Synthesis and Coordination Chemistry of Oxygen Rich Ligands:

***Bis*(oxoimidazolyl)hydroborato, *Tris*(oxoimidazolyl)hydroborato and *Tris*(2-pyridonyl)methane**

Ahmed Al-Harbi

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2014

ABSTRACT

Synthesis and Coordination Chemistry of Oxygen Rich Ligands:

***Bis*(oxoimidazolyl)hydroborato, *Tris*(oxoimidazolyl)hydroborato and *Tris*(2-pyridonyl)methane**

Ahmed Al-Harbi

In Chapter One, the sodium salt of *tris*(2-oxo-1-t-butylimidazolyl) hydroborate, [To^{But}]Na, as an [O_3] donor ligand has been prepared. The yield for this reaction was low because there is a significant amount of side product in which the double bond of the oxoimidazole starting material is reduced. Treatment of sodium borohydride with bezannulated oxoimidazole at high temperature leads to the generation of the sodium salt of *tris*(2-oxo-1-R-methylbenimidazolyl) hydroborate in high yield, [To^{RBenz}]Na. These ligands have been prepared with different alkyl substituents, methyl, *t*-butyl and adamantyl, to achieve the desired steric environment. Furthermore, these benzannulated ligand have been used to synthesize a series [To^{RBenz}]Tl complexes, which exist as a discrete mononuclear complexes in the solid state. Finally, [To^{RBenz}]Tl complexes are more pyramidal than the sulfur counterpart, [Tm^{RBenz}]Tl, but less pyramidal than those in the *tris*(pyrazolyl)hydroborato counterpart, [Tp^{R,R}]Tl.

In Chapter Two, the properties of [To^R] ligands have been evaluated *versus* related L$_2$X ligands. [To^R] ligands are substantially more sterically demanding than the corresponding [Tm^R] sulfur donor ligand and related [O_3] donor ligands. However,

electronically, the [To^R] ligands exhibit weaker electron donating properties than other L$_2$X type ligands. Finally, the coordination chemistry of [To^R] ligands with various metal compounds has been briefly investigated.

The synthesis of a new class of bidentate ligands has been detailed in Chapter Three. Namely the *bis*(2-oxo-1-t-butylimidazolyl)hydroborato and *bis*(2-oxo-1-alkylbenzimidazolyl)hydroborato, [Bo^{Bu^t}] and [Bo^{RBenz}], have been synthesized *via* the reaction of MBH$_4$ with two equivalents of the respective 2-imidazolone. Chelation of [Bo^{Bu^t}] and [Bo^{MeBenz}] to a metal center results in a flexible 8-membered ring that is capable of adopting a "boat-like" conformation that allows for secondary M•••H–B interactions.

Chapter Four describes the synthesis of [Bo^{RBenz}]$_2$Zr(CH$_2$Ph)$_2$ and [To^{RBenz}]Zr(CH$_2$Ph)$_3$ with different alkyl substituents. Treatment of [To^{Bu^tBenz}]Zr(CH$_2$Ph)$_3$ with ([PhNHMe$_2$][B{C$_6$F$_5$}$_4$]) in a coordinating solvent, Et$_2$O, generates {[To^{Bu^tBenz}]Zr(CH$_2$Ph)$_2$(OEt$_2$)}{B(C$_6$F$_5$)$_4$} which exhibit a very low activity for ethylene polymerization. However, a coordinatively unsaturated cationic zirconium alkyl complex was obtained by the treatment of ([PhNHMe$_2$][B{C$_6$F$_5$}$_4$]) with [To^{Bu^tBenz}]Zr(CH$_2$Ph)$_3$ or [To^{AdBenz}]Zr(CH$_2$Ph)$_3$ which generate [To^{Bu^tBenz}]Zr(CH$_2$Ph)$_2$[B(C$_6$F$_5$)$_4$] or [To^{AdBenz}]Zr(CH$_2$Ph)$_2$[B(C$_6$F$_5$)$_4$], respectively. Moderate activity for ethylene polymerization was obtained for t-butyl while high activity was obtained for the adamantyl derivatives.

Finally, Chapter Five describes the synthesis of new oxygen-rich ligands, namely *tris*(2-pyridonyl)methane, [Tpom^R]H. They are obtained *via* the reaction of 2-pyridones with CHX$_3$ and K$_2$CO$_3$ in the presence of [Bu$^n_4$N]Br, followed by acid-catalyzed isomerization with camphorsulfonic acid. These compounds provide access to a new class of L$_3$X alkyl ligands that feature oxygen donors and are capable of forming metallacarbatranes, as exemplified by [κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t. In addition, the [Tpom^{But}] ligand also allows isolation of a monovalent thallium alkyl compound, [Tpom^{But}]Tl, in which the Tl–C bond is long and has little covalent character.

TABLE OF CONTENTS

LIST OF FIGURES

Chapter 1

Chapter 2

Chapter 3

Chapter 5.

LIST OF TABLES

Chapter 4.

Chapter 5.

LIST OF SCHEMES

Chapter 1.

Chapter 3.

Chapter 4.

ACKNOWLEDGMENTS

When the word "Acknowledgment" comes to my mind, I immediately think of two individuals who helped and supported me all the way, my Mother and my Wife. No words, sentences or phrases can capture their help, support and devotion they have shown for me over the last seven years. Even though my mother is ten thousand miles away, she always remembers me in her thoughts and prayers. As for my wife, what she has done for me is beyond comprehension. She gave me seven years of her life with full devotion and passion, which are things that can only be seen in fictional romantic movies. I hope I will have the opportunity to pay her back in the near future. Finally, I would like to mention my kids in this acknowledgment, even though the word "acknowledgment" is not the best word for some of them. For example, my sons Rayyan and Basel were not very cooperative with me while I was writing this thesis. On the flip side, my daughter Lujain is the walking angel in my house and I am very gratefully to her help, support and love. Finally, I would like to mention the latest edition to my family, my newly born daughter, Jumana. Her recent arrival provided me with enough energy to finish this thesis.

More than 10% of my life has been spent pursing a Ph.D degree which has turned out to be one of the most rewarding experiences of my life. During my time at Columbia University, I have had the pleasure to work for Professor Gerard Parkin. He is one hell

of character, personally and intellectually. There are many good things I have learned from him, but space and lack of a good English vocabulary does not permit to list them all. But if I have to single out the most important one he has taught me, then it is how to be "Critical" about everything. I knew what the word "Critical" meant before I start working for him but I rarely practice it. Apart from the fact that "being critical" is not going to be welcomed by my wife, especially when we go shopping, but I am sure it will help me with my future endeavors. No words can express my gratefulness to Ged for everything he has taught me during my Ph.D stint.

These five years have also been very rewarding as it has given me the opportunity to get to know numerous good and close friends through the lab. The twins for example, even though they are small in stature, their actions left a big impact on me and my fellow labmates. They are marvelous chemists and are very passionate about the subject. They taught me several chemical techniques including how to reach to a schlenck line even if you are little. My year companion, Yi has one of the biggest hearts I have ever encountered. She was a great help in my research, especially when it came to calculations since she did them all. Also thanks to Charlie's Angels, Ashley, Ava and Neena. Ashley, thanks for being a great desk mate. Ava, thanks for giving me a hand with various experiments, including variable temperature NMR. Thanks to Neena for her help with many issues including the O_3 project. Thanks also to Serge, Josh and

Michelle for the numerous thought-providing and intellectual discussion about chemistry. I wish all my colleagues in Parkin lab the best including the new Rookie, Patrick!!!

Finally, I would like to say that I started to have mixed feelings lately regarding leaving the lab. The happy part is that I am missing my family and Saudi Arabia after being in America for the last five years. Therefore, I am eager to go back. But the sad part is that I got used working with you guys as everyday colleagues. I am going to miss you all and I hope we will meet again sometime soon. Finally, I would like to say to my colleagues "I am sorry if there was any shortfall from my side to any of you guys".

Written by **Ahmed Al-Harbi** during his subway rid to lab

Edited by his ten years old daughter **Lujain**.

This thesis is dedicated to

the most important three individuals in my life:

my parents and my wife.

Chapter 1

Synthesis and Structural Characterization of *Tris*(2-oxo-1-*t*-butylimidazolyl) and *Tris*(2-oxo-1-R-benzimidazolyl)hydroborato Ligands: A New Class of Tripodal Oxygen Donor Ligand

Table of Contents

1.1   Introduction

Since the discovery of the hydro*tris*(pyrazolyl)borate anion, [Tp^{R,R}][1], by Trofimenko in

1966 as a C_3 symmetric [N_3] donor ligand system, tripodal boron-centered ligands have

become an active field of research whether in developing a new class of ligands donors

or in their use as a molecular support for different transition and main group metals.[2]

They are of significant interest for many reasons, including the fact that they are

electronically analogous to the cyclopentadienyl ligand, L$_2$X class according to the

covalent bond classification,[3] which has been the center of investigation in the

organometallic field since the discovery of metallocenes. [Tp^{R,R}] ligands have been

employed in diverse applications, such as homogeneous catalysis and modeling of

biological systems.[2] Approximately three decades after Trofimenko's discovery,

Riordan et al.[4] and Spicer et al.[5] have developed poly(methylthiomethyl)borate [RTt]

and hydro*tris*(mercaptoimidazolyl)borate [Tm^R], respectively. In both cases, they are

[S_3] donor ligands and softer L$_2$X ligands than the [Tp]. In 1999, Nocera et al. developed

an anionic [P_3] tripodal boron centered ligand.[6] Six years later, Smith and coworker

developed a carbene based [C_3] donor ligand that is boron-centered.[7] Finally,

hydro*tris*(selenoimidazolyl)borate, [Tse^R], one of the most electron donating L$_2$X type

ligands, was developed in our lab as a [Se_3] donor ligand[8] (Figure 1).

[Tp$^{R,R'}$], N_3 [Tm^R] when E = S, S_3 Tris(carbene)borate, C_3 PhBP$_3^R$, P_3
                        [Tse^R] when E = Se, Se$_3$
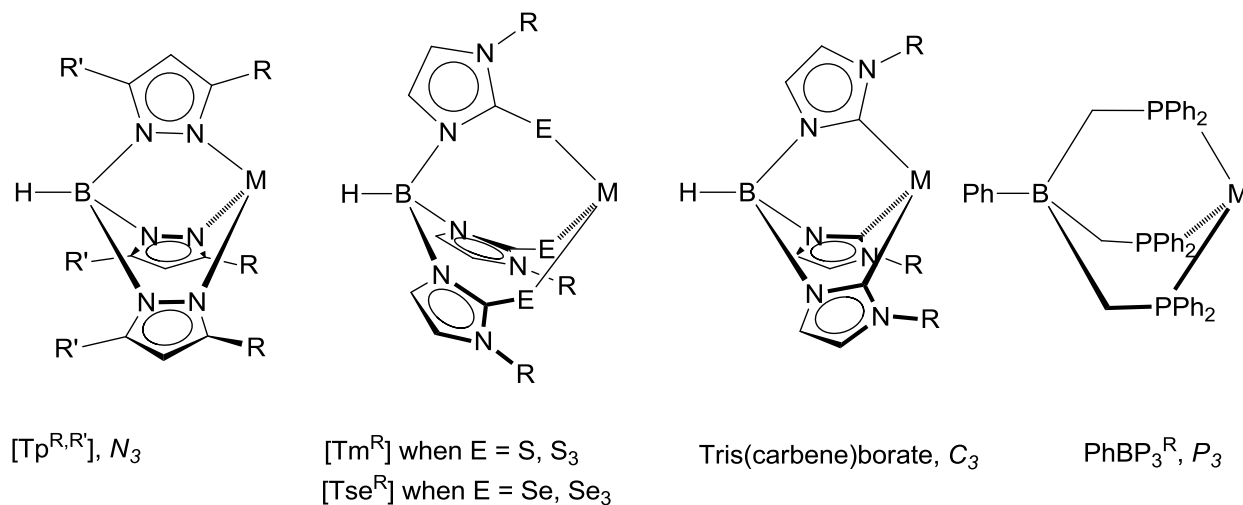
Figure 1. Examples of tripodal boron-centered ligands with different donor arrays.

In this chapter, we extend the series of chalcogen donor ligands, [Tm^R] and [Tse^R], to that of the lightest member, with the synthesis of the [O_3] donor counterpart, namely the *tris*(oxoimidazolyl) ligand system, [To^R].

1.1.1   Motivation for The Synthesis of an Oxygen Rich L$_2$X type ligand

By a method analogous to the synthesis of [Tm^R][5] and [Tse^R][8] *via* the reaction of borohydride with mercapto or selenoimidazole, respectively, we predicted that an [O_3] donor ligand could be obtained *via* the reaction of borohydride and an oxoimidazole. Our motivation came from the fact that tripodal L$_2$X [O_3] donors are not common; the field is dominated by the [CpCo{P(O)(OR)$_2$}$_3$] ligand system (Figure 2) which comes from an inefficient synthetic pathway.[9] The *tris*(phthalimidyl)hydroborato ligand has been reported.[10] However, since there is no structural verification of either the ligand or its complexes, the true nature of these compounds remains unknown.
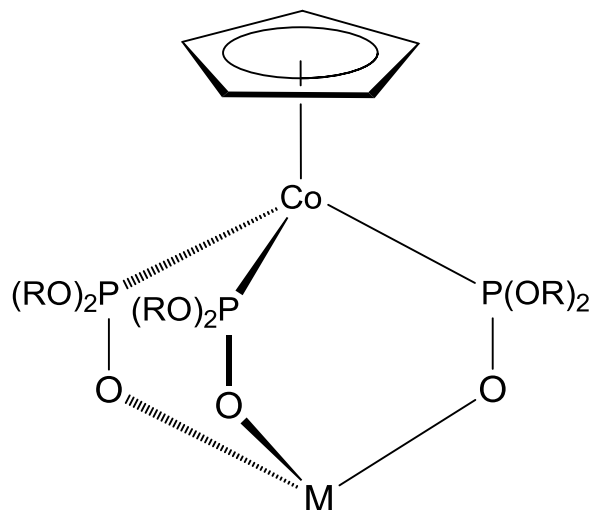
Figure 2. The Kläui ligand, [CpCo{P(O)(OR)$_2$}$_3$].

One key feature of the [Tp^{R,R}], [Tm^R] and [Tse^R] ligands is that the sterics can be easily

tailored for many different applications. For example in the [Tp^{R,R}] case, substitution at

the 3-position of the pyrazolyl group provides an effective method to manipulate the

steric environment around the metal center.[2] On the contrary, the location of the R

substituents of [CpCo{P(O)(OR)$_2$}$_3$] are such that they do not create a sterically

demanding binding pocket, as we will see in chapter 2. An L$_2$X [O_3] donor ligand that is

more sterically demanding than [CpCo{P(O)(OR)$_2$}$_3$] would, therefore, provide a means

for developing the coordination chemistry of metal centers in an oxygen rich

environment. Such ligands have the potential for mimicking molecular species that are

grafted to oxide surfaces *via* three oxygen atoms, as illustrated by the binding of

zirconium hydride, alkoxide, and acetylacetone moieties to silica surfaces.[11]

1.2 Reaction of 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one with Sodium Borohydride

In order to synthesize the [To^R] ligand, we initially set out to synthesize the oxoimidazolyl precursor of the ligand, 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one, following a published procedure.[12] The imidazole was synthesized *via* a two-step reaction: first, the *t*-butylamine was treated with *tert*-butyl isocyanate,[13] one of the common isocyanates, and then the intermediate was cyclized under acidic conditions (Scheme 1).
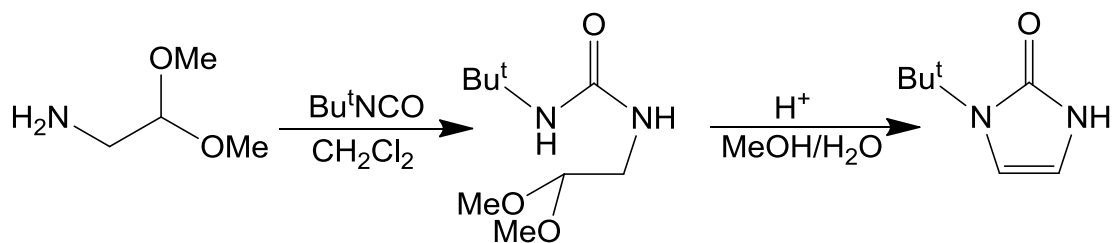
Scheme 1. Two-step synthesis of 1-*tert*-butyl-1,3-dihydro-imidazol-2-one.

During efforts to optimize the reaction conditions of this reaction, we noticed that it is important to use a dilute solution for the cyclization step, (< 0.25 M), in order to avoid an intermolecular reaction which produces a polymeric side product[14] (Scheme 2).
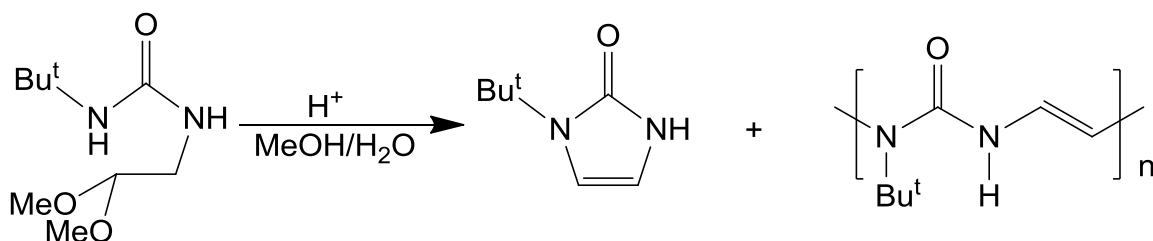
Scheme 2. Intra vs. intermolecular products for ring closing step.

Based on a CSD search,[15] there are few structurally characterized 2-imidazolone compounds in the literature. Therefore, yellow block crystals of 1-t-butyl-1,3-dihydro-2*H*-imidazol-2-one suitable for X-ray diffraction were obtained from slow evaporation of CH_2Cl_2 solution (Figure 3).
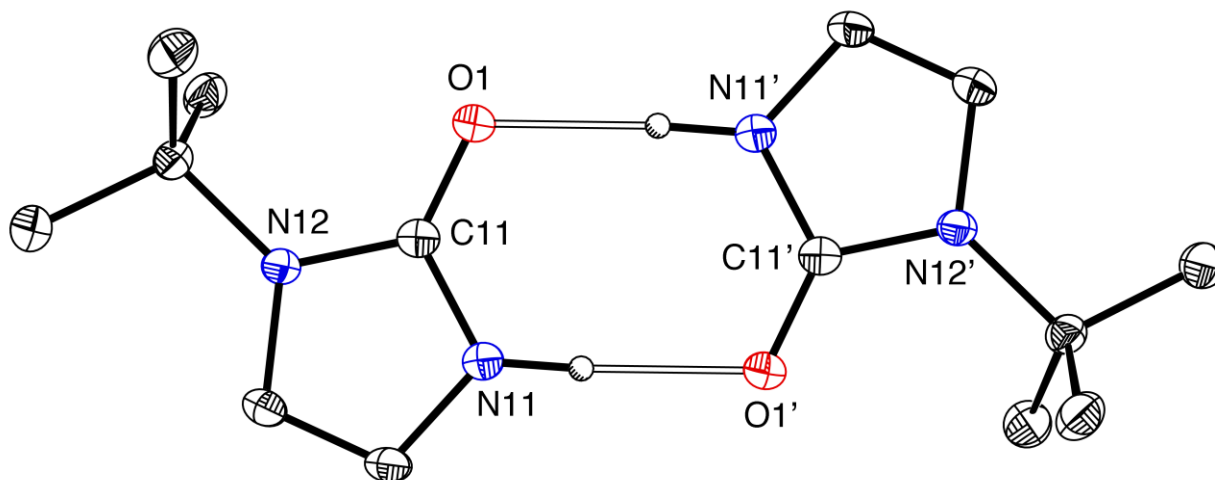
Figure 3. Hydrogen bonded dimeric structure of 1-*tert*-butyl-1,3-dihydro-imidazol-2-one.

Treatment of 1-*tert*-butyl-4-imidazolin-2-one with different metal borohydrides, Na, Li or K, in different solvent systems leads to the desired products along with an unexpected side product, 1-*tert*-butylimidazolidinone. This side product was formed as a result of the reduction of the 1-*tert*-butyl-1,3-dihydro-imidazol-2-one's double bond during a period of extended heating (Scheme 3). This result was established by ^{1}H NMR spectroscopy and by X-ray diffraction (Figure 4).
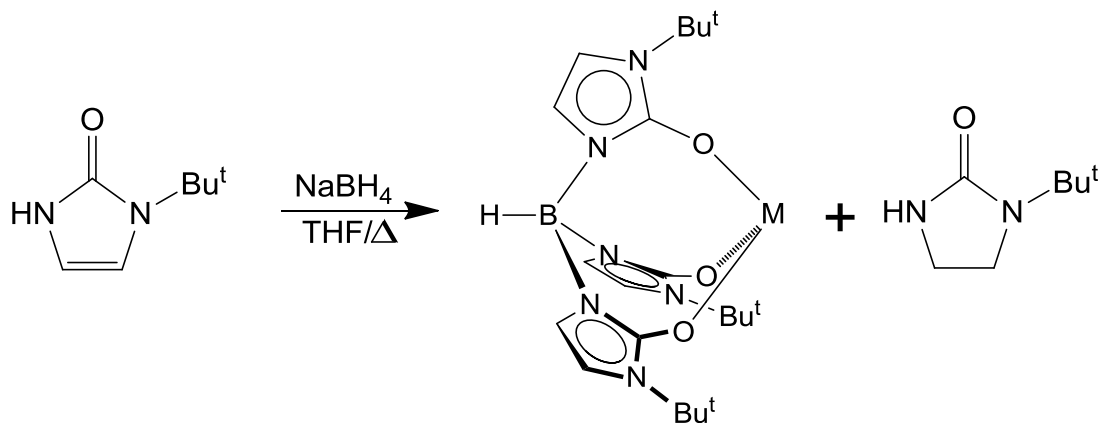
Scheme 3. Reaction of 3 eq. of 1-*tert*-butyl-1,3-dihydro-imidazol-2-one and NaBH$_4$.
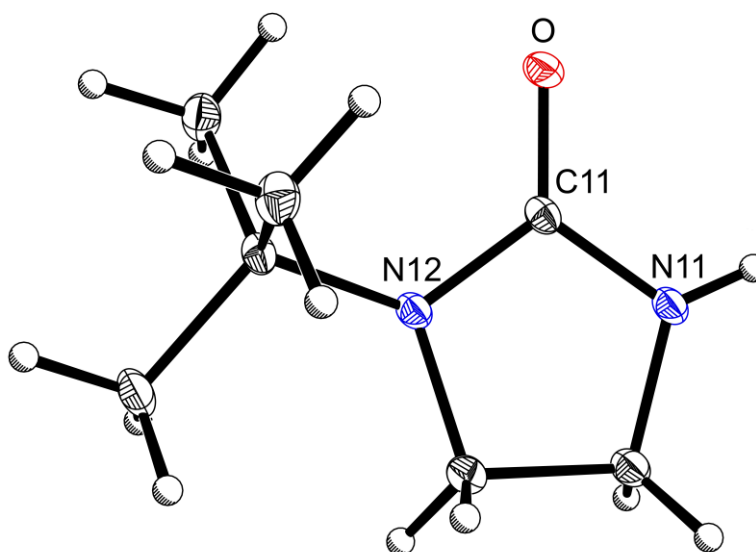
Figure 4. Molecular structure of 1-t-butylimidazolidinone.

Though the side product was generated in high yield, we managed to obtain [To$^{Bu^t}$]Na in adequate purity. The volatile matter was removed from the reaction mixture and the residue was dissolved in pentane. The pentane solution generated colorless block crystals of [To$^{Bu^t}$]Na. X-ray diffraction indicates that [To$^{Bu^t}$]Na is dinuclear in the solid state (Figure 5).
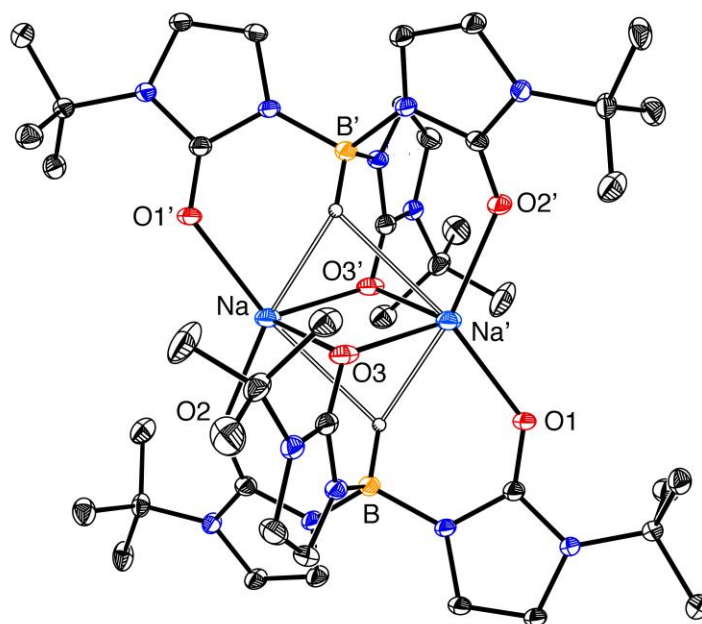
Figure 5. Molecular structure of {[To$^{Bu^t}$]Na}$_2$.

1.3   Synthesis of Benzannulated Ligands: [To^{MeBenz}]Na

We searched for an alternative to 1-*tert*-butyl-1,3-dihydro-imidazol-2-one as a building block for constructing the [To^R] ligands due to *i*) production of a side product in a significant amount as result of the reduction of the double bond *ii*) difficulty in obtaining pure product of the ligand. We thought that the annulation of the imidazole ring might help to circumvent this unwanted side-product since aromatic rings are less prone to reduction than isolated double bonds. A survey of the literature revealed that one of the most practical ways to synthesize 1-methylbenzimidazolinone is *via* a Hofmann-type-rearrangement of 2-methylaminobenzamide[16] (Scheme 4).
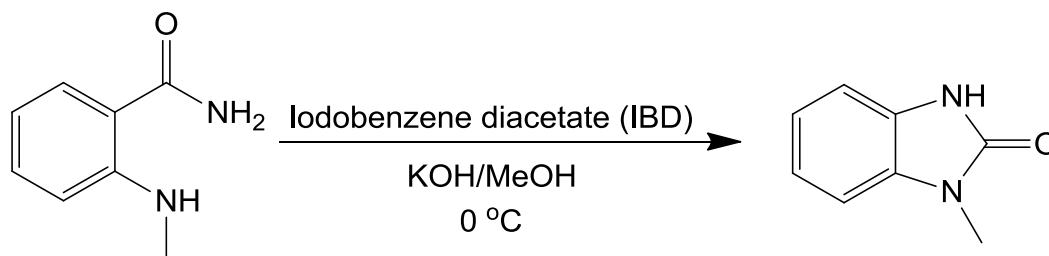
Scheme 4. Synthesis of 1-methyl-1,3-dihydro-benzimidazol-2-one.

The X-ray structure was not previously reported and we were able to crystalize 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-one from CH_2Cl_2 (Figure 6).
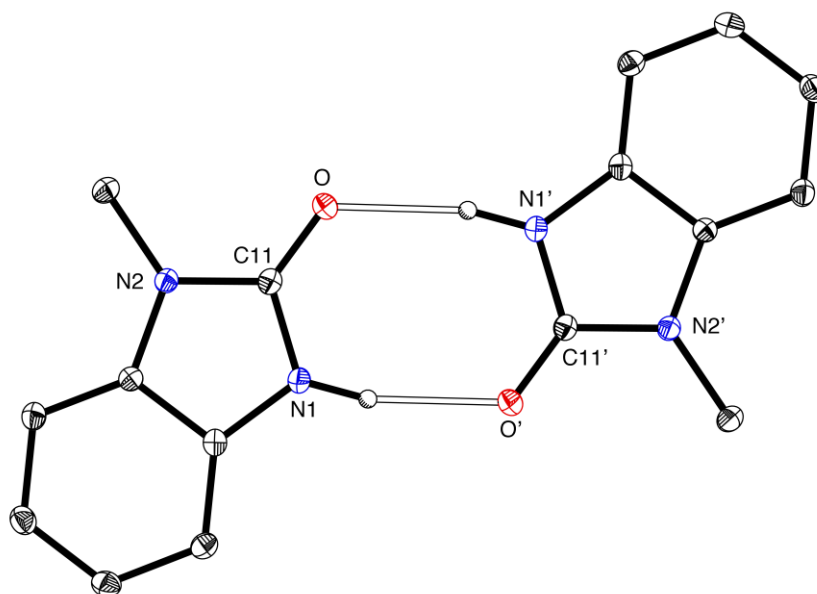
Figure 6. Hydrogen bonded dimeric structure of 1-methyl-1,3-dihydrobenzimidazol-2-one.

The dimeric structure of the methylbenzimidazolone compound, H(obenzim^Me), is distinct from those of both the mercapto[17] and seleno[18] counterparts which possess polymeric "head-to-tail" structures.

Treatment of $NaBH_4$ with three equivalents of 1-methyl-2-benzimidazolinone in either

benzene or tetrahydrofuran at elevated temperatures (140 ˚C) led only to the formation

of *bis*(oxobenzoimdazolyl)borate, [Bo[MeBenz]]Na, rather than the desired product, namely

tris(oxobenzoimdazolyl)borato [To[MeBenz]]. This result was established by ^{1}H NMR

spectroscopy (Scheme 5).
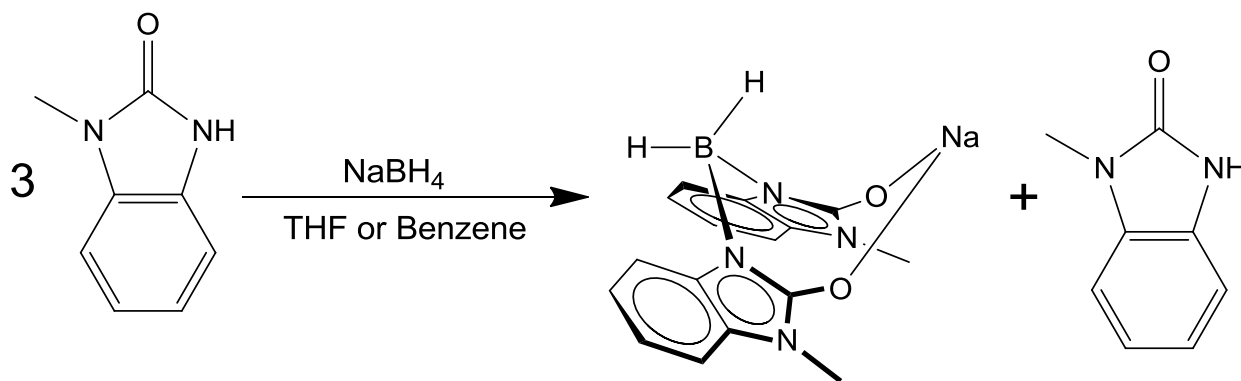
Scheme 5. Treatment of 3 eq. of 1-methy-1,3-dihydro-benzimidazol-2-one and $NaBH_4$ at

elevated temperature.

Additional evidence supporting the formation of [Bo[MeBenz]] ligands was provided by a

test reaction with ZnI_2, which produced crystals of composition {[Bo[MeBenz]]ZnI}$_2$, which

were isolated and characterized by X-ray diffraction. Chapter 3 will be devoted to the

synthesis and characterization of the bidendate version of the ligand, *bis*(2-

oxoimidazolyl)hydroborato ligand.

A suggestion by a coworker, Wesley Sattler, led to an examination of the effects of using

a higher boiling, coordinating solvent. Indeed, diglyme offered a reproducible synthesis

of [To[MeBenz]]Na•diglyme in excellent yield of greater than 80% (Scheme 6).
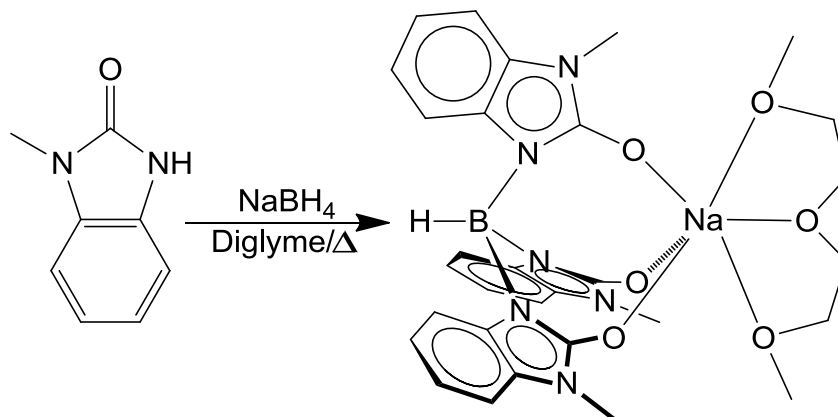
Scheme 6. Synthesis of [To^MeBenz]Na•diglyme.

The X-ray structure of [To^MeBenz]Na•diglyme, (Figure 7), reveals a fully coordinated diglyme molecule. The ability to obtain the *tris* motif when diglyme is used as solvent may be attributed to the enhanced reactivity of $NaBH_4$ by chelation of the sodium cation.
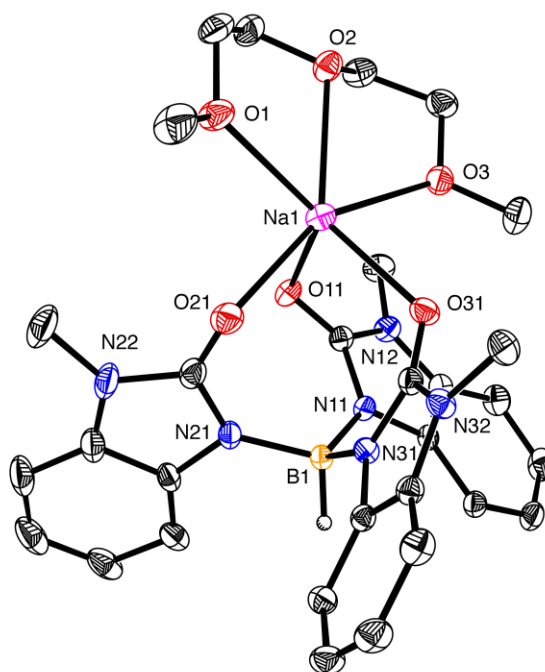
Figure 7. Molecular structure of [To^MeBenz]Na•diglyme.

1.4   Preparation of [To^RBenz]Na (Bu^t, Ad)

Increasing the steric bulk of the [To^R] ligand by replacing the methyl substituent with a bulkier alkyl group, for example *tert*-butyl or adamantyl, may cause the ligand to bond with different coordination modes, which may result in metal complexes that have different properties. For example, replacing the methyl group with mesityl in the case of [Tm^R] has allowed the isolation of monomeric species of {[Tm^Mes]Zn(HOMe)}^+.[19] Therefore, 1-*tert*-butyl-1,3-dihydro-benzimidazol-2-one was prepared in order to examine the *tert*-butyl substituent steric bulk impact. It was synthesized according to reported procedure[20] by Benjamin Kriegle, a visiting summer undergraduate, under my supervision (Scheme 7). Crystals of 1-*tert*-butyl-1,3-dihydro-benzimidazol-2-one were obtained from CH_2Cl_2 solution (Figure 8).
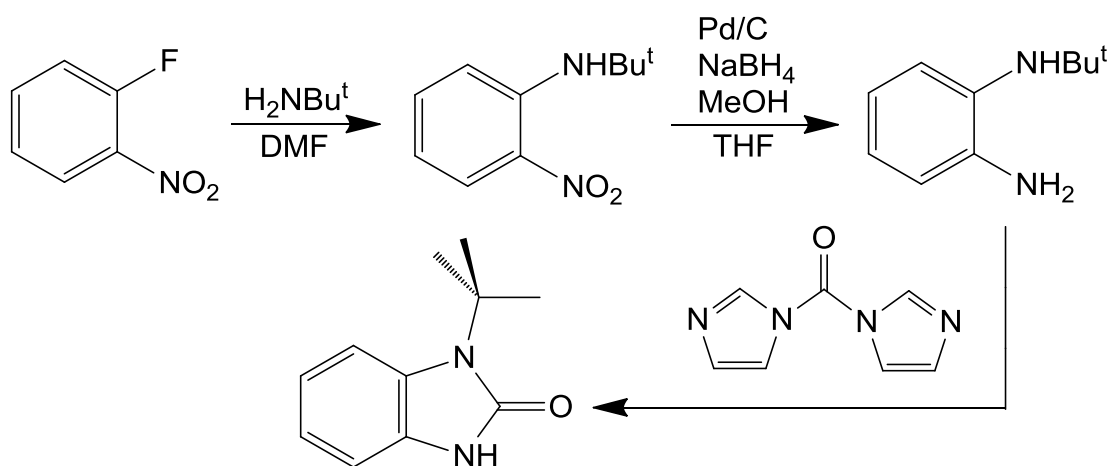
Scheme 7. Synthesis of 1-*t*-butyl-1,3-dihydro-benzimidazol-2-one.
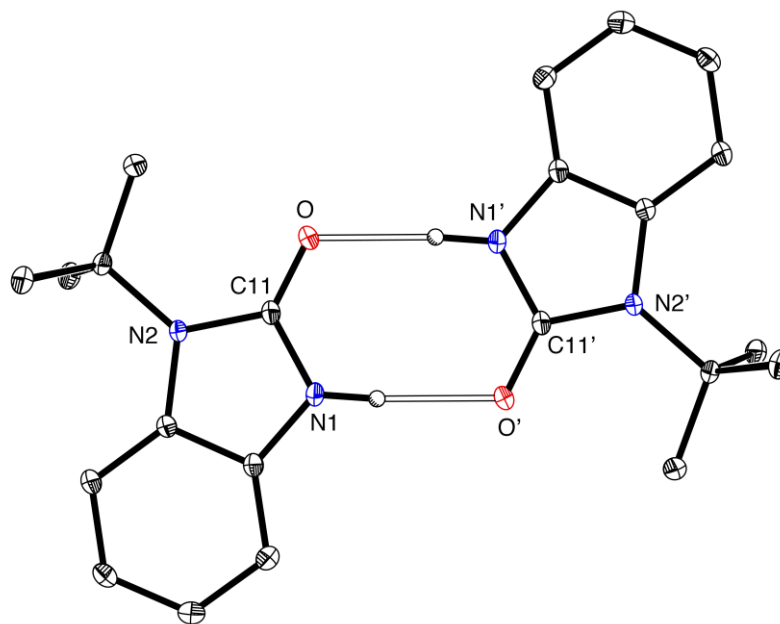
Figure 8. Hydrogen bonded dimeric structure of 1-t-butyl-1,3-dihydro-benzimidazol-2-one.

We then employed this procedure to synthesize a bulkier derivative, namely the 1-adamantyl-1,3-dihydro-benzimidazol-2-one,[21] and crystals suitable for X-ray diffraction were obtained from CH_2Cl_2 solution (Figure 9)
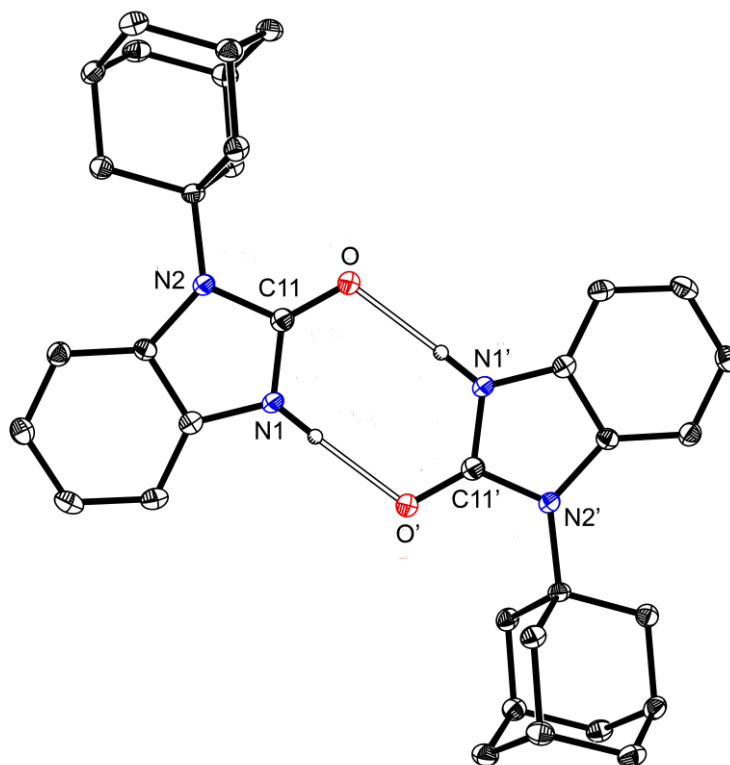
Figure 9. Hydrogen bonded dimeric structure of 1-adamantyl-1,3-dihydro-benzimidazol-2-one.

Benzannulated oxoimidazole compounds with different alkyl groups can be synthesized from the alkyl amine precursor (Scheme 7). However, we still find that the Hofmann-type-rearrangement of 2-methylaminobenzamide is the preferred method for the synthesis of 1-methyl-1,3-dihydro-benzimidazol-2-one since methylamine is a gas which has a strong fish odor (Scheme 4). The [To$^{Bu^tBenz}$]Na and [To^{AdBenz}]Na complexes have been synthesized by a method similar to [To^{MeBenz}]Na, by the reaction of NaBH$_4$ with the appropriate benzimidazole-2-one in diglyme at 185 °C (Scheme 8). The X-ray structures of [To$^{Bu^tBenz}$]Na and [To^{AdBenz}]Na reveal that, unlike the methyl version, the sodium is not fully coordinated by diglyme, since only two out of the three oxygen

atoms coordinate in the solid state (Figures 10 and 11). This might be due to the steric
bulk created by *t*-butyl or adamantyl groups.
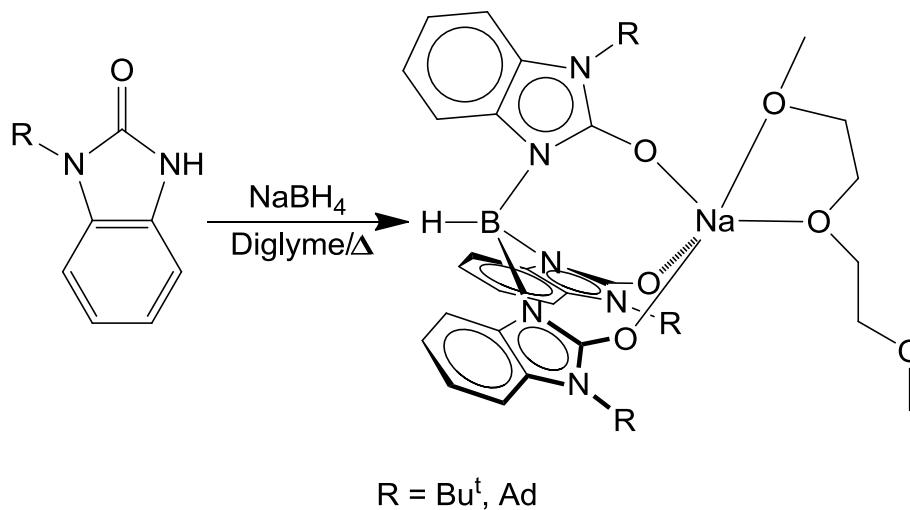
R = Bu^t, Ad

Scheme 8. Synthesis of [To^{RBenz}]Na(diglyme), R = Bu^t, Ad.
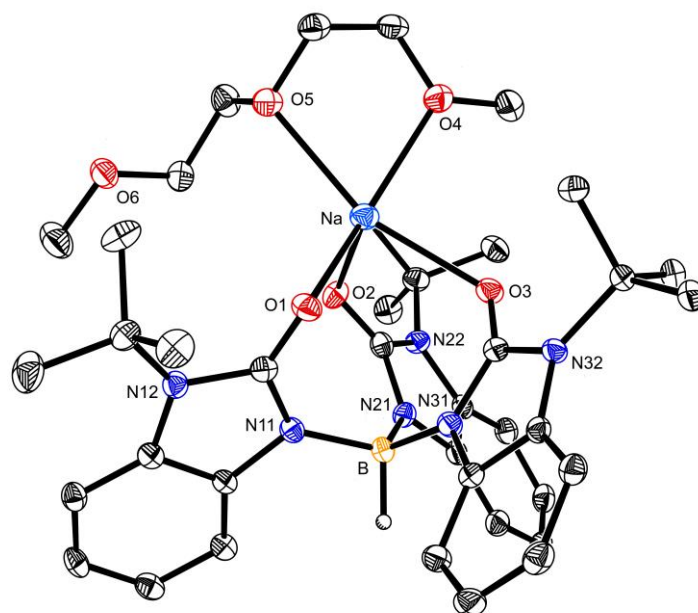
Figure 10. Molecular structure of [To$^{Bu^tBenz}$]Na·diglyme.
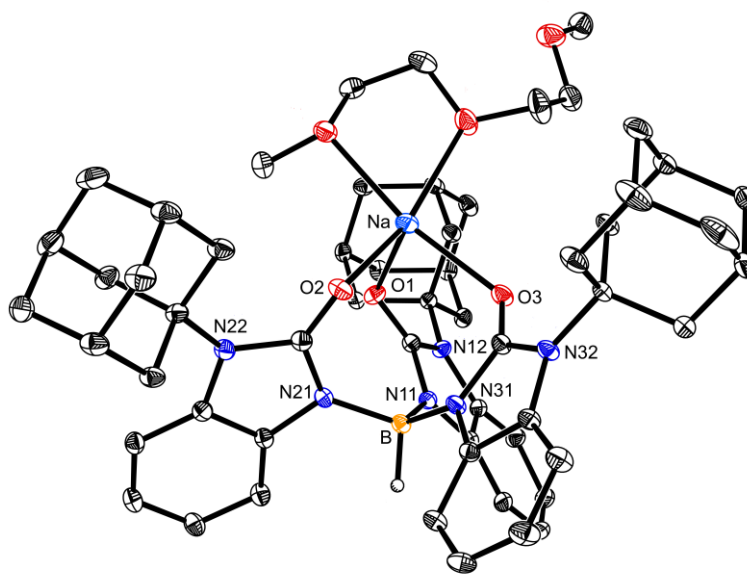
Figure 11. Molecular structure of [To^{AdBenz}]Na·diglyme.

1.5   Synthesis of the Thallium Counterpart: [To^{RBenz}]Tl

The alkali metal complexes, [To^{RBenz}]Na, are useful ligand-transfer reagents for the synthesis of the thallium derivative. There are many motivating factors for obtaining the thallium derivative. First, we are interested in how [To^R] ligands bind to thallium *versus* other related L$_2$X ligands, eg. [Tp^{R,R}] and [Tm^R]. Second, in many cases thallium derivatives are of use as ligand-transfer reagents due to the driving force provided by the precipitation of TlX or decomposition of TlR.[22] Finally, the process of converting [To^{RBenz}]Na to its thallium counterpart is an effective means for purifying the ligand by removing excess starting materials or coordinating solvent.[2]

Treatment of [To^{RBenz}]Na ,dissolved in methanol or THF with an aqueous solution of TlOAc led to immediate precipitation of the [To^{RBenz}]Tl (Scheme 9). The suspension was filtered and the precipitate was washed with water and dried *in vacuo* to generate the product with good yield and excellent purity. Crystals of [To^{MeBenz}]Tl (Figure 12), [To$^{Bu^tBenz}$]Tl (Figure 13) and [To^{AdBenz}]Tl (Figure 14) may be obtained from diffusion of pentane into a benzene solution, ether, and diffusion of pentane into a toluene solution, respectively, and their molecular structures were determined *via* X-ray diffraction.
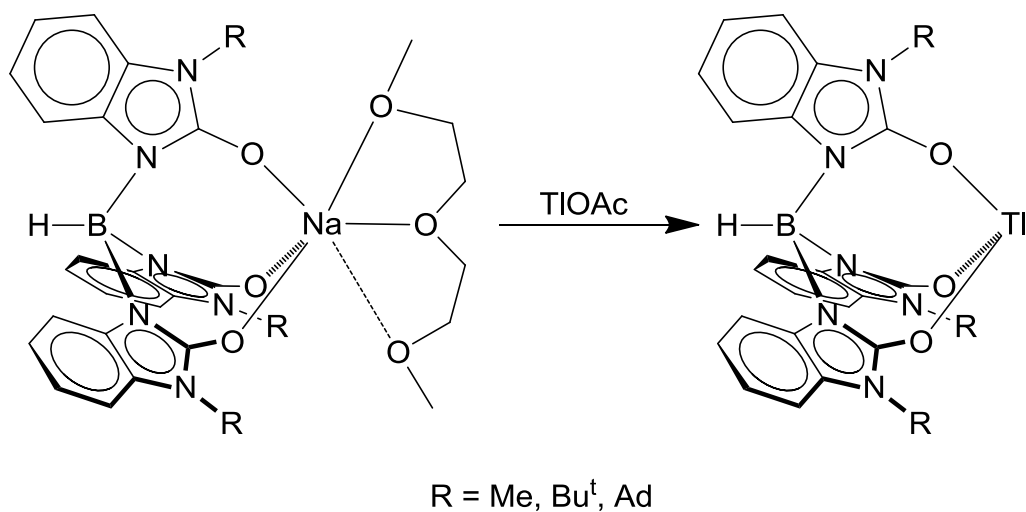
R = Me, Bu^t, Ad

Scheme 9. Synthesis of [To^{RBenz}]Tl, R = Me, Bu^t or Ad.
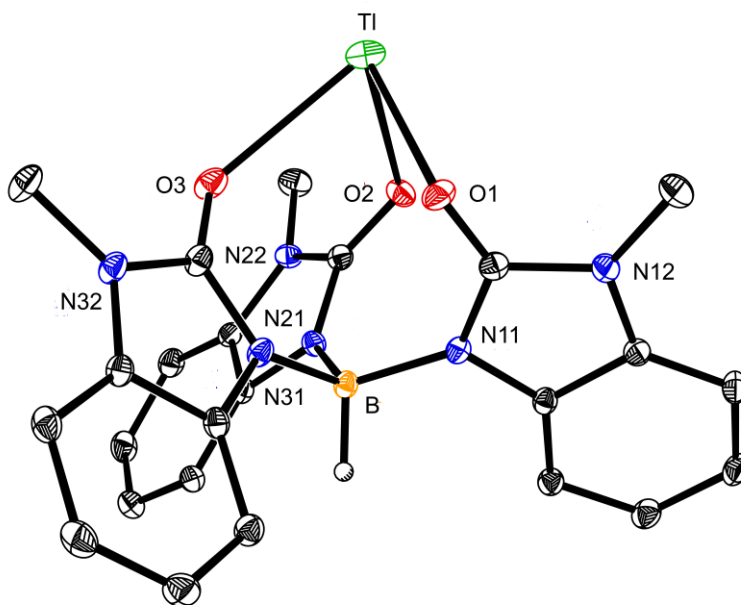
Figure 12. Molecular structure of [To^MeBenz]Tl.
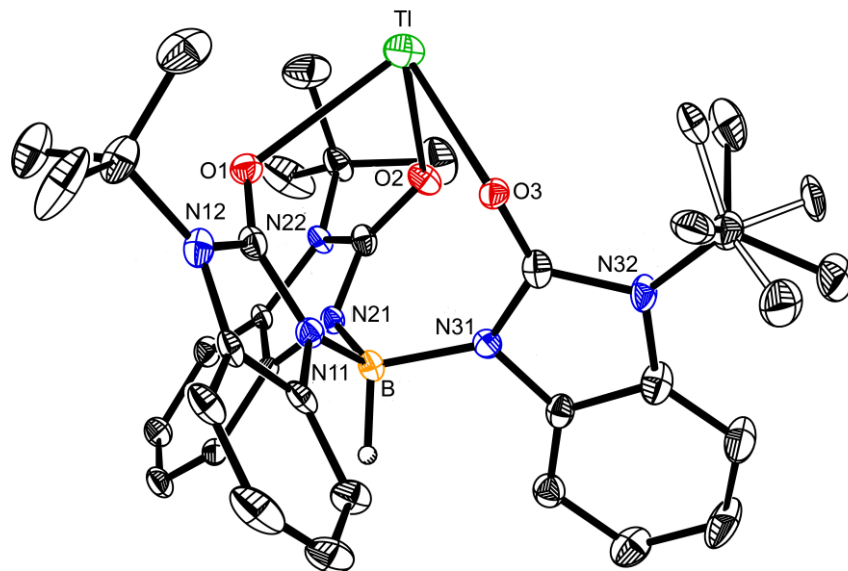
Figure 13. Molecular structure of [To^ButBenz]Tl.
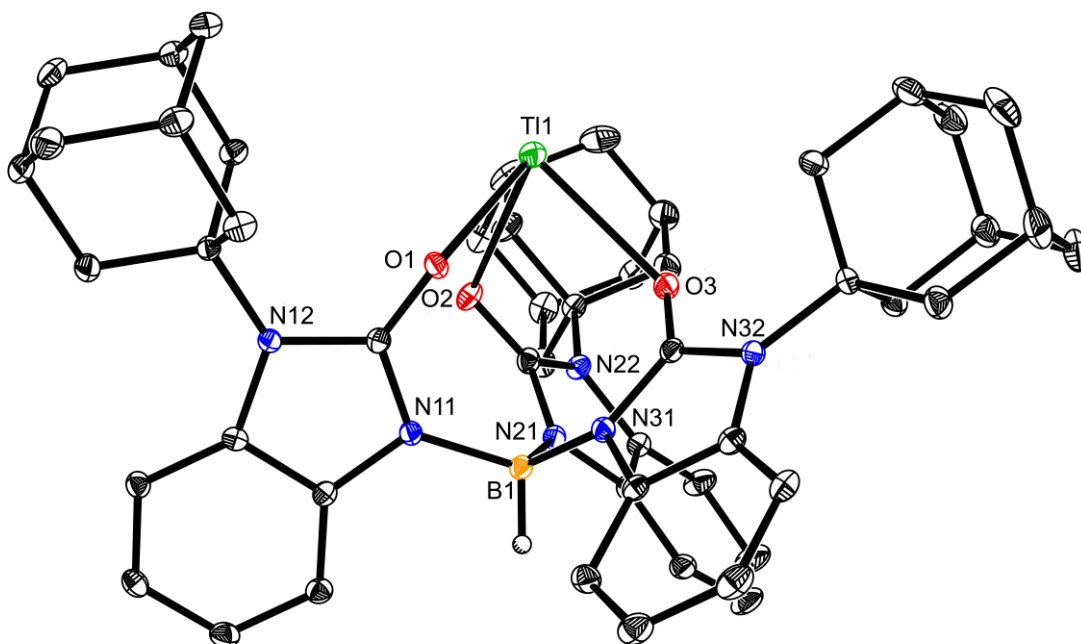
Figure 14. Molecular structure of [To^{AdBenz}]Tl.

Interestingly, [To^{RBenz}]Tl ,where R = Me, Bu^t , Ad, exist as discrete mononuclear complexes in the solid state since the shortest Tl•••Tl contact is 4.88 Å for [To^{MeBenz}]Tl, 6.81 Å for [To^{Bu^tBenz}]Tl and 7.41 Å for [To^{AdBenz}]Tl. Therefore, it is evident that there is no direct interaction. This is in marked contrast to [Tm^R]Tl. For example, when R = Ph, Bu^t, {[Tm^R]Tl}₂ is dinuclear in which two sulfurs of the ligand span the two metal centers whereas the third sulfur bridges them.[23] The coordination geometry of [To^{RBenz}]Tl more closely resembles the *tris*(pyrazolyl)-hydroborato counterparts, [Tp]Tl,[24] since they exist as monomeric complexes with symmetrically coordinated tridentate ligands.

The average O–Tl–O bond angles in [To^{RBenz}]Tl are quite acute, since it is 79.09° for [To^{MeBenz}]Tl, 79.77° for [To^{Bu^tBenz}]Tl and 78.41° for [To^{AdBenz}]Tl, and thus the thallium

centers are highly pyramidal (Table 1). Degree of pyramidality for MX_3 center can be obtained by measuring how much the sum of E–Tl–E departs from 360°, *i.e.* $P = 360° - \Sigma(E–M–E)$.[25] Similar values of pyramidality were obtained for $(Py)Fe(\mu\text{-}Ar^{Tol}CO_2)_3Tl$[26] where the thallium(I) center is fused between three Fe(II) carboxylate moties. [To^{RBenz}]Tl complexes are more pyramidal than the sulfur counterpart, [Tm^{RBenz}]Tl,[27] but less pyramidal than those in the *tris*(pyrazolyl)hydroborato counterpart, [Tp]Tl.[28]

Table 1. Metric data and pyramidality (*P*) of various tripodal thallium compounds.

	(Tl–E$_{av}$)/Å	Tl•••B/Å	(E–Tl–E$_{av}$)/°	Pyramidality (P)
				P = 360°– Σ(E–Tl–E)
[To^{MeBenz}]Tl	2.56	4.02	79.09	122.7
[To$^{Bu^tBenz}$]Tl	2.52	4.14	79.77	120.7
[To^{AdBenz}]Tl	2.51	4.17	78.41	124.8
[Tm^{MeBenz}]Tl	3.00	4.39	85.53	103.4
[Tm$^{Bu^tBenz}$]Tl	2.90	4.14	88.81	93.6
[Tp^{Me2}]Tl	2.52	3.62	74.64	136.09
[Tp$^{Bu^t,Me}$]Tl	2.50	3.53	77.87	126.39
[Tp^{Tripp}]Tl	2.74	3.63	76.01	131.98
$(Py)Fe(\mu\text{-}Ar^{Tol}CO_2)_3Tl$	2.65	–	78.8	123.6

1.6   Conclusion

The sodium salt of *tris*(2-oxo-1-t-butylimidazolyl) hydroborato, [To$^{Bu^t}$], as an [O_3] donor ligand has been prepared. The yield for this reaction is low because there is a significant

amount of side product in which the double bond of the oxoimidazole starting material is reduced. Treatment of sodium borohydride with benzannulated oxoimidazole at high temperature leads to the generation of *tris*(2-oxo-1-R-methylbenzimidazolyl) hydroborate in high yield. These ligands have been prepared with different alkyl substituents, methyl, *t*-butyl and adamantyl, to achieve the desired steric environment. Furthermore, these benzannulated ligands have been used to synthesize a series of [To^{RBenz}]Tl complexes, which exist as discrete mononuclear complexes in the solid state. Finally, the [To^{RBenz}]Tl complexes are more pyramidal than the sulfur counterparts, [Tm^{RBenz}]Tl, but less pyramidal than those in the *tris*(pyrazolyl)hydroborato, [Tp^{R,R}]Tl.

1.7   Experimental Section

1.7.1   General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[29] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 DRX, Bruker 400 AVIII, Brucker 400 Cyber-enabled Avance III and Bruker Avance 500 DMX spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C$_6$D$_5$H; 7.26 for CHCl$_3$ and 2.50 for d_6-DMSO).[30] ^{13}C NMR spectra are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 77.16 for CDCl$_3$, 128.06 for

C_6D_6, 54.00 for CD_2Cl_2 and 39.52 for d_6-DMSO).[30] Coupling constants are given in hertz.

Infrared spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Jeol JMS-HX110H Tandem Double-Focusing Mass Spectrometer with a 10 kV accelerated voltage equipped with FAB ion source. 1-*tert*-Butyl-1,3-dihydro-2*H*-imidazol-2-one,[12] 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-one[16] and 1-t-butyl-1,3-dihydro-2*H*-benzimidazol-2-one[20] were prepared by the literature methods. $NaBH_4$ (Aldrich), TlOAc (Aldrich) and 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-thione (Aldrich) were obtained commercially and used as received.

1.7.2   X-ray Structure Determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer and crystal data, data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2008/4).[31]

1.7.3   Synthesis of 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one

A mixture of N-(2,2-ethoxylethyl)-N-*t*-butylurea (7.0 g, 30 mmol), 1M H_2SO_4 (4 mL) and water (5 mL) in MeOH (200 mL) was heated at 60 °C for overnight. Then the mixture was cooled to room temperature and neutralized with NaOH (1 M). The volatile components were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (*ca.* 500 mL) and washed with saturated solution of $NaHCO_3$ (*ca.* 500 mL). The organic layer

was collected and dried over Na$_2$SO$_4$, after which the volatile components were removed *in vacuo* to leave behind yellow solid. The solid was dissolved in a minimum amount of CH$_2$Cl$_2$ for crystallization to obtained yellow crystals of 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one (3.0 g, 71.0%).

1.7.4 Synthesis of {[To$^{Bu^t}$]Na}$_2$

A mixture of 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one (200 mg, 1.43 mmol) and NaBH$_4$ (18 mg, 0.47 mmol) was placed in an ampoule and treated with THF (4 mL). The mixture was heated at 180 °C for 9 days and cooled to room temperature. The volatile components were removed *in vacuo* and the residue obtained was crystallized from pentane (*ca.* 5 mL) and dried to give [To$^{Bu^t}$]Na as colorless crystals (14 mg, 7%). ^{1}H NMR (C$_6$D$_6$): 1.37 [s, 27H of HB{C$_2$N$_2$H$_2$[C(C$\underline{H}_3$)$_3$]CO}$_3$], 6.08 [d, $^3J_{H-H}$ = 3, 3H of HB{C$_2$N$_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$], 6.62 [br, 3H of HB{C$_2$N$_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 28.5 [9 C, HB{C$_2$N$_2$H$_2$[C($\underline{C}$H$_3$)$_3$]CO}$_3$], 53.9 [3 C, HB{C$_2$N$_2$H$_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_3$], 107.7 [3 C, HB{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_3$], 112.3 [3 C, HB{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_3$], 157.6 [3 C, HB{C$_2$N$_2$H$_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_3$]. FAB-MS: *m/z* = 475.3 [M + Na]$^+$, M = [To$^{Bu^t}$]Na. The formation of [To$^{Bu^t}$]Na, however, is accompanied side reactions, in one of which the C=C double bond of the imidazolone ring is reduced, thereby resulting in the formation of 1-t-butylimidazolidinone, which was identified by ^{1}H NMR spectroscopy and X–ray diffraction. ^{1}H NMR for 1-t-butylimidazolidinone (C$_6$D$_6$): 1.29 [s, 9H of

C$_2$H$_4$NHN[C(C$\underline{H}_3$)$_3$]CO], 2.43 [t, $^3J_{\text{H-H}}$ = 8, 2H of C$_2\underline{H}_4$NHN[C(CH$_3$)$_3$]CO], 2.69 [t, $^3J_{\text{H-H}}$ = 8, 2H of C$_2\underline{H}_4$NHN[C(CH$_3$)$_3$]CO], NH not observed.

1.7.5 Synthesis of 1-methyl-1,3-dihydro-benzimidazol-2-one

Iodobenzene diacetate (6.4g, 20 mmol) was added portion wise to ice cooled mixture of 2-methylaminobenzamide (3.0g, 20 mmol) and KOH (2.6g, 40 mmol) in 100 mL MeOH. The ice was removed and the mixture was stirred for one hour. The mixture was neutralized with HCl (1 M). Then hexane (*ca.* 100 mL) was added and stirred for one hour to extract the formed iodobenzene. The methanol layer was collected and the volatile components were removed *in vacuo*. The resulted residue was dissolved in CH$_2$Cl$_2$ (*ca.* 500 mL) and washed with saturated aqueous solution of NaHCO$_3$ (400 mL). The organic layer was collected and dried over Na$_2$SO$_4$, after which the volatile components were removed *in vacuo* leaving behind light brown solid. The solid was dissolved in a minimum amount of CH$_2$Cl$_2$ for crystallization to obtained off-white crystals of 1-methyl-1,3-dihydro-benzimidazol-2-one (2.0 g, 68%).

1.7.6 Synthesis of [To$^{\text{MeBenz}}$]Na(diglyme)

A mixture of 1-methyl-2-benzimidazolinone (700 mg, 4.73 mmol) and NaBH$_4$ (51 mg, 1.35 mmol) was placed in an ampoule and treated with diglyme (*ca.* 10 mL). The mixture was heated at 175 $^\circ$C for 1 week, cooled to room temperature and filtered. The precipitate was washed with pentane (*ca.* 5 mL) and dried *in vacuo*, yielding [To$^{\text{MeBenz}}$]Na•diglyme as a white solid (650 mg, 79%). Analysis calcd. for

[To^{MeBenz}]Na•diglyme: C, 59.0%; H, 5.9%; N 13.8%. Found: C, 58.8%; H, 4.9%; N 14.6%.

^{1}H NMR (C$_6$D$_6$): 2.74 [s, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_3$], 3.10 [s, 6H of 2C$\underline{H}_3$ for

diglyme], 3.30 [t, $^3J_{H-H}$ = 5, 4H of 2C$\underline{H}_2$ for diglyme], 3.43[t, $^3J_{H-H}$ = 5, 4H of 2C$\underline{H}_2$ for

diglyme], 5.40 [b, ^{1}H of $\underline{H}$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 6.54 [d, $^3J_{H-H}$ = 7, 3H of

HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 6.94 [m, 6H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 7.59[d, $^3J_{H-H}$ = 7, 3H

of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 26.2[3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$],

58.7 [2 C, methyl of the diglyme], 70.6 [2 C, methylene of the diglyme], 72.0[2 C,

methylene of the diglyme], 106.9 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 111.8 [3 C,

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 120.4 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 121.6[3 C,

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 131.9 [3 C, HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$], 134.8[3 C,

HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$], 159.7 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_3$]. FAB-MS: m/z = 476.3

[M]$^+$, M = [To^{MeBenz}]Na. IR Data (KBr disk, cm^{-1}): 3424 (br), 3054 (w), 2931 (m), 2887 (m),

2425 (w) [ν_{BH}], 1699 (s), 1674 (s), 1602 (m), 1544 (w), 1495 (s), 1433 (s), 1390 (s), 1377 (s),

1316 (m), 1299 (s), 1212 (m), 1160 (m), 1121 (s), 1088 (s), 1017 (m), 853 (m), 768 (s), 736 (s),

693 (m), 669 (w), 620 (m), 564 (m), 511 (m), 445 (m). Colorless blocks of

[To^{MeBenz}]Na•diglyme suitable for X-ray were obtained from diglyme.

1.7.7 Synthesis of [To^{ButBenz}]Na(diglyme)

A mixture of 1-*tert*-Butyl-2-benzimidazolinone (824 mg, 4.33 mmol) and NaBH$_4$ (54.0

mg, 1.44 mmol) was placed in an ampoule and treated with diglyme (*ca.* 10 mL). The

mixture was heated at 190 °C for 4 days, cooled to room temperature where yellow

crystals formed. The crystals were filtered and washed with Et$_2$O (*ca.* 5 mL) and dried *in vacuo*, yielding [To^{ButBenz}]Na•diglyme as a yellow crystals (790 mg, 74.5%). Analysis calcd. for [To^{ButBenz}]Na•diglyme: C, 63.6%; H, 7.4%; N, 11.4. Found: C, 62.8%; H, 7.2%; N, 11.0%. ^{1}H NMR (C$_6$D$_6$): 1.58 [s, 27H of HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 3.15 [s, 6H of 2CH$_3$ for diglyme], 3.18 [t, $^{3}J_{H-H}$ = 5, 4H of 2CH$_2$ for diglyme], 3.39 [t, $^{3}J_{H-H}$ = 5, 4H of 2CH$_2$ for diglyme], 6.90 [m, 6H of HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 7.19 [m, 3H of HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 7.54 [d, $^{3}J_{H-H}$ = 7, 3H of HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 29.7 [9 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 56.9 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 59.1 [2 C, methyl of the diglyme], 69.4 [2 C, methylene of the diglyme], 71.1 [2 C, methylene of the diglyme], 110.9 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 111.9 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 119.2 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 120.7 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 131.6 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 136.0 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 160.0 [3C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$]. FAB-MS: *m/z* = 602.3 [M]$^{+}$, M = [To^{ButBenz}]Na. Yellowish blocks of [To^{ButBenz}]Na•diglyme suitable for X-ray were obtained from diglyme.

