INVESTIGATIONS INTO RARE COORDINATION ENVIRONMENTS OF AL, P AND PD SPECIES: SYNTHESIS AND APPLICATIONS

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By

Shih-Chang Wu

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ABSTRACT

This research work includes three parts, with the first section describing the synthesis and applications of neutral 3-coordinate aluminum complexes. As demonstrated in this part, aluminum complexes in a 3-coordinate geometry can be formed only with a ring size greater than or equal to a 6-member ring when supported by diamido ligands. It is found that 1,2-diamido ligands designed for 5-member ring formations can accommodate the formation of only 4-coordinate dinuclear species, which show no activity when used as a single component catalyst in the ring-opening polymerization (ROP) of cyclic esters under specified reaction conditions. Three-coordinate neutral (1,4-diamido)AlMe complexes are successfully synthesized, revealing a higher activity in the ROP of cyclic esters than the existing 6-member analogues under the same reaction conditions. A detailed discussion of the structure-reactivity relationship of Al catalysts in the ROP of cyclic esters is presented.

The second part of this thesis project consists of investigations into the applications of 1,4-diamido ligands for the formation of 3-coordinate NHP (*N*-heterocyclic phosphine) and 2-coordinate NHP^+ cations (phosphenium cations). These novel NHP species are the first to be shown in a 7-member ring supported by 1,4-diamido ligands. Various *N*-substituents in the 1,4-diamido ligands are examined for the formation of a cyclic structure based on their steric hindrance. It is found that a Dipp (2,6-diisopropylphenyl) group is unable to allow for the formation of a 7-member NHP due to its excessive steric bulk. The less bulky mesityl (2,4,6-trimethylphenyl) group at the *N*-positions in the ligands leads to successful formation of these novel NHPs and NHP^+ species. Furthermore, an investigation is carried out to explore their π-accepting property by means of ^{31}P NMR studies. The NHP and NHP^+ species synthesized in this project show chemical shifts downfield relative to the existing 5- and 6-member analogues in

^{31}P NMR experiments, suggesting a high potential of 7-member NHPs to be used as π-acceptor ligands. The second section also examined the resulting NHPs and NHP^{+} species for coordinating to various metals.

The last part of this research work is dedicated to presenting the first example of chelating κ^3–triNHC (tri-*N*-heterocyclic carbene) ligands that allow for the formation of (triNHC)Pd(II) complexes in a meridional fashion, wherein the triNHC ligand coordinates to the metal center in a pseudo-meridional fashion. Novel $[(triNHC)^{Me}PdX]X$ (X = Cl or acetate) complexes are successfully synthesized, and they display extraordinary stability against air and heat. Low activities of the resulting complexes are found in promoting C-C coupling reactions, possibly due to the low solubility of the resulting complexes in organic solvents. Various attempts to change the *N*-substituents to groups other than methyls are conducted to improve the solubility of the complexes in organic solvents for higher activities in C-C coupling reactions. The results from these attempted modifications to these complexes are discussed in detail.

All complexes are characterized by standard spectral methods such as mass spectrometry, X-ray crystallography, elemental analysis, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy.

