, *m*-terphenyl and a modified  $\beta$ -diketiminato. Both the *m*-terphenyl and  $\beta$ -diketiminato are noted for their large, bulky shape and section I illustrates how their shape can influence metal compounds. Section I.4 states, idealistically, a few goals of general inorganic chemistry and how the two ligands are related to those goals.

Section 2 focuses on the chemistry of *m*-terphenyl. The synthesis of *m*-terphenyl iodide is described in section 2.2 using a modified synthesis. The change in functional group on *m*-terphenyl to carboxylic acid is also shown in section 2.2 using a previously established synthesis. The coordination aspect of *m*-terphenyl carboxylate is demonstrated with new compounds with cationic lithium.

The other ligand discussed in section 3 is a modified  $\beta$ -diketiminato, denoted knicnac. This begins with some recent  $\beta$ -diketiminato chemistry and proposals to modify

$\beta$ -diketiminato. The synthesis of the modified  $\beta$ -diketiminato was a reported procedure is written in section 3.4. A demonstration on how the new ligand, knicnac, behaves similarly to  $\beta$ -diketiminato is depicted in section 3.6 that leads to possible future work in this field as extensions to bulky ligand chemistry and other chemistry available to  $\beta$ -diketiminato.

The closing statements of the thesis summarize the results obtained for the progress on *m*-terphenyl and  $\beta$ -diketiminato. Experimental details and synthetic procedures is detailed in section section 2.6 and 3.8 for *m*-terphenyl and  $\beta$ -diketiminato respectively. A general experimental and crystallographic details can be found in section 2.6.1 and 2.6.2, which are applicable to both *m*-terphenyl and  $\beta$ -diketiminato experimental work. All references are found at the end of the thesis.

## 2 The Synthesis, Functionalization, and Coordination of *m*-Terphenyls:

### 2.1 Ligand Performance and the *m*-Terphenyl:

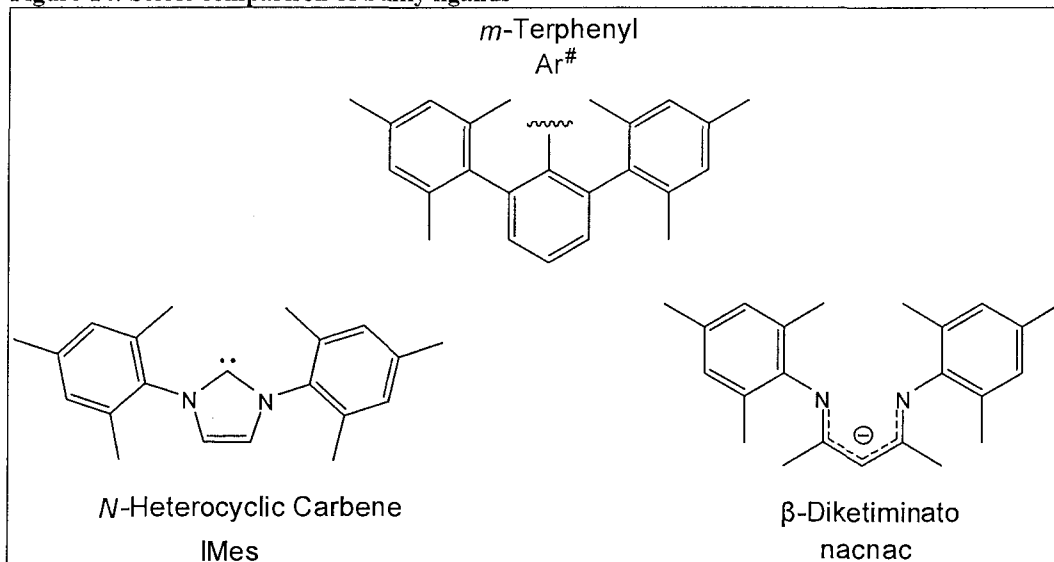
As a ligand, *m*-terphenyl embodies many of the desired characteristics. The very bulky size and unique ‘bowl-shape’ are ideal for low-valent synthesis, enforcing a lower coordination using steric bulk. Yet the ligand also contains many other qualities that make it a strong tool for inorganic chemists. In changing the functional groups, the direct bonding interaction, electronic tuneability, can be adjusted to give the desired bond strength and interaction. Playing the role of the ligand, *m*-terphenyl undergoes few undesirable side reactions, owing to its hydrocarbon framework. Synthetic accessibility in ligands is important to inorganic chemists. The *m*-terphenyl framework is prepared in two-steps, one of which is a very simple bench-top experiment. All of these qualities make *m*-terphenyl desirable for systematic study of the relationship between ligand and center.

The electronic tuneability of *m*-terphenyl is achieved via varying functional groups at the bonding position. Synthetically, numerous *ipso* substitutions have been established predominantly starting from the *m*-terphenyl halide.<sup>19-23, 26</sup> Changing the functional group on the *m*-terphenyl directly modifies the bonding properties of the ligand and varies the chemistry differently from phosphines to amides.

Due to its hydrocarbon framework, *m*-terphenyl as a ligand is relatively inert to most chemical reactions, allowing functional group transformations and metal-ligand binding to occur with the aryl groups maintaining chemical innocence. Yet it has been reported that flanking C-H protons can be involved in cyclometallation as often these protons are chemically accessible to a low-valent metal center.<sup>49</sup>

As mentioned in section 1.2, the bulkiness of *m*-terphenyl is one of the initial attractive points to *m*-terphenyl. The ‘bowl’ shape of *m*-terphenyl is mimicked similarly by nacnac and some *N*-heterocyclic carbenes, Figure 14, that creates a steric pocket such that low valency is enforced by being placed inside the *m*-terphenyl ‘bowl’.<sup>36</sup>

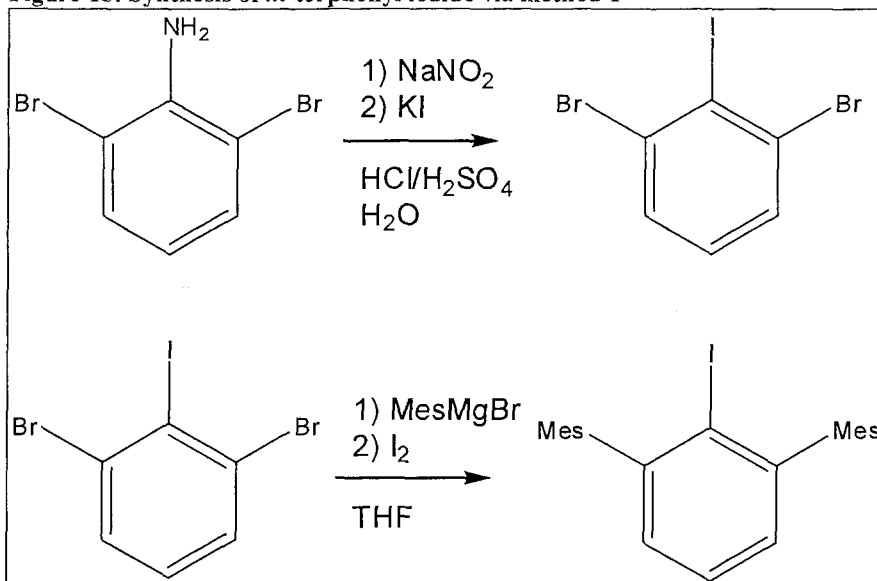
**Figure 14: Steric comparison of bulky ligands**



## 2.2 Synthesis and Functionalization of *m*-Terphenyls

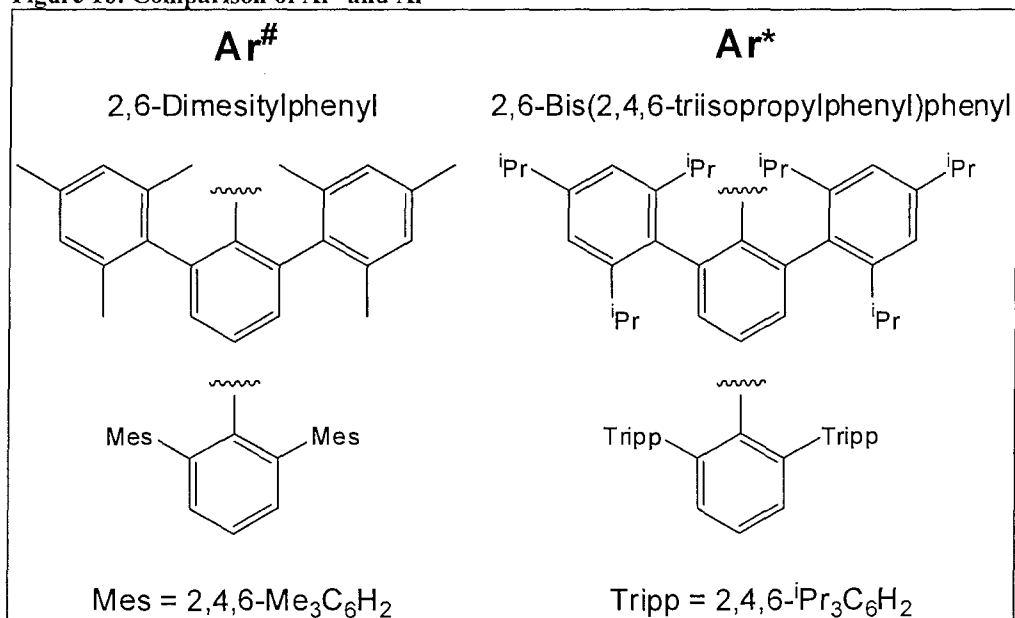
The synthesis of *m*-terphenyl precursors can be obtained in a minimal number of steps. The Clyburne group relied mainly on method 1, Figure 15, to synthesize *m*-terphenyl, which started with 2,6-dibromoaniline.<sup>50</sup> Utilizing a diazonium salt reaction, the first step proceeds to give the desired 2,6-dibromo-1-iodobenzene. The second step to generate *m*-terphenyl iodide is performed in an anhydrous atmosphere where an aryl Grignard reagent is used to replace bromine with 2,4,6-trimethylphenyl, mesityl. This reaction is suspected to proceed via a benzyne intermediate.<sup>50</sup> On quenching with iodine, the desired product is obtained.

Figure 15: Synthesis of *m*-terphenyl iodide via method 1



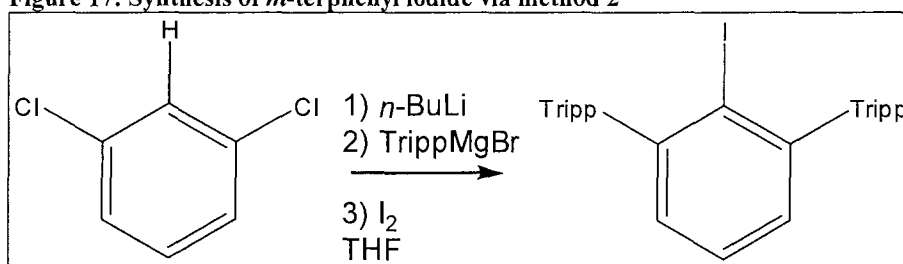
While the synthesis is easy to learn, the preparation still requires two steps. The starting material, 2,6-dibromoaniline is listed as a rare material in many chemical catalogues and is an expensive material to use in large quantities. Typically, the group has used 2,6-dibromoaniline in moderate quantities of about ten grams at maximum.<sup>8</sup>

Figure 16: Comparison of  $\text{Ar}^\#$  and  $\text{Ar}^*$



An improved procedure was developed for the Ar\*, Figure 16, version of *m*-terphenyl iodide.<sup>25</sup> In Figure 17, instead of starting at 2,6-dibromoaniline, method 2 began with 1,3-dichlorobenzene. The synthesis can be performed in one pot. The isolation procedure and purification procedure was described, using an extraction, vacuum distillation, and vacuum sublimation. This synthesis also described a large-scale reaction which resulted in large quantities of product.