1.7.8   Synthesis of 1-Adamantyl-1,3-dihydro-benzimidazol-2-one

1.7.8.1 Synthesis of Adamantyl-(2-nitrophenyl)-amine

A mixture of 1-fluoro-2-nitrobenzene (10.0 g, 70.4 mmol) and 1-adamantylamine (9.5g , 63.0 mmol) was placed in round-bottom flask and treated with DMF (*ca.* 70 mL). The mixture was heated at 70 °C for 4 days during which a precipitate was formed. The

mixture was cooled to room temperature where more precipitate formed. The mixture was filtered and the solid was collected and added to saturated aqueous solution of NaCl (200 mL) in erlenmeyer flask. The resulted mixture was extracted with ethyl acetate (*ca.* 700 mL). The organic layer was collected and dried over Na_2SO_4, after which the volatile components were removed *in vacuo* to yield adamantyl-(2-nitrophenyl)-amine as an orange crystalline material (10.0g, 58.4%). Analysis calcd. for adamantyl-(2-nitrophenyl)-amine: C, 70.6%; H, 7.4%; N, 10.3% Found: C, 70.6%; H, 7.6%; N, 10.3%. ^{1}H NMR (C_6H_6): 1.42 [m, 6H of $(C_4H_4)C_2(NO_2)(NHC_{10}\underline{H}_{15})$], 1.73 [br, 6H of $(C_4H_4)C_2(NO_2)(NHC_{10}\underline{H}_{15})$], 1.80 [br, 3H of $(C_4H_4)C_2(NO_2)(NHC_{10}\underline{H}_{15})$], 6.20 [m, 1H of $(C_4\underline{H}_4)C_2(NO_2)(NHC_{10}H_{15})$], 6.89 [m, 2H of $(C_4\underline{H}_4)C_2(NO_2)(NHC_{10}H_{15})$], 8.20 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 1H of $(C_4\underline{H}_4)C_2(NO_2)(NHC_{10}H_{15})$], 8.35 [br, 1H of $(C_4H_4)C_2(NO_2)(N\underline{H}C_{10}H_{15})$]. $^{13}C\{^1H\}$ NMR (C_6H_6): 29.8 [3C of $(C_4H_4)C_2(NO_2)(NH\underline{C}_{10}H_{15})$], 36.3 [3C of $(C_4H_4)C_2(NO_2)(NH\underline{C}_{10}H_{15})$], 42.3 [3C of $(C_4H_4)C_2(NO_2)(NH\underline{C}_{10}H_{15})$], 52.5 [1C of $(C_4H_4)C_2(NO_2)(NH\underline{C}_{10}H_{15})$], 114.8 [1C of $(\underline{C}_4H_4)C_2(NO_2)(NHC_{10}H_{15})$], 116.8 [1C of $(\underline{C}_4H_4)C_2(NO_2)(NHC_{10}H_{15})$], 127.8 [1C of $(\underline{C}_4H_4)C_2(NO_2)[NHC_{10}H_{15}]$], 133.5 [1C of $(C_4H_4)\underline{C}_2(NO_2)(NHC_{10}H_{15})$], 134.7 [1C of $(\underline{C}_4H_4)C_2(NO_2)(NHC_{10}H_{15})$], 144.9 [1C of $(C_4H_4)\underline{C}_2(NO_2)(NHC_{10}H_{15})$]. FAB-MS: *m/z* = 272.15 [M][+], M = Adamantyl-(2-nitrophenyl)-amine.

1.7.8.2 Synthesis of N-adamantyl-benzene-1,2-diamine

Methanol (40.0 mL) was added in a dropwise manner to a mixture of adamantyl-(2-nitrophenyl)-amine (4.5 g, 16.5 mmol), $NaBH_4$ (2.0 g, 52.9 mmol) and 5% Pd/C (2 gram) in THF (*ca.* 150 mL). The addition was slow enough to prevent overheating of the mixture. The addition, also, was carried out in an open system due to the continuous generation of hydrogen gas. After the complete addition of methanol, the mixture was stirred for one hour then filtered through pad of celite. The filtrate was collected and poured into saturated solution of ammonium chloride (200 mL) and extracted with ethyl acetate (2 × *ca.* 100 mL). The organic layer was collected and dried over Na_2SO_4, after which the volatile components were removed *in vacuo* to yield a brown powder of crude N-adamantyl-benzene-1,2-diamine (3.8 g, 95.0%) which is used for the next step without any further purification. ^1H NMR (C_6H_6): 1.47 [m, 6H of $(C_4H_4)C_2(NH_2)(NHC_{10}\underline{H}_{15})$], 1.70 [br, 6H of $(C_4H_4)C_2(NH_2)(NHC_{10}\underline{H}_{15})$], 1.90 [br, 3H of $(C_4H_4)C_2(NH_2)(NHC_{10}\underline{H}_{15})$], 6.54 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 1H of $(C_4\underline{H}_4)C_2(NH_2)(NHC_{10}H_{15})$], 6.77 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 1H of $(C_4\underline{H}_4)C_2(NH_2)(NHC_{10}H_{15})$], 6.89 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 1H of $(C_4\underline{H}_4)C_2(NH_2)(NHC_{10}H_{15})$], 6.94 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 1H of $(C_4\underline{H}_4)C_2(NH_2)(NHC_{10}H_{15})$]. $^{13}C\{^1H\}$ NMR (C_6H_6): 30.1 [3C of $(C_4H_4)C_2(NH_2)(NH\underline{C}_{10}H_{15})$], 36.8 [3C of $(C_4H_4)C_2(NH_2)(NH\underline{C}_{10}H_{15})$], 43.6 [3C of $(C_4H_4)C_2(NH_2)(NH\underline{C}_{10}H_{15})$], 53.4 [1C of $(C_4H_4)C_2(NH_2)(NH\underline{C}_{10}H_{15})$], 116.2 [1C of $(\underline{C}_4H_4)C_2(NH_2)(NHC_{10}H_{15})$], 118.4 [1C of $(\underline{C}_4H_4)C_2(NH_2)(NHC_{10}H_{15})$], 124.1 [1C of $(\underline{C}_4H_4)C_2(NH_2)(NHC_{10}H_{15})$], 126.6 [1C of $(\underline{C}_4H_4)C_2(NH_2)(NHC_{10}H_{15})$], 131.9 [1C of $(C_4H_4)\underline{C}_2(NH_2)(NHC_{10}H_{15})$], 143.6 [1C of

$(C_4H_4)\underline{C}_2(NH_2)(NHC_{10}H_{15})]$. FAB-MS: *m/z* = 242.37 [M]$^+$, M = N-adamantyl-benzene-1,2-diamine.

1.7.8.3 Synthesis of 1-Adamantyl-1,3-dihydro-benzimidazol-2-one

A mixture of N-adamantyl-benzene-1,2-diamine (3.8 g, 15.7 mmol) and 1,1′-carbonyl-diimidazole (4.2 g, 25.9) was treated with anhydrous THF (150 mL). The mixture was stirred for 48 hours at room temperature then poured into 1M aqueous solution of HCl (*ca.* 200 mL). The resulted mixture was extracted with ethyl acetate (2 × *ca.* 200 mL). The organic layer was collected and dried over Na_2SO_4 after which the volatile components were removed *in vacuo* to give of 1-adamantyl-2-benzimidazolinone as a light brown powder (4.0g, 95.1%). Analysis calcd. for 1-adamantyl-2-benzimidazolinone: C, 76.1%; H, 7.5%; N, 10.4 Found: C, 76.2%; H, 7.6%; N, 10.4%. ^{1}H NMR (C_6D_6): 1.57 [m, 6H of $(C_4H_4)C_2N_2H[C_{10}\underline{H}_{15}]CO$], 1.97 [br, 3H of $(C_4H_4)C_2N_2H[C_{10}\underline{H}_{15}]CO$], 2.55 [br, 6H of $(C_4H_4)C_2N_2H[C_{10}\underline{H}_{15}]CO$], 6.86 [m, 3H of $(C_4\underline{H}_4)C_2N_2H[C_{10}H_{15}]CO$], 7.26 [m, 1H of $(C_4\underline{H}_4)C_2N_2H[C_{10}H_{15}]CO$], 10.54 [br, 1H of $(C_4H_4)C_2N_2\underline{H}[C_{10}H_{15}]CO$]. ^{13}C{^{1}H} NMR ($C_6D_6$): 30.2 [3C of $(C_4H_4)C_2N_2H[\underline{C}_{10}H_{15}]CO$], 36.4 [3C of $(C_4H_4)C_2N_2H[\underline{C}_{10}H_{15}]CO$], 40.8 [6C of $(C_4H_4)C_2N_2H[\underline{C}_{10}H_{15}]CO$], 60.2 [1C of $(C_4H_4)C_2N_2H[\underline{C}_{10}H_{15}]CO$], 109.7 [1C of $(\underline{C}_4H_4)C_2N_2H[C_{10}H_{15}]CO$], 112.7 [1C of $(\underline{C}_4H_4)C_2N_2H[C_{10}H_{15}]CO$], 120.5 [1C of $(\underline{C}_4H_4)C_2N_2H[C_{10}H_{15}]CO$], 120.9 [1C of $(\underline{C}_4H_4)C_2N_2H[C_{10}H_{15}]CO$], 129.5 [1C of $(C_4H_4)\underline{C}_2N_2H[C_{10}H_{15}]CO$], 130.6 [1C of $(C_4H_4)\underline{C}_2N_2H[C_{10}H_{15}]CO$], 156.3 [1C of $(C_4H_4)C_2N_2H[C_{10}H_{15}]\underline{C}O$]. FAB-MS: *m/z* = 268.33 [M]$^+$, M = 1-admantyl-2-

benzimidazolinone. Colorless blocks of 1-adamantyl-2-benzimidazolinone suitable for X-ray were obtained from CH_2Cl_2.

1.7.9 Synthesis of [To^{AdBenz}]Na(diglyme)

A mixture of 1-adamantyl-2-benzimidazolinone (700 mg, 2.6 mmol) and NaBH$_4$ (33 mg, 0.9 mmol) was placed in an ampoule and treated with diglyme (*ca.* 6 mL). The mixture was heated at 190 °C for 4 days, cooled to room temperature where yellow crystals formed. In case of no crystals formed at room temperature, the mixture can be cooled in an ice-bath to 0 °C to enhance the formation of crystals of the product. The crystals were filtered and dried *in vacuo*, yielding [To^{AdBenz}]Na•diglyme as a yellow crystals (400 mg, 45.8%). Analysis calcd. for [To^{MeBenz}]Na•1.5diglyme: C, 69.4 %; H, 7.7 %; N, 8.1 % Found: C, 68.9%; H, 6.9%; N, 8.01%. ^{1}H NMR (C$_6$D$_6$): 1.54 [m, 18H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}_{15}$]CO}$_3$], 1.90 [br, 9H of HB{(C$_4H_4$)C$_2N_2$[C$_{10}$$\underline{H}_{15}$]CO}$_3$], 2.45 [br, 18H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}_{15}$]CO}$_3$], 3.18 [s, 6H of 2C$\underline{H}_3$ for diglyme], 3.29 [t, $^3J_{H-H}$ = 4, 4H of 2C$\underline{H}_2$ for diglyme], 3.46[t, $^3J_{H-H}$ = 4, 4H of 2C$\underline{H}_2$ for diglyme], 6.92 [m, 6H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_3$], 7.33 [m, 3H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_3$], 7.55 [d, $^3J_{H-H}$ = 6, 3H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_3$] . ^{13}C{^{1}H} NMR (C$_6D_6$): 30.4 [9C of HB{(C$_4H_4$)C$_2N_2$[$\underline{C}_{10}H_{15}$]CO}$_3$], 36.7 [9C of HB{(C$_4H_4$)C$_2N_2$[$\underline{C}_{10}H_{15}$]CO}$_3$], 40.9 [9C of HB{(C$_4H_4$)C$_2N_2$[$\underline{C}_{10}H_{15}$]CO}$_3$], Not showing [3C of HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$], 59.1 [2 C, methyl of the diglyme], 70.0 [2 C, methylene of the diglyme], 71.4 [2 C, methylene of the diglyme], 111.6 [3C of HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 112.0 [3C of

HB{($\underline{C}_4H_4$)C_2N_2[$C_{10}H_{15}$]CO}$_3$], 119.2 [3C of HB{($\underline{C}_4H_4$)C_2N_2[$C_{10}H_{15}$]CO}$_3$], 120.6 [3C of

HB{($\underline{C}_4H_4$)C_2N_2[$C_{10}H_{15}$]CO}$_3$], 131.3 [3C of HB{(C_4H_4)$\underline{C}_2N_2$[$C_{10}H_{15}$]CO}$_3$], 136.0 [3C of

HB{(C_4H_4)$\underline{C}_2N_2$[$C_{10}H_{15}$]CO}$_3$], 159.9 [3C of HB{(C_4H_4)C_2N_2[$C_{10}H_{15}$]$\underline{C}$O}$_3$]. FAB-MS: m/z =

836.46 [M]$^+$, M = [To^{AdBenz}]Na. Yellowish blocks of [To^{AdBenz}]Na•diglyme suitable for X-

ray were obtained from diglyme.

1.7.10 Synthesis of [To^{MeBenz}]Tl

[To^{MeBenz}]Na•diglyme (230 mg, 0.38 mmol) was dissolved in MeOH (*ca.* 22 mL) and

filtered to obtain clear solution. The clear solution was treated with solution of TlOAc

(149 mg, 0.57 mmol) in distilled water (*ca.* 80 mL), resulting in the formation of a white

precipitate in a colorless solution. The mixture was stirred at room temperature for 30

minutes then filtered. The precipitate was washed with water (2 × *ca.* 10 mL) and dried

in air overnight then dried *in vacuo* yielding off-white powder of [To^{MeBenz}]Tl (180 mg,

72.0%). Analysis calcd. for [To^{MeBenz}]Tl•0.5C_6H_6: C, 46.6%; H, 3.6%; N, 12.1%. Found: C,

46.2%; H, 3.4%; N, 11.8%. ^{1}H NMR (C_6D_6): 2.74 [s, 9H of HB{(C_4H_4)C_2N_2(C$\underline{H}_3$)CO}$_3$], 6.58

[m, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH$_3$)CO}$_3$], 6.98 [m, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH$_3$)CO}$_3$], 7.63 [d,

3H of HB{($C_4\underline{H}_4$)C_2N_2(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 26.2[3 C,

HB{(C_4H_4)C_2N_2($\underline{C}$H$_3$)CO}$_3$], 107.2 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH$_3$)CO}$_3$], 111.9 [3 C,

HB{($\underline{C}_4H_4$)C_2N_2(CH$_3$)CO}$_3$], 120.5 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH$_3$)CO}$_3$], 121.7 [3 C,

HB{($\underline{C}_4H_4$)C_2N_2(CH$_3$)CO}$_3$], 131.9 [3C, HB{(C_4H_4)$\underline{C}_2N_2$(CH$_3$)CO}$_3$], 134.4 [3C,

HB{(C_4H_4)$\underline{C}_2N_2$(CH$_3$)CO}$_3$], 159.8 [3C, HB{(C_4H_4)C_2N_2(CH$_3$)$\underline{C}$O}$_3$]. FAB-MS: m/z = 658.2

[M]⁺, M = [To^MeBenz]Tl. Colorless block of [To^MeBenz]Tl suitable for X-ray were obtained

from diffusion of pentane into solution of [To^MeBenz]Tl in benzene.

1.7.11 Synthesis of [To^Bu^tBenz]Tl

[To^Bu^tBenz]Na•diglyme (500 mg, 0.68 mmol) was dissolved in MeOH (*ca.* 8 mL) and

filtered to obtain clear solution. The resulted clear solution was treated with a solution

of thallium (I) acetate (357 mg, 1.36 mmol) in water (*ca.* 10 mL), resulting in the

formation of a yellow precipitate in a light yellow solution. The mixture was stirred at

room temperature for 30 minutes then filtered. The precipitate was washed with water

(2 × *ca.* 10 mL) and dried in air overnight then dried *in vacuo* yielding yellow powder of

[To^Bu^tBenz]Tl (440 mg, 82.6%). Analysis calcd. for [To^Bu^tBenz]Tl: C, 50.6%; H, 5.1%; N, 10.7%.

Found: C, 50.8%; H, 5.2%; N, 10.6%. ^{1}H NMR (C$_6$D$_6$): 1.47 [s, 27H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 6.90 [m, 6H of HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 7.15 [d, ^{3}J$_{H-}$

$_H$ = 10, 3H of HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 7.56 [d, ^{3}J$_{H-H}$ = 10, 3H of

HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 30.1 [m, 9 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 57.6 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 111.8 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 112.2 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 120.1 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 121.2 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 131.3 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 135.0 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$], 160.2 [3C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$]. FAB-MS: *m/z* = 784.3 [M]⁺, M = [To^Bu^tBenz]Tl. Colorless

plate of [To^Bu^tBenz]Tl suitable for X-ray were obtained from diethylether.

1.7.12 Synthesis of [To^{AdBenz}]Tl

[To^{AdBenz}]Na•diglyme (218 mg, 0.22 mmol) was dissolved in THF (*ca.* 75 mL) and filtered

to obtain clear solution. The resulted clear solution was treated with a solution of

thallium (I) acetate (90.0 mg, 0.34 mmol) in water (*ca.* 100 mL), resulting in the

formation of a white precipitate in a colorless solution. The mixture was stirred at room

temperature for one hour then filtered. The precipitate was washed with water (2 × *ca.*

25 mL) and dried in air overnight and then dried *in vacuo* yielding off-white powder of

[To^{AdBenz}]Tl•THF (150 mg, 67.1%). Analysis calcd. for [To^{AdBenz}]Tl•THF: C, 60.6 %; H,

6.1%; N, 7.7. Found: C, 60.7%; H, 6.1%; N, 7.4%. ^{1}H NMR (C$_6$H$_6$): 1.42 [m, 4H of 2C$\underline{H}_2$ for

THF], 1.47 [m, 18H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}\underline{H}_{15}$]CO}$_3$], 1.85 [br, 9H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}\underline{H}_{15}$]CO}$_3$], 2.42 [br, 18H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}\underline{H}_{15}$]CO}$_3$], 3.58 [m, 4H

of 2C$\underline{H}_2$ for THF], 6.95 [m, 6H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 7.33 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1,

3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 7.59 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 3H of

HB{(C$_4\underline{H}_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6$H$_6$): 25.8 [2 C, methylene of the THF], 30.2

[9C of HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$], 36.4 [9C of HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$], 41.4 [br, 9C

of HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$], 60.0 [3C of HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$], 67.8 [2 C,

methylene of the THF], 112.3 [3C of H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 112.5[3C of

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 120.0 [3C of HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 121.1 [3C of

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 131.1 [3C of HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 135.0 [3C of

HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$], 160.0 [3C of HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$[C$_{10}$H$_{15}\underline{C}$O}$_3$]. FAB-MS: *m/z* =

1018.44 [M]$^+$, M = [To^{AdBenz}]Tl. Colorless plates of [To^{AdBenz}]Tl suitable for X-ray were

obtained from toluene.

1.8   Crystallographic Data

Table 2. Crystal, intensity collection and refinement data.

	H(obenzim$^{Bu^t}$)	[To$^{Bu^t}$]Na
lattice	Monoclinic	Triclinic
formula	$C_{11}H_{14}N_2O_2$	$C_{42}H_{68}B_2N_{12}O_6Na_2$
formula weight	190.24	904.68
space group	$P2_1/n$	$P\text{-}1$
$a/\text{Å}$	11.2515(19)	10.357(3)
$b/\text{Å}$	7.9498(14)	10.900(3)
$c/\text{Å}$	11.536(2)	12.135(4)
$\alpha/°$	90	104.306(5)
$\beta/°$	106.507(2)	92.511(5)
$\gamma/°$	90	108.015(5)
$V/\text{Å}^3$	989.3(3)	1251.6(6)
Z	4	1
temperature (K)	125(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.277	1.200
μ (Mo Kα), mm^{-1}	0.084	0.096
θ max, deg.	29.57	26.37
no. of data collected	14457	15155
no. of data used	2766	5123
no. of parameters	134	302
R_1 [$I > 2\sigma(I)$]	0.0389	0.0568
wR_2 [$I > 2\sigma(I)$]	0.1090	0.0784
R_1 [all data]	0.0463	0.1517
wR_2 [all data]	0.1154	0.0932
GOF	1.063	1.092
R_{int}	0.1007	0.0880

Table 2. (cont.) Crystal, intensity collection and refinement data.

	1-t-butyl-imidazolidinone	H(obenzim^{Me})
lattice	Monoclinic	Monoclinic
formula	$C_7H_{14}N_2O$	$C_8H_8N_2O$
formula weight	142.20	148.16
space group	$P2_1/c$	$P2_1/n$
$a/Å$	12.2165(13)	9.2105(16)
$b/Å$	6.1075(3)	5.5849(10)
$c/Å$	10.7386(11)	13.456(2)
$\alpha/°$	90	90
$\beta/°$	96.338(2)	91.481(2)
$\gamma/°$	90	90
$V/Å^3$	796.33(14)	707.0(2)
Z	4	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.186	1.392
μ (Mo Kα), mm^{-1}	0.081	0.095
θ max, deg.	30.50	30.69
no. of data collected	12129	10956
no. of data used	2430	2181
no. of parameters	98	105
R_1 [$I > 2\sigma(I)$]	0.0473	0.0478
wR_2 [$I > 2\sigma(I)$]	0.1277	0.1057
R_1 [all data]	0.0655	0.0752
wR_2 [all data]	0.1420	0.1183
GOF	1.037	1.040
R_{int}	0.0431	0.0623

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[To$^{\text{MeBenz}}$]Na	H(obenzim$^{\text{But}}$)
lattice	Triclinic	Monoclinic
formula	$C_{30}H_{36}BN_6O_6Na$	$C_{11}H_{14}N_2O$
formula weight	610.45	190.24
space group	P-1	$P2_1/n$
$a/\text{Å}$	13.7551(9)	11.2515(19)
$b/\text{Å}$	14.9081(10)	7.9498(14)
$c/\text{Å}$	15.2676(10)	11.536(2)
$\alpha/°$	82.3230(10)	90
$\beta/°$	89.7710(10)	106.507(2)
$\gamma/°$	81.6210(10)	90
$V/\text{Å}^3$	3069.2(4)	989.3(3)
Z	4	4
temperature (K)	200(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.321	1.277
μ (Mo Kα), mm^{-1}	0.105	0.084
θ max, deg.	32.57	29.57
no. of data collected	52297	14457
no. of data used	20703	2766
no. of parameters	811	134
R_1 [$I > 2\sigma(I)$]	0.0494	0.0392
wR_2 [$I > 2\sigma(I)$]	0.1178	0.1090
R_1 [all data]	0.1003	0.0463
wR_2 [all data]	0.1427	0.1154
GOF	1.021	1.063
R_{int}	0.0373	0.0289

Table 2. (cont.) Crystal, intensity collection and refinement data.

	H(obenzim^{Ad})	[To$^{Bu^tBenz}$]Na
lattice	Monoclinic	Monoclinic
formula	$C_{30}H_{36}BN_6NaO_6$	$C_{39}H_{54}BN_6O_6Na$
formula weight	610.45	736.68
space group	C_2/c	$P2_1/n$
$a/\text{Å}$	19.693(5)	14.4606(17)
$b/\text{Å}$	6.7643(16)	16.942(2)
$c/\text{Å}$	21.751(5)	16.2001(19)
$\alpha/°$	90	90
$\beta/°$	112.503(3)	104.238(2)
$\gamma/°$	90	90
$V/\text{Å}^3$	2676.9	3847.0(8)
Z	8	4
temperature (K)	130(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.332	1.272
μ (Mo Kα), mm^{-1}	0.084	0.095
θ max, deg.	28.28	28.28
no. of data collected	17902	53216
no. of data used	3310	9555
no. of parameters	185	493
R_1 [$I > 2\sigma(I)$]	0.0593	0.0563
wR_2 [$I > 2\sigma(I)$]	0.1049	0.0849
R_1 [all data]	0.1423	0.1641
wR_2 [all data]	0.1316	0.1092
GOF	1.029	1.043
R_{int}	0.1388	0.1615

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[To^{AdBenz}]Na	[To^{MeBenz}]Tl
lattice	Monoclinic	Triclinic
formula	$C_{57}H_{72}BN_6 O_6Na$	$C_{27}H_{25}BN_6O_3Tl$
formula weight	971.01	696.71
space group	*Cc*	*P-1*
$a/Å$	12.591(5)	8.9623(7)
$b/Å$	22.702(10)	11.8473(9)
$c/Å$	17.362(7)	12.5574(9)
$α/°$	90	88.5470(10)
$β/°$	96.671(6)	88.3440(10)
$γ/°$	90	75.8500(10)
$V/Å^3$	4929(4)	1292.11(17)
Z	4	2
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.308	1.791
μ (Mo Kα), mm^{-1}	0.092	6.292
θ max, deg.	26.80	30.51
no. of data collected	10239	20917
no. of data used	5221	7831
no. of parameters	647	350
R_1 [$I > 2σ(I)$]	0.0730	0.0207
wR_2 [$I > 2σ(I)$]	0.1461	0.0501
R_1 [all data]	0.1175	0.0235
wR_2 [all data]	0.1629	0.0511
GOF	1.036	1.037
R_{int}	0.1105	0.0209

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[To$^{Bu^tBenz}$]Tl	[To^{AdBenz}]Tl
lattice	Monoclinic	Triclinic
formula	$C_{37}H_{50}BN_6O_6Na$	$C_{54.5}H_{62}BN_6O_3Tl$
formula weight	858.01	1064.28
space group	$P2_1/c$	P-1
a/Å	16.633(3)	13.1614(17)
b/Å	17.757(3)	15.858(2)
c/Å	12.807(2)	23.642(3)
α/°	90	98.831(2)
β/°	103.682(2)	101.050(2)
γ/°	90	101.050(2)
V/Å^3	3675.3(10)	102.309(2)
Z	4	4
temperature (K)	150(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.551	1.526
μ (Mo Kα), mm^{-1}	4.442	3.538
θ max, deg.	28.28	32.79
no. of data collected	50589	80820
no. of data used	9125	31750
no. of parameters	488	1117
R_1 [$I > 2\sigma(I)$]	0.0602	0.0368
wR_2 [$I > 2\sigma(I)$]	0.1307	0.0825
R_1 [all data]	0.1294	0.0578
wR_2 [all data]	0.1579	0.0878
GOF	1.023	1.013
R_{int}	0.1432	0.0409

1.9   References and Notes.

(1)   Trofimenko, S. *J. Am. Chem. Soc*. **1966**, 88, 1842-1844.

(2)   (a) *Scorpionate- The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**. (b) *Scorpionate II: Chelating Borate Ligands*, C. Pettinari, Imperial College Press, London, **2008**.

(3)   (a) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148. (b) Parkin, G. in *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1.01; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2006.

(4)   Ge, P.; Haggerty, B. S.; Rheingold, A. L.; Riordan, C. G. *J. Am. Chem Soc*. **1994**, 8406-8407.

(5)   Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *J. Chem. Soc., Chem. Commun*. **1996**, 1975-1976.

(6)   (a) Barnery, A. A.; Heyduk, A. F.; Nocera, D. G. *Chem. Commun.*, **1999**, 2379-2380. (b) Peter, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am Chem. Soc.*, **1999**, 121, 9871-9872.

(7)   Nieto, I.; Cervantes-Lee, F.; Smith, J. M. *Chem Commun.*, **2005**, 3811-3813.

(8)   Minoura**,** M.; Landry, V. K.; Melnick, J. G.; Pang, K.; Marchio, L.; Parkin, G. *Chem. Commun.*, **2006,** 3990-3992.

(9)   (a) Kläui, W.; Asbahr, H. O.; Schramm, G.; Englert, U. *Chem. Ber*. **1997**, 130, 1223
        1229. (b) Leung, W. -H.; Zhang, Q. -F.; Yi, X. -Y.; *Coord. Chem. Rev.*, **2007**, 251,
        2266-2279. (c) Kläui, W. *Angew. Chem. Int. Ed. Engl.*, **1990**, 29, 627-637.

(10)   Zaidi, S. A. A.; Jaria, M.; Siddiqi, Z. A. *Synth. React. Inorg. Met.-Org. Chem.* **1986**,
        16, 1067-1087.

(11)   (a) Salinier, V.; Corker, J. M.; Lefebvre. F.; Bayard, F.; Dufaud, V.; Basset, J. M.
        Adv. Synth. Catal., **2009**, 351, 2155-2167. (b) Salinier, V.; Niccolai, G. P.; Dufaud,
        V.; Basset, *J. M. Adv. Synth. Catal*. **2009**, 351, 2168-2177.

(12)   H. Quast and U. Nahr, *Chem. Ber*. **1984**, 117, 2761-2778.

(13)   Sheehan, J. C.; Cruickshank, P. A. *Org. Synth. Coll.*, **1973**, 5, 555-558.

(14)   We had e-mail correspondence with H. Quast, the author of the procedure, and
        he confirmed this observation.

(15)   Cambridge Structural Database (Version 5.34). *3D Search and Research Using the
        Cambridge Structural Database*, Allen, F. H.; Kennard, O. *Chemical Design
        Automation News* **1993**, *8* (1), pp 1 & 31-37.

(16)   Prakash, O.; Batra, H.; Kaur, H.; Sharma, P. K.; Sharma, V.; Singh, S. P.;
        Moriarty, R. M. *Synthesis* **2001**, 541-543.

(17)   Khan, H.; Badshah, A.; Shaheen, F.; Gieck, C.; Qureshi, R. A. *Acta Cryst*. **2008**,

E64, o1141.

(18)   Palmer, J. H.; Parkin, G. *Polyhedron* **2013**, 52, 658-668.

(19)   Kimblin, C.**;** Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Chem Commun*. **1999**, 2301-2302.

(20)   Zhang, P.; Terefenko, E. A.; Bray, J.; Deecher, D.; Fensome, A.; Harrison, J.; Kim, C.; Koury, E.; Mark, L.; McComas, C. C.; Mugford, C. A.; Trybulski, E. J.; Vu, A. T.; Whiteside, G. T.; Mahaney, P. E. *J. Med. Chem.* **2009**, 52, 5703-5711.

(21)   [Tm[Ad]]K has been synthesized in our lab: Yurkerwich, K.; Yurkerwich, M.; Parkin, G. *Inorg. Chem*. **2011**, 50, 12284-12295.

(22)   (a) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *Dalton Trans.* **2000,** 1267-1274. (b) Han, R.; Parkin, G. *Organometallics* **1991**, *10*, 1010-1020. (c) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291-393. (d) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107-216.

(23)   (a) Kimblin, C.; Bridgewater, B. M.; HAscall, T.; Parkin, G. *Dalton Trans*. **2000**, 1267-1274. (b) Yurkerwich, K.; Buccella, D.; Melnick, J. G.; Parkin, G. *Chem. Commun*. **2008**, 3305-3307.

(24)   Janiak, C.; Temizfemir, S., Scharmann, T. *Z.anorg. allg. Chem*. 624, **1998**, 755-756.

(25)   Yurkerwich, K.; Rong, Y.; Parkin, G. *Acta Crystallogr*. **2013**, *C69*, 963–967.

(26)   Lee, D.; Lippard, S. J. *Inorg. Chem*. **2002**, 41, 2704-2719.

(27)   Rong, Y.; Palmer, J. Parkin, G. *Dalton Trans. Accepted manuscript.*

(28)   (a) Janiak, C.; Braun, L.; Girgsdies, F. *J. Chem. Soc., Dalton Trans.* **1999**, *3*, 3133–3136. (b) Yoon, K.; Parkin, G. *Polyhedron* **1995**, *14*, 811–821. (c) Fillebeen, T.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 3787–3790.

(29)   (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23. (b) Burger, B. J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98. (c) Shriver, D. F.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.

(30)   Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

(31)   (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981. (b) Sheldrick, G. M. *Acta Crystallogr.***2008**, *A64*, 112-122.

Chapter 2

Coordination Chemistry of the *tris*(2-oxo-1-R-imidazolyl)hydroborato Ligand with Transition and Main Group Metals: Steric and Electronics Evaluation of the [To^R] ligand

Table of Contents

Reproduced in part from:

Al-Harbi, A.; Sattler, W.; Sattler, A.; Parkin, G. *Chem. Commun.* **2011**, *47*, 3123-3125.

Al-Harbi, A.; Rong, Y.; Parkin, G. *Dalton Trans.* **2013**, 42, 11117-11127.

2.1   Introduction

As described in chapter one of this thesis, *tris*(2-oxo-1-alkylimidazolyl)hydroborato

ligands have been successfully synthesized in good yields. This has been mainly

achieved by annulation of the oxoimidazole starting materials which avoids any side

products. The primary goal of this chapter is to study the properties of these ligands in

terms of sterics and electronics, which may provide important information to help

harness the [To^R] ligand in the best way possible. Specifically, the electronic and steric

properties of these new ligands will be compared to those of other relevant L$_2$X[1] donors

by using the [L$_2$X]Re(CO)$_3$ framework. The assessment of the electron donation ability

of [To^R] ligands to that of other L$_2$X ligands can be achieved by the observation of the

ν_{CO} frequency of a series of related metal carbonyl derivatives.[2] On the other hand, the

Tolman cone angle,[3] a steric hindrance indicator, can be measured by using simple

geometrical calculations based on the molecular structure determined by X-ray

crystallography.[4] Fortunately, there is a library of reported X-ray structures and infrared

data of various [L$_2$X]Re(CO)$_3$[5] complexes which enable us to evaluate the [To^R] ligands.

Finally, the coordination chemistry of [To^R] ligands with various metal compounds will

be investigated.

2.2   Preparation of [To^R]Re(CO)$_3$ and Relevant L$_2$XRe(CO)$_3$ Complexes

[To^{MeBenz}]Re(CO)$_3$ and [To^{But}]Re(CO)$_3$ were prepared by the treatment of Re(CO)$_5$Br with

[To^{MeBenz}]Na•diglyme and [To^{But}]Na, respectively (Scheme 1). The molecular structures

of [To^{But}]Re(CO)$_3$ (Figure 1) and [To^{MeBenz}]Re(CO)$_3$ (Figure 2) have been determined by X-ray diffraction.
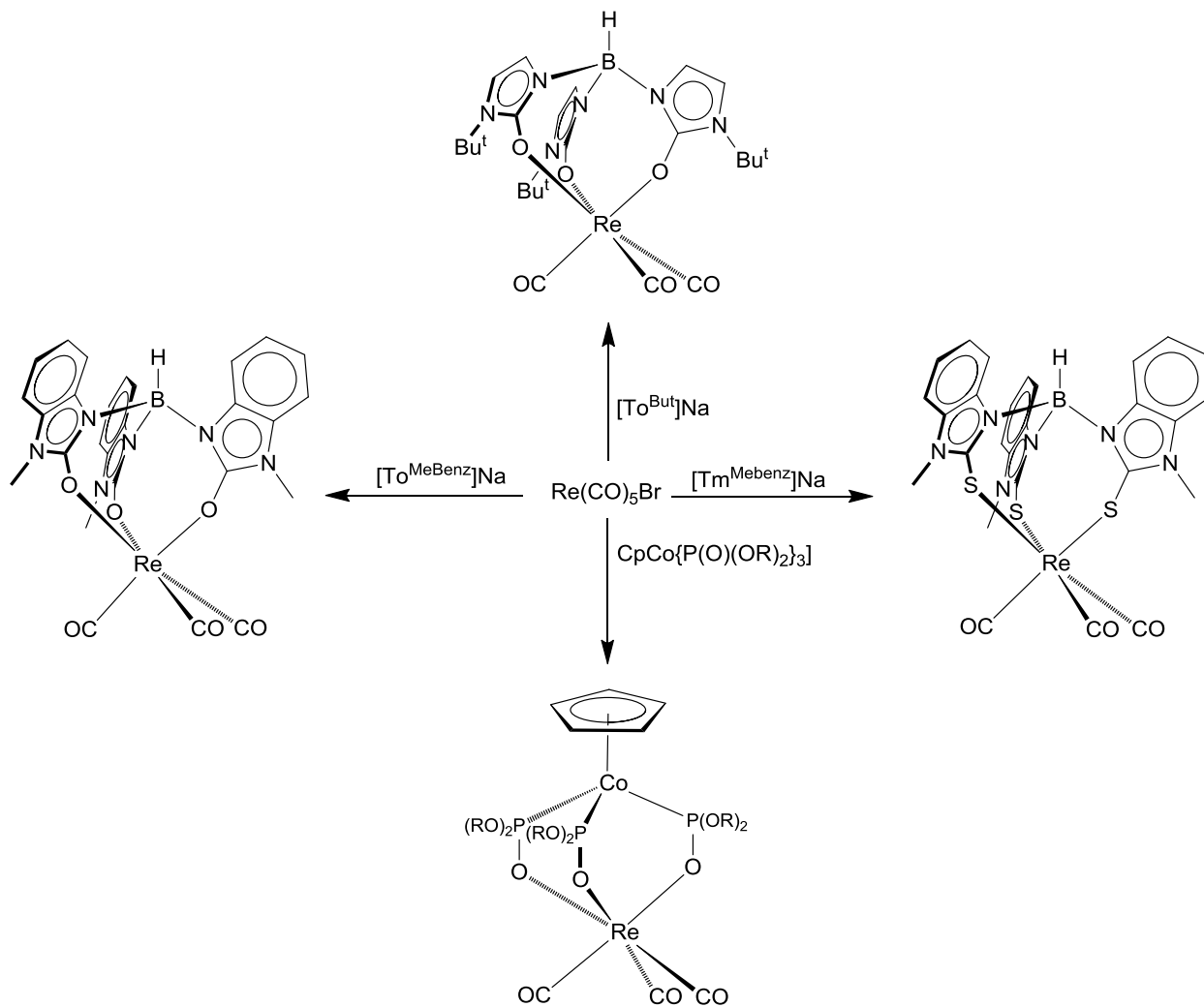
Scheme 1. Synthesis of [To^R]Re(CO)$_3$ and related [L$_2$X]Re(CO)$_3$ complexes.
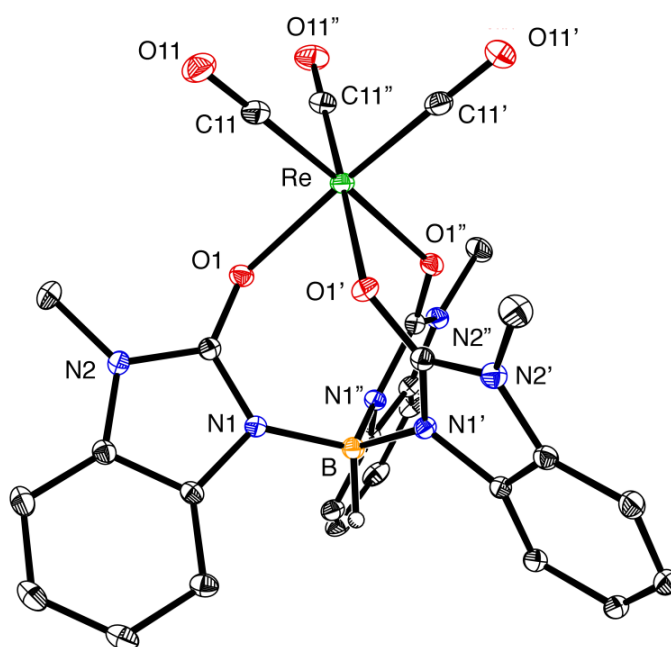
Figure 1. Molecular structure of [To$^{\text{MeBenz}}$]Re(CO)$_3$.
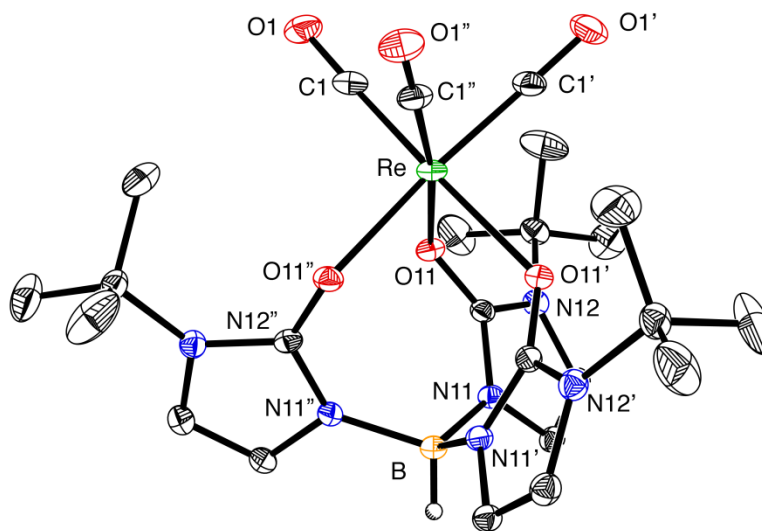
Figure 2. Molecular structure of [To$^{\text{Bu}^t}$]Re(CO)$_3$.

We also synthesized [Tm^{MeBenz}]Re(CO)$_3$ and [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$ for comparison

purposes since the former complex represents the corresponding [Tm^R][6] sulfur donor

and the latter is the only related L$_2$X type [O_3] donor ligands.[7] [To^{MeBenz}]Re(CO)$_3$ and

[CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$ were prepared by the treatment of Re(CO)$_5$Br with

{[Tm^{MeBenz}]Na}$_2$(THF)$_3$ and [CpCo{P(O)(OEt)$_2$}$_3$]Na, respectively (Scheme 1). Crystals of

[Tm^{MeBenz}]Re(CO)$_3$ (Figure 3) and [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$ (Figure 4) suitable for X-

ray diffraction were obtained by slow evaporation from benzene solution.
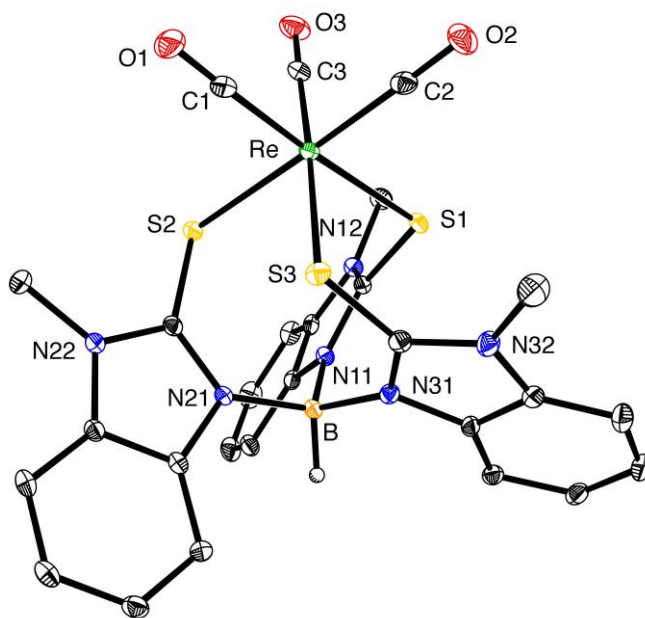
Figure 3. Molecular structure of [Tm^{MeBenz}]Re(CO)$_3$.
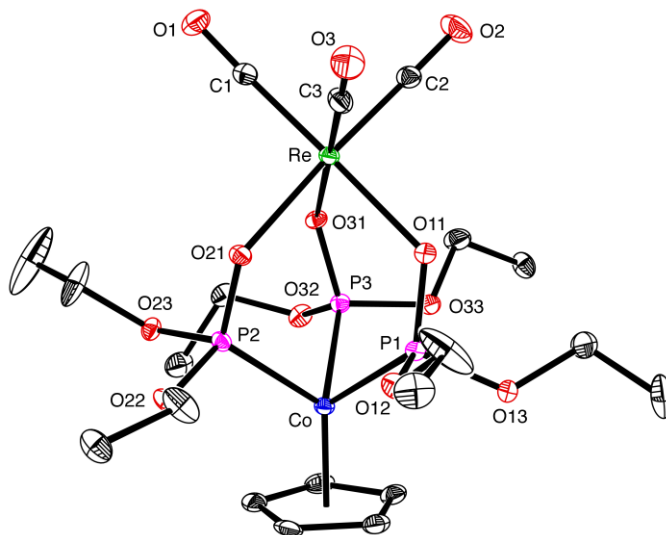
Figure 4. Molecular structure of [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$.

[Tm^{MeBenz}]Na was synthesized via the reaction of NaBH$_4$ with three equivalents of 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione in THF at elevated temperature (Scheme 2).
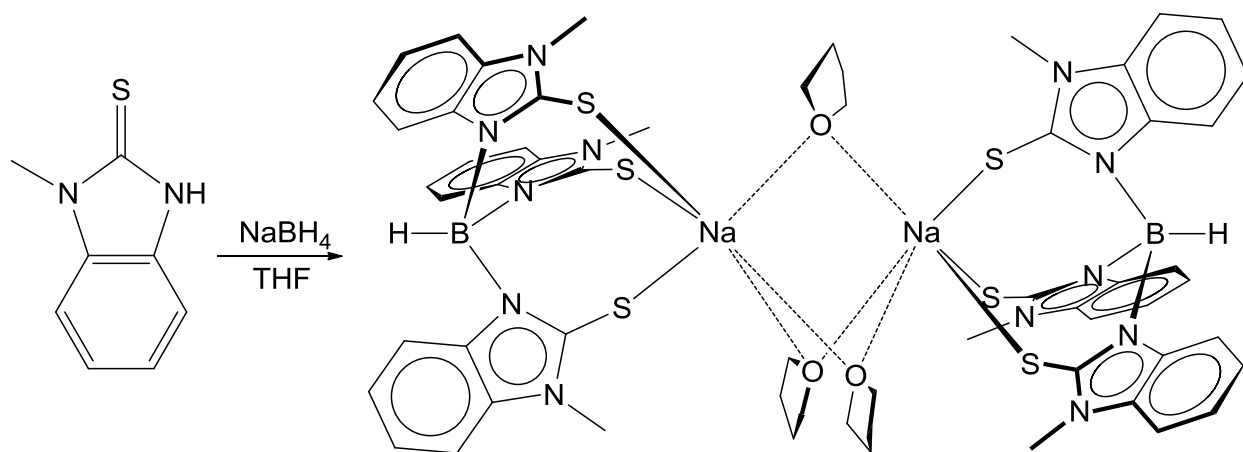
Scheme 2. Synthesis of {[Tm^{MeBenz}]Na}$_2$(THF)$_3$.

Colorless crystals of {[Tm^{MeBenz}]Na}$_2$(THF)$_3$ suitable for X-ray diffraction of were obtained by cooling down the reaction mixture to room temperature (Figure 5).
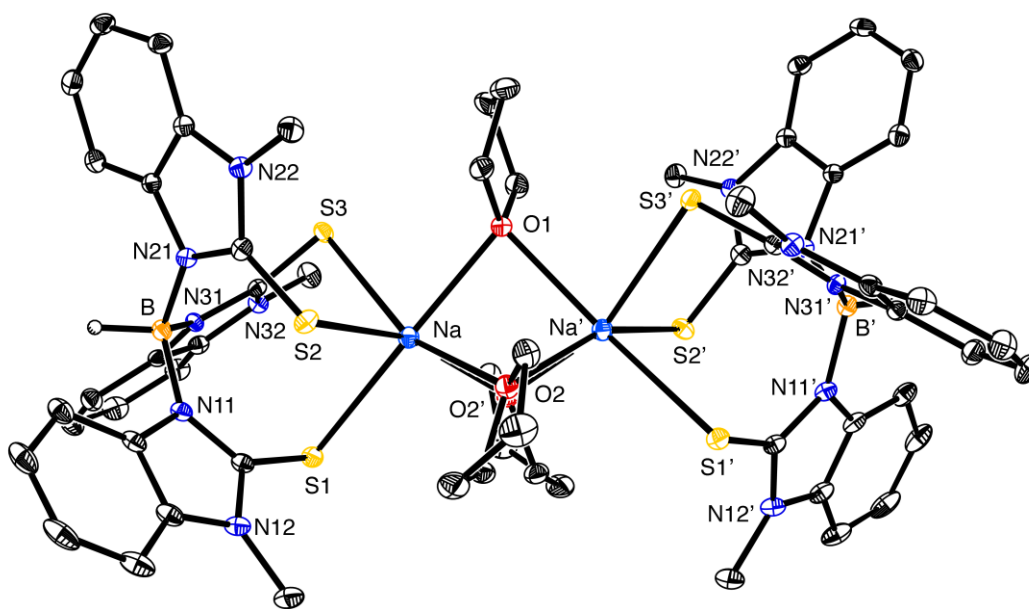
Figure 5. Molecular structure of {[Tm^{MeBenz}]Na}$_2$(THF)$_3$.

2.3   Steric Properties of [To$^{Bu^t}$] and [To^{MeBenz}] Ligands

The steric properties of the [To$^{Bu^t}$] and [To^{MeBenz}] ligands have been assessed by analysis of the crystallographic cone angles of the rhenium carbonyl compounds, [To$^{Bu^t}$]Re(CO)$_3$ and [To^{MeBenz}]Re(CO)$_3$. Crystallographic cone angles (Θ) were measured by using the procedure described by Mingos.[4] Specifically, the half-angle (θ_i) for each arm of the ligand is calculated as the maximum value of $\angle$ B–Re–H, where the hydrogen atom position takes into account the van der Waals radius of hydrogen (1.2 Å). The crystallographic cone angle for the ligand is then defined as $\Theta = (2/3) \Sigma\theta_i$ (Figure 6).
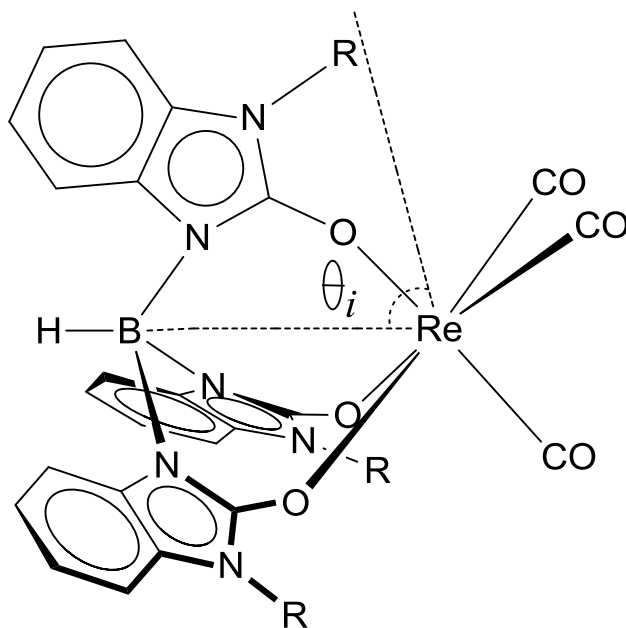
Figure 6. Tolman half cone angle for a complex of the type $[L_2X]Re(CO)_3$.

The cone angles of selected $[L_2X]Re(CO)_3$ compounds are summarized in Table 1. These cone angle values reveal that the $[To^{Bu^t}]$ (229°) and $[To^{MeBenz}]$ (196°) ligands are substantially more sterically demanding than the related $[O_3]$ donor ligand, $[CpCo\{P(O)(OEt)_2\}_3]$ (174°). In addition, $[To^R]$ ligands are more sterically demanding than the corresponding $[Tm^R]$ sulfur donor ligands based on the pairs comparison of the cone angles of $[To^R]Re(CO)_3$ and $[Tm^R]Re(CO)_3$ (Table 1). This is a consequence of the fact that the Re–O bonds are *ca.* 0.35 Å shorter than the Re–S bonds.

Table 1. Carbonyl ν_{CO} stretching frequency and cone angle values for various

$[L_2X]Re(CO)_3$ compounds.

$[L_2X]$	ν_{CO} (cm^{-1})	$\nu_{CO(av)}$ (cm^{-1})	Θ (°)
$[To^{Bu^t}]$	2018, 1887	1953	229
$[Tm^{Bu^t}]^a$	2008, 1880	1944	213
$[To^{MeBenz}]$	2026, 1894	1960	196
$[Tm^{MeBenz}]$	2014, 1895	1955	189
$[Tm^{Me}]^b$	2007, 1888	1948	191 and 183^b
$[Tm^{Ad}]^a$	2005, 1887	1946	232
$[CpCo\{P(O)(OEt)_2\}_3]$	2015, 1880	1948	174

a) Reference 5a. b) values for two crystallographically independent molecules in the

same asymmetric unit (CSD# QUSNOH).[8]

2.4 Electronic Properties of $[To^{Bu^t}]$ and $[To^{MeBenz}]$ Ligands

2.4.1 General Trend.

As mentioned previously, comparison of the electron donating properties of $[To^{Bu^t}]$ and

$[To^{MeBenz}]$ ligands to relevant L_2X ligands may be achieved by comparing the carbonyl

ν_{CO} stretching frequencies of $[To^R]Re(CO)_3$ with other $[L_2X]Re(CO)_3$ compounds

(Table 1).[5] Specifically, comparison of the ν_{CO} stretching frequencies of $[To^R]Re(CO)_3$ and

$[CpCo\{P(O)(OEt)_2\}_3]Re(CO)_3$ indicates that the metal centers of $[To^R]Re(CO)_3$ are less

electron rich than that of $[CpCo\{P(O)(OEt)_2\}_3]Re(CO)_3$ (Table 1). Also the $[To^R]$ oxygen

ligand is less electron donating than the corresponding $[Tm^R]$ sulfur ligand based on

comparing the ν_{CO} stretching frequencies of $[To^R]Re(CO)_3$ and $[Tm^R]Re(CO)_3$. Based on these results and results that have been obtained by my colleagues Dr. Victoria Landry[9] and Dr. Kevin Yurkerwich,[5a] a general trend for electron donability of L_2X ligands can be established as follows: $[To^R] < [CpCo\{P(O)(OEt)_2\}_3] < [Tm^R] < [Tse^R]$. This trend is in accord with the electronegativity of the donor atoms. However, it is worth noting that π-donor effects could exert an opposite effect. For instance, $W(EBu^t)_3(NO)(py)$[10] and $[Tp^{Me_2}]Mo(NO)(ER)X$[11] show lower stretching frequencies for ν_{NO} when E = O than when E = S. This was justified by alkoxide being a better π-donor than the thiolate. The relative π-donor abilities of oxygen and sulfur are not well established though, with there being contradictory reports in the literature.[12] It is also worth noting that π-donor effects have been invoked to rationalize why $[Tm^R]$ ligands are generally more strongly electron donating than $[Tp^R]$ ligands.[13] However, based on the ν_{CO} stretching frequencies we obtained, it appears that π-donation is not a dominant factor when comparing $[To^R]Re(CO)_3$ with its sulfur counterpart.

2.4.2   Benzannulation Impact on $[To^R]$ and $[Tm^R]$ Ligands.

It is also worth noting that annulation of the imidazole ring has an impact on the electron donor properties of the $[To^R]$ ligands. Thus, $[To^{MeBenz}]$ is less electron donating than $[To^{Bu^t}]$ (Table 1). Likewise, benzannulation impacts the electron donor ability of $[Tm^R]$ in the same manner as $[To^R]$. For example, the ν_{CO} stretching frequencies of $[Tm^{MeBenz}]Re(CO)_3$ (2014 and 1895 cm^{-1}) are higher than those of $[Tm^{Me}]Re(CO)_3$ (2007

and 1888 cm^{-1}), [Tm^{But}]Re(CO)$_3$ (2008 and 1880 cm^{-1})[5a] and [Tm^{Ad}]Re(CO)$_3$ (2005 and 1887

cm^{-1}).[5a] This indicates that benzannulation decreases the electron donating properties of

the ligand. Furthermore, the similar electronic properties of the non-benzannulated

[Tm^R] ligands with different alkyl derivatives may be attributed to the fact that the alkyl

groups are well separated from the metal by four bonds.[5a]

2.5   Coordination Chemistry of [To^R] Ligands with Various Metal Compounds

2.5.1   [To^R] Complexes of Zirconium

We are particularly interested in the application of [To^R] ligands to early transition

metal chemistry on the basis that these ligands could allow access to analogues of bent

metallocenes in an oxygen rich environment. In this regard, the zirconium compounds

[To^{But}]ZrCl$_3$ and [To^{MeBenz}]ZrCl$_3$ may be obtained *via* the reactions of ZrCl$_4$ with [To^{But}]Na

and [To^{MeBenz}]Na, respectively (Scheme 3).
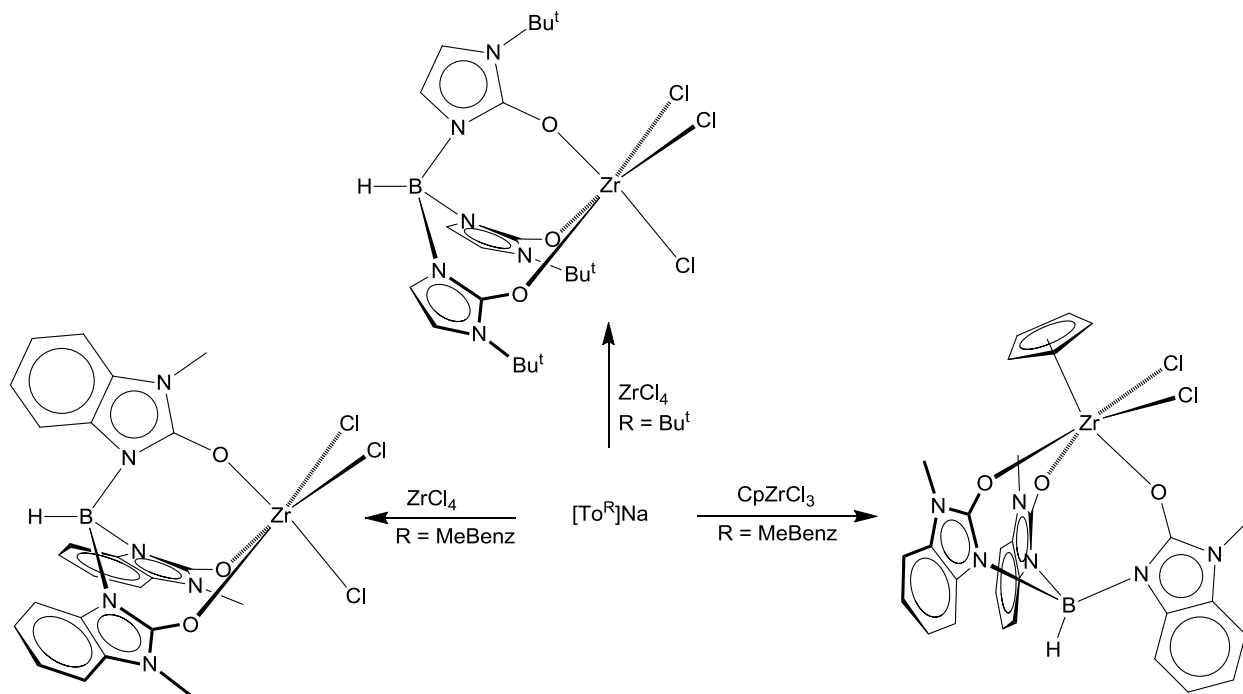
Scheme 3. Synthesis of [To^R] zirconium complexes.

The molecular structures of [To$^{Bu^t}$]ZrCl$_3$ and [To^{MeBenz}]ZrCl$_3$ have been determined by X–

ray diffraction, as illustrated in Figures 7 and 8, respectively. The two pseudoctahedral

complexes are clearly similar to the half-sandwich compound, CpZrCl$_3$. However,

CpZrCl$_3$ exists as a dimer[14] in the solid state unless a bulky Cp^R ligand such as the

pentaphenylcyclopentadienyl ligand is used.[15] The benzannulation has no impact on the

molecular structure of [To^{MeBenz}]ZrCl$_3$ which has a geometry and dimensions very

similar to [To$^{Bu^t}$]ZrCl$_3$.
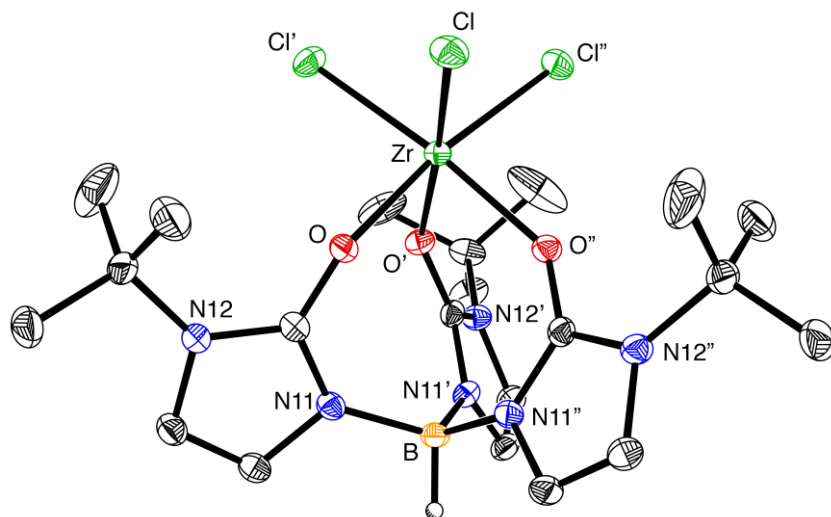
Figure 7. Molecular structure of [To$^{Bu^t}$]ZrCl$_3$.
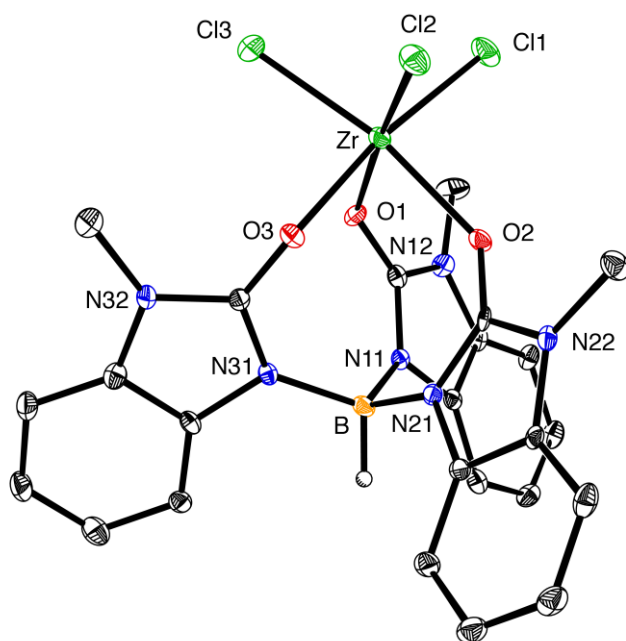
Figure 8. Molecular structure of [To^{MeBenz}]ZrCl$_3$.

Furthermore, the hybrid complex Cp[To^{MeBenz}]ZrCl$_2$ may be obtained *via* the reaction of [To^{MeBenz}]Na with CpZrCl$_3$ (Scheme 3). The molecular structure of Cp[To^{MeBenz}]ZrCl$_2$ has been determined by X–ray diffraction, as illustrated in Figure 9.
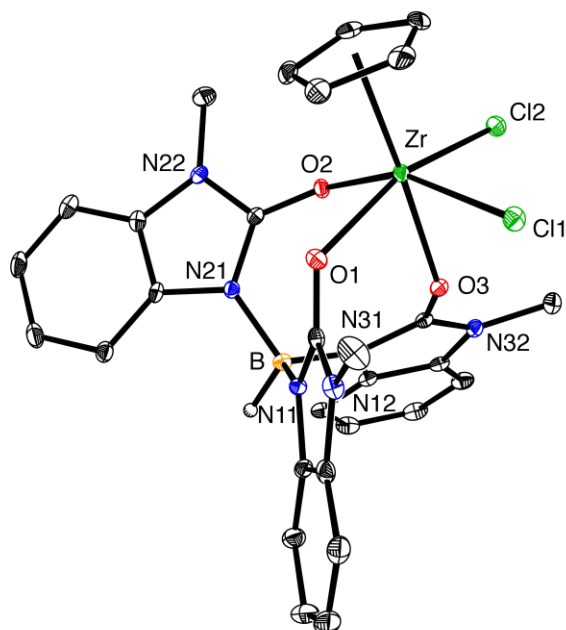
Figure 9. Molecular structure of Cp[To^{MeBenz}]ZrCl$_2$.

The ability to isolate Cp[To^{MeBenz}]ZrCl$_2$ is noteworthy because the corresponding

reaction of CpZrCl$_3$ with [CpCo{P(O)(OEt)$_2$}$_3$]Na does not yield

Cp[CpCo{P(O)(OEt)$_2$}$_3$]ZrCl$_2$, but results in preferential displacement of the

cyclopentadienyl ligand and the formation of [CpCo{P(O)(OEt)$_2$}$_3$]ZrCl$_3$.[16] The [To^{MeBenz}]

ligand provides a sought-after zirconocene analogue in which one of the

cyclopentadienyl ligands is replaced with an [O_3] donor array. In support of this

analogy, the geometry of Cp[To^{MeBenz}]ZrCl$_2$ bears a close resemblance to that of the bent

metallocene, Cp$_2$ZrCl$_2$ (Table 2).[17] For example, the Cp$_{cent}$–Zr–B angle of

Cp[To^{MeBenz}]ZrCl$_2$ (130.5°) is similar to the Cp$_{cent}$–Zr–Cp$_{cent}$ angle of Cp$_2$ZrCl$_2$ (129.2°),[17a]

while a bigger angle is observed in the case of Cp[Tm^{Me}]ZrCl$_2$ (133.5°).[18] The Cl–Zr–Cl

bond angles are 93.9° for Cp[To^{MeBenz}]ZrCl$_2$ and 97.0° for Cp$_2$ZrCl$_2$.

Table 2. Comparison of metrical data for Cp[To^MeBenz]ZrCl$_2$, Cp[Tm^Me]ZrCl$_2$ and Cp$_2$ZrCl$_2$.