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LIST OF ABBREVIATIONS

Ar..... Aromatic

BISBI.....2,2'-bis[(diphenylphosphino)methyl]-l,l'-biphenyl

Cat. .....Catalyst

CL.....Caprolactone

COD.....Cyclooctadiene

Cp.....Cyclopentadienyl

CPK.....Space-filling models

diNHC.....di-*N*-heterocyclic carbene

DIOP.....(2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

DIPHOS (dppe).....1,2-Bis(diphenylphosphino)ethane

Dipp.....2,6-diisopropylphenyl

DMF.....Dimethylformamide

DMSO.....Dimethyl sulfoxide

dppf..... .....1,1'- Bis(diphenylphosphino)ferrocene

dppp.....1,3-Bis(diphenylphosphino)propane

Et_2O.....Diethyl ether

Et_3N.....Triethylamine

KHMDS.....Potassium bis(trimethylsilyl)amide

MAO.....Methylaluminoxane

Me.....Methyl

Mes.....Mesityl = 2,4,6-trimethylphenyl

monoNHC.....mono-*N*-heterocyclic carbene

NHC.....*N*-heterocyclic carbene

NHP.....*N*-heterocyclic phosphine

NHP^+.....*N*-heterocyclic phosphenium cation

NMR.....Nuclear Magnetic Resonance

NR_3.....Tertiary amines

OAc.....Acetate

Oct.....Octoate

O^iPr.....Isoproxide

OTf.....Triflate, Trifluoromethanesulfonate

PCL.....Polycaprolactone

PE.....Polyethylene

Ph.....Phenyl

PPDL.....Polypentadecalactone

PR_3.....Tertiary phosphines

R_2P^+ ..... Phosphenium cation

ROP.....Ring-opening polymerization

sal.....Salicylaldiminato

SMes*.....Supermesityl = 2,4,6-tri-*tert*-butylphenyl

T-BDCP .....*trans*-l,2-bis[(diphenylphosphino)-methyl]cyclopropane

*t*Bu.....Tertiary butyl

THF.....Tetrahydrofuran

TiBA.....Triisobutylaluminum

TMS.....Trimethylsilyl

TON.....Turnover number

triNHC.....tri-*N*-heterocyclic carbene

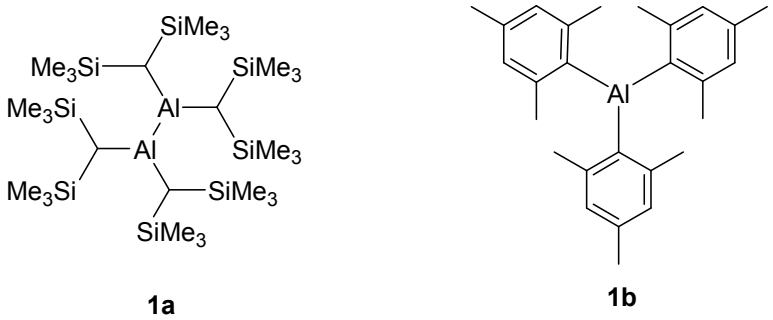
ε-CL.....ε-caprolactone

CHAPTER 1. INTRODUCTION

1.1 Rare Coordination Environments and Catalysis

Rare coordination environments represent coordination numbers of chemical species that are lower than normal, or a coordination geometry that the species do not commonly display. In catalysis, a lower coordination is thought to offer more available coordination sites for substrates to react, thereby allowing a facile catalytic initiation. In addition, the Lewis acidity of a metal-based catalyst, as required by most catalytic reactions, can be enhanced by a lower coordinate environment. In this research, rare coordination environments around aluminum, phosphorus, and palladium species are investigated.

The most commonly seen organoaluminum complexes exist in the form of 4-coordinate aluminum with an oxidation state of 3+. The simplest examples are commercially available Me_3Al and Et_3Al, which are 4-coordinate complexes bridged by alkyl groups. Smith *et al.* reported that 3-coordinate aluminum species existed in monomer-dimer equilibrium of liquid triisobutylaluminum (TiBA).[1] One early example of a well-characterized 3-coordinate organoaluminum complex was reported by Uhl *et al.* in the form of a dinuclear Al^{II} species, **1a** (Figure 1-1).[2] The key feature for accessing stable low-coordinate aluminum complexes such as **1a** lies in the use of sterically hindered Al substituents to protect the aluminum center and to prevent facile decompositions. A very bulky supermesityl thiolate (SMes*) ligand (supermesityl = 2,4,6-tri-*tert*-butylphenyl) was used to form a stable neutral 3-coordinate Al^{III} complex, $Al(SMes^*)_3$, in monomeric form.[3] Another representative example reported by Jerius *et al.* in 1985 was trimesitylaluminum **1b** (Figure 1-1).[4]



1a **1b**

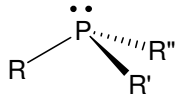
Figure 1-1. Examples of 3-coordinate Al complexes.

Although 3-coordinate aluminum complexes resembling those described above can be prepared with bulky ligands, no application of them are addressed in existing research on catalytic reactions.[5]

Phosphorus species have been seen mostly in 5+ and 3+ oxidation states. A significant number of organophosphorus compounds have also become commercially available. Organophosphorus(V) compounds can be categorized as phosphonic oxides $P(=O)R(OR)_2$ and phosphine oxides $R_3P(=O)$. Since the high oxidation state of P(V) compounds utilizes all the valence electrons of a phosphorus atom, much less attention has been given to them than to the P(III) species as a ligand.

In contrast, trivalent phosphines P(III), also referred to as phosphanes, exhibit reactivity levels different from P(V) species. The parent structure of the phosphine **2** (Figure 1-2) displays a trigonal pyramidal molecular geometry and accommodates a wide variety of R groups. In phosphines, phosphori exist in the oxidation state of 3+ and hold a lone pair available for donating to metal centers. The C-P-C bond angle in **2** can be tuned by varying the steric bulk of R groups, e.g. 98.6^o in trimethylphosphine, and 109.7^o when the methyl groups are replaced by *tert*-butyl groups. It is the donor property and tunable steric bulk that collectively make

phosphines good σ-donor ligands in coordination chemistry. Since there are diversified applications of σ-donating ability, investigations into utilizing phosphines as ligands have been by far one of the most abundant studies in coordination chemistry. In organometallic catalysis, the strong σ-donating property of the 3-coordinate phosphines is found to stabilize the metal center better than most ligands. Therefore, phosphine-based metal catalysts usually result in longer catalytic lifetimes and higher efficiencies.



