Spring 5-1-2019

A Closer Look at the Synthesis and Characterization of Alkaline Earth Metal Tetraarylborates and Heteroleptic Tetraarylborate Pyrazolates

Ashley Clements

Recommended Citation

Clements, Ashley, "A Closer Look at the Synthesis and Characterization of Alkaline Earth Metal Tetraarylborates and Heteroleptic Tetraarylborate Pyrazolates" (2019). *Syracuse University Honors Program Capstone Projects*. 1112.
https://surface.syr.edu/honors_capstone/1112

A Closer Look at the Synthesis and Characterization of Alkaline Earth Metal Tetraarylborates and Heteroleptic Tetraarylborate Pyrazolates

A Capstone Project Submitted in Partial Fulfillment of the
Requirements of the Renée Crown University Honors Program at
Syracuse University

Ashley D. Clements

Candidate for Bachelor of Science in Chemistry
and Renée Crown University Honors
Spring 2019

Honors Capstone Project in Chemistry

Capstone Project Advisor: ____________________________
Dr. Karin Ruhlandt, Dean and
Distinguished Professor
of Chemistry

Capstone Project Reader: ____________________________
Dr. Miriam Gillett-Kunnath,
Research Assistant Professor
of Chemistry

Honors Director: ____________________________________
Dr. Danielle Smith, Director

Abstract

Compounds containing *s*-block metals are highly sought after as precursor materials for the Metal Organic Chemical Vapor Deposition (MOCVD) process with applications for novel and improved electronic materials. Previous work in the Ruhlandt Group has been focused on the synthesis and characterization of novel homoleptic alkaline earth (Ae) metal pyrazolate and tetraarylborate complexes, while understanding the importance of secondary interactions such as M-π in the isolation of these compounds. More recently, it was further proposed that the pyrazolate and tetraarylborate ligand systems combined with an Ae silyl amide *via* transamination may very well result in an improved heteroleptic MOCVD potential precursor due to the ligand systems' capability of extended M-π interactions. Herein are described efforts to further understand and successfully reproduce, with significantly improved yields from ~1 – 15% to 50% (ave.), these unprecedented Ae tetraarylborates $[Ae(B((3,5\text{-}Me_2)C_6H_3)_4)_2(thf)_n]$ (Ae = Ca, **1**†, n = 0; Ae = Sr, **2**†, n = 0; Ae = Ba, **3**†, n = 1) and $[Ae(B((4\text{-}t\text{Bu})C_6H_3)_4)_2(thf)_n]$ (Ae = Ba, **4**†, n = 0) and heteroleptic tetraarylborate pyrazolates $[Ae(thf)_2(Et_2O)_2(t\text{Bu}_2pz)][B((3,5\text{-}Me_2)C_6H_3)_4]$ (Ae = Ca, **5**†) and $[Ae(thf)_2(t\text{Bu}_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$ (Ae = Sr, **6**†; Ba, **7**†) that exhibit various ion association modes along with M-π interactions. In addition, little is known about the formation of these compounds; as such, there is still a need to examine and further explore the synthesis of various Lewis bases to provide an improved understanding towards the structure-function relationships of these complexes.

Executive Summary

The *s*-block metals comprising of alkali metals and alkaline earth metals (calcium, strontium, and barium) are sought after as precursor materials for the Metal Organic Chemical Vapor Deposition (MOCVD) process with applications for novel and improved electronic materials. While remarkable progress has been made towards the optimization of synthetic pathways and the exploration of alternative routes to overcome various synthetic challenges towards these compounds, significant restrictions and limitations remain. However, research in the Ruhlandt Group has seen that the importance of secondary non-covalent interactions, such as M-π, has played a key role in the isolation of novel alkali and alkaline earth metal complexes.

Previous work has focused on the synthesis of novel homoleptic alkaline earth (Ae) metal pyrazolate and tetraarylborate complexes. These ligand systems make for promising oxide-free MOCVD precursors. The pyrazolate and tetraarylborate ligands have a wide variety of binding modes which help stabilize organometallic compounds, thus making it useful for synthesis of Ae complexes. Homometallic pyrazolates with alkali, Ae, and rare earth metals are well-established and have been synthesized and characterized. Prior research in the Ruhlandt Group has led to the isolation of novel Ae pyrazolate compounds such as $[\{\mathrm{Ae}(t\mathrm{Bu}_2\mathrm{pz})_2\}_n]$ (Ae = Ca, n = 3; Ae = Sr, n = 4; Ae = Ba, n = 6) and more recently by Lavin and Woods, the tetraarylborates including $[\mathrm{Ae}(\mathrm{B}((3,5\text{-}\mathrm{Me}_2)\mathrm{C}_6\mathrm{H}_3)_4)_2(\mathrm{thf})_n]$ (Ae = Ca, **1**†, n = 0; Ae = Sr, **2**†, n = 0; Ae = Ba, **3**†, n = 1) and $[\mathrm{Ae}(\mathrm{B}((4\text{-}t\mathrm{Bu})\mathrm{C}_6\mathrm{H}_3)_4)_2(\mathrm{thf})_n]$ (Ae = Ba, **4**†, n = 0). The first part of this thesis focuses on efforts towards successfully reproducing these tetraarylborate complexes with improved yields.

It was proposed that reacting the pyrazolate and tetraarylborate ligands with $\mathrm{Ae}[\mathrm{N}(\mathrm{SiMe}_3)_2]_2(\mathrm{thf})_2$ (Ae = Ca, Sr, Ba) *via* transamination would result in mixed pyrazolate and tetraarylborate compounds similar to lanthanide work done by Deacon *et al.* Thus, the second part

of this thesis focuses on efforts towards successfully reproducing and upscaling these novel heteroleptic compounds such as $[Ae(thf)_2(Et_2O)_2(t\mathrm{Bu}_2pz)][B((3,5\text{-}Me_2)C_6H_3)_4]$ (Ae = Ca, **5**†) and $[Ae(thf)_2(t\mathrm{Bu}_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$ (Ae = Sr, **6**†; Ba, **7**†) initially synthesized by Lavin and Woods based on the well-understood homoleptic systems.

However, little is known about the formation of these Ae tetraarylborates and the heteroleptic tetraarylborate pyrazolate compounds; as such, there is a need to examine and further explore the synthesis and effects of various Lewis bases to provide an improved understanding towards these species *via* donor studies. Initial work towards this goal are explored in the final part of this work.

Table of Contents:

List of Illustrative Material

Figures

Tables

Equations

Abbreviations

Lower case letters denote coordinating donor, capitalized denote solvent

† Previously synthesized compounds by Lavin and Woods in the Ruhlandt Group

tBu_2pzH	3,5-di-*tert*-butylpyrazole
$[BAr_4]^-$	tetraarylborate
-Ar	aryl
-*t*Bu	*tert*-butyl
-Ph	phenyl
-Me	methyl
M-H	metal-hydrogen agostic interactions
M-π	metal-π secondary interactions
THF, thf	tetrahydrofuran
DME, dme	1,2-dimethoxyethane
TMEDA, tmeda	N, N, N’, N’-tetramethylethylenediamine
PMDTA, pmdta	N, N, N’, N”, N”-pentamethylethylenetriamine
py	pyridine
Et_2O	diethyl ether
Ae	heavy alkaline earth metal (Ca, Sr, Ba)
MOCVD	Metal Organic Chemical Vapor Deposition

Acknowledgements

I would first like to thank my faculty mentor and advisor, Professor Karin Ruhlandt, for allowing me to work for her research group during my time at Syracuse University. Additionally, my undergraduate research experience would not have been possible without the help and advice of Doctor Miriam Gillett-Kunnath, who taught me inorganic chemistry techniques and helped me improve both my synthesis techniques and report generation skills. Thank you to the Syracuse University Chemistry and Forensic Science faculty and staff who mentored me throughout my time at Syracuse, particularly Doctor Timothy Korter and Doctor Jon Zubieta, who read my thesis and provided me with guidance. I would also like to thank the America Chemical Society for allowing me to present my research at their National Meeting and Exposition in the spring of 2019.

Thank you to my friends and family for your constant encouragement and support during my studies at Syracuse University.

Lastly, I would like to thank the Renée Crown University Honors Program for providing me with the guidance and funding to conduct and present my research.

CHAPTER 1:

Introduction

1.1 The Alkaline Earth Metals

The *s*-block elements are located on the far left in the periodic table and consist of alkali metals and alkaline earth metals. The alkaline earth metals are comprised of beryllium (Be), magnesium (Mg), calcium (Ca), strontium, (Sr), and barium (Ba), and occur naturally in minerals and salts found in the earth's crust and the oceans.[1] These elements have valence electron configurations of ns^2 and are highly electropositive, thus making them susceptible to the loss of valence electrons in order to form a positively charged cation (Table 1.1).[2] These metals are highly oxo- and hydrophilic and therefore require strict water-free conditions and synthesis must therefore be performed under a strict inert gas environment.[3-8]

Table 1.1 Alkaline earth metal properties.[1-3]

Element	Electron Configuration (m^0)	1st Ionization Energy	Electronegativity	Charge Radius
Ca	[Ar]$4s^2$	6.11	1.04	2.0
Sr	[Kr]$5s^2$	5.69	0.99	1.8
Ba	[Xe]$6s^2$	5.21	0.97	1.5

Alkaline earth metals play a variety of roles in synthetic chemistry and are used in many materials such as semiconductors.[9] Additionally, calcium-containing reagents have been found to be environmentally benign, allowing for potential applications in green chemistry.[5,6] Compounds synthesized using heavy alkaline earth metals can also be utilized as potential precursors for Metal Organic Chemical Vapor Deposition (MOCVD).[9]

There are many factors affecting the bonding characteristics of *s*-block metals, particularly the size of the metal, the strength of the metal-ligand bond, and the properties of the ligand.[3] These make the resulting structures difficult to predict, especially when the multiple potential ion-association modes of these metals are taken into account. Previous research has indicated that a contact pair is favored for covalent metal-ligand bonds, while ion separation is common in heavier metals with a weak metal-ligand bond (*c.f.* Chapter 2).[3]

1.2 Secondary Non-Covalent Interactions

It has been observed that non-covalent interactions, particularly M-π and agostic interactions (M···H—C) are critical to the stabilization of the Ae metal centers.[3-8] The aromaticity of the tetraarylborate and deprotonated pyrazolate ligand systems (*c.f.* 1.3) allow for these secondary interactions to occur between the ligand and the highly electropositive metal center of the complex. When these weak interactions are combined with sterically hindered ligands or are in the presence of neutral donors or Lewis bases, the resulting complex can lead to ideal precursors for MOCVD that are volatile and able to sublime intact. The cut-off values for these secondary non-covalent interactions have been well-studied in the Ruhlandt Group, as seen in Table 1.2.[3-8]

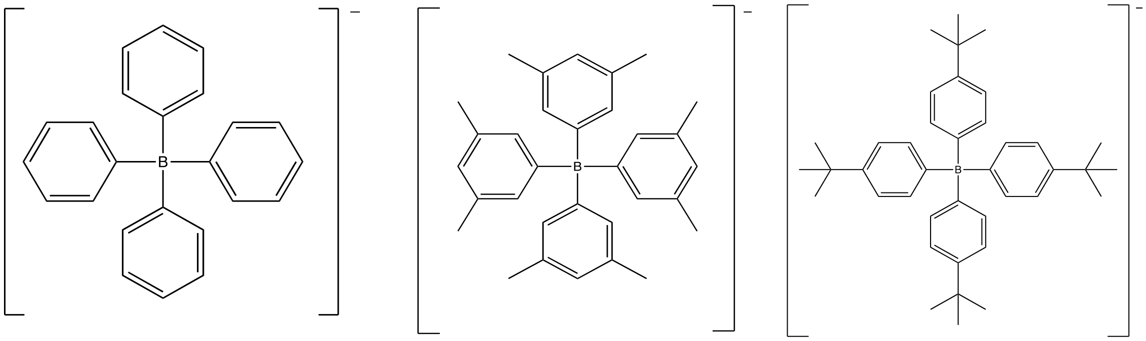
Table 1.2 Cut-off values for M-π and agostic interactions (M···H—C) fall within the range of the sum of van der Waals radii (Σ (r_{wA} + r_{wC}) for a metal-carbon bond for alkaline earth metals.[3-8]

Ae^{2+}	**CN**	**r_{ion}**	**r_W** (H = 1.1.) (Å)	**$\Sigma(r_{wAe} + r_{wH})$** (Ae —H) (Å)	**Cut-off Value** (Ae···H—C) (Å)
Ca	6	1.00	2.31	3.41	3.10
Sr	6	1.18	2.49	3.59	3.25
Ba	6	1.35	2.68	3.78	3.30

1.3 Selected Ligand Systems

1.3.1 The Tetraarylborate Ligand System

The tetraarylborate ligand system is a large anionic ligand that primarily participates in M-π and agostic M-H interactions, and is generally used as a “counterion” to stabilize cationic compounds (Figure 1.1).[12] Because the negative charge throughout the delocalized system is stabilized by the aryl groups, this ligand is very stable when exposed to air and water.[12,13]



- 24 e^- π system
- Stable in air and water
- Easily substituted aromatic rings
- Capable of M-ligand π interactions

- BPh_4^- (a)
- $B((3,5\text{-}Me_2)(C_6H_3))_4^-$ (b)
- $B((4\text{-}t\text{Bu})(C_6H_4))_4^-$ (c)

Figure 1.1 The tetraarylborate ligand system.

M-π interactions between tetraarylborate ligands and metal cations were first observed with transition metal complexes,[12] and later extended to studies of lanthanide interactions with the ligand system.[14] Previous research conducted within the Ruhlandt Group studied this M-π coordination using alkyl-substituted tetraarylborates and a diethyl ether solvent.[13,15,16] This research yielded compounds with low coordination numbers where M-ligand π secondary interactions are primarily responsible for the saturation of the metal,[15] and showed that multiple factors help contribute to the saturation of the metal center of the compound (*c.f.* Chapter 2).