	Cp[Tm^Me]ZrCl$_2$	Cp$_2$ZrCl$_2$	Cp[To^MeBenz]ZrCl$_2$
Zr–C$_{range}$/ Å	2.51-2.57	2.47-2.52	2.51-2.57
Zr–C$_{av}$/ Å	2.54	2.50	2.54
Zr–C$_{cent}$/ Å	2.26	2.20	2.24
Zr–Cl/ Å	2.52	2.45	2.48
Cl–Zr–Cl/deg	97.9˚	97.0˚	93.9˚
Cp$_{cent}$–Zr–Y/deg	133.5˚ (Y = B)	129.2˚ (Y = Cp$_{cent}$)	130.5˚ (Y = B)

2.5.2 Complexes of the [To^MeBenz] ligand with Fe, Co and Zn

Less oxophilic metals have also been coordinated to the [To^R] ligands. For example, treatment of [To^MeBenz]Na with ZnI$_2$ led to the generation of pseudotetrahedral complex of [To^MeBenz]ZnI (Scheme 4). The molecular structure of [To^MeBenz]ZnI (Figure 10) has been determined by X-ray diffraction. It resembles the [Tm^Me]ZnI[19] complex since both of them adopt a κ^3-coordination mode. However, the geometry of [Tm^Me]ZnI is more tetrahedral than that of [To^MeBenz]ZnI, with a four-coordinate τ_4 geometry index[20] of 0.92 *versus* 0.86 for [To^MeBenz]ZnI. This is mainly because the average S–Zn–S angle, 105.61˚, in [Tm^Me]ZnI is closer to a tetrahedral value than the average angle O–Zr–O in [To^MeBenz]ZnI, 99.97˚.
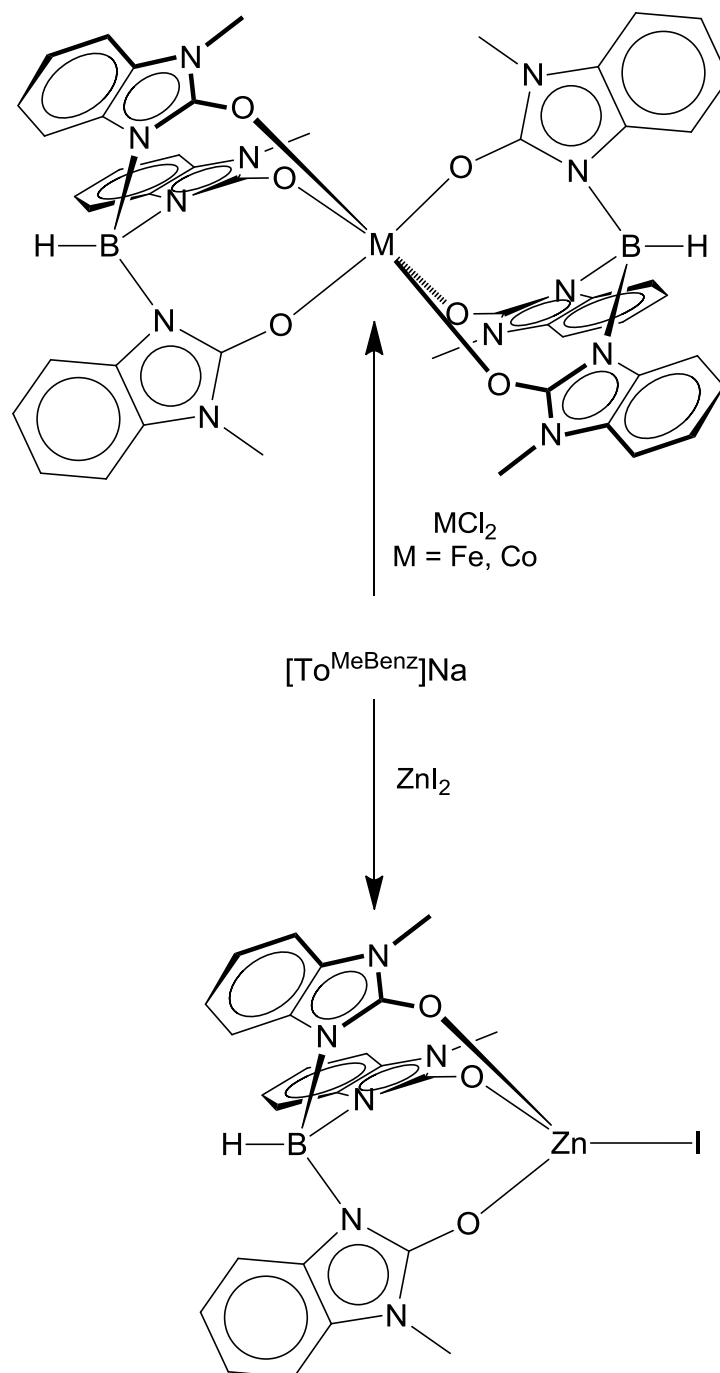
Scheme 4. Reaction of [To^MeBenz]Na with ZnI_2 and MCl_2 (M = Fe, Co).
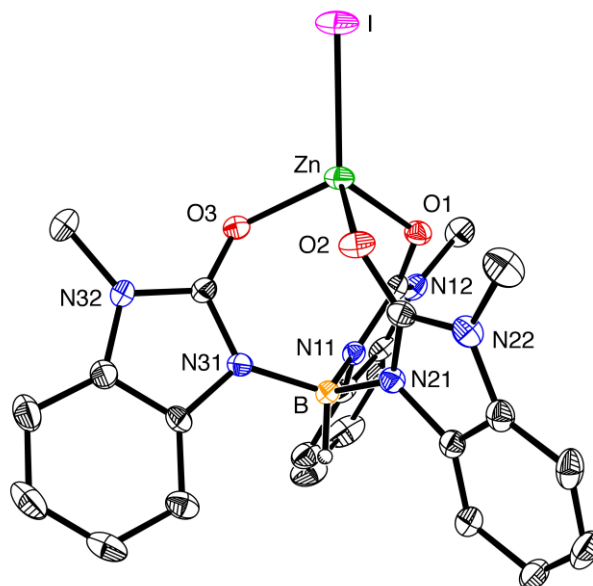
Figure 10. Molecular structure of [To^{MeBenz}]ZnI.

Also, treatment of [To^{MeBenz}]Na with FeCl$_2$ and CoCl$_2$ led to paramagnetic complexes of [To^{MeBenz}]$_2$Fe and [To^{MeBenz}]$_2$Co, respectively (Scheme 4). The molecular structures of [To^{MeBenz}]$_2$Fe (Figure 11) and [To^{MeBenz}]$_2$Co (Figure 12) have been determined by X-ray diffraction. In the case of [To^{MeBenz}]$_2$Fe, the [To^{MeBenz}] ligand adopts a κ^3-coordination mode that resembles the coordination mode of the [Tm^{Me}] ligand in [Tm^{Me}]$_2$Fe.[21] The isolation of [To^{MeBenz}]$_2$Co is of interest because the sulfur counterpart, namely [Tm^{Me}]$_2$Co, has not been isolated.[22,23] In addition, [To^{MeBenz}]$_2$M (M = Fe, Co) adopts a totally different type of structure to that of [Tm^{Ph}]$_2$M. Specifically, while both [To^{MeBenz}]$_2$Fe and [To^{MeBenz}]$_2$Co adopt octahedral structures with κ^3-O_3 coordination of the ligand, [Tm^{Ph}]$_2$Fe and [Tm^{Ph}]$_2$Co exhibit coordination *via* only two of the sulfur donors of each ligand with the coordination sphere being completed by interaction with the two B–H groups.[24]
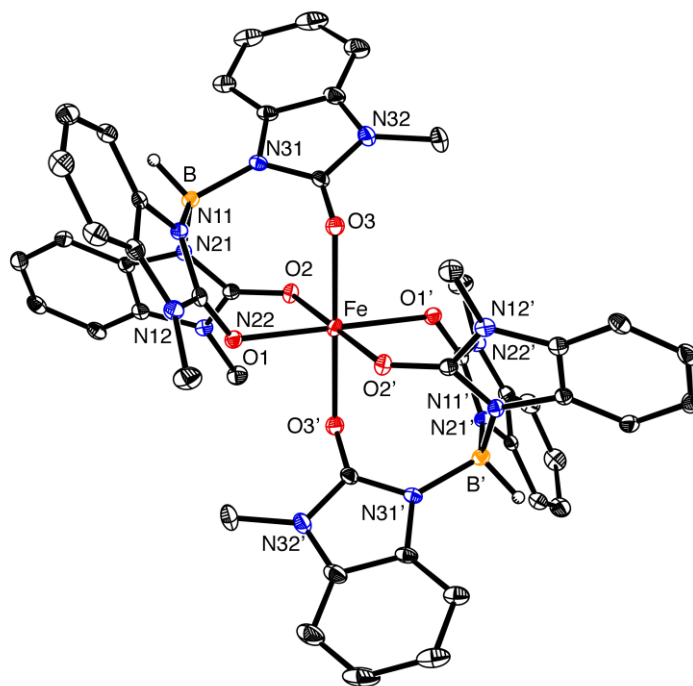
Figure 11. Molecular structure of [To^MeBenz]$_2$Fe.
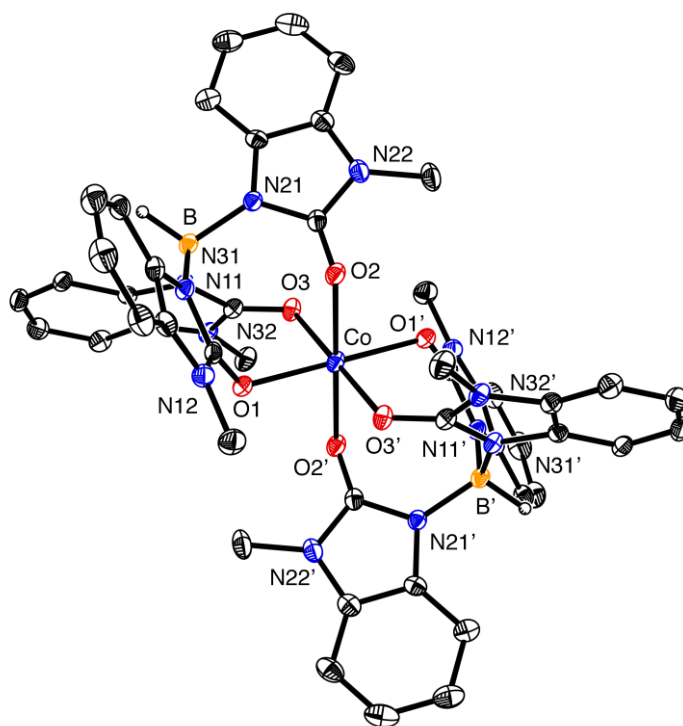
Figure 12. Molecular structure of [To^MeBenz]$_2$Co.

2.5.3   Complexes of the [To^MeBenz] ligand with Cu

We have also obtained a [To^R] copper complex by the treatment of [To^MeBenz]Na with

[Me$_3$PCuCl]$_4$ in benzene to yield [To^MeBenz]Cu(PMe$_3$) (Scheme 5). The molecular

structure of [To^MeBenz]Cu(PMe$_3$) has been determined by X–ray diffraction (Figure 13).

For comparison purposes, we have synthesized the sulfur counterpart. Specifically, the

treatment of {[Tm^MeBenz]Na(THF)$_3$}$_2$ with [Me$_3$PCuCl]$_4$ produces the copper compound,

[Tm^MeBenz]CuPMe$_3$ (Scheme 5). Also, the molecular structure of [Tm^MeBenz]CuPMe$_3$ has

been determined by X-ray diffraction, as illustrated in Figure 14. Both structures adopt a

κ^3-coordination mode; however, the tetrahedral [S_3P] motif in [Tm^MeBenz]CuPMe$_3$ is much

closer to an ideal tetrahedron with a four-coordinate τ_4 geometry index[20] of 0.96

compared to that of [To^MeBenz]CuPMe$_3$ (0.73).
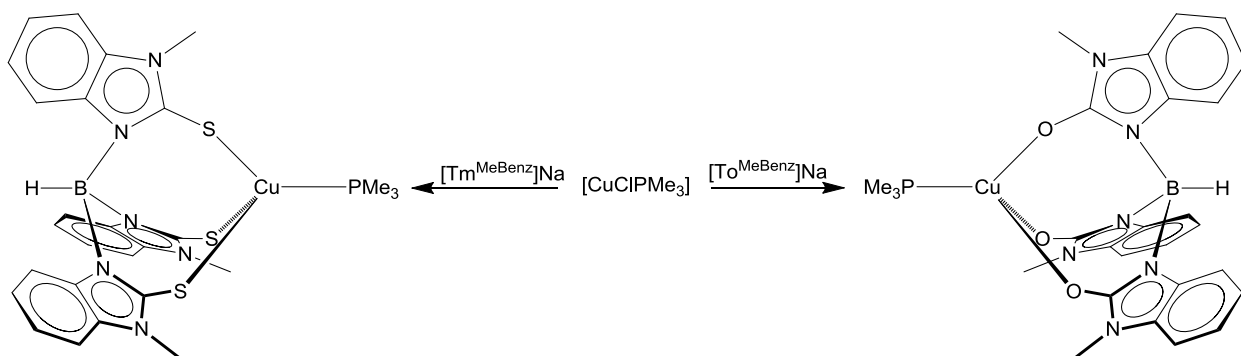
Scheme 5. Synthesis of [To^MeBenz]CuPMe$_3$ and [Tm^MeBenz]CuPMe$_3$.
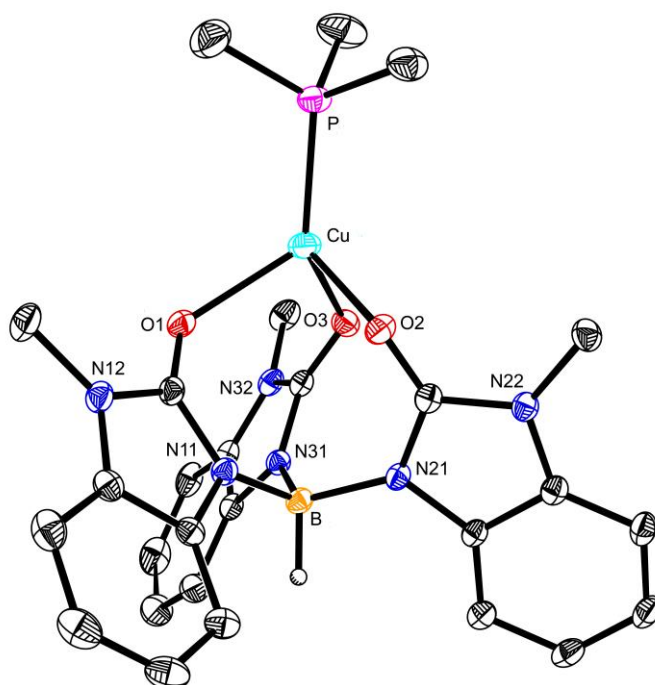
Figure 13. Molecular structure of [To^{MeBenz}]CuPMe₃.
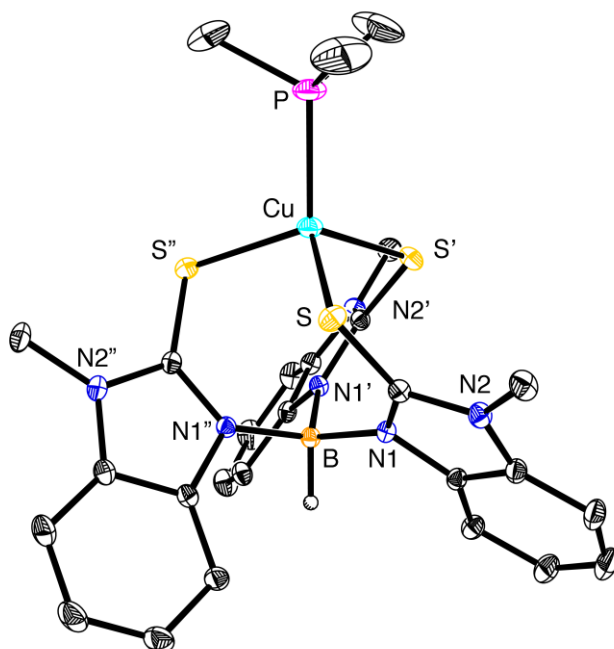
Figure 14. Molecular structure of [Tm^{MeBenz}]CuPMe₃.

2.6 Conclusion

After describing the synthesis of [To^R] ligands in the previous chapter, we have shown in this chapter that these ligands are substantially more sterically demanding than the corresponding [Tm^R] sulfur donor ligands and the related [O_3] donor ligands. However, electronically, the [To^R] ligands exhibit weaker electron donating properties than related L$_2$X type ligands. Finally, the coordination chemistry of [To^R] ligands with various metal compounds has been briefly investigated.

2.7 Experimental Section

2.7.1 General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[25] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 DRX, Bruker 400 AVIII, Brucker 400 Cyber-enabled Avance III and Bruker Avance 500 DMX spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C$_6$D$_5$H, 7.26 for CHCl$_3$ and 2.50 for d_6-DMSO).[26] ^{13}C NMR spectra are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 77.16 for CDCl$_3$, 128.06 for C$_6$D$_6$, 54.00 for CD$_2$Cl$_2$ and 39.52 for d_6-DMSO).[26] Coupling constants are given in hertz. [31]P chemical shifts are reported in ppm relative to 85% H$_3$PO$_4$ ($\delta = 0$) and were

referenced using P(OMe)$_3$ (δ = 141.0) as an external standard.[27] Infrared spectra were

recorded on a Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass

spectra were obtained on a Jeol JMS-HX110H Tandem Double-Focusing Mass

Spectrometer with a 10 kV accelerated voltage equipped with a FAB ion source.

[Me$_3$PCuCl]$_4$,[28] 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one,[29]1-methyl-1,3-dihydro-2*H*-

benzimidazol-2-one[30] and 1-t-butyl-1,3-dihydro-2*H*-benzimidazol-2-one were prepared

by the literature methods. NaBH$_4$ (Aldrich), ZnI$_2$ (Aldrich), CoCl$_2$ (Aldrich), FeCl$_2$

(Strem Chemicals), ZrCl$_4$ (Aldrich), CpZrCl$_3$ (Aldrich), Re(CO)$_5$Br (Strem Chemicals)

and 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-thione (Aldrich) were obtained

commercially and used as received.

2.7.2   X-ray Structure Determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer

and crystal data, data collection and refinement parameters are summarized in Table 1.

The structures were solved using direct methods and standard difference map

techniques, and were refined by full-matrix least-squares procedures on F^2 with

SHELXTL (Version 2008/4).[31]

2.7.3   Synthesis of [To$^{\text{MeBenz}}$]Re(CO)$_3$

A mixture of [To$^{\text{MeBenz}}$]Na•diglyme (40 mg, 0.07 mmol) and Re(CO)$_5$Br (27 mg, 0.07

mmol) was placed in an ampoule, treated with benzene (*ca.* 5 mL) and heated overnight

at 70 °C. The reaction mixture was filtered and the volatile components were removed

from the filtrate *in vacuo.* The residue obtained was washed with acetonitrile (ca. 5 mL) to give [To^{MeBenz}]Re(CO)$_3$ as a white powder (24 mg, 50%). Analysis calcd. for [To^{MeBenz}]Re(CO)$_3$: C, 44.8%; H, 3.1%; N 11.6%. Found: C, 44.6%; H, 3.2%; N, 11.4%. ^{1}H NMR (C$_6$D$_6$) : 2.81 [s, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_3$], 6.37 [d, $^3J_{H-H}$ = 8, 3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 6.88 [t, $^3J_{H-H}$ = 8, 3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 6.99 [t, $^3J_{H-H}$ =8, 3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 7.57 [d, $^3J_{H-H}$ =8, 3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 27.0 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$], 109.1 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 112.2 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 122.1 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 122.7 [3C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 131.2 [HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$], 132.8 [HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$], 161.0 [HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_3$]. FAB-MS: *m/z* = 724.1 [M]$^+$, M = [To^{MeBenz}]Re(CO)$_3$. IR Data (KBr disk, cm^{-1}): 2938 (w), 2457(w) [ν_{BH}], 2022 (s) [ν_{CO}], 1911 (s) [ν_{CO}], 1637 (s), 1588 (s), 1490 (m), 1448 (m), 1399 (m), 1302 (w), 1232 (w), 1158 (w), 1126 (w), 1099 (w), 764 (w). IR Data (CH$_2$Cl$_2$, cm^{-1}): 2026 (m) [ν_{CO}], 1894 (s) [ν_{CO}].

2.7.4   Synthesis of [To^{But}]Re(CO)$_3$

A mixture of [To^{But}]Na (14 mg, 0.03 mmol) and Re(CO)$_5$Br (15 mg, 0.04 mmol) was treated with benzene (*ca.* 1 mL) and heated at 70 °C overnight, during which period a small amount of colorless crystals of [To^{But}]Re(CO)$_3$ suitable for X-ray diffraction were deposited and isolated by filtration. The filtrate was lyophilized, resulting in a white powder. The residue was dissolved in hexane/Et$_2$O (*ca.* 50:50) to give a solution from

which colorless crystals of [To^{But}]Re(CO)$_3$ were obtained by slow evaporation (8 mg,

37%). ^{1}H NMR (C$_6$D$_6$): 1.29 [s, 27H of HB{C$_2$N$_2$H$_2$[C(C$\underline{H}_3$)$_3$]CO}$_3$], 5.87 [d, $^3J_{H-H}$ = 3, 3H of

HB{C$_2$N$_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$], 6.28 [d, $^3J_{H-H}$ = 3, 3H of HB{C$_2$N$_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$]. ^{13}C{^{1}H}

NMR (C$_6$D$_6$): 29.1 [9 C, HB{C$_2$N$_2$H$_2$[C($\underline{C}$H$_3$)$_3$]CO}$_3$], 55.9 [3 C, HB{C$_2$N$_2$H$_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_3$],

110.4 [3 C, HB{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_3$], 116.8 [3 C, HB{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_3$], 157.0 [3 C,

HB{C$_2$N$_2$H$_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_3$]. FAB-MS: m/z = 700.6 [M]$^+$, M = [To^{But}]Re(CO)$_3$ superimposed

by [M+1]$^+$; m/z = 672.6 [M-CO]$^+$, M = [To^{But}]Re(CO)$_3$. IR Data (KBr disk, cm^{-1}): IR Data

(KBr disk, cm^{-1}): 2979 (m), 2925 (m), 2431 (w) [ν_{BH}], 2017 (vs) [ν_{CO}], 1879 (vs) [ν_{CO}], 1621

(s), 1587 (s), 1436 (m), 1370 (w), 1215 (m), 1194 (m), 1085 (w), 805 (w), 773 (w), 743 (w),

680 (w). IR Data (CH$_2$Cl$_2$, cm^{-1}): 2018 (m) [ν_{CO}], 1887 (s) [ν_{CO}].

2.7.5 Synthesis of [Tm^{MeBenz}]Na

A mixture of 1-methyl-2-benzimidazole-2-thione (300 mg, 1.83 mmol) and NaBH$_4$ (22

mg, 0.58 mmol) was placed in an ampoule and treated with THF (*ca.* 5 mL). The

mixture was heated at 160 °C for 1 week. After this period, the mixture was filtered and

the precipitate was dried *in vacuo* to give {[Tm^{MeBenz}]Na}$_2$(THF)$_3$ as an off-white powder

(200 mg, 56%). Analysis calcd. for {[Tm^{MeBenz}]Na}$_2$(THF)$_3$: C, 56.7%; H, 5.9%; N, 13.2%.

Found: C, 56.6%; H, 5.2%; N, 13.5%. ^{1}H NMR for {[Tm^{MeBenz}]Na}$_2$(THF)$_3$ (d_6-DMSO): 1.76

[m, 12H of 3CH$_2$ of THF], 3.60 [m, 12H of 3CH$_2$ of THF], 3.64 [s, 18H of

HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CS}$_3$], 6.74 [t, $^3J_{H-H}$ = 7, 6H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 6.86 [b, 6H

of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 6.94 [t, $^3J_{H-H}$ = 8, 6H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 7.19 [d, $^3J_{H-}$

$_H$ = 8, 6H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CS}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 25.1 [6 C, CH$_2$ of the THF],

30.3 [6 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CS}$_3$], 67.0 [6 C, CH$_2$ of the THF], 107.7 [6 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 112.6 [6 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 120.3 [6 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 121.0 [6 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 133.8 [6 C,

HB{(C$_4$H$_4$)$\underline{C}$$_2N_2$(CH$_3$)CS}$_3$], 136.6 [6 C, HB{(C$_4H_4$)$\underline{C}$$_2N_2$(CH$_3$)CS}$_3$], 172.8 [6 C,

HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$S}$_3$]. FAB-MS: m/z = 525.2 [M+1]$^+$, M = [Tm^{MeBenz}]Na. IR Data (KBr

disk, cm^{-1}): 3450 (br), 3052 (w), 2929 (w), 2868 (w), 2423 (w) [v$_{BH}$], 1620 (m), 1544 (w),

1484 (s), 1460 (w), 1432 (s), 1344 (s), 1293 (s), 1230 (m), 1190 (m), 1158 (m), 1092 (m), 997

(m), 858 (w), 813 (m), 742 (s), 620 (m), 555 (m), 421 (m).

[Tm^{MeBenz}]Na free of THF may be obtained by washing with Et$_2$O. ^{1}H NMR for

[Tm^{MeBenz}]Na (d_6-DMSO): 3.64 [s, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}$$_3$)CS}$_3$], 6.74 [t, ^{3}J$_{H-H}$ = 7, 3H of

HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CS}$_3$], 6.87 [b,3H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CS}$_3$], 6.94 [t, ^{3}J$_{H-H}$ = 8, 3H of

HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CS}$_3$], 7.18 [d, ^{3}J$_{H-H}$ = 8, 3H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CS}$_3$]. ^{13}C{^{1}H}

NMR (d_6-DMSO): 30.3 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CS}$_3$], 107.7 [3 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 112.6 [3 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 120.3 [3 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 121.0 [3 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CS}$_3$], 133.8 [3 C,

HB{(C$_4$H$_4$)$\underline{C}$$_2N_2$(CH$_3$)CS}$_3$], 136.6 [3 C, HB{(C$_4H_4$)$\underline{C}$$_2N_2$(CH$_3$)CS}$_3$], 172.8 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$S}$_3$].

2.7.6   Synthesis of [Tm$^{\text{MeBenz}}$]Re(CO)$_3$

A mixture of [Tm$^{\text{MeBenz}}$]Na•1.5THF (50 mg, 0.08 mmol) and Re(CO)$_5$Br (33 mg, 0.08

mmol) was placed in an ampoule, treated with THF (*ca.* 5 mL) and heated overnight at

70 °C. The mixture was filtered and the volatile components were removed from the

filtrate *in vacuo.* The residue obtained was washed with acetonitrile (*ca.* 5 mL) to give

[Tm$^{\text{MeBenz}}$]Re(CO)$_3$ as white powder (20 mg, 33%). Crystals suitable for X-ray diffraction

were obtained from slow evaporation from a solution in benzene. Analysis calcd. for

[Tm$^{\text{MeBenz}}$]Re(CO)$_3$•1.8C$_6$H$_6$: C, 49.8%; H, 3.6%; N, 9.2%. Found: C, 49.4%; H, 4.6%; N,

9.0%. ^{1}H NMR (C$_6$D$_6$): 3.08 [s, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{\text{H}}_3$)CS}$_3$], 6.54 [d, $^3J_{\text{H-H}}$ = 8, 3H of

HB{(C$_4\underline{\text{H}}_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 6.96 [m, 6H of HB{(C$_4\underline{\text{H}}_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 7.58 [d, $^3J_{\text{H-H}}$ = 8, 3H

of HB{(C$_4\underline{\text{H}}_4$)C$_2$N$_2$(CH$_3$)CS}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 30.6 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{\text{C}}$H$_3$)CS}$_3$],

110.8 [3C, HB{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 113.3 [3C, HB{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 123.7 [3C,

HB{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 124.1 [3C, HB{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_3$], 133.7

[HB{(C$_4$H$_4$)$\underline{\text{C}}_2$N$_2$(CH$_3$)CS}$_3$], 135.7 [HB{(C$_4$H$_4$)$\underline{\text{C}}_2$N$_2$(CH$_3$)CS}$_3$], 167.5

[HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{\text{C}}$S}$_3$]. FAB-MS: *m/z* = 772.1 [M]$^+$, M = [Tm$^{\text{MeBenz}}$]Re(CO)$_3$. IR Data

(KBr disk, cm^{-1}): 2925 (m), 2010 (s) [ν_{CO}], 1922 (s) [ν_{CO}], 1478 (m), 1439 (m), 1409 (m), 1363

(m), 1293 (m), 1233 (w), 1193 (w), 1149 (w), 1120 (w), 1094 (w), 1014 (w), 853 (m), 812

(m), 749 (m), 672 (w), 624 (m), 556 (w), 516 (w), 482 (w), 437 (w), 420 (w). IR Data

(CH$_2$Cl$_2$, cm^{-1}): 2014 (m) [ν_{CO}], 1895 (m) [ν_{CO}].

2.7.7   Synthesis of [CpCo{P(O)(OEt)₂}₃]Re(CO)₃

A mixture of [CpCo{P(O)(OEt)$_2$}$_3$]Na (69 mg, 0.12 mmol) and Re(CO)$_5$Br (50 mg, 0.12 mmol) was placed in an ampoule, treated with THF (*ca.* 8 mL) and heated for 3 days at 60 °C. After this period, the mixture was filtered and the volatile components were removed from the filtrate *in vacuo*. The residue was washed with hexane and dissolved in benzene for crystallization to yield yellow crystals (40 mg, 41%). Analysis calcd. [L$_{OET}$]Re(CO)$_3$: C, 29.8% ; H, 4.4%. Found: C, 29.6%; H, 4.1%. ^{1}H NMR (C$_6$D$_6$): 1.15 [t, $^3J_{H-H}$ = 7, 18 H of C$_5$H$_5$Co{OP(CH$_2$C$\underline{H}_3$)$_2$}$_3$], 4.07 [m, 12 H of C$_5$H$_5$Co{OP(C$\underline{H}_2$CH$_3$)$_2$}$_3$], 4.76 [s, 5H of C$_5\underline{H}_5$Co{OP(CH$_2$CH$_3$)$_2$}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): ^{13}C{^{1}H} NMR (C$_6$D$_6$): 16.8 [m, 6 C of C$_5$H$_5$Co{OP(CH$_2$C$\underline{H}_3$)$_2$}$_3$], 61.4 [m, 6 C of C$_5$H$_5$Co{OP($\underline{C}$H$_2$CH$_3$)$_2$}$_3$], 89.3 [s, 5 C of $\underline{C}_5$H$_5$Co{OP(CH$_2$CH$_3$)$_2$}$_3$]. IR Data (KBr disk, cm^{-1}): 2982 (s), 2903 (m), 2367 (w), 2346 (w), 2013 (vs) [ν$_{CO}$], 1873 (vs) [ν$_{CO}$], 1688 (vw), 1656 (vw), 1478 (w), 1441 (m), 1388 (m), 1115 (vs), 1041 (vs), 936 (vs), 839 (s), 776 (s), 740 (s), 671 (vw), 655 (w), 631 (m), 590 (s), 529 (w), 510 (m). IR Data (CH$_2$Cl$_2$, cm^{-1}): 2015 (s) [ν$_{CO}$], 1880 (s) [ν$_{CO}$]. MS: *m/z* = 806.38 [M]$^+$, M = [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$.

2.7.8   Synthesis of [To$^{Bu^t}$]ZrCl₃

A mixture of [To$^{Bu^t}$]Na (16 mg, 0.04 mmol) and ZrCl$_4$ (12.3 mg, 0.05 mmol) was treated with benzene (*ca.* 1 mL) and heated at 60 °C for 4 hours, during which period a small amount of colorless crystals of [To$^{Bu^t}$]ZrCl$_3$ suitable for X-ray diffraction were deposited. The mixture was filtered and the residue was extracted with chloroform (3 × *ca.* 3 mL).

The volatile components were removed *in vacuo* and the residue obtained was washed with hexanes (*ca.* 3 mL), yielding [To^{But}]ZrCl$_3$ as an off-white powder (6 mg, 27%). ^{1}H NMR (C$_6$D$_6$): 1.66 [s, 27H of HB{C$_2$N$_2$H$_2$[C(C$\underline{H}_3$)$_3$]CO}$_3$], 6.46 [d, $^3J_{H-H}$ = 3, 3H of HB{C$_2$N$_2$$\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$], 6.50 [d, $^3J_{H-H}$ = 3, 3H of HB{C$_2$N$_2$$\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 29.4 [9 C, HB{C$_2N_2H_2$[C($\underline{C}H_3$)$_3$]CO}$_3$], 57.9 [3 C, HB{C$_2N_2H_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_3$], 110.7 [3 C, HB{$\underline{C}_2N_2H_2$[C(CH$_3$)$_3$]CO}$_3$], 119.0 [3 C, HB{$\underline{C}_2N_2H_2$[C(CH$_3$)$_3$]CO}$_3$], 152.7 [3 C, HB{C$_2N_2H_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_3$].

2.7.9 Synthesis of [To^{MeBenz}]ZrCl$_3$

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and ZrCl$_4$ (18 mg, 0.08 mmol) was placed in an ampoule, treated with dichloromethane (*ca.* 6 mL) and heated overnight at 50 °C. After this period, the mixture was filtered and the volatile components were removed from the filtrate *in vacuo.* The solid residue was washed with acetonitrile (*ca.* 3 mL) and hexane (*ca.* 3 mL) to yield [To^{MeBenz}]ZrCl$_3$ as a white powder (14 mg, 33%). ^{1}H NMR (C$_6$D$_6$): 2.96 [s, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_3$], 6.33 [d, $^3J_{H-H}$ = 8, 3H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_3$], 6.85 [t, $^3J_{H-H}$ = 8, 3H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_3$], 7.00 [t, $^3J_{H-H}$ = 8, 3H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_3$], 7.56 [d, $^3J_{H-H}$ = 8, 3H of HB{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (CDCl$_3$): 28.9 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$], 109.8 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 113.2 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 123.5 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 123.7 [3C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 128.5 [3 C, HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$], 130.7 [3 C,

HB{(C$_4$H$_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], [3 C,HB{(C$_4H_4$)C$_2N_2$(CH$_3$)$\underline{C}$O}$_3$] not observed. ^{13}C{^{1}H} NMR

(CD$_2$Cl$_2$): 29.2 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$], 110.3 [3 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$],

113.7 [3 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 123.9 [3 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 124.1 [3C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 131.2 [3 C, HB{(C$_4H_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], 132.6 [3 C,

HB{(C$_4$H$_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], 158.8 [3 C,HB{(C$_4H_4$)C$_2N_2$(CH$_3$)$\underline{C}$O}$_3$]. Analysis calcd. for

[To^{MeBenz}]ZrCl$_3$•CH$_2$Cl$_2$: C, 40.8%; H, 3.3%; N, 11.4%. Found: C, 41.0%; H, 3.4%; N, 11.0%.

2.7.10 Synthesis of Cp[To^{MeBenz}]ZrCl$_2$

A mixture of CpZrCl$_3$ (18 mg, 0.07 mmol) and [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol)

was placed in an ampoule and treated with benzene (*ca.* 5 mL). The mixture was stirred

at room temperature for a period of 2 hours during which it became a suspension. The

mixture was treated with *n*-hexane (*ca.* 5 mL) to precipitate more material, which was

isolated by filtration. The precipitate was washed with *n*-hexane, dried *in vacuo*, and

then extracted with dichloromethane (*ca.* 5 mL). The volatile components were removed

in vacuo to give [To^{MeBenz}]CpZrCl$_2$ as a white powder (30 mg, 67%). Crystals suitable for

X-ray diffraction were obtained from slow evaporation from a solution in benzene.

Analysis calcd. for Cp[To^{MeBenz}]ZrCl$_2$: C, 51.2%; H, 4.0%; N, 12.3%. Found: C, 50.8%; H,

3.9%; N, 11.3%. ^{1}H NMR (C$_6$D$_6$): 2.88 [s, 6H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}$$_3$)CO}$_3$], 3.23 [s, 3H of

HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}$$_3$)CO}$_3$], 6.31 [d, ^{3}J$_{H-H}$ = 8, 1H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$], 6.51 [d, ^{3}J$_{H-H}$ = 8, 2H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$], 6.69 [s, 5H of C$_5$$\underline{H}$$_5$], 6.78 [t, ^{3}J$_{H-H}$ = 8, 1H of

HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$], 6.95 [m, 4H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$], 7.06 [t, ^{3}J$_{H-H}$ = 8, 1H

of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$], 7.48 [d, $^3J_{H-H}$ = 8, 1H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$], 7.67 [d,

$^3J_{H-H}$ = 8, 2H of HB{(C$_4$$\underline{H}$$_4$)C$_2N_2$(CH$_3$)CO}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 28.0 [2 C,

HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$], 29.1 [1 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$], 109.2 [2 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 109.4 [1 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 111.6 [1 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 112.9 [2 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 118.2 [5 C, $\underline{C}$$_5H_5$],

122.1 [1 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 122.4 [1 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 122.6 [2 C,

HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 123.1 [2C, HB{($\underline{C}$$_4H_4$)C$_2N_2$(CH$_3$)CO}$_3$], 131.0 [2C,

HB{(C$_4$H$_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], 131.5 [1C, HB{(C$_4H_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], 132.6 [1C,

HB{(C$_4$H$_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], 133.1 [2C, HB{(C$_4H_4$)$\underline{C}$$_2N_2$(CH$_3$)CO}$_3$], 159.1 [1C,

HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_3$], 159.6 [2C, HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_3$].

2.7.11 Synthesis of [To^{MeBenz}]ZnI

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and ZnI$_2$ (21 mg, 0.07 mmol) was

treated with dichloromethane (*ca.* 8 mL) resulting in the immediate deposition of a

white precipitate. The mixture was stirred for *ca.* 4 hours at room temperature, allowed

to settle and then filtered. The filtrate was concentrated to *ca.* 3 mL and treated with

pentane (*ca.* 10 mL), thereby resulting in the formation of a precipitate. The mixture was

filtered and the volatile components were removed from the filtrate *in vacuo* to give

[To^{MeBenz}]ZnI as white powder (20 mg, 47%). Crystals of composition

[To^{MeBenz}]ZnI•CH$_2$Cl$_2$ suitable for X-ray diffraction were obtained from a solution in

dichloromethane. Analysis calcd. for [To^{MeBenz}]ZnI•CH$_2$Cl$_2$: C, 41.1%; H, 3.3%; N, 11.5%.

Found: C, 41.7%; H, 3.1%; N, 11.1. ^{1}H NMR (C$_6$D$_6$): 2.48 [s, 9H of

HB{(C$_4$H$_4$)C$_2$N$_2$(C<u>H</u>$_3$)CO}$_3$], 6.37 [d, ^{3}J$_{H-H}$ = 8, 3H of HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 6.88 – 7.00

[m, 6H of HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 7.60 [d, ^{3}J$_{H-H}$ = 8, 3H of HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$].

^{13}C{^{1}H} NMR (C$_6$D$_6$): 26.6 [9 C, HB{(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>H$_3$)CO}$_3$], 109.0 [3 C,

HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 112.4 [3 C, HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 122.1 [3 C,

HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 122.6 [3C, HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 131.3 [3C,

HB{(C$_4$H$_4$)<u>C</u>$_2$N$_2$(CH$_3$)CO}$_3$], 133.3[3C, HB{(C$_4$H$_4$)<u>C</u>$_2$N$_2$(CH$_3$)CO}$_3$], [3C,

HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)<u>C</u>O}$_3$] not observed.

2.7.12 Synthesis of [To^{MeBenz}]$_2$Co

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and CoCl$_2$ (4 mg, 0.03 mmol) was

placed in an ampoule, treated with dichloromethane (*ca.* 5 mL) and heated overnight at

60 ˚C. After this period, the volatile components were removed *in vacuo* and the solid

residue was washed sequentially with hexane (*ca.* 3 mL) and acetonitrile (*ca.* 5 mL). The

residue was extracted into warm chloroform (2 × *ca.* 5 mL) and the volatile components

were removed from the extract *in vacuo* to give [To^{MeBenz}]$_2$Co as a lilac powder (20 mg,

67%). Crystals suitable for X-ray diffraction were obtained from a solution in

chloroform. Analysis calcd. [To^{MeBenz}]$_2$Co: C, 59.7%; H, 4.6%; N, 17.4%. Found: C, 59.3%;

H, 4.1%; N, 16.1 %. μ$_{eff}$ (Evans Method, room temperature): 5.5 μ$_B$. ^{1}H NMR (CDCl$_3$):

-7.01 [s, 18H of HB{(C$_4$H$_4$)C$_2$N$_2$(C<u>H</u>$_3$)CO}$_3$], 2.07 [d, ^{3}J$_{H-H}$ = 7, 6H of

HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 6.72 [t, ^{3}J$_{H-H}$ = 7, 6H of HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 8.67 [d, ^{3}J$_{H-H}$

= 7, 6H of HB{$(C_4\underline{H}_4)C_2N_2(CH_3)CO$}$_3$], 16.75 [t, $^3J_{H-H}$ = 7, 3H of HB{$(C_4\underline{H}_4)C_2N_2(CH_3)CO$}$_3$].

FAB-MS: m/z = 965.3 [M]$^+$, M = [To^{MeBenz}]$_2$Co. IR Data (KBr disk, cm^{-1}): 3446 (br), 3054

(w), 2927 (m), 2855 (w), 2426 (w) [ν_{BH}], 2228 (w), 1629 (s), 1601 (s), 1544 (w), 1494 (s),

1440 (m), 1397 (m), 1300 (m), 1223 (m), 1148 (m), 1124 (m), 1095 (m), 1013 (w), 996 (w),

847 (m), 771 (m), 735 (m).

2.7.13 Synthesis of [To^{MeBenz}]$_2$Fe

A mixture of [To^{MeBenz}]Na•diglyme (50 mg, 0.08 mmol) and FeCl$_2$ (5 mg, 0.04 mmol) was

placed in an ampoule, treated with chloroform (*ca.* 5 mL) and heated overnight at 60 °C.

After this period, the volatile components were removed *in vacuo* and the solid residue

was washed sequentially with hexane (*ca.* 5 mL) and acetonitrile (*ca.* 5 mL). The residue

was extracted into warm chloroform (2 × *ca.* 5 mL) and the volatile components were

removed from the extract *in vacuo* to give [To^{MeBenz}]$_2$Fe as a very pale powder (24 mg,

61%). Crystals suitable for X-ray diffraction were obtained from a solution in

chloroform. μ_{eff} (Evans Method, room temperature): 3.8 μ_B. ^{1}H NMR (CDCl$_3$): -23.3 [s,

18H of HB{$(C_4H_4)C_2N_2(C\underline{H}_3)CO$}$_3$], 0.5 [br, 6H of HB{$(C_4\underline{H}_4)C_2N_2(CH_3)CO$}$_3$], 7.4 [br, 6H

of HB{$(C_4\underline{H}_4)C_2N_2(CH_3)CO$}$_3$], 11.9 [br, 6H of HB{$(C_4\underline{H}_4)C_2N_2(CH_3)CO$}$_3$], 25.7 [br, 6H of

HB{$(C_4\underline{H}_4)C_2N_2(CH_3)CO$}$_3$]. FAB-MS: m/z = 962.3 [M]$^+$, M = [To^{MeBenz}]$_2$Fe. IR Data (KBr

disk, cm^{-1}): 3450 (br), 2923 (m), 2848 (w), 2434 (w) [ν_{BH}], 1637 (s), 1629 (s), 1601 (m), 1544

(w), 1510 (w), 1493 (m), 1440 (m), 1397 (m), 1299 (w), 1219 (w), 1152 (w), 1124 (m), 1094

(w), 1014 (w), 844 (w), 769 (m), 735 (m).

2.7.14 [To^{MeBenz}]CuPMe$_3$

A mixture of [To^{MeBenz}]Na•diglyme (20 mg, 0.03 mmol) and [Me$_3$PCuCl]$_4$ (5.7 mg, 0.008 mmol) was treated with benzene (*ca.* 3 mL). The resulting suspension was mixed with a pipette for several minutes and then filtered. Then the filtrate was lyophilized and the solid obtained was washed with pentane (*ca.* 3 mL) to give [To^{MeBenz}]CuPMe$_3$ as white powder (10 mg, 51 %). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a benzene solution. ^{1}H NMR (C$_6$D$_6$): 0.82 [d, $^2J_{P-H}$= 4, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(C$\underline{H}_3$)$_3$], 2.76 [s, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_3$CuP(CH$_3$)$_3$], 6.53 ["d", $^3J_{H-H}$ = 8, 3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 6.98 [m, 6H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 7.66 ["d", $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 3H of HB{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 14.9 [d, $^1J_{P-C}$ = 25, 3 C, HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP($\underline{C}$H$_3$)$_3$], 26.2 [3 C, HB{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_3$CuP(CH$_3$)$_3$], 107.0 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 111.7 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 120.3 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 121.5 [3 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 132.0 [3 C, HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 134.8 [3C, HB{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_3$CuP(CH$_3$)$_3$], 159.9 [3C, HB{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_3$CuP(CH$_3$)$_3$]. ^{31}P{^{1}H} NMR (C$_6$D$_6$): -46.9.

2.7.15 [Tm^MeBenz]CuPMe₃

A mixture of {[Tm^MeBenz]Na}₂(THF)₃ (23 mg, 0.02 mmol) and [Me₃PCuCl]₄ (4.0 mg, 0.006

mmol) was treated with benzene (*ca.* 3 mL). The resulted suspension was mixed with a

pipette for several minutes and then filtered. Then the filtrate was lyophilized and the

solid obtained was washed with pentane (*ca.* 3 mL) to give [Tm^MeBenz]CuPMe₃ as white

powder (8 mg, 55%). Crystals suitable for X-ray diffraction were obtained by slow

diffusion of pentane into a benzene solution. Analysis calcd. for [Tm^MeBenz]CuPMe₃: C,

50.6%; H, 4.9%; N, 13.1%. Found: C, 50.9%; H, 4.9%; N, 12.8%. ^{1}H NMR (C₆D₆): 1.09 [d,

$^2J_{P-H}$= 5, 9H of HB{(C₄H₄)C₂N₂(CH₃)CS}₃CuP(C$\underline{H}$₃)₃], 3.18 [s, 9H of

HB{(C₄H₄)C₂N₂(C$\underline{H}$₃)CS}₃CuP(CH₃)₃], 6.63 ["d", $^3J_{H-H}$ = 8, 3H of

HB{(C₄$\underline{H}$₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃], 6.93 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 3H of

HB{(C₄$\underline{H}$₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃], 6.97 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 3H of

HB{(C₄$\underline{H}$₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃], 7.59 ["d", $^3J_{H-H}$ = 8, 3H of

HB{(C₄$\underline{H}$₄)C₂N₂(CH₃)CS}CuP(CH₃)₃]. ^{13}C{^{1}H} NMR (C₆D₆): 15.9 [d, $^1J_{P-C}$ = 15, 3 C,

HB{(C₄H₄)C₂N₂(CH₃)CS}₃CuP($\underline{C}$H₃)₃], 30.3 [3 C, HB{(C₄H₄)C₂N₂($\underline{C}$H₃)CS}₃CuP(CH₃)₃],

108.8 [3 C, HB{($\underline{C}$₄H₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃], 112.9 [3 C,

HB{($\underline{C}$₄H₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃], 122.3 [3 C, HB{($\underline{C}$₄H₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃],

122.9 [3 C, HB{($\underline{C}$₄H₄)C₂N₂(CH₃)CS}₃CuP(CH₃)₃], 134.3 [3 C,

HB{(C₄H₄)$\underline{C}$₂N₂(CH₃)CS}₃CuP(CH₃)₃], 137.5 [3C, HB{(C₄H₄)$\underline{C}$₂N₂(CH₃)CS}₃CuP(CH₃)₃],

171.2 [3C, HB{(C₄H₄)C₂N₂(CH₃)$\underline{C}$S}₃CuP(CH₃)₃]. ^{31}P{^{1}H} NMR (C₆D₆): -49.6. IR Data

(ATR, cm^{-1}): 3057 (w), 2962 (w), 2935 (w), 2898 (w), 2449 (w), 2431 (w), 1483 (m), 1430

(m), 1399 (m), 1342 (vs), 1294 (m), 1231 (w), 1191 (m), 1156 (w), 1123 (w), 1090 (m), 1015 (m), 998 (w), 950 (s), 855 (m), 813 (m), 736 (s), 668 (w), 632 (w), 619 (s), 568 (m), 557 (m), 437 (m), 419 (s).

2.8 Crystallographic Data

Table 3. Crystal, intensity collection and refinement data.

	[To^{MeBenz}]Re(CO)$_3$	[To^{But}]Re(CO)$_3$
lattice	Rhombohedral	Trigonal
formula	C$_{27}$H$_{22}$BN$_6$O$_6$Re	C$_{42}$H$_{52}$BN$_6$O$_6$Re
formula weight	723.52	933.91
space group	*R-3*	*P-3*
a/Å	15.5893(14)	16.131(2)
b/Å	15.5893(14)	16.131(2)
c/Å	19.0929(14)	9.6857(14)
α/°	90	90
β/°	90	90
γ/°	120	120
V/Å³	4018.4(6)	2182.6(6)
Z	6	2
temperature (K)	123(2)	200(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.794	1.421
μ (Mo Kα), mm^{-1}	4.590	2.835
θ max, deg.	32.71	30.71
no. of data collected	23365	34854
no. of data used	3200	4523
no. of parameters	127	175
R_1 [$I > 2\sigma(I)$]	0.0167	0.0363
wR_2 [$I > 2\sigma(I)$]	0.0410	0.0586
R_1 [all data]	0.0187	0.0822
wR_2 [all data]	0.0418	0.0714
GOF	1.063	1.131
R_{int}	0.0271	0.0818

Table 3 (cont.) Crystal, intensity collection and refinementdata.

	[Tm^{MeBenz}]Na	[Tm^{MeBenz}]Re(CO)$_3$
lattice	Triclinic	Monoclinic
formula	C$_{30}$H$_{36}$BN$_6$NaO$_6$	C$_{33}$H$_{28}$BN$_6$O$_3$ReS$_3$
formula weight	610.45	849.80
space group	P-1	$P2_1/c$
a/Å	13.7551(9)	16.147(3)
b/Å	14.9081(10)	10.510(2)
c/Å	15.2676(10)	19.719(4)
α/°	82.3230(10)	90
β/°	89.7710(10)	93.087(3)
γ/°	81.6210(10)	90
V/Å^3	3069.2(4)	3341.5(12)
Z	4	4
temperature (K)	200(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.321	1.689
μ (Mo Kα), mm^{-1}	0.105	3.868
θ max, deg.	32.57	32.75
no. of data collected	52297	56925
no. of data used	20703	11778
no. of parameters	811	431
R_1 [$I > 2\sigma(I)$]	0.0494	0.0311
wR_2 [$I > 2\sigma(I)$]	0.1178	0.0577
R_1 [all data]	0.1003	0.0516
wR_2 [all data]	0.1427	0.0635
GOF	1.021	1.000
R_{int}	0.0373	0.0557

Table 3 (cont.) Crystal, intensity collection and refinement data.

	[CpCo{P(O)(OEt)$_2$}$_3$]-Re(CO)$_3$	[To$^{\text{Bu}^{\text{t}}}$]ZrCl$_3$
lattice	Monoclinic	Trigonal
formula	C$_{20}$H$_{35}$CoO$_{12}$P$_3$Re	C$_{39}$H$_{52}$BCl$_3$N$_6$O$_3$Zr
formula weight	805.52	861.25
space group	$P2_1/n$	$P\text{-}3$
a/Å	11.4131(7)	16.242(2)
b/Å	18.4005(11)	16.242(2)
c/Å	13.6761(8)	9.4661(14)
α/°	90	90
β/°	92.8560(10)	90
γ/°	90	120
V/Å^3	2868.5(3)	2162.6(5)
Z	4	2
temperature (K)	125(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.865	1.323
μ (Mo Kα), mm^{-1}	5.018	0.482
θ max, deg.	32.48	30.50
no. of data collected	48946	35051
no. of data used	10043	4410
no. of parameters	341	111
R_1 [$I > 2\sigma(I)$]	0.0355	0.0436
wR_2 [$I > 2\sigma(I)$]	0.0601	0.1087
R_1 [all data]	0.0694	0.0607
wR_2 [all data]	0.0686	0.1139
GOF	1.001	1.093
R_{int}	0.0705	0.0541

Table 3. (cont.) Crystal, intensity collection and refinement data.

	Cp[To^{MeBenz}]ZrCl$_2$	[To$^{Bu^t}$]ZrCl$_3$
lattice	Triclinic	Triclinic
formula	C$_{35}$H$_{33}$BCl$_2$N$_6$O$_3$Zr	C$_{25.5}$H$_{25}$BCl$_3$IN$_6$O$_3$Zn
formula weight	758.60	772.95
space group	*P-1*	*P-1*
a/Å	10.0122(17)	9.361(5)
b/Å	12.326(2)	11.221(7)
c/Å	15.991(3)	17.165(13)
α/°	69.229(2)	96.785(11)
β/°	72.820(2)	103.212(11)
γ/°	71.988(2)	113.522(8)
V/Å³	1716.0(5)	1564.5(18)
Z	2	2
temperature (K)	125(2)	200(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.468	1.641
μ (Mo Kα), mm^{-1}	0.521	2.065
θ max, deg.	30.61	30.15
no. of data collected	28027	24328
no. of data used	10491	9138
no. of parameters	439	368
R_1 [$I > 2\sigma(I)$]	0.0483	0.0520
wR_2 [$I > 2\sigma(I)$]	0.0798	0.1122
R_1 [all data]	0.0939	0.1108
wR_2 [all data]	0.0922	0.1336
GOF	1.002	1.009
R_{int}	0.0722	0.0531

Table 3. (cont.) Crystal, intensity collection and refinement data.

	[To^{MeBenz}]$_2$Fe	[To^{MeBenz}]$_2$Co
lattice	Triclinic	Triclinic
formula	C$_{50}$H$_{46}$B$_2$Cl$_6$FeN$_{12}$O$_6$	C$_{50}$H$_{46}$B$_2$Cl$_6$CoN$_{12}$O$_6$
formula weight	1201.16	1204.24
space group	*P-1*	*P-1*
a/Å	9.765(7)	11.027(2)
b/Å	11.496(8)	11.171(2)
c/Å	13.698(9)	11.536(2)
α/°	87.906(10)	85.955(3)
β/°	69.479(10)	78.386(3)
γ/°	72.277(10)	74.761(3)
V/Å³	1367.6(16)	1342.8(4)
Z	1	1
temperature (K)	125(2)	160(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.458	1.489
μ (Mo Kα), mm^{-1}	0.629	0.680
θ max, deg.	30.62	30.47
no. of data collected	16628	21660
no. of data used	8255	8101
no. of parameters	356	356
R_1 [$I > 2\sigma(I)$]	0.0670	0.0637
wR_2 [$I > 2\sigma(I)$]	0.1219	0.1400
R_1 [all data]	0.1569	0.1520
wR_2 [all data]	0.1527	0.1701
GOF	1.000	1.000
R_{int}	0.0727	0.0761

Table 3. (cont.) Crystal, intensity collection and refinement data.

	[To$^{\text{MeBenz}}$]CuPMe$_3$	[Tm$^{\text{MeBenz}}$]CuPMe$_3$
lattice	Triclinic	Trigonal
formula	C$_{50}$H$_{34}$BCuN$_6$O$_3$PCu	C$_{96}$H$_{104}$B$_2$N$_{12}$S$_6$P$_2$Cu$_2$
formula weight	631.95	1828.91
space group	P-1	P-3
a/Å	9.463(2)	15.4166(7)
b/Å	11.773(3)	15.4166(7)
c/Å	15.140(4)	11.4883(6)
α/°	91.189(4)	90
β/°	103.845(4)	90
γ/°	103.714(4)	120
V/Å^3	1585.8(6)	2364.6(2)
Z	2	1
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.324	1.284
μ (Mo Kα), mm^{-1}	0.779	0.668
θ max, deg.	31.51	32.60
no. of data collected	27076	40931
no. of data used	10413	5563
no. of parameters	389	215
R_1 [$I > 2\sigma(I)$]	0.0498	0.0321
wR_2 [$I > 2\sigma(I)$]	0.1209	0.0804
R_1 [all data]	0.0970	0.0447
wR_2 [all data]	0.1414	0.0890
GOF	1.024	1.051
R_{int}	0.0422	0.0261

2.9   References and Notes.

(1)   (a) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148. (b) Parkin, G. in *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1.01; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2006.

(2)   See, for example, reference 5g and Zachmanglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc*. **2002**, 124, 9525-9546.

(3)   (a) Tolman, C.A. *J. Am. Chem. Soc.* **1970**, 92, 2956-2965. (b) Tolman, C. A. *Chem. Rev.* **1977**, 313-348.

(4)   Müller, T. E.; Mingos, D. M. P. *Transition Met. Chem.***1995**, 20, 533-539.

(5)   For compilations of X-ray structures and IR spectroscopic data on $[L_2X]Re(CO)_3$ and $[L_2X]Mn(CO)_3$ compounds: (a) Yurkerwich, K.; Yurkerwich, M.; Parkin, G. *Inorg. Chem*. **2011**, 50, 12284-12295. (b) Minoura, M.; Landry, V. K.; Melnick, J. G.; Pang, K.; Marchiò, L.; Parkin, G. *Chem. Commun.* **2006**, 3990-3992. (c) Landry, V. K.; Pang, K.; Quan, S. M.; Parkin, G. *Dalton Trans.* **2007**, 820-824. (d) Garcia, R.; Paulo, A.; Santos, I. *Inorg. Chim. Acta* **2009**, *362*, 4315-4327. (e) Graham, L. A.; Fout, A. R.; Kuehne, K. R.; White, J. L.; Mookherji, B.; Marks, F. M.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2005**, 171-180. (f) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428-2432. (g) Bergman, R. G.; Cundari, T. R.; Gillespie, A. M.; Gunnoe, T. B.; Harman, W. D.; Klinckman, T. R.; Temple, M. D.; White, D. P. *Organometallics* **2003**, *22*, 2331-2337.

(6)   (a) Spicer, M. D.; Reglinski, J. *Eur. J. Inorg. Chem.* **2009**, 1553-1574. (b) Parkin, G. *New J. Chem.* **2007**, *31*, 1996-2014. (c) Smith, J. M. *Comm. Inorg. Chem.* **2008**, *29*, 189-233.

(7)   (a) Kläui, W.; Asbahr, H. O.; Schramm, G.; Englert, U. *Chem. Ber.* **1997**, *130*, 1223-1229. (b) Leung, W.-H.; Zhang, Q.-F.; Yi, X.-Y. *Coord. Chem. Rev.* **2007**, *251*, 2266-2279. (c) Kläui, W. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 627-637.

(8)   Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *Organomet. Chem.* **2001**, *632*, 41-48.

(9)   Referance 5b, 5c and Victoria K. Landry Ph.D thesis.

(10)   Chisholm, M. H.; Davidson, E. R.; Huffman, J. C.; Quinlan, K. B. *J. Am. Chem. Soc.* **2001**, *123*, 9652-9664.

(11)   McCleverty, J. A. *Chem. Soc. Rev.* **1983**, *12*, 331-360.

(12)   See, for example: (a) Kapp, J.; Schade, C.; El-Nahasa, A. M.; Schleyer, P. v. R. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2236-2238. (b) Marchand, C. M.; Pidun, U.; Frenking, G.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 11078-11085.

(13)   See, for example refernces 3b, 3c, 3d and (a) Schwalbe, M.; Andrikopoulos, P. C.; Armstrong, D. R.; Reglinski, J.; Spicer, M. D. *Eur. J. Inorg. Chem.* **2007**, 1351-1360. (b) Garner, M.; Lehmann, M. A.; Reglinski, J.; Spicer, M. D. *Organometallics* **2001**, *20*, 5233-5236. (c) Graham, L. A.; Fout, A. R.; Kuehne, K. R.; White, J. L.;

Mookherji, B.; Marks, F. M.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2005**, 171-180.

(14) (a) Martin, A.; Mena, M.; Palacios, F. *J. Organomet. Chem.* **1994**, 480, C10-C11. (b) Braun, L. F.; Dreier, T.; Christy, M.; Petersen, J. L. *Inorg. Chem.* **2004,** 43, 3976-3987. (c) Knuppel, S.; Wang, C.; Kehr, G.; Frohlich, R.; Erker, G. *J. Organomet. Chem.* **2005**, 690, 14-32. (d) Krutko, D. P.; Borzov, M. V.;Veksler, E. N.; Churakov, A. V.; Kuzmina, L. G. . *J. Organomet. Chem.* **2005**, 690, 4036-4048.   (e) Lee, S. H.; Wu, C. J.; Yoo, J.; Kwak, J. Yun, H.; Lee, B. Y. *J. Organomet. Chem.* **2008**, 693, 457-467. (f) Park, J. H.; Do, S. H.; Cyriac, A.; Yun, H.; Lee, B. Y. *Dalton Trans*. **2010**, 39, 9994-10002.

(15) Greene, D. L.; Villalta, O. A.; Macias, D. M.; Gonzalez, A.; Tikkanen, W.; Schick, B.; Kanatardjieff, K. *Inorg. Chem. Commun*. **1999**, 2, 311-314.

(16) Ward, T. R.; Duclos, S.; Therrien, B.; Schenk, K. *Organometallics* **1998**, *17*, 2490-2494.

(17) (a) Repo, T.; Klinga, M.; Mutikainen, I.; Su, Y. C.; Leskelä, M.; Polamo, M. *Acta Chem. Scand.* **1996**, *50*, 1116-1120. (b) Corey, J. Y.; Zhu, X.-H.; Brammer, L.; Rath, N. P. *Acta Cryst.* **1995**, *C51*, 565-567.

(18) Buccella, D.; Shultz, A.; Melnick, J. G.; Konopka, F.; Parkin, G. *Organometallics* **2006**, *25*, 5496-5499.

(19)   Cassidy, I.; Garner, M.; Kennedy, A. R.; Potts, G. B. S.; Reglinski, J.; Slavin, P. A.; Spicer, M. D. *Eur. J. Inorg. Chem.* **2002**,1235-1239.

(20) τ_4 = [360 − (α + β)]/141, where α + β is the sum of the two largest angles. See: Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955-964.

(21)   Garner, M.; Lewinski, K.; Pattek-Janczyk, A.; Reglinski, J.; Sieklucka, B.; Spicer, M. D. Szaleniec, M. *Dalton Trans.* **2003**, 1181–1185.

(22)   Dodds, C. A.; Lehmann, M. A.; Ojo, J. F.; Reglinski, J.; Spicer, M. D. *Inorg. Chem.* **2004**, *43*, 4927-4934.

(23)   Senda, S.; Ohki, Y.; Hirayama, T.; Toda, D.; Chen, J.-L.; Matsumoto, T.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **2006**, *45*, 9914-9925.

(24)   Kimblin, C.; Churchill, D. G.; Bridgewater, B. M.; Girard, J. N.; Quarless, D. A.; Parkin, G. *Polyhedron* **2001**, *20*, 1891–1896.

(25)   (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23. (b) Burger, B. J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98. (c) Shriver, D. F.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York,1986.

(26)   Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

(27)   "Nuclear Magnetic Resonance Spectroscopy" Nelson, J. H. Prentice Hall, New Jersey (2003), p 79.

(28)   Schmidbaur, H.; Adlkofer, J.; Schwirten, K. *Chem. Ber*. **1972**, 105, 3382-3388.

(29)   H. Quast and U. Nahr, *Chem. Ber*. **1984**, 117, 2761.

(30)   Prakash, O.; Batra, H.; Kaur, H.; Sharma, P. K.; Sharma, V.; Singh, S. and Moriarty R., *Synthesis* **2001**, 4, 541-543.

(31)   (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

Chapter 3

Synthesis and Structural Characterization of *Bis*(2-oxoimidazolyl)hydroborato Complexes: A New Class of Bidentate Oxygen Donor Ligand

Table of Contents

Reproduced in part from:

3.1 Introduction

One major advantage of the boron-centered synthetic strategy is that X, LX, and L_2X

type ligands, according to the covalent bond classification system,[1] can be obtained by

simply altering the stoichiometry of the reaction. The synthesis of the

bis(pyrazolyl)borate, *bis*(mercaptoimidazolyl)borate and *bis*(selenoimidazolyl)borate as

bidentate donors ligands of $[N_2]$,[2] $[S_2]$[3] and $[Se_2]$,[4] respectively, have been published.

Among the ligands, the $[N_2]$[2] and $[S_2]$[5,6] donors have enjoyed widespread applications.

 We have described in chapter one the synthesis of the *tris*(oxoimidazolyl)borate ligands

which provide L_2X type tridentate $[O_3]$ donors ligands. In this chapter, we will present

the logical extension of this synthesis by reporting the related $[O_2]$ donor,

bis(oxoimidazolyl)borate [Bo^R], *via* treatment of two equivalents of imidazolone and

metal borohydride.

Bidentate ligands with $[O_2]$ donors that belong to the LX class are dominated by κ^2-

carboxylate[7] and κ^2-acetylacetonate[8] that respectively result in 4 and 6-membered rings

upon coordination. However, coordination of the [Bo^R] ligands to a metal center results

in a flexible 8-membered ring.[9,10] This helps in the adoption of a "boat-like"[11]

conformation that allows for secondary M•••H–B interactions (Figure 1). Similar 3-

center–2-electron M•••H–B interactions have been observed in the structure of several

bis(pyrazolyl)hydroborato,[2] *bis*(mercaptoimidazolyl)hydroborato[3] and

bis(selenoimidazolyl)hydroborato[4] metal complexes.
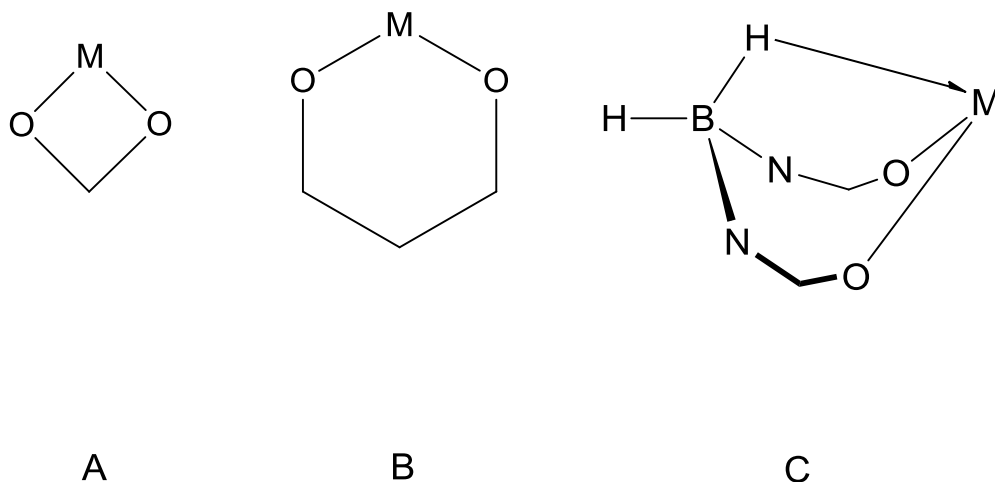
Figure 1. Coordination geometries of a. κ^2-carboxylate, b. κ^2-acetylacetonate, c. *bis*(oxoimidazolyl)borate.

The coordination chemistry of the [Bo^R] ligand with various metal compounds, mainly main group metals, will be investigated to provide a complete profile for this type of ligand. In addition, the [Bo^R] ligands will be compared to the sulfur and selenium counterpart in terms of coordination chemistry when applicable.

3.2 Alkali Metal Bo Complexes

3.2.1 Lithium Complexes of [Bo^R] ligands

3.2.1.1 [Bo$^{Bu^t}$]Li

Treatment of two equivalents of 1-tert-butyl-2-imidazolin-2-one with MBH_4, M = Li, Na, in THF at elevated temperatures results in the formation of [Bo$^{Bu^t}$]M (Scheme 1). Unlike [To$^{Bu^t}$]Na, [Bo$^{Bu^t}$]M was obtained in good yield without any major side products resulting from the reduction of the double bond of imidazolone. The reduction of the

double bond of imidazolone when making [To^R] ligand may be attributed to the high temperature needed.
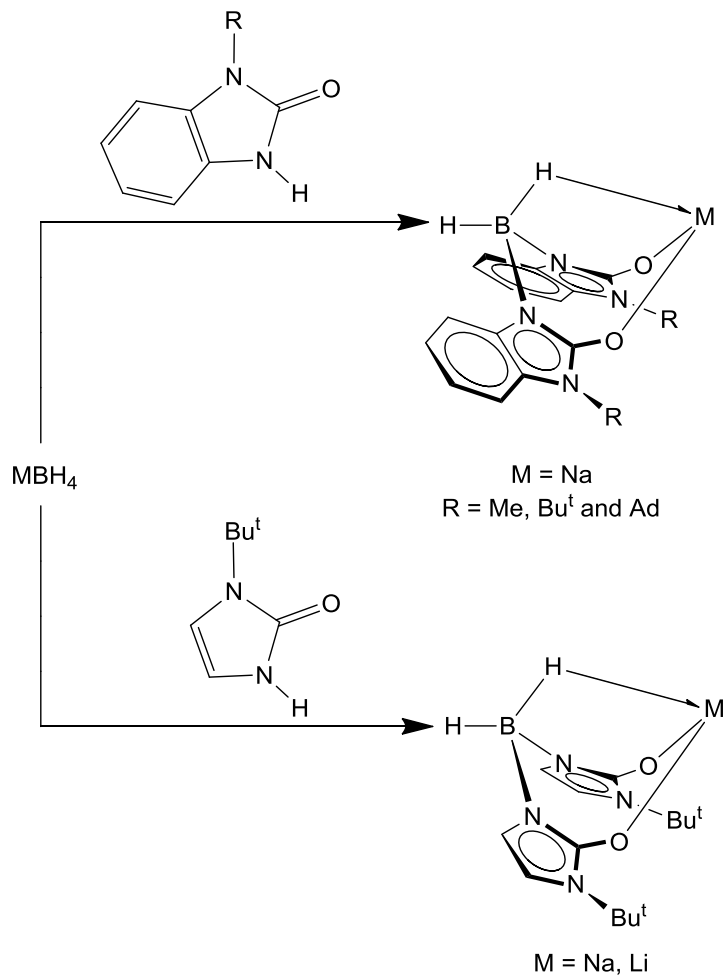
Scheme 1. Synthesis of [Bo^R]M.