2

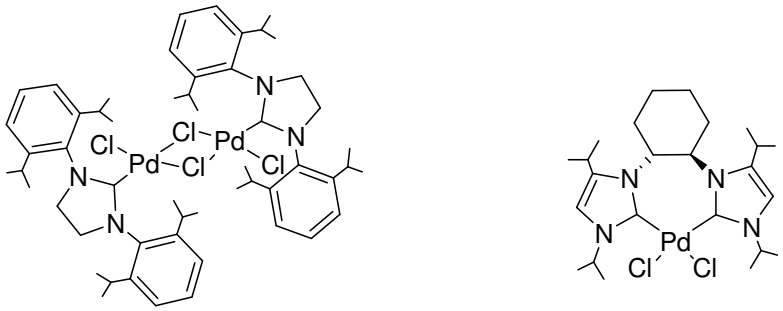
R, R', R" = alkyl, aryl groups

Figure 1-2. Structure of a phosphine P(III) species.

Although 3-coordinate P(III) species have been well studied, the less common 2-coordinate P(III) species have not been explored to the same extent. Two-coordinate phospheniums ($R_2P^+ X^-$) exist mainly as cationic species, in which the positive charge is assumed to attenuate their donor ability, thus making the species weaker σ-donors. Moreover, a positive charge introduced on the P atom becomes a major factor in providing π-acceptor properties to 2-coordinate phosphenium species. The σ-donor and π-acceptor properties of 2-coordinate phosphenium cationic species could launch an interesting field of study in coordination chemistry and catalysis.

N-Heterocyclic carbene-palladium ((NHC)Pd) complexes are extensively studied in cross-coupling reactions because of their excellent catalytic activities. Palladium in well-defined (NHC)Pd complexes exists in the oxidation states of Pd(0), Pd(II) and Pd(IV), wherein

(NHC)Pd(II) is most commonly reported. The simple (NHC)Pd(II) complexes assume a square planar geometry around the Pd center, as represented in a commercially available monodentate (diNHC)Pd(II) **3** (Figure 1-3). Complexes of (diNHC)Pd(II) incorporating chelating diNHC ligands are more stable than that of monodentate (NHC)Pd(II) through chelate effects; therefore, the study of (diNHC)Pd(II) in catalysis has been second only to their monoNHC analogues. A representative example of bidentate (diNHC)Pd(II) complex **4** (Figure 1-3) is a mononuclear species stabilized by the diNHC ligand while the environment around Pd center is a square planar geometry.[6]



3 **4**

Figure 1-3. Examples of mono(NHC)Pd(II) **3** and chelating (diNHC)Pd(II) **4** complexes.[7]

While there has been extensive study of palladium chemistry with monoNHC and diNHC ligands to form well-defined complexes in catalytic applications, (triNHC)Pd(II) complexes incorporating chelating triNHC ligands are unknown. The investigation of coordination patterns and catalytic activities of Pd complexes incorporating NHCs is of great interest based on the assumption that multiple NHCs should provide higher stability to the complex.

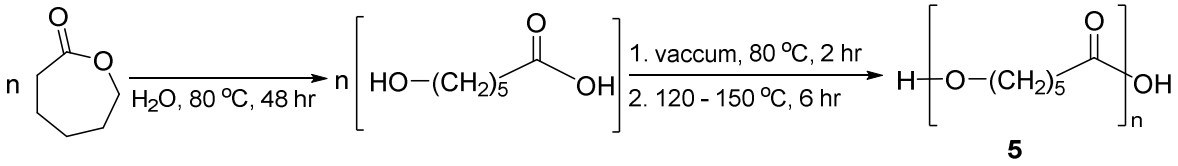
1.2 Lactone Polymerization

1.2.1 Ring-Opening Polymerization (ROP)

Polylactones are polymers consisting of repeating lactone units. Polycaprolactone (PCL) is a polymer important for its mechanical properties, miscibility with a large range of other polymers, biodegradability and biocompatibility. Polymer **5** (Scheme 1-1) offers an example of polycaprolactone (PCL) derived from a 6-carbon monomer known as ε-caprolactone (ε-CL). It is the biocompatibility of polycaprolactone that makes **5** an important material for various applications, such as tissue engineering, implantation of artificial organs, prostheses, ophthalmology, dentistry, bone repair, drug delivery, and many other biomedical fields.[8]

One route to prepare PCL was the polycondensation of 6-hydroxylhexanoic acid, which was generated by hydrolysis of ε-caprolactone (Scheme 1-1).[9]

Scheme 1-1. Polycondensation of ε-caprolactone to form polycaprolactone.[9]