**Figure 17: Synthesis of *m*-terphenyl iodide via method 2**



Previously, the group synthesized *m*-terphenyl via method 1 and obtained Ar<sup>#</sup> as its largest ligand. The synthesis for Ar\* described in method 2 was modified to Ar<sup>#</sup> in order to obtain a large quantity of Ar<sup>#</sup>.

The synthesis was performed by adapting the quantities used to synthesize Ar\* to match Ar<sup>#</sup>. The scale was cut to half to make purification and handling simpler. Furthermore, purification was performed without the need for a vacuum distillation. The vacuum distillation step removes 2,4,6-trimethyliodobenzene, a side-product formed when using a large excess of Grignard reagent. The vacuum sublimation step was similarly removed. Instead, a more favorable crystallization step was developed. The contents obtained post-extraction were redissolved in boiling isopropanol. Crystalline material deposited after overnight standing and was collected using vacuum filtration.

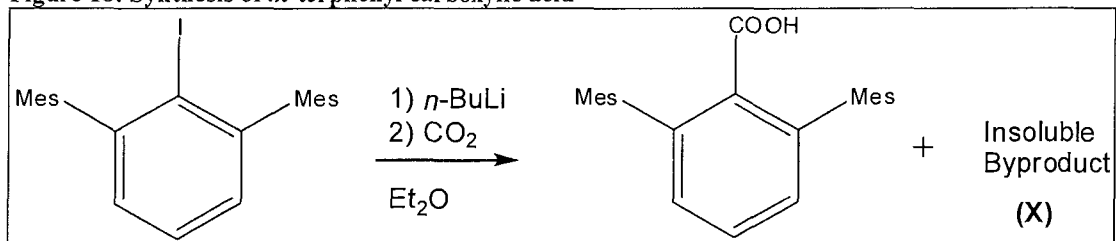
The new synthesis provided technical access to large amounts of *m*-terphenyl in a minimal amount of steps, while limiting the cost of the starting materials. The

modification of the Power synthesis eliminated two potentially more difficult steps in favor of one simple and cleaner stage.<sup>8, 25</sup> The starting materials are easier to handle. In one-step, the synthesis utilizes only easy-to-handle liquid reagents, 1,3-dichlorobenzene, 1.6 M *n*-butyl lithium, 1.0 M mesitylmagnesium bromide, and THF as the solvent. Comparing method 1 to method 2, the use of 1,3-dichlorobenzene simplifies the procedure considerably, removing one step from the synthesis. In cost, 1,3-dichlorobenzene is less expensive than the former precursor, 2,6-dibromoaniline. The synthesis also results in a high quantity of product compared to method 1.<sup>8, 25</sup>

The methodology used in the purification of Ar<sup>#</sup>I was also extended to the synthesis of Ar\*<sup>#</sup>I. It was found that the synthetic technique and purification procedure worked similarly to produce large amounts of Ar\*<sup>#</sup>I, an even more desired bulkier ligand. For this synthesis, the Grignard reagent was prepared in contrast to the Ar<sup>#</sup>I synthesis where the Grignard reagent was purchased.<sup>19</sup>

Functionalization of Ar<sup>#</sup>I to Ar<sup>#</sup>COOH was achieved via lithiation followed by carboxylation, Figure 18.<sup>8, 26</sup> The synthesis was performed as previously reported. Though the procedure was followed, the yield of Ar<sup>#</sup>COOH, 26 %, was found to be drastically lower than the original report, 78%.<sup>8</sup>

**Figure 18: Synthesis of *m*-terphenyl carboxylic acid**





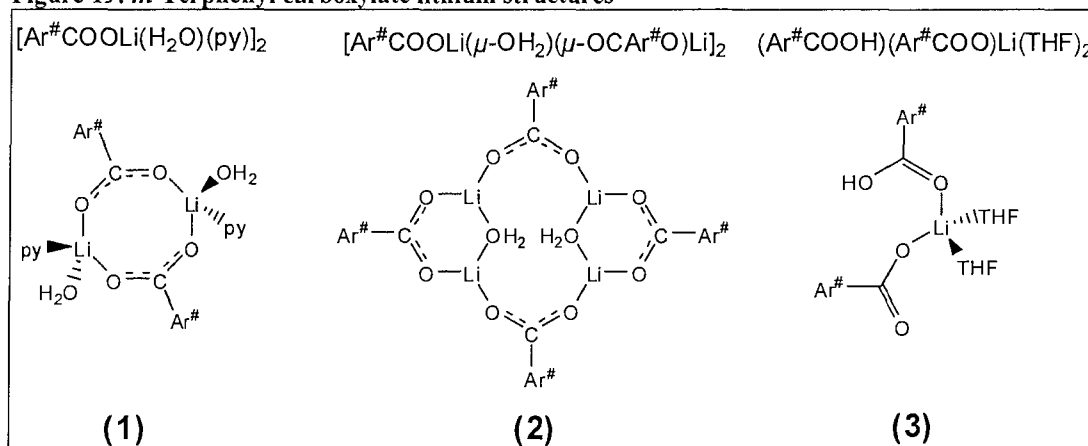
### 2.3 Coordination of *m*-Terphenyl Carboxylate to Cationic Lithium

An unusual byproduct was isolated during the synthesis of Ar<sup>#</sup>COOH. On quenching the solution with HCl/H<sub>2</sub>O, an insoluble white material (X) appeared on the two-phase boundary. The material was removed by gravity filtration and the remaining filtrate was handled to give the final Ar<sup>#</sup>COOH desired product.

The compound (X) was not documented in past reports of Ar<sup>#</sup>COOH synthesis.<sup>8</sup> Further attempts at the synthesis consistently produced the material despite varying the reaction temperature, time, and scale. In qualitatively observing the amounts of (X) and product collected, it would seem as if the insoluble material is vastly hindering the yield of the product.

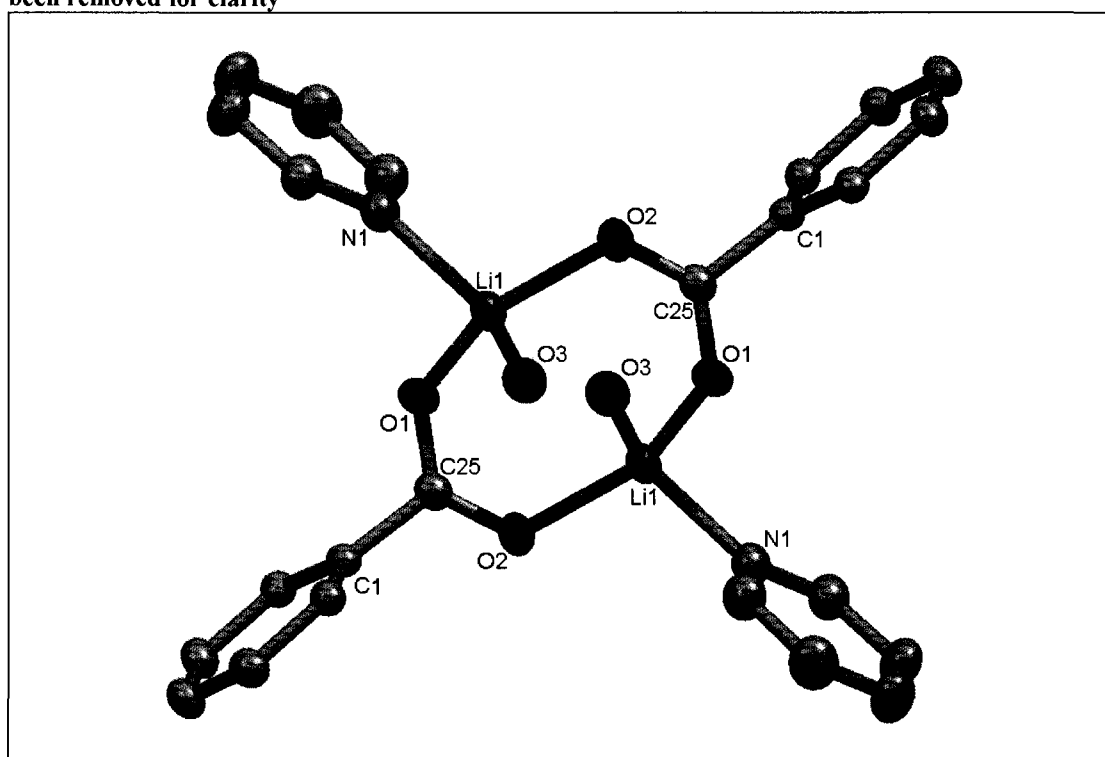
Further analysis of (X) proved difficult as the material was difficult to dissolve in conventional organic solvents. A method was eventually formed to analyze the material via grinding the solid powder in a mortar and pestle into a fine solid. The resulting material could be dissolved with some effort into acetone, THF, and pyridine and the solids were allowed to crystallize under evaporating solvent.

**Figure 19: *m*-Terphenyl carboxylate lithium structures**



Three different structures, Figure 19, were obtained shows possible components in (X). In pyridine, the crystalline material revealed an eight-membered ring of *m*-terphenyl carboxylate and lithium. Like other structures determined for *m*-terphenyl carboxylate, lithium complexes similarly adopt an eight-membered ring as illustrated for other elements such as tin, aluminum, zinc, germanium, and others.<sup>4, 8</sup>

**Figure 20: Crystal structure of  $[\text{Ar}^{\#}\text{COOLi}(\text{H}_2\text{O})(\text{py})]_2$  (1).** Thermal ellipsoids are shown at 50% probability and all hydrogen atoms and mesityl groups have been removed for clarity



The pyridine adduct obtained,  $[\text{Ar}^{\#}\text{COOLi}(\text{H}_2\text{O})(\text{py})]_2$  (1), was similar to previously prepared  $\text{M}_2\text{C}_2\text{O}_4$  structures synthesized within the Clyburne group. The eight-membered ring for *m*-terphenyl carboxylate coordination has become signature and the further synthesis of another eight-membered ring leads to this geometry being the preferred formation for this ligand.

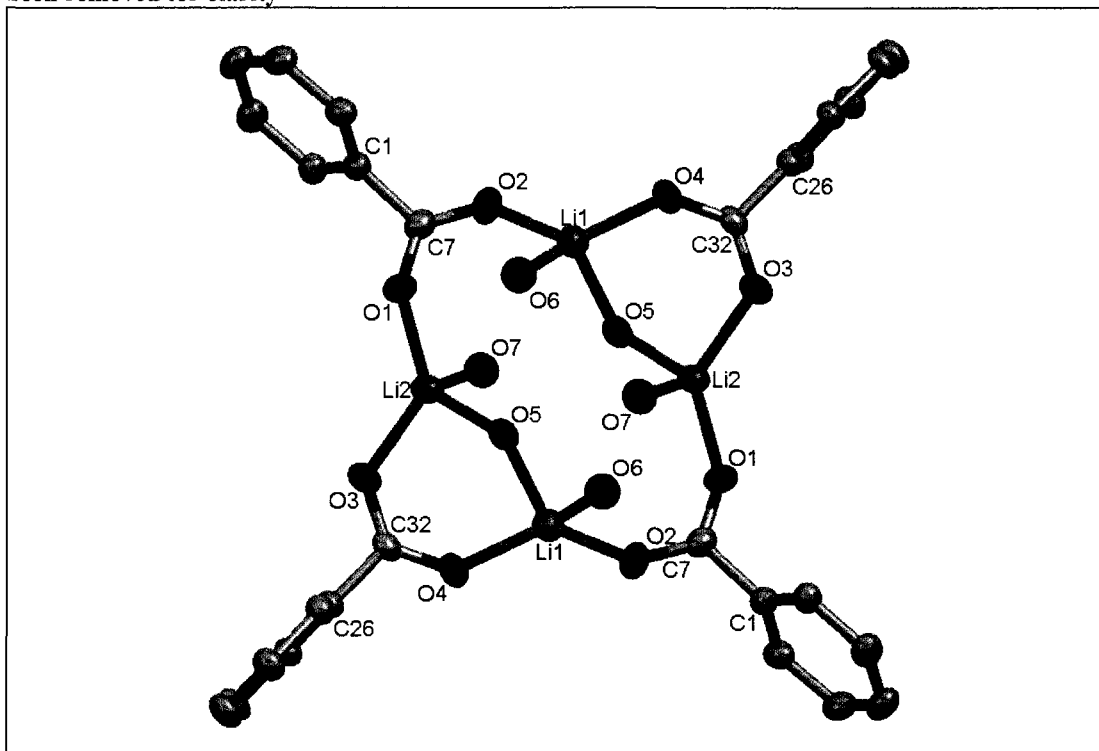
**Table 2: Selected structural data for [Ar<sup>#</sup>COOLi(H<sub>2</sub>O)(py)]<sub>2</sub> (1)**

Bond	Length (Å)	Bond	Angle (°)
N1-Li1	2.073	O1-Li1-O2	124.66
O3-Li1	1.965	O1-C25-O2	125.84
Li1-O2	1.952	O1-Li1-O3	114.23
Li1-O1	1.944	O1-Li1-N1	105.38
		N1-Li1-O3	100.29

Coordination of *m*-terphenyl carboxylate to lithium has been reported previously. The structure obtained was similarly a dimeric species as an eight-membered ring, [Ar<sup>#</sup>COOLi(Et<sub>2</sub>O)]<sub>2</sub>.<sup>51</sup> Yet the lithium atoms are believed to be trigonal planar with only one solvent molecule, diethyl ether, coordinating to each lithium atom. Little was suggested about this structure in the report, though the formulation of a three-coordinate lithium atom seems to be odd considering that the usual tetrahedral compound synthesized with the exact same ligand with a well-known coordination number.