Colorless crystals of composition [Bo$^{Bu^t}$]Li suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a benzene solution (Figure 2.). The molecular structure is dinuclear in nature where one of the oxygen atoms serves as a bridge between the two metal centers, resulting in an [M$_2$O$_2$] core. This type of bridging mode has been observed previously in [Bm^R] systems.[3]

A common feature of the molecular structures of many [Bo^R] compounds is that the [O_2] bidentate coordination is supplemented by interaction with one of the H–B groups. Therefore, besides the fact that the lithium is supported by three oxygens (one terminal and two bridging) a secondary Li•••H–B interaction ($d_{Li•••H}$ = 2.11 Å and $d_{Li•••B}$ = 2.81 Å) is observed. This interaction is associated with a "boat-like" conformation of the [Bo$^{Bu^t}$] ligand that allows the H–B group to be in proximity to the lithium center.
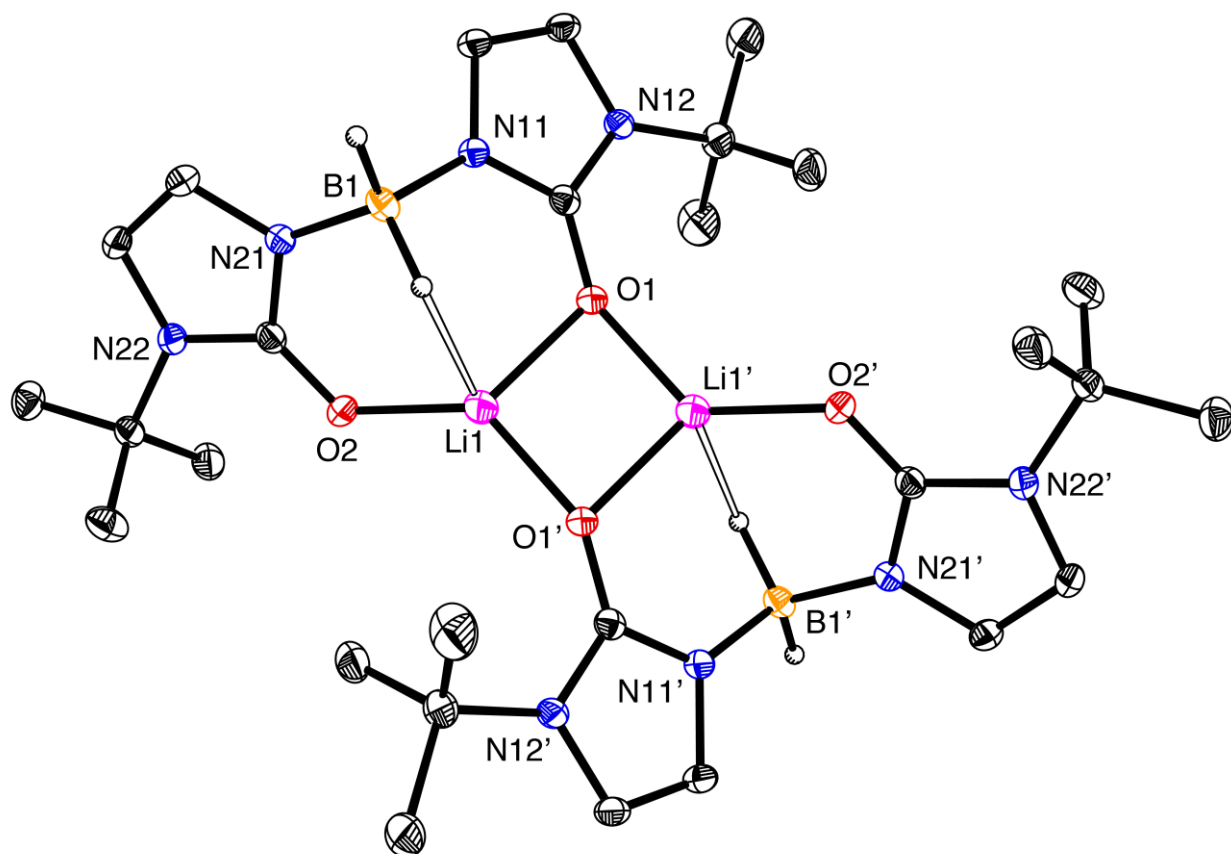
Figure 2. Molecular structure of {[Bo$^{Bu^t}$]Li}$_2$ (only one of the crystallographically independent molecules is shown).

Crystals of composition $[Bo^{Bu^t}]Li\cdot CH_2Cl_2$ suitable for X-ray diffraction were also obtained by vapor diffusion of pentane into a solution of $[Bo^{Bu^t}]Li$ in CH_2Cl_2 (Figures 3 and 4). The asymmetric unit possesses two crystallographically independent dimeric molecules of which one exhibits interactions between the lithium centers and CH_2Cl_2 molecules. Despite this interaction, the structures of the $\{[Bo^{Bu^t}]Li\}_2$ moieties are very similar.
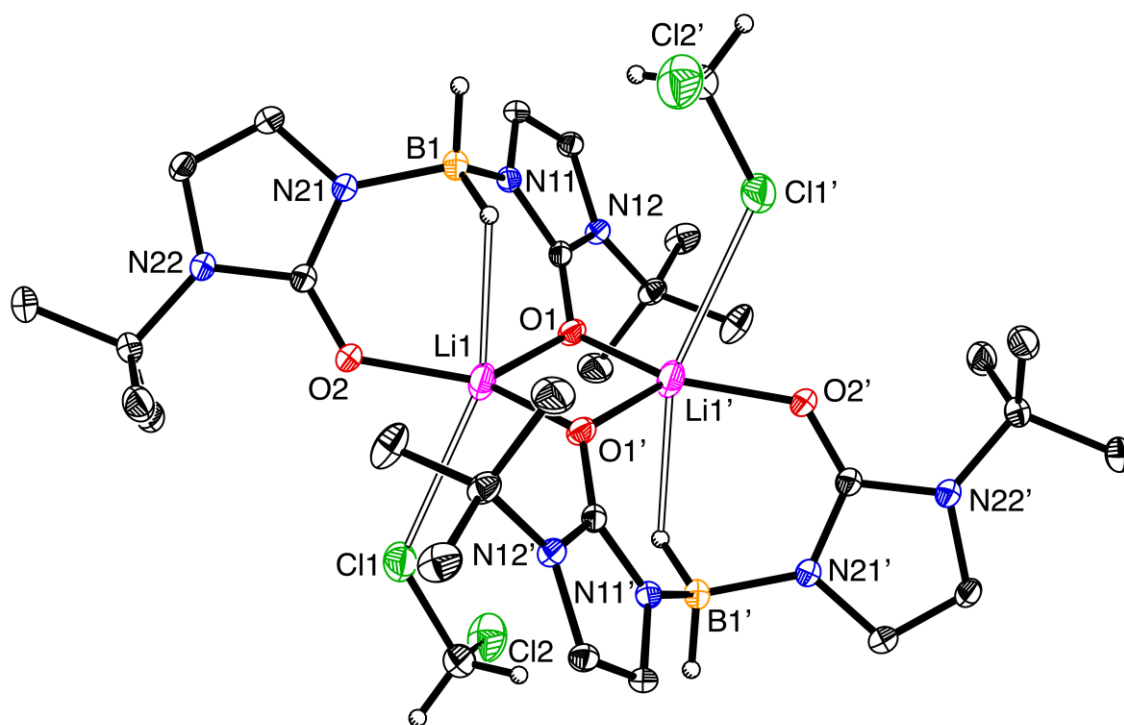
Figure 3. Molecular structure of $\{[Bo^{Bu^t}]Li\}_2\cdot(CH_2Cl_2)_2$ (only one of the crystallographically independent molecules is shown).
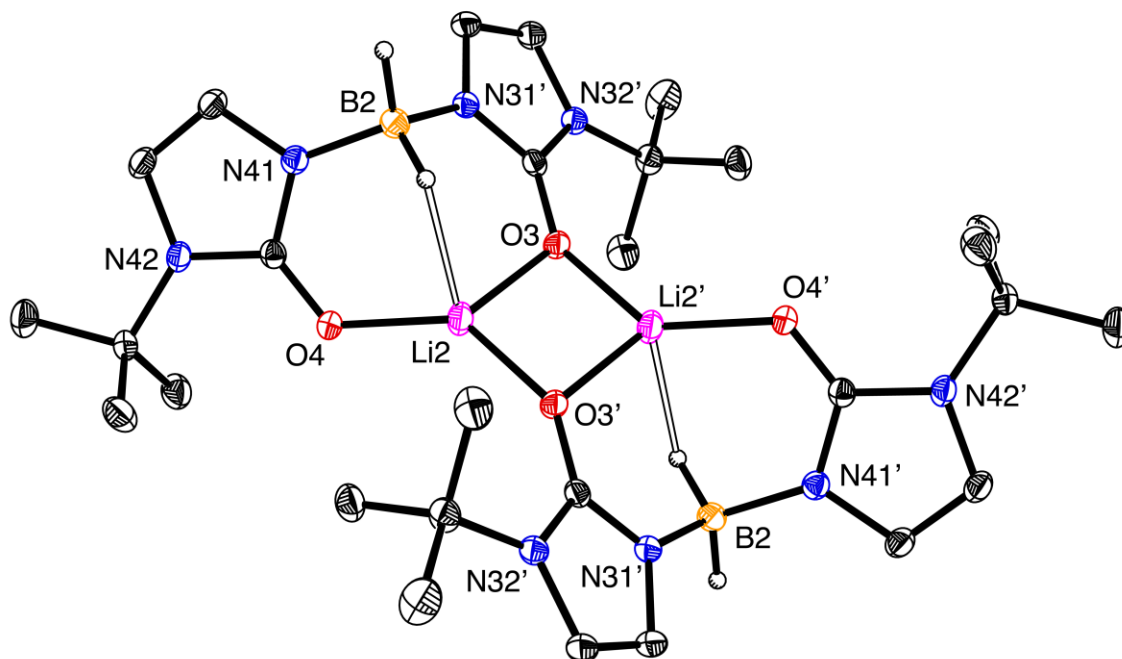
Figure 4. Molecular structure of $\{[Bo^{Bu^t}]Li\}_2 \bullet (CH_2Cl_2)$ (only one of the crystallographically independent molecules is shown).

3.2.2 Sodium Complexes of [Bo^R] ligands

3.2.2.1 [Bo$^{Bu^t}$]Na

Similar to the synthesis of [Bo$^{Bu^t}$]Li, treatment of two equivalents of 1-tert-butyl-2-imidazolin-2-one with NaBH$_4$ in THF at elevated temperature results in the formation of [Bo$^{Bu^t}$]Na. Crystals of composition [Bo$^{Bu^t}$]Na•diglyme suitable for X-ray diffraction were obtained from a solution of [Bo$^{Bu^t}$]Na in hexane and diglyme (Figure 5). X-ray diffraction indicates that [Bo$^{Bu^t}$]Na•diglyme is mononuclear in the solid state and sodium metal is supported by five oxygen atoms, two from the ligand and three from

diglyme, along with a 3-center–2-electron Na•••H–B secondary interaction ($d_{\text{Na•••H}}$ = 2.37

Å and $d_{\text{Na•••B}}$ = 3.20 Å).
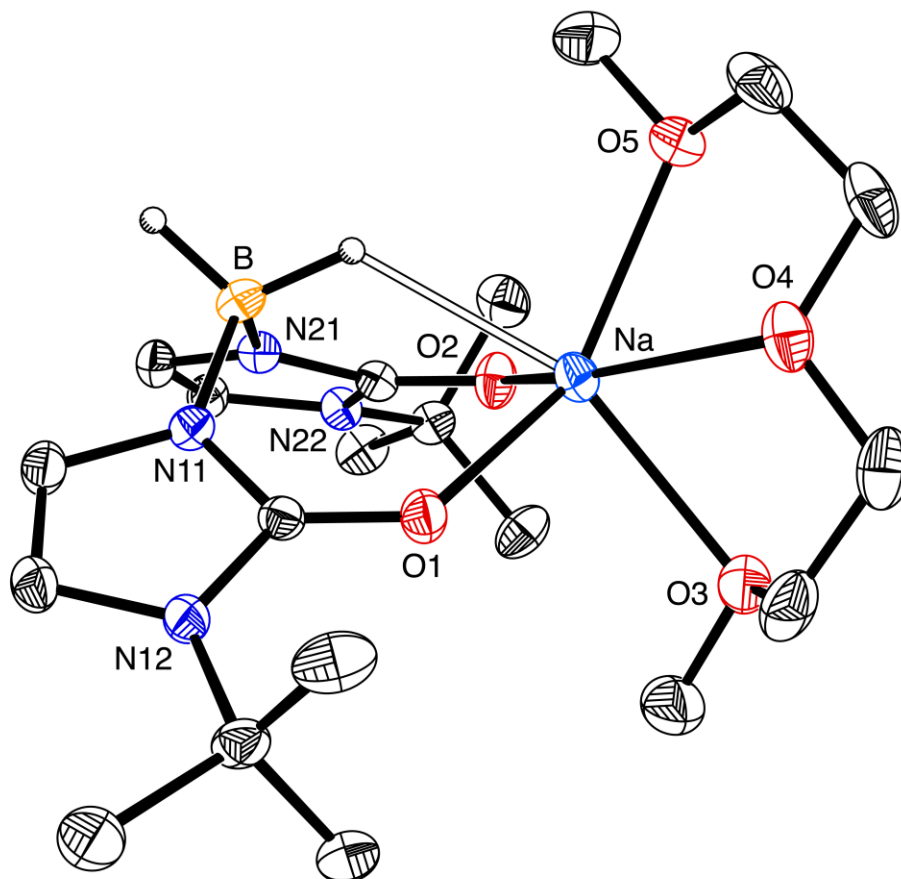
Figure 5. Molecular structure of [Bo$^{\text{But}}$]Na•diglyme.

However, a dinuclear structure of composition {[Bo$^{\text{But}}$]Na}$_2$•diglyme was obtained from

a 2:1 ratio of [Bo$^{\text{But}}$]Na and diglyme in hexane (Figure 6). Three-center–2-electron

M•••H–B interactions are observed in both molecular structures; the M•••H bond

distance for the mononuclear complex is 2.37 Å, but the M•••H distances are 2.53 and

2.47 Å for the dinuclear complex.
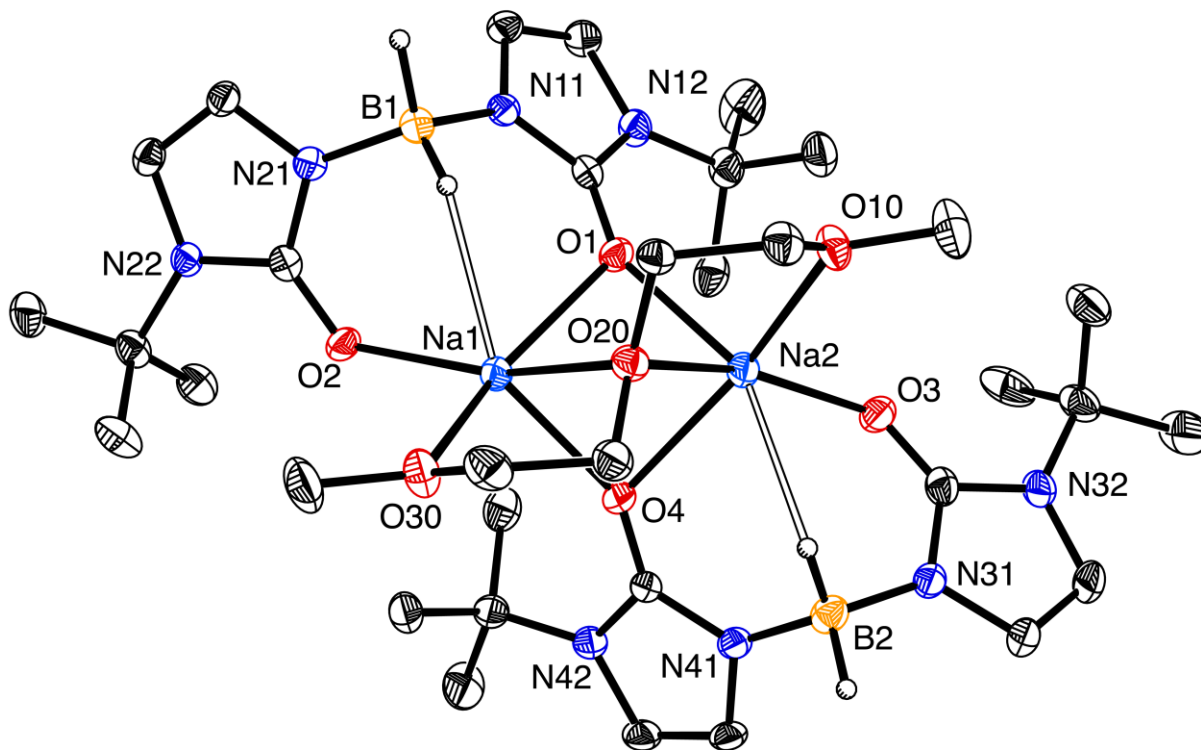
Figure 6. Molecular structure of {[Bo$^{Bu^t}$]Na}$_2$•diglyme.

3.2.2.2 [Bo^{RBenz}]Na, R = Me, t-Bu and Ad

We have also used an annulated imidazolone as precursor for the synthesis of [Bo^{RBenz}] ligands. Specifically, treatment of 1-R-1,3-dihydro-benzimidazol-2-one with NaBH$_4$ in toluene (when R = methyl) or THF (when R = *t*-But or Adamantyl) result in the generation of the respective ligand. Toluene is used as the reaction solvent in the methyl case because the product precipitates out from the reaction mixture which makes it easy for product isolation. For the methyl case, crystals of composition {[Bo^{MeBenz}]Na(diglyme)}$_2$ suitable for X-ray diffraction were obtained from mixture of diglyme and hexane (Figure 7). The molecular structure is dinuclear in nature but the

two sodium metals are in different coordination environments. One of the sodium centers is fully coordinated by diglyme and has no M•••H–B interaction ($d_{Na•••H}$ = 2.80 Å and $d_{Na•••B}$ = 3.50 Å) while the other sodium center is involved in a more pronounced 3-center–2-electron M•••H–B interaction ($d_{Na•••H}$ = 2.48 Å and $d_{Na•••B}$ = 3.20 Å) and only two of the three oxygens of diglyme coordinate to the metal center.
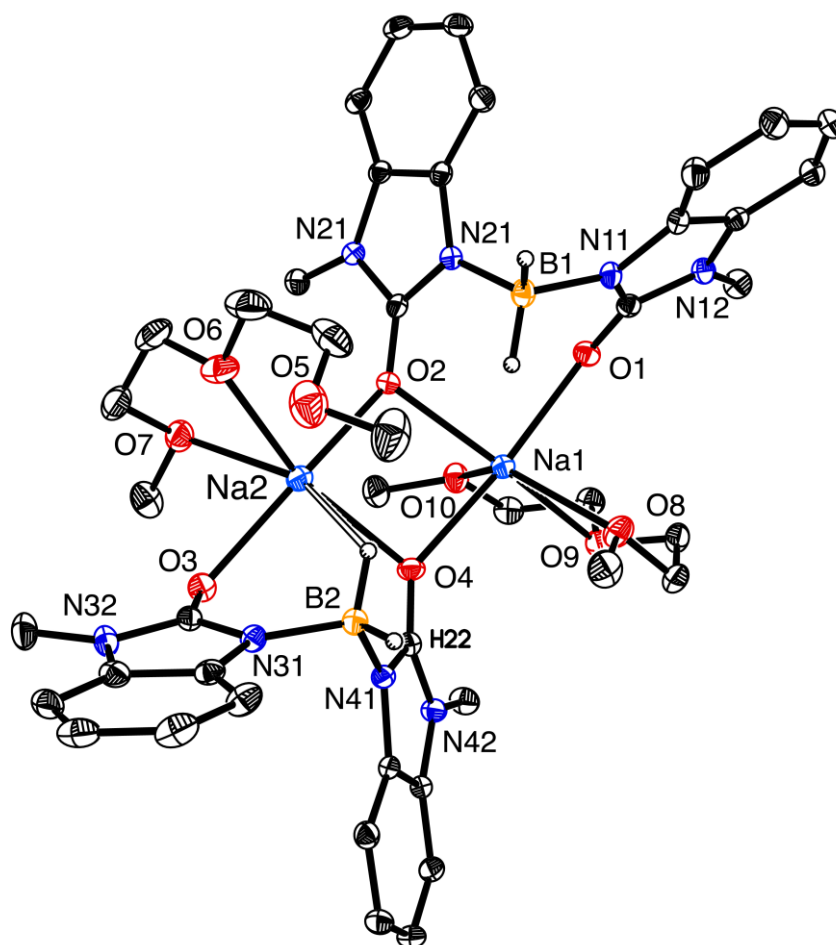
Figure 7. Molecular structure of {[Bo^{MeBenz}]Na(diglyme)}$_2$.

On the other hand, crystals of composition {[Bo^{RBenz}]Na•THF}$_2$, R = *t*-But or Ad, suitable for X-ray diffraction were obtained from a THF solution (Figures 8 and 9). In both cases,

the molecular structures are dimeric in nature. Although the coordination number of the sodium in this complex is only four, the 3-center–2-electron M•••H–B interaction is less pronounced than the previous cases. For example, the M•••H–B distance for {[Bo$^{Bu^tBenz}$]Na•THF}$_2$ is 3.10 Å while it is 3.49 Å for {[Bo^{AdBenz}]Na•THF}$_2$. This difference may be attributed to the steric bulk of the alkyl group.
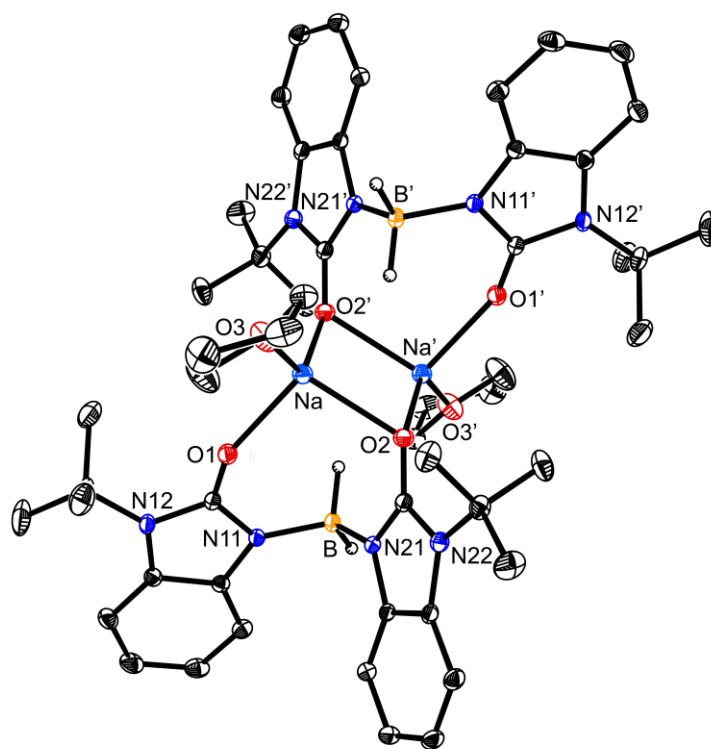
Figure 8. Molecular structure of {[Bo$^{Bu^tBenz}$]Na•THF}$_2$.
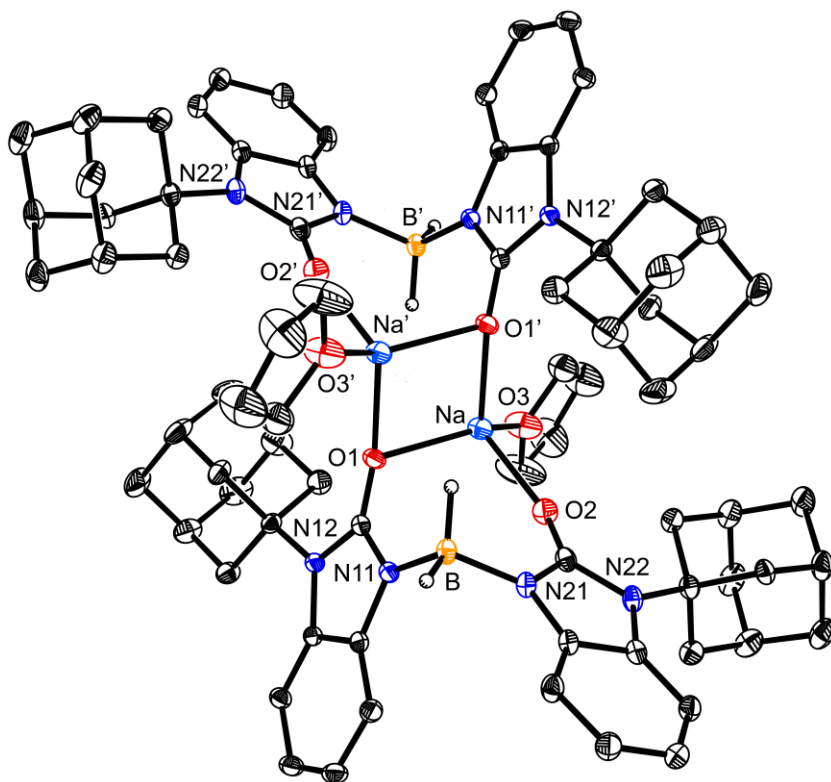
Figure 9. Molecular structure of $\{[\text{Bo}^{\text{AdBenz}}]\text{Na}\cdot\text{THF}\}_2$.

3.3 [Bo^R]Tl

The alkali metal complexes, [Bo^R]M, are useful ligand transfer reagents for the synthesis

of other derivatives. For example, treatment of $\{[\text{Bo}^{\text{Bu}^t}]\text{Li}\}_2$ with TlOAc gives [Bo$^{\text{Bu}^t}$]Tl

(Scheme 2). [Bo$^{\text{MeBenz}}$]Tl, [Bo$^{\text{Bu}^t\text{Benz}}$]Tl and [Bo$^{\text{AdBenz}}$]Tl have also been synthesized. All of

the [Bo^R]Tl complexes have been structurally characterized by X-ray diffraction, Figures

10, 11 and 12, except the [Bo$^{\text{AdBenz}}$]Tl complex due to the inability to grow crystals

suitable for X-ray diffraction. Notably, [Bo^R]Tl exists as a discrete mononuclear complex

with the shortest Tl•••Tl contact being 5.99 Å for [Bo$^{\text{Bu}^t}$]Tl, 4.63 Å for [Bo$^{\text{MeBenz}}$]Tl and

5.42 Å for [Bo$^{Bu^tBenz}$]Tl. The coordination geometry of thallium in [Bo^R]Tl is also supplemented by a secondary Tl•••H–B interaction, which results in a "boat-like" conformation of the [Bo^R] ligand and allows the B–H group to be in proximity to the metal center. This coordination geometry resembles that of the *bis*(pyrazolyl)hydroborato counterparts, [Bp^R]Tl.[12] However, the structures of the sulfur counterparts, {[Bm^R]Tl}$_x$, exist in totally different coordination geometries. For example, for the t-butyl-substituted derivative, {[Bm$^{Bu^t}$]Tl}$_2$, the structure is dimeric where one of the sulfur atoms of the [Bm$^{Bu^t}$] ligand bridges the two thallium centers.[13] On the other hand, the methyl-substituted derivative {[Bm^{Me}]Tl}$_x$ is polymeric with bridging mercaptoimidazolyl groups.[3a,14] Tl(I) compounds supported by bidentate [O_2] donor LX type ligands have been previously reported; however, unlike the [Bo^R]Tl, these complexes exhibit a variety of intermolecular interactions.[15]
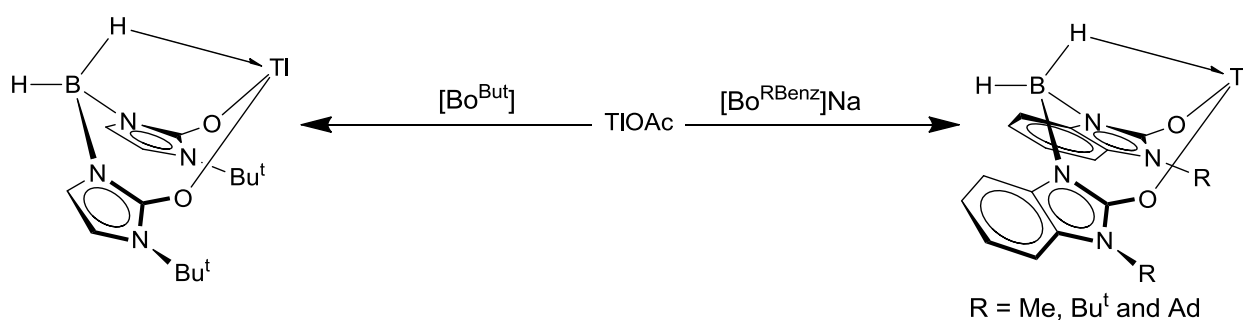
Scheme 2. Synthesis of [Bo^R]Tl.
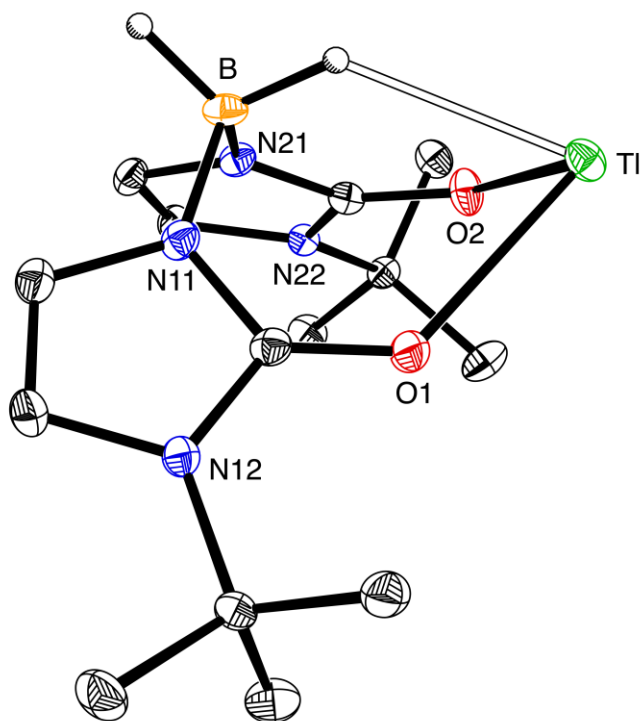
Figure 10. Molecular structure of [Bo$^{Bu^t}$]Tl.
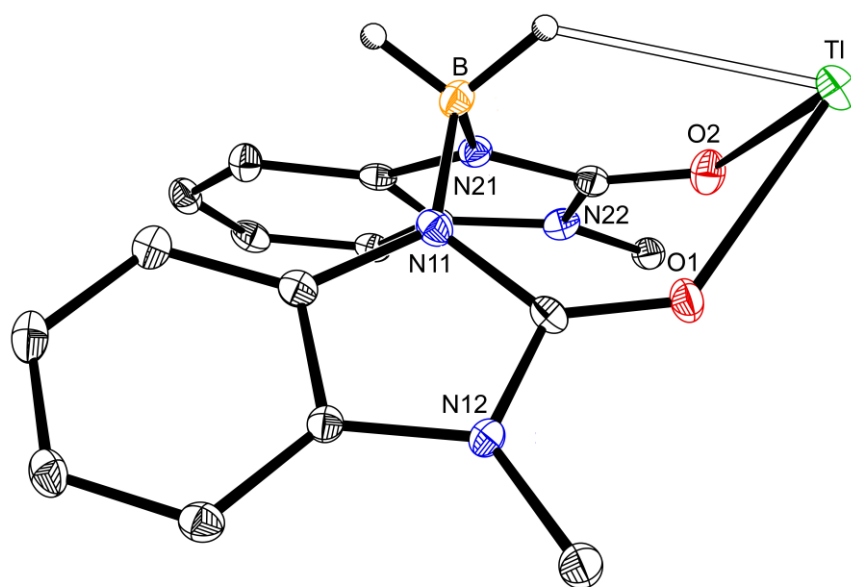
Figure 11. Molecular structure of [Bo^{MeBenz}]Tl.
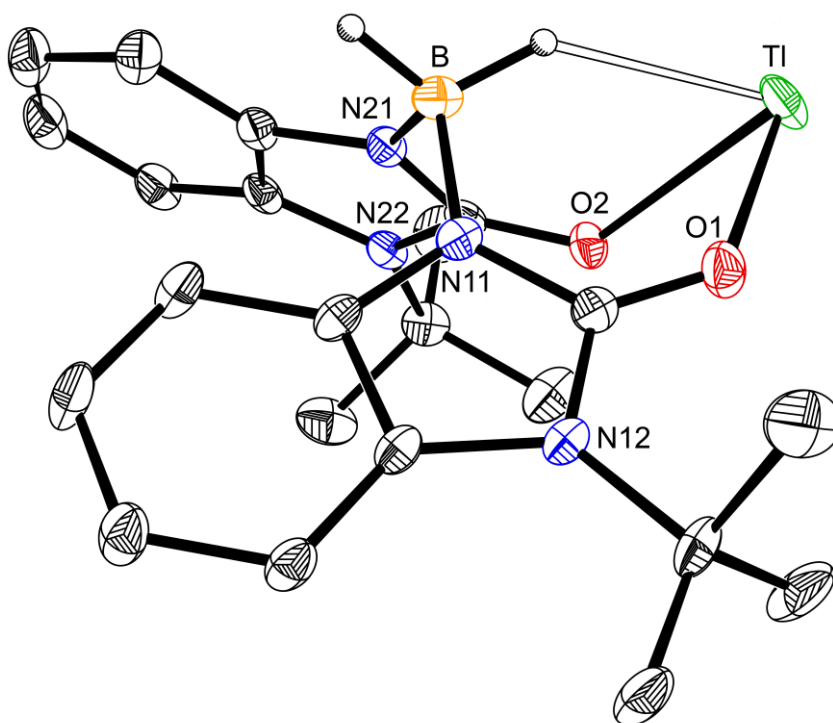
Figure 12. Molecular structure of [Bo$^{Bu^tBenz}$]Tl.

3.4   {[Bo^{MeBenz}]ZnI}$_2$

The zinc iodide compound, {[Bo^{MeBenz}]ZnI}$_2$, may be obtained *via* the treatment of

[Bo^{MeBenz}]Na with ZnI$_2$ (Scheme 3). The molecular structure of {[Bo^{MeBenz}]ZnI}$_2$ has been

determined by X–ray diffraction (Figure 13), demonstrating that the compound is

dinuclear with an oxygen atom of each [Bo^{MeBenz}] ligand bridging the two metal centers.

The selenium counterpart has similar dimeric coordination geometry.[4a] An interesting

difference between the two structures is that the two Zn-O bond lengths in the [Zn$_2$O$_2$]

core of {[Bo^{MeBenz}]ZnI}$_2$ are much more similar than the two pairs of Zn–Se bond lengths

in the [Zn$_2$Se$_2$] core of {[Bse^{Me}]ZnI}$_2$. Specifically, the two pairs of Zn–O bond lengths are

2.008(2) Å and 2.201(2) Å, whereas the two pairs of Zn–Se bond lengths are 2.452(1) Å

and 2.826(1) Å. This trend is in accord with density functional theory calculations performed on {[Bo^{MeBenz}]ZnI}$_2$ (0.083 Å, average value) and {[Bse^{Me}]ZnI}$_2$ (0.415 Å, average value).[16] On the other hand, these dinuclear structures, {[Bo^{MeBenz}]ZnI}$_2$ and {[Bse^{Me}]ZnI}$_2$, are distinct from the monomeric mercapto counterpart, [Bm^{Me}]ZnI.[3a,b]
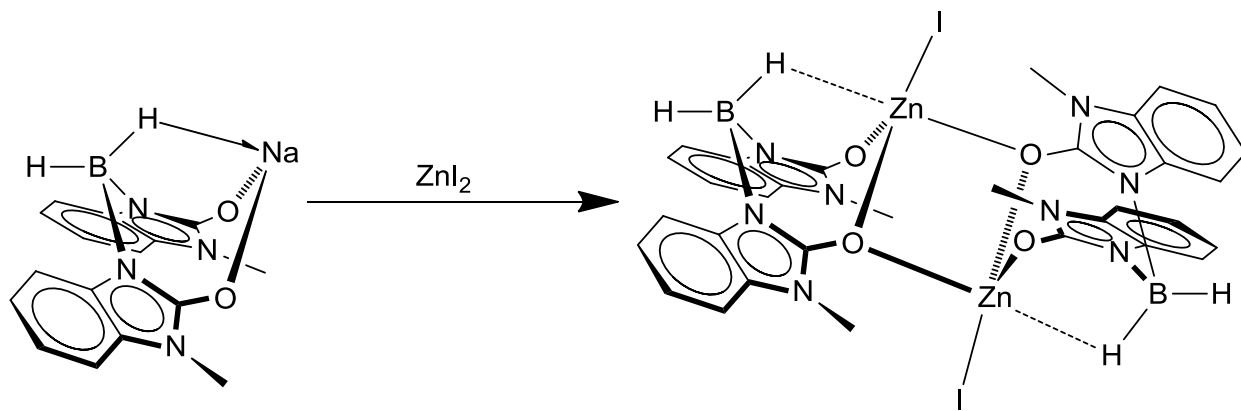
Scheme 3. Synthesis of {[Bo^{MeBenz}]ZnI}$_2$.
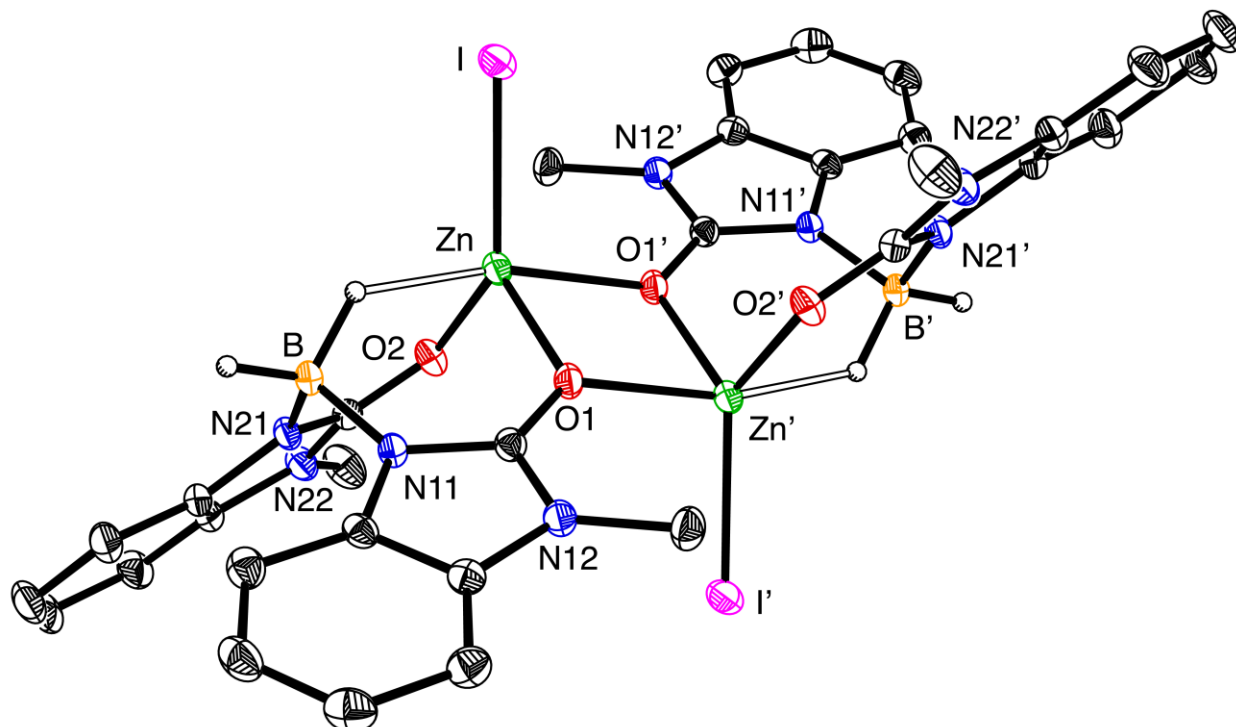
Figure 13. Molecular structure of {[Bo^{MeBenz}]ZnI}$_2$.

A 3–center–2–electron Zn•••H–B interaction ($d_{Zn•••H}$ = 1.97 Å and $d_{Zn•••B}$ = 2.85 Å)[17]

occupies an axial position in the trigonal bipyramid coordination environment of the

zinc. The trigonal plane is occupied by [O,O,I] whereas the apical positions are occupied

by the bridging oxygen and the Zn•••H–B interaction. There are other reported zinc

complexes that exhibit 3–center–2–electron B–H•••Zn interactions.[3a,b]

3.5 Gallium Iodide Supported by [Bo^{MeBenz}] Ligand

The [Bo^{MeBenz}] ligand is also effective for coordinating gallium metal. For example,

treatment of [Bo^{MeBenz}]Na with GaI$_3$ results in the formation of [Bo^{MeBenz}]GaI$_2$ while

{[Bo^{MeBenz}]GaI}$_2$ is formed as result of the reaction of [Bo^{MeBenz}]Na and "GaI"[18,19,20] (Scheme

4). The latter gallium complex features a Ga–Ga bond and the transformation is

formally accompanied by disproportionation, in accord with the previously reported reactivity of "GaI".[5b,19,20] Also, the [Bo^R] ligand is effective in supporting a interconversion between the two gallium complexes, [Bo^MeBenz]GaI$_2$ and {[Bo^MeBenz]GaI}$_2$. Specifically, the Ga–Ga bond of {[Bo^MeBenz]GaI}$_2$ can be cleaved by I$_2$ to give [Bo^MeBenz]GaI$_2$, while {[Bo^MeBenz]GaI}$_2$ can be regenerated by treatment of [Bo^MeBenz]GaI$_2$ with KC$_8$ (Scheme 4).
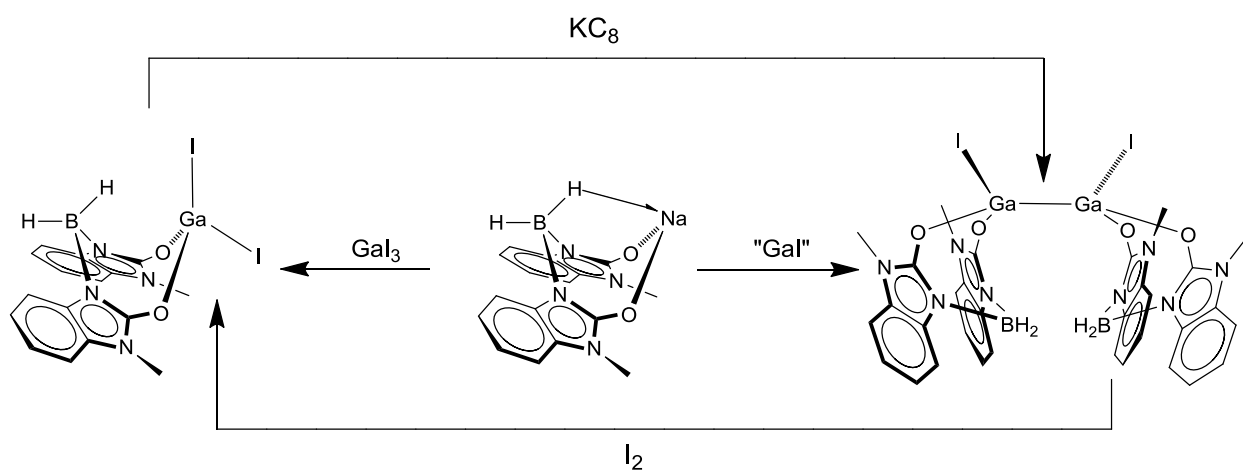
Scheme 4. Synthesis and interconversion of [Bo^MeBenz]GaI$_2$ and {[Bo^MeBenz]GaI}$_2$.

The molecular structures of [Bo^MeBenz]GaI$_2$ (Figure 14) and {[Bo^MeBenz]GaI}$_2$ (Figure 15) have been determined by X-ray diffraction. Even though there is no Ga•••H–B interaction, a noteworthy feature of both structures is that the [Bo^MeBenz]Ga moieties adopt a "boat-like" conformation, whereas those for [Bm^R]Ga in the mercapto counterparts, [Bm^R]GaI$_2$ and {[Bm^R]GaI}$_2$ are "chair-like" (Figure 16).[5b]
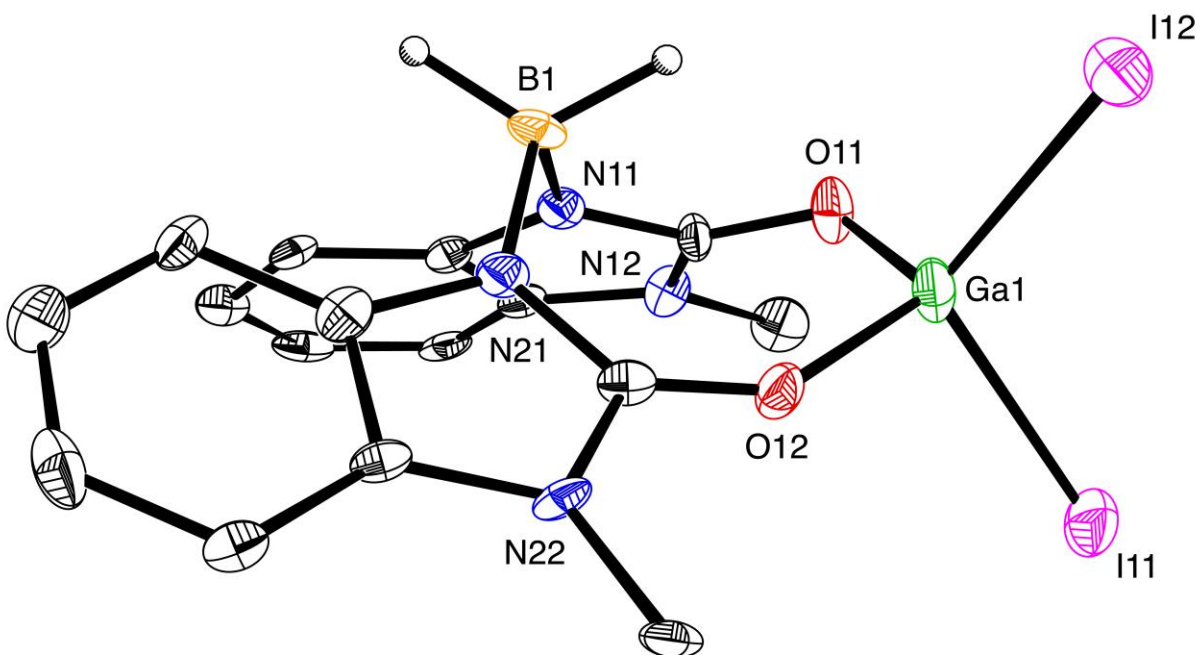
Figure 14. Molecular structure of [Bo^{MeBenz}]GaI$_2$.
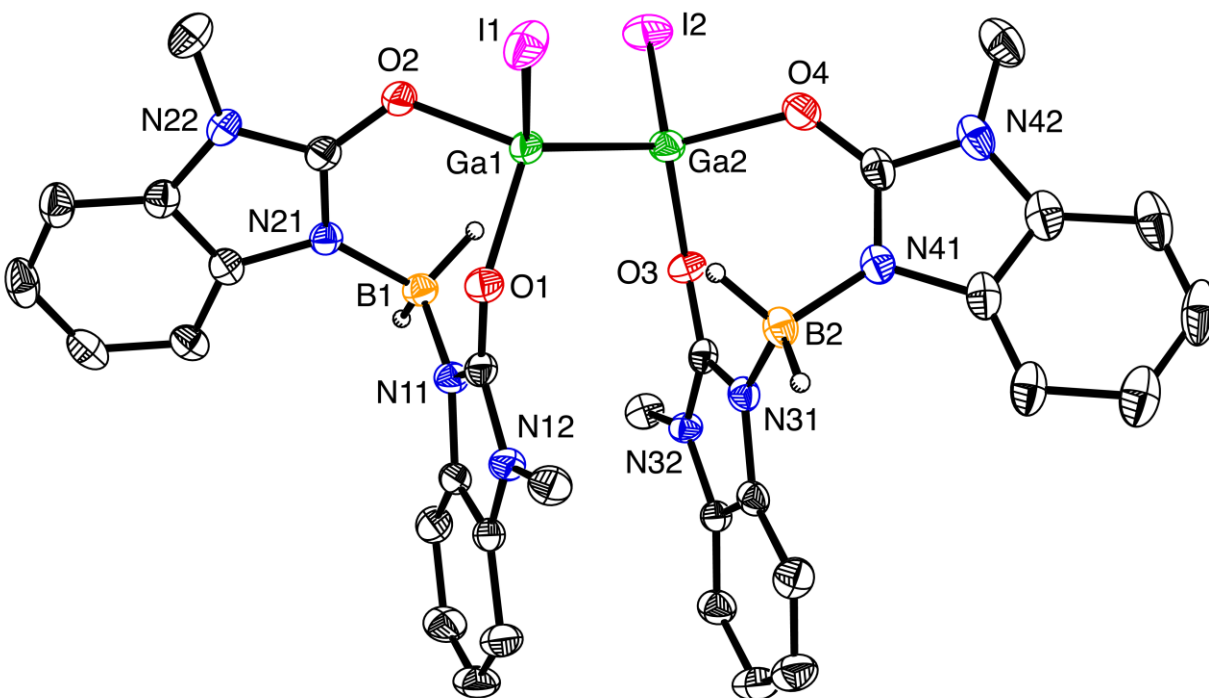
Figure 15. Molecular structure of {[Bo^{MeBenz}]GaI}$_2$.
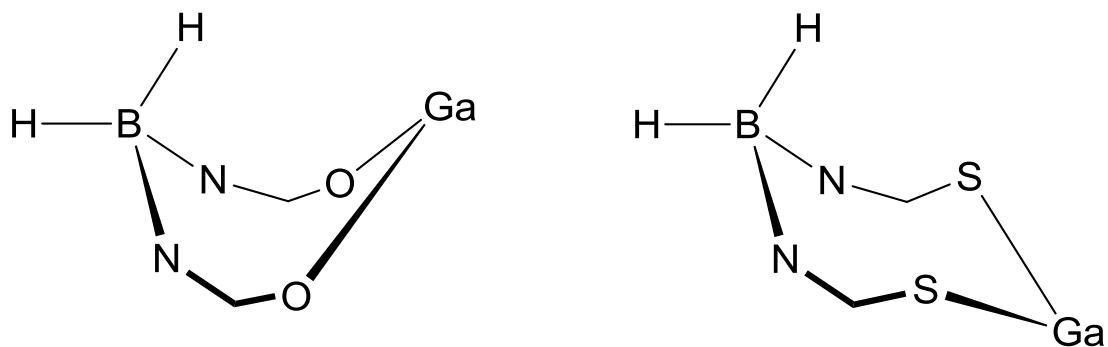
Figure 16. Coordination geometry of [Bo^{MeBenz}]Ga and [Bo^{MeBenz}]Ga motives: "boat-like" vs. "chair-like".

This is not the only difference in conformation between the structures of {[Bo^{MeBenz}]GaI}$_2$ and {[Bm^R]GaI}$_2$, since the two [Bm^R]GaI moieties of the latter adopt a *trans* conformation while the two [Bo^{MeBenz}]GaI moieties adopt an approximately eclipsed conformation in which the I–Ga–Ga–O torsion angles are 18.9° and 20.8°. Also, the I–Ga–Ga–I torsion angle is 101.9°, in contrast to a value of 180° for {[Bm^R]GaI}$_2$.[5b] Despite all these conformational differences, however, the Ga–Ga bond length for {[Bo^{MeBenz}]GaI}$_2$ [2.3995(6) Å] is comparable to the values in the mercapto counterparts, {[Bm^{But}]GaI}$_2$ [2.423(2) Å] and {[Bm^{Me}]GaI}$_2$ [2.414(2) Å].[5b]

3.6   [Bo^{MeBenz}]CuPMe$_3$

The use of [Bo^R] ligands is not restricted to main group metals; the ligands are also of use in transition metal chemistry. For example, treatment of [Bo^{MeBenz}]Na with [Me$_3$PCuCl]$_4$ yields [Bo^{MeBenz}]Cu(PMe$_3$) (Scheme 5). The molecular structure of [Bo^{MeBenz}]Cu(PMe$_3$) has been determined by X–ray diffraction (Figure 17). For

comparison purposes, we have also synthesized the sulfur counterpart. Specifically, {μ-[Bm[MeBenz]]Na(THF)$_2$}$_2$ has been treated with [Me$_3$PCuCl]$_4$ to produce the copper compound, [Bm[MeBenz]]CuPMe$_3$ (Scheme 5). The molecular structure of [Bm[MeBenz]]CuPMe$_3$ has been determined by X-ray diffraction, as illustrated in Figure 18. In both cases, the trigonal planar primary coordination sphere is supplemented by a Cu•••H–B interaction [$d_{Cu•••H}$ = 1.81 for [Bo[MeBenz]]Cu(PMe$_3$) and $d_{Cu•••H}$ = 1.90 Å for [Bm[MeBenz]]Cu(PMe$_3$)]. In accord with the presence of a Cu•••H–B interaction, the [Bo[MeBenz]] and [Bm[MeBenz]] ligands adopt a boat-like configuration. Furthermore, the Cu•••H–B interactions result in overall geometries that are trigonal monopyramidal. The τ_4 geometric indices of [Bo[MeBenz]]CuPMe$_3$ and [Bm[MeBenz]]CuPMe$_3$, 0.73 and 0.79 respectively, indicate that [Bm[MeBenz]]CuPMe$_3$ is closer to a trigonal monopyramid (0.85) than is [Bo[MeBenz]]CuPMe$_3$.[22] This is mainly due to the primary trigonal planar coordination of the [O$_2$CuP] core, deviating more from planarity than the [S$_2$CuP] core, as evidenced by the sums of the E–Cu–E and E–Cu–P angles in [Bo[MeBenz]]Cu(PMe$_3$) (350.6°) and [Bm[MeBenz]]Cu(PMe$_3$) (355.8°). The difference in the two P–Cu–O bond angles (15.3°) is considerably greater than the difference in the two P–Cu–S bond angles (2.0°). Comparing the primary trigonal planar coordination of [O$_2$CuP] in [Bo[MeBenz]]CuPMe$_3$ to that in [acac[R2]]Cu(PR′$_3$),[23] we find that both classes have O–Cu–O bond angles that are close to 90°. However, the Cu–O bond lengths for [Bo[MeBenz]]Cu(PMe$_3$) [2.017(2) Å and 2.073(2) Å] are slightly longer than those of [acac[R2]]Cu(PR′$_3$), *e.g.* [acac[(CF3)2]]Cu(PMe$_3$) [1.990(8) Å and 2.034(7) Å].[23b]
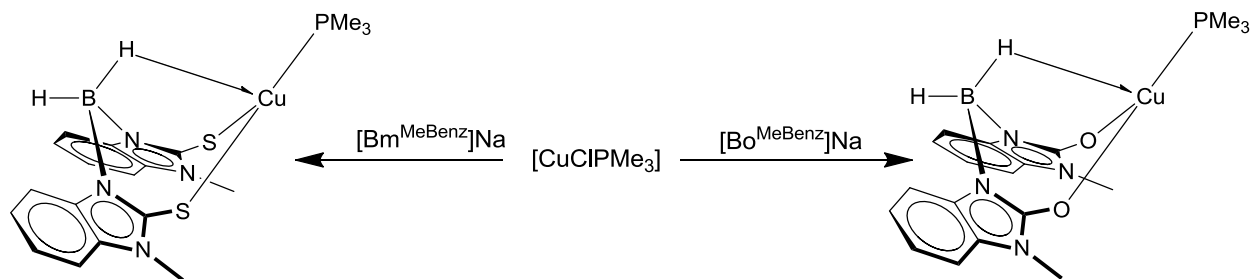
Scheme 5. Synthesis of [Bo^MeBenz]CuPMe_3 and [Bm^MeBenz]CuPMe_3.
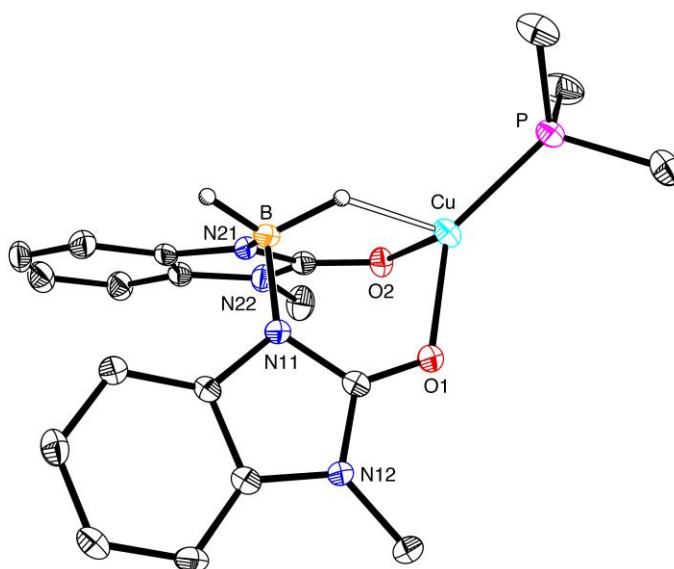
Figure 17. Molecular structure of [Bo^MeBenz]CuPMe_3.
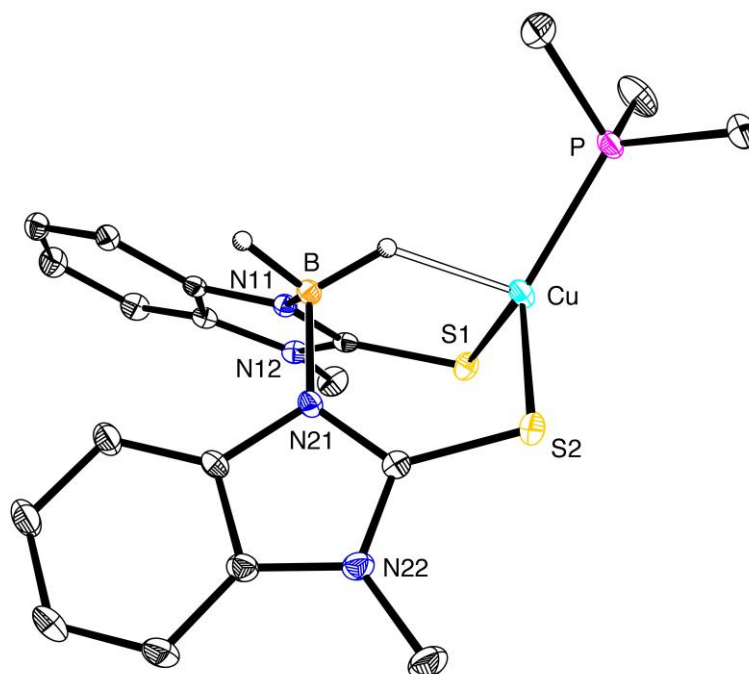
Figure 18. Molecular structure of [Bm^{MeBenz}]CuPMe$_3$.

3.7 General Structural Features for the [Bo^R] Ligand

A summary of the key structural data for various {[Bo^R]M} is illustrated in Table 1. As expected, the C–O bonds are slightly longer than those of the respective oxoimidazole. Secondly, the M–O$_{bridge}$ bonds are slightly longer than the corresponding M–O$_{term}$ bonds in structures where one of the oxygen donors bridge two metal centers. Finally as mentioned before, one of the most important features of the [Bo^R] ligand and also its selenium and sulfur counterparts is a flexible 8-membered ring.

Table 1. Selected metrical data for [Bo^R]M Complexes.[a]

	d(M–O$_{term}$)/Å	d(M–O$_{br}$)/Å	d(M···B)/Å	d(M···H)/Å	Δd/Å[b]
[[Bo^{MeBenz}]Cu(PMe$_3$)	2.05		2.78	1.81	0.73
{[Bo^{MeBenz}]ZnI}$_2$	1.96	2.11	2.85	1.97	0.89
[Bo$^{Bu^t}$]Tl	2.51		3.41	2.49	0.90
[Bo$^{Bu^t}$]Na(dig)	2.25		3.20	2.37	0.95
{[Bo$^{Bu^t}$]Li}$_2$	1.83	1.90	2.81	2.11	0.98
{[Bo$^{Bu^t}$]Na}$_2$(dig)	2.24	2.31	3.23	2.49	0.99
{[Bo^{MeBenz}]Na(dig)}$_2$	2.32	2.32	3.35	2.64	1.03
{[Bo^{MeBenz}]GaI}$_2$	1.90		3.32	2.75	1.42
[Bo^{MeBenz}]GaI$_2$	1.86		3.40	2.79	1.54

(a) Average values listed where appropriate. (b) $\Delta d = d$(M···B) - d(M–O$_{term}$).

This allows the B–H moiety to adjust its position to accommodate a 3-center-2-electron M···H–B interaction if required to supplement the bidentate [O_2] coordination. For example, the M···B distance is 2.78 Å for [Bo^{MeBenz}]Cu(PMe$_3$) and 3.41 Å for [Bo$^{Bu^t}$]Tl where both complexes possess M···H–B interaction. We devised a numerical gauge to indicate the significance of M···H–B interactions. This is simply accomplished by comparing the M···B distance relative to the average terminal M–O distances, *i.e.* $\Delta d = d$(M···B) – d(M–O$_{term}$). Based on this gauge, the most significant M···H–B interaction is in [Bo^{MeBenz}]Cu(PMe$_3$) (Δd = 0.73 Å), while the least significant interaction is in

[Bo^{MeBenz}]GaI$_2$ (Δd = 1.54 Å). Both results are reasonable with respect to common

coordination modes for each metal. The M•••H–B interaction in the former case leads to

a ML$_3$X complex, which is common for copper(I). For the latter complex, four-

coordinate gallium is a common motif and results due to the absence of any interaction

with the B–H group.[24]

3.8   Conclusion

A new class of bidentate ligands that features oxygen donors, namely the *bis*(2-oxo-1-t-

butylimidazolyl)hydroborato and *bis*(2-oxo-1-alkylbenzimidazolyl)hydroborato ligands,

[Bo$^{Bu^t}$] and [Bo^{RBenz}], has been synthesized *via* the reaction of MBH$_4$ with two equivalents

of the respective 2-imidazolone. Chelation of [Bo$^{Bu^t}$] and [Bo^{RBenz}] to a metal center

results in a flexible 8-membered ring that is capable of adopting a "boat-like"

conformation that allows for secondary M•••H–B interactions.

3.9   Experimental Section

3.9.1   General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and

Schlenk techniques under a nitrogen or argon atmosphere.[25] Solvents were purified and

degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX,

Bruker 400 DRX, Bruker 400 Cyber-enabled Avance III and Bruker Avance 500 DMX

spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to SiMe$_4$ (δ = 0) and

were referenced internally with respect to the protio solvent impurity (δ 7.16 for C$_6$D$_5$H,

5.32 for $CDHCl_2$ and 2.50 for d_6-DMSO).[26] ^{13}C NMR spectra are reported in ppm relative

to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for

C_6D_6, 53.84 for CD_2Cl_2 and 39.52 for d_6-DMSO).[26] ^{31}P chemical shifts are reported in ppm

relative to 85% H_3PO_4 ($\delta = 0$) and were referenced using $P(OMe)_3$ ($\delta = 141.0$) as an

external standard.[27] Coupling constants are given in hertz. Infrared spectra were

recorded on PerkinElmer Spectrum Two spectrometer and are reported in cm^{-1}. Mass

spectra were obtained on a Jeol JMS-HX110H Tandem Double-Focusing Mass

Spectrometer with a 10 kV accelerated voltage equipped with FAB ion source. $NaBH_4$

(Aldrich), $LiBH_4$ (Strem), GaI_3 (Strem), ZnI_2 (Aldrich) and TlOAc (Aldrich) were

obtained commercially and used as received while 1-*tert*-butyl-1,3-dihydro-2*H*-

imidazol-2-one,[28] 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-one,[29] 1-tert-butyl-1,3-

dihydro-benzimidazol-2-one,[30] $[Me_3PCuCl]_4$,[31] and "GaI"[18] were prepared by the

literature methods.

3.9.2   X-ray Structure Determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer

and crystal data, data collection and refinement parameters are summarized in Table 2.

The structures were solved using direct methods and standard difference map

techniques, and were refined by full-matrix least-squares procedures on F^2 with

SHELXTL (Version 2008/4).[32]

3.9.3   Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.6 (release 110, 2009) suite of *ab initio* quantum chemistry programs.[33] Geometry optimizations were performed with the B3LYP density functional[34] using the 6-31G** (H, C, N, O, B) and LAV3P (Se, Zn, I) basis sets,[35] and atomic coordinates are listed in Table 3.

3.9.4   Synthesis [Bo$^{Bu^t}$]Li

A mixture of 1-tert-butyl-1,3-dihydro-2*H*-imidazol-2-one (440 mg, 3.14 mmol) and LiBH$_4$ (34.1 mg, 1.57 mmol) was placed in a Fischer-Porter style bottle (3 oz),[36] treated with THF (*ca.* 6 mL) and heated at 100 °C overnight. The solvent was removed *in vacuo* and the residue obtained was extracted into benzene (*ca.* 6 mL) and lyophilized to yield {[Bo$^{Bu^t}$]Li}$_2$(THF) as a white powder (350 mg, 67%). Analysis calcd. for [Bo$^{Bu^t}$]Li·0.1CH$_2$Cl$_2$: C, 55.2%; H, 8.0%; N, 18.3%. Found: C, 55.2%; H, 7.9%; N, 18.0%. ^{1}H NMR (C$_6$D$_6$): 1.28 [s, 18H of H$_2$B{C$_2$N$_2$H$_2$[C(C$\underline{H}_3$)$_3$]CO}$_2$], 1.38 [m, 2H of 0.5 THF], 3.60 [m, 2H of 0.5 THF], 5.96 [d, $^3J_{H-H}$ = 3, 2H of H$_2$B{C$_2$N$_2$$\underline{H}_2$[C(CH$_3$)$_3$]CO}$_2$], 6.50 [d, $^3J_{H-H}$ = 3, 2H of H$_2$B{C$_2$N$_2$$\underline{H}_2$[C(CH$_3$)$_3$]CO}$_2$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 25.7 [2 C, 0.5 THF], 28.6 [6 C, H$_2$B{C$_2$N$_2$H$_2$[C($\underline{C}$H$_3$)$_3$]CO}$_2$], 54.4 [2 C, H$_2$B{C$_2$N$_2$H$_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_2$], 68.0 [2 C, 0.5 THF], 108.1 [2 C, H$_2$B{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_2$], 116.3 [2 C, H$_2$B{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_2$], 157.4 [2 C, H$_2$B{C$_2$N$_2$H$_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_2$]. IR Data (ATR, cm^{-1}): 2972 (m), 2935 (w), 2878 (w), 2378 (w), 2340 (w), 1628 (s), 1595 (vs), 1480 (m), 1427 (s), 1396 (w), 1366 (m), 1270 (m), 1216 (m), 1184 (s), 1138 (s), 1078 (m), 1054 (w), 1029 (w), 982 (w), 900 (w), 828 (w), 796 (m) 776 (m),

664 (vs), 585 (m), 554 (m), 458 (s). FAB-MS: m/z = 297.3 [M-1]$^+$, M = [Bo^{But}]Li. Crystals of composition [Bo^{But}]Li were obtained by vapor diffusion of pentane into a solution of [Bo^{But}]Li in benzene. Crystals of composition [Bo^{But}]Li•CH$_2$Cl$_2$ were obtained by vapor diffusion of pentane into a solution of [Bo^{But}]Li in CH$_2$Cl$_2$.