1.3.2 The Pyrazole Ligand System

Pyrazole is a ring consisting of three carbon atoms and two nitrogen atoms that becomes aromatic upon deprotonation of the compound (Figure 1.2)[13, 17]

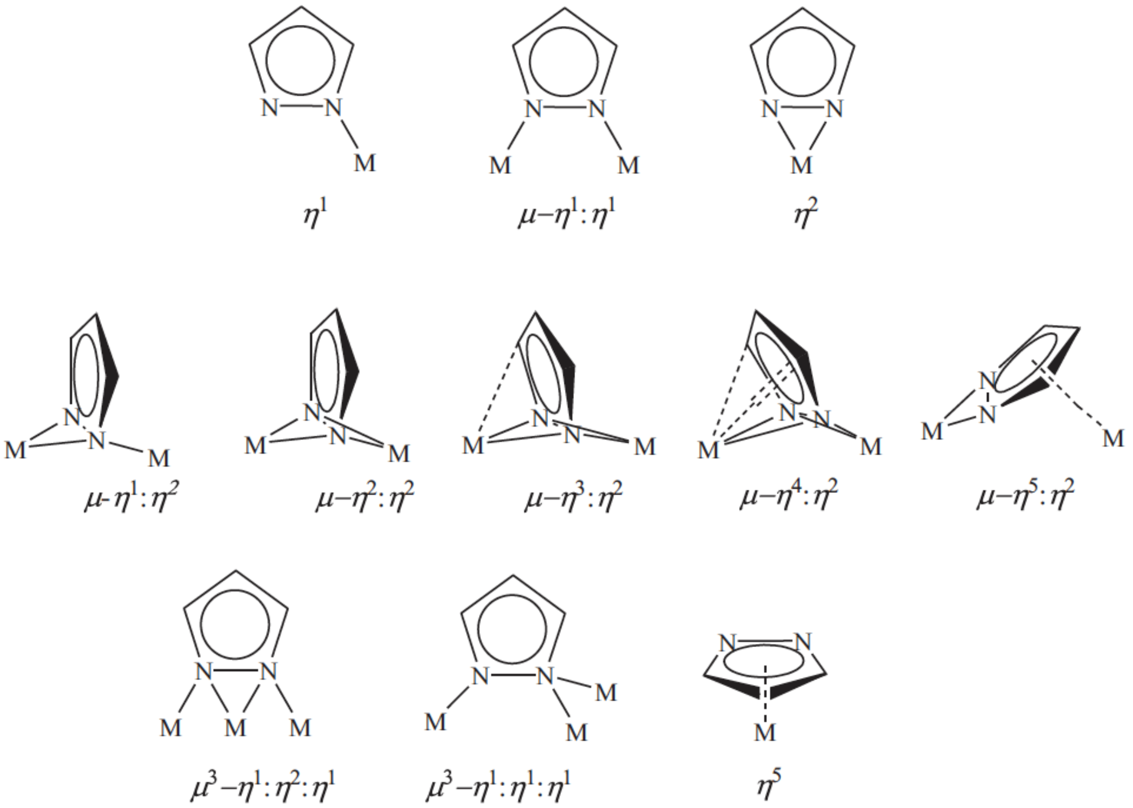
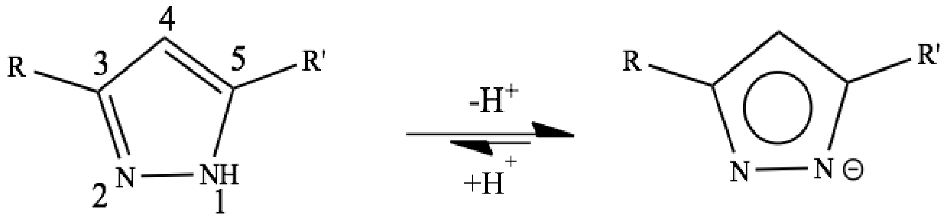


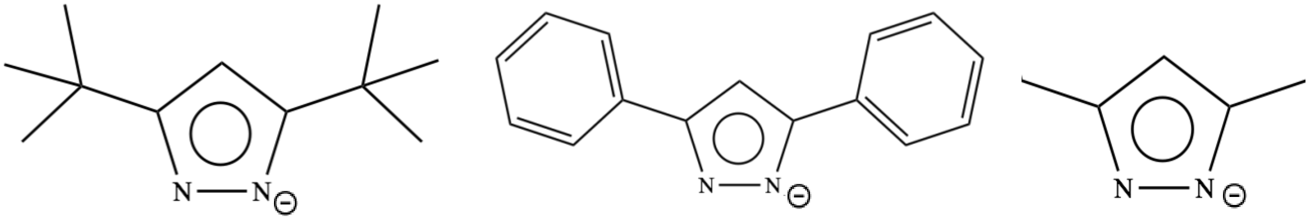
Figure 1.2 The aromaticity of pyrazole.[17]

Once the pyrazole is deprotonated, it can bind to a metal cation and create a stable pyrazolate compound, and the aromaticity of the ligand allows for M-π interactions.[17] In addition, the solubility of the ligand can be adjusted by substituting various alkyl and aryl groups onto the 3- and 5- positions of the pyrazole (Figures 1.3 and 1.4). The list of potential groups includes -H, -CH_3, -*t*Bu, and -Ph. Metal pyrazolate compounds with various substituted groups can then be studied in order to evaluate the effects of solubility and reactivity on the formation of these compounds.[13]



- Heterocyclic compound
- Becomes aromatic upon deprotonation
- Multiple substitution possibilities, in order to study the effect of ligand bulk substitutions on the 3,5 position
    - 3,5-di-*tert*-butylpyrazole ($t\mathrm{Bu}_2\mathrm{pzH}$), R = 3,5-$t\mathrm{Bu}_2$
    - 3,5-dimethylpyrazole ($\mathrm{Me}_2\mathrm{pzH}$), R = 3,5-$\mathrm{Me}_2$
    - 3,5-diphenylpyrazole ($\mathrm{Ph}_2\mathrm{pzH}$), R = 3,5-$\mathrm{Ph}_2$

Figure 1.3 The pyrazole ligand system.



$t\mathrm{Bu}_2\mathrm{pz}^-$ $\mathrm{Ph}_2\mathrm{pz}^-$ $\mathrm{Me}_2\mathrm{pz}^-$

Figure 1.4: Substitution possibilities for the pyrazole ligand system.

1.4 Selected Lewis Bases

In addition to the M-π interactions with the aryl rings of the ligand systems, there is a need to examine the secondary interactions with the metal center and neutral Lewis bases as it might further contribute to the compounds' saturation and volatility. These oxygen-and nitrogen- Lewis bases/neutral co-ligands/donors can help to further saturate the metal ion center, resulting in varied structure-function relationships. Lewis bases with varying hapticities, as seen in Figure 1.5 below, can be studied in order to determine which systems can result in the most stable complex that is also volatile enough to sublime intact and can thus be further tested in order to determine their potential as MOCVD precursors.

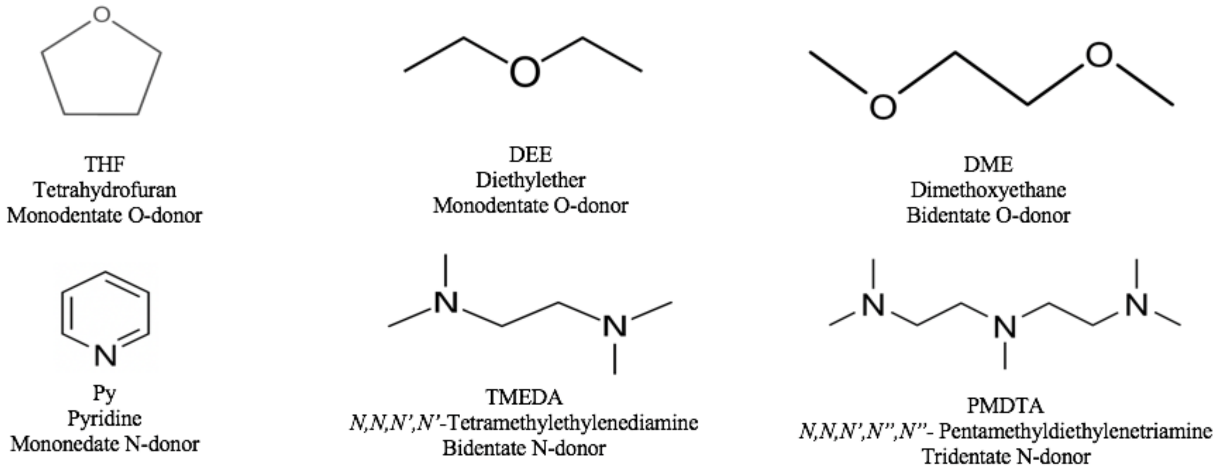


Figure 1.5 Potential Lewis bases or donors.

1.5 Goals

1.5.1 Alkaline Earth Metal Tetraarylborate Compounds and Donor Studies

Previous work in the Ruhlandt Group by Lavin and Woods synthesized a family of tetraarylborate compounds: $[Ae(B((3,5\text{-}Me_2)C_6H_3)_4)_2(thf)_n]$ (Ae = Ca, **1**†, n = 0; Ae = Sr, **2**†, n = 0; Ae = Ba, **3**†, n = 1) and $[Ae(B((4\text{-}t\text{Bu})C_6H_3)_4)_2(thf)_n]$ (Ae = Ba, **4**†, n = 0).[15] However, reproducible and scalable yields were lacking. Herein describes successful efforts towards this end by repeating the synthesis of these compounds and characterizing them in order to obtain publishable data. These compounds will then be subjected to donor studies with various Lewis bases such as pyridine and TMEDA and initially characterized using $^{1}H/^{13}C$ NMR.

1.5.2 Alkaline Earth Metal Heteroleptic Pyrazolate Tetraarylborate Compounds and Donor Studies

The second goal of this project is to reproduce compounds previously synthesized by Lavin and Woods in the Ruhlandt Group: $[Ae(thf)_2(Et_2O)_2(t\text{Bu}_2pz)][B((3,5\text{-}Me_2)C_6H_3)_4]$ (Ae = Ca, **5**†) and $[Ae(thf)_2(t\text{Bu}_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$ (Ae = Sr, **6**†; Ba, **7**†).[13] By synthesizing reproducible data, these compounds can be studied in order to further the understanding of M-π interactions of the tetraarylborate and pyrazolate ligand systems. These compounds will then be subjected to donor studies with various Lewis bases such as pyridine and TMEDA and initially characterized using ^{1}H/^{13}C NMR.

1.6 References

1 Atkins, P. W. *Shriver & Atkins' Inorganic Chemistry*. Oxford University Press, **2010.**

2 Cotton, F. A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. *Advanced Inorganic Chemistry*. Wiley-Interscience, **1999.**

3 Torvisco, A. and Ruhlandt-Senge, K. *Inorg. Chem.*, **2011**, *50*, 12223.

4 Torvisco, A. *Evaluating the Structure Determining Factors of Alkali and Alkaline Earth Metal Amides*. Syracuse University PhD Thesis, **2010.**

5 Goos, A. *Heavy Main-Group Metal Coordination Chemistry: A study of metal size, co-ligand, and secondary interactions*. Syracuse University PhD Thesis, **2015.**

6 Alexander, J. S. and Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2002**, 2761.

7 Buchanan, W. D.; Allis, D. G.; Ruhlandt-Senge, K. *Chem. Comm.* **2010**, *46*, 4449.

8 Gillett-Kunnath, M. M. *Heavy Alkaline Earth Metal Amides: Synthetic and Structural Investigations*. Syracuse University PhD Thesis, **2008.**

9 Marks, T. J.; et al. *Chem. Vapor Deposition.* **2000**, *6*, 180.

10 Imamoto, T. *Lanthanides in Organic Synthesis*. Academic Press, **1994**.

11 Evans, C. H. *Biochemistry of Lanthanides*. Plenum, **1991.**

12 Strauss, S. H. *The Search for Larger and More Weakly Coordinating Anions*. **1993.**

13 Woods, J. J. *Structural Variations Involving s-block Metal Pyrazolates*. Syracuse University Honors Program Capstone Thesis, **2016**.

14 Schaverien, C. J. *Organometallics*. **1992**, *11*, 3476.

15 Lavin, C. M.; Allis, D. G.; Clements, A. D. Goos, A. G.; Woods, J. J.; Gillet-Kunnath, M. M.; Ruhlandt-Senge, K. *Inorg. Chem.* submitted May **2019.**

16 Verma, A.; Guino-o, M.; Gillett-Kunnath, M.; Teng, W.; Ruhlandt-Senge, K. *Z. Anorg. Allg. Chemie.* **2009**, *635*, 903.

17 Kumar, K. A. and Jayaroopa, P. *Int. J. PharmTech. Res.* **2013**, *5*, 1473.

18 Torvisco, A.; O'Brien, A. Y.; Ruhlandt-Senge, K. *Coord. Chem. Rev.* **2011**, *255*, 1268.

CHAPTER 2:

Reproducibility and Extension of Alkaline Earth Metal Tetraarylborates

2.1 Introduction

In order to understand the relationship between the structure and function of an alkaline earth metal, the factors responsible for association and coordination trends must be studied. Depending on the metal, ligand, and co-ligand, these alkaline earth metal species can have different ion association modes such as contact, contact/separated, and separated, as seen in Figure 2.1.[1-8]

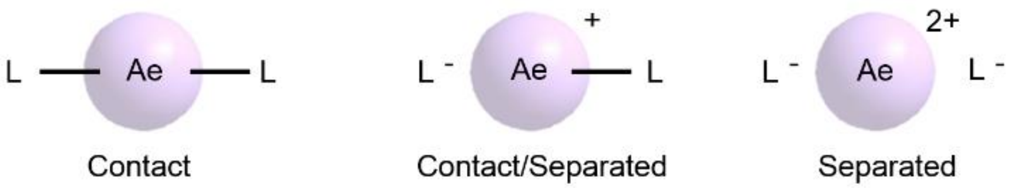
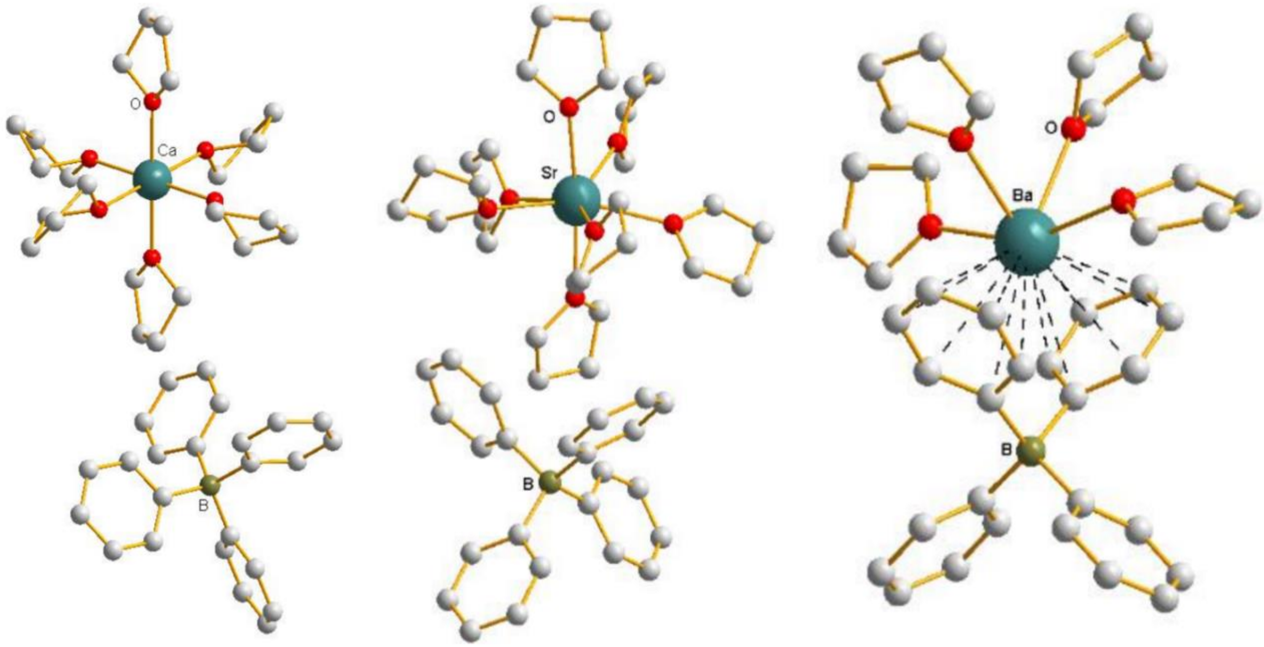


Figure 2.1 Possible alkaline earth metal ion association modes (Ae = alkaline earth metal, L = ligand).[1-8]

Prior research has been conducted that observed separated ions $[Ae(thf)_n][BPh_4]_2$ (Ae = Ca, n = 6; Sr, n = 7) for calcium and strontium, while the barium species appears as the contact/separated ion $[Ba((\eta^6\text{-}C_6H_5)_2BPh_2(thf)_4][BPh_4]_2$ with multiple M-π interactions, seen in Figure 2.2.[9,10] This indicates that many factors, including the properties of the metal, co-ligand, and ligand, affect the ion association and therefore the reactivity of the compounds.