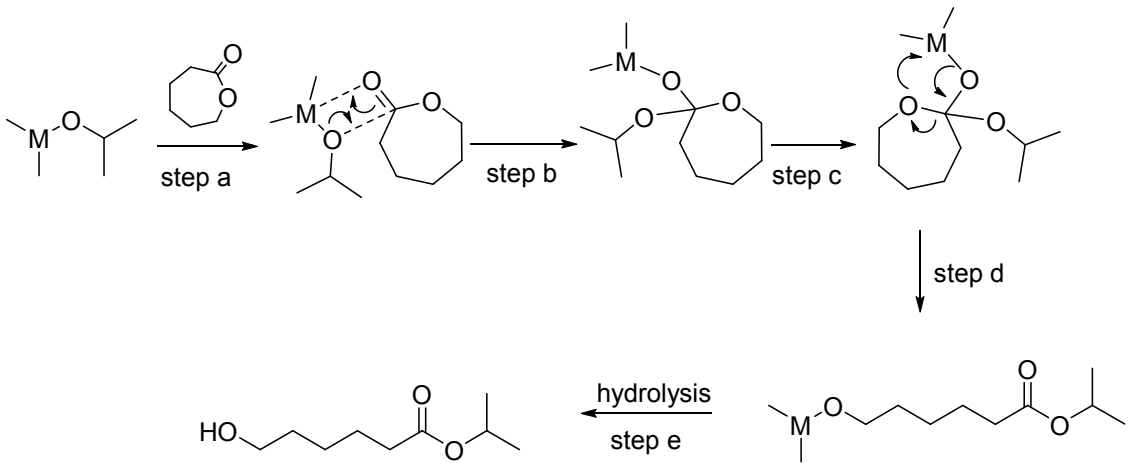
5

A representative pathway to synthesizing caprolactone oligomers by polycondensation was reported by Braud *et al.* (Scheme 1-1).[9b] Compound **5** was formed by heating an aqueous solution of ε-caprolactone at 80°C for two days, after which the lactone underwent ring-opening to form 6-hydroxylhexanoic acid, followed by drying at elevated temperatures (80 ~ 150°C) *in vacuo* to remove water.

Compared to the rigorous reaction conditions that polycondensation requires, a more facile catalyzed ROP route is preferred. Several pathways for catalyzed ROP reactions of

polyesters have been studied, such as anionic, cationic, monomer-activated and coordination-insertion pathways. Coordination-insertion ROP was widely adopted as the most efficient pathway to obtain high molecular weight polymers at facile reaction conditions. Stridsberg *et al.* proposed a mechanism (Scheme 1-2) showing that the coordination-insertion ROP behaves similarly to that of anionic ROP; therefore, it is also referred to as a pseudo-anionic ROP pathway.[9a, 10]

Scheme 1-2. The general pathway for the ROP of a cyclic ester by the coordination-insertion mechanism.[9a, 10]

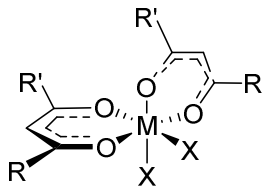


The coordination-insertion mechanism that the ROP of caprolactone polymerization reactions proceed by is directed by metal complexes (Scheme 1-2).[10a] After the initial coordination of the monomer to the metal center (step a), a metal-oxygen bond is formed (step b). Subsequent conformational changes and insertions of the monomer into the metal-oxygen bond (steps c and d) take place until it is terminated by hydrolysis, forming a hydroxyl end group (step

e). Step d is a combination of insertion and ring-opening and is commonly accepted as the rate-limiting step of the polymerization reaction. The coordination-insertion type of polymerization is thought to yield well-controlled polymers through living polymerization.[11] A wide variety of metal complexes was chosen to investigate their performance in ROP reactions, including Sn, Ti, Zr, Mg, Zn, V, Mo, and Al complexes.

Möller *et al.* reported the application of $Sn(OTf)_2$ and $Sc(OTf)_3$ for the polymerization of ε-caprolactone.[12] At 1.0 mol % catalyst loading, a yield of 100% is obtained by the combination of $Sn(OTf)_2$ as the precatalyst with ethanol as the initiator at 20°C for 2 days. With the temperature raised to 65°C, it still required 18 hours to achieve a comparable yield.

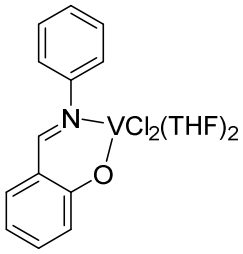
In addition, some titanium and zirconium complexes have been investigated in the ROP reactions of ε-caprolactone. Eisen *et al.* presented their results with (dialkoxide)Ti(IV) and (dialkoxide)Zr(IV)Cl_2 complexes, both with β-diketonate as the ancillary ligand.[13] The zirconium complex **6b** (Figure 1-4) performed marginally better than the titanium analogue **6a**, since **6a** required a longer reaction time to achieve comparable conversions. However, a reaction temperature of 120°C was deemed necessary for both catalysts.