3.9.5   Synthesis of [Bo^{But}]Na

A mixture of 1-tert-butyl-1,3-dihydro-2H-imidazol-2-one (410 mg, 2.93 mmol) and NaBH$_4$ (55.4 mg, 1.46 mmol) was placed in a Fischer-Porter style bottle (3 oz),[36] treated with THF (*ca.* 6 mL) and heated at 100 °C overnight. The solvent was removed *in vacuo* and the residue obtained was extracted into benzene (*ca.* 5 mL) and lyophilized to yield [Bo^{But}]Na as white powder (320 mg, 70%). ^{1}H NMR (C$_6$D$_6$): 1.37 [s, 18H of H$_2$B{C$_2$N$_2$H$_2$[C(C$\underline{H}_3$)$_3$]CO}$_2$], 6.02 [d, $^3J_{H-H}$ = 3, 2H of H$_2$B{C$_2$N$_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_2$], 6.52 [d, $^3J_{H-H}$ = 3, 2H of H$_2$B{C$_2$N$_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_2$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 28.7 [6 C, H$_2$B{C$_2$N$_2$H$_2$[C($\underline{C}$H$_3$)$_3$]CO}$_2$], 53.8 [2 C, H$_2$B{C$_2$N$_2$H$_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_2$], 107.0 [2 C, H$_2$B{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_2$], 116.6 [2 C, H$_2$B{$\underline{C}_2$N$_2$H$_2$[C(CH$_3$)$_3$]CO}$_2$], 157.5 [2 C, H$_2$B{C$_2$N$_2$H$_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_2$]. IR Data (ATR, cm^{-1}): 2972 (m), 2926 (br), 2368 (br), 1617 (vs), 1480 (w), 1454 (m), 1421 (vs), 1364 (s), 1264 (s), 1214 (s), 1182 (vs), 1138 (vs), 1075 (m), 1027 (m), 976 (m), 790 (m), 774 (m), 700 (m), 654 (vs), 555 (m), 463 (w), 430 (w). FAB-MS: m/z = 337.3 [M+Na]$^+$, 313.3 [M–1]$^+$, M = [Bo^{But}]Na$_.$. Crystals of composition [Bo^{But}]Na•diglyme were obtained from a solution of [Bo^{But}]Na (*ca.* 50 mg, 0.16 mmol) and excess of diglyme (*ca.* 50 mg, 0.37 mmol) in hexane (*ca.* 2 mL), while crystals of

composition {[Bo$^{Bu^t}$]Na}$_2$•diglyme were obtained from a solution of [Bo$^{Bu^t}$]Na (50 mg, 0.16 mmol) and diglyme (10 mg, 0.07 mmol) in hexane (*ca.* 2 mL).

3.9.6   Synthesis of [Bo^{MeBenz}]Na

A mixture of 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-one (520 mg, 3.51 mmol) and NaBH$_4$ (66.4 mg, 1.76 mmol) was placed in a thick-walled ampoule capable of withstanding pressure and treated with toluene (*ca.* 10 mL). The mixture was heated at 145 °C for 4 days in a fume hood (*CAUTION!*), allowed to cool to room temperature and then filtered. The precipitate was washed sequentially with CH$_2$Cl$_2$ (*ca.* 10 mL) and pentane (*ca.* 10 mL) and dried *in vacuo* to give [Bo^{MeBenz}]Na as a white solid (370 mg, 64%). ^{1}H NMR (DMSO): 3.22 [s, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_2$], 6.82 [m, 6H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 7.47 [d, $^3J_{H-H}$ = 7, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]. ^{13}C{^{1}H} NMR (DMSO): 26.5 [2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_2$], 105.5 [2 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 110.9 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 118.3 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 119.5[2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 131.3 [2 C, H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_2$], 135.2 [2 C, H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_2$], 158.2 [2C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_2$]. IR Data (ATR, cm^{-1}): 3649 (w), 3238 (br), 3060 (w), 2412 (br), 2383 (br), 1620 (vs), 1596 (vs), 1488 (s), 1440 (s), 1393 (s), 1320 (m), 1216 (m), 1140 (s), 1122 (s), 1097 (s), 1020 (w), 1002 (m), 983 (w), 914 (w), 870 (w), 821 (w), 794 (w), 766 (s), 729 (vs), 717 (vs), 657 (w), 630 (w), 611 (m), 576 (m), 554 (s), 442 (m). FAB-MS: *m/z* =

329.2 [M-1]$^+$, M = [Bo^{MeBenz}]Na. Crystals of composition {[Bo^{MeBenz}]Na(diglyme)}$_2$ suitable

for X-ray diffraction were obtained from a mixture of diglyme and hexanes.

3.9.7 Synthesis of [Bo$^{Bu^tBenz}$]Na

A mixture of 1-*tert*-butyl-2-benzimidazolinone (700 mg, 3.68 mmol) and NaBH$_4$ (69.6

mg, 1.84 mmol) was placed in an ampoule and treated with THF (*ca.* 10 mL). The

mixture was heated at 140 °C for one day, and then cooled to room temperature.

Addition of pentane (*ca.* 10 mL) results in the formation of an off-white precipitate. The

precipitate was filtered and dried *in vacuo,* yielding [Bo$^{Bu^tBenz}$]Na•THF as an off-white

powder (600 mg, 67%). Analysis calcd. for [[Bo$^{Bu^tBenz}$]Na: C, 63.8%; H, 6.8%; N 13.5%.

Found: C, 62.9%; H, 7.7%; N 11.5%. ^{1}H NMR (C$_6$D$_6$): 1.37 [m, 4H of 2C$\underline{H}_2$ for THF], 1.52

[s, 18H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C(C$\underline{H}_3$)$_3$]CO}$_2$], 3.54 [m, 4H of 2C$\underline{H}_2$ for THF], 6.87 [t, 2H of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C(C$\underline{H}_3$)$_3$]CO}$_2$], 7.06 [t, 2H of H$_2$B{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_2$], 7.15 [d, 2H of

H$_2$B{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_2$], 8.05 [d, ^{3}J$_{H-H}$ = 7, 2H of H$_2$B{(C$_4$$\underline{H}_4$)C$_2N_2$(CH$_3$)CO}$_2$]. ^{13}C{^{1}H}

NMR (C$_6$D$_6$): 25.7 [2 C, methylene of the THF], 29.7 [6 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C($\underline{C}$H$_3$)$_3$]CO}$_2$],

57.4 [2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_2$], 67.9 [2 C, methylene of the THF], 111.8 [2 C,

H$_2$B{($\underline{C}$$_4H_4$)C$_2N_2$[C(CH$_3$)$_3$]CO}$_2$], 112.5 [2 C, H$_2$B{($\underline{C}$$_4H_4$)C$_2N_2$[C(CH$_3$)$_3$]CO}$_2$], 119.7 [2 C,

H$_2$B{($\underline{C}$$_4H_4$)C$_2N_2$[C(CH$_3$)$_3$]CO}$_2$], 121.1 [2 C, HB{($\underline{C}$$_4H_4$)C$_2N_2$[C(CH$_3$)$_3$]CO}$_2$], 131.2 [2 C,

H$_2$B{($\underline{C}$$_4H_4$)$\underline{C}_2N_2$[C(CH$_3$)$_3$]CO}$_2$], 135.9.0 [2 C, H$_2$B{(C$_4H_4$)$\underline{C}_2N_2$[C(CH$_3$)$_3$]CO}$_2$], 160.7 [2C,

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_2$]. FAB-MS: *m/z* = 413.3 [M-1]$^+$, M = [To$^{Bu^tBenz}$]Na.

Yellowish blocks of [Bo$^{\text{But Benz}}$]Na•2THF suitable for X-ray diffraction were obtained from the reaction mixture.

3.9.8   Synthesis of [Bo$^{\text{AdBenz}}$]Na

A mixture of 1-admantyl-2-benzimidazolinone (478 mg, 1.78 mmol) and NaBH$_4$ (33.7 mg, 0.89 mmol) was placed in an ampoule and treated with THF (*ca.* 7 mL). The mixture was heated at 150 °C for one day, and then cooled to room temperature. Addition of pentane (*ca.* 20 mL) results in the formation of off-white precipitate. The precipitate was filtered and dried *in vacuo,* yielding [Bo$^{\text{AdBenz}}$]Na•2THF as an off-white powder (400 mg, 70%). Analysis calcd. for [[Bo$^{\text{AdBenz}}$]Na•2THF: C, 70.6%; H, 7.2%; N 7.8%. Found: C, 69.1%; H, 7.2%; N 8.3%. ^{1}H NMR (DMSO): 1.73 [m, 12H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{\text{H}}_{15}$]CO}$_2$], 1.78 [m, 4H of 2C$\underline{\text{H}}_2$ for THF], 2.15 [br, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{\text{H}}_{15}$]CO}$_2$], 2.51 [br, 12H of H$_2$B{(C$_4H_4$)C$_2N_2$[C$_{10}$$\underline{\text{H}}_{15}$]CO}$_2$], 3.62 [m, 4H of 2C$\underline{\text{H}}_2$ for THF], 6.62 [t, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_2$], 6.72 [t, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_2$], 7.22 [d, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_2$], 7.62 [t, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_2$] . ^{13}C{^{1}H} NMR (DMSO): 25.1 [2 C, methylene of the THF], 29.3 [6C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[$\underline{\text{C}}_{10}H_{15}$]CO}$_2$], 35.9 [6C of H$_2$B{(C$_4H_4$)C$_2N_2$[$\underline{\text{C}}_{10}H_{15}$]CO}$_2$], 40.3 [6C of H$_2$B{(C$_4H_4$)C$_2N_2$[$\underline{\text{C}}_{10}H_{15}$]CO}$_2$], 57.9 [2C of H$_2$B{(C$_4H_4$)C$_2N_2$[$\underline{\text{C}}_{10}H_{15}$]CO}$_2$], 67.0 [2 C, methylene of the THF], 109.5 [2C of H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 111.4 [2C of H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 117.4 [2C of H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 118.5 [2C of H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 130.1 [2C of

$H_2B\{(C_4H_4)\underline{C}_2N_2[C_{10}H_{15}]CO\}_2]$, 135.8 [2C of $H_2B\{(C_4H_4)\underline{C}_2N_2[C_{10}H_{15}]CO\}_2]$, 157.7 [2C of $H_2B\{(C_4H_4)C_2N_2[C_{10}H_{15}]\underline{C}O\}_2]$. FAB-MS: m/z = 593.6 [M+Na]$^+$, M = [Bo^{MeBenz}]Na. Colorless blocks of [[Bo^{AdBenz}]Na•THF suitable for X-ray differaction were obtained from reaction mixture at room temperature.

3.9.9 Synthesis of [Bo$^{Bu^t}$]Tl

A filtered solution of {[Bo$^{Bu^t}$]Li}$_2$(THF) (95 mg, 0.14 mmol) in MeOH (*ca.* 2 mL) was treated with a solution of thallium(I) acetate (125 mg, 0.47 mmol) in water (*ca.* 10 mL), thereby resulting in the immediate formation of a white precipitate. The mixture was stirred for one hour and filtered. The precipitate was dried *in vacuo* overnight yielding [Bo$^{Bu^t}$]Tl as a white powder (55 mg, 40%). Analysis calcd. for [Bo$^{Bu^t}$]Tl: C, 33.9%; H, 4.9%; N, 11.3%. Found: C, 33.7%; H, 4.6%; N. 11.1%. ^{1}H NMR (C$_6$D$_6$): 1.32 [s, 18H of $H_2B\{C_2N_2H_2[C(C\underline{H}_3)_3]CO\}_2]$, 6.09 [d, $^3J_{H-H}$ = 3, 2H of $H_2B\{C_2N_2\underline{H}_2[C(CH_3)_3]CO\}_2]$, 6.52 [d, $^3J_{H-H}$ = 3, 2H of $H_2B\{C_2N_2\underline{H}_2[C(CH_3)_3]CO\}_2]$. ^{13}C{^{1}H} NMR (C$_6D_6$): 28.3 [6 C, $H_2B\{C_2N_2H_2[C(\underline{C}H_3)_3]CO\}_2]$, 54.0 [2 C, $H_2B\{C_2N_2H_2[\underline{C}(CH_3)_3]CO\}_2]$, 108.1 [2 C, $H_2B\{\underline{C}_2N_2H_2[C(CH_3)_3]CO\}_2]$, 116.2 [2 C, $H_2B\{\underline{C}_2N_2H_2[C(CH_3)_3]CO\}_2]$, 159.3 [2 C, $H_2B\{C_2N_2H_2[C(CH_3)_3]\underline{C}O\}_2]$. FAB-MS: m/z = 496.2 [M]$^+$ and 495.2 [M-1]$^+$ (overlapping), M = [Bo$^{Bu^t}$]Tl. Crystals of composition [Bo$^{Bu^t}$]Tl suitable for X-ray diffraction were obtained by vapor diffusion into a benzene solution.

3.9.10 Synthesis of [Bo$^{\text{MeBenz}}$]Tl

[Bo$^{\text{MeBenz}}$]Na (200 mg, 0.61 mmol) was dissolved in MeOH (*ca.* 10 mL) and filtered to

obtain a clear solution. The clear solution was treated with solution of thallium(I)

acetate (200 mg, 0.76 mmol) in water (*ca.* 10 mL) which results in the immediate

formation of a white precipitate. The mixture was stirred for 30 minutes and then

filtered. The residue was washed with water (2 × *ca.* 50 mL) and dried *in vacuo*

overnight yielding an off-white powder of [Bo$^{\text{MeBenz}}$]Tl (220 mg, 71%). Analysis calcd. for

[Bo$^{\text{MeBenz}}$]Tl: C, 37.6%; H, 3.2%; N, 11.0%. Found: C, 37.8%; H, 3.0%; N, 10.9%. ^{1}H NMR

(DMSO): 3.32 [s, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{\text{H}}_3$)CO}$_2$], 6.80 [m, 6H of

H$_2$B{(C$_4\underline{\text{H}}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 7.47 [m, 2H of H$_2$B{(C$_4\underline{\text{H}}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]. ^{13}C{^{1}H} NMR

(DMSO): 26.4[2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{\text{C}}$H$_3$)CO}$_2$], 105.4 [2 C, HB{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$],

111.0 [2 C, H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 118.2 [2 C, H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 119.5 [2 C,

H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 131.3 [2 C, H$_2$B{(C$_4$H$_4$)$\underline{\text{C}}_2$N$_2$(CH$_3$)CO}$_2$], 135.1 [2 C,

H$_2$B{(C$_4$H$_4$)$\underline{\text{C}}_2$N$_2$(CH$_3$)CO}$_2$], 158.3 [2C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{\text{C}}$O}$_2$]. Colorless plate of

[Bo$^{\text{MeBenz}}$]Tl suitable for X-ray were obtained from CH$_2$Cl$_2$ solution.

3.9.11 Synthesis of [Bo$^{\text{Bu}^{\text{t}}\text{Benz}}$]Tl

[Bo$^{\text{Bu}^{\text{t}}\text{Benz}}$]Na•THF (200 mg, 0.41 mmol) was dissolved in MeOH (*ca.* 5 mL) and filtered to

obtain a clear solution. The clear solution was treated with a solution of thallium(I)

acetate (130 mg, 0.49 mmol) in water (*ca.* 5 mL) which results in immediate formation

of white precipitate. The mixture was stirred for one hour and then filtered. The residue

was washed with water (*ca.* 10 mL) and dried *in vacuo* overnight yielding an off-white

powder of [Bo$^{\text{But Benz}}$]Tl (200 mg, 82%). Analysis calcd. for [Bo$^{\text{But Benz}}$]Tl: C, 44.4%; H, 4.7%;

N 9.4%. Found: C, 44.5%; H, 4.64%; N 9.2%.^{1}H NMR (C$_6$D$_6$): 1.53 [s, 18H of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C(C$\underline{H}_3$)$_3$]CO}$_2$], 6.88 [t, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$],

7.09 [t, $^3J_{\text{H-H}}$ = 9, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 7.15 [d, $^3J_{\text{H-H}}$ = 8, 2H of

H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 8.00 [d, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]. ^{13}C{^{1}H}

NMR (C$_6$D$_6$): 29.6 [m, 6 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C(C$\underline{H}_3$)$_3$]CO}$_2$], 57.6 [2 C,

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_2$], 111.9 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 112.6 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 119.8 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 121.1 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 131.6 [2 C, H$_2$B{($\underline{C}_4$H$_4$)$\underline{C}_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 135.6 [2 C,

H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$[C(CH$_3$)$_3$]CO}$_2$], 162.1 [2C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_2$]. FAB-MS: *m/z*

= 596.3 [M]$^+$, M = [Bo$^{\text{But Benz}}$]Tl. Colorless plate of [Bo$^{\text{But Benz}}$]Tl suitable for X-ray diffraction

were obtained from benzene.

3.9.12 Synthesis of [Bo$^{\text{AdBenz}}$]Tl

[Bo$^{\text{AdBenz}}$]Na•THF (300 mg, 0.47 mmol) was dissolved in THF (*ca.* 18 mL) and filtered to

obtain a clear solution. The clear solution is treated with solution of thallium(I) acetate

(330 mg, 1.25 mmol) in water (*ca.* 50 mL) which result in immediate formation of a

white precipitate. The mixture was stirred for one hour and then filtered. The residue

was washed with water (2 × *ca.* 50 mL) and dried *in vacuo* overnight yielding an off-

white powder of {[Bo$^{\text{AdBenz}}$]Tl}$_2$•THF (290 mg, 79%). Analysis calcd. For

{[Bo$^{\text{AdBenz}}$]Tl}$_2$•THF: C, 54.9%; H, 5.6%; N 7.1%. Found: C, 55.0%; H, 5.6%; N 6.9%. ^{1}H

NMR (DMSO): 1.73 [m, 12H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 1.78 [m, 4H of 2CH$_2$ for

THF], 2.15 [br, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 2.52 [br, 12H of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 3.62 [m, 4H of 2CH$_2$ for THF], 6.62 [t, $^3J_{\text{H-H}}$ = 8, 2H of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 6.72 [t, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 7.22

[d, $^3J_{\text{H-H}}$ = 8, 2H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 7.62 [t, $^3J_{\text{H-H}}$ = 8, 2H of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$]. ^{13}C{^{1}H} NMR (DMSO): 25.1 [2 C, methylene of the THF],

29.3 [6C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 35.9 [6C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 40.3

[6C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 57.9 [2C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 67.0 [2 C,

methylene of the THF], 109.4 [2C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 111.6 [2C of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 117.3 [2C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 118.4 [2C of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 130.1 [2C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 135.9 [2C of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$], 157.6 [2C of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_2$]. FAB-MS: m/z =

957.7 [M+Tl]$^+$, M = [Bo$^{\text{AdBenz}}$]Tl.

3.9.13 Synthesis of {[Bo$^{\text{MeBenz}}$]ZnI$_2$]}$_2$

A mixture of [Bo$^{\text{MeBenz}}$]Na (30 mg, 0.09 mmol) and ZnI$_2$ (40 mg, 0.13 mmol) was placed in

a thick-walled ampoule capable of withstanding pressure and treated with CH$_2$Cl$_2$ (*ca.* 2

mL). The mixture was heated at 60°C for 2 hours in a fume hood (*CARE!*) and allowed

to cool to room temperature. CH$_2$Cl$_2$ (*ca.* 10 mL) was added to the mixture, which was

stirred for few minutes and then filtered. The solvent was removed *in vacuo* and the

residue obtained was dissolved in benzene (*ca.* 5 mL) and then lyophilized to yield

{[Bo^{MeBenz}]ZnI}$_2$ as a white powder (22 mg, 49%). Analysis calcd. for

{[Bo^{MeBenz}]ZnI}$_2$•2(CH$_2$Cl$_2$): C, 34.9%; H, 3.1%; N, 9.6%. Found: C, 34.4%; H, 2.6%; N,

9.5%. ^{1}H NMR (CD$_2$Cl$_2$): 3.50 [s, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_2$], 7.06 [d, $^3J_{H-H}$ = 8, 2H

of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 7.12 [t, $^3J_{H-H}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]], 7.18 [t,

$^3J_{H-H}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]], 7.65 [d, $^3J_{H-H}$ = 8, 2H of

H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 27.9 [2 C,

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_2$], 108.3 [2 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 112.5 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 121.6 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 122.2 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 131.4 [2 C, H$_2$B{($\underline{C}_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_2$], 133.7 [2 C,

H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_2$], 159.8 [2C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_2$]. IR Data (ATR, cm^{-1}):

3334 (br), 2936 (w), 2439 (br), 2288 (br), 1613 (s), 1591 (vs), 1556 (vs), 1488 (s), 1453 (s),

1405 (s), 1325 (m), 1298 (m), 1257 (m), 1235 (m), 1120 (s), 1100 (s), 1046 (m), 998 (m), 926

(m), 873 (m), 821 (w), 789 (m), 746 (vs), 718 (s), 656 (m), 620 (m), 592 (m), 577 (s), 560 (s),

519 (s), 497 (m), 445 (s), 430 (s). FAB-MS: *m/z* = 497.2 [M]$^+$, M= [Bo^{MeBenz}]ZnI. Crystals of

composition {[Bo^{MeBenz}]ZnI}$_2$ were obtained from pumping down solution of CH$_2$Cl$_2$ and

crystals of composition {[Bo^{MeBenz}]ZnI}$_2$•2(CH$_2$Cl$_2$) were obtained from the reaction

mixture.

3.9.14 Synthesis of [Bo^{MeBenz}]GaI$_2$

A mixture of [Bo^{MeBenz}]Na (20 mg, 0.06 mmol) and GaI$_3$ (27 mg, 0.06 mmol) was treated

with benzene (*ca.* 4 mL). The resulting suspension was mixed with a pipette for several

minutes and then filtered. The filtrate was lyophilized and the solid obtained was

washed with pentane (*ca.* 2 mL) to give [Bo^{MeBenz}]GaI$_2$ as a white powder (10 mg, 26%).

^{1}H NMR (C$_6$D$_6$): 2.58 [s, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO}$_2$], 6.33 [d, $^3J_{H-H}$ = 8, 2H of

H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 6.88 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$],

7.05 [dt, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 7.77 [d, $^3J_{H-H}$ = 8, 2H of

H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO}$_2$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 27.4 [2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CO}$_2$],

109.3 [2 C, HB{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_3$], 113.8 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 122.8 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 123.5 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$], 130.4 [2 C,

H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_2$], 133.0 [2 C, H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO}$_2$], 156.3 [2C,

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$O}$_2$]. Crystals of composition [Bo^{MeBenz}]GaI$_2$ were obtained by

vapor diffusion of hexane into a benzene solution.

3.9.15 Synthesis of {[Bo^{MeBenz}]GaI}$_2$

A mixture of [Bo^{MeBenz}]Na (10 mg, 0.03 mmol) and "GaI" (6.0 mg, 0.03 mmol) was treated

with benzene (*ca.* 1 mL). The mixture was stirred for *ca.* 30 minutes and filtered.

Hexane was was added and allowed to diffuse into the benzene solution, thereby

resulting in the formation of colorless crystals of {[Bo^{MeBenz}]GaI}$_2$ (6.0 mg, 40%). Analysis

calcd. for {[Bo^{MeBenz}]GaI}$_2$·0.8C$_6$H$_6$: C, 41.3%; H, 3.5%; N, 10.5%. Found: C, 40.9%; H,

3.4%; N, 10.0%. ^{1}H NMR (C_6D_6): 2.75 [s, 6H of $H_2B\{(C_4H_4)C_2N_2(C\underline{H}_3)CO\}_2$], 6.23 [d, $^3J_{H-H}$ =

8, 2H of $H_2B\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_2$], 6.78 [t, $^3J_{H-H}$ = 8, 2H of $H_2B\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_2$],

6.91 [t, $^3J_{H-H}$ = 7, 2H of $H_2B\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_2$, 7.48 [d, $^3J_{H-H}$ = 8, 2H of

$H_2B\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 27.4 [2 C, $H_2B\{(C_4H_4)C_2N_2(\underline{C}H_3)CO\}_2$],

109.0 [2 C, $HB\{(\underline{C}_4H_4)C_2N_2(CH_3)CO\}_2$], 112.7 [2 C, $H_2B\{(\underline{C}_4H_4)C_2N_2(CH_3)CO\}_2$], 122.1 [2 C,

$H_2B\{(\underline{C}_4H_4)C_2N_2(CH_3)CO\}_2$], 122.8 [2 C, $H_2B\{(\underline{C}_4H_4)C_2N_2(CH_3)CO\}_2$], 130.7 [2 C,

$H_2B\{(C_4H_4)\underline{C}_2N_2(CH_3)CO\}_2$], 133.0 [2 C, $H_2B\{(C_4H_4)\underline{C}_2N_2(CH_3)CO\}_2$], 157.6 [2C,

$H_2B\{(C_4H_4)C_2N_2(CH_3)\underline{C}O\}_2$].

3.9.16 Interconversion of $\{[Bo^{MeBenz}]GaI\}_2$ and $[Bo^{MeBenz}]GaI_2$

A solution of $\{[Bo^{MeBenz}]GaI\}_2$ (*ca.* 10 mg, 0.01 mmol) in C_6D_6 (*ca.* 1 mL) was titrated with

a solution of I_2 in C_6D_6 (*ca.* 0.01 M). The reaction was monitored by ^{1}H NMR

spectroscopy, thereby demonstrating the formation of $[Bo^{MeBenz}]GaI_2$. The solution was

then treated with KC_8 (*ca.* 4 mg), thereby resulting in the regeneration of $\{[Bo^{MeBenz}]GaI\}_2$

as indicated by ^{1}H NMR spectroscopy.

3.9.17 Synthesis of $[Bo^{MeBenz}]CuPMe_3$

A mixture of $[Bo^{MeBenz}]Na$ (40 mg, 0.12 mmol) and $[Me_3PCuCl]_4$ (15.9 mg, 0.02 mmol)

was treated with benzene (*ca.* 2 mL). The suspension was mixed with a pipette for

several minutes and then filtered. Pentane (*ca.* 2 mL) was added slowly to the filtrate

until the solution became turbid, which was then placed at -16 °C, thereby depositing

colorless crystals of $[Bo^{MeBenz}]CuPMe_3$ (15.0 mg, 37%). Analysis calcd. for

[Bo$^{\text{MeBenz}}$]CuPMe$_3$•0.3C$_6$H$_6$: C, 53.1%; H, 5.7%; N, 11.9%. Found: C, 53.5%; H, 5.6%; N,

11.5%. Crystals of composition [Bo$^{\text{MeBenz}}$]CuPMe$_3$•0.5C$_5$H$_{12}$ suitable for X-ray diffraction

were obtained from diffusion of pentane into toluene at -16 °C. ^{1}H NMR (C$_6$D$_6$): 0.81 [d,

^{2}J$_{\text{P-H}}$=7, 9H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$CuP(C$\underline{\text{H}}_3$)$_3$], 2.85 [s, 6H of

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{\text{H}}_3$)CO}$_2$CuP(CH$_3$)$_3$], 6.45 [d, ^{3}J$_{\text{H-H}}$= 8, 2H of

H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 6.92 [t, ^{3}J$_{\text{H-H}}$= 8, 2H of

H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 7.11 [t, ^{3}J$_{\text{H -H}}$= 8, 2H of

H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 7.99 [d, ^{3}J$_{\text{H-H}}$= 8, 2H of

H$_2$B{(C$_4$$\underline{\text{H}}_4$)C$_2N_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 15.5 [3 C, ^{1}J$_{\text{P-C}}$ = 23,

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$CuP($\underline{\text{C}}$H$_3$)$_3$], 26.7 [2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{\text{C}}$H$_3$)CO}$_2$CuP(CH$_3$)$_3$],

107.2 [2 C, H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 112.2 [2 C,

H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 120.4 [2 C, H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$],

121.6 [2 C, H$_2$B{($\underline{\text{C}}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 132.1 [2 C,

H$_2$B{(C$_4$H$_4$)$\underline{\text{C}}_2$N$_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$], 134.7 [2C, H$_2$B{(C$_4$H$_4$)$\underline{\text{C}}_2$N$_2$(CH$_3$)CO}$_2$CuP(CH$_3$)$_3$],

161.7 [2C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{\text{C}}$O}$_2$CuP(CH$_3$)$_3$]. ^{31}P NMR (C$_6$D$_6$): –47.3.

3.9.18 Synthesis of [Bm$^{\text{MeBenz}}$]Na

A mixture of 1-methyl-2-benzimidazole-2-thione (500 mg, 3.05 mmol) and NaBH$_4$ (57.6

mg, 1.52 mmol) was placed in a Fischer-Porter style bottle (3 oz),[36] treated with THF (*ca.*

4 mL) and heated at 100 °C overnight. The mixture was allowed to cool to room

temperature and then placed at –10 °C, thereby depositing large colorless crystals of

{μ-[Bm^{MeBenz}]Na(THF)$_2$}$_2$. The mixture was then placed at –78 $^\circ$C, resulting in further

deposition. The mixture was filtered and the precipitate was dried *in vacuo* to give

{μ-[Bm^{MeBenz}]Na(THF)$_2$}$_2$ as a white solid (300 mg, 39%). The filtrate was allowed to sit at

room temperature for two days, over which period additional {μ-[Bm^{MeBenz}]Na(THF)$_2$}$_2$

was deposited, isolated by filtration and dried *in vacuo* (160 mg, total yield 60%).

Analysis calcd. for {μ-[Bm^{MeBenz}]Na(THF)$_2$}$_2$: C, 56.9%; H, 6.4%; N, 11.1%. Found: C,

56.8%; H, 6.1%; N, 11.0%. ^{1}H NMR for {Bm^{MeBenz}]Na}(THF)$_2$ (d_6-DMSO): 1.76 [m, 8H of 2

THF], 3.60 [m, 8H of 2 THF], 3.64 [s, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CS}$_2$], 6.93 [m, 4H of

H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$], 7.09 ["d", ^{3}J$_{H-H}$ = 7, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$], 8.18

["d", ^{3}J$_{H-H}$ = 7, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$]. ^{13}C{^{1}H} NMR (DMSO): 25.1 [4 C, CH$_2$ of

the THF], 30.5 [2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CS}$_2$], 67.0 [4 C, CH$_2$ of the THF], 107.2 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$], 114.3 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$], 120.4 [2 C,

H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$], 120.8 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$], 133.4 [2 C,

H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CS}$_2$], 137.2 [2 C, H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CS}$_2$], 172.3 [2C,

H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$S}$_2$]. FAB-MS: *m/z* = 385.1 [M + Na]$^+$, M = [Bm^{MeBenz}]Na. IR Data

(ATR, cm^{-1}): 3051 (w), 3016 (w), 2969 (m), 2875 (m), 2444 (br), 1607 (w), 1483 (m), 1461

(w), 1435 (m), 1422 (w), 1388 (m), 1337 (vs), 1311 (s), 1238 (m), 1178 (m), 1156 (w), 1117

(m), 1092 (m), 1044 (m), 1023 (m), 1018 (w), 980 (m), 917 (w), 887 (m), 767 (s), 745 (s), 652

(w), 420 (s).

3.9.19 Synthesis of [Bm^{MeBenz}]CuPMe$_3$

A mixture of {μ-[Bm^{MeBenz}]Na(THF)$_2$}$_2$ (30 mg, 0.03 mmol) and [Me$_3$PCuCl]$_4$ (9.0 mg, 0.01 mmol) was treated with benzene (*ca.* 4 mL). The resulted suspension was mixed with a pipette for several minutes and then filtered. The filtrate was lyophilized and the solid obtained was washed with pentane (*ca.* 3 mL) to give [Bm^{MeBenz}]CuPMe$_3$ as a white powder (15 mg, 61%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a benzene solution. Analysis calcd. for [Bm^{MeBenz}]CuPMe$_3$: C, 47.7%; H, 5.3%; N, 11.7%. Found: C, 47.9%; H, 5.0%; N, 11.5%. ^{1}H NMR (C$_6$D$_6$): 0.91 [d, $^2J_{P-H}$= 5, 9H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(C$\underline{H}_3$)$_3$], 3.10 [s, 6H of H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CS}$_2$CuP(CH$_3$)$_3$], 6.43 [d, $^3J_{H-H}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 6.87 [t, $^3J_{H-H}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 7.01 [t, $^3J_{H-H}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 7.96 [d, $^3J_{H-H}$ = 8, 2H of H$_2$B{(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 15.6 [d, $^1J_{P-C}$ = 19, 3 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP($\underline{C}$H$_3$)$_3$], 30.7 [2 C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$($\underline{C}$H$_3$)CS}$_2$CuP(CH$_3$)$_3$], 108.8 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 114.0 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 122.0 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 122.6 [2 C, H$_2$B{($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 134.7 [2 C, H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], 137.5 [2C, H$_2$B{(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CS}$_2$CuP(CH$_3$)$_3$], not showing [2C, H$_2$B{(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)$\underline{C}$S}$_2$CuP(CH$_3$)$_3$]. ^{31}P{^{1}H} (C$_6$D$_6$): -47.9. IR Data (ATR, cm^{-1}): 3059 (w), 2965 (w), 2900 (w), 2390 (br), 2260 (br), 1613 (w), 1483 (m), 1436

(m), 1398 (m), 1376 (m), 1344 (s), 1301 (m), 1235 (m), 1176 (w), 1153 (w), 1116 (m), 1097

(m), 1017 (w), 981 (w), 952 (m), 845 (w), 794 (w), 734 (vs), 700 (w), 650 (w), 612 (w), 553

(m), 435 (w), 419 (s), 402 (w).

3.10 Crystallographic Data

Table 2. Crystal, intensity collection and refinement data.

	[Bo$^{Bu^t}$]Li	[Bo$^{Bu^t}$]Li·0.5CH$_2$Cl$_2$
lattice	Triclinic	Triclinic
formula	C$_{28}$H$_{48}$B$_2$Li$_2$N$_8$O$_4$	C$_{29}$H$_{50}$B$_2$Cl$_2$Li$_2$N$_8$O$_4$
formula weight	596.24	681.17
space group	P-1	P-1
a/Å	9.7018(13)	9.4956(11)
b/Å	11.7027(16)	12.2278(14)
c/Å	15.355(2)	16.2888(18)
α/°	101.550(2)	89.903(2)
β/°	100.886(2)	74.243(2)
γ/°	96.742(2)	85.331(2)
V/Å^3	1655.4(4)	1813.8(4)
Z	2	2
temperature (K)	130(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.196	1.247
μ (Mo Kα), mm^{-1}	0.079	0.223
θ max, deg.	25.51	31.02
no. of data collected	18873	30106
no. of data used	6184	11448
no. of parameters	425	452
R_1 [$I > 2\sigma(I)$]	0.0504	0.0590
wR_2 [$I > 2\sigma(I)$]	0.0794	0.1450
R_1 [all data]	0.0952	0.1094
wR_2 [all data]	0.0909	0.1694
GOF	1.165	1.056
R_{int}	0.0692	0.0488

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[Bo$^{Bu^t}$]Na·diglyme	{[Bo$^{Bu^t}$]Na}$_2$·diglyme
lattice	Monoclinic	Monoclinic
formula	$C_{20}H_{38}BN_4NaO_5$	$C_{40}H_{76}B_2N_8Na_2O_7$
formula weight	448.34	848.69
space group	$P2_1/n$	Cc
$a/\text{Å}$	9.546(2)	23.626(3)
$b/\text{Å}$	9.704(2)	15.8447(18)
$c/\text{Å}$	27.190(6)	17.432(2)
$\alpha/°$	90	90
$\beta/°$	97.744(4)	128.969(2)
$\gamma/°$	90	90
$V/\text{Å}^3$	2495.9(10)	5073.7(10)
Z	4	4
temperature (K)	130(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.193	1.111
μ (Mo Kα), mm^{-1}	0.099	0.090
θ max, deg.	31.09	28.28
no. of data collected	40047	34739
no. of data used	7870	12506
no. of parameters	296	509
R_1 [$I > 2\sigma(I)$]	0.0617	0.0513
wR_2 [$I > 2\sigma(I)$]	0.1145	0.0628
R_1 [all data]	0.1640	0.0995
wR_2 [all data]	0.1450	0.0687
GOF	1.003	1.016
R_{int}	0.1159	0.0706

Table 2. (cont.) Crystal, intensity collection and refinement data.

	{[Bo^{MeBenz}]Na(diglyme)}$_2$	{[Bo$^{Bu^tBenz}$]Na(THF)}$_2$
lattice	Triclinic	Monoclinic
formula	$C_{44}H_{60}B_2N_8Na_2O_{10}$	$C_{26}H_{36}BN_4O_3Na$
formula weight	928.60	486.39
space group	$P\text{-}1$	$P2_1/c$
$a/\text{Å}$	11.2105(11)	10.097(2)
$b/\text{Å}$	11.7527(11)	12.902(3)
$c/\text{Å}$	19.0172(18)	20.081(5)
$\alpha/°$	76.2150(10)	90
$\beta/°$	79.2350(10)	91.683(4)
$\gamma/°$	82.7380(10)	90
$V/\text{Å}^3$	2381.8(4)	2614.7(11)
Z	2	4
temperature (K)	130(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.295	1.236
μ (Mo Kα), mm^{-1}	0.107	0.095
θ max, deg.	32.02	31.58
no. of data collected	41548	43750
no. of data used	16150	8728
no. of parameters	619	330
R_1 [$I > 2\sigma(I)$]	0.0599	0.0595
wR_2 [$I > 2\sigma(I)$]	0.1377	0.1619
R_1 [all data]	0.1233	0.0907
wR_2 [all data]	0.1658	0.1860
GOF	1.024	1.059
R_{int}	0.0516	0.0495

Table 2. (cont.) Crystal, intensity collection and refinement data.

	$\{[Bo^{AdBenz}]Na(THF)\}_2$	$[Bo^{Bu^t}]Tl$
lattice	Triclinic	Monoclinic
formula	$C_{84}H_{110}B_2N_8O_8Na_2$	$C_{14}H_{24}BN_4O_2Tl$
formula weight	1427.40	495.55
space group	$P\text{-}1$	$P2_1/c$
$a/Å$	11.5310(9)	13.5424(10)
$b/Å$	12.0586(9)	5.9912(5)
$c/Å$	15.2849(12)	22.3075(17)
$\alpha/°$	104.8730(10)	90
$\beta/°$	98.0770(10)	105.2950(10)
$\gamma/°$	110.0860(10)	90
$V/Å^3$	1867.0(2)	1745.8(2)
Z	1	4
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.270	1.885
μ (Mo Kα), mm^{-1}	0.091	9.262
θ max, deg.	31.14	32.80
no. of data collected	30965	29121
no. of data used	11834	6148
no. of parameters	538	207
R_1 [$I > 2\sigma(I)$]	0.0603	0.0263
wR_2 [$I > 2\sigma(I)$]	0.1588	0.0512
R_1 [all data]	0.0860	0.0406
wR_2 [all data]	0.1768	0.0549
GOF	1.058	1.025
R_{int}	0.0276	0.0433

Table 2. (cont.) Crystal, intensity collection and refinement data.

	{[Bo^{MeBenz}]Tl}	{[Bo$^{Bu^tBenz}$]Tl}
lattice	Triclinic	Monoclinic
formula	C$_{16}$H$_{16}$BN$_4$O$_2$Tl	C$_{22}$H$_{28}$BN$_4$O$_2$Tl
formula weight	511.51	595.66
space group	P-1	$P2_1/c$
a/Å	8.7572(13)	9.6961(10)
b/Å	8.8944(13)	26.190(3)
c/Å	11.2406(16)	9.8721(10)
α/°	111.184(2)	90
β/°	94.055(2)	118.0950(10)
γ/°	102.591(2)	90
V/Å^3	785.9(2)	2211.5(4)
Z	2	4
temperature (K)	150(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	2.162	1.789
μ (Mo Kα), mm^{-1}	10.292	7.329
θ max, deg.	31.50	30.75
no. of data collected	13257	35591
no. of data used	5163	6872
no. of parameters	227	316
R_1 [$I > 2\sigma(I)$]	0.0398	0.0374
wR_2 [$I > 2\sigma(I)$]	0.0669	0.0750
R_1 [all data]	0.0625	0.0524
wR_2 [all data]	0.0723	0.0798
GOF	1.040	1.069
R_{int}	0.0503	0.0386

Table 2. (cont.) Crystal, intensity collection and refinement data.

	{[Bo^{MeBenz}]ZnI}$_2$	{[Bo^{MeBenz}]ZnI}$_2$ •2(CH$_2$Cl$_2$)
lattice	Triclinic	Triclinic
formula	C$_{32}$H$_{32}$B$_2$I$_2$N$_8$O$_4$Zn$_2$	C$_{34}$H$_{36}$B$_2$Cl$_4$I$_2$N$_8$O$_4$Zn$_2$
formula weight	998.82	1168.67
space group	P-1	P-1
a/Å	8.797(3)	8.9863(11)
b/Å	10.599(4)	10.5954(13)
c/Å	11.305(4)	12.2767(14)
α/°	68.735(5)	74.050(2)
β/°	78.585(5)	72.881(2)
γ/°	67.408(5)	68.703(2)
V/Å^3	904.8(5)	1022.2(2)
Z	1	1
temperature (K)	200(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.833	1.899
μ (Mo Kα), mm^{-1}	3.080	2.994
θ max, deg.	29.57	31.02
no. of data collected	13690	16936
no. of data used	5055	6444
no. of parameters	236	263
R_1 [$I > 2\sigma(I)$]	0.0344	0.0408
wR_2 [$I > 2\sigma(I)$]	0.0739	0.0675
R_1 [all data]	0.0556	0.0694
wR_2 [all data]	0.0811	0.0748
GOF	1.008	1.071
R_{int}	0.0333	0.0510

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[Bo^{MeBenz}]GaI$_2$	{[Bo^{MeBenz}]GaI}$_2$
lattice	Orthorhombic	Monoclinic
formula	C$_{16}$H$_{16}$BGaI$_2$N$_4$O$_2$	C$_{47}$H$_{51}$B$_2$Ga$_2$I$_2$N$_8$O$_4$
formula weight	630.66	1206.82
space group	$Pbca$	$P2_1/n$
a/Å	20.5059(18)	16.6643(12)
b/Å	15.3790(14)	16.3434(11)
c/Å	24.714(2)	18.5556(13)
α/°	90	90
β/°	90	96.9820(10)
γ/°	90	90
V/Å^3	7793.7(12)	5016.2(6)
Z	16	4
temperature (K)	130(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	2.150	1.598
μ (Mo Kα), mm^{-1}	4.599	2.355
θ max, deg.	23.26	28.28
no. of data collected	68595	68652
no. of data used	5600	12435
no. of parameters	467	555
R_1 [$I > 2\sigma(I)$]	0.0682	0.0458
wR_2 [$I > 2\sigma(I)$]	0.1618	0.0758
R_1 [all data]	0.1268	0.0959
wR_2 [all data]	0.1912	0.0853
GOF	1.230	1.029
R_{int}	0.2089	0.0798

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[Bo$^{\text{MeBenz}}$]CuPMe$_3$	{μ-[Bm$^{\text{MeBenz}}$]Na(THF)$_2$}$_2$
lattice	Triclinic	Triclinic
formula	C$_{21.50}$H$_{31}$BCuN$_4$O$_2$P	C$_{48}$H$_{64}$B$_2$N$_8$Na$_2$O$_4$S$_4$
formula weight	482.82	1012.91
space group	*P-1*	*P-1*
a/Å	8.8727(12)	10.2914(9)
b/Å	10.0513(14)	10.6050(9)
c/Å	14.569(2)	12.5970(11)
α/°	90.266(2)	111.1290(10)
β/°	101.055(2)	94.9240(10)
γ/°	112.945(2)	95.1530(10)
V/Å^3	1169.8(3)	1266.85(19)
Z	2	1
temperature (K)	130(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.371	1.328
μ (Mo Kα), mm^{-1}	1.027	0.257
θ max, deg.	30.97	30.51
no. of data collected	19535	20510
no. of data used	7374	7686
no. of parameters	266	317
R_1 [$I > 2\sigma(I)$]	0.0576	0.0500
wR_2 [$I > 2\sigma(I)$]	0.0879	0.1268
R_1 [all data]	0.1226	0.0718
wR_2 [all data]	0.0981	0.1396
GOF	1.009	1.077
R_{int}	0.0761	0.0356

Table 2. (cont.) Crystal, intensity collection and refinement data.

	[Bm$^{\text{MeBenz}}$]CuPMe$_3$
lattice	Monoclinic
formula	C$_{19}$H$_{25}$BN$_4$S$_2$PCu
formula weight	478.87
space group	$P2_1/c$
a/Å	15.943(2)
b/Å	8.8788(11)
c/Å	16.066(2)
α/°	90
β/°	103.346(2)
γ/°	90
V/Å^3	2212.7(5)
Z	4
temperature (K)	150(2)
radiation (λ, Å)	0.71073
ρ (calcd.), g cm^{-3}	1.437
μ (Mo Kα), mm^{-1}	1.261
θ max, deg.	32.73
no. of data collected	37547
no. of data used	7811
no. of parameters	266
R_1 [$I > 2\sigma(I)$]	0.0310
wR_2 [$I > 2\sigma(I)$]	0.0789
R_1 [all data]	0.0432
wR_2 [all data]	0.0848
GOF	1.041
R_{int}	0.0359

Table 3. Cartesian coordinates for geometry optimized structures of {[Bo^{MeBenz}]ZnI}$_2$ and

{[Bse^{Me}]ZnI}$_2$.

{[Bo^{MeBenz}]ZnI}$_2$

(-2181.80813350053 Hartrees)

atom	x	y	z
Zn	3.261304282	5.689300341	0.290430918
B	3.070991509	8.359393026	-0.899339917
H	3.333955752	9.520188815	-0.746008397
H	3.447463046	7.743544471	0.082822383
I	3.806442841	5.823746711	2.8617267
O	1.341701745	5.916938715	-0.551322617
O	4.483470108	5.697785236	-1.315610639
N	1.522386324	8.207111944	-1.020766748
N	-0.51048119	7.290452266	-1.045757043
N	3.822739151	7.805526282	-2.144212145
N	5.141718312	6.504784911	-3.393045003
C	-1.588464531	6.31494868	-0.951154376
H	-1.375440848	5.605239307	-0.152228125
H	-1.722477571	5.781598149	-1.896109429
H	-2.508289738	6.846248581	-0.699542645
C	0.824435964	7.056947394	-0.857692294
C	-0.677285583	8.645574677	-1.338670543
C	0.601862497	9.222237987	-1.298433143
C	0.767953606	10.59287122	-1.494062585
H	1.746040912	11.05290131	-1.419300666
C	-0.37278647	11.35087208	-1.759797417
H	-0.272654896	12.42066679	-1.916624833
C	-1.644559489	10.76297271	-1.823462492
H	-2.510779664	11.38131392	-2.03841594
C	-1.818912843	9.395196121	-1.609626104
H	-2.803057341	8.94099628	-1.657694589
C	5.928315391	5.359813392	-3.808373459
H	5.853322811	4.596571284	-3.034583748

H	6.978613209	5.64086328	-3.939625243
H	5.543922484	4.955173133	-4.74981545
C	4.468315272	6.608746149	-2.201077914
C	4.917943257	7.666634278	-4.130151475
C	4.086958602	8.481531083	-3.342150994
C	3.676401665	9.727742078	-3.806376071
H	3.026801507	10.36064083	-3.214546046
C	4.121464519	10.12865019	-5.068509582
H	3.813871818	11.09599292	-5.454359492
C	4.950825517	9.310728066	-5.846802251
H	5.27707248	9.653305706	-6.824072682
C	5.364905788	8.05788787	-5.387231225
H	6.006904089	7.420279898	-5.98655755
Zn	0.725105587	3.800896138	-0.597217662
B	0.931542178	1.381295999	1.103913551
H	0.615673468	0.227995657	1.208220948
H	0.486763393	1.821717951	0.056634943
I	0.03826053	3.281561456	-3.072186162
O	2.707879882	3.598637549	0.078516753
O	-0.341829147	4.133060933	1.090292759
N	2.491387788	1.472829142	1.055558483
N	4.54364929	2.278133574	0.72669728
N	0.333627446	2.209725966	2.276293924
N	-0.753591449	3.833425141	3.357921699
C	5.636071187	3.158936065	0.346016909
H	5.296911667	3.856696292	-0.418009447
H	6.004206601	3.717024319	1.212262519
H	6.445275568	2.55244135	-0.069528699
C	3.205708551	2.524738829	0.594382256
C	4.69715388	1.01975998	1.307605925
C	3.40389127	0.505145058	1.489042346
C	3.219917079	-0.777841297	2.003174486
H	2.228299424	-1.202481585	2.1036531
C	4.359230543	-1.501039335	2.357760473
H	4.245175815	-2.50140767	2.764356006

C	5.646742004	-0.967407646	2.198489141
H	6.510595984	-1.55579609	2.492427784
C	5.83831788	0.306546776	1.663201871
H	6.83288261	0.721431783	1.536666641
C	-1.397902164	5.106017315	3.61383516
H	-1.413177761	5.673243816	2.683785826
H	-2.424720973	4.954574834	3.963095489
H	-0.839677533	5.669878267	4.367755651
C	-0.248760852	3.432373608	2.146657652
C	-0.475348628	2.846418093	4.301279068
C	0.206826669	1.82535647	3.617621184
C	0.625360682	0.683832232	4.295182492
H	1.161522481	-0.106839024	3.785737407
C	0.343423898	0.598919809	5.660943502
H	0.663213845	-0.280108627	6.212648067
C	-0.335439535	1.622828401	6.334069509
H	-0.534315197	1.526121267	7.39713339
C	-0.75875494	2.770850112	5.660246026
H	-1.282612463	3.568528073	6.177206912

{[Bse^{Me}]ZnI}$_2$

(-1303.12161101306 Hartrees)

atom	x	y	z
Zn	-0.216378136	2.716238423	-1.426464843
I	0.259902668	3.556350515	-3.884133142
B	-3.053808921	3.599415392	-0.346403118
H	-2.206895928	3.455352502	-1.195178991
H	-4.057564956	4.056547982	-0.827364369
Se	0.329730279	3.954435121	0.776873603
Se	-1.531919273	0.456363862	-1.16129541
N	-2.562794521	4.593485664	0.752488885
N	-1.387837704	5.724698927	2.219473429
N	-3.409806685	2.207304165	0.301918199
N	-3.67421734	0.067813806	0.72179909
C	-1.318001021	4.772098779	1.250236502

C	-3.41651215	5.466349163	1.413059505
H	-4.460556274	5.526257179	1.151981452
C	-2.698000631	6.16474896	2.327858576
H	-2.985172957	6.929826649	3.03106472
C	-0.259302207	6.212515997	3.002592302
H	0.504547939	6.630116722	2.342328441
H	0.183292654	5.39578435	3.578112778
H	-0.620635807	6.985312033	3.682453376
C	-2.936633138	0.973164737	0.0285486
C	-4.455380922	2.065348407	1.200857065
H	-5.000425316	2.919468818	1.567140098
C	-4.620674252	0.745411435	1.468379566
H	-5.313328635	0.226758279	2.111255224
C	-3.508640089	-1.384252747	0.702204649
H	-3.340033022	-1.719121718	-0.322587064
H	-4.425536992	-1.835077329	1.084975295
H	-2.662983212	-1.678172361	1.329300742
Zn	0.666963352	-0.776286336	0.413967688
I	-0.136503637	-1.089312899	2.92411404
B	3.550771032	-2.056902902	-0.040350362
H	2.679904911	-1.619828832	0.673434466
H	4.55477921	-2.268208147	0.589781229
Se	0.381889065	-2.58166372	-1.45665574
Se	2.239780498	1.228499679	-0.224414115
N	3.093321685	-3.410948565	-0.667412978
N	1.92959339	-5.004460713	-1.622698832
N	3.870782892	-1.027127094	-1.186808832
N	4.113727878	0.796993201	-2.383005859
C	1.895437502	-3.705490384	-1.219751311
C	3.882635198	-4.549741401	-0.71641457
H	4.878145413	-4.552894481	-0.303112774
C	3.170801813	-5.541046839	-1.312274607
H	3.42040517	-6.565578401	-1.53687047
C	0.829691718	-5.716278192	-2.259904024
H	-0.064193006	-5.658011822	-1.634869219

H	0.603648964	-5.277004868	-3.234893283
H	1.121952177	-6.759484787	-2.388337707
C	3.456452355	0.249968464	-1.328047515
C	4.796967499	-1.28394544	-2.184113784
H	5.269726605	-2.248281676	-2.275590984
C	4.951669337	-0.159350633	-2.929179425
H	5.569597732	0.051077405	-3.787110356
C	3.979245077	2.172743479	-2.856816169
H	4.166869552	2.868320374	-2.035800795
H	4.716976697	2.334042132	-3.643994168
H	2.977708091	2.352525763	-3.254257712

3.11 References and Notes.

(1)   (a) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148. (b) Parkin, G. in *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1.01; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2006.

(2)   (a) *Scorpionate- The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**. (b) *Scorpionate II: Chelating Borate Ligands*, C. Pettinari, Imperial College Press, London, **2008**.

(3)   (a) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 891-897. (b) Kimblin, C.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 5680-5681. (c) Al-Harbi, A.; Rong, Y.; Parkin, G. *Dalton Trans.* **2013**, 42, 11117-11127.

(4)   (a) Landry, V. K.; Buccella, D.; Pang, K.; Parkin, G. *Dalton Trans.* **2007**, 866-870. (b) Landry, V. K.; Parkin, G. *Polyhedron* **2007**, *26*, 4751-4757.

(5)   (a) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *Dalton Trans.* **2000,** 1267-1274. (b) Yurkerwich, K.; Coleman, F.; Parkin, G. *Dalton Trans.* **2010**, *39, 6939 – 6942.

(6)   See, for example:
(a) Rabinovich, D. *Struct. Bond.* **2006**, *120*, 143-162. (b) Abernethy, R. J.; Foreman, M. R. S.-J.; Hill, A. F.; Tshabang, N.; Willis, A. C.; Young, R. D. *Organometallics* **2008**, *27*, 4455–4463. (c) Kuan, S. L.; Leong, W. K.; Webster, R. D.; Goh, L. Y.

Organometallics **2012**, *31*, 273–281. (d) Hill, A. F.; Smith, M. K. *Organometallics* **2007**, *26*, 3900–3903.

(7)   (a) Mehrotra, R. C.; Bohra, R. "Metal Carboxylates", Academic Press, London, 1983. (b) Carrell, C. J.; Carrell, H. L.; Erlebacher, J.; Glusker, J. P. *J. Am. Chem. Soc.* **1988**, *110,* 8651-8656.

(8)   (a) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. "Metal κ^2-Diketonates and Allied Derivatives", Academic Press, London, 1978. (b) Otway, D. J.; Rees, W. S. *Coord. Chem. Rev.* **2000**, *210*, 279-328. (c) Pike, R. M. *Coord. Chem. Rev.* **1967**, *2*, 163-172.

(9)   For other examples of LX [O_2] donor ligands that form 8-membered rings see: (a) Pettinari, C.; Marchetti, F.; Pettinari, R.; Martini, D.; Drozdov, A.; Troyanov, S. *J. Chem. Soc. Dalton Trans.* **2001**, 1790-1797. (b) Tsai, C. Y.; Li, C. Y.; Lin, C. H.; Huang, B. H.; Ko, B. T. *Inorg. Chem. Commun.* **2011**, *14*, 271-275.

(10)   For examples of X_2 [O_2] donor ligands that form 8-membered rings see: Kawaguchi, H.; Matsuo, T. *J. Organomet. Chem.* **2004**, *689*, 4228-4243.

(11)   A variety of descriptions have been given for the conformations of 8-membered ring systems but these classifications are less easy to apply when the ring contains several different types of atoms. Therefore, we only use the simplified "boat-like" and "chair-like" descriptions in this article.

(12)   (a) Dowling, C.; Ghosh, P.; Parkin, G. *Polyhedron* **1997**, *16*, 3469-3473. (b) Ghosh, P.; Rheingold, A. L.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 5464-5467. (c) Fillebeen, T.;

Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 3787-3790. (d) Johnson, D. M.; Eichhorn, D. M.; Moore, C. E.; Mwania, T. M.; Zhao, N. *J. Chem. Crystallogr.* **2012**, *42*, 746-751. (e) Craven, E.; Mutlu, E.; Lundberg, D.; Temizdemir, S.; Dechert, S.; Brombacher, H.; Janiak, C. *Polyhedron* **2002**, *21*, 553-562. (f) Adams, H.; Batten, S. R.; Davies, G. M.; Duriska, M. B.; Jeffery, J. C.; Jensen, P.; Lu, J. Z.; Motson, G. R.; Coles, S. J.; Hursthouse, M. B.; Ward, M. D. *Dalton Trans.* **2005**, 1910-1923.

(13)   Alvarez, H. M.; Gillespie, P. A.; Gause, C. D.; Rheingold, A.L.; Golen, J. A.; Rabinovich, D. *Polyhedron* **2004**, 23, 617-622.

(14)   Thallium(I) often forms polymeric arrays. See, for example:
(a) Akhbari, K.; Morsali, A. *Coord. Chem. Rev.* **2010**, *254*, 1977-2006. (b) Gade, L. H. *Dalton Trans.* **2003**, 267-278.

(15)   (a) Atencio, R.; Barbera, J.; Cativiela, C.; Lahoz, F. J.; Serrano, J. L.; Zurbano, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 11558-11559. (b) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E.; Pérez, J. *Organometallics* **2004**, *23*, 774-782. (c) Askarinejad, A.; Morsali, A.; Zhu, L. G. *Solid State Sci.* **2006**, *8*, 537-540.

(16)   The calculation was performed by Dr. Yi Rong.

(17)   Similar values are observed for a second polymorph: $d_{Zn \cdots H}$ = 2.07 Å and $d_{Zn \cdots B}$ = 2.87 Å.

(18)   Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9*, 2763.

(19)   Baker, R. J.; Jones, C. *Dalton Trans.* **2005**, 1341-1348.

(20)   Widdifield, C. M.; Jurca, T.; Richeson, D. S.; Bryce, D. L. *Polyhedron* **2012**, *35*, 96-100.

(21)   Schnepf, A.; Doriat, C.; Möllhausen, E.; Schnöckel, H. *Chem. Commun.* **1997**, 2111-2112.

(22) τ_4 = [360 – (α + β)]/141, where α + β is the sum of the two largest angles. See: Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955-964.

(23)   (a) Shin, H. K.; Hampden-Smith, M. J.; Duesler, E. N.; Kodas, T. T. *Polyhedron* **1991**, *10*, 645-647. (b) Shin, H. K.; Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424-431. (c) Shin, H.-K.; Hampden-Smith, M. J.; Duesler, E. N.; Kodas, T. T. *Can. J. Chem.* **1992**, *70*, 2954-2966. (d) Chi, K. M.; Corbitt, T. S.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *J. Organomet. Chem.* **1993**, *449*, 181-189. (e) Herberhold, M.; Milius, W.; Akkus, N. *Z. Naturforsch. (B)* **2004**, *59*, 843-849.

(24)   Hutchison, A. R.; Mitra, A.; Atwood, D. A. *Main Group Chem.* **2005**, *4*, 187-200.

(25)   (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23. (b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.;

American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98. (c) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.

(26)   Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

(27)   "Nuclear Magnetic Resonance Spectroscopy" Nelson, J. H. Prentice Hall, New Jersey (2003), p 79.

(28)   Quast, H.; Nahr, U. *Chem. Ber.* **1984**, *117*, 2761-2778.

(29)   Prakash, O.; Batra, H.; Kaur, H.; Sharma, P. K.; Sharma, V.; Singh, S. P.; Moriarty, R. M. *Synthesis* **2001**, 541-543.

(30)   Zhang, P.; Terefenko, E. A.; Bray, J.; Deecher, D.; Fensome, A.; Harrison, J.; Kim, C.; Koury, E.; Mark, L.; McComas, C. C.; Mugford, C. A.; Trybulski, E. J.; Vu, A. T.; Whiteside, G. T.; Mahaney, P. E. *J. Med. Chem.* **2009**, 52, 5703-5711.

(31)   Schmidbaur, H.; Adlkofer, J.; Schwirten, K. *Chem. Ber*. **1972**, 105, 3382-3388.

(32)   (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

(33)   Jaguar 7.6, Schrödinger, LLC, New York, NY 2009.

(34)   (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Becke, A. D. *Phys. Rev. A*
         1988, *38*, 3098-3100. (c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*,
         785-789. (d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200-1211.
         (e) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent
         Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

(35)   (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283. (b) Wadt, W. R.; Hay,
         P. J. *J. Chem. Phys.* **1985**, *82*, 284-298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**,
         82, 299-310.

(36)   Lab-Crest® glass pressure reaction vessels, Andrews Glass Company, Vineland,
         NJ.

Chapter 4

Synthesis and Structural Characterization of *Bis and Tris*(2-oxoimidazolyl)borate Zirconium Benzyl Complexes: Potential Ethylene Polymerization Precatalysts

Table of Contents

Reproduced in part from:

Rong, Y.; Al-Harbi, A.; Parkin, G. *Organometallics* **2013**, 31, 8208-8217.

4.1 Introduction

In the previous three chapters, we detailed the synthesis and the structural characterization of *bis* and *tris*(oxoimidazolyl)hydroborato ligands. We have also studied the coordination chemistry of these ligands with various main group and transition metals. Eager to find an application for these oxygen rich and hard donor ligands,[1] we decided to employ them for early transition metals in olefin polymerization.

Following the Ziegler-Natta discovery of the $TiCl_4/Al(C_2H_5)_3$ system, olefin polymerization has become one of the most active areas in the field of organometallic and polymer chemistry.[2,3] Since the Ziegler-Natta system is heterogeneous, understanding of the polymerization mechanism is limited. The later discovery of a homogeneous single-site system based on metallocene[4] catalysts brought this process to the molecular level. The replacement of the activator, methylaluminoxane, (MAO) with fluoroaryl boranes or borates made it possible to monitor this homogeneous system *via* spectroscopy.[5] However, due to the growing patent minefield around the metallocene systems, the use of non-metallocene catalyst systems has increased over the last two decades.[6] For example, *tris*(pyrazolyl)borate ($[Tp^{R,R}]$) ligands have been used in olefin polymerization since they are electronically analogous to the cyclopentadineyl ligand.[7] Good ethylene polymerization activities have been obtained from $[Tp^{R,R}]ZrCl_3/MAO$[7a] or $[Tp^*]Zr(CH_2Ph)_3/[Ph_3C][B\{C_6F_5\}_4]$[7n] systems.

In this chapter, we describe the synthesis and structural characterization of

$[Bo^{RBenz}]_2Zr(CH_2Ph)_2$ and $[To^{RBenz}]Zr(CH_2Ph)_3$. In addition, they are examined as olefin

polymerization precatalysts.

4.2   Synthesis of [Bo^{RBenz}] and [To^{RBenz}] Zirconium Benzyl Complexes

There are two possible routes that can be considered for the synthesis of

$[To^{RBenz}]Zr(CH_2Ph)_3$ (Scheme 1). The first one is alkylation of $[To^{RBenz}]ZrCl_3$[8] while the

second is *via* treatment of $[To^{RBenz}]Tl$ with tetrabenzylzirconium to generate

$[To^{RBenz}]Zr(CH_2Ph)_3$ and bibenzyl as a by-product. We found that the latter is more

convenient since the reaction of $[To^{RBenz}]Tl$ and tetrabenzylzirconium is instantaneous

and the purification of the product is straightforward.
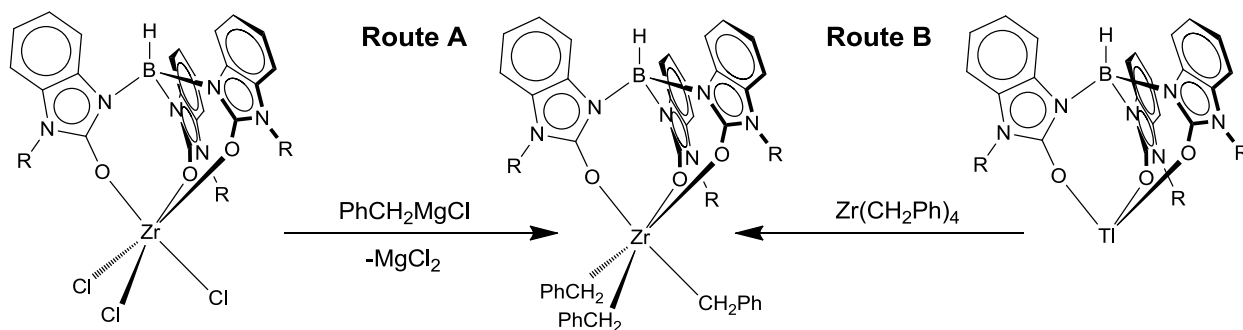
Scheme 1. Different possible routes for the synthesis of $[To^{RBenz}]Zr(CH_2Ph)_3$.

4.2.1   Synthesis and Structural Characterization of Tetrabenzylzirconium

The synthesis of tetrabenzylzirconium was reported in 1969.[9] $Zr(CH_2Ph)_4$ was

synthesized *via* the reaction of $PhCH_2MgCl$[10] with $ZrCl_4$ by a modification of the

literature method.[9b] During the work-up process, orange block crystals of the $Zr(CH_2Ph)_4$ were obtained by removing the volatile component from toluene solution. Based on X-ray diffraction examination, the crystals are a monoclinic form of $Zr(CH_2Ph)_4$ (Figure 1).
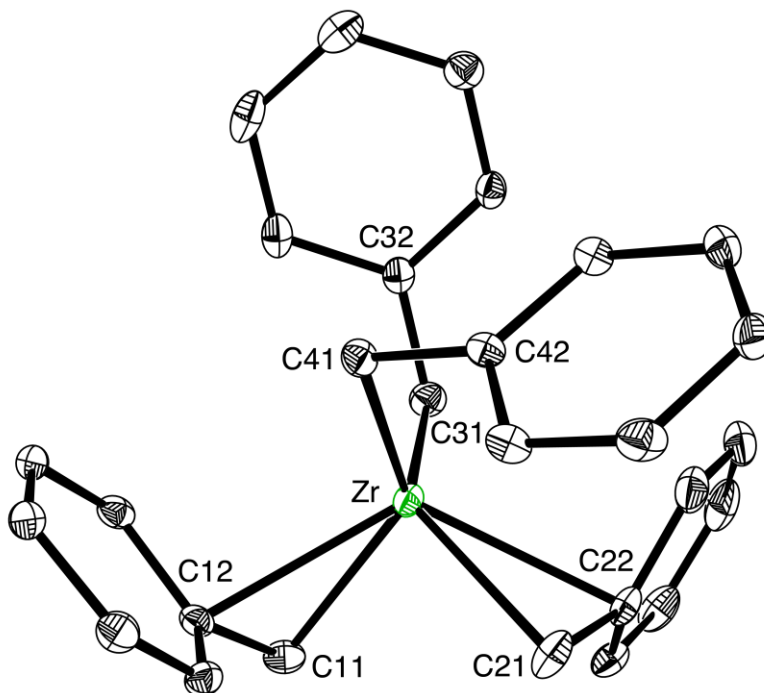
Figure 1. Molecular structure of monoclinic $Zr(CH_2Ph)_4$.