Using acetone as the crystallization solvent, a different ring structure was obtained, (**2**), Figure 21. The size of the ring doubled to make a sixteen-membered ring supported by lithium and *m*-terphenyl carboxylate as before. This structure illustrates that while an eight-membered ring may be the preferred geometry, rings of the monomer Ar-COO-M are not restricted to an eight-membered ring and may adopt larger rings under the correct conditions.

**Figure 21: Crystal structure of  $[\text{Ar}^{\#}\text{COOLi}(\mu\text{-OH}_2)(\mu\text{-OCAr}^{\#}\text{O})\text{Li}]_2$  (2).** Thermal ellipsoids are shown at 50% probability and all hydrogen atoms and mesityl groups have been removed for clarity



**Table 3: Selected structural data for  $[\text{Ar}^{\#}\text{COOLi}(\mu\text{-OH}_2)(\mu\text{-OCAr}^{\#}\text{O})\text{Li}]_2$  (2)**

Bond	Length (Å)	Bond	Angle (°)
Li1-O4	1.904	O4-Li1-O6	106.21
Li1-O6	2.001	O4-Li1-O5	97.930
Li1-O2	1.920	O4-Li1-O2	134.27
Li1-O5	2.047	O2-Li1-O5	104.82
Li2-O3	1.900	O2-Li1-O6	100.58
Li2-O5	2.057	O5-Li1-O6	113.01
Li2-O7	1.977	O3-Li2-O5	95.940
Li2-O1	1.900	O3-Li2-O7	110.00
Li1-Li2	3.174	O3-Li1-O1	128.65
		O5-Li2-O7	108.95
		O5-Li2-O1	107.91
		O7-Li2-O1	104.20

The last structure, (3), Figure 22, obtained which indicates the insoluble material contains lithium and *m*-terphenyl carboxylate was crystallized from THF. The resulting structure differed significantly from other structures obtained combining metals and *m*-

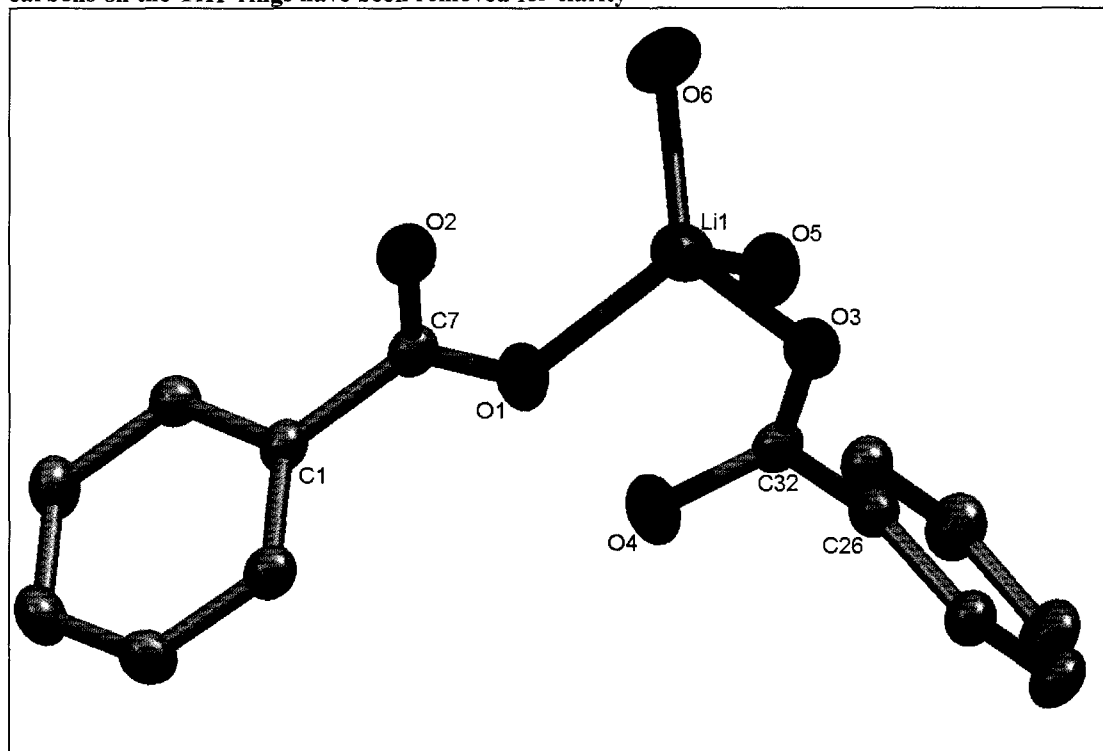
terphenyl carboxylate. The structure was observed to be monomeric lithium supported by an anionic *m*-terphenyl carboxylate and a neutral *m*-terphenyl carboxylic acid.

**Table 4: Selected structural data for  $(\text{Ar}^{\#}\text{COOH})(\text{Ar}^{\#}\text{COO})\text{Li}(\text{THF})_2$  (3)**

Bond	Length (Å)	Bond	Angle (°)
Li1-O3	2.074	O3-Li1-O6	103.31
Li1-O6	1.921	O3-Li1-O5	108.98
Li1-O5	1.933	O3-Li1-O1	96.840
Li1-O1	1.911	O1-Li1-O5	113.18
		O1-Li1-O6	117.05
		O5-Li1-O6	114.92

**Figure 22: Crystal structure of  $(\text{Ar}^{\#}\text{COOH})(\text{Ar}^{\#}\text{COO})\text{Li}(\text{THF})_2$  (3).**

Thermal ellipsoids are shown at 50% probability and all hydrogen atoms, mesityl groups, and carbons on the THF rings have been removed for clarity



Despite the introduction of a large, bulky *m*-terphenyl carboxylate functionality to the lithium cations, there negligible change in the observed bond lengths compared to previously synthesized lithium benzoates.<sup>52-54</sup> Compounds such as lithium anthranilate

and lithium salicylate contain Li-O bond lengths of almost the same bond length, in the range of 1.9-2.0 Å, when the carboxylate is univalent.

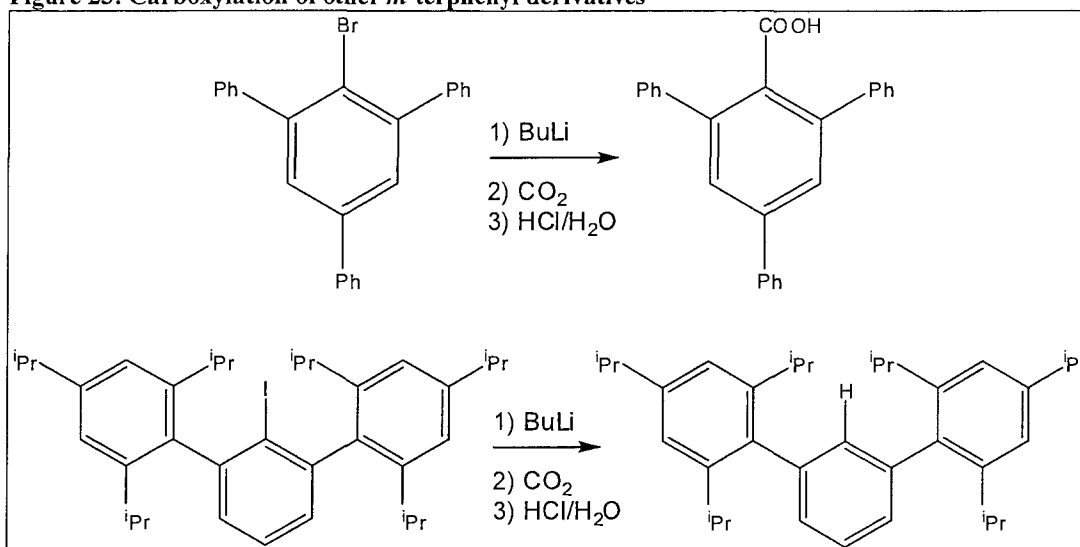
Though there are concerns with the conversion of Ar<sup>#</sup>I to Ar<sup>#</sup>COOH due to the consistent formation of insoluble Ar<sup>#</sup>COOLi, the synthesis of **(3)** shows partial protonation of *m*-terphenyl carboxylate. Thus, conversion to the desired Ar<sup>#</sup>COOH goes to at least a stage wherein the charge neutral Ar<sup>#</sup>COOH becomes a coordinating ligand.

Though the material was difficult to study by NMR techniques due to its insolubility, the three structures obtained indicate the material contains at least *m*-terphenyl carboxylate and lithium as anion and cation pairs. The synthesis is described as the lithiation by *n*-butyl lithium, followed by addition of gaseous CO<sub>2</sub>, then quenching the reaction with HCl/H<sub>2</sub>O. The fact *m*-terphenyl carboxylate is present, suggests an incomplete quenching of the material, leaving *m*-terphenyl carboxylate lithium as the undissolved material. It is too ionic to fully dissolve in organic solvent, being composed of a strong ionic lithium to R-COO<sup>-</sup> bond and too organic to dissolve in water, having three phenyl rings composing a huge hydrocarbon framework. Despite identification of these two key parts in material **(X)**, the exact structure is unknown. Solvent particles, such as water or diethyl ether, may be contained in the material. Also the exact coordination structure could play a role in the material's inability to dissolve in aqueous or organic solvents.