I: $[Ca(thf)_6][BPh_4]_2$ **II:** $[Sr(thf)_7][BPh_4]_2$ **III:** $[Ba(thf)_4(BPh_4)][BPh_4]$

Figure 2.2 Previously synthesized separated ions for Ca (I) and Sr (II) tetraarylborate and Ba (III) contact/separated complex.[9,10] Hydrogen atoms and the second uncoordinated tetraarylborate are omitted for clarity.

Studies by previous Syracuse University Ruhlandt Group students Catherine Lavin and Joshua Woods assess the impact of aryl substitution in a family of heavy alkaline earth metal tetraarylborates.[11-13] Based on prior syntheses, $Ae[N(SiMe_3)_2]_2(thf)_2$ (Ae = Ca, Sr, Ba) were treated with alkyl-substituted tetraarylborate $[BAr_4]^-$ in diethyl ether and yielded compounds $[Ae(B((3,5\text{-}Me_2)C_6H_3)_4)_2(thf)_n]$ (Ae = Ca, **1**†, n = 0; Ae = Sr, **2**†, n = 0; Ae = Ba, **3**†, n = 1) and $[Ba\{B((4\text{-}t\mathrm{Bu})C_6H_4)_4\}_2]\cdot Et_2O$, **4**†, as seen in Equation 2.1 below, *via* transamination.[7-9] However, these compounds were obtained at very low yields and were not able to be systematically synthesized and reproduced. Thus, there was a need to successfully reproduce these compounds with increased yields in order to attain publishable results. Compounds **1-4**† were all successfully synthesized and characterized *via* ^{1}H, ^{11}B, ^{13}C NMR, infrared (IR) spectroscopy, and single crystal X-ray diffraction (SCXRD)[11-13]

$$Ae[N(SiMe_3)_2]_2(thf)_2 + 2HNEt_3BAr_4 \xrightarrow{Et_2O} [Ae(BAr_4)_2(thf)_n] + 2HN(SiMe_3)_2 + 2NEt_3$$

Ae = Ca, Sr, Ba
Ar = $((3,5\text{-}Me_2)C_6H_3)$, $((4\text{-}t\text{Bu})C_6H_4)$

Equation 2.1 Synthesis of Ae tetraarylborates, Ae = Ca, Ar = $((3,5\text{-}Me_2)C_6H_3)$, n = 0, **1**†**;** Ae = Sr, Ar = $((3,5\text{-}Me_2)C_6H_3)$, n = 0, **2**†**;** Ae = Ba, Ar = $((3,5\text{-}Me_2)C_6H_3)$, n = 1, **3**†**;** Ae = Ba, Ar = $((4\text{-}t\text{Bu})C_6H_4)$, n = 0, **4**†.[11-13]

2.2 Results and Discussion

2.2.1 Synthetic Chemistry

In order to successfully reproduce Compounds **1-4**†, several initial starting materials were synthesized. The $Ae[N(SiMe_3)_2]_2(thf)_2$ (Ae = Ca, Sr, Ba) were synthesized *via* Redox Transmetallation Ligand Exchange (RTLE)/Redox Transmetallation Protolysis (RTP) using previous synthetic methods as seen in Equation 2.2 below.[14] This one-pot synthesis was time- and cost-effective, as readily available triphenylbismuth was added to mechanically filed Ae in tetrahydrofuran (THF). The metal was activated under sonication and after several days and well-established work-up protocols, the Ae silyl amides were isolated in high yields.[14]

$$Ae_{(s)} + {}^{2}/_{3}\ BiPh_3 + 2HN(SiMe_3)_2 \rightarrow Ae[N(SiMe_3)_2]_2(thf)_2 + {}^{2}/_{3}\ Bi_{(s)} + 2HPh$$

Ae = Ca, Sr, Ba

Equation 2.2 Synthesis of Ae amide starting materials.[14]

The tetraarylborates were synthesized *via* a Grignard reaction following well-established protocols and work done by Lavin et. al., as seen in Equation 2.3.[11,12] The resulting tetraarylborate was then carefully monitored and heated under vacuum for several days to ensure complete dryness. This step, highlighted by Lavin et. al., was critical as any presence of water would prevent the target compounds from forming, and if the temperature was heated over 80 °C, the tetraarylborate would start to decompose.[11]

$$4\ Mg_{(s)} + 4ArBr \xrightarrow{THF} 4ArMgBr \xrightarrow{KBF_4} \xrightarrow{[HEt_3N]^+[Cl]^-} [HEt_3N]^+[BAr_4]^-$$

Ar = $((3,5\text{-}Me_2)C_6H_3)$, $((4\text{-}t\text{Bu})C_6H_4)$

$((3,5\text{-}Me)C_6H_3)$ $((4\text{-}t\text{Bu})C_6H_4)$

Equation 2.3 Synthesis of tetraarylborates.[7]

Compounds **1-4**[†] were then synthesized *via* transamination, as previously mentioned in Equation 2.1 above. However, instead of running the reactions on the Schlenk-line under inert gas, the reactions were fire-sealed in heavy-walled Carius tubes (*c.f.* Chapter 4). This reaction was driven by the pK_a of $HN(SiMe_3)_2$ (pK_a = 30) and the high solubility of the free amine.[11-13] All reactions were conducted under strict inert gas conditions, and the reaction in the sealed Carius tube was left to heat for several days at 60 °C (Compounds **1**[†], **3**[†], **4**[†]) and 35 °C (Compound **2**[†]). For the successful reproducible synthesis of these homoleptic compounds, synthetic techniques were modified from Lavin and Woods by using as little Et_2O as possible, resulting in over a 57% reduction in solvent volume which allowed for a more concentrated solution and ability to heat the reaction at various temperatures. Additionally, the reactions were slowly heated and visually monitored over several days with a slow increase in temperature in order to ensure the progression of the reaction. Equally important was that the temperature was slowly lowered back to room temperature over many days after heating to further induce crystal formation and hence increasing yields from 9% - 15% to 40% - 60% (Table 2.1).[11-13] The entire reaction occurred over several weeks versus the five to seven days as previously carried out by Lavin and Woods. The family of Compounds **1-4**[†] were successfully repeated using the modified procedures, ensuring reproducibility with improved yields. The ^1H NMR and other spectroscopic analysis for the compounds confirmed the presence of the complexes. For example, the ^1H NMR spectrum for Compound **2**[†] showed peaks at 7.29 ppm and 6.53 ppm confirming the aryl rings and at 2.10 ppm confirming the alkyl-substituents of the (3,5-Me_2)-tetraarylborate ligand system (*c.f.* Chapter 4 for more details). Thus, these results were finally able to be added to the manuscript in preparation and most recently submitted for review.[13]

Table 2.1 Summary of Reactions for Compounds **1-4**[†].

Compound	Temperature (℃) | Days	Observation	Yield (%)
[Ca(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$], **1**[†]	60 | 7	White crystals	40
[Sr(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$], **2**[†]	35 | 7	Tan crystals	40
[Ba(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$], **3**[†]	60 | 7	White-tan crystals	40
[Ba(B((4-tBu)C$_6$H$_4$)$_4$)$_2$], **4**[†]	60 | 7	White crystals	40
[Ca(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$], **1**[†]	60 | 7	White crystals	60
[Sr(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$], **2**[†]	35 | 7	Tan crystals	60
[Ba(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$], **3**[†]	60 | 7	White-tan crystals	60
[Ba(B((4-tBu)C$_6$H$_4$)$_4$)$_2$], **4**[†]	60 | 7	White crystals	60

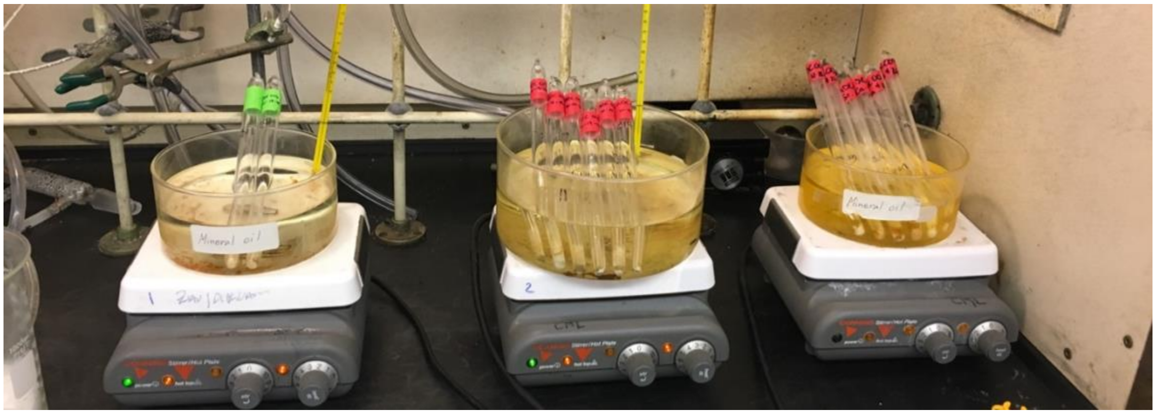


Figure 2.3 Reactions in Carius tubes monitored at various temperatures to induce crystallization

2.2.2 Structural Aspects of Compounds 1-4[†]

Compounds **1-4**[†] were characterized using single crystal X-ray crystallography. A summary of pertinent details obtained from characterization are provided in Table 2.2.[11-13] The compounds were additionally characterized with ^{1}H, ^{13}C, and ^{11}B nuclear magnetic resonance (NMR) spectroscopy as well as infrared (IR) spectroscopy.[11-13] This data is listed in the Experimental (*c.f.* Chapter 4).

Table 2.2 Crystallographic data for Compounds **1-4**†.[11-13]

	1	**2**	**3**	**4**
empirical formula	$C_{64}H_{72}B_2Ca$	$C_{64}H_{72}B_2Sr$	$C_{74}H_{95}B_2BaNOSi_2$	$C_{88}H_{124}B_2BaO_2$
formula weight	902.91	950.45	1229.64	1372.82
a (Å)	25.7853(14)	26.248(11)	13.0292(11)	22.6717(13)
b (Å)	16.7675(14)	16.835(11)	17.9564(15)	20.4230(13)
c (Å)	14.9589(9)	15.012(7)	30.913(3)	19.1338(11)
α (°)	90	90	90	90
β (°)	123.562(2)	124.428(16)	96.991(2)	114.628(2)
γ (°)	90	90	90	90
V (Å^3)	5389.3(6)	5472(5)	7178.4(11)	8053.5(8)
Z	4	4	4	4
space group	C2/c	C2/c	$P2_1/n$	C2/c
d_{calc} (Mg/m^3)	1.113	1.154	1.138	1.132
linear abs. coeff. (mm^{-1})	0.155	1.023	0.627	0.537
T (K)	90(2)	95(2)	90(2)	90(2)
2θ range (°)	1.540-33.230	1.818-31.612	1.314-27.101	1.404-27.023
no. of indep. reflns.	10285	9043	15748	8804
no. of parameters	323	323	791	489
R_1, wR_2 (all data)	0.0660, 0.1251	0.0385, 0.0805	0.1242, 0.2389	0.0403, 0.0836
R_1, wR_2 (>2σ)	0.0437, 0.1125	0.0303, 0.0760	0.0779, 0.2106	0.0321, 0.0787

2.2.2.1 Structural Characterization of Compounds 1-4†

Prior research observed separated ions in $[Ae(thf)_n][BPh_4]_2$ (Ae = Ca, n = 6; Sr, n = 7) for calcium and strontium, while the barium species complex showed a contact/separated ion $[Ba((\eta^6\text{-}C_6H_5)_2BPh_2(thf)_4][BPh_4]_2$ with multiple M-π interactions (Figure 2.2).[9,10] This demonstrated how many factors including the properties of the metal, co-ligand, and ligand affect the ion association and reactivity of these compounds. The previously synthesized Compounds **1-4**† all exhibited multiple M-π interactions yielding non-conventional contact molecules (Figures 2.4 – 2.7). Non-covalent interactions were assigned using established cut-off values (*c.f.* 1.2).[4-8]

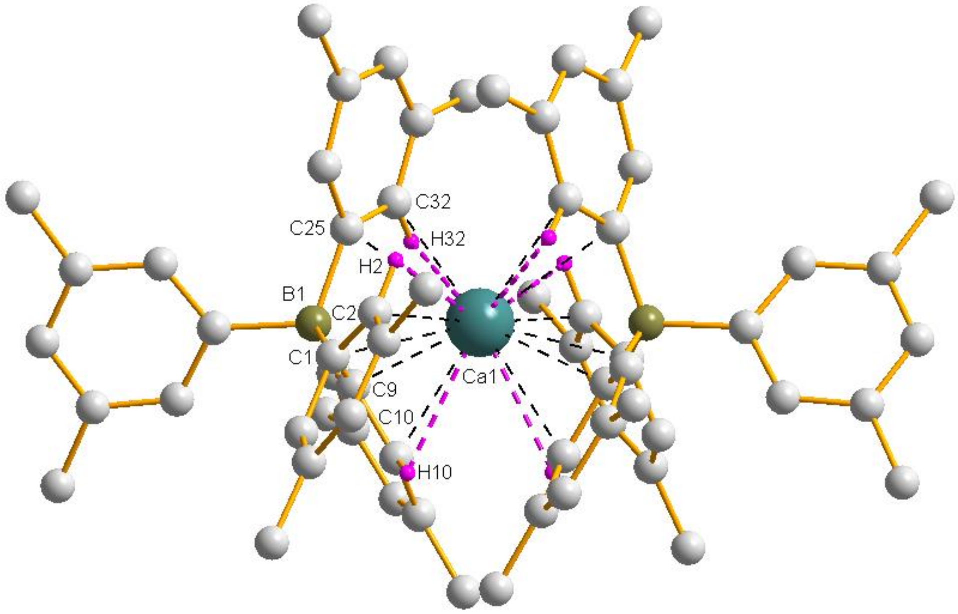


Figure 2.4 Crystal structure of **1**† $[Ca\{B((3,5\text{-}Me_2)C_6H_3)_4\}_2]$; hydrogen atoms omitted for clarity; second $[BAr_4]^-$ is generated by the symmetry transformation -x + 1, y, -z + 1/2. (Ca1-C1),2,9,10,25,32 as 2.763(1), 2.816(1), 2.745(1), 2.869(1), 2.723(1), 2.910(1) Å and Ca1-H2,10,32 as 2.64(1), 2.75(2), 2.88(2) Å, respectively.)[11-13]