This crystal form differs from a previously reported orthorhombic structure[11] with respect to the benzyl conformation and the zirconium–benzyl interactions. Specifically, The benzyl ligands in orthorhombic $Zr(CH_2Ph)_4$ are arranged in such a manner as to give an approximate S_4 molecular symmetry, the molecular structure in the monoclinic form (Figure 1) deviates considerably from the orthorhombic form (Figure 2). One of the major factors that remove the S_4 symmetry for the monoclinic structure is that one of the

benzyl ligands points in a direction that destroys the C_2 axis. In addition to this variation in conformation, the zirconium–benzyl interactions in the two polymorphs are also different. For example, the Zr–CH_2–Ph bond angles for the monoclinic form span a range of 25.1°, which is substantially greater than those spanned in the orthorhombic form (12.1°). Furthermore, acute (81.6°) and obtuse (106.7°) bond angles for Zr–CH_2–Ph are observed in the monoclinic Zr(CH_2Ph)$_4$ form while a narrow range of Zr–CH_2–Ph bond angle is observed for the orthorhombic form, 87.0° – 99.1°. My colleague Yi Rong conducted a full analysis of the M•••C distances involving the phenyl group for the two crystal forms to investigate the hapticity of the benzyl ligands prompted by a report by Andersen.[12] She concluded that in the monoclinic form, two of the benzyl ligands coordinate in an η^2 manner while the other two coordinate in an η^1 manner. However, in the orthorhombic crystal form, three of the benzyl ligands coordinate in an η^2 fashion and one in an η^1 fashion.
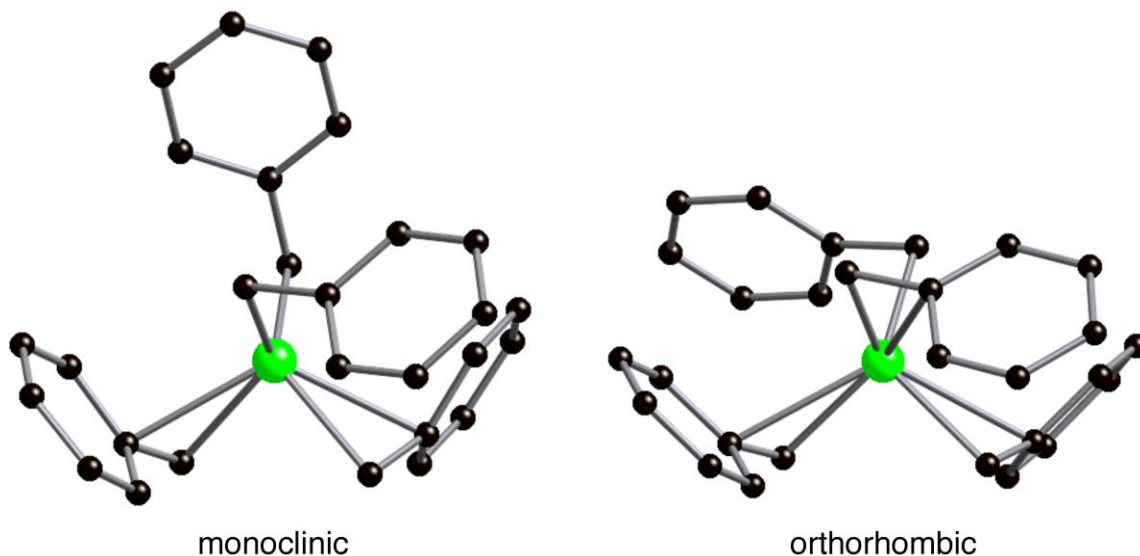
Figure 2. Comparison of the molecular structures of monoclinic (left) and orthorhombic (right) forms of $Zr(CH_2Ph)_4$.

Finally, It also worth noting that in solution the benzyl ligands are chemically equivalent on the NMR time-scale while the solid state $^{13}C\{^1H\}$ NMR spectrum exhibits a 1:1:2 set of signals for the four methylene carbon atoms at 76.4, 74.2 and 70.9 ppm, respectively (Figure 3). This is consistent with the inequivalent nature of the benzyl ligands.
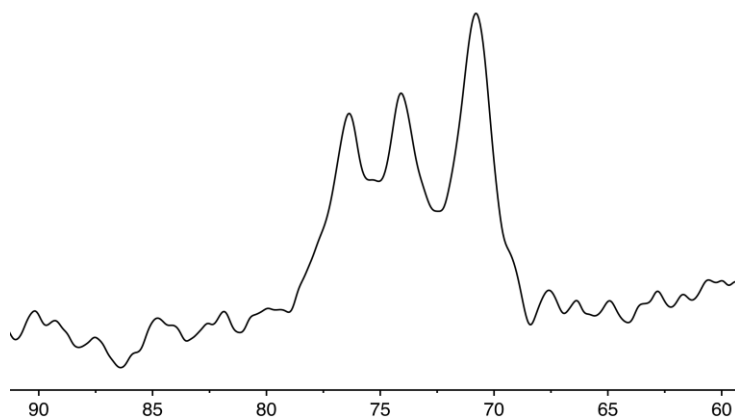

Figure 3. Methylene region of solid state ^{13}C NMR spectrum of $Zr(CH_2Ph)_4$.

4.2.2   Synthesis and Structural Characterization of [Bo^{RBenz}]$_2$Zr(CH$_2$Ph)$_2$

Treatment of two equivalents of [Bo^{RBenz}]Tl (R = Me or Ad) with tetrabenzylzirconium in benzene at room temperature leads to the generation of [Bo^{RBenz}]$_2$Zr(CH$_2$Ph)$_2$, along with thallium and bibenzyl as by-products (Scheme 2). However, isolation of [Bo^{RBenz}]Zr(CH$_2$Ph)$_3$ by the reaction of one equivalent of [Bo^{RBenz}]Tl with tetrabenzylzirconium proved to be difficult since it produces a mixture of products. [Bo^{RBnez}]$_2$Zr(CH$_2$Ph)$_2$ was simply purified by filtering the mixture to remove the thallium by-product followed by addition of pentane to the filtrate to precipitate the product. Crystals of composition [Bo^{MeBenz}]$_2$Zr(CH$_2$Ph)$_2$ (Figure 4) and [Bo^{AdBenz}]$_2$Zr(CH$_2$Ph)$_2$ (Figure 5) suitable for X-ray diffraction were obtained by vapor diffusion of pentane into toluene at -15 °C. In both alkyl derivatives, the zirconium benzyl motif is supported by four oxygen atoms and two 3-center–2-electron Zr•••H–B secondary interactions. The Zr•••H–B distances for both alkyl derivatives are similar despite the big difference in steric bulk between the methyl ($d_{Zr•••H1}$ = 2.46 Å, $d_{Zr•••H2}$ = 2.68 Å) and adamantyl groups ($d_{Zr•••H1}$ = 2.45 Å, $d_{Zr•••H2}$ = 2.65 Å). However, there is clearly an impact on the M–CH$_2$–Ph bond angles as a result of steric bulk since the bond angles for the methyl derivative are 119.3° and 119.4°, while the M–CH$_2$–Ph bond angles for the adamantyl derivative are 121.1° and 128.0°.
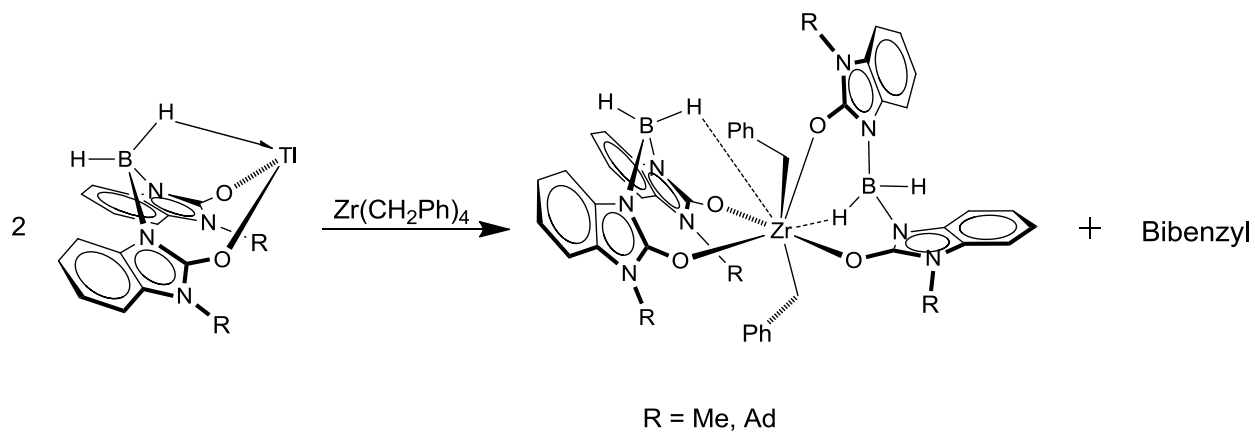
Scheme 2. Synthesis of [Bo^{RBenz}]$_2$Zr(CH$_2$Ph)$_2$.
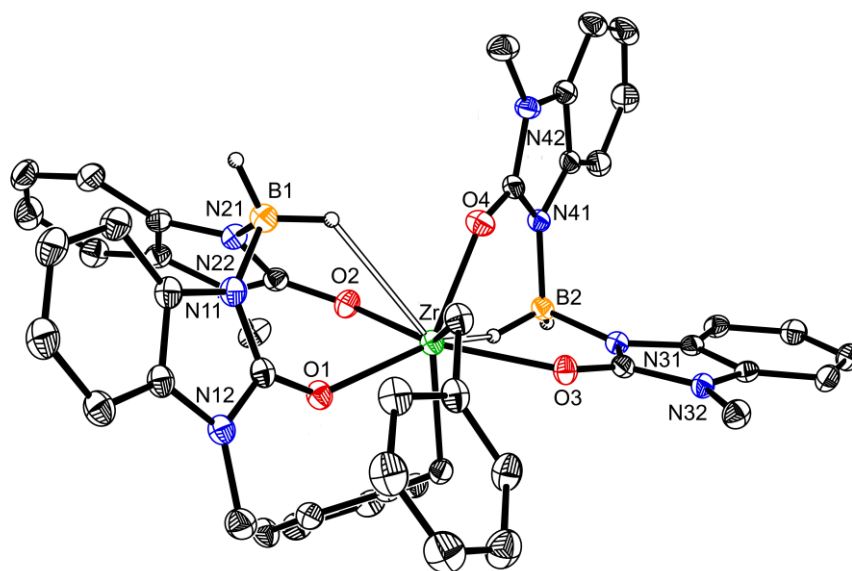
Figure 4. Molecular structure of [Bo^{MeBenz}]$_2$Zr(CH$_2$Ph)$_2$.
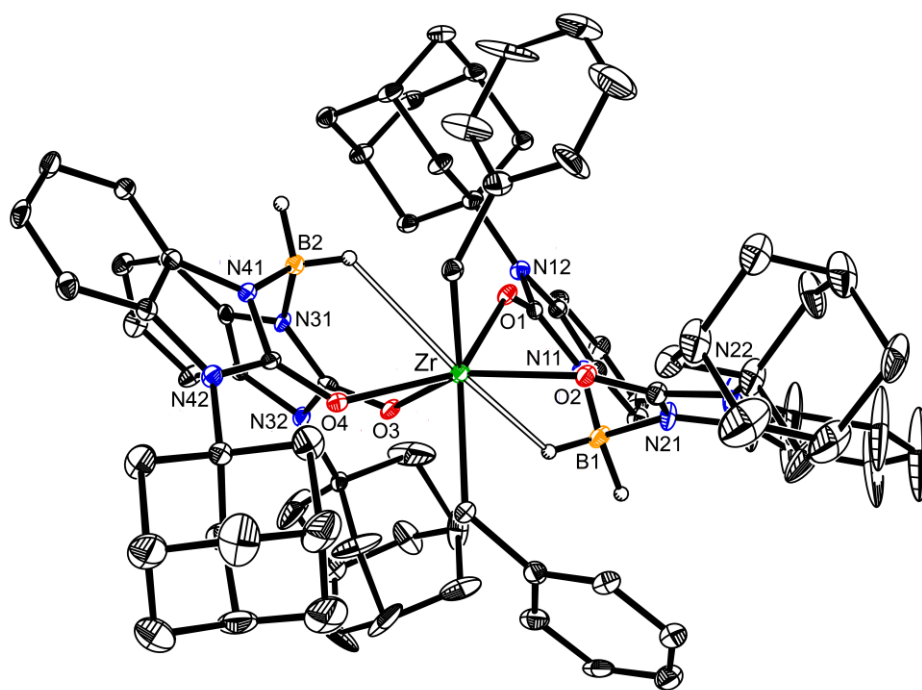
Figure 5. Molecular structure of [Bo^{AdBenz}]$_2$Zr(CH$_2$Ph)$_2$.

4.2.3   Synthesis and Structural Characterization of [To^{RBenz}]Zr(CH$_2$Ph)$_3$

Treatment of [To^{RBenz}]Tl , where R = Me, Bu^t and Ad, with tetrabenzylzirconium in benzene or toluene results in the generation of [To^{RBenz}]Zr(CH$_2$Ph)$_3$ along with bibenzyl and thallium as by-products (Scheme 3). The products are purified in a very similar way to the purification of [Bo^{RBenz}]$_2$Zr(CH$_2$Ph)$_2$. Fortunately, we were able obtain molecular structures of all the three different alkyl derivatives *via* X-ray diffraction (Figures 6, 7 and 8). From the X-ray structures of [To^{RBenz}]Zr(CH$_2$Ph)$_3$, we can clearly observe the influence of the alkyl group steric bulk on the Zr–CH$_2$–Ph bond angles. For example, the Zr–CH$_2$–Ph bond angles in the C_3 rhombohedral crystalline forms of t-butyl and adamantyl derivatives are 120.9° and 122.7° respectively, while the same

angles in the monoclinic crystalline form of $[To^{MeBenz}]Zr(CH_2Ph)_3$ are 94.5°, 115.6° and

121.4°. Thus in the methyl case, one of the benzyl ligands coordinates in an η^2 manner

since the Zr–CH$_2$–Ph bond angle is less than 97° while the other two benzyl ligands

coordinate in an η^1 manner. All the benzyl ligands for the t-butyl and adamantyl

derivative coordinate in an η^1 manner.

R = Me, Bu^t,Ad
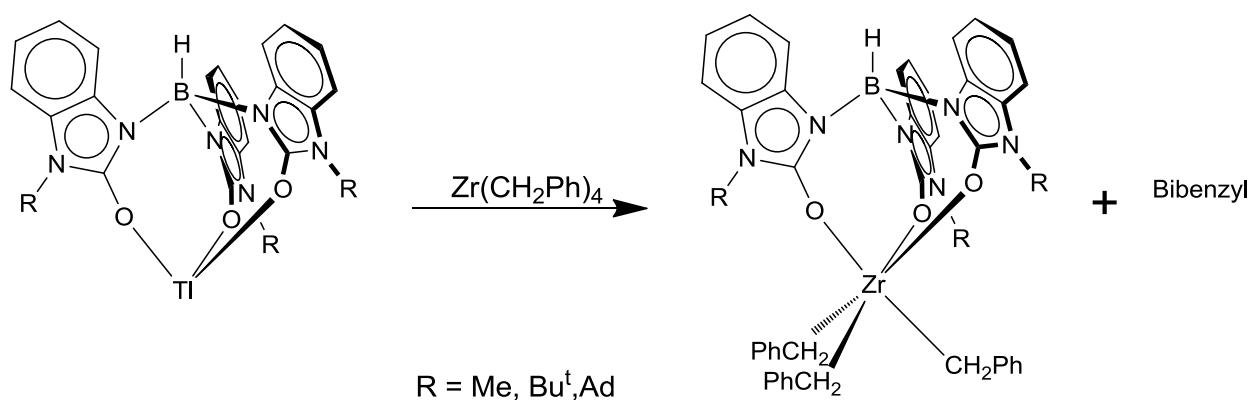
Scheme 3. Synthesis of $[To^{RBenz}]Zr(CH_2Ph)_3$.
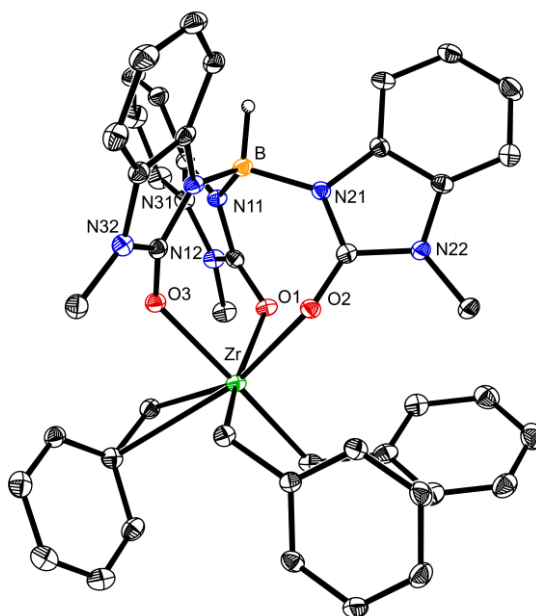
Figure 6. Molecular structure of $[To^{MeBenz}]Zr(CH_2Ph)_3$.
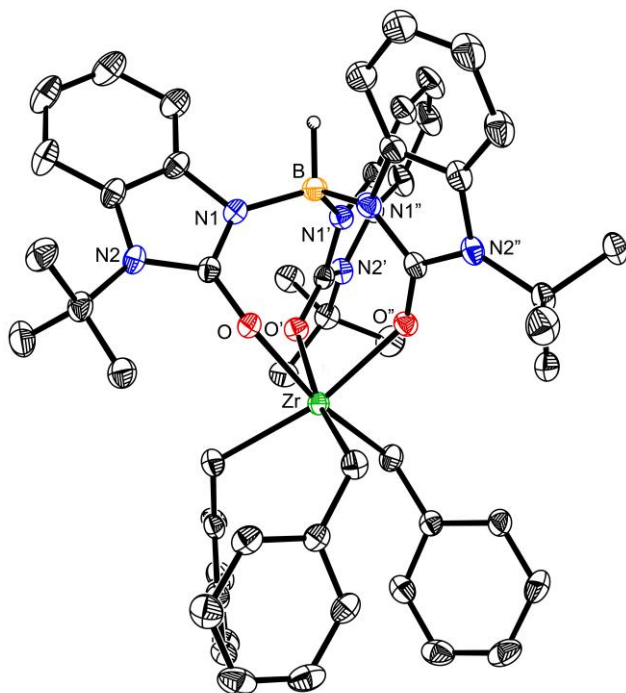
Figure 7. Molecular structure of [To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_3$.
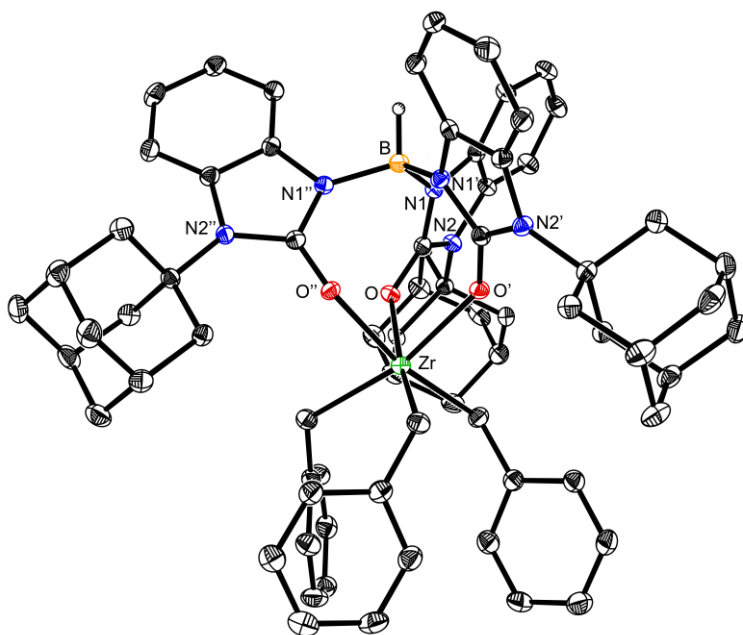
Figure 8. Molecular structure of [To^{AdBenz}]Zr(CH$_2$Ph)$_3$.

4.3 Activation of *Tris*(2-oxoimidazolyl)borate Zirconium Benzyl Complexes: Generation of Polymerization Catalysts

Active olefin polymerization catalysts from $[L_nMR_m]$ are normally obtained by alkyl abstraction or protonolysis to generate the unsaturated cationic alkyl complex $[L_nMR_{m-1}]^+$. Alkyl abstraction is normally achieved *via* the treatment of metal alkyl with trityl tetrakis(pentafluorophenyl)borate ($[Ph_3C][B\{C_6F_5\}_4]$) or *tris*(pentafluorophenyl)borane ($B\{C_6F_5\}_3$), while alkyl protonolysis is achieved by the use of dimethylanilinium tetrakis(pentafluorophenyl)borate ($[PhNHMe_2][B\{C_6F_5\}_4]$) or Brookhart's acid ($[\{Et_2O\}_2H][B\{C_6F_5\}_4]$).[5]

Treatment of $[To^{But Benz}]Zr(CH_2Ph)_3$ with $[PhNHMe_2][B\{C_6F_5\}_4]$ in diethylether leads to the protonolysis of one of the benzyl ligands generating the cationic species $\{[To^{But Benz}]Zr(CH_2Ph)_2(OEt_2)\}\{B(C_6F_5)_4\}$ (Scheme 4). Yellow blocks suitable for X-ray diffraction were obtained by slow diffusion of pentane into ether solution (Figure 9). However, this species, $\{[To^{But Benz}]Zr(CH_2Ph)_2(OEt_2)\}\{B(C_6F_5)_4\}$, exhibits very low activity for ethylene polymerization at 25 °C and 1 atm of ethylene. This might be explained by the strong coordination of Et_2O to zirconium which prevents the monomer insertion.
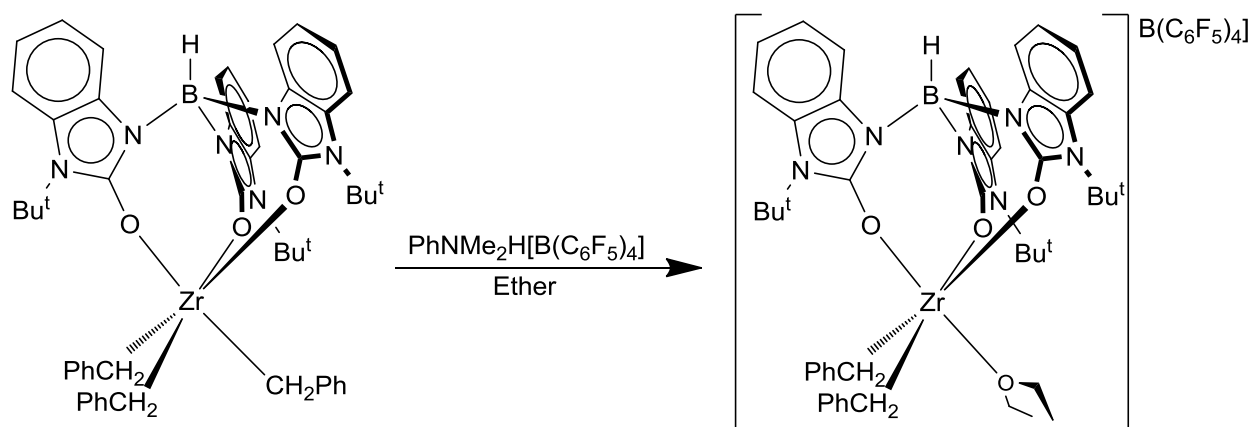
Scheme 4. Synthesis of {[To^{Bu^tBenz}]Zr(CH_2Ph)_2(OEt_2)}{B(C_6F_5)_4}.
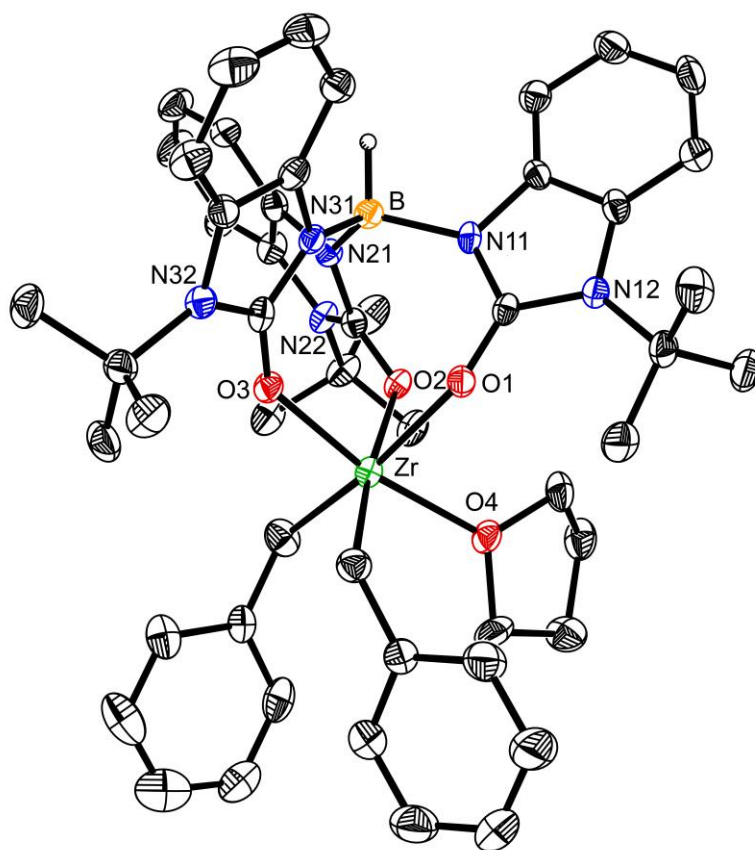
Figure 9. Molecular structure of {[To^{Bu^tBenz}]Zr(CH_2Ph)_2(OEt_2)}{B(C_6F_5)_4}.

In contrast, treatment of $[To^{Bu^tBenz}]Zr(CH_2Ph)_3$ or $[To^{AdBenz}]Zr(CH_2Ph)_3$ with

$([PhNHMe_2][B\{C_6F_5\}_4])$ in a non-coordinating solvent ,benzene, result in the *in situ*

generation of $\{[To^{Bu^tBenz}]Zr(CH_2Ph)_3\}\{B(C_6F_5)_4\}$ and $\{[To^{AdBenz}]Zr(CH_2Ph)_3\}\{B(C_6F_5)_4\}$,

respectively (Scheme 5). According to ^{1}H NMR spectra, the generated dimethylaniline

as a by-product for both protonolysis does not coordinate to the activated species which

makes the active species a truly "coordinatively unsaturated cationic alkyl complex".[13]

Addition of ethylene to $\{[To^{Bu^tBenz}]Zr(CH_2Ph)_2\}\{B(C_6F_5)_4\}$ results in the production of

polyethylene with moderate activity, 45 kg PE [mol Zr]$^{-1}$[h]$^{-1}$[atm C$_2$H$_4$]$^{-1}$, while a higher

activity was obtained in the case of $\{[To^{AdBenz}]Zr(CH_2Ph)_2\}\{B(C_6F_5)_4\}$,

160 kg PE [mol Zr]$^{-1}$[h]$^{-1}$[atm C$_2$H$_4$]$^{-1}$.[14]
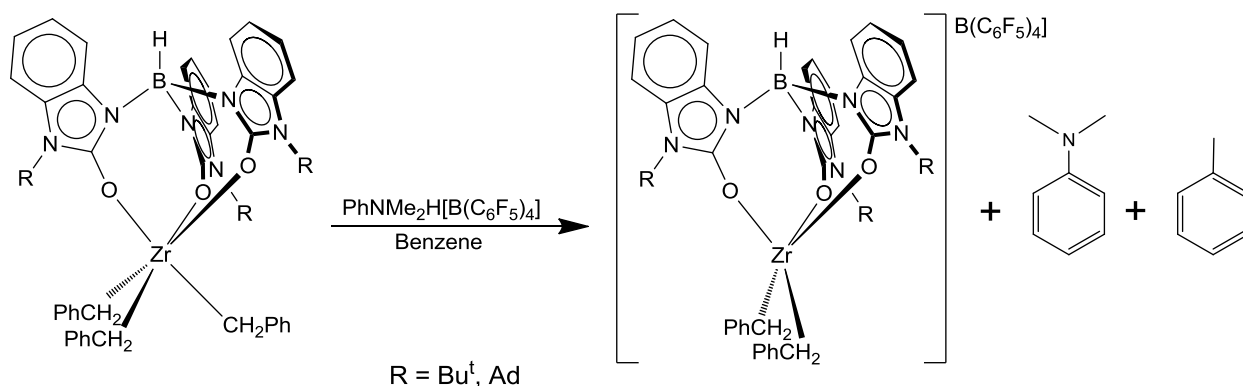
Scheme 5. *In situ* generation of $\{[To^{Bu^tBenz}]Zr(CH_2Ph)_2\}\{B(C_6F_5)_4\}$ and

$\{[To^{AdBenz}]Zr(CH_2Ph)_2\}\{B(C_6F_5)_4\}$.

4.4　Conclusion

We have described the synthesis of $[Bo^{RBenz}]_2Zr(CH_2Ph)_2$ and $[To^{RBenz}]Zr(CH_2Ph)_3$ with

different alkyl substituents. Treatment of $[To^{Bu^tBenz}]Zr(CH_2Ph)_3$ with

$([PhNHMe_2][B\{C_6F_5\}_4])$ in a coordinating solvent, Et_2O, generates

$\{[To^{Bu^tBenz}]Zr(CH_2Ph)_2(OEt_2)\}\{B(C_6F_5)_4\}$ which exhibits a very low activity for ethylene

polymerization. However, a coordinatively unsaturated cationic zirconium alkyl

complex was obtained by the use of $([PhNHMe_2][B\{C_6F_5\}_4])$ with $[To^{Bu^tBenz}]Zr(CH_2Ph)_3$ or

$[To^{AdBenz}]Zr(CH_2Ph)_3$ generating $[To^{Bu^tBenz}]Zr(CH_2Ph)_2[B(C_6F_5)_4]$ or

$[To^{AdBenz}]Zr(CH_2Ph)_2[B(C_6F_5)_4]$, respectively. Moderate activity for ethylene

polymerization was obtained for t-butyl while high activity was obtained for the

adamantyl derivatives.

4.5　Experimental Section

4.5.1　General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and

Schlenk techniques under an argon atmosphere.[15] Solvents were purified and degassed

by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker

400 DRX, Bruker 400 Cyber-enabled Avance III and Bruker Avance 500 DMX

spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and

were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H

and 5.32 for $CDHCl_2$).[16] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$)

and were referenced internally with respect to the solvent (δ 128.06 for C_6D_6, 53.84 for CD_2Cl_2).[16] Coupling constants are given in hertz. Solid-state $^{13}C\{^1H\}$ NMR experiments were performed on a Bruker 400 Cyber-enabled Avance III at a field of 9.40 T (corresponding to a ^{13}C resonance frequency of 100.62 MHz) using the CP-MAS pulse sequence, with an acquisition time of 0.03 seconds and a spin rate of 10^4 Hz. Solid state ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced externally to the methylene peak of adamantane ($\delta = 38.5$).[17]

4.5.2   X-ray Structure Determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer and crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2008/4).[18]

4.5.3   Synthesis of Tetrabenzylzirconium

A solution of benzylchloride (13.6 g, 0.11 mol) in THF (200 mL) was slowly added to a stirred suspension of magnesium turnings (11.0 g, 0.45 mol) in THF (50 mL) over a period for *ca*. 1 hour, such that the temperature of the reaction vessel was maintained at *ca.* 25 °C. The mixture was stirred at room temperature overnight and then filtered. The volatile components were removed from the filtrate *in vacuo* to give $PhCH_2MgCl$ as an off-white powder that was treated sequentially with $ZrCl_4$ (6.0 g, 0.026 mol) and Et_2O

(150 mL) at -15 °C. The mixture was stirred at -15 °C overnight and filtered at 0 °C. The precipitate was washed with Et_2O (200 mL) at 0°C and then extracted into toluene (200 mL and 100 mL). The volatile components were removed from each extraction *in vacuo*, resulting in the formation of $Zr(CH_2Ph)_4$ as orange crystalline blocks suitable for X-ray diffraction (2.1 g and 1.0 g, 26 %). The synthesis and the purification of tetrabenzylzirconium were conducted in the absence of light to avoid any photochemical decomposition. ^{1}H NMR (C_6D_6): 1.55 [s, 8H of $Zr\{(C\underline{H}_2)C_6H_5\}_4$], 6.38 [d, $^3J_{H-H}$ = 7, 8H$_{ortho}$ of $Zr\{(CH_2)C_6\underline{H}_5\}_4$], 6.96 [t, $^3J_{H-H}$ = 7, 4H$_{para}$ of $Zr\{(CH_2)C_6\underline{H}_5\}_4$], 7.06 [t, $^3J_{H-H}$ = 7, 8H$_{meta}$ of $Zr\{(CH_2)C_6\underline{H}_5\}_4$]. ^{13}C NMR ($C_6D_6$): 72.5 [tt, $^1J_{C-H}$= 135, $^3J_{C-H}$ = 4, 4C of $Zr\{(\underline{C}H_2)C_6H_5\}_4$], 124.5 [dt, $^1J_{C-H}$= 162, $^3J_{C-H}$ = 8, 4C$_{para}$ of $Zr\{(CH_2)\underline{C}_6H_5\}_4$], 128.7 [m, 8C$_{ortho}$ of $Zr\{(CH_2)\underline{C}_6H_5\}_4$], 131.0 [dd, $^1J_{C-H}$= 159, $^3J_{C-H}$ = 8, 8C$_{meta}$ of $Zr\{(CH_2)\underline{C}_6H_5\}_4$], 139.5 [s, 4C$_{ipso}$ of $Zr\{(CH_2)\underline{C}_6H_5\}_4$]. Solid-state ^{13}C{^{1}H} NMR (only CH_2 group listed): 76.4 (1C), 74.0 (1C), 70.4 (2C) at –10°C; 76.4 (1C), 74.2 (1C), 70.9 (2C) at room temperature; 76.4 (1C), 74.4 (1C), 71.1 (2C) at 50°C.

4.5.4   Synthesis of [Bo^{MeBenz}]$_2$Zr(CH$_2$Ph)$_2$

A mixture of $Zr(CH_2Ph)_4$ (17.8 mg, 0.04 mmol) and [Bo^{MeBenz}]Tl (40.0 mg, 0.04 mmol) was treated with benzene (*ca.* 2 mL). The mixture was stirred for 5 minutes, which resulted in the immediate formation of Tl. The mixture was filtered to remove the Tl, then pentane (*ca.* 20 mL) was added to the filtrate to precipitate out the product. The mother liquor was decanted from the final product. The product was washed with pentane (*ca.*

10 mL) and dried *in vacuo* to remove any volatile matter yielding a yellow powder of

[Bo^{MeBenz}]$_2$Zr(CH$_2$Ph)$_2$ (18.0 mg, 52%). ^{1}H NMR (C$_6$D$_6$): 2.76 [s, 12H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 3.21 [s, 4H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{C$\underline{H}_2$(C$_6$H$_5$)}$_2$], 6.35 [d, $^3J_{H-H}$ = 8, 4H of

{H$_2$B[(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 6.70 [t, $^3J_{H-H}$ = 8, 2H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6\underline{H}_5$)}$_2$], 6.88 ["dt", $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 4H of

{H$_2$B[(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 7.08 [m, 8H of

{H$_2$B[(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6\underline{H}_5$)}$_2$], 7.33 [d, $^3J_{H-H}$ = 8, 6H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6\underline{H}_5$)}$_2$], 7.83 [d, $^3J_{H-H}$ = 8, 4H of

{H$_2$B[(C$_4\underline{H}_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6\underline{H}_5$)}$_2$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 34.5 [4 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$\underline{H}_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 71.2 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{$\underline{C}$H$_2$(C$_6$H$_5$)}$_2$], 108.6 [4 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 112.5 [4 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 120.1 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 121.7 [4 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 122.7 [4 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 127.1 [4 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 127.4 [4 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 131.2 [4C,

{H$_2$B[(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 133.4 [4C,

{H$_2$B[(C$_4$H$_4$)$\underline{C}_2$N$_2$(CH$_3$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 152.1 [2C,

$\{H_2B[(C_4H_4)C_2N_2(CH_3)CO]_2\}_2Zr\{CH_2(\underline{C}_6H_5)\}_2]$, 160.5 [4C,

$\{H_2B[(C_4H_4)C_2N_2(CH_3)\underline{C}O]_2\}_2Zr\{CH_2(C_6H_5)\}_2]$. Yellow block crystals of

$[Bo^{MeBenz}]_2Zr(CH_2Ph)_2$ suitable for X-ray diffraction were obtained from slow diffusion of

pentane into a toluene solution of $[Bo^{MeBenz}]_2Zr(CH_2Ph)_2$ at -15 °C.

4.5.5 Synthesis of $[Bo^{AdBenz}]_2Zr(CH_2Ph)_2$

A mixture of $Zr(CH_2Ph)_4$ (17.3 mg, 0.04 mmol) and $[Bo^{AdBenz}]Tl\cdot0.5THF$ (60 mg, 0.08

mmol) was treated with toluene (*ca.* 4 mL). The mixture was stirred for 10 minutes,

which resulted in the immediate formation of Tl. The mixture was filtered to remove

the Tl, and pentane (*ca.* 20 mL) was added to the filtrate to precipitate out the product.

The mother liquor was decanted from the final product. The product was washed with

pentane (*ca.* 10 mL) and dried *in vacuo* to remove any volatile matter yielding a yellow

powder of $[Bo^{AdBenz}]_2Zr(CH_2Ph)_2$ (25.0 mg, 49%). ^1H NMR (C_6D_6): 1.46 [br, 3H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}\underline{H}_{15})CO]_2\}_2Zr\{CH_2(C_6H_5)\}_2]$, 1.54 [br, 3H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}\underline{H}_{15})CO]_2\}_2Zr\{CH_2(C_6H_5)\}_2]$, 1.60 [m, 18H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}\underline{H}_{15})CO]_2\}_2Zr\{CH_2(C_6H_5)\}_2]$, 1.95 [br, 18H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}\underline{H}_{15})CO]_2\}_2Zr\{CH_2(C_6\underline{H}_5)\}_2]$, 2.15 [br, 6H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}\underline{H}_{15})CO]_2\}_2Zr\{CH_2(C_6H_5)\}_2]$, 2.71 [m, 12H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}\underline{H}_{15})CO]_2\}_2Zr\{CH_2(C_6H_5)\}_2]$, 2.92 [d, $^2J_{H-H}$ = 10, 2H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}H_{15})CO]_2\}_2Zr\{C\underline{H}_2(C_6H_5)\}_2]$, 3.77 [d, $^2J_{H-H}$ = 10, 2H of

$\{H_2B[(C_4H_4)C_2N_2(C_{10}H_{15})CO]_2\}_2Zr\{C\underline{H}_2(C_6H_5)\}_2]$, 6.54 [t, $^2J_{H-H}$ = 8, 2H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$<u>H</u>$_5$)}$_2$], 6.80 [t, ^{2}J$_{H-H}$ = 10, 2H of

{H$_2$B[(C$_4$<u>H</u>$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 6.93 [t, 2 H of

{H$_2$B[(C$_4$<u>H</u>$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 7.06 [overlapped peaks, 10 H of

{H$_2$B[(<u>C</u>$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$<u>H</u>$_5$)}$_2$], 7.33 [d, ^{2}J$_{H-H}$ = 8, 2H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$<u>H</u>$_5$)}$_2$], 7.44 [d, ^{2}J$_{H-H}$ = 7, 4H of

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$<u>H</u>$_5$)}$_2$], 7.75 [d, ^{2}J$_{H-H}$ = 8, 2H of

{H$_2$B[(C$_4$<u>H</u>$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 7.97 [d, ^{2}J$_{H-H}$ = 8, 2H of

{H$_2$B[(C$_4$<u>H</u>$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 30.2 [6 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 30.3 [6 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 36.2 [6 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 36.3 [6 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 40.3 [6 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 41.2 [6 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 60.9 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 61.1 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(<u>C</u>$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 74.3 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{<u>C</u>H$_2$(C$_6$H$_5$)}$_2$], 113.1 [2 C,

{H$_2$B[(<u>C</u>$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 113.2 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 113.8 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 114.2 [2 C,

{H$_2$B[(<u>C</u>$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 119.9 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 120.7 [2 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 120.9 [2 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 121.6 [2 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 121.8 [2 C,

{H$_2$B[($\underline{C}_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 126.6 [4 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 127.1 [4 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 130.3 [2 C,

{H$_2$B[(C$_4$H$_4$)$\underline{C}_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 130.6 [2 C,

{H$_2$B[(C$_4$H$_4$)$\underline{C}_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 133.7 [2 C,

{H$_2$B[(C$_4$H$_4$)$\underline{C}_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 133.8 [2 C,

{H$_2$B[(C$_4$H$_4$)$\underline{C}_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 153.1 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)CO]$_2$}$_2$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_2$], 160.2 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)$\underline{C}$O]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$], 162.0 [2 C,

{H$_2$B[(C$_4$H$_4$)C$_2$N$_2$(C$_{10}$H$_{15}$)$\underline{C}$O]$_2$}$_2$Zr{CH$_2$(C$_6$H$_5$)}$_2$]. Yellow block of [Bo^{AdBenz}]$_2$Zr(CH$_2$Ph)$_2$

suitable for X-ray were obtained from a mixture of pentane/toluene solution of

[Bo^{AdBenz}]$_2$Zr(CH$_2$Ph)$_2$ at -15 °C.

4.5.6   Synthesis of [To^{MeBenz}]Zr(CH$_2$Ph)$_3$

A solution of Zr(CH$_2$Ph)$_4$ (27.7 mg, 0.06 mmol) in benzene (*ca.* 6 mL) was added to

[To^{MeBenz}]Tl (40.0 mg, 0.06 mmol). The mixture was stirred for 10 min, which resulted in

the immediate formation of Tl. The mixture was filtered to remove the Tl, and pentane

(*ca.* 20 mL) was added to the filterate to precipitate out the product. The mother liquor

was decanted from the final product. The product was washed with pentane (*ca.* 5 mL)

and dried *in vacuo* to remove any volatile matter yielding a yellow powder of

[To^{MeBenz}]Zr(CH$_2$Ph)$_3$ (20.0 mg, 40%). Analysis calcd. for [To^{MeBenz}]Zr(CH$_2$Ph)$_3$: C, 64.5%;

H, 5.5%; N, 10.8%. Found: C, 5.4%; H, 6.1%; N, 10.6%. ^{1}H NMR (C$_6$D$_6$): 2.41 [s, 9H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$\underline{H}_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 2.99 [s, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{C$\underline{H}_2$(C$_6$H$_5$)}$_3$], 6.51 [d, ^{3}J$_{H-H}$ = 7, 3H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 6.87 [t, ^{3}J$_{H-H}$ = 7, 3H of

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$$\underline{H}_5$)}$_3$], 6.92 [dt, ^{3}J$_{H-H}$ = 7, ^{4}J$_{H-H}$ = 1, 3H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 6.99 [dt, ^{3}J$_{H-H}$ = 7, ^{4}J$_{H-H}$ = 1, 3H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 7.11 [t, ^{3}J$_{H-H}$ = 7, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$$\underline{H}_5$)}$_3$], 7.18 [d, ^{3}J$_{H-H}$ = 7, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$$\underline{H}_5$)}$_3$], 7.62 [d, ^{3}J$_{H-H}$ = 8, 3H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 27.0 [9 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}$H$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 75.9 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{$\underline{C}$H$_2$(C$_6$H$_5$)}$_3$], 108.9 [3 C,

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 112.5 [3 C,

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{C$\underline{H}_2$(C$_6$H$_5$)}$_3$], 120.7 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$($\underline{C}_6$H$_5$)}$_3$], 122.4 [3 C,

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 122.9 [3 C,

HB{($\underline{C}_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 127.6 [6 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C̲$_6$H$_5$)}$_3$], under solvent peak [6C,

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C̲$_6$H$_5$)}$_3$], 131.0 [3C,

HB{(C$_4$H$_4$)C̲$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 133.0 [3C,

HB{(C$_4$H$_4$)C̲$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 148.5 [3C,

HB{(C$_4$H$_4$)C̲$_2$N$_2$[CH$_3$]CO}$_3$Zr{CH$_2$(C̲$_6$H$_5$)}$_3$], 159.9 [3C,

HB{(C$_4$H$_4$)C$_2$N$_2$[CH$_3$]C̲O}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$]. Yellow block crystals of [To^{MeBenz}]Zr(CH$_2$Ph)$_3$

suitable for X-ray were obtained from a CH$_2$Cl$_2$ solution of [To^{MeBenz}]Zr(CH$_2$Ph)$_3$.

4.5.7   Synthesis of [To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_3$

A solution of Zr(CH$_2$Ph)$_4$ (23 mg, 0.05 mmol) in benzene (*ca.* 6 mL) was added to

[To$^{Bu^tBenz}$]Tl (40mg, 0.05). The mixture was stirred for 10 min, which resulted in the

immediate formation of Tl. The mixture was filtered to remove the Tl. Slow diffusion of

pentane to the toluene solution at -15 °C leads to the growth of yellow block crystals.

The crystals were washed with pentane (*ca.* 5 mL) and dried *in vacuo* to remove any

volatile matter yielding [To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_3$ (27.0 mg, 57%). Analysis calcd. for

[To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_3$: C, 68.5%; H, 6.5%; N, 8.9%. Found: C, 67.5%; H, 6.5%; N 8.5%. ^{1}H

NMR (C$_6$D$_6$): 1.36 [s, 27H of HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH̲$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 3.20 [s, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH̲$_2$(C$_6$H$_5$)}$_3$], 6.82 [t, $^3J_{H-H}$ = 8, 3H of

HB{(C$_4$H̲$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 6.89 [t, $^3J_{H-H}$ = 8, 3H of

HB{(C$_4$H̲$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 6.94 [t, $^3J_{H-H}$ = 7, 3H of

HB{(C$_4$H̲$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H̲$_5$)}$_3$], 6.99 [d, $^3J_{H-H}$ = 8, 3H of

HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 7.20 [d, $^3J_{\text{H-H}}$ = 7, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$<u>H</u>$_5$)}$_3$], 7.26 [d, $^3J_{\text{H-H}}$ = 7, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$<u>H</u>$_5$)}$_3$], 7.50 [d, $^3J_{\text{H-H}}$ = 8, 3H of

HB{(C$_4$<u>H</u>$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 29.7 [9 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(C<u>CH</u>$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 59.4 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[<u>C</u>(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 79.8 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{<u>C</u>H$_2$(C$_6$H$_5$)}$_3$], 113.1 [3 C,

HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 114.2 [3 C,

HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 120.9 [3 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(<u>C</u>$_6$H$_5$)}$_3$], 122.0 [3 C,

HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 122.7 [3 C,

HB{(<u>C</u>$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 126.8 [6 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(<u>C</u>$_6$H$_5$)}$_3$], 128.4 [6C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(<u>C</u>$_6$H$_5$)}$_3$], 130.6 [3C,

HB{(C$_4$H$_4$)<u>C</u>$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 134.0 [3C,

HB{(C$_4$H$_4$)<u>C</u>$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 151.2 [3C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO}$_3$Zr{CH$_2$(<u>C</u>$_6$H$_5$)}$_3$], 159.9 [3C,

HB{(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]<u>C</u>O}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$]. Yellow block of [To$^{\text{Bu}^{\text{t}}\text{Benz}}$]Zr(CH$_2$Ph)$_3$

suitable for X-ray were obtained from slow diffusion of pentane into a toluene solution

of [To$^{\text{Bu}^{\text{t}}\text{Benz}}$]Zr(CH$_2$Ph)$_3$ at -15 °C.

4.5.8 Synthesis of [To^{AdBenz}]Zr(CH$_2$Ph)$_3$

A solution of Zr(CH$_2$Ph)$_4$ (17.2 mg, 0.038 mmol) in benzene (*ca.* 4 mL) was added to

[To^{AdBenz}]Tl•THF (41.0 mg, 0.038 mmol). The mixture was stirred for 10 min, which

resulted in the immediate formation of Tl. The mixture was filtered to remove the Tl,

and pentane (*ca.* 15 mL) was added to the mixture to precipitate out the product. The

mother liquor was decanted from the final product. The product was washed with

pentane (*ca.* 5 mL) and dried *in vacuo* to remove any volatile matter yielding a yellow

powder of [To^{AdBenz}]Zr(CH$_2$Ph)$_3$ (27 mg, 61%). Analysis calcd. for

[To^{AdBenz}]Zr(CH$_2$Ph)$_3$•0.4CH$_2$Cl$_2$: C, 71.7%; H, 6.6%; N, 6.9%. Found: C, 71.7%; H, 7.1%;

N, 6.9 %. ^{1}H NMR (C$_6$D$_6$): 1.40 [m, 18H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$],

1.87 [br, 9H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 2.37 [br, 18H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 3.18 [s, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$Zr{C$\underline{H}_2$(C$_6$H$_5$)}$_3$], 6.90 [dt, ^{3}J$_{H-H}$ = 8, ^{4}J$_{H-H}$ = 1, 3H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$Zr{CH$_2$(C$_6$$\underline{H}_5$)}$_3$], 6.95 [m, 6H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 7.09 [dd, ^{3}J$_{H-H}$ = 7, ^{4}J$_{H-H}$ = 1, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$Zr{CH$_2$(C$_6$$\underline{H}_5$)}$_3$], 7.26 [t, ^{3}J$_{H-H}$ = 7, 6H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$Zr{CH$_2$(C$_6$$\underline{H}_5$)}$_3$], 7.30 [d, ^{3}J$_{H-H}$ = 8, 3H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 7.58 [dd, ^{3}J$_{H-H}$ = 8, ^{4}J$_{H-H}$ = 1, 3H of

HB{(C$_4$$\underline{H}_4$)C$_2N_2$[C$_{10}H_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 30.1 [9 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 35.9 [9 C,

HB{(C$_4$H$_4$)C$_2$N$_2$[$\underline{C}_{10}$H$_{15}$]CO}$_3$Zr{CH$_2$(C$_6$H$_5$)}$_3$], 40.8 [9 C,

yellow block crystals of $\{[\text{To}^{\text{Bu}^t\text{Benz}}]\text{Zr}(\text{CH}_2\text{Ph})_2\}\{\text{Et}_2\text{O}\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$. The crystals were washed

with pentane (*ca.* 3 mL) and left to dry (15.0 mg, 30%). ^{1}H NMR (CD$_2$Cl$_2$): 1.23 [6H,

methyl of the ether], 1.71 [s, 27H of HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(C$\underline{\text{H}}_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6$H$_5$)$\}_2$], 2.38

[s, 4H of HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$C$\underline{\text{H}}_2$(C$_6$H$_5$)$\}_2$], 3.85 [4H, methylene of the

ether], 6.84 [d, $^3J_{\text{H-H}}$ = 8, 4H of HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6\underline{\text{H}}_5$)$\}_2$], 7.01 [t, $^3J_{\text{H-H}}$ =

8, 2H of HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6\underline{\text{H}}_5$)$\}_2$], 7.24 [t, $^3J_{\text{H-H}}$ = 8, 4H of

HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6\underline{\text{H}}_5$)$\}_2$], 7.30 [m, 6H of

HB$\{$(C$_4\underline{\text{H}}_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6$H$_5$)$\}_2$], 7.54 [m, 3H of

HB$\{$(C$_4\underline{\text{H}}_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6$H$_5$)$\}_2$], 7.64 [m, 3H of

HB$\{$(C$_4\underline{\text{H}}_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6$H$_5$)$\}_2$]. Yellow block crystals of

$\{[\text{To}^{\text{Bu}^t\text{Benz}}]\text{Zr}(\text{CH}_2\text{Ph})_2\}\{\text{Et}_2\text{O}\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$ suitable for X-ray were obtained from slow

diffusion of pentane into an Et$_2$O solution of $\{[\text{To}^{\text{Bu}^t\text{Benz}}]\text{Zr}(\text{CH}_2\text{Ph})_2(\text{Et}_2\text{O})\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$ at -15

°C.

4.5.10 Generation of $\{[\text{To}^{\text{Bu}^t\text{Benz}}]\text{Zr}(\text{CH}_2\text{Ph})_2\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$

A solution of [To$^{\text{Bu}^t\text{Benz}}$]Zr(CH$_2$Ph)$_3$ (10 mg, 0.01 mmol) in C$_6$D$_6$ (*ca.* 2 mL) was added to

[PhNHMe$_2$][B$\{$C$_6$F$_5\}_4$] (8.5 mg, 0.01 mmol). The mixture was mixed with a pipet for two

minutes for *ca.* 2 min then filtered. ^{1}H NMR (C$_6$D$_6$) for the mixture

($\{[\text{To}^{\text{Bu}^t\text{Benz}}]\text{Zr}(\text{CH}_2\text{Ph})_2\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$ + Me$_2$NPh + Toluene): 1.71 [s, 27H of

HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(C$\underline{\text{H}}_3$)$_3$]CO$\}_3$Zr$\{$CH$_2$(C$_6$H$_5$)$\}_2$], 2.11 [s, 3H for the methyl group in

toluene], 2.16 [s, 4H of HB$\{$(C$_4$H$_4$)C$_2$N$_2$[C(CH$_3$)$_3$]CO$\}_3$Zr$\{$C$\underline{\text{H}}_2$(C$_6$H$_5$)$\}_2$], 2.52 [s, 6H for the

dimethyl groups in dimethylaniline], 6.64 [d, 3H], 6.81 [m, 6H], 6.87 [m, 4H], 6.93 [m,

6H], 7.02 [m, 9H], 7.13 [m, 3H], 7.24 [m, 2H], 7.40 [m, 2H].

4.5.11 Generation of {[To^{AdBenz}]Zr(CH$_2$Ph)$_2$}{B(C$_6$F$_5$)$_4$}

A solution of [To^{AdBenz}]Zr(CH$_2$Ph)$_3$ (7 mg, 0.006 mmol) in C$_6$D$_6$ (*ca.* 2 mL) was added to

[PhNHMe$_2$][B{C$_6$F$_5$}$_4$] *(4.7 mg, 0.006 mmol)*. The mixture was mixed with a pipet for *ca.* 2

minutes then filtered and filtered. ^{1}H NMR (C$_6$D$_6$) for the mixture

({[To^{AdBenz}]Zr(CH$_2$Ph)$_2$}{B(C$_6$F$_5$)$_4$} + Me$_2$NPh + Toluene**):** 1.43 [m, 18H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}$$_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 1.86 [br, 9H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}$$_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 2.09 [br, 18H of

HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$$\underline{H}$$_{15}$]CO}$_3$Zr{CH$_2$(C$_6H_5$)}$_3$], 2.11 [s, 3H for the methyl group in toluene],

2.12 [s, 4H of HB{(C$_4$H$_4$)C$_2$N$_2$[C$_{10}$H$_{15}$]CO}$_3$Zr{C$\underline{H}$$_2$(C$_6H_5$)}$_2$], 2.53 [s, 6H, $\underline{Me}$$_2$NPh], 6.64 [d,

2H, Me$_2$N$\underline{Ph}$],6.80 [d, 1H, Me$_2$N$\underline{Ph}$], 7.00 [overlapped peaks, 14H], 7.14 [peak under

solvent], 7.19 ["t", 2H], 7.24 [d, 2H, Me$_2$N$\underline{Ph}$], 7.31 [d, 3H], 7.45 [d, 3H].

4.5.12 Ethylene Polymerization using {[To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_2$}{B(C$_6$F$_5$)$_4$}

Benzene (*ca.* 4mL) was added to the generated solution in section 4.5.10 (0.007 mmol of

{[To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_2$}{B(C$_6$F$_5$)$_4$} in *ca.* 2 mL C$_6$D$_6$) to make up the total solution volume

of *ca.* 6 mL and poured into a schlenck. The mixture was stirred at room temperature

then degassed and treated with 1 ethylene (1 atm). The reaction mixture was stirred at

room temperature for 10 minutes while the pressure of ethylene was maintained at 1

atm. Then the mixture was quenched with methanol (*ca.* 5 mL) followed by dilute HCl

(1M, 20 mL). The polymer was collected by filtration and washed again by methanol (*ca.* 10 mL) then dried *in vacuo* to constant weight. The yield of polyethylene is 80 mg, corresponding to activity of 45 kg PE [mol Zr]$^{-1}$[h]$^{-1}$[atm C$_2$H$_4$]$^{-1}$.

4.5.13 Ethylene Polymerization using {[To^{AdBenz}]Zr(CH$_2$Ph)$_2$}{B(C$_6$F$_5$)$_4$}

Benzene (*ca.* 4mL) was added to the generated solution in section 4.5.11 (0.007 mmol of {[To^{AdBenz}]Zr(CH$_2$Ph)$_2$}{B(C$_6$F$_5$)$_4$} in ca. 2 mL C$_6$D$_6$) to make up the total solution volume of *ca.* 6 mL and poured into a schlenk. The mixture was stirred at room temperature then degassed and treated with 1 ethylene (1 atm). The reaction mixture was stirred at room temperature for 10 minutes while the pressure of ethylene was maintained at 1 atm. Then the mixture was quenched with methanol (*ca.* 5 mL) followed by dilute HCl (1M, 20 mL). The polymer was collected by filtration and washed again by methanol (*ca.* 10 mL) then dried *in vacuo* to constant weight. The yield of polyethylene is 160 mg, corresponding to activity of 160 kg PE [mol Zr]$^{-1}$[h]$^{-1}$[atm C$_2$H$_4$]$^{-1}$.

4.6 Crystallographic Data

Table 1. Crystal, intensity collection and refinement data.

	$Zr(CH_2Ph)_4$	$[Bo^{MeBenz}]_2Zr(CH_2Ph)_2$
lattice	Monoclinic	Triclinic
formula	$C_{28}H_{28}Zr$	$C_{56.50}H_{58}B_2N_8O_4Zr$
formula weight	455.72	1025.95
space group	$P2_1$	$P\text{-}1$
$a/\text{Å}$	10.2238(10)	11.2036(7)
$b/\text{Å}$	9.6635(9)	13.1590(9)
$c/\text{Å}$	11.2356(2)	20.7159(14)
$\alpha/°$	90	106.9080(10)
$\beta/°$	101.2950(2)	97.3150(10)
$\gamma/°$	90	96.3260(10)
$V/\text{Å}^3$	1088(18)	2863.2(3)
Z	2	2
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.390	1.190
μ (Mo Kα), mm^{-1}	0.516	0.241
θ max, deg.	32.45	30.68
no. of data collected	18886	46845
no. of data used	7475	17593
no. of parameters	262	571
R_1 [$I > 2\sigma(I)$]	0.0377	0.0472
wR_2 [$I > 2\sigma(I)$]	0.0640	0.0869
R_1 [all data]	0.0560	0.0790
wR_2 [all data]	0.0697	0.0934
GOF	1.012	1.019
R_{int}	0.0414	0.0546

Table 1. (cont.) Crystal, intensity collection and refinement data.

	[Bo^{AdBenz}]$_2$Zr(CH$_2$Ph)$_2$	[To^{MeBenz}]Zr(CH$_2$Ph)$_3$
lattice	Orthorhombic	Monoclinic
formula	C$_{89}$H$_{101}$B$_2$N$_8$O$_4$Zr	C$_{46.5}$H$_{46}$BN$_6$O$_3$ZrCl$_3$
formula weight	1459.62	945.27
space group	*Pbca*	*P-1*
a/Å	19.8594(16)	12.421(15)
b/Å	22.5384(18)	13.7095(16)
c/Å	34.248(3)	14.3580(17)
α/°	90	64.594(2)
β/°	90	72.960(2)
γ/°	90	78.419(2)
V/Å^3	15329(2)	2158.0(4)
Z	8	2
temperature (K)	150(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.265	1.455
μ (Mo Kα), mm^{-1}	0.201	0.490
θ max, deg.	24.71	31.31
no. of data collected	156891	36500
no. of data used	13077	13915
no. of parameters	862	539
R_1 [$I > 2\sigma(I)$]	0.1027	0.0605
wR_2 [$I > 2\sigma(I)$]	0.2336	0.1440
R_1 [all data]	0.1793	0.0978
wR_2 [all data]	0.2619	0.1596
GOF	1.219	1.023
R_{int}	0.2446	0.0629

Table 1. (cont.) Crystal, intensity collection and refinement data.

	[To$^{Bu^tBenz}$]Zr(CH$_2$Ph)$_3$	[To^{AdBenz}]Zr(CH$_2$Ph)$_3$
lattice	Rhombohedral	Rhombohedral
formula	C$_{77.50}$H$_{91}$BN$_6$O$_3$Zr	C$_{75.50}$H$_{86}$BN$_6$O$_3$ZrCl$_7$
formula weight	1256.59	1475.68
space group	R-3	R-3
a/Å	18.7511(13)	19.462(3)
b/Å	18.7511(13)	19.462(3)
c/Å	33.834(2)	31.762(4)
α/°	90	90
β/°	90	90
γ/°	120	120
V/Å^3	10302.4(12)	10418(2)
Z	6	6
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.215	1.411
μ (Mo Kα), mm^{-1}	0.212	0.481
θ max, deg.	32.03	26.37
no. of data collected	49968	42344
no. of data used	7747	4752
no. of parameters	265	279
R_1 [$I > 2\sigma(I)$]	0.0474	0.0566
wR_2 [$I > 2\sigma(I)$]	0.1344	0.1334
R_1 [all data]	0.0626	0.0829
wR_2 [all data]	0.1429	0.1437
GOF	1.083	1.058
R_{int}	0.0384	0.0975

Table 1. (cont.) Crystal, intensity collection and refinement data.

	$\{[\text{To}^{\text{Bu}^{\text{t}}\text{Benz}}]\text{Zr}(\text{CH}_2\text{Ph})_2(\text{OEt}_2)\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$
lattice	Triclinic
formula	$C_{85}H_{86.93}B_2N_6O_4ZrF_{20}$
formula weight	1749.38
space group	*P-1*
$a/\text{Å}$	16.257(2)
$b/\text{Å}$	17.277(3)
$c/\text{Å}$	18.379(3)
$\alpha/°$	65.836(2)
$\beta/°$	66.000(2)
$\gamma/°$	89.873(2)
$V/\text{Å}^3$	4218.1(11)
Z	2
temperature (K)	150(2)
radiation (λ, Å)	0.71073
ρ (calcd.), g cm^{-3}	1.377
μ (Mo Kα), mm^{-1}	0.227
θ max, deg.	26.37
no. of data collected	50995
no. of data used	17251
no. of parameters	996
R_1 [$I > 2\sigma(I)$]	0.0587
wR_2 [$I > 2\sigma(I)$]	0.0859
R_1 [all data]	0.1259
wR_2 [all data]	0.0951
GOF	1.005
R_{int}	0.0942

4.7 References and Notes.

(1)   (a) Pearson, R. G. *J. Chem. Edu*. **1968**, 581-587. (b) Pearson, R. G. *J. Chem. Edu*. **1968**, 643-648.

(2)   (a) Ziegler, K., Holzkamp, E., Breil, H., Martin, H. *Angew. Chem*. **1955**, 67, 541-547. (b) Ziegler, K. *Angew Chem*. **1964**, 76, 545-553.

(3)   (a) Natta, G. *Angew Chem*. **1956**, 68, 393-403. (b) Natta, G. *Angew Chem*. **1964**, 76, 553-566.

(4)   Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.*, **1980**, 18, 99-149.

(5)   Chen, E. Y.; Marks, T. J. *Chem. Rev*. **2000**, 100, 1391-1434.

(6)   Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev*. **2003**, 103, 283-315.

(7)   (a) Nakazawa. H.; Ika, S.; Imoka, K.; Kai, Y.; Yano, T. *J. Mol. Catal A: Chem*, **1998**, 132, 33-41. (b) Karam. A.; Jimeno, M.; Lezama, J.; Catari, E.; Figueroa, A.; Rojas, D. B. *J. Mol. Catal A:Chem*, **2001**, 176, 65-72. (c) Karam. A.; Cases, A.; Catari, A.; Perkerar, S.; Albornoz, A.; Mendez, B. *J. Mol. Catal A:Chem*, **2005**, 238, 233-240. (d) Karam. A.; Pastran, J.; Casas, E., Mendez, B. *Polym. Bull*. **2005**, 55, 11-17. (e) Murtuza, S.; Casagrande Jr., O. L.; Jordan, R. F., *Organometallics***, 2002**, 21, 1882-1890. (f) Lopez-Linares, F. Diaz, B. A., Ortrga, H., Karam A., Agrifoglio, G. Gonzalez, E. *J. Mol. Catal A:Chem*, **2002**, 179, 87-92. (g) Gil, M. P. Dos Santos, J. H. Z.; Casagrands Jr, O. L. Simplico, L. M. T.; Da Rocha, Z. N. *Macromol. Chem. Phys*. **2001**, 202, 319-324. (h) Gil, M. P.; Dos Santos, J. H. Z.; Casagrands Jr, O. L.

Simplicio, L. M. T.; Da Rocha, Z. N.; *J. Mol. Catal. A: Chem.* **2005**, 238, 96-101. (i) Junges, F.; de Souza, R. F.; dos Santos, J. H. Z. Casagrands Jr, O. L. *Macromol. Mater. Eng.* **2005**, 290, 72-77. (j) Kunrath, F. A.; Mauler, R. S.; de Souza, R. F.; Casagrands Jr, O. L. *Macromol. Chem. Phys.* **2002**, 203, 2058-2068. (k) Asandei, A. D.; Moran, I. W. *J. Polm Sci. Part A: Polym Chem.* **2005**, 43, 6039-6047. (l) Kunrath, F. A.; de Souza, R. F.; Casagrands Jr, O. L. *Macromol. Rapid Commun.* **2000**, 21, 277-280. (m) Janiak, C. Lange, K. C. H.; Scharmann, T. G. *Appl. Organomet. Chem.* **2000**, 14, 316-324. (n) Lee, H.; Jordan, R. F. *JACS*, **2005**, 127, 9384-9385.

(8)   For example group 4 metal [Tp^{R,R}]M alkyl complexes are difficult to prepare by alkylation of [Tp^{R,R}]MCl$_3$ and their chemistry is virtually unexplored. (a) Lee, H.; Nienkemper, K.; Jordan, R. F. *Organometallics* **2008**, 27, 5075-5081. (b) Reger, D. L.; Tarquini, M. E. Lebioda, L. *Organometallics* **1983**, 2, 1763-1769. (c) Ipaktschi, J.; Sulzbach, W. *J. Organomet. Chem.* **1992**, 426, 59-70.

(9)   (a) Zucchini, U.; Giannini, U.; Albizzati, E.; D'Angelo, R. *J. Chem. Soc. D, Chem. Commun.* **1969**, 1174-1175. (b) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357-372.

(10)   Benkeser, R. A.; Snyder, D. C. *J. Org. Chem.* **1982,** *47*, 1243-1249.