Formation of **(X)** seems to be unique to Ar<sup>#</sup>I as the starting material. The carboxylation of 2,4,6-triphenyl-1-iodobenzene is performed cleanly and produces no significant byproduct. For bulkier *m*-terphenyls such as Ar<sup>\*</sup>I, the carboxylation reaction does not work and the resulting product obtained is Ar<sup>\*</sup>H, the defunctionalization of *m*-

terphenyl. To date, no synthesis of Ar<sup>#</sup>COOH has been reported, yet the bonding of *N*-heterocyclic carbene with Dipp aryl groups to carbon dioxide has been illustrated, yet its reversibility suggests the bulky Dipp groups facilitates loss of CO<sub>2</sub>.<sup>55</sup>

**Figure 23: Carboxylation of other *m*-terphenyl derivatives**



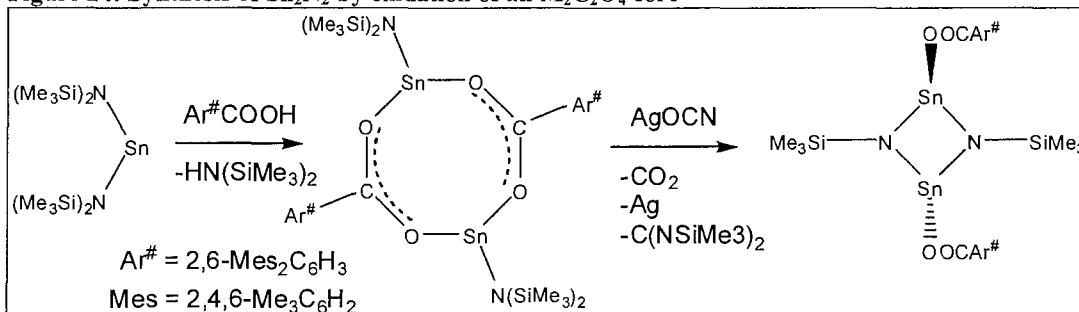
#### 2.4 Coordination of *m*-Terphenyl Carboxylate to Tin (II)

The coordination chemistry of ArCOO<sup>-</sup> as an anionic ligand to simple main group and transition metals has been well established within the Clyburne group.<sup>2, 4, 56</sup> The simplicity of introducing the neutral carboxylic acid, Ar<sup>#</sup>COOH, to metals bearing strongly basic ligands, M-L, results consistently in the loss of L-H followed by coordination to form Ar<sup>#</sup>COO-M in a dimeric cyclic compound.

Of particular interest within the group is the oxidative chemistry of some of these compounds. The dimeric tin(II) compound obtained from the reaction of Ar<sup>#</sup>COOH and Sn(TMS)<sub>2</sub> is the typical product between neutral acid and metal source.<sup>2</sup> While other compounds made in this manner typically contain the metal in its highest oxidation state, this M<sub>2</sub>C<sub>2</sub>O<sub>4</sub> contains tin in the Sn(II) oxidation state. Oxidation of the ring was achieved

previously using AgOCN, Figure 24, producing a new heterocycle containing a Sn<sub>2</sub>N<sub>2</sub> core.<sup>2</sup>

Figure 24: Synthesis of Sn<sub>2</sub>N<sub>2</sub> by oxidation of an M<sub>2</sub>C<sub>2</sub>O<sub>4</sub> core



The Sn<sub>2</sub>N<sub>2</sub> ring molecule presented shows unique chemistry. Formally, the tin atoms are in the Sn(III) oxidation state, indicating a potential diradical, two radicals in the same molecule. The molecule is EPR, electron paramagnetic resonance, silent and the material shows no magnetic behavior, despite the Lewis structure designation.<sup>2</sup> There are similar reports of four-membered X<sub>2</sub>Y<sub>2</sub> compounds that are isoelectronic to the Clyburne group Sn<sub>2</sub>N<sub>2</sub> ring, all of which share the same interesting magnetic behavior.<sup>5, 49, 57, 58</sup>

Repetition of the synthesis was attempted using the previously prepared Ar<sup>#</sup>COOH and Sn(TMS)<sub>2</sub> followed by oxidation of the resulting eight-membered ring. The resulting material that was isolated was AgN(TMS)<sub>2</sub> and characterized by X-ray crystallography, which indicated there may be multiple pathways of this reaction.

## 2.5 Future Work: *m*-Terphenyl

The improved synthesis of *m*-terphenyl gives further study into its functionalization and coordination a strong push. With an improved quantity of *m*-terphenyl, researchers in the field are less restricted by the cost and time requirement in prepare the *m*-terphenyl ligand.



The isolated material that shows signs of containing *m*-terphenyl carboxylate and lithium as anion cation pairs respectively remains a chemical mystery. Fundamentally, it is unusual that it forms and persists in an undissolved state in both aqueous and organic solvents. As a material, the compound is noted for its insolubility in both water and organic solvents, yet it is suspected to be composed of an ion pair as lithium cation and *m*-terphenyl carboxylate anion. Synthetically, it still remains a challenge to convert this remaining material into the original desired material, *m*-terphenyl carboxylic acid. If the material does contain ions of *m*-terphenyl carboxylate and lithium, it seems logical that some simple method can remove lithium and replace it with the desired proton. Thus the material remains a challenge to the Clyburne group to determine its exact composition, nature, and potential usage.

The coordination chemistry of *m*-terphenyl carboxylate seemed to be rigorously shown in previous work.<sup>2, 4, 33</sup> The introduction of Ar<sup>#</sup>COOH, or other aryl derivatives, with a metal bearing a strongly basic ligand almost exclusively formed a dimeric product in an eight-membered ring. Yet, the oxidation of the Sn<sub>2</sub>C<sub>2</sub>O<sub>4</sub> heterocycle giving a four-membered ring indicates that other ring sizes and coordination geometries are possible for these compounds.<sup>2</sup> Furthermore, the lithium compounds prepared as monomers and as a sixteen-membered ring indicate further coordination geometries are possible for 2,6-dimesitylbenzoate. To date, little is known about the formation of rings and reasons for the observed structures, despite using the same-sized ligand.

The four-membered ring previously synthesized was a very unusual molecule that still demands further insight into its structure. It remains a source of contention how the proposed biradicaloid attains singlet-state dynamics.<sup>59</sup> Similar molecules synthesized

have been observed to have the same problems in determining the bonding in their respective molecules. Synthetic and theoretical work can continue on this molecule to better understand the unusual bonding scheme.

## **2.6 Experimental:**

### **2.6.1 General**

An argon-atmosphere MBraun UL-99-245 dry box and standard Schlenk techniques on a double manifold vacuum line were used in the manipulation of air and moisture sensitive compounds. Solution-state NMR was recorded in five millimeter tubes at Dalhousie University on a Bruker Avance 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C) and <sup>13</sup>C spectra are calibrated to the signal of the solvent.

Infrared spectra were obtained using a Bruker Vertex 70 spectrometer with the percent transmittance values reported in cm<sup>-1</sup>. Melting points were measured using a Mel-Temp apparatus and are uncorrected.

Anhydrous solvents were purchased from Aldrich and used without further purification. All other reagents and solvents were purchased from commercial sources including Aldrich and Alfa Aesar and were used without further purification unless otherwise noted.

### **2.6.2 Crystallographic Studies**

Data for all X-ray crystallographic studies were collected by Dr. Gabriele Schatte at the Saskatchewan Structural Science Centre. The crystal was coated with oil (Paratone

8277, Exxon), and was collected on top of the nylon fibre of a CryoLoop<sup>TM</sup> (diameter of the nylon fibre: 10 microns; loop diameter 0.2-0.3 mm; Hampton Research, USA) that had previously been attached using epoxy to a metallic pin. All measurements were made on a Nonius Kappa CCD 4-Circa Kappa FR540C diffractometer using monochromated Mo K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at the temperature indicated in the appendix. Cell parameters were initially retrieved using the COLLECT<sup>60</sup> software, and then refined with the HKL DENZO and SCALEPACK software,<sup>61</sup> that was also used for data reduction. The structure was solved by direct methods using SIR-97<sup>62</sup> and refined by full-matrix least-squares method on F2 with SHELX97-2.<sup>63</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined, unless otherwise indicated in the text. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom.

### 2.6.2 Synthesis of Ar<sup>#</sup>I

In a three-neck flask, 1,3-dichlorobenzene (19 mL, 166 mmol) was added to anhydrous THF (175 mL). The solution was cooled in a dry ice/acetone bath (-78 °C). A solution of *n*-butyl lithium, 1.6 M in hexanes, was added dropwise (110 mL, 176 mmol). After addition was completed, the mixture was stirred for one hour. Mesitylmagnesium bromide, 1.0M in THF, was added dropwise (400 mL, 400 mmol). On completion, the mixture was allowed to slowly warm to room temperature and stirring was continued overnight. The next day, the mixture was heated to reflux (70 °C) for two hours. The flask was cooled to room temperature and placed in an ice bath. Iodine (67 g, 264 mmol) was added slowly to the mixture. The materials were allowed to stir overnight. The

mixture was quenched with 2 M sodium bisulfite (200 mL), distilled water (200 mL) and diethyl ether (300 mL). Precipitating salts were removed by gravity filtration. The biphasic mixture was then put into a separatory funnel and the organic layer was removed. The aqueous layer was washed twice with diethyl ether (500 mL) and the organic extracts were collected. The extracts were concentrated on the rotary evaporator. The material was then dissolved in boiling isopropanol (3 L). The solution was cooled to room temperature and placed in the freezer for crystallization overnight. Product was collected by vacuum filtration using cold isopropanol (500 mL x3) to wash. Yield 24.13 g (55 %). The  $^1\text{H}$  NMR spectrum and melting point was the same as previously reported.<sup>8</sup>

25,50

### 2.6.3 Synthesis of TrippMgBr in THF

In an inert atmosphere, anhydrous THF (175 mL), TrippBr (50 mL, 197 mmol), and Mg (5.30 g, 218 mmol) were added to a Schlenk flask. Over an ice bath, 1,2-dibromoethane (2.4 mL) was added dropwise via syringe. The mixture was stirred at room temperature for thirty minutes. The mixture was heated to reflux (50 °C) for two hours. After, the mixture was allowed to cool to room temperature. Additional THF (80 mL) was added and was stirred overnight at room temperature. The mixture was filtered and was ready to use.

### 2.6.4 Synthesis of Ar\*I

In a three-neck flask, 1,3-dichlorobenzene (9.5 mL, 83 mmol) was added to anhydrous THF (75 mL). The flask was cooled with a dry ice/acetone bath (-78 °C). A

solution of *n*-butyl lithium, 1.6 M in hexanes, was added (55 mL, 88 mmol), was added dropwise to the mixture. The mixture was stirred for one hour at -78 °C. After one hour, the previously prepared TrippMgBr solution (~300 mL) was added. The mixture was stirred overnight at room temperature. The solution was heated to reflux for two hours. After two hours, the solution was allowed to cool to room temperature and then the flask placed in an ice bath. Iodine (28.9 g, 114 mmol) was then added slowly, briefly exposing the flask head to the atmosphere while adding. The mixture was stirred overnight at room temperature. After overnight stirring, sodium bisulfite solution, 2 M, was added (300 mL) and the mixture was transferred to a separatory funnel using water (200 mL) to wash. The organic layer was separated and the aqueous layer was washed with diethyl ether (500 mL x2). The organic layers were collected and concentrated on the rotary evaporator. The crude product was redissolved in 2.25 L of boiling isopropanol. A clear yellow solution resulted and was allowed to cool to room temperature and then the materials were placed in the freezer overnight. Product deposited on overnight cooling and was collected by vacuum filtration using cold isopropanol (500 mL x3) to wash. Yield: 30.12 g (99 %). The material is believed to contain solvent on weighing. The <sup>1</sup>H NMR spectrum and melting point was similar to those already reported.<sup>25</sup>

### 2.6.5 Synthesis of Ar<sup>#</sup>COOH

To a three-neck flask, 2,6-dimesityl-1-iodobenzene (41.75 g, 94.81 mmol) and anhydrous diethyl ether (375 mL) were added. A solution of *n*-butyl lithium, 1.6 M in hexanes, was added dropwise (80 mL, 128 mmol). The solution was stirred for three hours at room temperature. After three hours, gaseous CO<sub>2</sub> was bubbled into the solution

using a pipet immersed into the solution. After two hours, all the diethyl ether had evaporated and a white solid deposited. Diethyl ether was added (900 mL) to wash the product. Added 1 M HCl (150 mL) and gently stirred the solution. The solution formed a layer of white undissolved material. Added water (600 mL) to solution and stirred the solution. The white material (**X**) was removed by vacuum filtration. The filtrate was recollected and diethyl ether was used to wash. The filtrate was put into a separatory funnel and the organic layer was collected. The aqueous layer was washed twice with diethyl ether (500 mL x2) and the organic extracts were collected and concentrated on the rotary evaporator. The solid was washed in toluene (100 mL) and a white powdery solid was obtained by vacuum filtration. Yield: 8.77 g (26 %). The  $^1\text{H}$  NMR spectrum and melting point were the same as previously reported.<sup>8</sup> Additionally isolated 14.92 g of insoluble white material (**X**) m.p. 358-369 °C. IR (KBr Pellet) 3232 (br), 2917 (vs), 2727 (w), 1735 (vs), 1613 (m), 1579 (m), 1436 (s), 1364 (s), 1215 (s), 1128 (s), 1061 (m), 1032 (m), 822 (s), 699 (s), 574 (s), 441 (w).