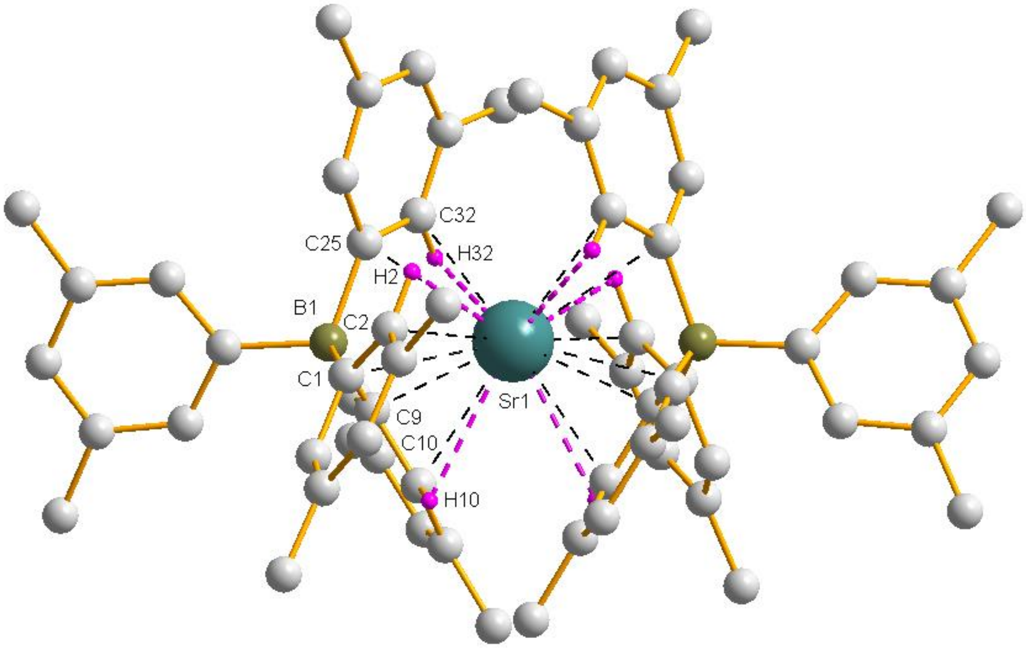


Figure 2.5 Crystal structure of **2**† $[Sr\{B((3,5\text{-}Me_2)C_6H_3)_4\}_2]$; hydrogen atoms not participating in agostic interactions are omitted for clarity; second $[BAr_4]^-$ is generated by the symmetry transformation -x + 1, y, -z + 1/2. (Sr1-C1,2,9,10,25,32 as 2.894(2), 2.906(2), 2.868(2), 2.943(2), 2.837(2), 2.965(2) Å and Sr1-H2,10,32 as 2.75(1), 2.81(2), and 2.95(2) Å, respectively.) [11-13]

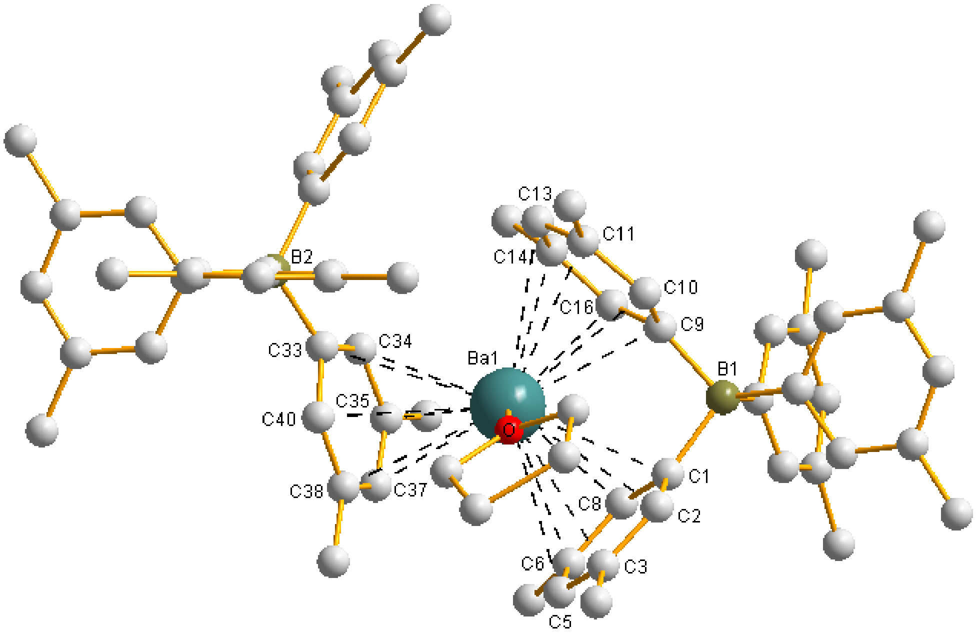


Figure 2.6 Crystal structure of Compound **3**† $[Ba\{B((3,5\text{-}Me_2)C_6H_3)_4\}_2(thf)]\cdot HN(SiMe_3)_2$; hydrogen atoms omitted for clarity. (Ba1-C1,2,3,5,6,8,9,10,11,13,14,16,33,34,35,37,38,40 as 3.139(6), 3.142(6), 3.275(6), 3.374(6), 3.400(6), 3.224(7), 3.117(5), 3.084(6), 3.168(6), 3.283(7), 3.353(7), 3.204(5), 3.398(6), 3.204(6), 3.087(7), 3.102(7), 3.189(6), 3.301(7) Å, respectively.)[11-13]

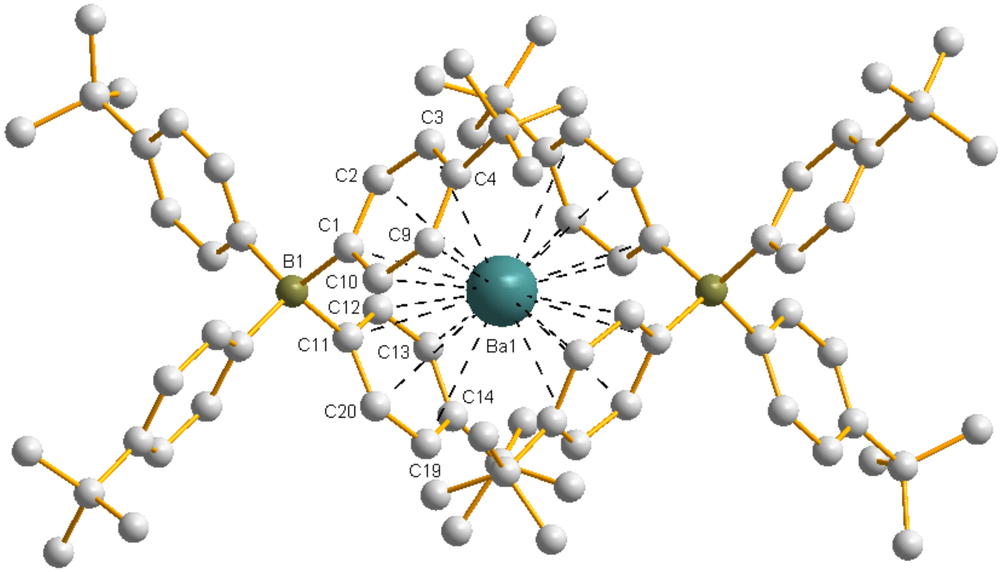


Figure 2.7 Crystal, structure of Compound **4**† $[Ba\{B((4\text{-}t\mathrm{Bu})C_6H_4)_4\}_2]\cdot Et_2O$; hydrogen atoms omitted for clarity; second $[BAr_4]^-$ is generated by the symmetry transformation -x + 1, y, -z + 1/2. (Ba1-C1,2,3,9,10,11,12,13,19,20 as 3.100(2), 3.137(2), 3.336(2), 3.366(2), 3.156(2), 3.120(2), 3.158(2), 3.391(2), 3.425(1), 3.207(2) Å, respectively.)[11-13]

Compounds **1-4**† all show a direct relationship between the number of M-π interactions and the metal size, a similar observation to previous research on alkali metal tetraarylborates.[15-18] Compounds **1**† and **2**† show no donor solvent present in these contact ion association complexes, but as the metal cation size increases such as in Compound **3**†, the metal center forms M-π interactions with the ligand in the presence of a thf coordinated donor. However, in Compound **4**†, the steric bulk of the *tert*-butyl substituents on the tetraarylborate ligands prevented the donor solvent from interacting with the barium center and an unprecedented complete donor free contact ion association complex for a barium metal center was finally achieved. Additionally, aryl-metal coordination generally results in the distortion of the tetrahedral boron environment as shown in Table 2.3.

Table 2.3 Comparison of M-π interactions and C-B-C angles (°).[11-13]

Compound	# of M-π	C-B-C (range)
1†	12: 6 x η^2	105.4(1)-111.4(1)
2†	12: 6 x η^2	105.6(1)-111.4(1)
3† (B2)	6: 1 x η^6	106.2(5)-112.1(5)
4†	20: 4 x η^5	102.3(1)-112.7(2)
3† (B1)	12: 2 x η^6	101.0(4)-115.6(5)

2.3 Donor Studies

Once the compounds were successfully synthesized, Lewis bases were introduced in order to examine the effects of various hapticities on the structure-function relationship and M-π interactions. Donors were added to the compounds and left to crystallize under argon gas. NMR studies are currently being conducted in order to characterize these new compounds. The compounds successfully dissolved in the donor solvent, shown in Figure 2.8 and Table 2.4.

$$\mathrm{Ae[N(SiMe_3)_2]_2(thf)_2 + 2HNEt_3BAr_4 + Donor \rightarrow [Ae(BAr_4)_2(thf)_n(Donor)_m] + 2HN(SiMe_3)_2 + 2NEt_3}$$

Equation 2.4 Synthesis of homoleptic donor compounds.

Table 2.4 Summary of donor studies reactions for Compounds **1-4**†.

Compound	Donor | ml	Observation
$[Ca(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$, **1**†	py | 1.5	Pale yellow solution
$[Sr(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$, **2**†	py | 1.5	Pale yellow solution
$[Ba(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$, **3**†	py | 1.5	Pale yellow solution
$[Ba(B((4\text{-}tBu)C_6H_4)_4)_2]$, **4**†	py | 1.5	Pale yellow solution
$[Ca(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$, **1**†	TMEDA | 1.5	Pale yellow solution
$[Sr(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$, **2**†	TMEDA | 1.5	Pale yellow solution
$[Ba(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$, **3**†	TMEDA | 1.5	Pale yellow solution
$[Ba(B((4\text{-}tBu)C_6H_4)_4)_2]$, **4**†	TMEDA | 1.5	Pale yellow solution

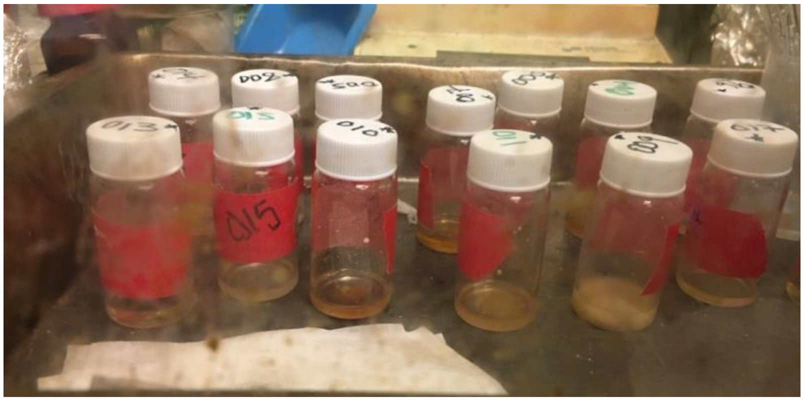


Figure 2.8 Reactions of tetraarylborate compounds with donor solvents.

2.4 Conclusions and Future Work

Compounds **1-4**† are the first examples of heavy alkaline earth metal alkyl-substituted tetraarylborates. These temperamental compounds required slow incremental increases in temperature for the reaction to proceed in the first week, followed by a slow decrease in temperature to further induce crystallization with improved yields over the following weeks. It is established that the formation of contact ion pairs is heavily dependent on the use of the weakly-coordinating diethyl ether rather than THF as a solvent.[9,10] However, although the solvent has been shown to affect the ion association mode of the tetraarylborate complexes, the major influencing factor remains unidentified, and further research must be conducted in order to determine this.

Donor studies are currently being conducted using pyridine (py) and TMEDA in order to investigate the effect of Lewis bases on the stabilization of the metal cation center of Compounds **1-4**[†]. Future work will expand on these studies and introduce different Lewis bases with various hapticities to study the resulting M-π interactions. In addition, sublimation studies will be conducted in order to test the viability of these compounds as potential precursors for MOCVD.

2.5 References

1 Goos, A. G.; Rosado Flores, P. J.; Takahashi, Y.; Ruhlandt-Senge, K. *In Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd, **2011**.

2 Buchanan, W. D.; Allis, D. G.; Ruhlandt-Senge, K. *Chem. Comm.* **2010**, *46*, 4449.

3 Guino-o, M. A.; Torvisco, A.; Teng, W.; Ruhlandt-Senge, K. *Inorg. Chem. Acta.* **2012**, *389*, 122.

4 Torvisco, A. and Ruhlandt-Senge, K. *Inorg. Chem.* **2011**, *50*, 12223.

5 Torvisco, A. *Evaluating the Structure Determining Factors of Alkali and Alkaline Earth Metal Amides.* Syracuse University PhD Thesis, **2010.**

6 Goos, A. *Heavy Main-Group Metal Coordination Chemistry: A study of metal size, co-ligand, and secondary interactions.* Syracuse University PhD Thesis, **2015.**

7 Alexander, J. S. and Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2002**, 2761.

8 Gillett-Kunnath, M. M. *Heavy Alkaline Earth Metal Amides: Synthetic and Structural Investigations*. Syracuse University PhD Thesis, **2008.**

9 Langer, J.; Krieck, S.; Gorls, H.; Seidel, W.; Westerhausen, M. *New J. Chem.* **2010**, *34*, 1667.

10 Hitzbleck, J. *Syntheses and Structural Survey of Novel Alkaline Earth and Rare Earth Metal Complexes.* Syracuse University PhD Thesis, **2004.**

11 Lavin, C.M. and Ruhlandt-Senge, K., **2017**, *unpublished results*.

12 Woods, J. J. *Structural Variations Involving s-block Metal Pyrazolates.* Syracuse University Honors Program Capstone Thesis, **2016**.

13 Lavin, C. M.; Allis, D. G.; Clements, A. D.; Goos, A. G.; Woods, J. J.; Gillett-Kunnath, M. M.; Ruhlandt-Senge, K. *Inorg. Chem.* submitted, May **2019**.

14 Gillett-Kunnath, M. M.; MacLellan, J. G.; Forsyth, C. M.; Andrews, P. C.; Deacon, G. B.; Ruhlandt-Senge, K. *Chem. Comm.* **2008**, *37*, 4490.

15 Behrens, U.; Hoffmann, F.; Olbrich, F. *Organometallics*. **2012**, *31*, 905.

16 Pajzderska, A.; Maluszynska, H.; Wasicki, J. *Naturforsch.* **2002,** 847.

17 Bryan, J. C. *Z. Kristallogr.* **2000.** *215*, 621.

18 Hoffmann, D.; Bauer, W.; Hampel, F.; van Elkema Hommes, N. J. R.; v. R. Schleyer, P.; Otto, P.; Piper, U.; Stalke, D.; Wright, D.S.; Snaith, R. *J. Am. Chem. Soc.* **1994,** *116*, 528.