6a: M = Ti; X = O^{t}Bu; R = Me; R' = Me_2N
6b: M = Zr; X = Cl; R = ^{t}Bu; R' = OMe

Figure 1-4. (β-Diketonate)Ti(IV) **6a**, and (β-diketonate)Zr(IV) **6b** complexes.

Vanadium complexes have also been studied for ROP reactions of ε-caprolactone. Clowes *et al.* investigated the performance of (phenoxyimine)V(III) complex **7** (Figure 1-5) in PCL reactions and found that a 100% yield can be achieved only under a rather harsh condition: 72 hours, 80°C, monomer to metal ratio of 400, and addition of benzyl alcohol as the initiator.[14]



7

Figure 1-5. (Phenoxyimine)V(III) complex.[14]

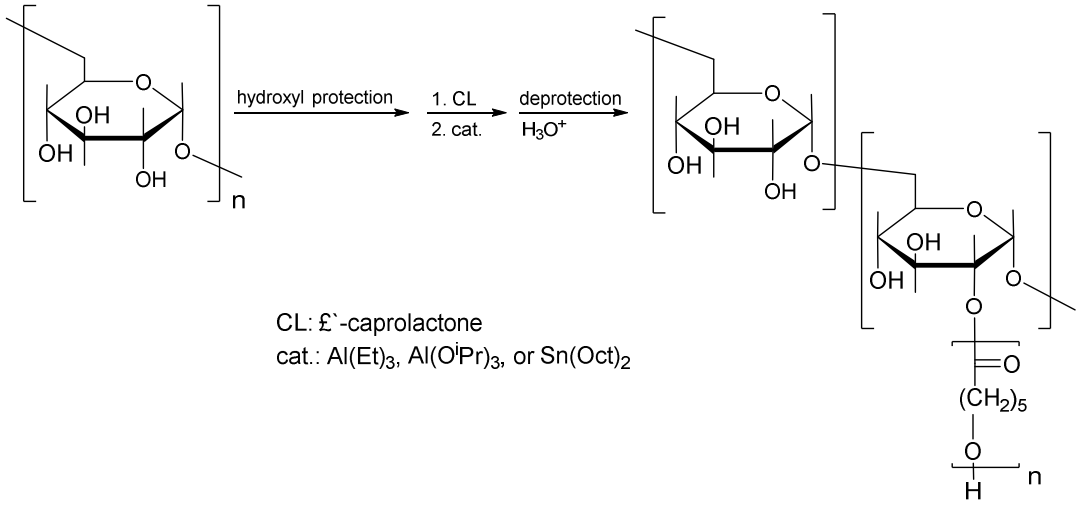
Mahha *et al.* evaluated the performance of heteropolyacid HPA-2 ($H_5[PMo_{10}V_2O_{40}]$) containing Mo(VI) and V(V) metals in the oligomerization of ε-caprolactone. A quantitative yield can be obtained solely by 12 hours at 60 ^oC with methanol as the reaction solvent, based on 7.5% mol of HPA-2. However, the catalyst became inactive under inert atmosphere, possibly due to reduction of the metal centers.[15]

Sarazin *et al.* looked into the catalytic activity of ROP reactions for ε-caprolactone with 4-coordinate cationic zinc and magnesium species stabilized by diethyl ether, such as $[(Et_2O)_3ZnCH_2CH_3][B(C_6F_5)_4]$ and $[(Et_2O)_3MgCH_2CH_2CH_2CH_3][B(C_6F_5)_4]$. The Zn complex exhibited a conversion around 94% for 120 hours at 22°C while the Mg complex was inactive in the ROP of ε-caprolactone.[16]

Tin and aluminum-based catalysts have been widely adopted for the ROP of lactones.

Notably, Dubois *et al.* developed a three-step procedure to synthesize a wide range of PCL-grafted dextran copolymers.[17] As illustrated in Scheme 1-3, the procedure consisted of controlled hydroxyl protection of the dextran moiety, ring-opening polymerization of ε-CL with metal catalysts, and removal of the protecting groups under mild acidic conditions. The critical step in the ROP of ε-CL took place in the presence of a tin or aluminum-based catalyst: stannous octoate $Sn(Oct)_2$, triethylaluminum $AlEt_3$, or aluminum isoproxide $Al(O^iPr)_3$. It is thought that the initiation step of the ROP reaction is driven by metal alkoxide species. Even in the presence of $AlEt_3$, aluminum alkoxide was formed with the free hydroxyl groups in dextran. However, all the catalysts must be accompanied with a rather harsh reaction condition, at least 60 ^oC and 44 hours, to achieve satisfactory results in ROP reactions.