(11)   (a) Tedesco, C.; Immirzi, A.; Proto, A. *Acta Crystallogr. Sect. B, Struct. Sci.* **1998**, *B54*, 431-437. (b) Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 1511-1512. (c) Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.; Pioli, A. J. P. *J. Chem. Soc. D., Chem. Commun.* **1971**, 677.

(12) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293-298.

(13) Examples of dimethylanaline coordinating to activated zirconium species:
(a) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, 371-386.
(b) Wilson, P. A.; Wright, J. A.; Oganesyan, V. S.; Lancaster, S. J.; Bochmann, M.
Organometallics **2008**, 6371-6374.

(14) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Int. Ed*. **1999**, 28, 428-
447.

(15) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic
Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society:
Washington, DC, 1987; Chapter 2, pp 6-23. (b) Burger, B.J.; Bercaw, J. E. in
Experimental Organometallic Chemistry; Wayda, A. L.; Darensbourg, M. Y., Eds.;
American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.
(c) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*,
2nd Edition; Wiley-Interscience: New York, 1986.

(16) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.;
Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

(17) Morcombe, C. R.; Zilm, K. W. *J. Magn. Reson.* **2003,** *162*, 479-486.

(18) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and
Displaying Crystal Structures from Diffraction Data; University of Göttingen,

Göttingen, Federal Republic of Germany, 1981. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

Chapter 5

Synthesis and Structural Characterization of *Tris*(2-pyridonyl)methyl Complexes of Zinc and Thallium: A New Class of Metallacarbatranes and a Monovalent Thallium Alkyl Compound

Table of Contents

5.1   Introduction

Development of facially-coordinating C_3 L_2X type tripodal ligands is currently an active field, among which, ligands that encompass nitrogen $[N_3]$[1] or sulfur $[S_3]$[2] donor arrays have enjoyed widespread applications. We have contributed to these activities by developing new $[O_3]$ donor ligands that belong to the L_2X type, namely *tris*(oxoimidazolyl)borate.

Multidentate oxygen-donor ligands are well established and have diverse applications, as illustrated by their use to mimic oxide surfaces.[3,4] They have been synthesized in many different electronic forms including L_2X[5], L_3,[6] X_3,[7] X_4[8] and LX_3[9,10], but not L_3X according to covalent bond classifications (L = 2-electron donor, X = 1-electron donor).[11] In addition to simple tridentate $[O_3]$ donor ligands, C_3 symmetric tetradentate tripodal variants are also known, in which the bridgehead donor may also bind to the metal. The majority of such ligands, however, belong to the classification LX_3, in which the bridgehead is an L-type nitrogen atom donor.[12,13] Therefore, we set out to develop a C_3 symmetric tetradentate tripodal oxygen rich donor ligand that belongs to the L_3X[14] donor system (Figure 1).
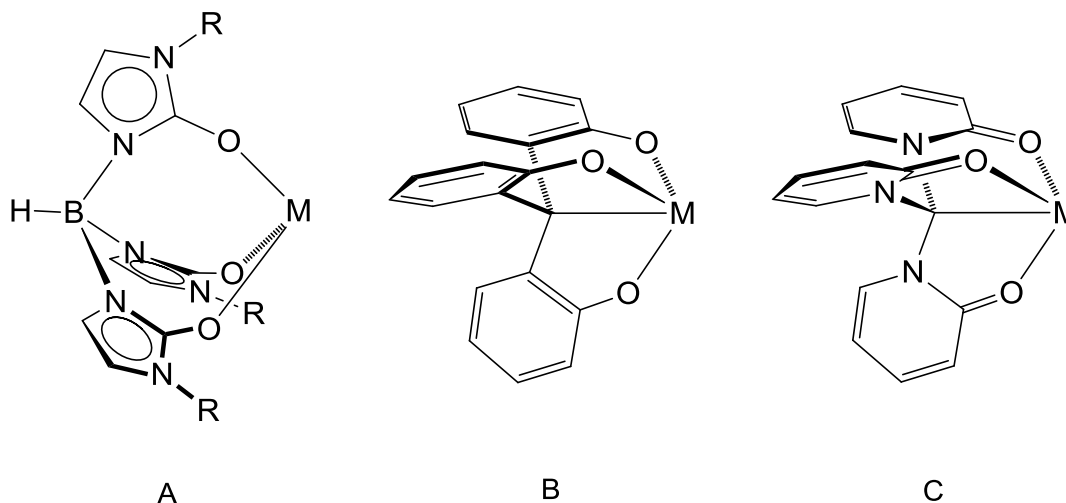
Figure 1. Different type of oxygen rich ligands according to the CBC method: a. L_2X, b. X_4, c. L_3X (target complex).

In addition to creating a new class of L_3X [CO_3] donor ligands in which the X-type bridgehead donor is a carbon atom, these ligands have enabled the isolation of a new class of metallacarbatrane compounds, including a monovalent thallium alkyl compound.

5.2 Synthesis of the ligands

Based on previous reports for the acid catalyzed rearrangement of *tris*(1-R-organo-imidazol-2-ylthio)methanes to *tris*(imidazole-2-thione)methanes,[15] we apply the same synthetic approach to obtain our target ligand, *tris*(2-pyridonyl)methane. Specifically, *tris*(pyridin-2-yloxy)methane was synthesized first, followed by treatment with acid to generate the thermodynamic product as shown in Scheme 1.
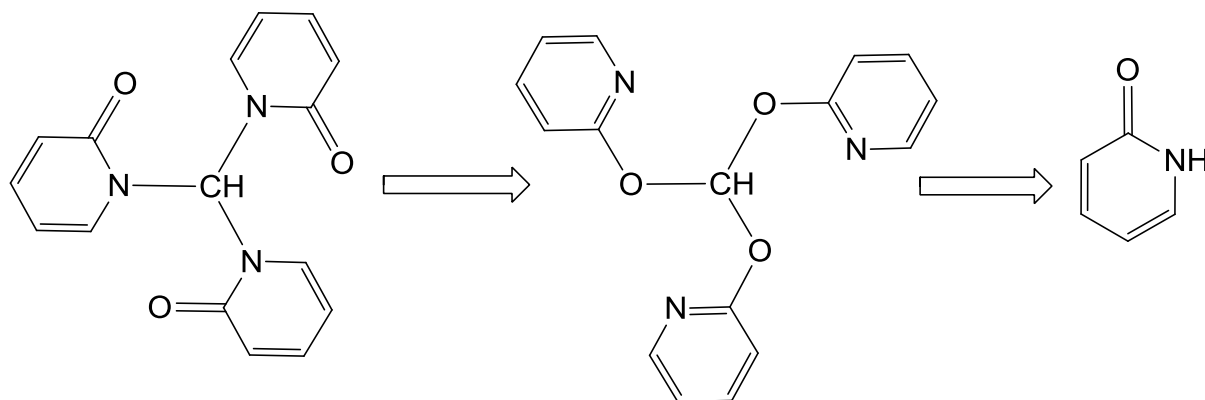
Scheme 1. Retrosynthetic analysis of *tris*(2-pyridonyl)methane.

Specifically, treatment of 2-pyridone with $CHCl_3$ and K_2CO_3 in the presence of

$[Bu^n_4N]Br$ as a phase transfer agent yields an isomeric mixture of $HC(OC_5H_4N)_3$ and

$HC(OC_5H_4N)_2(NC_5H_4O)$, as shown in Scheme 2. Treatment of $HC(OC_5H_4N)_3$

$HC(OC_5H_4N)_2(NC_5H_4O)$, or a mixture of the two, with camphorsulfonic acid (CSA) in a

THF and toluene mixture at reflux leads to $HC(OC_5H_4N)(NC_5H_4O)_2$. However, *tris*(2-

pyridonyl)methane, [Tpom]H, is obtained when the isomerization reaction conducted

at higher temperature, 175 °C (Scheme 2).
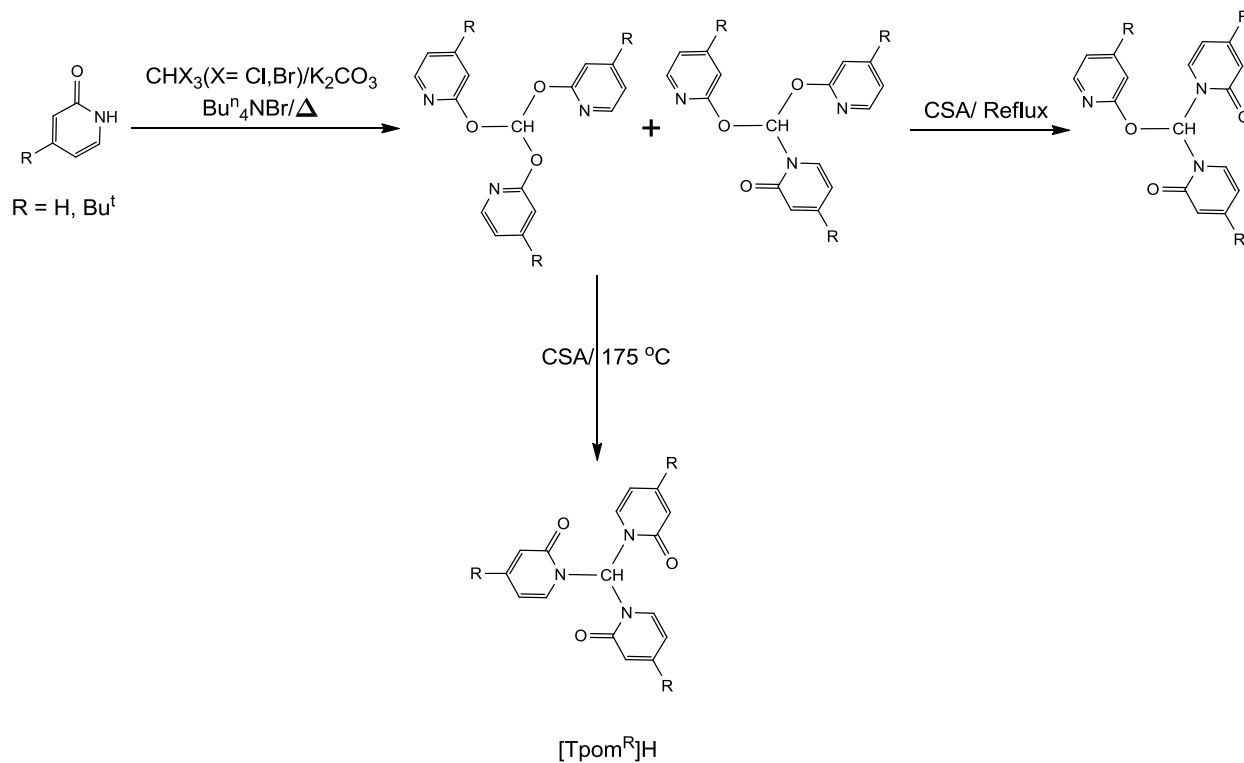
Scheme 2. Reaction of 2-pyridone with CHX$_3$ followed by acidic isomerization of the products.

Fortunately, we obtained crystals and determined the molecular structures of all of the isomeric products *via* X-ray diffraction as shown in Figures 2, 3, 4 and 5.
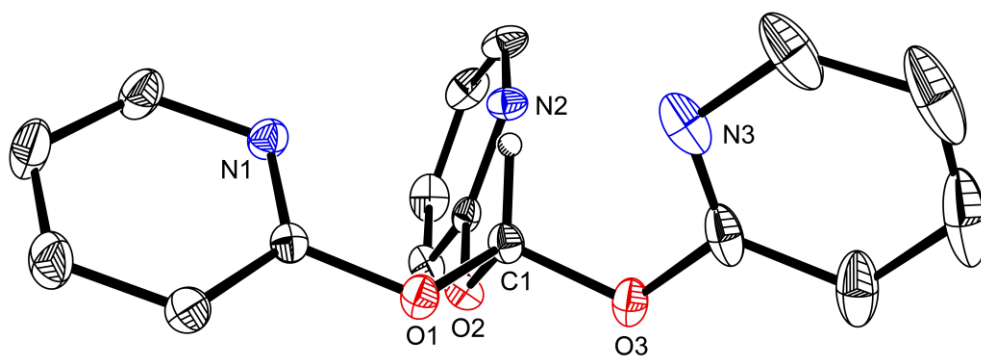
Figure 2. Molecular structure of HC(OC$_5$H$_4$N)$_3$.
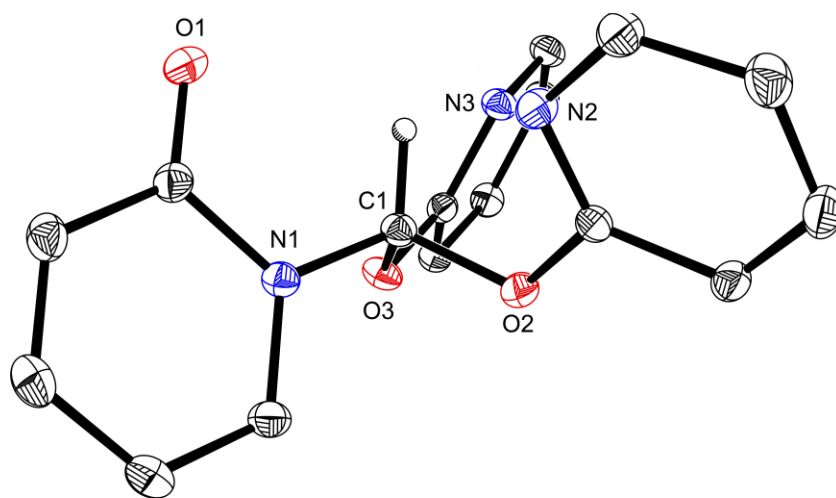
Figure 3. Molecular structure of HC(OC$_5$H$_4$N)$_2$(NC$_5$H$_4$O).
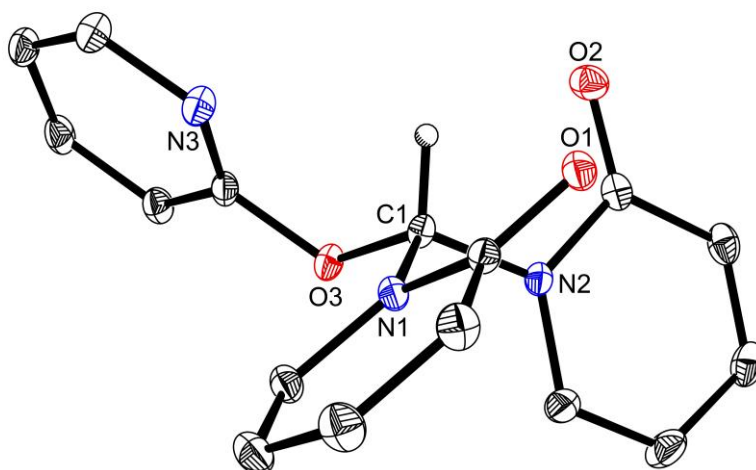
Figure 4. Molecular structure of $HC(OC_5H_4N)(NC_5H_4O)_2$.
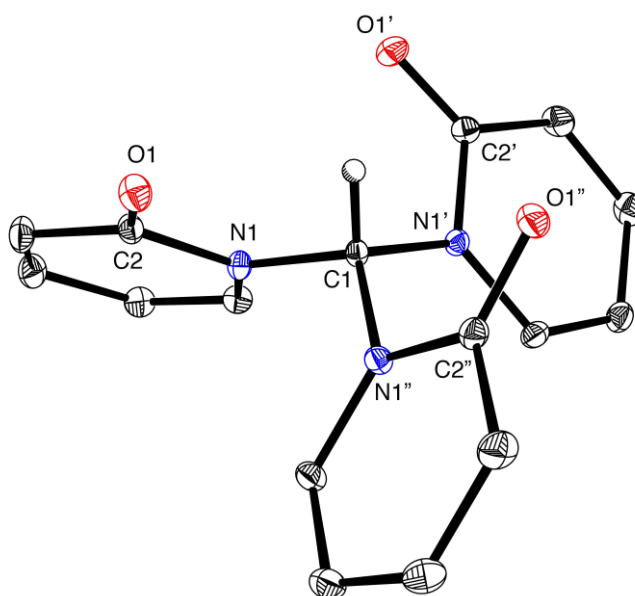
Figure 5. Molecular structure of $HC(NC_5H_4O)_3$.

Due to solubility issues associated with *tris*(2-pyridonyl)methane, we used 4-tert-butyl-

2-[1*H*]-pyridone instead of 2-pyridone as a starting material to produce a more soluble

ligand. It is synthesized according to the reported procedure[16] where 4-t-butylpyridine-

N-oxide[17] is generated by the oxidation of the 4-tert-butylpyridine. Then the N-oxide

compound reacts with acetic anhydride at high temperature followed by hydrolysis to

generate the pyridone derivative. (Scheme 3)
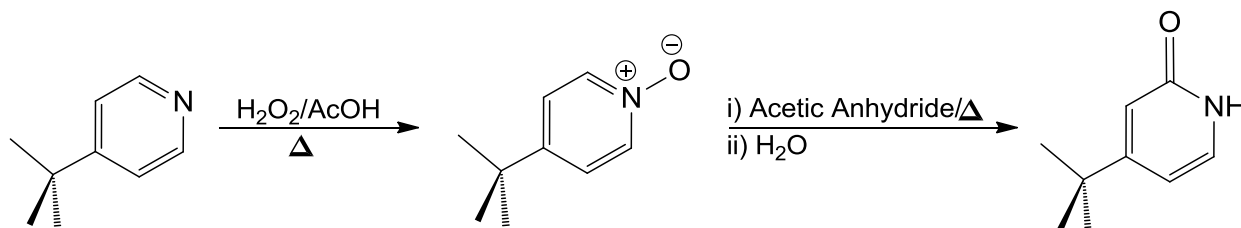
Scheme 3. Synthesis of 4-tert-butyl-2-[1*H*]-pyridone.

Colorless crystals of 4-tert-butyl-2-[1*H*]-pyridone were obtained from a hexane solution

and the molecular structure was determined by X-ray diffraction (Figure 6).
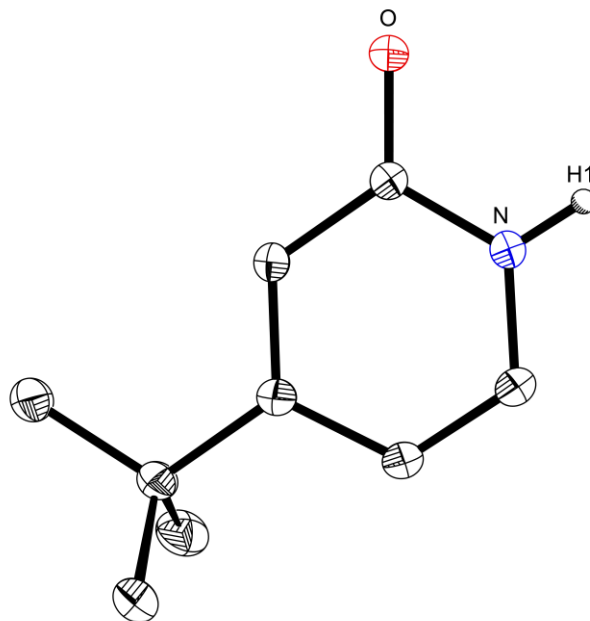
Figure 6. Molecular structure of 4-tert-butyl-2-[1*H*]-pyridone.

The t-butyl derivative, [Tpom^{But}]H, was obtained *via* a synthetic procedure similar to

[Tpom]H which result in [Tpom^{But}]H being more soluble than [Tpom]H, Scheme 2. The

molecular structures of all the isomeric products of the *t*-butyl derivative have been

determined by X-ray diffraction as shown in Figures 7, 8, 9 and 10.
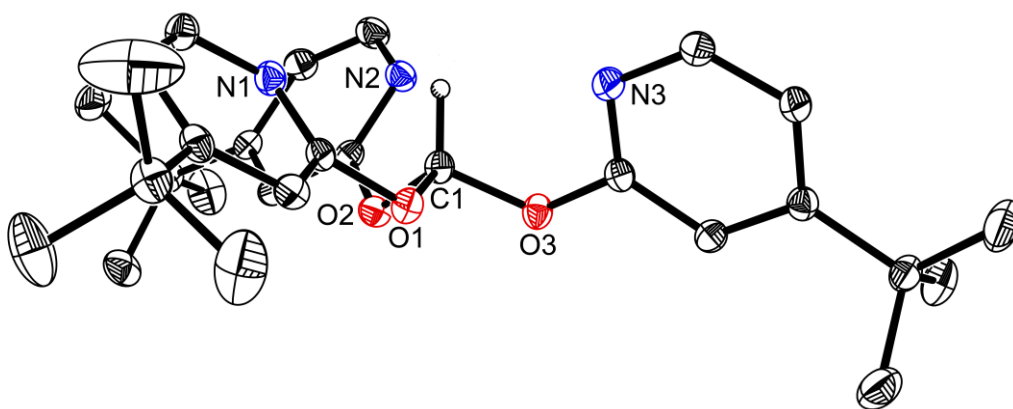
Figure 7. Molecular structure of HC(OC$_5$H$_3$Bu^{t}N)$_3$.
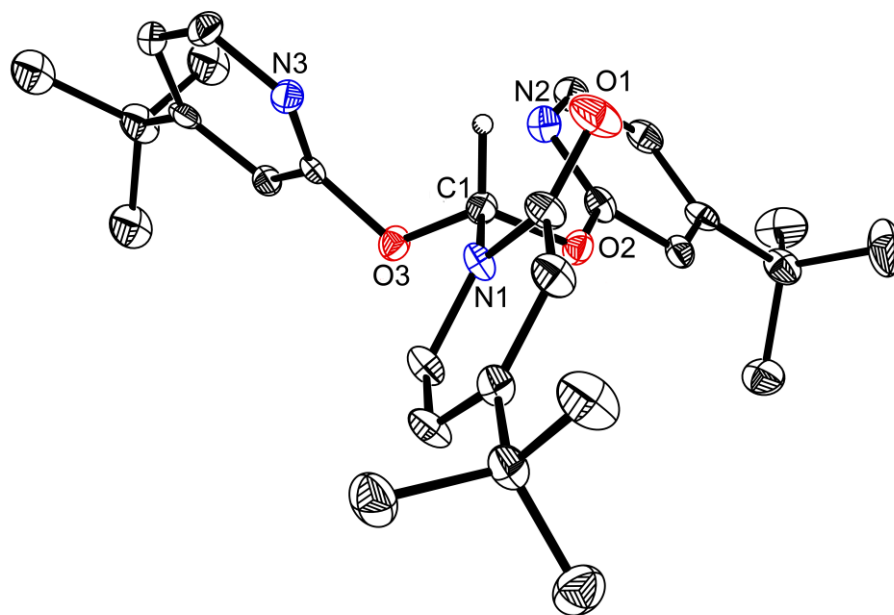
Figure 8. Molecular structure of $HC(OC_5H_3Bu^tN)_2(NC_5H_3Bu^tO)$.
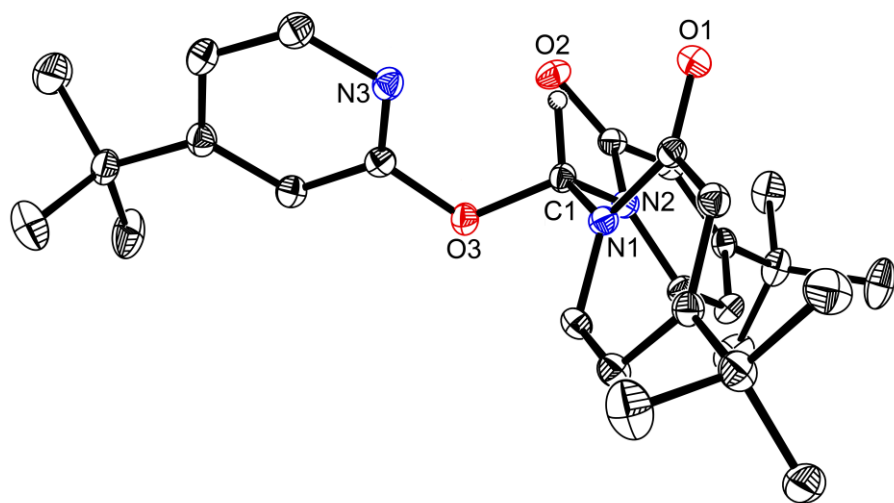
Figure 9. Molecular structure of $HC(OC_5H_3Bu^tN)(NC_5H_3Bu^tO)_2$.
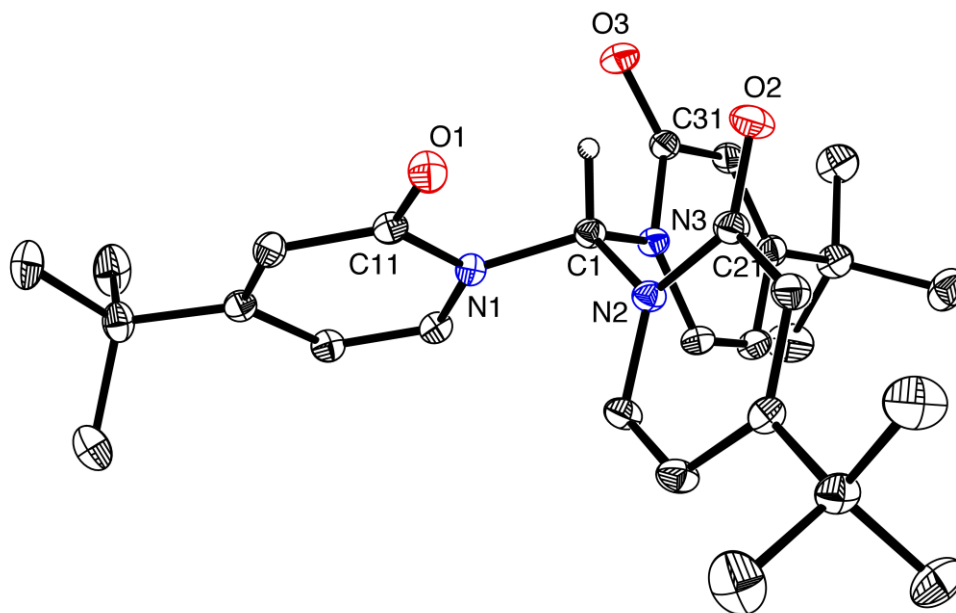
Figure 10. Molecular structure of HC(NC$_5$H$_3$Bu^{t}O)$_3$.

According to the molecular structures of both [Tpom]H and [Tpom$^{Bu^t}$]H, as shown in Figures 5 and 10, the conformation adopted is one in which the three oxygen atoms are on the same side as the C–H group. As such, the ligands are ideally suited for coordinating *via* the oxygen atoms following metalation of the C–H bond.

5.3 *Tris*(2-pyridonyl)methyl Complexes of Zinc

5.3.1 [Tpom^R]ZnN(TMS)$_2$: Effect of Alkyl Substitution

Treatment of Zn[N(SiMe$_3$)$_2$]$_2$ with [Tpom]H or [Tpom$^{Bu^t}$]H gives [κ^3-Tpom]ZnN(SiMe$_3$)$_2$ or [κ^4-Tpom$^{Bu^t}$]ZnN(SiMe$_3$)$_2$, respectively, as illustrated in Scheme 4.
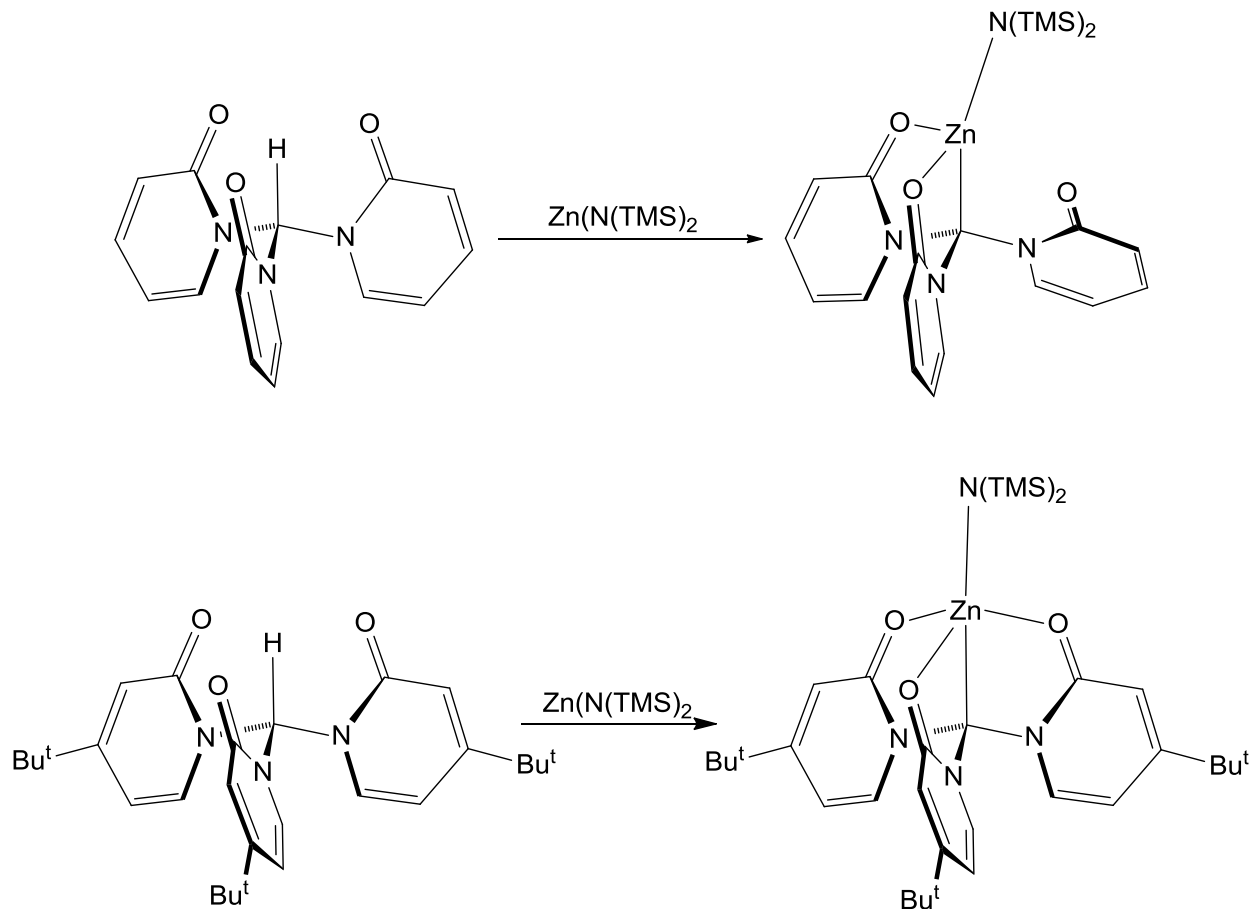
Scheme 4. Synthesis of $[\kappa^x\text{-Tpom}^R]Zn[N(SiMe_3)_2]$, X = 3 when R = H, and X = 4 when R = t-but.

An interesting difference that arises from the presence of the *t*-butyl substituent is that the $[\text{Tpom}^{Bu^t}]$ ligand binds to the zinc center in a manner that approaches a κ^4-coordination mode while [Tpom] ligand adopts a κ^3-coordination mode.[18] This observation is based on the X-ray structures of $[\kappa^4\text{-Tpom}^{Bu^t}]ZnN(SiMe_3)_2$ (Figure 11) and $[\kappa^3\text{-Tpom}]ZnN(SiMe_3)_2$ (Figure 12).
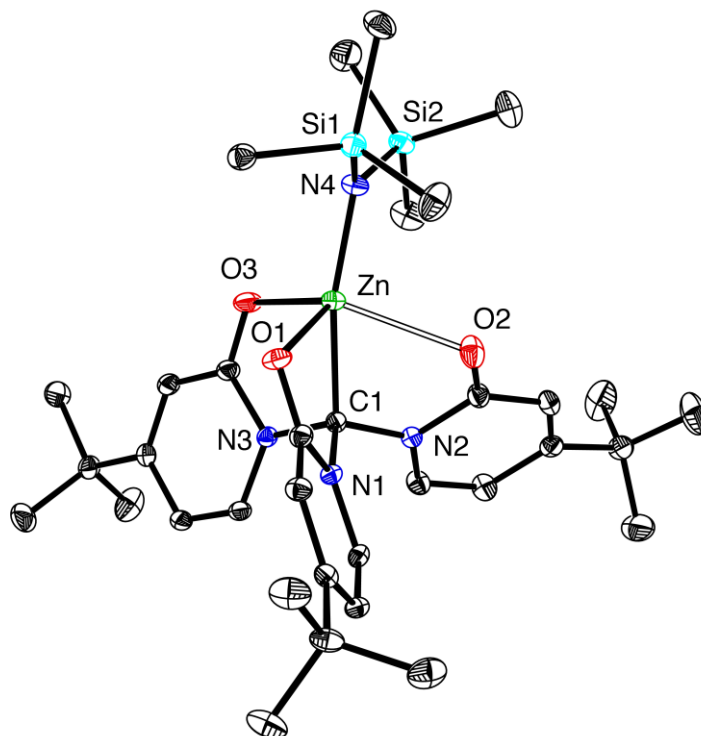
Figure 11. Molecular structure of [κ⁴-Tpom^Bu^t]Zn[N(SiMe₃)₂].
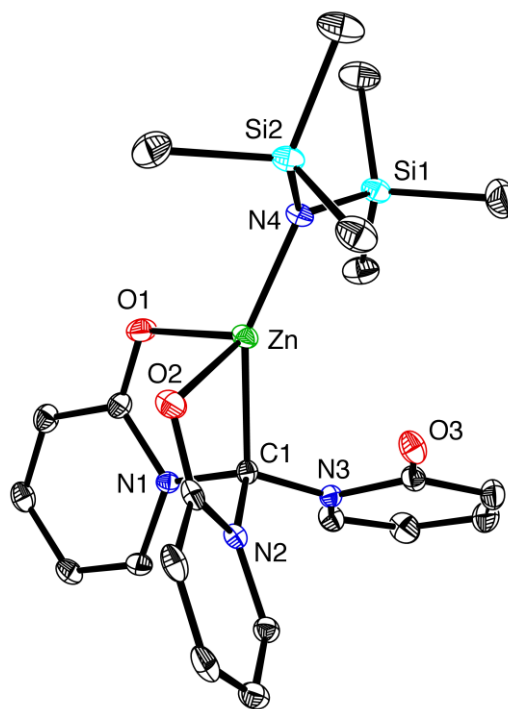
Figure 12. Molecular structure of [κ³-Tpom]Zn[N(SiMe₃)₂].

For both [κ³-Tpom]ZnN(SiMe$_3$)$_2$[19] and [κ⁴-Tpom$^{Bu^t}$]ZnN(SiMe$_3$)$_2$[20] complexes, two of the

Zn–O bonds are comparable to the average value for compounds listed in the

Cambridge Structural Database[21] (2.05 Å), the third Zn–O distance is considerably

longer, *i.e.* 2.866(2) Å and 2.401(1) Å, respectively. Based on the magnitude of these

distances, we conclude that there is a weak Zn–O secondary interaction for the

[Tpom$^{Bu^t}$] ligand but not for the [Tpom] derivative.

The three pyridonyl groups of [κ³-Tpom]Zn[N(SiMe$_3$)$_2$] are chemically equivalent on the

NMR time scale down to –77 °C based on variable temperature ^{1}H NMR spectroscopic

studies. This result indicates that there is either rapid exchange between the

coordinated and uncoordinated pyridonyl groups, such that the molecule is fluxional,

or that the molecule adopts a five-coordinate structure in solution. A different

observation was obtained for fluxional [κ³-Tptm]Zn[N(SiMe$_3$)$_2$] in solution; a spectrum

indicating two distinct pyridonyl environments starts to emerge at *ca.* -10°C.[22]

5.3.2 [κ⁴-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t: A Metallacarbatrane

Treatment of [κ⁴-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$] with 4-t-butylphenol in benzene leads to a

white precipitate of [κ⁴-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t (Scheme 5). Colorless crystals of [κ⁴-

Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t suitable for X-ray diffraction were obtained from a CH$_2$Cl$_2$

solution (Figure 13).
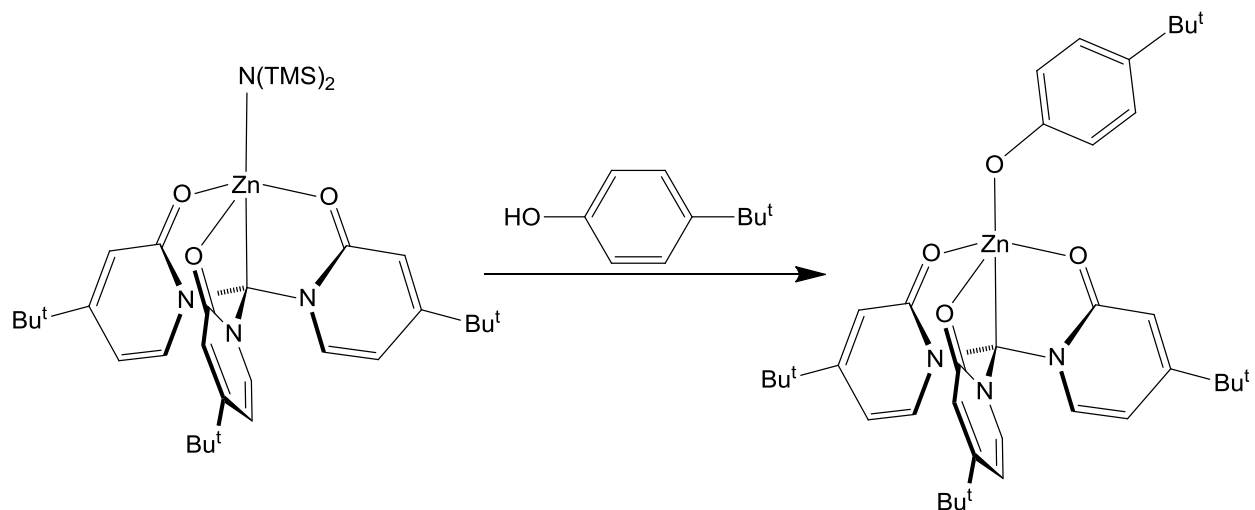
Scheme 5. Synthesis of [κ⁴-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t.
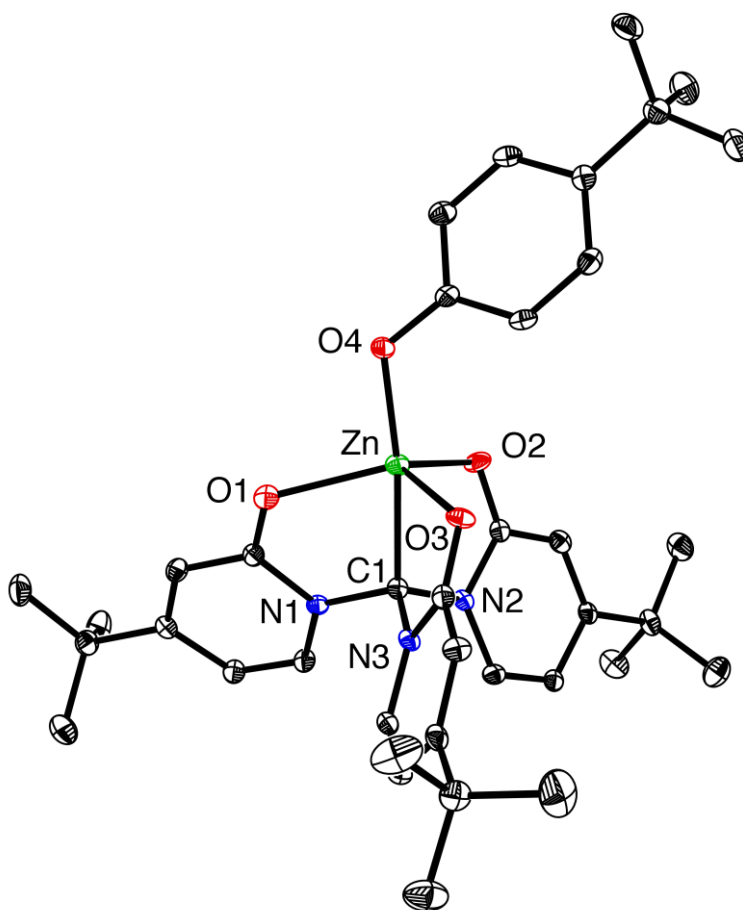
Figure 13. Molecular structure of [κ⁴-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t.

The range of Zn–O bond lengths [2.090(3) Å – 2.164(3) Å][23] for [κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t is much narrower than for [κ^4-Tpom^{But}]Zn[N(SiMe$_3$)$_2$] [2.096(1) Å – 2.401(1) Å] and [κ^3-Tpom]Zn[N(SiMe$_3$)$_2$] [2.095(2) Å – 2.866(2) Å]. Therefore, [κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t exhibits a well-defined atrane motif.[9,24]

Atranes are an interesting class of molecules that feature a tricyclic ring system in which the two bridgehead atoms are directly linked.[9,24] Originally, [κ^4-N(CH$_2$CH$_2$O)$_3$]E derivatives, in which one of the bridgehead atoms is nitrogen, were the only types of molecule described as having an atrane motif. Afterward, the term was expanded to include a variety of other systems. For instance, compounds in which nitrogen is not one of the bridgehead atoms have been described as atranes. If the linkers between the bridgehead atoms are not [CH$_2$CH$_2$O] groups, the complex is also described as an atrane. For example, tricyclic compounds that feature transannular M–B bonds have been referred to "metallaboratranes".[25] Therefore, [κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t would be classified as a "metallacarbatrane".[26]

Atranes derived from [Tpom^R] differ from [κ^4-N(CH$_2$CH$_2$O)$_3$]E and metallaboratrane derivatives by the fact that the transannular interaction is a normal covalent bond instead of a dative covalent bond.

The Zn–C bond lengths in [Tpom^R]ZnX (Table 1) are comparable to each other, but they are slightly longer than the mean Zn–C bond length of 2.01 Å for compounds listed in the Cambridge Structural Database.[21,27,28] On the contrary, the Zn–C bonds in

[Tpom^R]ZnX are shorter than those in *tris*(2-pyridylthio)methyl derivatives.[22,29,30] In both cases, the linkers contain the same numbers of atoms but they differ in nature and position, *i.e.* Zn–[NCS]–C *versus* Zn–[OCN]–C.

Table 1. Zn–C bond lengths in [Tpom^R]ZnX and related compounds.

	d(Zn–C)/Å
[κ^3-Tpom]Zn[N(SiMe$_3$)$_2$]	2.064(2)
[κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]	2.080(2)
[κ^4-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t	2.071(5)
[κ^3-Tptm]ZnH	2.105(3)
[κ^3-Tptm]ZnMe	2.098(2)
[κ^4-Tptm]ZnN$_3$	2.199(3)
[κ^4-Tptm]ZnNCO	2.194(3)

5.4   *Tris*(2-pyridonyl)methyl Complexes of Thallium: a Long Tl–C bond

We have seen in the previous sections the application of [Tpom^R] ligands to zinc chemistry. Here we show that the [Tpom^{Bu^t}] ligand also allows the isolation of a monovalent thallium alkyl complex. This is obtained *via* treatment of [Tpom^{Bu^t}]H with TlN(SiMe$_3$)$_2$, as shown in Scheme 6.

A

B
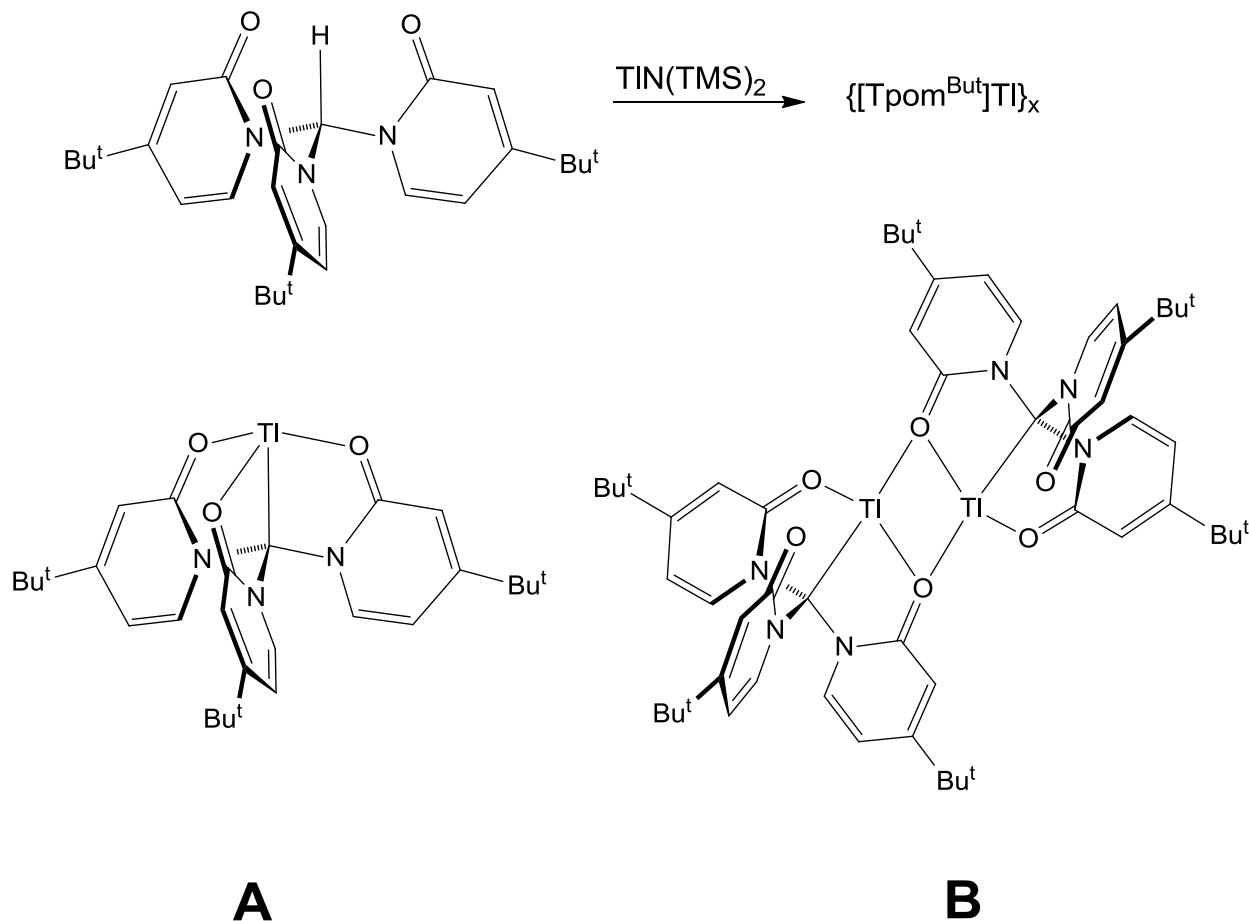
Scheme 6. Synthesis of {[Tpom^{But}]Tl}$_x$, A: x = 1 when crystalized from toluene,

B: x = 2 when crystalized from benzene.

The molecular structure of [Tpom^{But}]Tl as determined by X-ray diffraction has been

obtained in two different polymorphs. A monomeric complex, [Tpom^{But}]Tl (Figure 14),

is obtained by diffusion of hexane into a toluene solution while a dimeric complex,

{[Tpom^{But}]Tl}$_2$ (Figure 15), is obtained by diffusion of pentane into a benzene solution.

For [Tpom^{But}]Tl, the coordination environment surrounding the thallium is restricted to

less than one hemisphere. However in the case of {[Tpom^{But}]Tl}$_2$, one of the oxygen

atoms of the [Tpom^{But}] ligand serves as a bridge between two thallium centers. Pulsed

gradient spin-echo diffusion NMR spectroscopic experiments, however, indicate that dimeric {[κ³-Tpom$^{Bu^t}$]Tl}$_2$ does not persist in toluene and that the compound exists as a monomer in solution.

Figure 14. Molecular structure of [κ⁴-Tpom$^{Bu^t}$]Tl.
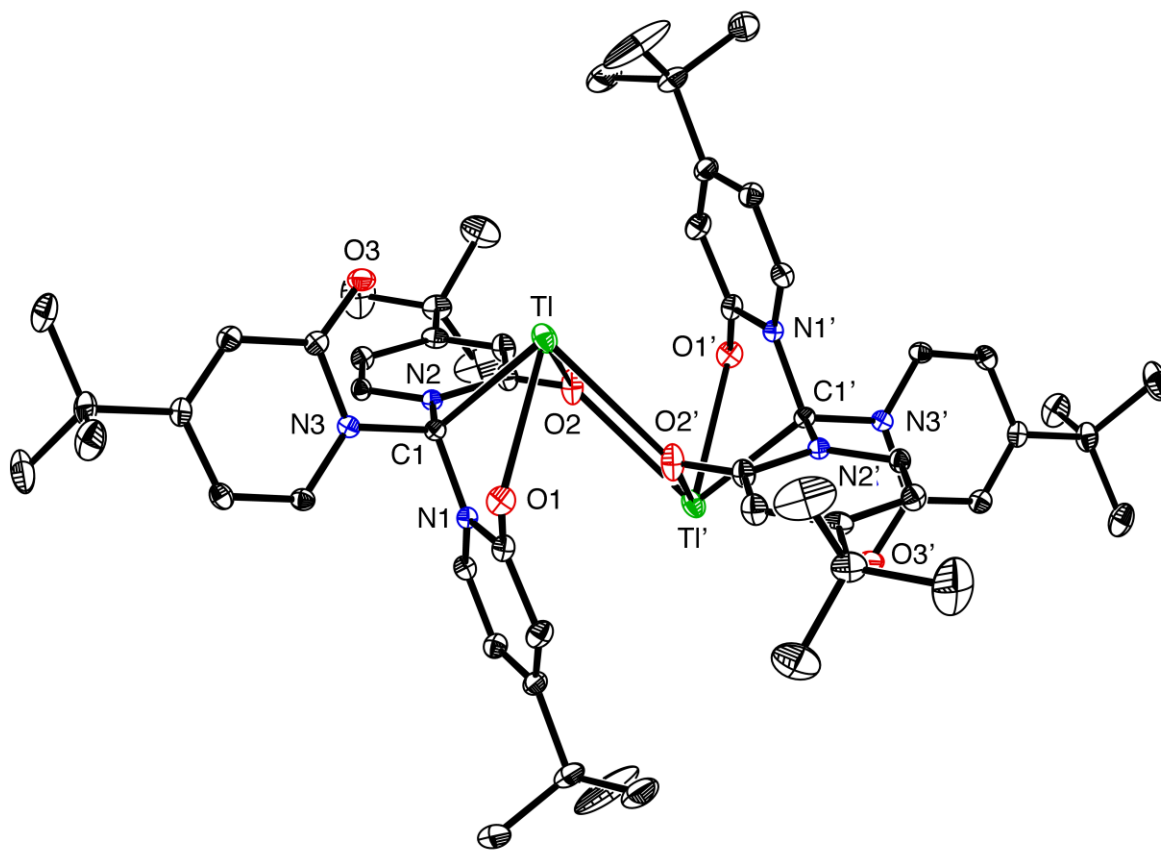
Figure 15. Molecular structure of {[κ³-Tpom$^{Bu^t}$]Tl}$_2$.

The mononuclear [Tpom$^{Bu^t}$]Tl crystal structure indicates that the coordination environment surrounding each thallium is restricted to less than one hemisphere of the atom. While this motif could be anticipated for mononuclear compounds that feature face-capping ligands, such as *tris*(pyrazolyl)borato complexes, [Tp$^{R,R'}$]Tl,[31] it is actually a general feature of monovalent thallium chemistry, and is commonly attributed to the presence of a lone pair on thallium.[32]

Simple monovalent organothallium compounds (RTl) are generally unstable and easily disproportionate to R$_3$Tl and elemental thallium.[31] They are mainly restricted to

cyclopentadienyl and arene derivatives,[31] and structurally characterized alkyl and aryl

compounds are uncommon. Also as a result of "thallophilic"[33] interactions,[34,35] many

monovalent thallium alkyl and aryl compounds exist as oligomers, *e.g.* dimeric $[Ar'Tl]_2$

$(Ar' = C_6H_3-2,6-\{C_6H_3-2,6-Pr^i_2\}_2)$,[36] trimeric $[Ar''Tl]_3$ $(Ar'' = C_6H_3-2,6-\{C_6H_3-2,6-Me_2\}_2)$,[36]

and tetrameric $\{Tl[C(SiMe_3)_3]\}_4$.[37] However, there is one monomeric compound listed in

the Cambridge Structural Database, namely the aryl compound Ar'''Tl $(Ar''' = C_6H_3-2,6-$

$\{C_6H_2-2,4,6-Pr^i_2\}_2)$.[38] Therefore, the isolation of $[Tpom^{Bu^t}]Tl$ is significant since it is rare

example of a structurally characterized monovalent thallium alkyl complex that is

devoid of "thallophilic" interactions.

The Tl–C and Tl–O bond lengths within $[Tpom^{Bu^t}]Tl$ also merit discussion. Though the

covalent radius of oxygen (0.66 Å) is smaller than that for carbon (0.76 Å),[28] the average

Tl–O bond length [2.681(3) Å] is significantly longer than the Tl–C bond length [2.490(7)

Å]. This observation is reproduced by density functional theory calculations.

Specifically, the calculated Tl–C bond length is 2.567 Å and the Tl–O bond lengths have

an average value of 2.627 Å. This suggests that the Tl–O interaction is secondary in

nature when compared to Tl–C interaction. In support of this suggestion, much shorter

Tl–O bonds (*e.g.* 2.401 Å) have been reported for other monovalent thallium

compounds.[39] Also the Tl–C bond length for $\{[Tpom^{Bu^t}]Tl\}_x$ is quite long when compared

to other monovalent thallium alkyl compounds as shown in Table 2.

Table 2. Tl–C bond lengths in monovalent thallium alkyl complexes.

	d(Tl–C)/Å
[Tpom^{But}]Tl	2.490(7)
{[Tpom^{But}]Tl}$_2$	2.790(2)
{Tl[C(SiMe$_3$)$_3$]}$_4$	2.37
[Ar'Tl]$_2$	2.313(5)
[Ar''Tl]$_3$	2.331(4)
Ar'''Tl	2.34(1)

Long Tl–C bond lengths comparable to that of [Tpom^{But}]Tl have been observed in {Tl[CH(SiMe$_3$){SiMe(OMe)$_2$}Li]}$_2$ (2.547 Å),[40] in which each thallium is attached to two alkyl groups, and [Tl$_2${C{(PPh$_2$)NSiMe$_3$}$_2$]$_2$ (2.525 Å),[41] in which the carbon atom bridges two thallium centers. At the other extreme, much shorter Tl–C bonds are observed in trivalent thallium compounds, *e.g.* [Bm^{But}]TlMe$_2$ (2.14 Å)[42] and Ar'Tl[B(C$_6$F$_5$)$_3$] (2.165 Å),[36] making it evident that Tl–C bonds span a very large range.

This can be rationalized by molecular orbital and natural bond orbital (NBO) analyses[43] since they indicate that the Tl–C bond has little covalent character (Figures 16 and 17). In addition to the presence of a lone pair on thallium, the NBO analysis also indicates the presence of a highly localized sp^3 hybridized lone pair on carbon.[44] Thus, this complex is better described as being zwitterionic. Generally, zwitterionic compounds that feature a formal negative charge on carbon are uncommon unless geometric factors

prevent the carbon lone pair from interacting with the metal.[14] Some examples have the lone pair on carbon pointing away from the metal center, as in the case of the *tris*(3,5-dimethylpyrazolyl)methyl complexes [C(pz^{Me_2})]ZnX.[45] In the [Tpom$^{Bu^t}$]Tl compounds, there is no significant Tl–C covalent interaction despite the fact that the *sp*^{3} hybrid carbon orbital points directly at thallium, thereby underscoring the uniqueness of the compound (Figures 18, 19 and 20).
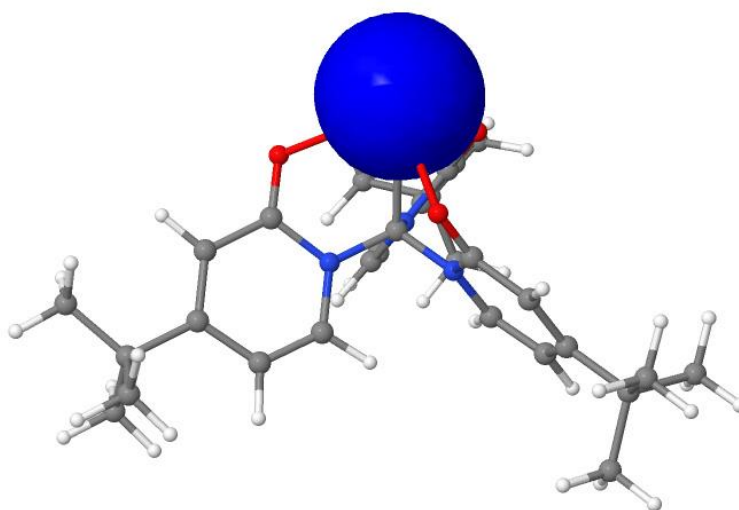
Figure 16. Natural bond orbital for Tl lone pair (96.76% 6s, 3.24% 6p character).
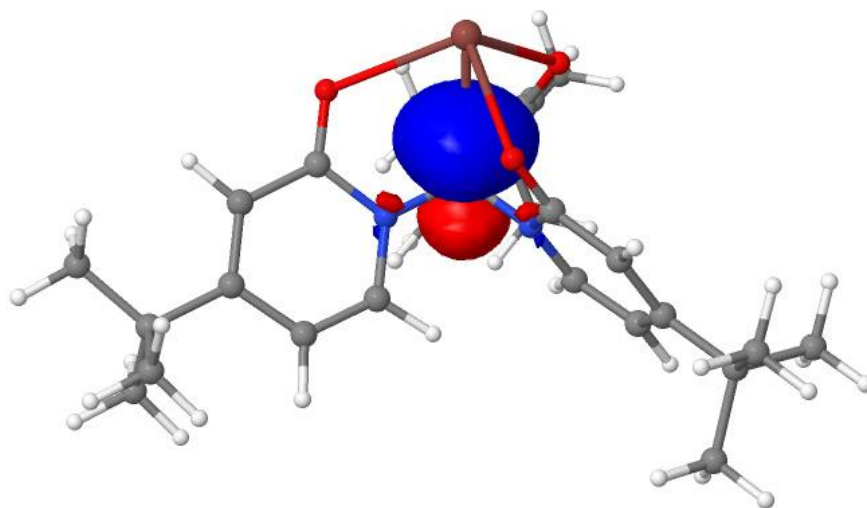
Figure 17. Natural bond orbital for C lone pair (22.68% 2s, 77.30% 2p and 0.02% of 3d character).
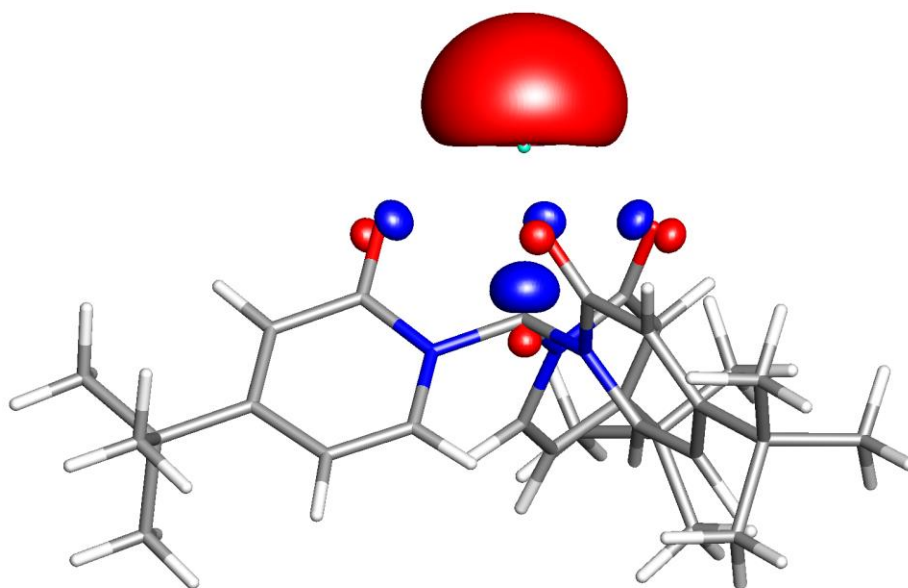
Figure 18. HOMO (Tl lone pair).
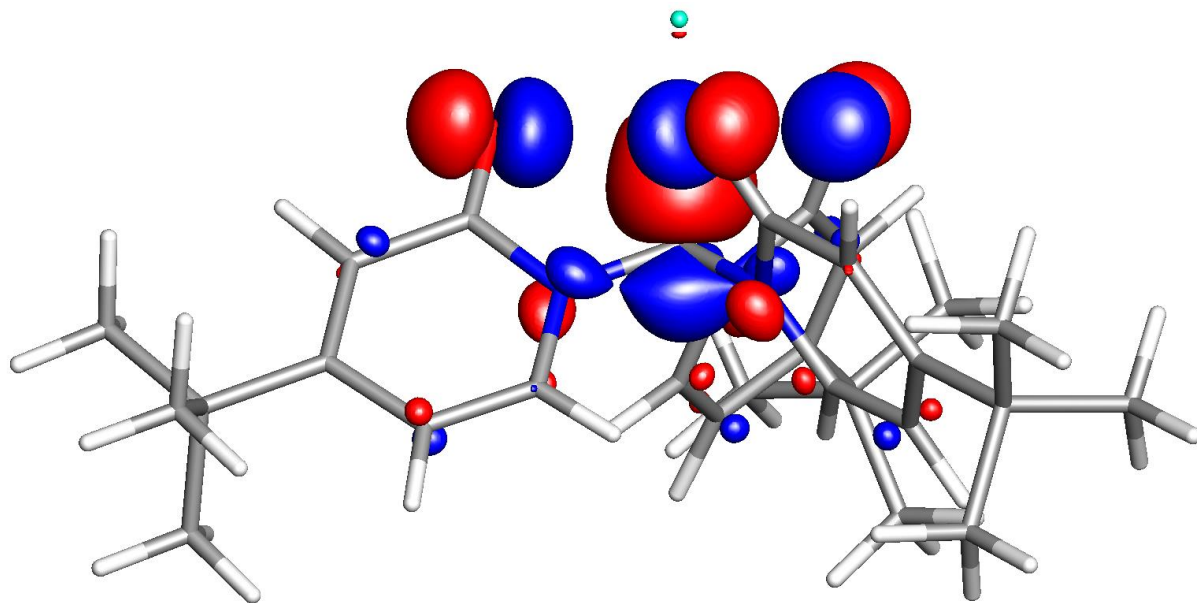
Figure 19. HOMO-1 (carbon lone pair).
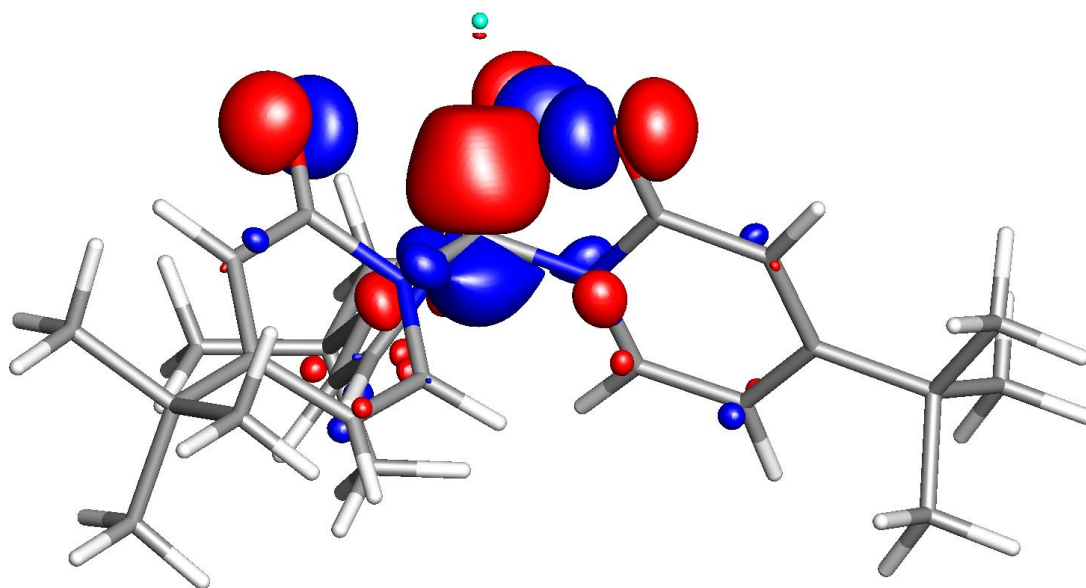
Figure 20. HOMO-1 (carbon lone pair, alternative view).

5.5 Conclusion

In summary, *tris*(2-pyridonyl)methane derivatives, namely [Tpom]H and [Tpom$^{\text{But}}$]H, may be obtained *via* the reaction of 2-pyridones with CHX_3 and K_2CO_3 in the presence of [Bu$^{\text{n}}_4$N]Br, followed by acid-catalyzed isomerization with camphorsulfonic acid. These compounds provide access to a new class of L_3X alkyl ligands that feature oxygen donors and are capable of forming metallacarbatranes, as exemplified by [κ^4-Tpom$^{\text{But}}$]ZnOC$_6$H$_4$Bu$^{\text{t}}$. In addition, the [Tpom$^{\text{But}}$] ligand also allows isolation of a monovalent thallium alkyl compound, [Tpom$^{\text{But}}$]Tl, in which the Tl–C bond is long and has little covalent character.

5.6 Experimental Section

5.6.1 General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere.[46] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, Bruker 400 Cyber-enabled Avance III and Bruker Avance 500 DMX spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C$_6$D$_5$H, 7.26 for CHCl$_3$, 5.32 for CDHCl$_2$ and 2.50 for d_6-DMSO).[47] ^{13}C NMR spectra are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for C$_6$D$_6$, 53.84 for CD$_2$Cl$_2$, 77.16 for CDCl$_3$, and 39.52 for d_6-

DMSO).[47] Coupling constants are given in hertz. Infrared spectra were recorded on

PerkinElmer Spectrum Two spectrometer and are reported in cm^{-1}. Mass spectra were

obtained on a Jeol JMS-HX110H Tandem Double-Focusing Mass Spectrometer with a 10

kV accelerated voltage equipped with FAB ion source. All chemicals were obtained

from Aldrich and Zn[N(SiMe$_3$)$_2$]$_2$[48] and TlN(SiMe$_3$)$_2$[49] were obtained by the literature

methods.

5.6.2   X-ray Structure Determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer

and crystal data, data collection and refinement parameters are summarized in Table 3.