#### 2.6.5 Synthesis of $[\text{Ar}^{\#}\text{COOLi}(\mu\text{-OH}_2)(\mu\text{-OCAr}^{\#}\text{O})\text{Li}]_2$ (**1**)

A sample of (**X**) (0.30 g) was placed in a mortar and pestle. The sample was finely ground into a fine powder. Using acetone (60 mL), the material partially dissolved into a cloudy mixture. The solution was filtered and the clear and colorless filtrate. The filtrate was allowed to evaporate dry overnight. Crystalline material appeared overnight and a small sample was removed (~5 mg) for crystallographic analysis.

### 2.6.6 Synthesis of $[\text{Ar}^{\#}\text{COOLi}(\text{H}_2\text{O})(\text{py})]_2$ (2)

A sample of (X) (0.05 g) was placed in a round-bottom flask. Pyridine (10 mL) was added to the flask and the material dissolved after a strong agitation of the solution and some gentle heating in a warm water bath. The solution was then left open to the atmosphere for solvent evaporation. The contents were allowed to evaporate until dryness. A sample was collected for X-ray crystallography (~5 mg). M.p. 388-392 °C (dec).

### 2.6.7 Synthesis of $(\text{Ar}^{\#}\text{COOH})(\text{Ar}^{\#}\text{COO})\text{Li}(\text{THF})_2$ (3)

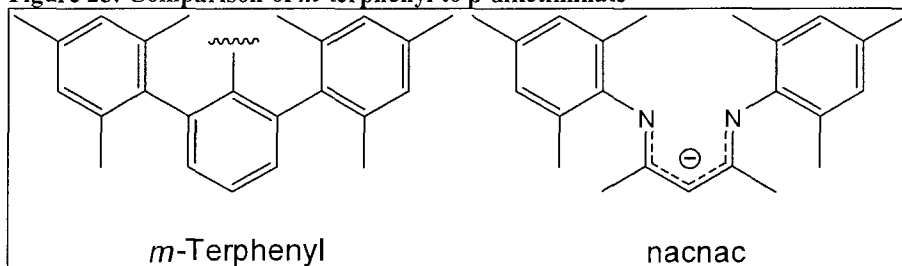
A sample of (X) (0.52 g) was placed in a mortar and pestle. The sample was finely ground into a fine powder. Using THF (60 mL), the material dissolved under a clear yellow solution. The solution was filtered and the filtrate was collected and the solvent was removed on the rotary evaporator. The remaining materials were dissolved again in a minimum amount of THF and the solvent was allowed to evaporate indefinitely. Crystalline material slowly deposited in the mother liquor and a sample was (~5 mg) removed for analysis by X-ray crystallography.

### 3 The Indirect Functionalization of Nacnac

#### 3.1 Recent Advances in Nacnac Chemistry

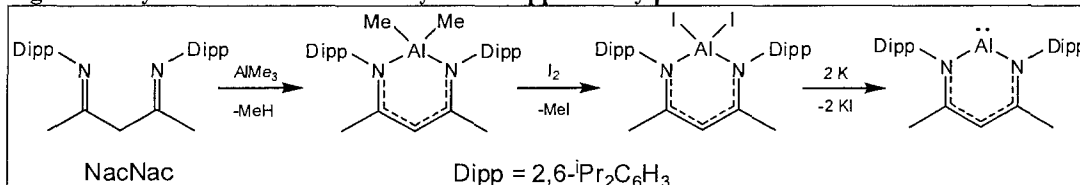
Nacnac, or  $\beta$ -diketiminates, can be compared directly to *m*-terphenyl, Figure 25. When drawn specifically, nacnac with aryl groups on the nitrogens achieves the same desired steric bowl effect that *m*-terphenyl creates. Thus, marked interest in nacnac within the Clyburne group was based on similar ligand geometries, a sterically encumbering “bowl” that has the ability to promote low-valency amongst inorganic compounds.

Figure 25: Comparison of *m*-terphenyl to  $\beta$ -diketiminates



As a ligand, nacnac has achieved a high amount of notice for supporting the first and only known aluminum ylidene compound.<sup>1</sup> The synthesis is depicted in Figure 26. Given aluminum's place on the periodic table as a strongly electropositive atom that is highly electron deficient, the isolation of such a compound is remarkable.

Figure 26: Synthesis of an aluminum ylidene supported by  $\beta$ -diketiminates



The existence of persistent aluminum ylidene is aided by three aspects that nacnac is able to provide, **Error! Reference source not found.**<sup>64</sup> The *m*-terphenyl-like ‘bowl’ configuration of nacnac discourages dimerization or ring formation of the aluminum ylidene fragment by sterically encumbering the Al fragment. The singlet state is highly



avored due to both of the nitrogen atoms donating to the aluminum atom that is attributed for singlet state ylidenes. The ring afforded by the nacnac ligand and Al fragment comprises a six-membered ring of six- $\pi$  electrons in an alternating fashion that satisfies the Hückle rule for aromaticity. While the aluminum heteroatom is significantly different from a simple aromatic ring such as benzene, the compound can be considered pseudo-aromatic.

### 3.2 Electronic Tuning of Nacnac

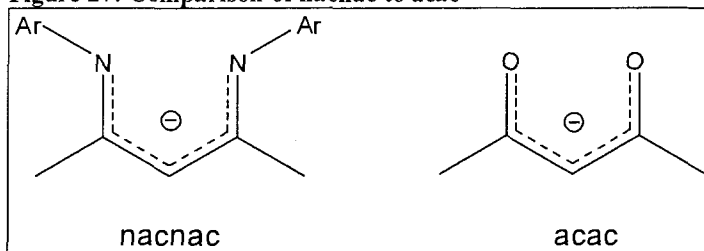
Despite advances in the synthesis of an aluminum ylidene using a nacnac framework, the corresponding boron ylidene has not been reported to date. The aluminum ylidene has unique reactive chemistry such as metallocyclopropene formation and its subsequent compound has been observed to react with small gaseous molecules. Such a boron derivative – considering boron’s affinity to form strong B-H bonds, yet chemically labile and accessible as hydride – is attractive to materials chemists for the possibility of hydrogen storage. Certainly there have been similar attempts to prepare boron ylidene in the same way aluminum ylidene is synthesized, yet to date, a monomeric boron ylidene has not been reported.

To isolate a boron ylidene, it would seem that that the three strengths of nacnac enforcing low-valency are not enough. Sterically, nacnac can be improved to make larger aryl groups on the nitrogen atoms. Such large nacnac compounds have been reported up to 2,6-diisopropylphenyl flanks, an already very bulky nacnac.

Another option is to modify the donor properties of nacnac, in a similar manner to the variance of functional groups on *m*-terphenyl, to achieve the desired ligand-donor

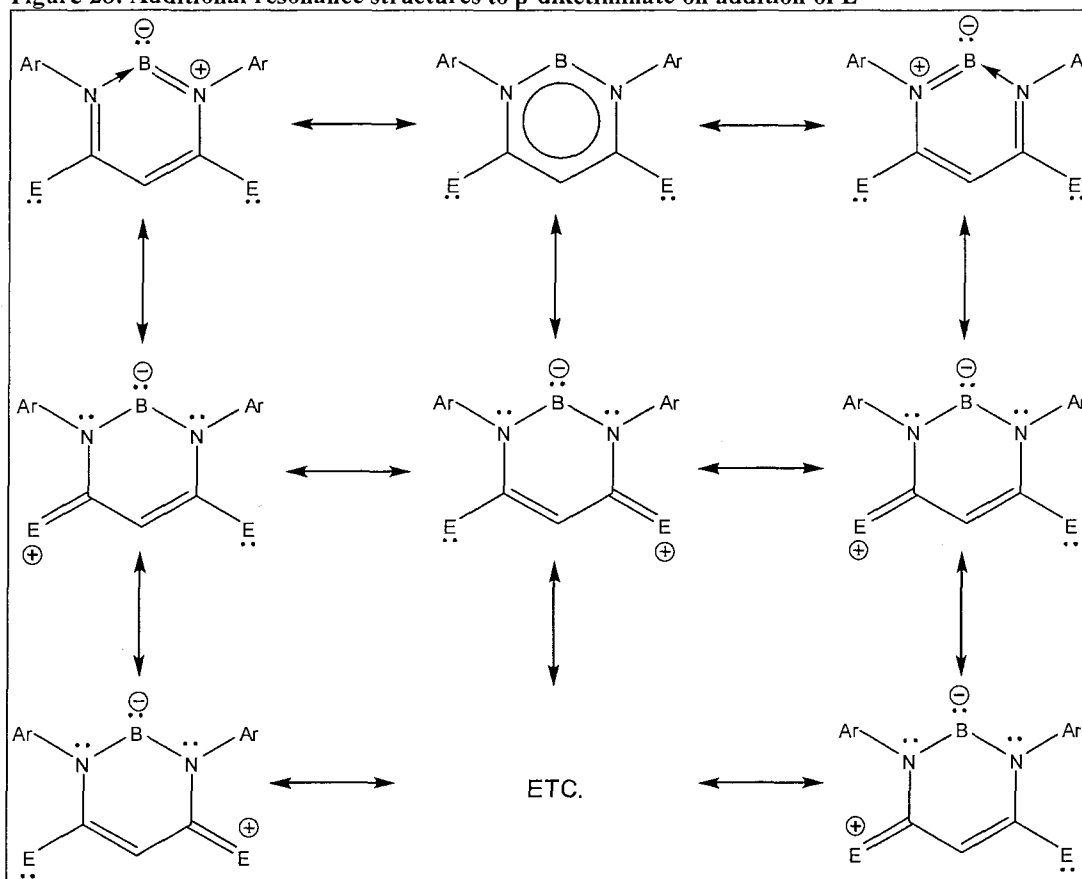
interaction. Yet nacnac, unlike *m*-terphenyl, is not an electronically tuneable ligand. In *m*-terphenyl, the functional group can be changed to match the desired bonding mode without affecting the aryl flanking group. In nacnac however, nitrogen is a requirement to achieve steric protection. The valency of nitrogen is mechanically needed to have an available bond for the nitrogen groups. For example, changing nitrogen to oxygen, Figure 27, a stronger donor atom, leads to the loss of coordination number and a loss in the aryl rings, changing nacnac to acac. While direct change in functionality may not be possible, there are other alternatives to modifying the electronic properties of nacnac while maintaining two nitrogen atoms in the appropriate positions.

**Figure 27: Comparison of nacnac to acac**



Noting the multiple resonance structures of a  $\beta$ -diketiminato ligand, the addition of an electron-donor group adjacent to the ring provides the added negative charge. The concept of adding electron donating groups to help stabilize the electron-deficient boron atom is visualized using Lewis structures containing electron-donating groups. In Figure 28, the addition of two electron-donating groups, denoted E, expands the possible resonance structures via electron addition into the ring. From basic Lewis structure theory, the addition of more resonance structures should help stabilize the potential boron ylidene. Though this is a very basic and crude justification, the Lewis theory has often been referred to for many complicated bonding schemes and remains the most visual and identifiable theoretical tool for chemists.