Scheme 1-3. Dextran grafted polycaprolactone.[17]

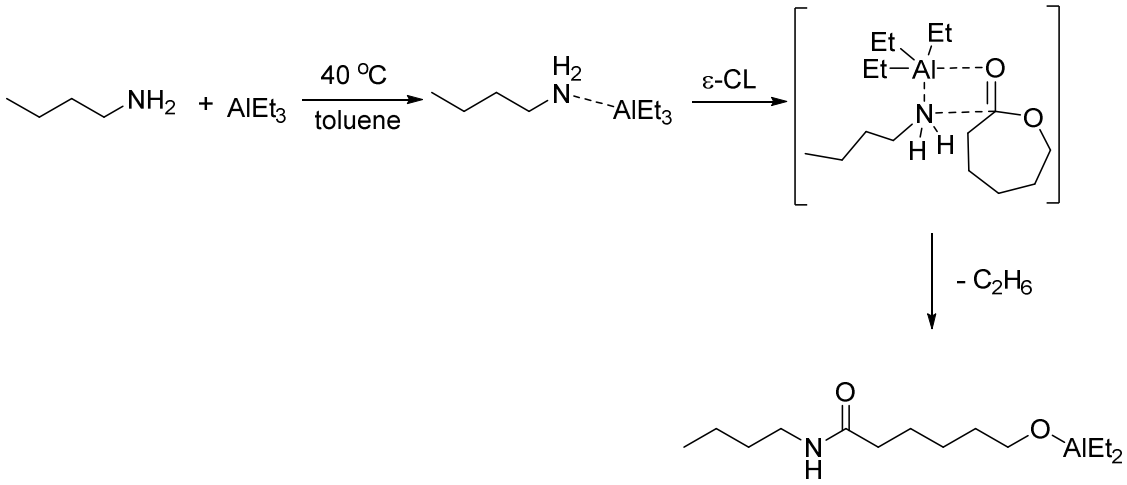


Although $Al(O^iPr)_3$ can be an effective catalyst in the ROP of caprolactones, an alcohol initiator must be added to allow the reaction to proceed at room temperature.[18] It was speculated that the polymerization with aluminum catalysts may not be limited to alkoxyl aluminum. Other

nucleophilic groups attached to aluminum may be as effective, such as an amine.[6, 19]

Dubois *et al.* investigated a triethylaluminum-amine system under the similar reaction conditions adopted by aluminum alkoxide in the ROP of ε-CL.[20] A mechanism of the initiation step was proposed (Scheme 1-4). $AlEt_3$ added with primary amines proved to be an effective initiator for PCL reactions, in that $AlEt_3$ activated the carbonyl group of the monomer and accordingly favored the nucleophilic addition of the amine (similar to that of alkoxide). This process appears in the proposed bracketed intermediate (Scheme 1-4), which was assumed to be the actual initiation step. As a result, a quantitative yield was obtained in 21 hours.

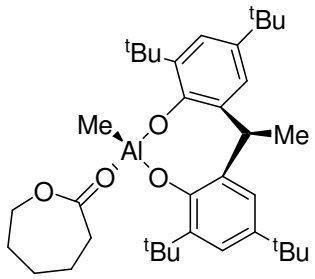
Scheme 1-4. Proposed initiation step of triethylaluminum-amine system.[20]



Combining the cost and effectiveness of various metal complexes in the ROP of lactone polymerizations, aluminum-based catalysts seem to be the most promising system for more investigations.

1.2.2 Role of Aluminum in Lactone Polymerization

The prevalence of Al complexes in lactone polymerization results from the high availability and low cost of Al precursors. Most researchers believe that Al catalysts in lactone polymerization proceed by coordination-insertion mechanism. However, evidence that proved this hypothesis was quite scarce until Lewiński *et al.* isolated the first Al and ε-CL adduct in a well-defined form.[21] Complex **8** (Figure 1-6) illustrates the resulting structure of (bisphenoxide)AlMe coordinated to a ε-CL, in which it displays a direct coordination between the acyl oxygen and aluminum center. The evidence becomes clear that for Al complexes, or for those not limited to Al in lactone polymerization, the acyl oxygen is the actual coordinating element that forms a sigma bond with the metal. This result offers a concrete evidence that the Lewis acidity of the Al center should be closely related and proportional to the rate of coordination.