The structures were solved using direct methods and standard difference map

techniques, and were refined by full-matrix least-squares procedures on F^2 with

SHELXTL (Version 2008/4).[50]

5.6.3   Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.7 (release 107)

suite of *ab initio* quantum chemistry programs.[51] Geometry optimizations were

performed with the B3LYP density functional[52] using the 6-31G** (C, H, N, O) and

LAV3P (Tl) basis sets, and atomic coordinates are listed in Table 4.[53] NBO calculations

were performed with NBO 5.0[54] as implemented in the Jaguar 7.7 (release 107) suite of

programs using the 6-31G** and LAV3P basis sets. Molecular orbital analyses were

performed with the aid of JIMP2,[55] which employs Fenske-Hall calculations and visualization using MOPLOT.[56]

5.6.4 Synthesis of $HC(OC_5H_4N)_3$ and $HC(OC_5H_4N)_2(NC_5H_4O)$

(a) A triphasic mixture of 2-pyridone (9.0 g, 94.6 mmol), $[Bu^n_4N]Br$ (0.6 g, 1.86 mmol) and K_2CO_3 (40 g, 289 mmol) in $CHCl_3$ (90 mL) and water (90 mL) was refluxed for 6 days. The mixture was allowed to cool to room temperature and was treated with water (*ca.* 500 mL) and CH_2Cl_2 (*ca.* 600 mL), resulting in the formation of two layers. The organic layer was separated, dried over Na_2SO_4 and filtered. The volatile components were removed *in vacuo* to give a dark brown residue that was subjected to column chromatography on silica gel. Elution with a mixture of ethylacetate and hexane (1:1 with 1% v/v Et_3N) produced $HC(OC_5H_4N)_3$ (600 mg, 6 %), while elution with a mixture of ethylacetate and hexane (2:1 with 1% v/v Et_3N) yielded $HC(OC_5H_4N)_2(NC_5H_4O)$ (750 mg, 8 %). Analysis calcd. for $HC(OC_5H_4N)_3$: C, 65.1%; H, 4.4%; N 14.2% Found: C, 65.2%; H, 3.8%; N 14.2%. ^1H NMR ($CDCl_3$): 6.86 [d, $^3J_{H-H}$ = 8, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 6.94 [m, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 7.61 [m, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 8.14 [m, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 9.28 [s, 1H of $C\underline{H}\{(OC)N(C_4H_4)\}_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 104.0 [1C of $\underline{C}H\{(OC)N(C_4H_4)\}_3$], 111.5 [3C of $CH\{(OC)N(\underline{C}_4H_4)(CO)\}_3$], 118.6 [3C of $CH\{(OC)N(\underline{C}_4H_4)\}_3$], 139.2 [3C of $CH\{(OC)N(\underline{C}_4H_4)\}_3$], 147.3 [3C of $CH\{(OC)N(\underline{C}_4H_4)\}_3$], 161.2 [3C of $CH\{(O\underline{C})N(C_4H_4)\}_3$]. FAB-MS: *m/z* = 296.16 $[M+1]^+$, M = $HC(OC_5H_4N)_3$. IR Data (ATR, cm^{-1}): 3015 (w), 2963 (w), 1658 (br), 1594 (s), 1573 (s), 1541 (w), 1468 (s), 1431

(s), 1356 (w), 1340 (w), 1284 (w), 1259 (s), 1231 (s), 1143 (w), 1102 (m), 1049 (vs), 1021

(vs), 990 (vs), 914 (m), 854 (m), 772 (vs), 735 (m), 664 (w), 615 (w), 559 (w), 513 (m), 496

(m). Colorless blocks of $HC(OC_5H_4N)_3$ suitable for X-ray diffraction were obtained from

mixture of ethylacetate and hexane Analysis calcd. for $HC(OC_5H_4N)_2(NC_5H_4O)$: C,

65.1%; H, 4.4%; N 14.2% Found: C, 65.4%; H, 3.9%; N 14.2%. ^{1}H NMR (CDCl$_3$): 6.20

["dt", $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 1, 1H of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}$], 6.58 [d, $^3J_{H-H}$ = 9, 1H of

$\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}$], 6.86 [d, $^3J_{H-H}$ = 8, 2H of

$\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$], 6.96 [m, 2H of $\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$],

7.31 [m, 1H of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}$], 7.63 [m, 2H of

$\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$], 7.79 [dd, $^3J_{H-H}$ = 7, $^3J_{H-H}$ = 2, 1H of

$\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}$], 8.15 [m, 2H of $\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$],

9.31 [s, 1H of $\{(C_4H_4)N(CO)\}_2C\underline{H}\{N(C_4H_4)(CO)\}$]. ^{13}C$\{^1H\}$ NMR (CDCl$_3$): 93.1 [1C of

$\{(C_4H_4)N(CO)\}_2\underline{C}H\{N(C_4H_4)(CO)\}$], 106.2 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}$], 111.0

[2C of $\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$], 119.0 [2C of

$\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$], 121.7 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}$], 132.1

[1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}$], 139.4 [2C of

$\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$], 139.9 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}$], 147.6

[2C of $\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}$], 160.7 [2C of

$\{(C_4H_4)N(\underline{C}O)\}_2CH\{N(C_4H_4)(CO)\}$], 161.6 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4H_4)(\underline{C}O)\}$]. FAB-

MS: m/z = 296.2 [M+1]$^+$, M = $HC(OC_5H_4N)_2(NC_5H_4O)$. IR Data (ATR, cm^{-1}): 3065 (w),

2963 (w), 1670 (s), 1595 (s), 1574 (m), 1537 (m), 1471 (s), 1432 (s), 1401 (w), 1364 (w), 1342

(w), 1292 (w), 1261 (m), 1226 (s), 1187 (w), 1176 (m), 1142 (m), 1117 (s), 1102 (s), 1067 (s),

1047 (s), 1020 (vs), 918 (s), 881 (m), 788 (s), 762 (vs), 672 (w), 647 (w), 630 (w), 618 (w),

603 (w), 575 (w), 557 (w), 513 (m), 494 (m). Colorless blocks of $HC(OC_5H_4N)_2(NC_5H_4O)$

suitable for X-ray were obtained from mixture of ethylacetate and hexane.

5.6.5 Synthesis of $HC(OC_5H_4N)(NC_5H_4O)_2$

$HC(OC_5H_4N)(NC_5H_4O)_2$ (330 mg, 1.12 mmol) and camphorsulfonic acid (35 mg, 0.15

mmol) were dissolved in a mixture of THF (1.5 mL) and toluene (3 mL) in a small

ampoule. The reaction was heated at 90 °C for 2 hours resulting in a white precipitate.

The solution was cooled to room temperature and filtered to isolate a white solid. The

solid was washed with Et_2O (3 × 1 mL) and dried *in vacuo* overnight (235 mg, 71%).

Anal. calcd. for $HC(OC_5H_4N)(NC_5H_4O)_2$: C, 65.1%; H, 4.4%; N, 14.2%. Found: C, 64.9 %;

H, 4.2 %; N, 14.4 %. ^1H NMR ($CDCl_3$): 6.19 [t, $^3J_{H-H}$ = 7 Hz, 2H of

$HC(OC_5H_4N)(NC_5\underline{H}_4O)_2$], 6.50 [d, $^3J_{H-H}$ = 9 Hz, 2H of $HC(OC_5H_4N)(NC_5\underline{H}_4O)_2$], 7.00 [d,

$^3J_{H-H}$ = 8 Hz, 1H of $HC(OC_5\underline{H}_4N)(NC_5H_4O)_2$], 7.03 [m, 1H of $HC(OC_5\underline{H}_4N)(NC_5H_4O)_2$],

7.32 [m, 2H of $HC(OC_5H_4N)(NC_5\underline{H}_4O)_2$], 7.69 [m, 1H of $HC(OC_5\underline{H}_4N)(NC_5H_4O)_2$], 7.99

[d, $^3J_{H-H}$ = 7 Hz, 2H of $HC(OC_5H_4N)(NC_5\underline{H}_4O)_2$], 8.15 [d, $^3J_{H-H}$ = 4 Hz, 1H of

$HC(OC_5\underline{H}_4N)(NC_5H_4O)_2$], 8.61 [s, 1H of $\underline{H}C(OC_5H_4N)(NC_5H_4O)_2$. $^{13}C\{^1H\}$ NMR ($CDCl_3$):

88.5 [s, 1C of $H\underline{C}(OC_5H_4N)(NC_5H_4O)_2$], 105.0 [s, 2C of $HC(OC_5H_4N)(N\underline{C}_5H_4O)_2$], 111.5 [s,

1C of $HC(O\underline{C}_5H_4N)(NC_5H_4O)_2$], 119.6 [s, 1C of $HC(O\underline{C}_5H_4N)(NC_5H_4O)_2$], 121.7 [s, 2C of

$HC(OC_5H_4N)(N\underline{C}_5H_4O)_2$], 136.3 [s, 2C of $HC(OC_5H_4N)(N\underline{C}_5H_4O)_2$], 139.9 [s, 1C of

HC(O$\underline{C}_5$H$_4$N)(NC$_5$H$_4$O)$_2$], 140.5 [s, 2C of HC(OC$_5$H$_4$N)(N$\underline{C}_5$H$_4$O)$_2$], 147.2 [s, 1C of

HC(O$\underline{C}_5$H$_4$N)(NC$_5$H$_4$O)$_2$], 160.0 [s, 1C of HC(O$\underline{C}_5$H$_4$N)(NC$_5$H$_4$O)$_2$], 162.3 [s, 2C of

HC(OC$_5$H$_4$N)(N$\underline{C}_5$H$_4$O)$_2$]. FAB-MS: m/z = 296.2 [M + H]$^+$. IR Data (ATR, cm^{-1}): 3098 (w),

1658 (vs), 15875 (s), 1534 (s), 1468 (m), 1430 (m), 1400 (w), 1358 (w), 1307 (w), 1263 (m),

1232 (s), 1175 (m), 1140 (m), 1113 (s), 1049 (s), 1018 (m), 991 (w), 910 (s), 887 (m), 866 (m),

849 (m), 778 (s), 761 (s), 734 (m), 655 (w), 631 (w), 583 (w), 569 (m), 552 (w), 517 (m), 500

(s). Colorless blocks of HC(OC$_5$H$_4$N)(NC$_5$H$_4$O)$_2$ suitable for X-ray were obtained from

solution of acetone.

5.6.6 Synthesis of HC(NC$_5$H$_4$O)$_3$

A mixture of HC(OC$_5$H$_4$N)$_3$ (392 mg, 1.33 mmol) and camphorsulfonic acid (40 mg, 0.17

mmol) in anhydrous toluene (*ca.* 2 mL) and THF (*ca.* 2 mL) was heated at 180 °C in a

sealed tube for 5 days. The mixture was allowed to cool to room temperature, thereby

depositing a brown precipitate. The mixture was filtered and the precipitate was

washed with Et$_2$O (*ca.* 5 mL) and acetone (*ca.* 5 mL) and dried *in vacuo* to give

HC(NC$_5$H$_4$O)$_3$ as a brown powder (110 mg, 28 %). Analysis calcd. for HC(NC$_5$H$_4$O)$_3$: C,

65.1%; H, 4.4%; N 14.2% Found: C, 65.1%; H, 3.8%; N 14.0%. ^{1}H NMR (DMSO): 6.39

["dt", $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 1, 3H of CH{N(C$_4\underline{H}_4$)(CO)}$_3$], 6.52 [d, $^3J_{H-H}$ = 9, 3H of

CH{N(C$_4\underline{H}_4$)(CO)}$_3$], 7.22 [dd, $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 1, 3H of CH{N(C$_4\underline{H}_4$)(CO)}$_3$], 7.57 [m, 3H of

CH{N(C$_4\underline{H}_4$)(CO)}$_3$], 8.53 [s, 1H of C$\underline{H}${N(C$_4$H$_4$)(CO)}$_3$]. ^{13}C{^{1}H} NMR (DMSO): 74.0 [1C

of $\underline{C}$H{N(C$_4$H$_4$)(CO)}$_3$], 107.0 [3C of CH{N($\underline{C}_4$H$_4$)(CO)}$_3$], 120.4 [3C of

CH{N($\underline{C}_4$H$_4$)(CO)}$_3$], 133.4 [3C of CH{N($\underline{C}_4$H$_4$)(CO)}$_3$], 141.3 [3C of CH{N($\underline{C}_4$H$_4$)(CO)}$_3$],

160.4 [3C of CH{N(C$_4$H$_4$)($\underline{C}$O)}$_3$]. FAB-MS: m/z = 296.2 [M+1]$^+$, M = HC(NC$_5$H$_4$O)$_3$. IR

Data (ATR, cm^{-1}): 3088 (w), 3034 (w), 1654 (vs), 1582 (vs), 1531 (vs), 1469 (w), 1458 (w),

1433 (w), 1399 (w), 1356 (w), 1304 (w), 1243 (s), 1182 (m), 1145 (m), 1133 (m), 1115 (m),

1094 (w), 1053 (w), 1019 (w), 994 (w), 952 (w), 903 (m), 852 (w), 807 (w), 764 (vs), 729

(m), 610 (w), 565 (m), 530 (m), 508 (s). Brown needle-shaped crystals of HC(NC$_5$H$_4$O)$_3$

suitable for X-ray diffraction were obtained from the reaction mixture.

5.6.7   Synthesis of 4-tert-butylpyridine-*N*-oxide

4-tert-butylpyridine-*N*-oxide was prepared by a modification of the literature method.[17]

Hydrogen peroxide (40 mL, 35% in water) was added to a mixture of 4-tert-

butylpyridine (18.5 g, 137 mmol) and glacial acetic acid (200 mL) and the mixture was

heated for 4 hours at 100 °C under an atmosphere of N$_2$. The mixture was allowed to

cool to room temperature, treated with another aliquot of hydrogen peroxide (40 mL,

35%) and heated for 4 hours at 100 °C. The mixture was allowed to cool to room

temperature, concentrated *in vacuo* to a volume of *ca.* 100 mL and neutralized with

NaOH (1 M). The mixture was extracted into CH$_2$Cl$_2$ (*ca.* 700 mL) and the organic layer

was collected and dried over Na$_2$SO$_4$, after which the volatile components were

removed *in vacuo* to yield a yellow solid which was washed with pentane (*ca.* 50 mL) to

yield 4-tert-butylpyridine-*N*-oxide (16.5 g, 80 %).

5.6.8 Synthesis of 4-tert-butyl-2-[1*H*]-pyridone

4-*tert*-Butyl-2-[1*H*]-pyridone was prepared by modification of a literature method.[16] A

mixture of 4-tert-butylpyridine-*N*-oxide (10.7 g, 70.8 mmol) and acetic anhydride (30

mL) was refluxed for 16 hours under an atmosphere of nitrogen. The mixture was

allowed to cool to room temperature and concentrated *in vacuo* to a volume of *ca.* 15 mL

and poured into ice water (600 mL). NaHCO$_3$ was added until the solution became

alkaline (pH = 8 - 9), and the resulting mixture was stirred for *ca.* 3 days and extracted

with ethylacetate (700 mL). The organic layer was collected and dried over Na$_2$SO$_4$,

after which the volatile components were removed *in vacuo* to give 4-tert-butyl-2-[*1H*]-

pyridone as a brown powder (5.9 g, 55 %). Analysis calcd. for 4-tert-butyl-2-[*1H*]-

pyridone: C, 71.5%; H, 8.7%; N 9.3% Found: C, 71.5%; H, 8.3%; N 9.0%. ^{1}H NMR (C$_6$D$_6$):

0.92 [s, 9H of HN(C$_3$H$_3$)(CC(C$\underline{H}_3$)$_3$)(CO)], 5.70 [dd, $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 1, 1H of

HN(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)], 6.68 [br, 1H of HN(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)], 6.88 [d, $^3J_{H-H}$ = 7,

1H of HN(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)CO)], not showing [1H of $\underline{H}$N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)]. ^{13}C{^{1}H}

NMR (C$_6$D$_6$): 29.6 [3C of HN(C$_3$H$_3$)(CC($\underline{C}$H$_3$)$_3$)(CO)], 34.8 [1C of

HN(C$_3$H$_3$)(C$\underline{C}$(CH$_3$)$_3$)(CO)], 105.3 [1C of HN($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)], 115.7 [1C of

HN($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)], 134.1 [1C of HN($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)], 165.0 [1C of

HN(C$_3$H$_3$)($\underline{C}$C(CH$_3$)$_3$)(CO)], 166.5 [1C of HN(C$_3$H$_3$)(CC(CH$_3$)$_3$)($\underline{C}$O)]. MS: *m/z* = 151.2

[M]$^+$, M = HNC$_5$H$_3$Bu^{t}O. IR Data (ATR, cm^{-1}): 2961 (m), 2868 (w), 1648 (s), 1605 (vs),

1553 (m), 1480 (m), 1459 (m), 1406 (s), 1364 (w), 1344 (w), 1330 (w), 1286 (s), 1259 (m),

1218 (m), 1201 (m), 1090 (m), 1038 (vs), 1022 (vs), 989 (vs), 938 (m), 858 (m), 836 (m), 789

(s), 739 (w), 708 (w), 657 (w), 573 (m), 541 (m), 519 (m), 470 (m). Colorless block of

$HNC_6H_3Bu^tO$ suitable for X-ray were obtained from hexanes.

5.6.9 Synthesis of $HC(OC_5H_3Bu^tN)_3$ and $HC(OC_5H_3Bu^tN)_2(NC_5H_3Bu^tO)$

(a) A triphasic mixture of 4-tert-butylpyridone (5.8 g, 38.4 mmol), $[Bu^n_4N]Br$ (0.5 g, 1.55

mmol) and K_2CO_3 (25 g, 180.9 mmol) in $CHBr_3$ (40 mL) and water (150 mL) was heated

at 110 °C for 5 days. The mixture was allowed to cool to room temperature and treated

with water (400 mL) and CH_2Cl_2 (700 mL). The organic layer was separated and dried

over Na_2SO_4, after which the solvent was removed *in vacuo* to give a dark brown residue

that was subjected to column chromatography on silica gel. Elution with a mixture of

ethylacetate and hexane (1:4 with 2% v/v Et_3N) gave $HC(OC_5H_3Bu^tN)_3$ (1.6 g, 27 %),

while elution with a mixture of ethylacetate and hexane (2:3 with 2% v/v Et_3N) yielded

$HC(OC_5H_3Bu^tN)_2(NC_5H_3Bu^tO)$ (600 mg, 10 %). Analysis calcd. for $HC(OC_5H_3Bu^tN)_3$: C,

72.5%; H, 8.0%; N 9.1% Found: C, 72.2%; H, 8.0%; N 9.0%. ^1H NMR ($CDCl_3$): 1.26 [s, 27H

of $CH\{(OC)N(C_3H_3)(CC(C\underline{H}_3)_3)\}_3$], 6.86 [d, $^4J_{H-H}$ = 1, 3H of $CH\{(OC)N(C_3\underline{H}_3)(CC(CH_3)_3)\}_3$],

6.95 [dd, $^3J_{H-H}$ = 5, $^4J_{H-H}$ = 2, 3H of $CH\{(OC)N(C_3\underline{H}_3)(CC(CH_3)_3)\}_3$], 8.07 [d, $^3J_{H-H}$ = 5, 3H of

$CH\{(OC)N(C_3\underline{H}_3)(CC(CH_3)_3)\}_3$], 9.32 [s, 1H of $C\underline{H}\{(OC)N(C_3H_3)(CC(CH_3)_3)\}_3$]. $^{13}C\{^1H\}$

NMR ($CDCl_3$): 30.6 [9C of $CH\{(OC)N(C_3H_3)(CC(\underline{C}H_3)_3)\}_3$], 34.9 [3C of

$CH\{(OC)N(C_3H_3)(C\underline{C}(CH_3)_3)\}_3$], 103.9 [1C of $\underline{C}H\{(OC)N(C_3H_3)(CC(CH_3)_3)\}_3$], 108.2 [3C of

$CH\{(OC)N(\underline{C}_3H_3)(CC(CH_3)_3)\}_3$], 116.2 [3C of $CH\{(OC)N(\underline{C}_3H_3)(CC(CH_3)_3)\}_3$], 147.0 [3C of

$CH\{(OC)N(\underline{C}_3H_3)(CC(CH_3)_3)\}_3$], 161.6 [3C of $CH\{(O\underline{C})N(C_3H_3)(CC(CH_3)_3)\}_3$], 163.7 [3C of

CH{(OC)N(C$_3$H$_3$)(CC(CH$_3$)$_3$)}$_3$]. FAB-MS: m/z = 464.3 [M+1]$^+$, M = HC(OC$_5$H$_3$Bu^{t}N)$_3$. IR

Data (ATR, cm^{-1}): 2967 (m), 2869 (w), 1604 (s), 1552 (m), 1481 (w), 1460 (w), 1406 (s), 1365

(w), 1343 (w), 1285 (s), 1262 (w), 1218 (m), 1199 (m), 1098 (w), 1036 (vs), 920 (m), 869

(m), 853 (m), 800 (m), 743 (w), 727 (w), 657 (m), 546 (w), 531 (m), 482 (w). Colorless

block of HC(OC$_5$H$_3$Bu^{t}N)$_3$ suitable for X-ray were obtained from mixture of hexane and

ethylacetate. Analysis calcd. for HC(OC$_5$H$_3$Bu^{t}N)$_2$(NC$_5$H$_3$Bu^{t}O): C, 72.5%; H, 8.0%; N

9.1% Found: C, 71.8%; H, 8.1%; N 9.0%. ^{1}H NMR (CDCl$_3$): 1.22 [s, 9H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(C$\underline{H}$$_3$)$_3$)(CO)}], 1.26 [s, 18H of

{(CC(C$\underline{H}$$_3$)$_3$)(C$_3H_3$)N(CO)}$_2$CH{N(C$_3H_3$)(CC(CH$_3$)$_3$)(CO)}], 6.26 [dd, ^{3}J$_{H-H}$= 7, ^{4}J$_{H-H}$= 2, 1H

of {(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$$\underline{H}$$_3$)(CC(CH$_3$)$_3$)(CO)}], 6.50 [d, ^{4}J$_{H-H}$= 2, 1H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$$\underline{H}$$_3$)(CC(CH$_3$)$_3$)(CO)}], 6.84 [d, ^{4}J$_{H-H}$= 1, 2H of

{(CC(CH$_3$)$_3$)(C$_3$$\underline{H}$$_3$)N(CO)}$_2$CH{N(C$_3H_3$)(CC(CH$_3$)$_3$)(CO)}], 6.96 [dd, ^{3}J$_{H-H}$= 5, ^{4}J$_{H-H}$= 2, 2H

of {(CC(CH$_3$)$_3$)(C$_3$$\underline{H}$$_3$)N(CO)}$_2$CH{N(C$_3H_3$)(CC(CH$_3$)$_3$)(CO)}], 7.72 [d, ^{3}J$_{H-H}$= 8, 1H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$$\underline{H}$$_3$)(CC(CH$_3$)$_3$)(CO)}], 8.06 [d, ^{3}J$_{H-H}$= 5, 2H of

{(CC(CH$_3$)$_3$)(C$_3$$\underline{H}$$_3$)N(CO)}$_2$CH{N(C$_3H_3$)(CC(CH$_3$)$_3$)(CO)}], 9.29 [s, 1H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$C$\underline{H}${N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}]. ^{13}C{^{1}H} NMR (CDCl$_3$): 29.7 [3C

of {(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(C$\underline{H}$$_3$)$_3$)(CO)}], 30.6 [6C of

{(CC(C$\underline{H}$$_3$)$_3$)(C$_3H_3$)N(CO)}$_2$CH{N(C$_3H_3$)(CC(CH$_3$)$_3$)(CO)}], 35.0 [2C of

{(C$\underline{C}$(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 35.1 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(C$\underline{C}$(CH$_3$)$_3$)(CO)}], 93.0 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$C$\underline{H}${N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 105.7 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 107.6[2C of

{(CC(CH$_3$)$_3$)($\underline{C}_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 116.3 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 116.6 [2C of

{(CC(CH$_3$)$_3$)($\underline{C}_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 130.8 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 147.2 [2C of

{(CC(CH$_3$)$_3$)($\underline{C}_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 161.2 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N($\underline{C}$O)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}], 162.0 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)($\underline{C}$O)}], 163.5 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)($\underline{C}$C(CH$_3$)$_3$)(CO)}], 163.9 [1C of

{($\underline{C}$C(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}$_2$CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}]. FAB-MS: m/z = 464.3 [M+1]$^+$, M

= HC(OC$_5$H$_3$Bu^{t}N)$_2$(NC$_5$H$_3$Bu^{t}O). IR Data (ATR, cm^{-1}): 2962 (m), 2869 (w), 1669 (s), 1605

(s), 1554 (m), 1532 (w), 1482 (m), 1407 (s), 1365 (w), 1343 (w), 1289 (m), 1258 (s), 1221 (m),

1196 (m), 1133 (m), 1077 (vs), 1016 (vs), 945 (m), 932 (m), 863 (m), 830 (m), 796 (s), 742

(w), 717 (w), 686 (m), 664 (m), 628 (m), 572 (m), 526 (m), 481 (m). Colorless crystals of

HC(OC$_5$H$_3$Bu^{t}N)$_2$(NC$_5$H$_3$Bu^{t}O) suitable for X-ray were obtained from the mixture of

hexane and ethylacetate.

5.6.10 Synthesis of HC(OC$_5$H$_3$Bu^{t}N)(NC$_5$H$_3$Bu^{t}O)$_2$

A mixture of HC(OC$_5$H$_3$Bu^{t}N)$_3$ (200 mg, 1.73 mmol) and camphorsulfonic acid (10 mg,

0.37 mmol) in anhydrous benzene (*ca*. 4 mL) was heated at 90 °C for 3 hours. After this

period, the mixture was lyophilized *in vacuo*, and the resulting residue was washed

with Et$_2$O (*ca.* 5 mL) and dried *in vacuo* to yield a white powder of

HC(OC$_5$H$_3$Bu^{t}N)(NC$_5$H$_3$Bu^{t}O)$_2$ (100 mg, 50%). Analysis calcd. for

HC(OC$_5$H$_3$Bu^{t}N)(NC$_5$H$_3$Bu^{t}O)$_2$: C, 72.5%; H, 8.0%; N 9.1% Found: C, 72.2%; H, 7.8%; N

9.1%. ^{1}H NMR (CDCl$_3$): 1.19 [s, 18H of {(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}

CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 1.28 [s, 9H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 6.23 [dd, $^3J_{H\text{-}H}$ = 8, $^4J_{H\text{-}H}$ = 2, 2H

of {(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 6.41 [d, $^4J_{H\text{-}H}$ = 2, 2H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 6.95 [br, 2H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 7.00 [d, $^3J_{H\text{-}H}$ = 5, $^4J_{H\text{-}H}$ = 2, 1H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 7.94 [d, $^3J_{H\text{-}H}$ = 8, 2H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 8.08 [d, $^3J_{H\text{-}H}$ = 5, 1H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 8.60 [s, 1H of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$]. ^{13}C{^{1}H} NMR (CDCl$_3$): 29.7 [6C

of {(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 30.6 [3C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 35.1 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 35.1 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 88.1 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 104.4 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 107.9[1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 116.1 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 117.2 [1C of

{(CC(CH$_3$)$_3$)(C̲$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 135.2 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C̲$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 146.6 [C of

{(CC(CH$_3$)$_3$)(C̲$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 160.6 [1C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(C̲O)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$], 162.8 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(C̲O)}$_2$], 164.3 [2C of

{(CC(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(C̲C(CH$_3$)$_3$)(CO)}$_2$], 164.7 [1C of

{(C̲C(CH$_3$)$_3$)(C$_3$H$_3$)N(CO)}CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_2$]. FAB-MS: *m/z* = 464.4 [M+1]$^+$, M

= HC(OC$_5$H$_3$Bu^{t}N)(NC$_5$H$_3$Bu^{t}O)$_2$. IR Data (ATR, cm^{-1}): 2964 (m), 2870 (w), 1666 (vs), 1598

(s), 1553 (m), 1530 (m), 1481 (m), 1406 (m), 1362 (m), 1326 (w), 1299 (w), 1277 (m), 1248

(m), 1224 (m), 1188 (m), 1122 (m), 1103 (m), 1062 (m), 1044 (s), 1022 (m), 954 (m), 927 (s),

867 (m), 833 (w), 792 (m), 779 (m), 743 (w), 689 (m), 663 (w), 557 (m), 525 (m), 463 (m).

Colorless crystals of HC(OC$_5$H$_3$Bu^{t}N)$_2$(NC$_5$H$_3$Bu^{t}O)$_2$ suitable for X-ray were obtained

from acetone solution.

5.6.11 Synthesis of HC(NC$_5$H$_3$Bu^{t}O)$_3$

A mixture of HC(OC$_5$H$_3$Bu^{t}N)$_3$ (800 mg, 1.73 mmol) and camphorsulfonic acid (85 mg,

0.37 mmol) in anhydrous toluene (*ca*. 5 mL) and THF (*ca*. 2 mL) was heated at 178 °C for

5 days. After this period, the mixture was allowed to cool to room temperature thereby

resulting in the formation of an off-white precipitate. The mixture was filtered and the

precipitate was washed with Et$_2$O (2 × 3 mL) and dried *in vacuo* to yield

HC(NC$_5$H$_3$Bu^{t}O)$_3$, [Tpom^{But}]H, as an off-white powder (300 mg, 38%). Analysis calcd.

for HC(NC$_5$H$_3$Bu^{t}O)$_3$: C, 72.5%; H, 8.0%; N 9.1% Found: C, 71.7%; H, 7.8%; N 8.8%. ^{1}H

NMR (CDCl$_3$): 1.22 [s, 27H of CH{N(C$_3$H$_3$)(CC(C$\underline{H}_3$)$_3$)(CO)}$_3$], 6.26 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 2,

3H of CH{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.46 [d, $^4J_{H-H}$ = 2, 3H of

CH{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 7.40 [d, $^3J_{H-H}$ = 8, 3H of CH{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)CO)}$_3$],

8.37 [s, 1H of C$\underline{H}${N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$]. ^{13}C{^{1}H} NMR (CDCl$_3$): 29.6 [9C of

CH{N(C$_3$H$_3$)(CC($\underline{C}$H$_3$)$_3$)(CO)}$_3$], 35.2 [3C of CH{N(C$_3$H$_3$)(C$\underline{C}$(CH$_3$)$_3$)(CO)}$_3$], 79.1 [1C of

$\underline{C}$H{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 105.8 [3C of CH{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 116.3 [3C of

CH{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 134.4 [3C of CH{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 162.4 [3C of

CH{N(C$_3$H$_3$)($\underline{C}$C(CH$_3$)$_3$)(CO)}$_3$], 164.6 [3C of CH{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)($\underline{C}$O)}$_3$]. MS: m/z =

464.3 [M+1]$^+$, M = HC(NC$_5$H$_3$Bu^{t}O)$_3$. IR Data (ATR, cm^{-1}): 3089 (w), 2967 (m), 2869 (w),

1666 (vs), 1597 (s), 1530 (m), 1475 (m), 1388 (m), 1368 (w), 1317 (w), 1249 (s), 1193 (s),

1118 (m), 1074 (m), 1023 (m), 955 (s), 885 (w), 858 (m), 796 (m), 779 (s), 743 (w), 688 (s),

621 (w), 603 (w), 568 (m), 552 (m), 526 (m), 466 (m). Colorless crystals of

HC(NC$_5$H$_3$Bu^{t}O)$_3$ suitable for X-ray were obtained from MeOH.

5.6.12 Synthesis of [κ^3-Tpom]ZnN(SiMe$_3$)$_2$

A mixture of [Tpom]H (18.0 mg, 0.06 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (20.0 mg, 0.05 mmol) in

C$_6$D$_6$ (*ca.* 2 mL) was heated for 3 weeks at 130 $^\circ$C in an NMR tube equipped with a J.

Young valve. The mixture was lyophilized and the residue obtained was extracted with

Et$_2$O (*ca.* 2 mL). The extract was cooled to -15 $^\circ$C, thereby depositing colorless crystals

of [κ^3-Tpom]ZnN(SiMe$_3$)$_2$, suitable for X-ray diffraction (10.0 mg, 32%). ^{1}H NMR (C$_6$D$_6$):

0.58 [s, 18H of {(C$\underline{H}_3$)$_3$Si}$_2$NZnC{N(C$_4$H$_4$)(CO)}$_3$], 5.45 ["dt", $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 2, 3H of

{(CH$_3$)$_3$Si}$_2$NZnC{N(C$_4$H$_4$)(CO)}$_3$], 6.38 [m, 3H of {(CH$_3$)$_3$Si}$_2$NZnC{N(C$_4$$\underline{H}_4$)(CO)}$_3$], 6.48

[m, 3H of {(CH$_3$)$_3$Si}$_2$NZnC{N(C$_4$$\underline{H}_4$)(CO)}$_3$], 6.55 [m, 3H of

{(CH$_3$)$_3$Si}$_2$NZnC{N(C$_4$$\underline{H}_4$)(CO)}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 5.8 [6C of

{(C$\underline{H}_3$)$_3$Si}$_2$NZnC{N(C$_4$H$_4$)(CO)}$_3$], 75.2 [1C of {(CH$_3$)$_3$Si}$_2$NZn$\underline{C}${N(C$_4$H$_4$)(CO)}$_3$], 108.1 [3C

of {(CH$_3$)$_3$Si}$_2$NZnC{N($\underline{C}_4$H$_4$)(CO)}$_3$], 120.8 [3C of {(CH$_3$)$_3$Si}$_2$NZnC{N($\underline{C}_4$H$_4$)(CO)}$_3$], 133.0

[3C of {(CH$_3$)$_3$Si}$_2$NZnC{N($\underline{C}_4$H$_4$)(CO)}$_3$], 139.2 [3C of {(CH$_3$)$_3$Si}$_2$NZnC{N($\underline{C}_4$H$_4$)(CO)}$_3$],

164.2 [3C of {(CH$_3$)$_3$Si}$_2$NZnC{N(C$_4$H$_4$)($\underline{C}$O)}$_3$].

5.6.13 Synthesis of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]

A mixture of [Tpom$^{Bu^t}$]H (30.0 mg, 0.06 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (30.0 mg, 0.08 mmol)

in C$_6$D$_6$ (*ca.* 1.2 mL) in an NMR tube equipped with a J. Young valve was heated at 120

°C for one week. After this period, the mixture was allowed to cool to room

temperature, during which period large colorless crystals of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]

were deposited (20.0 mg, 45 %). Crystals of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$] suitable for X-

ray diffraction were obtained from benzene. Analysis calcd. for [κ^4-

Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]: C, 59.3%; H, 7.9%; N, 8.1% Found: C, 58.9%; H, 7.6%; N 7.9%. ^{1}H

NMR (C$_6$D$_6$): 0.63 [s, 18H of {(C$\underline{H}_3$)$_3$Si}$_2$NZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 0.85 [s, 27H of

{(CH$_3$)$_3$Si}$_2$NZnC{N(C$_3$H$_3$)(CC(C$\underline{H}_3$)$_3$)(CO)}$_3$], 5.79 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 2, 3H of

{(CH$_3$)$_2$Si}$_2$NZnC{N(C$_3$$\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.65 [d, $^4J_{H-H}$ = 2, 3H of

{(CH$_3$)$_2$Si}$_2$NZnC{N(C$_3$$\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.93 [d, $^3J_{H-H}$ = 8, 3H of

{(CH$_3$)$_2$Si}$_2$NZnC{N(C$_3$$\underline{H}$$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$]. ^{13}C{^{1}H} NMR (C$_6D_6$): 5.9 [6C of

{($\underline{C}$H$_3$)$_3$Si}$_2$NZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 29.3 [9C of

{(CH$_3$)$_3$Si}$_2$NZnC{N(C$_3$H$_3$)(CC($\underline{C}$H$_3$)$_3$)(CO)}$_3$], 34.7 [3C of

{(CH$_3$)$_2$Si}$_2$NZnC{N(C$_3$H$_3$)(C$\underline{C}$(CH$_3$)$_3$)(CO)}$_3$], 74.9 [1C of

{(CH$_3$)$_2$Si}$_2$NZn$\underline{C}${N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 107.2 [3C of

{(CH$_3$)$_2$Si}$_2$NZnC{N($\underline{C}$$_3H_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 116.0 [3C of

{(CH$_3$)$_2$Si}$_2$NZnC{N($\underline{C}$$_3H_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 132.7 [3C of

{(CH$_3$)$_2$Si}$_2$NZnC{N($\underline{C}$$_3H_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 163.3 [3C of

{(CH$_3$)$_2$Si}$_2$NZnC{N(C$_3$H$_3$)($\underline{C}$C(CH$_3$)$_3$)(CO)}$_3$], 164.7 [3C of

{(CH$_3$)$_2$Si}$_2$NZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)($\underline{C}$O)}$_3$].

5.6.14 Synthesis of [κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t

A mixture of [κ^4-Tpom^{But}]Zn[N(SiMe$_3$)$_2$] (30.0 mg, 0.04) and 4-t-butylphenol (6.5 mg, 0.04

mmol) was treated with benzene (*ca.* 6 mL) and stirred for 10 minutes at room

temperature. After this period, the mixture was centrifuged and the supernatant was

decanted. Toluene (*ca.* 5 mL) was added and the mixture was stirred for few minutes.

Then mixture was centrifuged and the supernatant was decanted. The washing

procedure was repeated with pentane (*ca.* 5 mL) and the residue dried *in vacuo* to yield

[κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t as white powder (15 mg, 51%). Crystals of [κ^4-

Tpom^{But}]ZnOC$_6$H$_4$Bu^t suitable for X-ray diffraction were obtained from CH$_2$Cl$_2$.

Analysis calcd. for [κ^4-Tpom^{But}]ZnOC$_6$H$_4$Bu^t•0.7CH$_2$Cl$_2$: C, 63.1%; H, 6.9%; N, 5.7%

Found: C, 62.9%; H, 7.0%; N 5.3%. ^{1}H NMR (CD$_2$Cl$_2$): 1.25 [s, 27H of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(C$\underline{H}_3$)$_3$)(CO)}$_3$], 1.27 [s, 9H of

(C$\underline{H}_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.56 [d, ^{3}J$_{H-H}$ = 7, 3H of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.67 [d, ^{3}J$_{H-H}$ = 6, 2H of

(CH$_3$)$_3$CC(C$_2\underline{H}_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.79 [br, 3H of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 7.07 [d, ^{3}J$_{H-H}$ = 6, 2H of

(CH$_3$)$_3$CC(C$_2\underline{H}_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 7.48 [d, ^{3}J$_{H-H}$ = 7, 3H of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 29.7 [9C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC($\underline{C}$H$_3$)$_3$)(CO)}$_3$], 32.0 [3C of

($\underline{C}$H$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 33.9 [1C of

(CH$_3$)$_3\underline{C}$C(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 35.5 [3C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(C$\underline{C}$(CH$_3$)$_3$)(CO)}$_3$], 109.4 [3C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$$\underline{C}H_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 115.7 [3C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3\underline{C}$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 118.6 [2C of

(CH$_3$)$_3$CC($\underline{C}_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 126.0 [2C of

(CH$_3$)$_3$CC($\underline{C}_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 133.9 [3C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3\underline{C}$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 165.2 [3C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)($\underline{C}$C(CH$_3$)$_3$)(CO)}$_3$], 165.9 [3C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)($\underline{C}$O)}$_3$], not observed [1C of

(CH$_3$)$_3$C$\underline{C}$(C$_2$H$_2$)$_2$COZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$] , not observed [1C of

(CH$_3$)$_3$CC(C$_2$H$_2$)$_2\underline{C}$OZnC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$].

5.6.15 Synthesis of [Tpom$^{Bu^t}$]Tl

A mixture of [Tpom$^{Bu^t}$]H (10 mg, 0.02 mmol) and TlN(SiMe$_3$)$_2$ (20 mg, 0.05 mmol) was

treated with C$_6$D$_6$ (*ca.* 1 mL) in an NMR tube equipped with a J. Young valve and

monitored by ^{1}H NMR spectroscopy. The mixture was shaken occasionally and, after a

period of 4 days, the solvent was lyophilized. The solid obtained was washed with

pentane (*ca.* 2 mL) and dried *in vacuo* to give [Tpom$^{Bu^t}$]Tl as an amber solid (7.0 mg,

49%). Crystals of [Tpom$^{Bu^t}$]Tl suitable for X-ray diffraction were obtained by slow

diffusion of hexane into a toluene solution, whereas crystals of {[Tpom$^{Bu^t}$]Tl}$_2$ suitable

for X-ray diffraction were obtained by the slow diffusion of pentane into a benzene

solution. ^{1}H NMR (C$_6$D$_6$): 0.95 [s, 27H of TlC{N(C$_3$H$_3$)(CC(C$\underline{H}_3$)$_3$)(CO)}$_3$], 5.75 [dd, $^3J_{H-H}$ =

8, $^4J_{H-H}$ = 2, 3H of TlC{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.62 [d, $^4J_{H-H}$ = 2, 3H of

TlC{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 6.78 [d, $^3J_{H-H}$ = 8, 3H of TlC{N(C$_3\underline{H}_3$)(CC(CH$_3$)$_3$)(CO)}$_3$].

^{13}C{^{1}H} NMR (C$_6$D$_6$): 29.6 [9C of TlC{N(C$_3$H$_3$)(CC($\underline{C}$H$_3$)$_3$)(CO)}$_3$], 34.6 [3C of

TlC{N(C$_3$H$_3$)(C$\underline{C}$(CH$_3$)$_3$)(CO)}$_3$], 107.1 [3C of TlC{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 117.3 [3C of

TlC{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 133.9 [3C of TlC{N($\underline{C}_3$H$_3$)(CC(CH$_3$)$_3$)(CO)}$_3$], 161.4 [3C of

TlC{N(C$_3$H$_3$)($\underline{C}$C(CH$_3$)$_3$)(CO)}$_3$], 164.2 [3C of TlC{N(C$_3$H$_3$)(CC(CH$_3$)$_3$)($\underline{C}$O)}$_3$]. The self-

diffusion constant for [Tpom$^{Bu^t}$]Tl was determined by pulsed gradient spin-echo (PGSE)

diffusion NMR spectroscopic experiments employing the Bruker stebpg1s pulse

sequence, and the value of 6.27×10^{-10} m^{2}s^{-1} is comparable to that of [Tpom$^{Bu^t}$]H, $6.43 \times$

10^{-10} m^{2}s^{-1}, indicating that both molecules have similar hydrodynamic radii and that

[Tpom$^{Bu^t}$]Tl is a monomer in toluene solution.

5.7　Crystallographic Data

Table 3. Crystal, intensity collection and refinement data.

	$HC(OC_5H_4N)_3$	$HC(OC_5H_4N)_2(NC_5H_4O)$
lattice	Monoclinic	Orthorhombic
formula	$C_{16}H_{13}N_3O_3$	$C_{16}H_{13}N_3O_3$
formula weight	295.29	295.29
space group	$P2_1/c$	$P2_12_12_1$
a/Å	8.9795(16)	8.3122(3)
b/Å	9.7068(18)	10.8507(5)
c/Å	16.817(3)	15.4823(6)
α/°	90	90
β/°	92.703(3)	90
γ/°	90	90
V/Å^3	1464.2(5)	1396.40(10)
Z	4	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.340	1.405
μ (Mo Kα), mm^{-1}	0.095	0.100
θ max, deg.	30.65	32.52
no. of data collected	23167	24271
no. of data used	4514	4914
no. of parameters	200	200
R_1 [$I > 2\sigma(I)$]	0.0539	0.0400
wR_2 [$I > 2\sigma(I)$]	0.0854	0.0870
R_1 [all data]	0.1566	0.0552
wR_2 [all data]	0.1101	0.0942
GOF	1.000	1.018
R_{int}	0.1240	0.0390

Table 3. (cont.) Crystal, intensity collection and refinement data.

	HC(OC$_5$H$_4$N)(NC$_5$H$_4$O)$_2$	[Tpom]H
lattice	Monoclinic	Trigonal
formula	C$_{16}$H$_{13}$N$_3$O$_3$	C$_{16}$H$_{13}$N$_3$O$_3$
formula weight	295.29	295.29
space group	$P2_1$	$R3$
a/Å	8.439(3)	15.486(3)
b/Å	9.654(4)	15.486(3)
c/Å	9.538(4)	5.0769(11)
α/°	90	90
β/°	112.338(5)	90
γ/°	90	120
V/Å^3	718.8(4)	1054.4(4)
Z	2	3
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.364	1.395
μ (Mo Kα), mm^{-1}	0.097	0.099
θ max, deg.	32.36	31.64
no. of data collected	11954	5315
no. of data used	4795	1540
no. of parameters	200	67
R_1 [$I > 2\sigma(I)$]	0.0418	0.0404
wR_2 [$I > 2\sigma(I)$]	0.0926	0.1037
R_1 [all data]	0.0661	0.0451
wR_2 [all data]	0.1037	0.1063
GOF	1.030	1.060
R_{int}	0.0407	0.0380

Table 3. (cont.) Crystal, intensity collection and refinement data.

	4-t-butyl-2-pyridone	$HC(OC_5H_3Bu^tN)_3$
lattice	Triclinic	Monoclinic
formula	$C_9H_{13}NO$	$C_{28}H_{37}N_3O_3$
formula weight	151.20	463.61
space group	$P\text{-}1$	$P2_1/n$
a/Å	6.356(3)	11..3797(11)
b/Å	7.596(3)	16.8458(15)
c/Å	9.433(4)	13.7187(13)
α/°	81.064(6)	90
β/°	81.376(6)	100.3940(10)
γ/°	73.737(6)	90
V/Å³	429.2(3)	2586.7(4)
Z	2	4
temperature (K)	170(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm⁻³	1.170	1.190
μ (Mo Kα), mm⁻¹	0.076	0.078
θ max, deg.	30.78	32.17
no. of data collected	6914	43981
no. of data used	2644	8926
no. of parameters	107	316
R_1 [$I > 2\sigma(I)$]	0.0552	0.0608
wR_2 [$I > 2\sigma(I)$]	0.1302	0.1457
R_1 [all data]	0.1121	0.1242
wR_2 [all data]	0.1560	0.1723
GOF	1.019	1.066
R_{int}	0.0460	0.0711

Table 3. (cont.) Crystal, intensity collection and refinement data.

	HC(OC$_5$H$_3$Bu^{t}N)$_2$(NC$_5$H$_3$Bu^{t}O)	HC(OC$_5$H$_3$Bu^{t}N)(NC$_5$H$_3$Bu^{t}O)$_2$
lattice	Triclinic	Monoclinic
formula	C$_{28}$H$_{37}$N$_3$O$_3$	C$_{28}$H$_{37}$N$_3$O$_3$
formula weight	463.61	463.61
space group	*P-1*	*P2$_1$/c*
a/Å	10.340(4)	11.7988(16)
b/Å	11.806(5)	19.007(3)
c/Å	12.079(8)	11.9442(16)
α/°	104.041(7)	90
β/°	94.552(7)	103.317(2)
γ/°	114.598(5)	90
V/Å³	1273.1(11)	2606.5(6)
Z	2	4
temperature (K)	150(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.209	1.181
μ (Mo Kα), mm^{-1}	0.079	0.077
θ max, deg.	25.35	30.88
no. of data collected	10667	41584
no. of data used	4616	8145
no. of parameters	305	316
R_1 [$I > 2\sigma(I)$]	0.0876	0.0681
wR_2 [$I > 2\sigma(I)$]	0.1053	0.1459
R_1 [all data]	0.2268	0.1363
wR_2 [all data]	0.1230	0.1765
GOF	1.032	1.020
R_{int}	0.1628	0.0852

Table 3. (cont.) Crystal, intensity collection and refinement data.

	[Tpom$^{Bu^t}$]H	[κ^3-Tpom]Zn[N(SiMe$_3$)$_2$]
lattice	Monoclinic	Triclinic
formula	C$_{28}$H$_{37}$N$_3$O$_3$	C$_{26}$H$_{40}$N$_4$O$_4$Si$_2$Zn
formula weight	463.61	594.17
space group	$P2_1/c$	$P\text{-}1$
$a/\text{Å}$	11.8366(15)	10.347(3)
$b/\text{Å}$	18.801(2)	10.513(3)
$c/\text{Å}$	12.2176(16)	15.117(17)
$\alpha/°$	90	102.776(5)
$\beta/°$	106.441(2)	105.658(5)
$\gamma/°$	90	97.886(5)
$V/\text{Å}^3$	2607.7(6)	1509.9(8)
Z	4	2
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.181	1.307
μ (Mo Kα), mm^{-1}	0.077	0.929
θ max, deg.	30.75	30.63
no. of data collected	41441	24546
no. of data used	8080	9236
no. of parameters	316	342
R_1 [$I > 2\sigma(I)$]	0.0569	0.0508
wR_2 [$I > 2\sigma(I)$]	0.1401	0.0768
R_1 [all data]	0.0983	0.1087
wR_2 [all data]	0.1628	0.0905
GOF	1.023	1.002
R_{int}	0.0660	0.0708

Table 3. (cont.) Crystal, intensity collection and refinement data.

	[κ⁴-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]	[κ⁴-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t
lattice	Orthorhombic	Monoclinic
formula	C$_{46}$H$_{66}$N$_4$O$_3$Si$_2$Zn	C$_{42}$H$_{57}$Cl$_8$N$_3$O$_4$Zn
formula weight	844.58	1016.88
space group	$P2_12_12_1$	$P2_1/n$
$a/\text{Å}$	13.8655(11)	14.5805(16)
$b/\text{Å}$	15.0021(12)	14.0968(15)
$c/\text{Å}$	22.8550(18)	24.168(3)
$\alpha/°$	90	90
$\beta/°$	90	93.703(2)
$\gamma/°$	90	90
$V/\text{Å}^3$	4754.1(7)	4957.2(9)
Z	4	4
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.180	1.363
μ (Mo Kα), mm^{-1}	0.608	0.968
θ max, deg.	30.55	24.71
no. of data collected	76604	43118
no. of data used	14503	8462
no. of parameters	520	535
R_1 [$I > 2\sigma(I)$]	0.0361	0.0690
wR_2 [$I > 2\sigma(I)$]	0.0797	0.1524
R_1 [all data]	0.0536	0.1269
wR_2 [all data]	0.0877	0.1723
GOF	1.019	1.133
R_{int}	0.0473	0.1209

Table 3. (cont.) Crystal, intensity collection and refinement data.

	[Tpom$^{Bu^t}$]Tl	{[Tpom$^{Bu^t}$]Tl}$_2$
lattice	Trigonal	Monoclinic
formula	$C_{28}H_{36}N_3O_3Tl$	$C_{56}H_{72}N_6O_6Tl_2$
formula weight	666.97	1333.94
space group	*R-3*	*P2$_1$/n*
a/Å	15.492(4)	11.9498(15)
b/Å	15.492(4)	10.7516(13)
c/Å	19.782(5)	21.365(3)
α/°	90	90
β/°	90	92.803(2)
γ/°	120	90
V/Å^3	4111.6(16)	2741.7(6)
Z	6	2
temperature (K)	130(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.616	1.616
μ (Mo Kα), mm^{-1}	5.925	5.924
θ max, deg.	30.70	32.03
no. of data collected	21563	46294
no. of data used	2818	9456
no. of parameters	109	325
R_1 [$I > 2\sigma(I)$]	0.0383	0.0319
wR_2 [$I > 2\sigma(I)$]	0.0873	0.0720
R_1 [all data]	0.0508	0.0522
wR_2 [all data]	0.0927	0.0784
GOF	1.030	1.030
R_{int}	0.0739	0.0442

Table 4. Cartesian coordinates for geometry optimized structures of [Tpom^But]Tl.

[Tpom^But]Tl

-1480.69342327206 Hartrees

atom	x	y	z
Tl	-0.007073257	-0.005740297	5.696597513
O	1.934943045	1.277553268	4.495005443
N	0.524351765	1.278928468	2.669915594
C	-0.00425187	-0.006458295	3.129438362
C	1.538710846	1.858075805	3.467592075
C	2.061217616	3.117003615	3.002776322
H	2.844601074	3.527205422	3.626426019
C	1.600599825	3.763453864	1.881518183
C	2.159551246	5.107065595	1.389863846
C	2.714059091	4.926327838	-0.044756573
H	1.942341435	4.591971607	-0.744897729
H	3.525127639	4.19058726	-0.062755344
H	3.111138772	5.877097766	-0.417599495
C	1.021478962	6.156473013	1.372989306
H	0.608376755	6.303490595	2.376206927
H	0.200199517	5.86226972	0.712517564
H	1.404239112	7.120070512	1.018358512
C	3.29381858	5.631682083	2.288558761
H	2.951856816	5.804964372	3.313881573
H	3.663162964	6.585141224	1.896683764
H	4.139483402	4.937106735	2.322482743
C	0.543957854	3.13758469	1.151502454
H	0.113653003	3.599192799	0.270928134
C	0.054626046	1.932135655	1.559382558
H	-0.747231903	1.437461858	1.026064248
O	-2.077824626	1.06859008	4.472081143
N	-1.380502852	-0.186883669	2.666728642
C	-2.386740099	0.422542241	3.45389206
C	-3.738362187	0.249550069	2.988332828

H	-4.482886023	0.738135911	3.603072726
C	-4.071575235	-0.486887245	1.877258657
C	-5.51543148	-0.668587464	1.384938468
C	-5.627945527	-0.112144103	-0.055939262
H	-4.954299872	-0.625988818	-0.748576601
H	-5.387716518	0.956020468	-0.084456314
H	-6.649760239	-0.23949879	-0.430624269
C	-5.867102903	-2.176276852	1.38244938
H	-5.793993766	-2.598349569	2.39003085
H	-5.204547062	-2.752303011	0.72937179
H	-6.893197422	-2.322050192	1.026474686
C	-6.534002613	0.06859144	2.273663217
H	-6.518505238	-0.303569125	3.302986457
H	-7.54440146	-0.085229014	1.880757664
H	-6.347917562	1.147250961	2.296781843
C	-3.004689231	-1.108236296	1.15872644
H	-3.191895579	-1.723099416	0.28661202
C	-1.715060779	-0.933402335	1.566243465
H	-0.888774824	-1.394472435	1.040329207
O	0.154934838	-2.332592717	4.489036582
N	0.844555822	-1.103563485	2.662812326
C	0.852949748	-2.27214517	3.460533136
C	1.694176265	-3.344742075	2.995027539
H	1.671138609	-4.227058051	3.621065663
C	2.480547332	-3.261451282	1.871807635
C	3.38144461	-4.405135069	1.382002002
C	2.948616565	-4.809257793	-0.04890603
H	3.026634357	-3.975346453	-0.75324801
H	1.912122719	-5.162800209	-0.060638945
H	3.586675615	-5.618672624	-0.42089456
C	4.851211726	-3.919105366	1.356739594
H	5.183654006	-3.622994487	2.357004415
H	4.989991909	-3.062307777	0.690481352
H	5.507040359	-4.723379743	1.004786947
C	3.294002356	-5.647082182	2.287131302

H	3.615675307	-5.42719134	3.310105507
H	3.947357353	-6.434081289	1.89617418
H	2.27680582	-6.050115678	2.327299806
C	2.447651784	-2.035782425	1.138284025
H	3.056269669	-1.888400813	0.254248152
C	1.638542698	-1.017775209	1.547542893
H	1.598409236	-0.078133321	1.011389272

5.8 References and Notes.

(1)   (a) *Scorpionates – The Coordination Chemistry of Polypyrazolylborate Ligands*, S. Trofimenko, Imperial College Press, London, 1999. (b) *Scorpionates II: Chelating Borate Ligands*, C. Pettinari, Imperial College Press, London, 2008.

(2)   (a) Spicer, M. D.; Reglinski, J. *Eur. J. Inorg. Chem.* **2009**, 1553-1574. (b) Parkin, G. *New J. Chem.* **2007**, *31*, 1996-2014. (c) Smith, J. M. *Comm. Inorg. Chem.* **2008**, *29*, 189-233. (d) Riordan, C. G. *Coord. Chem. Rev.* **2010**, *254*, 1815-1825.

(3)   (a) Limberg, C. *Eur. J. Inorg. Chem.* **2007**, 3303-3314. (b) Quadrelli, E. A.; Basset, J. M. *Coord. Chem. Rev.* **2010**, *254*, 707-728. (c) Floriani, C. *Chem. Eur. J.* **1999**, *5*, 19-23.

(4)   (a) Salinier, V.; Corker, J. M.; Lefebvre, F.; Bayard, F.; Dufaud, V.; Basset, J. M. *Adv. Synth. Catal.* **2009**, *351*, 2155-2167. (b) Salinier, V.; Niccolai, G. P.; Dufaud, V.; Basset, J. M. *Adv. Synth. Catal.* **2009**, *351*, 2168-2177.

(5)   (a) Kläui, W.; Asbahr, H. O.; Schramm, G.; Englert, U. *Chem. Ber*. **1997**, 130, 1223 1229. (b) Leung, W. -H.; Zhang, Q. -F.; Yi, X. -Y.; *Coord. Chem. Rev*., **2007**, 251, 2266-2279. (c) Kläui, W. *Angew. Chem. Int. Ed. Engl*., **1990**, 29, 627-637.

(6)   (a) Roesky, H. W.; Gries, T.; Dhathathreyan, K. S.; Lueken, H. *Z. Anorg. Allg. Chem.* **1987**, *547*, 199-204. (b) Roesky, H. W.; Djarrah, H.; Thomas, M.; Krebs, B.; Henkel, G. *Z. Naturforsch.* **1983**, *38B*, 168-171.

(7)   (a) Dinger, M. B.; Scott, M. J. *Eur. J. Org. Chem.* **2000**, 2467-2478. (b) Dinger, M. B.; Scott, M. J. *Inorg. Chem.* **2000**, *39*, 1238-1254. (c) Dinger, M. B.; Scott, M. J. *Inorg. Chem.* **2001**, *40*, 856-864. (d) Akagi, F.; Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2005**, *127*, 11936-11937. (e) Akagi, F.; Matsuo, T.; Kawaguchi, H. *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 8778-8781. (f) Chaplin, A. B.; Harrison, J. A.; Nielson, A. J.; Shen, C.; Waters, J. M. *Dalton Trans.* **2004**, 2643-2648. (g) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 499-510. (h) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 511-519. (i) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 520-533. (j) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 1063-1069. (k) Michalczyk, L.; de Gala, S.; Bruno, J. W. *Organometallics* **2001**, *20*, 5547-5556. (l) Paz-Sandoval, M. A.; Fernández-Vincent, C.; Uribe, G.; Contreras, R.; Klaebe, A. *Polyhedron* **1988**, *7*, 679-684. (m) Livant, P.; Northcott, J.; Webb, T. R. *J. Organomet. Chem.* **2001**, *620*, 133-138. (n) Tanski, J. M.; Kelly, B. V.; Parkin, G. *Dalton Trans.* **2005**, 2442-2447. (o) Kelly, B. V.; Tanski, J. M.; Anzovino, M. B.; Parkin, G. *J. Chem. Crystallogr.* **2005**, *35*, 969-981. (p) Yasuda, M.; Nakajima, H.; Takeda, R.; Yoshioka, S.; Yamasaki, S.; Chiba, K.; Baba, A. *Chem. Eur. J.* **2011**, *17*, 3856-3867.

(8)   Kobayashi, J.; Goto, K.; Kawashima, T.; Schmidt, M. W.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 3703-3712.

(9)   (a) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233-295. (b) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483-489.

(10)   (a) Kawaguchi, H.; Matsuo, T. *J. Organomet. Chem.* **2004**, *689*, 4228-4243. (b) Kelly, B. V.; Weintrob, E. C.; Buccella, D.; Tanski, J. M.; Parkin, G. *Inorg. Chem.*

Commun. **2007**, *10*, 699-704. (c) Tong, L. H.; Wong, Y. L.; Lee, H. K.; Dilworth, J. R. *Inorg. Chim. Acta* **2012**, *383*, 91-97. (d) Worl, S.; Hellwinkel, D.; Pritzkow, H.; Hofmann, M.; Kramer, R. *Dalton Trans.* **2004**, 2750-2757.

(11)   (a) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148. (b) Parkin, G. in *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1.01; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2006. (c) Green, J. C.; Green, M. L. H.; Parkin, G. *Chem. Commun.* **2012**, *48*, 11481-11503.

(12)   (a) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233-295. (b) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483-489.

(13)   (a) Kawaguchi, H.; Matsuo, T. *J. Organomet. Chem.* **2004**, *689*, 4228-4243. (b) Kelly, B. V.; Weintrob, E. C.; Buccella, D.; Tanski, J. M.; Parkin, G. *Inorg. Chem. Commun.* **2007**, *10*, 699-704. (c) Tong, L. H.; Wong, Y. L.; Lee, H. K.; Dilworth, J. R. *Inorg. Chim. Acta* **2012**, *383*, 91-97. (d) Worl, S.; Hellwinkel, D.; Pritzkow, H.; Hofmann, M.; Kramer, R. *Dalton Trans.* **2004**, 2750-2757.

(14)   For other L_3X ligands, see: Kuzu, I.; Krummenacher, I.; Meyer, J.; Armbruster, F.; Breher, F. *Dalton Trans.* **2008**, 5836-5865.

(15)   Gwengo, C.; Silva, R. M.; Smith, M. D.; Lindeman, S. V.; Gardinier, J. R. *Inorg. Chim. Acta* **2009**, *362*, 4127-4136.

(16)   Witzel, B. E.; Shen, T. *US Patent #3,654,291 (1972).*

(17)   Bell, Z. R.; Motson, G. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Polyhedron* **2001**, 20, 2045-2053.

(18)   The zinc center is characterized by a four-coordinate τ_4 geometry index of 0.62, such that it is best described as possessing a "see-saw" geometry. See: Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955-964.

(19) d(Zn–O) = 2.095(2) Å and 2.104(2) Å.

(20) d(Zn–O) = 2.096(1) Å and 2.179(1) Å.

(21)   Cambridge Structural Database (Version 5.34). *3D Search and Research Using the Cambridge Structural Database*, Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8* (1), pp 1 & 31-37.

(22)   Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2011**, *133*, 9708-9711.

(23)   As would be expected, these Zn–O bond lengths are longer than that pertaining to the zinc-aryloxide interaction (1.89 Å)

(24)   (a) Voronkov, M. G. *Pure Appl. Chem.* **1966**, *13*, 35-59. (b) Voronkov, M. G.; Baryshok, V. P. *J. Organomet. Chem.* **1982**, *239*, 199-249. (c) Woronkow, M. G.; Seltschan, G. I.; Lapsina, A.; Pestunowitschich, W. A. *Z. Chem.* **1968**, *8*, 214-217.

(25)   (a) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem. Int. Edit.* **1999**, *38*, 2759-2761. (b) Braunschweig, H.; Dewhurst, R. D. *Dalton Trans.* **2011**,

40, 549-558. (c) Amgoune, A.; Bourissou, D. *Chem. Commun.* **2011**, *47*, 859-871.
(d) Parkin, G. *Organometallics* **2006**, *25*, 4744-4747.

(26) For some other compounds that can be classified as metallacarbatranes:
(a) Chakrabarti, N.; Sattler, W.; Parkin, G. *Polyhedron* **2013**, *58*, 235-246.
(b) Rong, Y.; Parkin, G. *Aust. J. Chem* in press (DOI: 10.1071/CH13263). (c)
Miyamoto, R.; Santo, R.; Matsushita, T.; Nishioka, T.; Ichimura, A.; Teki, Y.;
Kinoshita, I. *Dalton Trans.* **2005**, 3179-3186. (d) Halder, P.; Dey, A.; Paine, T. K.
Inorg. Chem. **2009**, *48*, 11501-11503. (e) Vieira, F. T.; de Lima, G. M.; Wardell, J. L.;
Wardell, S. M. S. V.; Krambrock, K.; Alcantara, A. F. d. C. *J. Organomet. Chem.*
2008, *693*, 1986-1990. (f) Pellei, M.; Lobbia, G. G.; Mancini, M.; Spagna, R.; Santini,
C. *J. Organomet. Chem.* **2006**, *691*, 1615-1621. (g) Miyamoto, R.; Hamazawa, R. T.;
Hirotsu, M.; Nishioka, T.; Kinoshita, I.; Wright, L. J. *Chem. Commun.* **2005**, 4047-
4049. (h) Kuwamura, N.; Kato, R.; Kitano, K.; Hirotsu, M.; Nishioka, T.;
Hashimoto, H.; Kinoshita, I. *Dalton Trans.* **2010**, *39*, 9988-9993.

(27) the sum of the covalent radii of zinc (1.22 Å) and sp^3 carbon (0.76 Å) is 1.98 Å

(28) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades,
E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

(29) (a) Sattler, W.; Parkin, G. *Chem. Sci.* **2012**, *3*, 2015-2019. (b) Sattler, W.; Parkin, G.
J. Am. Chem. Soc. **2012**, *134*, 17462-17465.

(30) Kitano, K.; Kuwamura, N.; Tanaka, R.; Santo, R.; Nishioka, T.; Ichimura, A.;
Kinoshita, I. *Chem. Commun.* **2008**, 1314-1316.

(31)   Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107-216.

(32)   See, for example, references 31, 33a, and:

(a) Kristiansson, O. *Eur. J. Inorg. Chem.* **2002**, 2355-2361. (b) Akhbari, K.; Morsali,

A. *Coord. Chem. Rev.* **2010**, *254*, 1977-2006.

(33)   (a) Wiesbrock, F.; Schmidbaur, H. *J. Am. Chem. Soc.* **2003**, *125*, 3622-3630. (b)

Childress, M. V.; Millar, D.; Alam, T. M.; Kreisel, K. A.; Yap, G. P. A.; Zakharov,

L. N.; Golen, J. A.; Rheingold, A. L.; Doerrer, L. H. *Inorg. Chem.* **2006**, *45*, 3864-

3877.

(34)   (a) Uhl, W. *Adv. Organomet. Chem.* **2004**, *51*, 53-108. (b) Uhl, W. *Rev. Inorg. Chem.*

1998, *18*, 239-282.

(35)   (a) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047-10064. (b) Power, P. P. *J.*

Chem. Soc. Dalton Trans. **1998**, 2939-2951. (c) Power, P. P. *J. Organomet. Chem.*

2004, *689*, 3904-3919. (d) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv.*

Organomet. Chem. **1999**, *44*, 1-65.

(36)   Wright, R. J.; Phillips, A. D.; Hino, S.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*,

4794-4799.

(37)   Uhl, W.; Keimling, S. U.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem. Int.*

Edit. Engl. **1997**, *36*, 64-65.

(38)   Niemeyer, M.; Power, P. P. *Angew. Chem. Int. Edit.* **1998**, *37*, 1277-1279.

(39)   Bylikin, S. Y.; Robson, D. A.; Male, N. A. H.; Rees, L. H.; Mountford, P.; Schröder, M. *J. Chem. Soc. Dalton Trans.* **2001**, 170-180.

(40)   Hitchcock, P. B.; Huang, Q.; Lappert, M. F.; Zhou, M. *Dalton Trans.* **2005**, 2988-2993.

(41)   Ma, G.; Ferguson, M. J.; Cavell, R. G. *Chem. Commun.* **2010**, *46*, 5370-5372.

(42)   Yurkerwich, K.; Coleman, F.; Parkin, G. *Dalton Trans.* **2010**, *39*, 6939 – 6942.

(43)   Calculations and NBO analyses were performed by Dr. Yi Rong.

(44)   Note that the three N–C–N bond angles of 109.4(3)° correspond closely to the tetrahedral value.

(45)   (a) Bigmore, H. R.; Meyer, J.; Krummenacher, I.; Rugger, H.; Clot, E.; Mountford, P.; Breher, F. *Chem. Eur. J.* **2008**, *14*, 5918-5934. (b) Cushion, M. G.; Meyer, J.; Health, A.; Schwarz, A. D.; Fernandez, I.; Breher, F.; Mountford, P. *Organometallics* **2010**, *29*, 1174-1190.

(46)   (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23. (b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.;

American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98. (c) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.

(47)   Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

(48)   Bochmann, M.; Bwembya, G.; Webb, K. J. *Inorg. Synth.* **1971**, 31, 19-24.

(49)   Klinkhammer, K. W.; Henkel, S. *J. Organomet. Chem.* **1994**, 480, 167-171.

(50)   (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

(51)   Jaguar 7.6, Schrödinger, LLC, New York, NY 2009.

(52)   (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100. (c) Lee, C. T.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789. (d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200-1211. (e) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

(53)   (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284-298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.

(54)   Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001); http://www.chem.wisc.edu/~nbo5.

(55)   (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768-775. (b) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320-3321. (c) Manson, J.; Webster, C. E.; Pérez, L. M.; Hall, M. B. http://www.chem.tamu.edu/jimp2/index.html

(56)   Version 2.0, June 1993; Lichtenberger, D. L. Department of Chemistry, University of Arizona, Tuscon, AZ 85721.