**Figure 28: Additional resonance structures to  $\beta$ -diketiminato on addition of E**

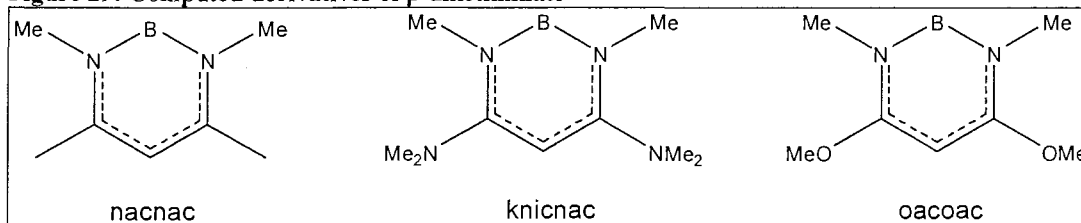


The substitution of electron donating groups at the noted positions would be necessary to create a more electron-rich nacnac ligand. Methoxy and dimethyl amino in particular were considered as strongly donating groups that would potentially add to a ylidene site on nacnac.

### 3.3 Calculations on the Electronic Tuning of Nacnac

Calculations were performed on potential models of modified nacnac ligands: methyl, methoxy, and dimethylamino, Figure 29. The model for these calculations was the singlet-triplet gap, a calculation commonly used to express the stabilization of a free ylidene.

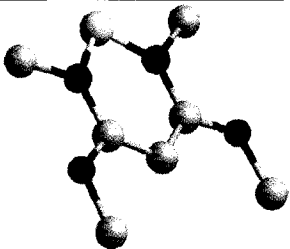
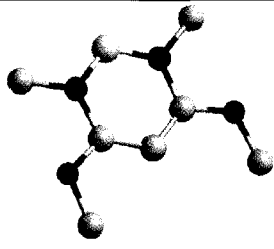
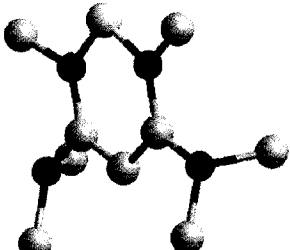
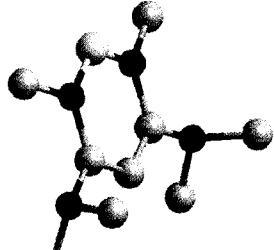
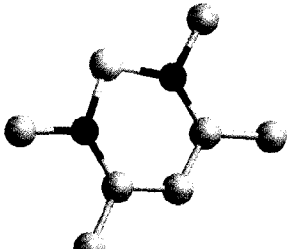
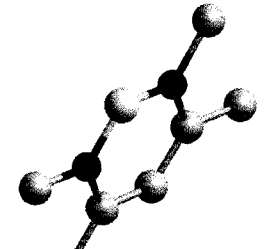
**Figure 29: Computed derivatives of  $\beta$ -diketiminate**



Using the Spartan '06 package, calculations were performed using the model of methyl groups in place of the aryl groups.<sup>65</sup> At the MP2/6-31-G\* level, the calculations were performed on the three different models representing different degrees of electron donation. The parameter determined was the singlet-to-triplet energy gap,  $\Delta E_{S \rightarrow T}$ , found by calculating energies for the singlet and triplet states and then comparing their differences.

On calculating each derivative as their corresponding boron ylidene, Table 5, it was determined that increasing the electron-donor character at the prescribed positions increased the singlet-triplet energy gap. Thus, replacing the methyl groups on nacnac with dimethylamino or methoxy groups has the effect of lowering the energy of the singlet state in relation to the triplet. This was expected when counting the increased number of resonance structures obtained when adding the donor atom E to those positions.

**Table 5: Computed MP2/6-31G\* structures of nacnac and modified derivatives**

Structure Type	Singlet Structure	Triplet Structure	$\Delta E_{S \rightarrow T}$ (kJ/mol)
oacoac			74.12 kJ/mol
knicnac			27.70 kJ/mol
nacnac			18.02 kJ/mol

The observed trend of increasing singlet-triplet energy gap when calculating boron ylidenes justifies the design and synthesis of electron-rich versions of nacnac. The best possible alternative, as shown by the MP2 calculations, was the methoxy derivative. Yet, to date, no synthesis for such a molecule has been reported.

The other alternative electron-donating nacnac compound utilized dimethylamino side groups. To some surprise, the parent compound KnicNac was found to be previously

known, synthesized, and characterized. The synthesis was reported in the early 1970s by H. G. Viehe and Z. Janousek and outlines the synthetic route to KnicNac.<sup>66-69</sup>

### 3.4 Synthesis of KnicNac

The synthesis uses dichloro-*N,N*-dimethylammonium chloride as a starting material. Commonly known as Viehe's salt or PI salt, the compound is named due to Viehe's extensive work providing multiple synthetic pathways to prepare the material, as well as demonstrating many novel reactions that Viehe's salt can perform with other functional groups.<sup>70-76</sup> Viehe's salt is a commercially available compound in moderate quantities of about 100 grams. It is highly sensitive to moisture and oxygen, quickly forming volatile byproducts on exposure to the atmosphere, as shown in Figure 30.<sup>77</sup>

**Figure 30: Atmospheric decomposition of Viehe's salt**

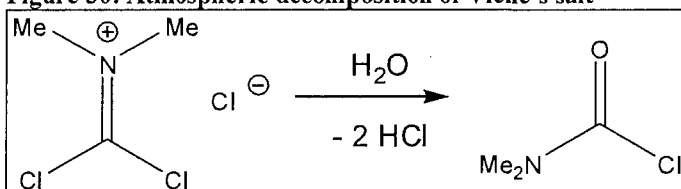
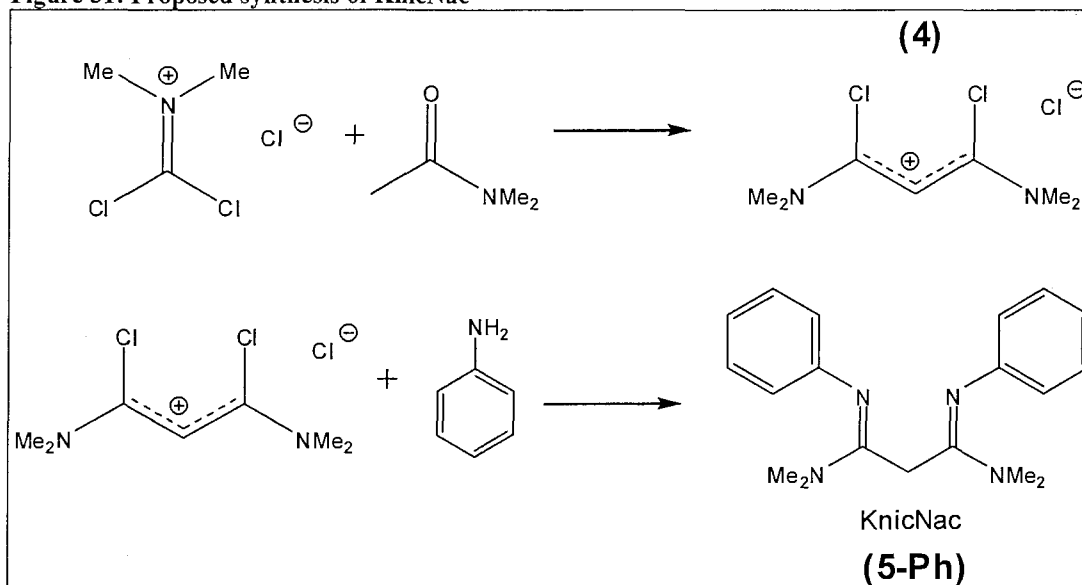


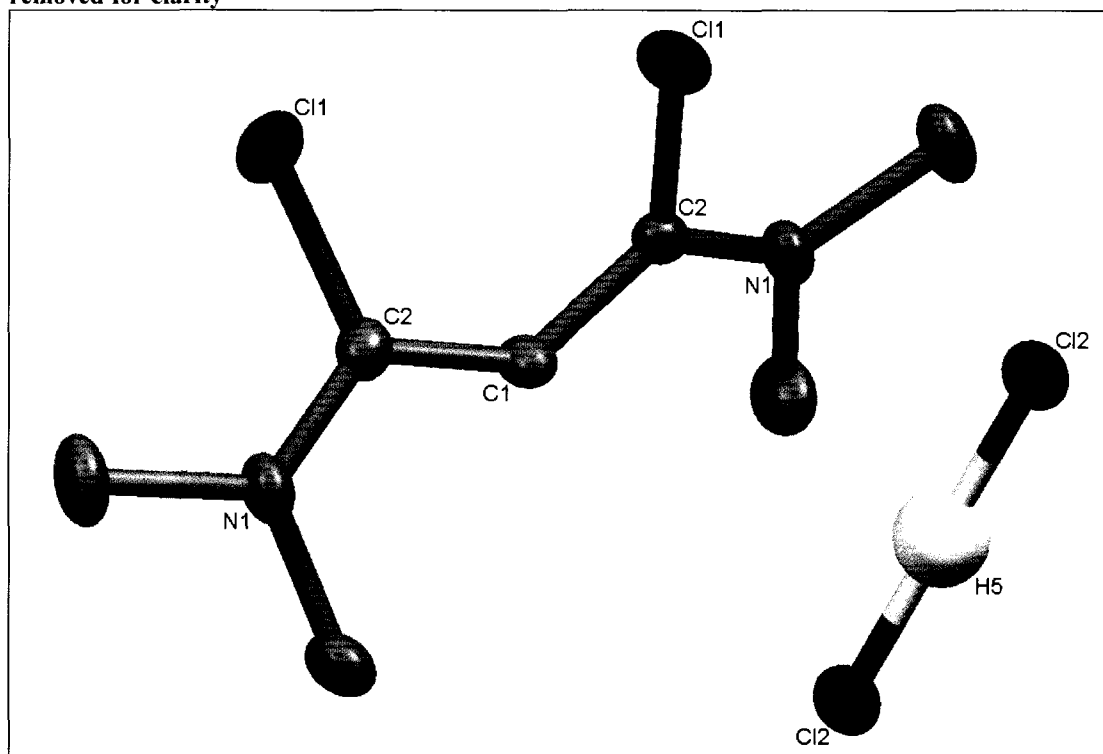
Figure 31 shows a particular reaction of interest, the reaction of PI salt with *N,N*-dimethylacetamide and its subsequent reaction with aniline. This unusual reaction gives 1,3-dimethylamino-1,3-dichlorotrimethine chloride, often abbreviated as the malonyl cyanine. The reaction has an interesting stoichiometry. The cyanine can be viewed as the reaction of one equivalent of Viehe's salt with one *N,N*-dimethylacetamide producing one mole of H<sub>2</sub>O, with the water molecule consumed by an additional equivalent of Viehe's salt.<sup>66, 67, 69, 76</sup>

Figure 31: Proposed synthesis of KnicNac



The synthesis of malonyl cyanine was repeated by slow addition of *N,N*-dimethylacetamide to Viehe's salt in dichloromethane. On isolation and analysis, the product was found to contain an additional HCl on crystallization in the form of an HCl<sub>2</sub> anion, hydrogen dichloride, [Cl-H-Cl]<sup>-</sup>, as the anion, Figure 32, which was not reported in the original accounts. Similar data was obtained for malonyl cyanine that matched the reported characteristics such as melting point and <sup>1</sup>H NMR spectrum.<sup>66, 69</sup>

**Figure 32:** Crystal structure of malonyl cyanine hydrogen dichloride  $[\text{Me}_2\text{NC}(\text{Cl})\text{CHC}(\text{Cl})\text{NMe}_2]^+[\text{HCl}_2]^-$  (**4**). Thermal ellipsoids are shown at 50% probability and all hydrogen atoms on the cation have been removed for clarity



Despite the success in obtaining a crystal structure of the cyanine, the reaction suffered from poor yields as a large amount of cyanine remained in solution and could only be isolated by crude methods. Consequently, the following reaction with an aniline derivative was difficult to perform with small quantities of cyanine. It was then decided to perform the reactions in tandem without complete isolation of the cyanine.