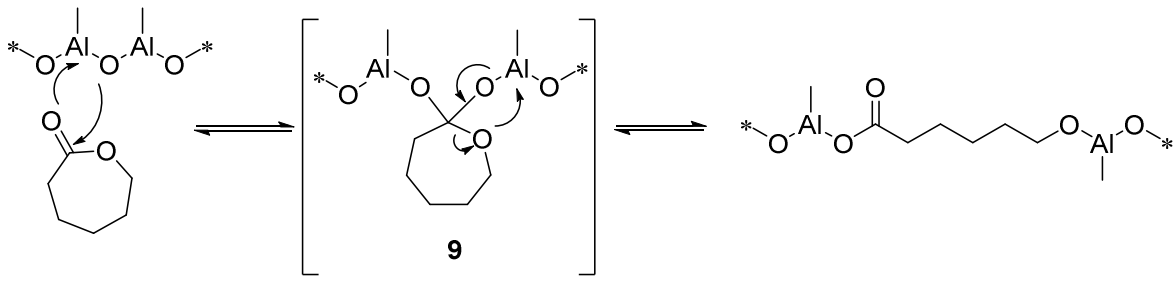
8

Figure 1-6. An example of Al complex coordinated to ε-CL through acyl oxygen, **8**.[21]

Meanwhile, a commercially available catalyst system containing methylaluminoxane (MAO) and trimethylaluminium (MAO/TMA) was investigated in the ROP of cyclic esters. Florjańczyk *et al.* reported on applying the system in PCL reactions and proposed that monomer

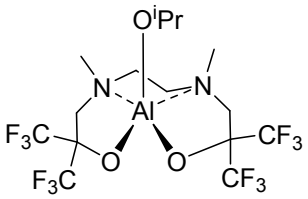
insertion into Al-O-Al bonds in MAO took place through intermediate **9** (Scheme 1-5). It was found that a yield of 89% can be obtained at 60°C for 20 hours.[9a, 22]

Scheme 1-5. Mechanism of the initiation step of the ROP of ε-CL catalyzed by MAO.[9a, 22]



It is commonly accepted that, in the first step, the coordination of acyl oxygen to the aluminum center will proceed at a higher rate if the Lewis acidity of the aluminum center is higher. Such promotion of PCL reactions with highly Lewis-acidic metals was also supported by various research groups.

Carpentier *et al.* claimed that incorporating a strong electron-withdrawing group, such as CF_3, to the diamino-dialkoxide ligand makes **10** (Figure 1-7) a better catalyst by increasing of the Lewis acidity of the Al center.[23] A total conversion of ε-CL to PCL can be obtained at [CL]/[Al] = 100 ratio in one hour at room temperature in the presence of isopropyl alcohol. As demonstrated by Carpentier with complex **10**, manipulating the electronic property of the ligand has been proven to be effective for increasing the Lewis acidity of metals.[23]

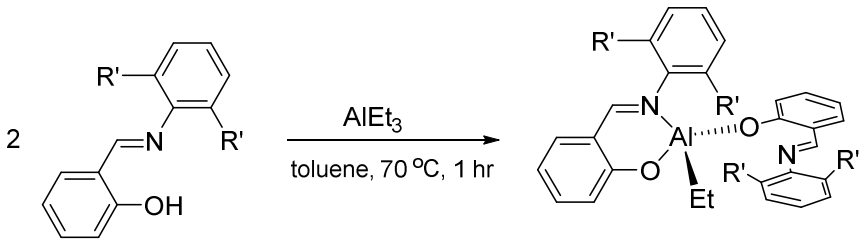


10

Figure 1-7. Al complex containing strong electron-withdrawing CF_3 groups, **10**.[23]

With salicylaldimine (Scheme 1-6) as the ligand system, electronic effects can be tuned by changing the substituents R' (Scheme 1-6) for a higher Lewis acidity in the resulting Al complexes. For instance, Nomura *et al.* performed a series of polymerization reactions with various salicylaldimine-aluminum complexes **11** (Scheme 1-6), in which the effects of different R' groups were investigated in PCL reactions.[24]

Scheme 1-6. Salicylaldimine-Al complex, **11**.[24]



salicylaldimine

11

11a: R' = *tert*-butyl
11b: R' = F
11c: R' = Cl

When the polymerization reaction took place in the presence of benzyl alcohol, **11b** and **11c** gave a higher activity than **11a**. The introduction of electronic-withdrawing groups as the R' moiety, such as that in **11b** (R' = F) and **11c** (R' = Cl), in the salicylaldimine ligand results in a higher Lewis acidity of the metal center, which further leads to increased activities in PCL reactions. Evidently, tuning the electronic properties of the ligands can be of great influence in increasing the Lewis acidity of the metal.

The role of aluminum in organoaluminum complexes serves as a Lewis acid center to which monomers coordinate in polymerization reactions. Various experimental results, as described above, have demonstrated that coordination between monomers and Al can be promoted by increasing the Lewis acidity of the metal complexes.