CHAPTER 3:

Reproducibility and Extension of Alkaline Earth Metal Tetraarylborate Pyrazolates

3.1 Introduction

It was proposed that reacting the pyrazolate and tetraarylborate ligands with $Ae[N(SiMe_3)_2]_2(thf)_2$ (Ae = Ca, Sr, Ba) *via* transamination would result in mixed pyrazolate and tetraarylborate compounds similar to lanthanide work done by Deacon *et. al.*, $[Yb(tBu_2pz)(thf)(BPh_4)]{\bullet}2C_6D_6$ (Figure 3.1).[1] Thus, Lavin and Woods were able to isolate $[Ae(thf)_2(Et_2O)_2(tBu_2pz)][B((3,5\text{-}Me_2)C_6H_3)_4]$ (Ae = Ca, **5**†) and $[Ae(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$ (Ae = Sr, **6**†; Ba, **7**†) by reacting the *tert*-butyl pyrazolates and tetraarylborates with the $Ae[N(SiMe_3)_2]_2(thf)_2$ amide *via* transamination.[2]

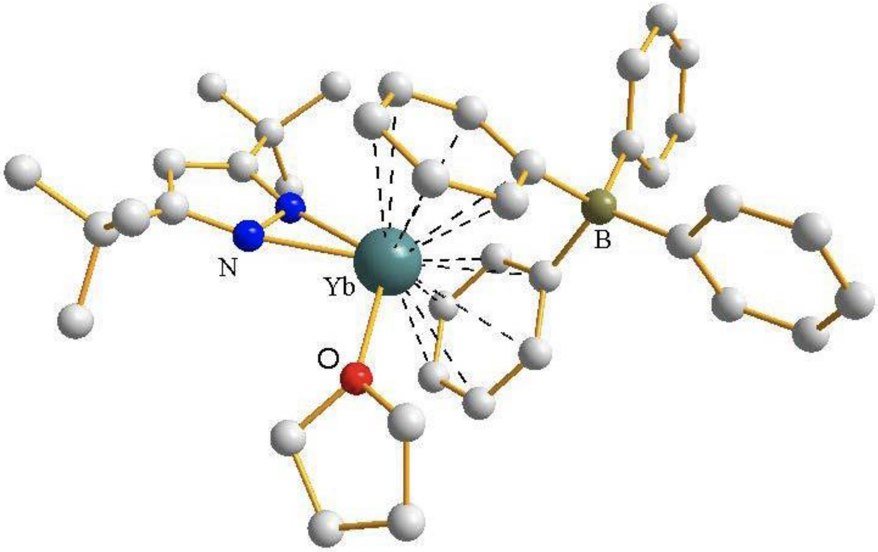


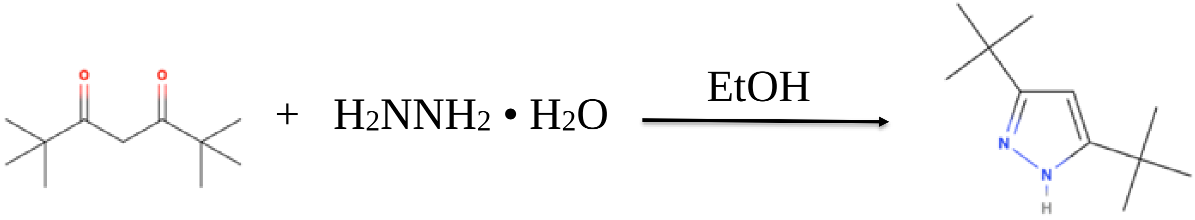
Figure 3.1 $[Yb(tBu_2pz)(thf)(BPh_4)]{\bullet}2C_6D_6$ showing the $\eta^6{:}\eta^6$ coordination of the $[BPh_4]^-$ ligand to Yb^{2+}.[1] Hydrogen atoms and C_6D_6 omitted for clarity.

However, Lavin and Woods had encountered difficulties when attempting to successfully reproduce these novel compounds that were isolated with yields ~ 0.1%.[2] After adjusting the ratios of the reactants and synthetic conditions, Compounds **5-7**† were synthesized and confirmed *via* single crystal X-ray diffractometry and nuclear resonance magnetic spectroscopy. Thus, the second part of this thesis focuses on these efforts towards successfully reproducing and upscaling these novel heteroleptic tetraarylborate and pyrazolates.

3.2 Results and Discussion

3.2.1 Synthetic Chemistry

Starting materials utilized in the synthesis of Compounds **5-7**† were $Ae[N(SiMe_3)_2]_2(thf)_2$ (Ae = Ca, Sr, Ba) and *t*Bu_2pzH. The pyrazole ligand was synthesized using established synthetic protocols from acetylene and diazomethane, shown in Equation 3.1.[4-9] In addition, the tetraarylborate was prepared *via* previously discussed synthetic methods (*c.f.* 2.2.1).[3]



Equation 3.1 Synthesis of the pyrazole ligand.[4-9]

Compounds **5-7**† were again synthesized *via* transamination as seen in Equation 3.2 below. The transamination was driven by the pK_a of *t*Bu_2pzH (pK_a = 13-15) and the high solubility of the free amine.[2] Learning from synthetic modifications to reproduce the Ae tetraarylborates (*c.f.* Chapter 2), all reactions were conducted under strict inert gas conditions, and the reaction was sealed in a Carius tube and left to heat for several days at 35 °C (beyond this temperature, slight decomposition was observed), followed by slow cooling to room temperature over many days in order to further induce crystallization. Synthetic techniques were further modified from Lavin and

Woods by adjusting the ratio of pyrazolate, tetraarylborate, and Ae silyl amide from 0.05 mmol to 0.5 mmol scale. This larger mmol scale helped to better visualize the reaction as it occurred, and yields were increased from ~1% to 40-60% (Table 3.1). Again, the entire reaction occurred over several weeks versus the five to seven days as previously carried out. The family of Compounds **5-7**† were repeated using the modified procedures, ensuring reproducibility with improved yields. When looking at the ^{1}H NMR spectra for these three compounds, there was a notable absence of a broad NH(pz) peak that normally appears between 10 and 12 ppm signifying that the free pyrazole had indeed coordinated to the Ae metal center. For example, Compound **7**† showed peaks that demonstrated the alkyl substituted tetraarylborate ligand system and the substituted pyrazolate ligand at 7.932, 6.746, 6.116, 3.240, 3.005, 2.181, 2.054, 1.320, and 1.089 ppm (i.e.: 7.932 (s, 8H, o-H (C_6H_3)), 6.746 (s, 4H, p-H (C_6H_3)),6.116 (s, 1H, H-4 (pz)), 3.240 (q, 2H, residual Et_2O), 3.005 (br m 8H, CH_2O (thf)), 2.181 (s, 24H(3,5-Me_2)), 2.054 (br t, 3H, residual Et_2O), 1.320 (s, 18H, H-*t*Bu (pz)), 1.089 (m, 8H, CH_2 (thf)). Et_2O resonances at $\delta\delta$ = 3.240, 2.054 are due to residual solvent that had not evaporated before the sample was taken; *c.f.* Chapter 4 for more details). Thus, these results were able to be added to a manuscript in preparation.

$$\mathrm{Ae[N(SiMe_3)_2]_2(thf)_2 + HNEt_3B((3,5\text{-}Me_2)C_6H_3)_4 + \mathit{t}Bu_2pzH \xrightarrow{Et_2O}}$$

$$\mathrm{[Ae(\mathit{t}Bu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)_x(thf)_m(Et_2O)_n][BAr_4]_y + 2HN(SiMe_3)_2 + NEt_3}$$

Ae = Ca, Sr, Ba

Equation 3.2 Synthesis of heteroleptic alkaline earth metal tetraarylborate pyrazolate compounds.

Table 3.1 Summary of reactions for Compounds **5-7**†**.**

Compound	Temperature (°C) | Days	Observation	Yield (%)
[Ca(thf)$_2$(Et$_2$O)$_2$(*t*Bu$_2$pz)][(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)], **5**†	35 | 7	White crystals	40
[Sr(thf)$_2$(*t*Bu$_2$pz)(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)], **6**†	35 | 7	White crystals	40
[Ba(thf)$_2$(*t*Bu$_2$pz)(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)]**, 7**†	35 | 7	White crystals	40
[Ca(thf)$_2$(Et$_2$O)$_2$(*t*Bu$_2$pz)][(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)], **5**†	35 | 7	White crystals	60
[Sr(thf)$_2$(*t*Bu$_2$pz)(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)], **6**†	35 | 7	White crystals	60
[Ba(thf)$_2$(*t*Bu$_2$pz)(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)]**, 7**†	35 | 7	White crystals	60

Figure 3.2 Reactions in Carius tubes monitored at various temperatures to induce crystallization.

3.2.2 Structural Aspects of Compounds 5-7†

Compounds **5-7**† were all analyzed using single crystal X-ray diffractometry. Important crystallographic data are provided below. Compounds **5-7**† were additionally analyzed using ^{1}H and ^{13}C NMR spectroscopy. For each compound, the NMR spectra confirmed the stoichiometry of Et_2O in the solution. Important data is provided in the Experimental (*c.f.* Chapter 4).

Table 3.2 Crystallographic data for Compounds **5-7**†.[2]

	5†	**6**†	**7**†
empirical formula	$C_{100}H_{120}BN_2O_5Ca$	$C_{51}H_{71}BSrN_2O_2$	$C_{51}H_{80}BBaN_2O_2$
formula weight	1480.86	842.52	901.32
a (Å)	20.9102(13)	19.2912(16)	19.253(19)
b (Å)	13.3936(13)	14.7453(13)	15.0325(14)
c (Å)	22.5102(18)	18.3176(14)	18.3661(18)
α (°)	90	90	90
β (°)	109.365(4)	113.851(2)	113.828
γ (°)	90	90	90
V ($Å^3$)	5947.6(8)	4765.5(7)	4862.4(8)
Z	2	4	4
crystal system	monoclinic	monoclinic	monoclinic
space group	Cc	$P2_1/c$	$P2_1/c$
d_{calc} (Mg/m^3)	0.827	1.174	1.231
linear abs. coeff. (mm^{-1})	0.092	1.170	0.855
T (K)	95(2)	95(2)	95(2)
2θ range (°)	1.838-30.612	1.800-28.726	2.225-30.615
# independent reflections	17986	12316	14940
# parameters	273	557	514
R_1, wR_2 (all data)	0.1757, 0.3989	0.0786, 0.0955	0.0498, 0.1926
R_1, wR_2 (>2σ)	0.1542, 0.3833	0.0428, 0.0842	0.0446, 0.1854

3.2.2.1 Structural Characterization of Compounds 5-7†

Compound **5**† showed a separated ion compound with no direct interactions between the metal center and the tetraarylborate. Upon using metals with a larger ionic radius such as Sr and Ba, M-π interactions between the metal center and borate were observed resulting in a contact ion association in Compounds **6**† and **7**†, similar to Deacon's [Yb(*t*Bu$_2$pz)(thf)(BPh$_4$)]•2C$_6$D$_6$ (Figure 3.1).[1] The increased size of the heavier Ae metal cation center allows for an increase in the number of possible secondary interactions within the complex contributing to its coordinative saturation. Thus, for each of the three compounds, the *t*Bu$_2$pz ligand appears to be a major influence on the coordination of the tetraarylborate, along with the size of the metal cation (Figures 3.3-3.5).

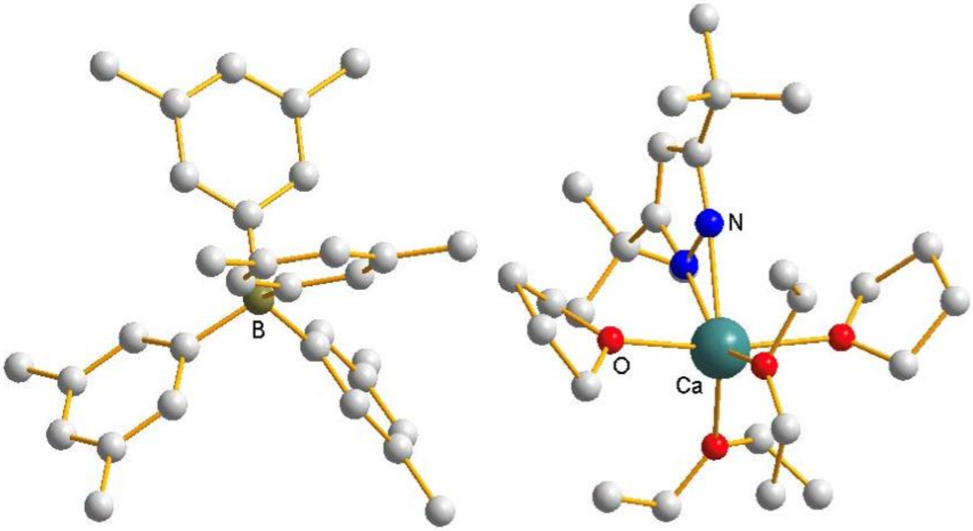


Figure 3.3 Crystal structure of Compound **5**† [Ca(thf)$_2$(Et$_2$O)$_2$(*t*Bu$_2$pz)][B((3,5-Me$_2$)C$_6$H$_3$)$_4$)]. Hydrogen atoms and disordered atoms omitted for clarity. (Ca1-N1, 2.271(8); Ca1-N2 , 2.342(8); Ca1-O, 2.362(7) – 2.371(9); B1-C, 1.647(12) – 1.666(12) Å, respectively.)[2]

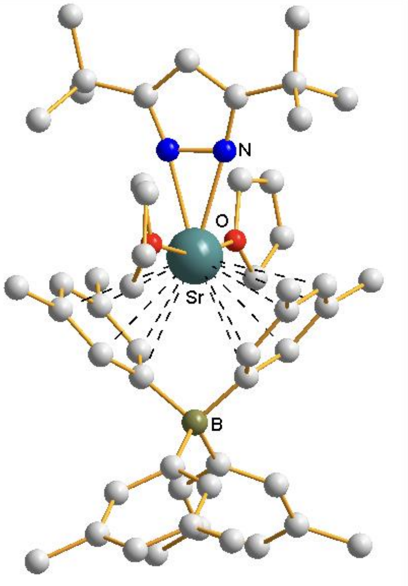


Figure 3.4 Crystal structure of Compound **6**† [Sr(thf)$_2$(*t*Bu$_2$pz)(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)]. M-π interactions are shown as dashed lines. Hydrogen atoms and disordered positions are removed for clarity. (Sr1-N1, 2.48(17); Sr1-N2 , 2.52(29); Sr1-O, 2.63(49) – 2.66(07); B1-C, 1.63(23) – 1.66(03); Sr-C, 2.99(92) – 3.26(6) Å, respectively.)[2]

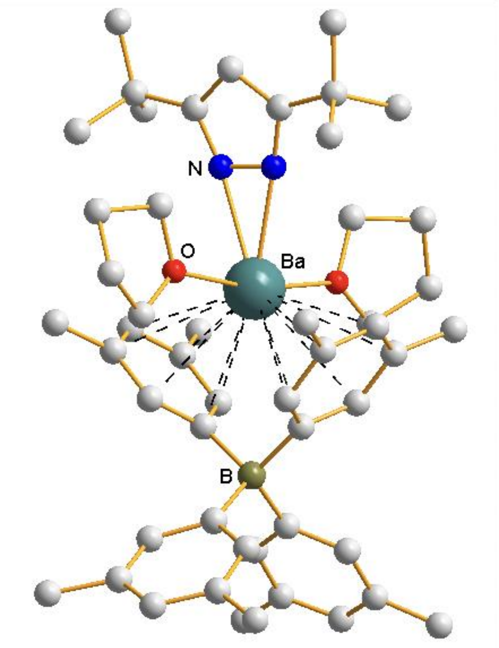


Figure 3.5 Crystal structure of Compound **7**† [Ba(thf)$_2$(*t*Bu$_2$pz)(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)]. M-π interactions are shown as dashed lines. Hydrogen atoms and disordered positions are removed for clarity. (Ba1-N1, 2.630(2); Ba1-N2 , 2.676(2); Ba1-O, 2.773(2) – 2.801(9); B1-C, 1.645(4) – 1.658(3); Ba-C, 3.139(2) – 3.357 (6) Å, respectively.)[2]

3.3 Donor Studies

Once the compounds were successfully synthesized, Lewis bases were introduced in order to examine the effects of various hapticities on the structure-function relationship and M-π interactions. Donors were added to the compounds and left to crystallize under argon gas. NMR studies are currently being conducted in order to characterize these new compounds. Compounds **5-7**† successfully dissolved in the donor solvent, shown in Figure 3.6 and Table 3.3.

$$\mathrm{Ae[N(SiMe_3)_2]_2(thf)_2 + HNEt_3B((3,5\text{-}Me_2)C_6H_3)_4 + \mathit{t}Bu_2pzH \xrightarrow{Donor}}$$

$$\mathrm{[Ae(\mathit{t}Bu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)_x(thf)_m(Donor)_n][BAr_4]_y + 2HN(SiMe_3)_2 + NEt_3}$$

Equation 3.3 Synthesis of heteroleptic donor compounds.