**Table 6: Selected structural data for malonyl cyanine hydrogen dichloride (**4**)**

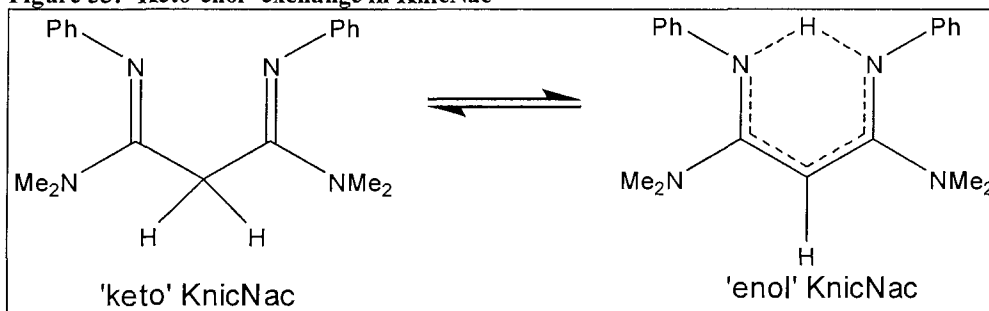
Bond	Length (Å)	Bond	Angle (°)
N1-C2	1.322	C11-C2-N1	116.28
Cl1-C2	1.721	C11-C2-C1	120.94
C2-C1	1.392	N1-C2-C1	122.65
Cl2-H	1.559	C2-C1-C2	130.25
		Cl2-H5-Cl2	180.00
		$\Sigma\alpha(\text{N1})$	359.75



A one-pot synthesis of KnicNac was developed starting from the original cyanine synthesis and then subsequently adding the aniline. An aqueous workup resulted in a white powder as the product. The resulting material was crystallized and a crystal structure was obtained, Figure 34.

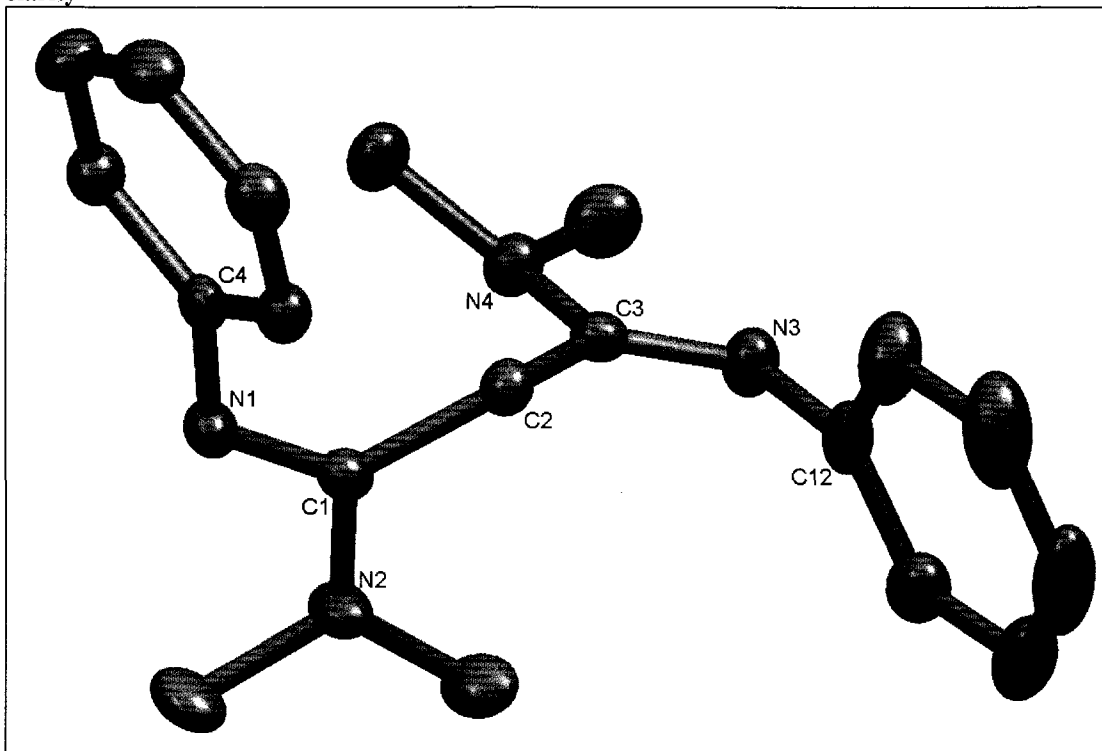
The  $\beta$ -diketones,  $\beta$ -diketimines are well known to exhibit ‘enolic’ behavior, where one of the methylene protons exchanges readily to form the ‘enol’ form.<sup>10, 78</sup> The identification of keto-enol exchange in AcAc and NacNac suggests the accessibility of the anionic forms nacnac and acac as ligands. In the  $^1\text{H}$  NMR of KnicNac, no distinguishable N-H proton could be identified, yet the assigned methylene signal had an inconsistent signal intensity, which may be attributed to possible exchange amongst the keto and enol forms of KnicNac.

**Figure 33: ‘Keto-enol’ exchange in KnicNac**



The steric tuneability of KnicNac was tested by changing the aryl group from phenyl to mesityl. As indicated before with the mesityl derivative of *m*-terphenyl carboxylate, mesityl flanking groups significantly increase the steric ‘bowl’ effect and can influence a reaction’s existence that is presumably based on sterics.<sup>2</sup> Thus, synthesis of a mesityl KnicNac ligand was desired to create a bulkier ligand for potential low-valent synthesis as well as to test the one-step reaction’s robustness.

**Figure 34: Crystal structure of KnicNac (5-Ph).**  
 Thermal ellipsoids are shown at 50% probability and all hydrogen atoms have been removed for clarity

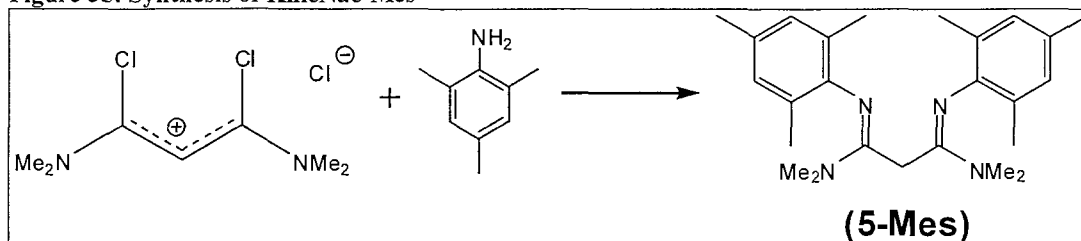


**Table 7: Selected structural data for KnicNac (5-Ph)**

Bond	Length (Å)	Bond	Angle (°)
C4-N1	1.408	C4-N1-C1	123.15
N1-C1	1.289	N1-C1-N2	117.38
C1-N2	1.362	N2-C1-C2	118.59
C1-C2	1.528	C1-C2-C3	118.10
C2-C3	1.522	N4-C3-C2	117.59
C3-N4	1.375	N4-C3-N3	117.93
C3-N3	1.288	C3-N3-C12	122.03
N3-C12	1.410	$\Sigma\alpha(\text{N2})$	359.40
		$\Sigma\alpha(\text{N4})$	351.47

The synthesis of KnicNac-Mes was performed in the exact same fashion as the KnicNac-Ph derivative, with the exchange of aniline and 2,4,6-trimethylaniline. The resulting product on isolation was a white powder (**5-Mes**). Although no single crystal of the material resulted, the NMR, IR, MS data, and bulk isolation obtained for this compound indicate successful synthesis of the mesityl derivative of KnicNac.

Figure 35: Synthesis of KnicNac-Mes



### 3.5 Base-Sensitive Chemistry

The chemistry of Viehe's salt is denoted as moisture sensitive. On exposure to the atmosphere, the salt rapidly decomposes into gaseous byproducts. Today, state-of-the-art laboratories utilize vacuum line techniques and inert atmosphere boxes to handle and manipulate air-sensitive materials.<sup>79</sup> The majority of these compounds are reactive towards free protons, such as those in H<sub>2</sub>O, water. The synthesis of a low-valent compound is typically dependent on being isolated from water, since a small proton can easily react with the low-valent center or the ligands attached to it. Thus, the elimination of the proton, the absence of water, is the first key to their isolation.

Despite the reaction of Viehe's salt and the malonyl cyanine to water, the chemistry of decomposition is inverted in comparison to typical air-sensitive chemistry. Both compounds are not reactive in the presence of free protons. In fact, determined by crystallography, malonyl cyanine contains one equivalent of HCl, a source of free proton, inside of it. Over the course of the reaction, several equivalents of hydrogen chloride gas are released, illustrating that free protons are inert in combination with the materials. Instead, these compounds are labile towards bases, lone pairs of electrons.<sup>80</sup> The fact that the material is sensitive to water is due to the oxygen in water, not the acidic protons.

This type of chemistry brings about many technical challenges. Chief amongst these is the development of techniques to handle base-sensitive chemicals in a laboratory where mainly acid-sensitive chemistry occurs. Inert-atmosphere dry box manipulations were typically discouraged since the majority of that chemistry was reserved for acid-sensitive chemistry. Many of the techniques used in these reactions were Schlenk techniques and carefully-planned manipulations in order to avoid the contamination of this chemistry with other chemistry within the group, such as the *m*-terphenyl coordination described in section 2, which is highly sensitive to free protons.

### 3.6 Knicnac as a Ligand:

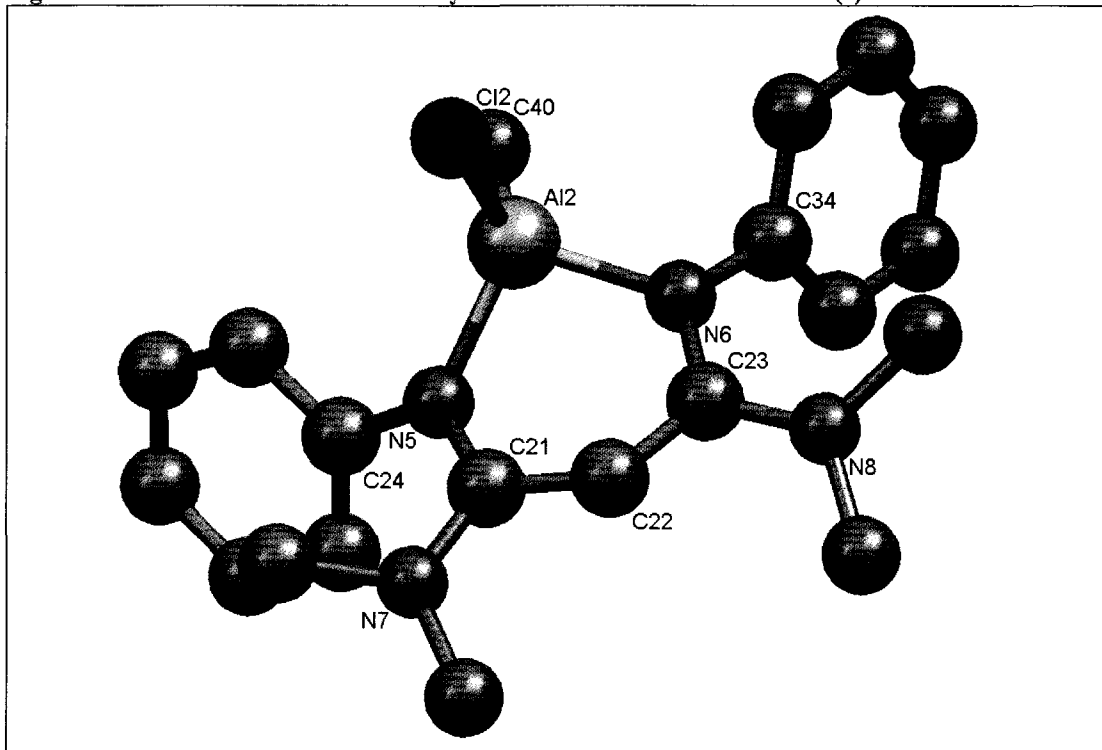
The design and goal of KnicNac was not to simply develop a novel synthesis for the compound, but to demonstrate its ability as a ligand, knicnac, comparable to nacnac-type  $\beta$ -diketiminates. A simple reaction of NacNac was its reaction with trimethylaluminum, forming a well-known nacnac-AlMe<sub>2</sub> adduct.<sup>1, 81</sup> Subsequent reactions with nacnac-AlMe<sub>2</sub> produce the low-valent aluminum ylidene.