Table 3.3 Summary of donor studies reactions for Compounds **5-7**†.

Compound	Donor | ml	Observation
$\mathrm{[Ca(thf)_2(Et_2O)_2(\mathit{t}Bu_2pz)][(B((3,5\text{-}Me_2)C_6H_3)_4)]}$, **5**†	py | 1.5	Pale yellow solution
$\mathrm{[Sr(thf)_2(\mathit{t}Bu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]}$, **6**†	py | 1.5	Pale yellow solution
$\mathrm{[Ba(thf)_2(\mathit{t}Bu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]}$**, 7**†	py | 1.5	Pale yellow solution
$\mathrm{[Ba(thf)_2(\mathit{t}Bu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]}$**, 7**†	TMEDA | 1.5	Pale yellow solution

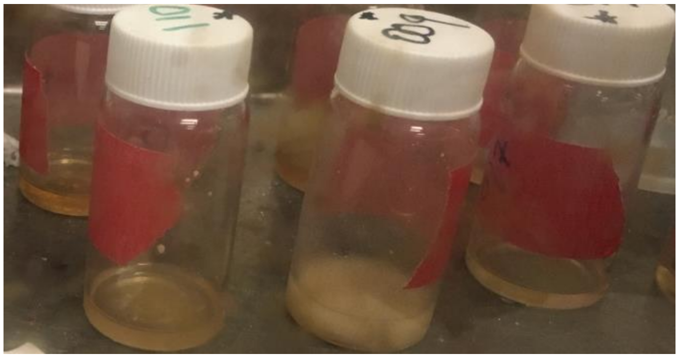


Figure 3.6 Reactions of tetraarylborate pyrazolate compounds with donor solvents.

3.4 Conclusions and Future Work

Compounds **5-7**† are the first examples of these heavy alkaline earth metal heteroleptic tetraarylborate pyrazolates. These compounds required slow incremental changes in temperature for the reaction to complete, and a gradual decrease in temperature to room temperature in order to further improve crystallization with improved yields over the following weeks.

Donor studies are currently being conducted using pyridine (Py) and TMEDA in order to examine the effect of Lewis bases on the stabilization of the metal cation of Compounds **5-7**†. Future work will expand on these donor studies and introduce different Lewis bases with varying hapticities in order to study the resulting structure-function relationships and M-π interactions (Figure 3.7). Finally, sublimation studies will be conducted in order to test the viability of these compounds as potential precursors for MOCVD.

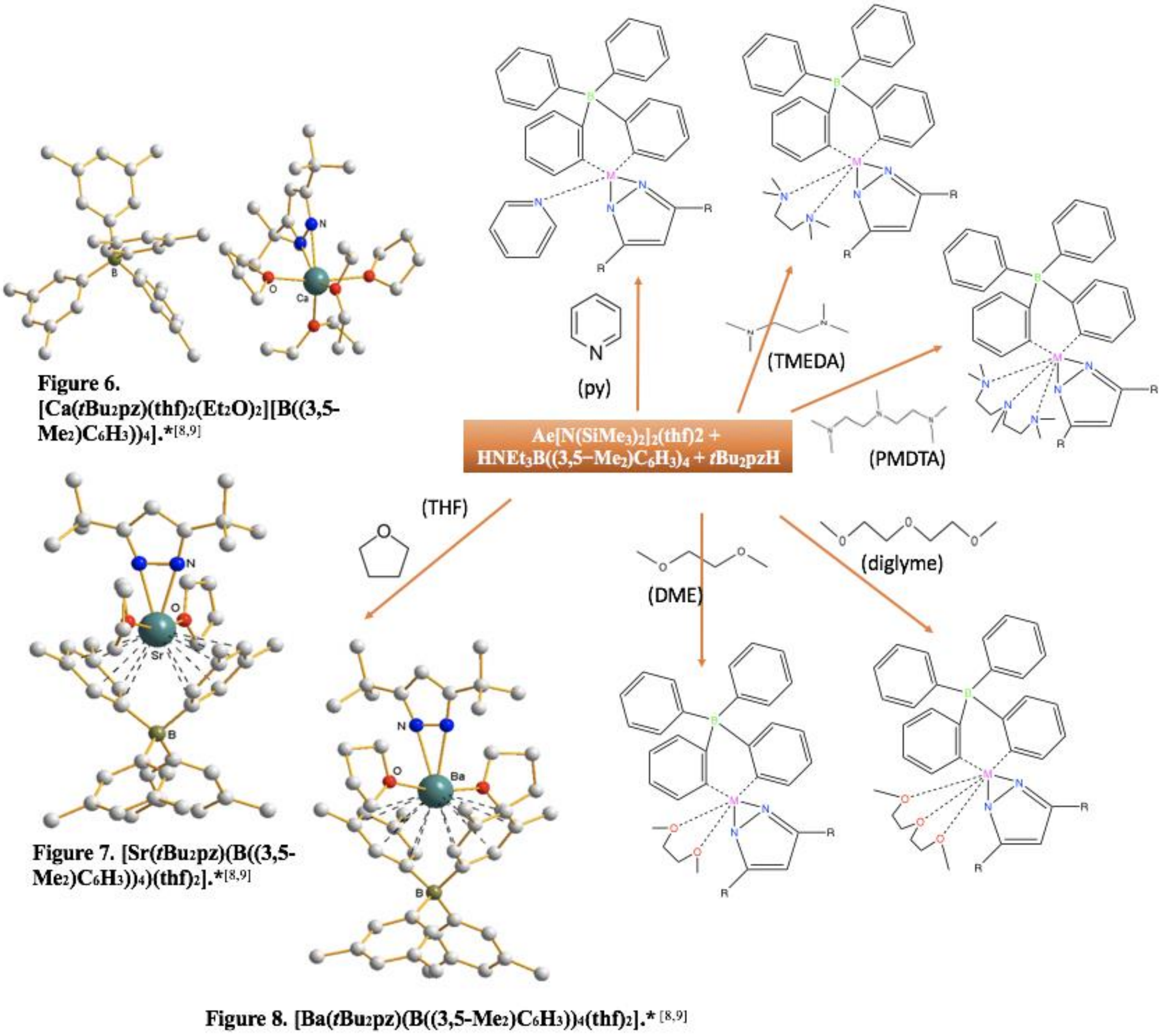


Figure 3.7 Future Lewis bases to examine for donor studies.

3.5 References

1 Deacon, G. B.; Forsyth, C. M.; Junk, P. C. *Eur. J. Inorg. Chem.*, **2005**, 817.

2 Woods, J. J. *Structural Variations Involving s-block Metal Pyrazolates*. Syracuse University Honors Program Capstone Thesis, **2016**.

3 Murphy, S.; Yang, X.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 2411.

4 Beaini, S.; Deacon, G. B.; Erven, A. P.; Junk, P. C.; Turner, D. R. *Chem. An Asian J.* **2007**, *2*, 539.

5 Lavin, C. M. and Ruhlandt-Senge, K., **2017**, *unpublished results*.

6 Hitzbleck, J.; O’Brien, A. Y.; Deacon, G. B.; Ruhlandt-Senge, K. *Inorg. Chem.* **2006**. *45*, 10329.

7 Stepaniuk, O. O; Matviienko, V. O.; Kontratov, I. S.; Vitruk, I. V.; Tolmachev, A. O. *Synthesis*. **2013**, *45*, 925.

8 Zhang, J.; Chen, S-H.; Yu, X-Q. *Tetrahedron*. **2011**, *67*, 9618.

9 Yang, G. and Raptis, G. *Inorg. Chim. Acta.* **2003,** *352*, 98.

CHAPTER 4:

Experimental

4.1 General Information

Due to the compounds being extremely air and water sensitive, all reactions were carried out under an argon atmosphere using standard Schlenk techniques.[1] The solvents and donors, including diethyl ether, dimethoxyethane, tetrahydrofuran, hexane, and toluene were obtained commercially (VWR), purified with a Vac-Atmosphere® solvent system, and degassed prior to use with three freeze-pump-thaw cycles.

1,1,1,3,3,3-hexamethyldisilazane (H-HMDS, Aldrich), pyridine (VWR), TMEDA (VWR) and PMDTA (VWR) were obtained commercially and refluxed over CaH_2 (Aldrich) overnight prior to vacuum distillation.[2] The alkaline earth metals were obtained commercially (Strem) at high purity +99.9% (Magnesium and calcium turnings or distilled ingots; strontium, and barium pieces under oil). Alkaline earth metal amides, $[Ae(N(SiMe_3)_2)(thf)_2]$ (Ae = Mg, Ca, Sr, Ba), were synthesized by literature procedures.[3] Pyrazoles were synthesized by a modified literature procedure by refluxing the corresponding diketone (Strem) with hydrazine monohydrate (Strem) in ethanol for 24 hours, recrystallized from acetone/hexane (VWR), and dried under vacuum for ≥24 hours.[4-6] Tetraarylborates were synthesized according to literature procedures[7-9] and dried at 80 °C under vacuum for three and a half days.[10-11]

X-ray quality crystals were removed from the Carius tube in the glove box and covered with hydrocarbon oil (Infeneum). X-ray data was collected under 100 K using a Bruker Kappa Apex II Duo CCD diffractometer with Mo_{Ka} radiation ($\lambda = 0.71073$ Å).[12] The crystals were attached to a MITEGEN® mount and remained under a nitrogen stream using a Cryocool LN-3 low-temperature device from Cryoindustries of America, Inc. Structure solution and refinement details were reported. All non-hydrogen atoms were refined anisotropically.[12]

4.1.1 Carius Tube Pressure

WARNING: Carius tube contents are under high pressure and measures must be taken to prevent tube bursting and potential injury. Tubes must be transported in metal sleeves and reactions must be heated behind a blast shield.

To avoid the risk of a Carius tube bursting, it was ensured that the working pressure inside the sealed tube never exceeded 10 bar. Using the ideal gas law (PV = nRT),[13] it was determined that about 3.75 mL of Et_2O would produce a pressure exceeding 10 bar at 60 °C. Reactions were monitored to ensure that the volume of the liquid inside the tubes did not change dramatically as the reaction progressed. Although it is difficult to determine the exact pressure as the reaction occurs, it can be assumed that the pressure did not exceed safe operating levels for any of the tubes.

4.2 Starting Materials

4.2.1 Redox Transmetallation Ligand Exchange/Protolysis (RTLE/RTP) General Procedure

The alkaline earth metal, triphenyl bismuth ($BiPh_3$, VWR) were combined in a Schlenk flask, then degassed THF and H-HMDS were added via a syringe. The reaction was stirred at room temperature overnight and sonicated for 12 days. All volatiles were then evacuated off and 40 mL of degassed hexane was added. The reaction was then filtered via a filter cannula and left to crystallize at -25 °C.[3]

4.2.1.1 Specific Synthesis

[Ca(N(SiMe$_3$)$_2$(thf)$_2$]:

Ca pieces (0.41 g / 10 mmol), BiPh$_3$ (1.32 g / 3 mmol), HMDS (1.50 g / 9 mmol). Yield = 78 %. ^{1}H NMR (C_6D_6) (ppm): 0.30 (s, 36H, SiMe$_3$); 1.22 (s, 8H, THF); 3.51 (s, 8H, THF). ^{13}C NMR (C_6D_6) (ppm): 5.4 (SiMe$_3$); 25.06 (THF); 69.17 (THF).

[Sr(N(SiMe$_3$)$_2$(thf)$_2$]:

Sr pieces (0.88 g / 10 mmol), HMDS (1.50 g / 9 mmol). Yield = 85 %. ^{1}H NMR (C_6D_6) (ppm): 0.34 (s, 36H, SiMe$_3$); 1.24 (s, 8H, THF); 3.51 (s, 8H, THF). ^{13}C NMR (C_6D_6) (ppm): 5.5 (SiMe$_3$); 25.06 (THF); 69.17 (THF).

[Ba(N(SiMe$_3$)$_2$(thf)$_2$]:

Ba pieces (1.37 g / 10mmol), BiPh$_3$ (1.32 g / 3 mmol), HMDS (1.50 g / 9 mmol). Yield = 90 %. ^{1}H NMR (C_6D_6) (ppm): 0.36 (s, 36H, SiMe$_3$); 1.26 (s, 8H, THF); 3.51 (s, 8H, THF). ^{13}C NMR (C_6D_6) (ppm): 5.7 (SiMe$_3$); 25.06 (THF); 69.17 (THF).

4.2.2 Pyrazole General Procedure

The diketone, hydrazine monohydrate ($H_2NNH_2{\bullet}H_2O$), and ethanol were combined in a 500 mL flask and closed with a rubber septum. A reflux condenser was attached to the flask, placed in a mineral bath, and set to heat at about 215 °C. The mixture was allowed to reflux for 24 hours, then placed in the rotavap until crystals started to form. The pyrazolates were recrystallized in a 1:4 mixture of hexane/acetone for 3 days.[4-6]

4.2.2.1 Specific Synthesis

***t*Bu$_2$pzH:**

2,2,6,6-Tetramethyl-3,5-heptanedione (9.214 g / 50 mmol), $H_2NNH_2{\bullet}H_2O$ (2.47 mL / 51 mmol), EtOH (250 mL). ^{1}H NMR (C_6D_6) (ppm): 12.29 (br, 1H; N-H (pz)); 6.12 (s, 6 H; C4-H(pz)); 1.38

(s, 108 H; *t*Bu-H). ^{13}C NMR (C_6D_6) (ppm): 15.1 (ipso-C(pz)); 97.1 (*C*H(pz)); 32.6 (*C*CH_3); 32.0, 31.9, 31.6 (C*C*H_3).

4.2.3 Tetraarylborate General Procedure

Tetraarylborates were synthesized according to literature procedures and dried at 80 °C under vacuum for four days. The borates were carefully monitored during this time to ensure that the temperature did not exceed 80 °C.[2,10-11]

4.2.3.1 Specific Synthesis

$HNEt_3B((3,5\text{-}Me_2)C_6H_4)_4$:

Aryl bromide: 5-bromo-*m*-xylene. Refluxed one hour during formation of Grignard reagent. ^{1}H NMR (CD_3CN) (ppm): 1.26 (t, 9H, CH_3); 2.12 (s, 24H, CH_3); 3.09 (q, 6H, CH_2); 6.48 (s, 4H, *p*-CHPh); 6.89 (s, 8H, *o*-CHPh). ^{11}B NMR (CD_3CN) (ppm): -6.88.

$HNEt_3B((4\text{-}tBu)C_6H_4)_4$:

Aryl bromide: 1-bromo-4-*tert*-butylbenezene. Refluxed three hours during formation of Grignard reagent. ^{1}H NMR (CD_3CN) (ppm): 1.25 (s, 45H, CH_3); 3.11 (q, 6H, CH_2); 7.04 (d, 8H, *m*-CHPh); 7.25 (m, 8H, *o*-CHPH). ^{11}B NMR (CD_3CN) (ppm): -7.23.

4.3 Tetraarylborate Compounds General Procedure

In the glove box, $[Ae(N(SiMe_3)_2(thf)_2]$ (Ae = Ca, Sr, Ba) and $HNEt_3BAr_4$ (Ar = $(3,5\text{-}Me_2)C_6H_3$, $(4\text{-}t\text{Bu})C_6H_4$) were combined in a Carius tube with about 1 mL of Et_2O. The tube was sealed under vacuum and heated in an oil bath for 7 days before slowly decreasing the temperature to room temperature to ensure a complete reaction.[10]

4.3.1 Specific Synthesis

[Ca(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$] (1†):

Ca[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (0.024 g / 0.05 mmol) and HNEt$_3$B((3,5-Me$_2$)C$_6$H$_3$)$_4$ (0.053 g / 0.10 mmol). The reaction was slowly heated up to 60 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 50.0% ave. Mp: decomposes between 115-117 °C (turns beige). ^{1}H NMR ([d$_6$]benzene): δ = 7.24 (s, 13H, *o*-C$_6$H$_3$), 6.57 (s, 8H, *p*-C$_6$H$_3$), 2.13 (s, 48H, CH$_3$) ppm. ^{11}B NMR ([d$_6$]benzene): δ = -7.22 ppm. ^{13}C NMR ([d$_6$]benzene): δ = 134.25 (*o*-C$_6$H$_3$), 126.78 (*p*-C$_6$H$_3$), 22.53 (CH$_3$) ppm. IR (cm^{-1}): ν 1576.66 (w), 1033.22 (w), 840.59(m). There is overlap of the C$_6$D$_6$ peak and *o*-C$_6$H$_3$ peak at 7.24 ppm, which resulted in the lower integration value of 13H instead of 16H.

[Sr(B((3,4-Me$_2$)C$_6$H$_3$)$_4$)$_2$] (2†):

Sr[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (0.028 g / 0.05 mmol) and HNEt$_3$B((3,5-Me$_2$)C$_6$H$_3$)$_4$ (0.053 g / 0.10 mmol). The reaction was slowly heated up to 35 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 50.0% ave. Mp: decomposes between 123-125 °C (turns beige). ^{1}H NMR ([d$_6$]benzene): δ = 7.29 (s, 16H, *o*-C$_6$H$_3$), 6.53 (s, 8H, *p*-C$_6$H$_3$), 2.10 (s, 48H, CH$_3$) ppm. ^{11}B NMR ([d$_6$]benzene): δ = -6.99 ppm. ^{13}C NMR ([d$_6$]benzene): δ = 138.31 (*o*-C$_6$H$_3$), 134.13 (*p*-C$_6$H$_3$), 22.40 (CH$_3$) ppm. IR(cm^{-1}): ν 1575.66 (w), 1034.00 (w), 841.46 (m).

[Ba(B((3,5-Me$_2$)C$_6$H$_3$)$_4$)$_2$(thf)] (3†):

Ba[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (0.031 g / 0.05 mmol) and HNEt$_3$B((3,5-Me$_2$)C$_6$H$_3$)$_4$ (0.053 g / 0.10 mmol). The reaction was slowly heated up to 60 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 50.0% ave. Mp: decomposes between 136-138 °C (turns beige). ^{1}H NMR (400 MHz, [D$_8$]benzene, 25°C]: δ = 7.46

(s, 16H, *o*-C_6H_3), 6.47 (s, 8H, *p*-C_6H_3), 3.44-3.47 (m, 4H, THF), 2.06 (s, 48H, CH_3), 1.34-1.37 (m, 4H THF) ppm. ^{11}B NMR (400 MHz, [D_6]benzene, 25°C]: δ = -6.26 ppm. ^{13}C NMR (400 MHz, [D_6]benzene, 25°C]: δ = 138.16 (*ipso*-C), 134.78 (*o*-C_6H_3), 126.88 (*p*- C_6H_3), 68.37 (THF), 26.03 (THF), 22.26 (CH_3) ppm. IR(cm^{-1}): ν 1577.75 (w), 1260.55 (w), 1020.57 (m), 841.36 (m), 799.60 (w).

$[Ba(B((4\text{-}t\mathrm{Bu})C_6H_4)_4)_2]$ ($4^\dagger$):

$Ba[N(SiMe_3)_2]_2(thf)_2$ (0.032 g / 0.05 mmol) and $HNEt_3B((4\text{-}t\mathrm{Bu})C_6H_4)_4$ (0.065 g / 0.10 mmol). The reaction was slowly heated up to 60 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 50.0%. ave. Mp: > 400 °C. ^{1}H NMR ([d_6]benzene): δ = 7.80 (d, 16H, $^2J_{H,H}$ = 7.2 Hz, *o*-C_6H_4), 7.26 (d, 16H, $^2J_{H,H}$ = 7.2 Hz, *p*-C_6H_4), 1.15 (s, 72H, CH_3) ppm. ^{11}B NMR ([d_6]benzene): δ = -6.55 ppm. ^{13}C NMR ([d_6]benzene): δ = 139.65 (*ipso*-C), 136.00 (*o*-C_6H_4), 125 (*m*-C_6H_4), 34.75 ($\boldsymbol{C}(CH_3)_3$), 31.71($C(\boldsymbol{C}H_3)_3$) ppm. IR(cm^{-1}): ν 1600.04 (w), 1265.65 (w), 1100.91 (w), 1021.20 (w), 837.47 (w), 808.11 (m).

4.4 Tetraarylborate Pyrazolate Compounds General Procedure

In the glove box, $[Ae(N(SiMe_3)_2(thf)_2]$ (Ae = Mg, Ca, Sr, Ba), $HNEt_3B((3,5\text{-}Me_2)C_6H_3)_4$ and *t*-Bu_2pzH were combined in a Carius tube with about 2 mL of Et_2O. The tube was sealed under vacuum and heated in an oil bath at 35 °C for 7 days and slowly returned to room temperature to ensure a complete reaction.[2,10-11]

4.4.1 Specific Synthesis

$[Ca(thf)_2(Et_2O)(t\mathrm{Bu}_2pz)][(B((3,5\text{-}Me_2)C_6H_3)_4]$ ($5^\dagger$):

$[Ca(N(SiMe_3)_2(thf)_2]$ (0.251 g / 0.5 mmol), $HNEt_3B((3,5\text{-}Me_2)C_6H_3)_4$ (0.279 g / 0.5 mmol), and *t*Bu_2pzH (0.1 g / 0.5 mmol). The reaction was slowly heated up to 35 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 40 - 60.0%. M.p. 74-96 °C (decomposed, tan), > 140 °C (dark red). IR (nujol): = 3158.92 (w), 2720.53 (m), 1574.29 (s), 1504.32 (m), 1376.42 (s), 1317.68 (w), 1251.64 (w), 1225.16 (w), 1149.65 (s), 1093.43 (m), 1051.03 (s), 1028.98 (m), 938.07 (w), 905.13 (m), 840.26 (s), 793.37 (s), 736.75 (s), 721.61 (m) cm-1. ^{1}H-NMR (400 MHz, [D_6]benzene): δ(ppm) = 7.849 (s, 8H, o-H(C_6H_3)), 6.701 (s, 4H, p-H (C_6H_3)), 6.031 (s, 1H, H-4 (pz)), 3.261 (q, 8H, CH_2 (Et_2O)), 3.185 (m, 8H, CH_2O (thf)), 2.130 (s, 24H, H (3,5-Me_2)), 1.247 (s, 18H, H-*t*Bu(pz)), 1.171 (m, 8H, CH_2(thf)), 1.112 (t, 12H, CH_3 (Et_2O)). ^{13}C-NMR (400 MHz, [D_6]benzene): δ(ppm) = 138.37 (C-4) (pz)), 133.72 (o-C (C_6H_3)), 126.97 (p-C (C_6H_3)), 68.80(CH_2O (thf)), 66.25 (CH_2O (Et_2O)), 32.25 ($C(CH_3)_3$ (*t*Bu_2pz)), 31.80 ($C(CH_3)_3$ (*t*Bu_2pz)), 25.74 (CH_2 (thf)), 22.29 (C (3,5-Me_2)), 15.91 (CH_3 (Et_2O)). ^{11}B-NMR (400 MHz, [D_6]benzene): δ(ppm) = -5.55.

[Sr(thf)$_2$(Et_2O)(*t*Bu_2pz)][(B((3,5-Me_2)C_6H_3)$_4$] (6†):

[Sr(N(SiMe_3)$_2$(thf)$_2$] (0.28 g / 0.5 mmol), HNEt_3B((3,5-Me_2)C_6H_3)$_4$ (0.268 g / 0.5 mmol), and *t*Bu_2pzH (0.048 g / 0.5 mmol). The reaction was slowly heated up to 35 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 40 - 60.0%. M.p. 121-129 °C (decomposed, yellow), >150 °C (dark brown). IR (nujol): = 3106.93 (w), 2722.42 (w), 1736.75 (w), 1582.25 (m), 1566.67 (w), 1402.70 (w), 1354.74 (s), 1294.89 (m), 1245.62 (m), 1152.64 (s), 1029.61 (s), 993.20 (m) 873.49 (m), 849.18 (s), 784.60 (s), 745.12 (s), 727.18 (s), 660.40 (w) cm^{-1}. ^{1}H-NMR (400MHz, [D_6]benzene): δ(ppm) = 7.934 (s, 8H, o-H (C_6H_3)), 6.783 (s, 4H, p-H (C_6H_3), 6.055 (s, 1H, H-4(pz)), 3.284 - 3.232 (br q, residual Et_2O), 3.111 (m, 8H, CH_2O (thf)), 2.177 (s, 24H (3,5-Me_2)), 1.295 (s, 18H H-*t*Bu (pz)), 1.163 – 1.092 (br, m, CH_2 (thf), residual Et_2O). Overlap of residual Et_2O and THF signals $\delta\delta$ = 1.16 – 1.09 made for unreliable integration. ^{13}C-NMR (400MHz, [D_6]benzene): δ(ppm) =138.15 (C-4 (pz)), 133.85

(o-C (C_6H_3)), 126.26 (p-C (C_6H_3)), 68.40 (CH_2O (thf)), 32.10 ($C(CH_3)_3$ (*t*Bu_2pz)), 31.67 ($C(CH_3)_3$ (*t*Bu_2pz)), 25.93 (CH_2 (thf)), 22.27 (C (3,5-Me_2)). Et_2O resonances are due to residual solvent that had not evaporated before the sample was taken. ^{11}B-NMR (400MHz, [D_6]benzene): δ(ppm) = -5.28.

[Ba(thf)$_2$(Et_2O)(*t*Bu_2pz)][(B((3,5-Me_2)C_6H_3)$_4$] (7†):

[Ba(N($SiMe_3$)$_2$(thf)$_2$] (0.149 g / 0.25 mmol), HNEt$_3$B((3,5-Me_2)C_6H_3)$_4$ (0.137 g / 0.25 mmol), and *t*Bu_2pzH (0.048 g / 0.25 mmol). The reaction was slowly heated up to 35 °C for 7 days with slow increments in temperature and then slowly reduced back to room temperature over 2 weeks. Yield: 40 - 60.0%. [Ba(N($SiMe_3$)$_2$(thf)$_2$] (0.03g / 0.05 mmol), HNEt$_3$B((3,5-Me_2)C_6H_3)$_4$ (0.027g / 0.05 mmol), and *t*Bu_2pzH (0.009g / 0.05 mmol). M.p. >137 °C (decomposed, opaque yellow). IR (nujol): = 3103.95 (w), 2723.11 (w), 1581.44 (w), 1376.82 (s), 1245.86 (m), 1222.99 (w), 1151.49 (m), 1033.58 (m), 993.36 (w), 877.49 (m), 782.16 (m), 742.98 (s), 742.97 (s) cm^{-1}. ^{1}H-NMR (400MHz, [D_6]benzene): δ(ppm) = 7.932 (s, 8H, o-H (C_6H_3)), 6.746 (s, 4H, p-H (C_6H_3)), 6.116 (s, 1H, H-4 (pz)), 3.240 (q, 2H, residual Et_2O), 3.005 (br m 8H, CH_2O (thf)), 2.181 (s, 24H (3,5-Me_2)), 2.054 (br t, 3H, residual Et_2O), 1.320 (s, 18H, H-*t*Bu (pz)), 1.089 (m, 8H, CH_2 (thf)). Et_2O resonances at $\delta\delta$ = 3.240, 2.054 are due to residual solvent that had not evaporated before the sample was taken. ^{13}C-NMR (400MHz, [D_6]benzene): δ(ppm) = 138.15 (C-4 (pz)), 134.61 (o-C (C_6H_3)), 126.32 (p-C (C_6H_3)), 68.42 (CH_2O (thf)), 66.24 (residual Et_2O), 32.30 ($C(CH_3)_3$ (*t*Bu_2pz)), 31.95 ($C(CH_3)_3$ (*t*Bu_2pz)), 25.73 (CH_2 (thf)), 22.22 (C (3,5-Me_2)), 15.89 (Residual Et_2O). Et_2O resonances at $\delta\delta$ = 66.25, 15.88 are due to residual solvent that had not evaporated before the sample was taken. ^{11}B-NMR (400MHz, [D_6]benzene): δ(ppm) =-5.18.

4.5 Donor Studies of Tetraarylborate Pyrazolate Compounds General Procedure

In the glove box, Compounds **1-7**† were combined in a vial with about 1.5 mL of either pyridine or TMEDA. The vial was then closed and left to sit under argon in order to induce crystallization. The crystals dissolved resulting in a pale-yellow solution. After several days, tiny colorless crystals can be seen forming.

4.6 References

1 Shriver, D. A. and Drezden, M. A. *The Manipulation of Air-Sensitive Compounds*, Wiley-Interscience, **1986.**

2 Woods, J. J. *Structural Variations Involving s-block Metal Pyrazolates.* Syracuse University Honors Program Capstone Thesis, **2016**.

3 Gillett-Kunnath, M. M.; Maclellan, J. G.; Forsyth, C. M.; Andrews, P. C.; Deacon, G. B.; Ruhlandt-Senge, K. *Chem. Commun.* **2008**, 4490.

4 Wen, J.; Fu, Y.; Zhang, R-Y.; Zhang J.; Chen, S-H.; Yu, X-Q. *Tetrahedron*, **2011**, *67*, 9618.

5 Yang, G. and Raptis, G. *Inorg. Chim. Acta* **2003**, *352*, 98.

6 Elguero, J.; Gonzalex, E.; Jacquier, R. *Bull. Soc. Chim. Fr.* **1968,** 707.

7 Murphy, S.; Yang, X.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 2411.

8 Deacon, G. B.; Gitlits, A.; Roesky, P. W.; Burgstein, M. R.; Lim, K. C.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **2001**, *7*, 127.

9 Hitzbleck, J.; O'Brien, A. Y.; Deacon, G. B.; Ruhlandt-Senge, K. *Inorg. Chem.* **2006**, *45*, 10329.

10 Lavin, C. M. and Ruhlandt-Senge, K., **2017**, *unpublished results*.

11 Lavin, C. M.; Allis, D. G.; Clements, A. D.; Goos, A. G.; Woods, J. J.; Gillett-Kunnath, M.M.; Ruhlandt-Senge, K., *Inorg. Chem.*, submitted, May **2019.**

12 Sheldrick, G. *Acta Cryst*., **2015**, A71, 3.

13 Holleman, A. F.; Wiberg, E.; Wilberg, N. *Inorganic Chemistry* **2001.**

I would like to thank the Renée Crown University Honors Program for providing me with funding that allowed me to travel to Orlando for the American Chemical Society Spring 2019 National Meeting and Exposition and present a poster detailing my research (see attached below).

A Closer Look at the Synthesis and Characterization of Alkaline Earth Metal Heteroleptic Tetraarylborate Pyrazolates

Ashley Clements, Joshua Woods, Catherine Lavin, Marina Cousins, Kim La, Miriam M. Gillett-Kunnath, and Karin Ruhlandt-Senge*
Department of Chemistry, CST 1-014, Syracuse University, Syracuse, NY, 13244

Introduction

Compounds containing *s*-block metals are highly sought after as precursor materials for the Metal Organic Chemical Vapor Deposition (MOCVD) process with applications for novel and improved electronic materials.[1] Previous work in the Ruhlandt group has been focused on the synthesis and characterization of novel homoleptic alkaline earth metal (Ae) pyrazolate and tetraarylborate complexes. Additionally, these ligand systems make for promising oxide free alkaline earth metal MOCVD precursors.