The introduction of NacNac to trimethylaluminum produces the expected coordination and loss of methane. The reaction utilizes the acidity of the center proton, which creates the anion of NacNac. Such a reaction has been reported for nacnac derivatives with *p*-tolyl and 2,6-diisopropylphenyl flanking aryl groups.<sup>81</sup>

Because knicnac is presumed analogous to nacnac in its ability to synthesize group 13 ylidenes, the reaction between the previously prepared free KnicNac and trimethylaluminum was desirable.<sup>1, 12, 13, 82</sup> This was to fulfill both the necessity to demonstrate knicnac's ability as a ligand in a manner similar to nacnac, loss of the acidic



**Figure 37: Ball and stick model of the crystal structure of Knicnac-AlMeCl (6)**



In the  $^1\text{H}$  NMR, two similar, yet distinguishable compounds could be observed. The compounds  $^1\text{H}$  NMR resonances appeared as twin signals slightly displaced from each other by about  $\pm 0.05$  ppm. All of the peaks appeared in the suggested position for a knicnac anion structure. Though quantitative determination of these peaks was difficult due to peak overlap, it was concluded that there existed at least two structures containing knicnac anionic ligands.

**Table 8: Selected structural data for Knicnac-AlMeCl (6)**

Bond	Length (Å)	Bond	Angle (°)
C4-N1	1.431	C4-N1-C1	121.00
C1-N4	1.360	C4-N1-Al1	122.51
C1-N3	1.369	N1-C1-N3	119.49
C1-C2	1.414	N1-C1-C2	121.58
N1-Al1	1.884	C1-C2-C3	127.54
Al1-Cl1	2.130	N3-C1-C2	118.90
Al1-C20	1.960	C1-N1-Al1	115.68
		N1-Al1-N2	97.03
		N1-Al1-Cl1	108.68
		N1-Al1-C20	116.34
		Cl1-Al1-C20	112.86
		$\Sigma\alpha(\text{N7})$	358.93
		$\Sigma\alpha(\text{N8})$	359.13

The exact nature of the reaction that forms knicnac-AlMeCl is still unknown. Though it seems via  $^1\text{H}$  NMR that two such compounds exist in solution, it cannot be assumed that one is converted directly from the other. The synthesis of nacnac-AlMeCl has been reported via two methods. First preparing nacnac-AlCl<sub>2</sub>, the stoichiometric replacement of chloride with methyl lithium was achieved and reported to make nacnac-AlMeCl.<sup>81</sup> Alternately, using the hydrochloride salt of the starting material NacNac•HCl, introduction of trimethylaluminum in a 1:1 mixture similarly produced nacnac-AlMeCl.<sup>81</sup> At this stage, the possibilities for the formation of knicnac-AlMeCl include the following: ligand disassociation and association with an abundance of solvent particles;  $\sigma$ -bond metathesis to exchange methyl for chloride with dichloromethane; small amounts of hydrochloride salts in the KnicNac product; or chloride impurity in the reacting trimethylaluminum.

Nevertheless, the isolation of knicnac-AlMeCl illustrates an example of knicnac acting as a ligand. The loss of at least one proton to form the anionic ligand shows that

the model of knicnac as a nacnac analogue is valid and opens the chemistry of KnicNac to many of the successes shared by the  $\beta$ -diketiminato.<sup>1, 12, 13, 64, 82</sup>

The success of nacnac as a ligand is well-noted for both transition metal and main group chemistry.<sup>64</sup> Whether it be polymerization catalysts, interesting metal-ligand interactions, or as previously mentioned, the isolation of group 13 ylidenes, the chemistry of nacnac may be extended to that of knicnac since they share similar structures.<sup>64</sup> Yet as shown by even Lewis theory, the addition of dimethylamino gives added and unique properties to knicnac as a source of strongly donating nacnac that has the potential to open currently unknown chemistry.

### 3.7 Future Work: Functionalized Electron-Donating Nacnac Ligands

The work done on KnicNac, *m*-terphenyls, and ‘bowl’ shape structures is designed to be a foundation. Research is often designated as fundamental or applied. With knicnac, it is clearly a start to learning more about its fundamental properties as a ligand as well as important applied characteristics as a ligand-metal compound.

The boron ylidene remains an interest and challenge to chemists. The stabilization of such an electron-deficient atom is yet to be accomplished despite numerous attempts at ligand designs emulating nacnac’s success with the aluminum ylidene. The use of such a compound in organoboron chemistry, boron-hydrides, and energy storage keeps interest in such a boron ylidene high.

Nacnac owes an impressive amount of chemical research ranging from simple ligand-metal interactions to extensive research in its polymerization properties.<sup>83-85</sup> Knicnac is comparable to nacnac with the addition of nitrogen-containing electron-donor



groups. Knicnac contains the similar bonding, sterics, and structure of nacnac. Knicnac is distinct from nacnac in that it is a stronger electron donor. It therefore can be introduced into nacnac systems to extend electron-donating properties.

### **3.8 Experimental:**

#### **3.8.1 General**

General experimental details can be found in section 2.6.1.

#### **3.8.2 Crystallographic Studies**

Details for the collection of crystallographic data can be found in section 2.6.2.

#### **3.8.3 Synthesis of Malonyl Cyanine [Me<sub>2</sub>NC(Cl)CHC(Cl)NMe<sub>2</sub><sup>+</sup>][HCl<sub>2</sub><sup>-</sup>] (4)**

In an inert atmosphere, dichloromethylene-*N,N*-dimethylammonium chloride (32.51 g, 200.1 mmol) was weighed in a Schlenk flask and dichloromethane (200 mL) was added. *N,N*-dimethylacetamide (8.5 mL, 91 mmol) was added dropwise to the solution at 0 °C. The solution was then heated to reflux for three hours. The loss of HCl was observed and was allowed to exit the apparatus through a CaCl<sub>2</sub> drying tube. The solution was heated to reflux for four hours. The solution turned to a clear orange solution with some signs of undissolved material. The liquid was removed via cannula to a new flask. The solution was evacuated to remove solvent until the material began to precipitate. Anhydrous benzene was then added to the solution comprising about 25 % of the remaining volume. The solution was then put into the freezer for crystallization. Overnight, small amounts of crystalline material deposited and it was collected by

filtration. Yield: 7.20 g (34 %) m.p. 119-121 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 6.1 (s, 1H), 3.7 (s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz) δ 158.9, 90.5, 45.0. IR (nujol mull) ν 2923 (br), 1111 (m), 723 (m), 618 (w), 552 (w).

#### 3.8.4 Synthesis KnicNac-Ph (5-Ph)

Under an inert atmosphere, anhydrous dichloromethane (150 mL) was added to dichloromethylene-*N,N*-dimethylammonium chloride (16.82 g, 103.5 mmol) in a Schlenk flask. Via syringe, *N,N*-dimethylacetamide (4.6 mL, 49.5 mmol) was added dropwise to the solution at room temperature. The mixture was then heated to reflux (50 °C) for five hours. After five hours, the mixture was allowed to cool to room temperature. The material was exhaustively evacuated to remove the solvent. Chloroform (150 mL) was added to the flask. Previously distilled anhydrous aniline was then added dropwise (12 mL, 130 mmol) to the solution at room temperature. The mixture was heated to reflux for six hours. After six hours, the solution was cooled to room temperature. Concentrated KOH (1-2mL) was then added dropwise to the solution and the mixture was stirred at room temperature. After five minutes, water (50 mL) was added. The mixture was transferred to a separatory funnel. The organic layer was extracted and the aqueous layer was washed with chloroform (100 mL x2). The organic extracts were dried with anhydrous magnesium sulfate and then passed through a gravity filter. The extracts were concentrated on the rotary evaporator. Acetone and hexanes in a 1:1 mixture were then added to the liquid. The mixture was then put in the sonicator and gently agitated. The product was collected by vacuum filtration and washed with ice cold acetone/hexanes. Yield: 6.201 g (41 %) m.p. 216-221 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.00 (t, J = 7.7

Hz, 4H), 6.87 (t,  $J = 7.5$  Hz, 2H), 6.80 (d,  $J = 7.9$  Hz, 4H), 3.91 (s, 2H), 3.04 (s, 12H), 1.78 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  128.7, 122.8, 119.7, 72.4, 40.3. IR (KBr Pellet) 3267 (br, w), 2930 (w), 1638 (vs), 1595 (vs), 1572 (vs), 1494 (m) 1446 (m), 1400 (m), 1332 (w), 1307 (w), 1255 (w), 1160 (w), 1063 (w), 1039 (w), 752 (m), 695 (m).

### 3.8.5 Synthesis of KnicNac-Mes (5-Mes)

The same synthetic procedure was applied as for the phenyl derivative up to the addition of aniline. Instead, previously dried and distilled 2,4,6-trimethylaniline (15 mL, 110 mmol) was used. The same extraction and isolation procedure was used yielding the final product. Yield: 3.180 g (16 %) m.p. 221-222 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  6.92 (s, 4H), 3.69 (s, 2H), 2.65 (s, 6H), 2.31 (s, 6H), 2.24 (s, 12H), 2.20 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  161.1, 139.2, 133.8, 131.9, 129.8, 42.2, 42.0, 36.8, 31.1, 21.2, 19.0. IR (KBr Pellet) 3179 (m), 2895 (s), 2613 (br), 1705 (vs), 1636 (vs, br), 1428 (s), 1360 (m), 1337 (m), 1225 (m), 867 (s), 700 (m), 530 (w).

### 3.8.6 Synthesis of Knicnac-AlMeCl (6)

Under an inert atmosphere, anhydrous pentane (25 mL) was added to a round bottom flask containing 0.41 g (3.2 mmol) of KnicNac-Ph (**5-Ph**). While stirring, trimethylaluminum (1.3 mL of 1.0M in hexanes) was added dropwise. The solution bubbled gently on addition and the undissolved material started slowly dissolving into solution. A small amount of undissolved material persisted and an additional 0.5 mL of trimethylaluminum was added. The solution was stirred overnight in an inert, open

atmosphere. The solution was filter through celite. The remaining solvent was removed by exhaustive evacuation. The mixture was redissolved in a minimum amount of anhydrous dichloromethane (2-3 mL). The mixture was allowed to lose solvent by evaporation overnight. Crystals were removed from the mother liquor for X-ray analysis.

#### **4 Conclusion:**

The work performed on *m*-terphenyl has resulted in the material being more accessible for future studies on its properties as a ligand. With the synthesis of the precursor, *m*-terphenyl iodide in a simple, one-step, high-yield, large quantity synthesis, obtaining the material for more advanced studies is more straightforward.

It seemed that *m*-terphenyl carboxylate chemistry was well-defined by previous synthesis of very repeatable structures. Yet the discovery of lithium-based carboxylate compounds that were not constrained in their ring size, including the first monomeric *m*-terphenyl carboxylate, indicates there is more unknown chemistry to this ligand and metal compounds.

The functionalization of nacnac presents a way of improving a tried and tested ligand support for low-valent synthesis. With the synthesis mapped and material obtainable in useable quantities, the coordination chemistry of knicnac, first illustrated with an AlMeCl compound, can be performed. Knicnac chemistry has a promising future.

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