The pyrazolate and tetraarylborate ligands have a wide range of binding modes which help stabilize organometallic compounds, making the ligand system highly attractive for the synthesis of alkaline earth metal complexes. Homometallic pyrazolates with alkali, Ae, and rare earth metals are well established and have been synthesized and characterized.[2-4] Examples prepared in the Ruhlandt group include $[\{Ae(tBu_2pz)_2\}_n]$ (Ae = Ca, n = 3; Ae = Sr, n = 4 (Figure 1); Ae = Ba, n = 6)[2,3] and tetraarylborates including $[Ae(B((3,5\text{-}Me_2)C_6H_3)_4)_2(thf)_n]$ (Ae = Ca, n = 0 (Figure 2); Ae = Sr, n = 0; Ae = Ba, n = 1).[5] We here propose the prepared heteroleptic pyrazolate and tetraarylborate compounds *via* transamination with $Ae[N(SiMe_3)_2]_2(thf)_2$ (Ae = Mg, Ca, Sr, Ba) similar to the lanthanide work done by Deacon *et. al.*[6]

Little is known about heteroleptic compounds as the nature of Lewis bases, concentration, temperature, and solubility play a major role in the synthesis of these species. Synthetic studies will be supplemented by theoretical studies to examine the impact of non covalent interactions.

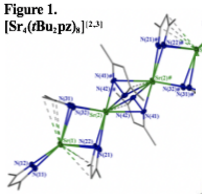


Figure 1. $[Sr_4(tBu_2pz)_8]$[2,3]

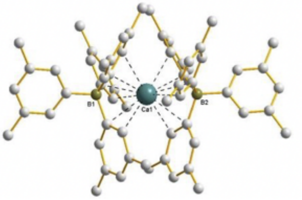


Figure 2. $Ca(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$.[5]

I. The Tetraarylborate Ligand System

- 24 e⁻ π system
- Stable in air and water
- Easily substituted aromatic rings
- Capable of M-ligand π interactions

- BPh_4 (a)
- $B((4\text{-}tBu)(C_6H_4))_4$ (b)
- $B((3,5\text{-}Me_2)(C_6H_3))_4$ (c)

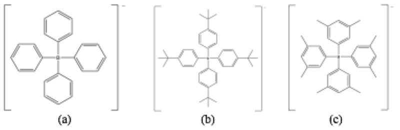


Figure 3. The tetraarylborate system.[7]

II. The Pyrazole Ligand System

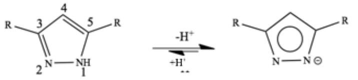


Figure 4. The pyrazole ligand.

- Heterocyclic compound
- Becomes aromatic upon deprotonation
- Multiple substitution possibilities, in order to study the effect of ligand bulk substitutions on the 3,5 position
  - 3,5-di-*tert*-butylpyrazole (tBu_2pzH), R = 3,5-tBu_2
  - 3,5-dimethylpyrazole (Me_2pzH), R = 3,5-Me_2
  - 3,5-diphenylpyrazole (Ph_2pzH), R = 3,5-Ph_2

Results

III. Synthesis of Homoleptic Arylborates

$$Ae[N(SiMe_3)_2]_2(thf)_2 + 2HNEt_3BAr_4 \xrightarrow[\Delta]{Et_2O} [Ae(BAr_4)_2(thf)_n] + 2HN(SiMe_3)_2 + 2NEt_3$$

Synthesis via Transamination:

- Alkaline earth amides (Ae = Ca, Sr, Ba) and $HNEt_3BAr_4$ (Ar = Ph, (4-*t*Bu)(C_6H_4), (3,5-Me_2)(C_6H_4)) were combined in a 1:2 ratio using diethyl ether as a solvent and sealed in a Carius tube. Results were reproduced.[5,9]
- All reactions were carried out under inert gas conditions
- Donor studies are being conducted to examine the role of the Lewis base on the structural features of the target compounds

Transamination:

- High solubility of amide
- Easy removal of free silylamine
- Driven by pK_a RRpzH (pK_a = 13-15); $HN(SiMe_3)_2$ (pK_a = 30);
- $HNEt_3$ (pK_a = 9)

IV. Synthesis of Heteroleptic Arylborate Pyrazolates

$$Ae[N(SiMe_3)_2]_2(thf)_2 + HNEt_3B((3,5\text{-}Me_2)C_6H_3)_4 + tBu_2pzH \xrightarrow[\Delta]{Et_2O}$$

$$[Ae(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)_x(thf)_m(Et_2O)_n][BAr_4]_y + 2HN(SiMe_3)_2 + NEt_3$$

Synthesis via Transamination:

- Alkaline earth amides (Ae = Ca, Sr, Ba) were combined with borate and *tert*-butyl pyrazolate using diethyl ether as a solvent and sealed in a Carius tube. Results were reproduced.[5,8]
- All reactions were carried out under inert gas conditions.

Figure 5. Sealing a Carius tube.

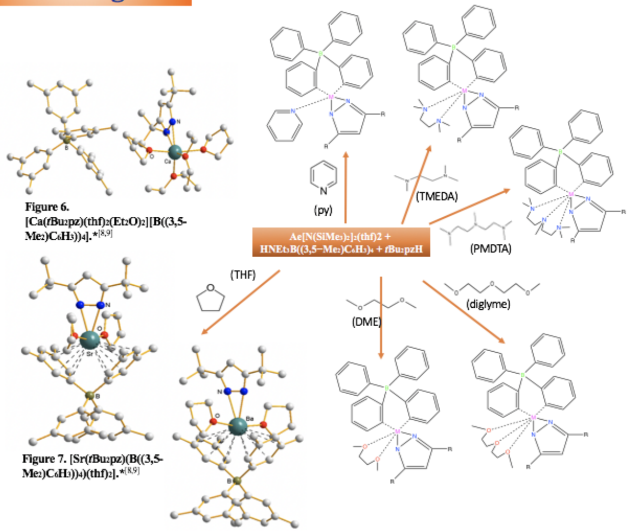
V. Results

Summary of Reactions

Experiment #	Compound*	Temperature (℃)	Observation
ADC-004	$Ca(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$	35	White crystals
ADC-005	$Sr(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$	35	White crystals
ADC-006	$Ba(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$	35	White crystals
ADC-007	$Mg(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$	35	White crystals
ADC-008	$Ba(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$	35	White crystals
ADC-009	$Mg(thf)_2(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3)_4)]$	35	White crystals
ADC-010	$[Ca(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$	60	White crystals
ADC-011	$[Sr(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$	35	Tan crystals
ADC-012	$[Ba(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$	60	White-tan crystals
ADC-013	$[Ba(B((4\text{-}tBu)C_6H_4)_4)_2]$	60	White crystals
ADC-014	$[Ca(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$	60	White crystals
ADC-015	$[Sr(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$	35	Tan crystals
ADC-016	$[Ba(B((3,5\text{-}Me_2)C_6H_3)_4)_2]$	60	White-tan crystals
ADC-017	$[Ba(B((4\text{-}tBu)C_6H_4)_4)_2]$	60	White crystals

* Lewis bases will be added to the compounds, further crystallized, and characterized using Single Crystal X-Ray Diffraction and ¹H NMR studies.

Work in Progress



$Ae[N(SiMe_3)_2]_2(thf)2$ + $HNEt_3B((3,5\text{-}Me_2)C_6H_3)_4 + tBu_2pzH$

Figure 6. $[Ca(tBu_2pz)(thf)_2(Et_2O)_2][B((3,5\text{-}Me_2)C_6H_3))_4]$.*[8,9]

Figure 7. $[Sr(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3))_4)(thf)_2]$.*[8,9]

Figure 8. $[Ba(tBu_2pz)(B((3,5\text{-}Me_2)C_6H_3))_4(thf)_2]$.* [8,9]

Scheme 1. Exploring the Coordination Effect of Donors with Various Hapticity. Hydrogen atoms omitted for clarity. (M = Mg, Ca, Sr, Ba)

Outlook

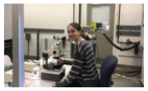
- Characterization of reaction crystals *via* M.p., IR and NMR spectroscopy, and Single Crystal X-ray Crystallography
- Perform sublimation studies to test viability of compounds as potential MOCVD precursors
- Use RR'pzH to further understand structure/function relationships

References

1. Marks, T. J.; et al. *Chem. Vapor Deposition* **2000**, *6*, 180.
2. Hitzbleck, J.; Deacon, G. B.; Ruhlandt-Senge, K. *Angew. Chem. Int. Ed.* **2004**, 5218-5220.
3. Hitzbleck, J.; O'Brien, A.; Forsyth, C. et al, *Chem. Eur. J.* **2004**,*10*, 3315-3323.
4. Corte-Llamas, S.; Hernandez-Lamoneda, R.; Velazquez-Carmona, M. et. al. *Inorg. Chem* **2006,** *45*, 286-294.
5. Lavin, C. M.; Woods, J. J.; Goos, A.; Allis, D. G.; Gillett-Kunnath, M. M.; Ruhlandt, K. *in prep.* **2016**.
6. Deacon, G. B.; Forsyth, C. M.; Junk, P. C. *Eur. J. Inorg. Chem.* **2005**, 817.
7. O. O. Stepaniuk, V. O. Matviienko, I. S. Kontratov, I. V. Vitruk, A. O. Tolmachev, *Synthesis*, **2013**, *45*, 925-930.
8. Woods, J. "Structural Variations Involving s-block Metal Pyrazolates. **2016**, Syracuse University Honors Program Capstone Thesis.
9. Lavin, C. M.; Woods, J. J.; Clements, A.; La, K.; Cousins, M.; Gillett-Kunnath, M. M.; Ruhlandt, K. *in prep.* **2019**.

Acknowledgements

Ruhlandt Research Group
Syracuse University Chemistry Department
Renée Crown University Honors Program



ASHLEY CLEMENTS

Phone: (817) 798-7483 | **Email:** ashclem23@gmail.com
Address: 1102 Brighton Place · Syracuse, NY 13210
LinkedIn: https://www.linkedin.com/in/ashley-clements-1157a715b/

SUMMARY OF QUALIFICATIONS

Hardworking and trained undergraduate student in chemistry and forensic science with an accelerated graduation date (Fall 2016 – Spring 2019) and 1.5+ years of research experience in a graduate chemistry laboratory. Displays strong analytical, leadership, and time management skills. Currently seeking a position which will effectively utilize acquired skills and areas of expertise as follows:

- Research/Analysis
- Chromatography
- Spectroscopy Techniques
- Crystallography (working knowledge)
- Forensic Science
- Organic and Inorganic Synthesis Techniques
- Schlenk Line Techniques
- Report Generation
- Internet Proficiency
- Microsoft Office
- Detail-Oriented
- Innovative
- Team Building

EDUCATION

Syracuse University | Bachelor of Science - Chemistry (Aug. 2016 – Present | Anticipated Grad. 2019)
Current GPA: 3.81
Currently in the Renee Crown Honors Society and pursuing a Degree with Distinction in Chemistry
Notable Courses: Honors General Chemistry, Organic Chemistry, Physical Chemistry, Inorganic Chemistry, Introduction to Chemical Research, Structural and Physical Biochemistry

Syracuse University | Minor - Forensic Science (Aug. 2017 – Present | Anticipated Grad. 2019)
Notable Courses: Advanced Forensic Science, Latent Prints, Bloodstain Pattern Analysis, Criminology, Forensic Chemical Analysis

RESEARCH EXPERIENCE

Syracuse University Aug. 2016 - Present

Undergraduate Research *(Oct. 2017 - Present)*
Advisor: Dean Karin Ruhlandt
Mentor: Dr. Miriam Gillett-Kunnath
Project: Synthesis and characterization of alkaline earth metal heteroleptic tetraarylborate pyrazolates via air-free Schlenk line techniques
Characterization Techniques: Single Crystal X-ray Diffraction, ^{1}H NMR, ^{13}C NMR, IR, melting point

Undergraduate Academic Experience *(Aug. 2016 – Present)*
Chemistry laboratory techniques through academic courses
Characterization Techniques: Ultraviolet-Visible Spectroscopy, IR and FTIR Spectroscopy, Fluorescence Spectroscopy, Thin Layer Chromatography, SDS-PAGE gel electrophoresis, Gas Chromatography-Mass Spectrometry, Raman Spectroscopy

WORK EXPERIENCE

Syracuse University Aug. 2017 – Present

Tutor *(Jan. 2019 – Present)*
Assisted student athletes with schoolwork from classes such as Calculus, General Chemistry, Organic Chemistry, and Introduction to Forensic Science; learned listening and leadership skills

Carrier Dome Concessions Worker *(Aug. 2017 – Present)*
Managed cash register; food service; learned customer service and interpersonal communication skills

Panera Bread May 2018 – Aug. 2018

Cashier

Assisted and served customers; kept the store presentable; learned organization and time management skills

Journeys Sep. 2014 - Aug. 2016

Assistant Manager *(May 2016 – Aug. 2016)*

Monitored store inventory; trained new employees; closed cash registers and managed the bank deposit

Sales Associate *(Sep. 2014 – Apr 2016),*

Engaged with and assisted customers; kept the store presentable; assisted with store inventory

PRESENTATIONS AND PUBLICATIONS

Clements, A.; Woods, J.; Lavin, C. M.; Cousins, M.; La, K.; Allis, D. G.; Gillett-Kunnath, M. M.; Ruhlandt-Senge, K. *A Closer Look at the Synthesis and Characterization of Alkaline Earth Metal Heteroleptic Tetraarylborate Pyrazolates.* Abstracts, 257th ACS National Meeting and Exposition, Orlando, FL, United States, March 31 – April 4, **2019**.

Lavin, C. M.; Allis, D. G.; **Clements, A.D.**; Goos, A. G.; Woods, J. J.; Gillett-Kunnath, M. M.; Ruhlandt-Senge, K. *To bind or not to bind: The role of M-π interactions in the coordination chemistry of heavy alkaline earth metal tetraarylborates. Inorg. Chem.,* in preparation, **2019**.

Lavin, C. M.; Woods, J. J.; **Clements, A.D.**; Goos, A.; Allis, D. G.; Gillett-Kunnath, M. M.; Ruhlandt-Senge, K. *Influence of M-π interactions on ion association in a novel class of Group II tetraarylborate pyrazolate compounds: Synthetic, structural, and computational investigations. Inorg. Chem.,* in preparation, **2019**.

HONORS AND AWARDS

- Dean's List – 2016-2018
- Renee Crown University Honors Crown Funding Award – Fall 2018
- Invitation to collaborate with crystallographer in Canada – Spring 2019
- Syracuse University LC Smith Scholarship – 2016-2019
- Member of American Chemical Society (ACS) – 2018-Present
- Obtained grant to attend ACS National Conference – Spring 2019

EXTRACURRICULAR ACTIVITIES AND COMMUNITY SERVICE

Syracuse University Apr. 2017 - Present

Volunteer

- OttoTHON Dance Marathon – 2018
- Homecoming Dean's Team Liquid Nitrogen Ice Cream Demonstration – 2018
- Green Chemistry Think Tank – 2018
- Orange Seeds's The Big Event – 2017-2018

Milton J. Rubenstein Museum of Science and Technology (MOST) Oct. 2018 - Present

Volunteer

- Technology Alliance of Central New York (TACNY) Jr. Café Scientifique Magical Matter – 2018
- NYS STEAM Syracuse University Chemistry Booth – 2018

REFERENCES

Available upon request

“Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.”

~ Marie Curie (1867-1934)