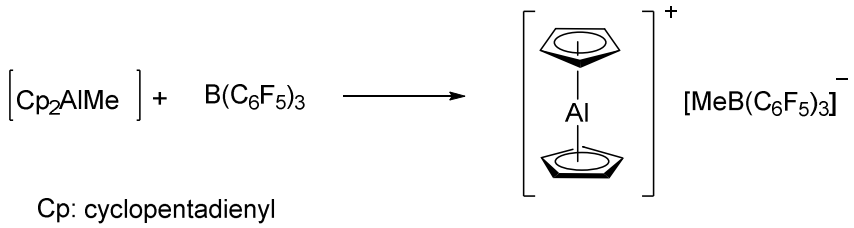
Alternatively, the enhancement of Lewis acidity of a metal complex can be achieved by changing the coordination environment around the metal centers, such as by lowering the coordination number or introducing a positive charge to the metal center.

1.2.3 Low-coordinate Aluminum Complexes in Lactone Polymerization

Trialkylaluminum complexes exist mainly in dimeric or polymeric forms, which might in part contribute to their diminished polymerization activities. Therefore, several approaches were developed to enhance the activities of organoaluminum complexes by increasing the Lewis acidity of the metal centers through incorporating a positive charge to the complexes or by decreasing the coordination number around the aluminum centers.

It was thought that incorporating a positive charge to the metal center could enhance the Lewis acidity of a complex so as to increase the rate of coordination between the monomer and the metal. Transformations of organoaluminum complexes into cationic species have been studied intensively to improve catalytic activities in polymerization reactions, including preparations of the type AlR_2^+ and $(LX^-)AlR^+$ (LX^- = monoanionic bidentate ligand, R = alkyl, aryl). For example, complex **12** $[(Cp_2Al)]^+[MeB(C_6F_5)_3]^-$ was prepared and claimed to be highly Lewis acidic due to the presence of a positive charge at the metal center.[25] Although **12** (Scheme 1-7) was active in olefin polymerization, there has been no report of the complex in lactone polymerizations.[25]

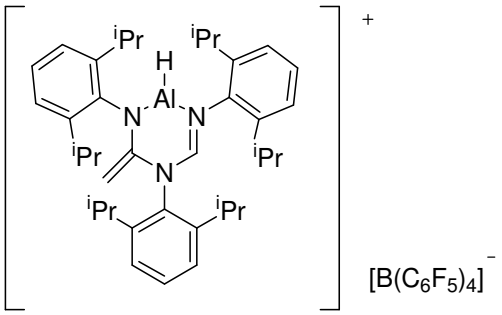
Scheme 1-7. An example of cationic Al complex.[25]



Cp: cyclopentadienyl
Me: methyl

12

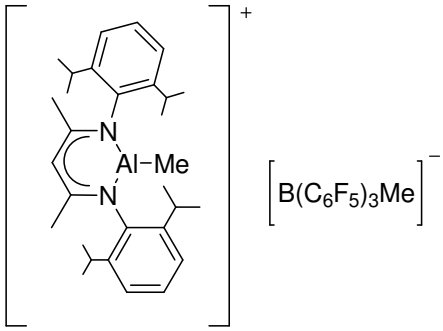
In an example of related research, Stephen *et al.* reported the synthesis of a cationic 3-coordinate Al complex **13** (Figure 1-8) with a sterically demanding *N*-imidoylamidine ligand.[26] The cationic 3-coordinate aluminum complex was made possible by utilizing the steric hindrance of the bulky diisopropylphenyl (Dipp) substituents on the nitrogens. Although **13** was reported as the first 3-coordinate Al-hydride complex, there has been no application of **13** in catalytic reactions.



13

Figure 1-8. A cationic 3-coordinate Al complex.[26]

Some other cationic aluminum complexes in a 3-coordinate geometry have also been reported. The scenario accomplished by incorporating bulky ligands to the metal center seemed to be the best approach for maintaining a 3-coordinate environment. Jordan *et al.* reported the introduction of a bulky β-diketiminate ligand to form a (β-diketiminate)AlMe complex **14** (Figure 1-9).[27] Although the synthesis was successful, no subsequent applications of **14** in polymerization reactions have been presented.[28]



14

Figure 1-9. A [(β-diketiminate)AlMe]$^{+}$ cationic complex.[27]

The commonly accepted mechanism that the ROP of cyclic esters proceed by is coordination-insertion, and the lack of application of the cationic species **12**, **13** and **14** is likely due to a different mechanistic route for which these complexes were suited. First, the incorporation of a positive charge in these complexes may have increased the Lewis acidity of the metal, but the negatively charged counterion may compete with the monomers for coordinating to the growing polymer chain. Consequently, a cationic polymerization process is more likely to occur. Second, for a reason not clear, the presence of a non-nucleophilic counterion in the ionic complexes may bring a reverse effect in initiating ROP reactions. Therefore, although the combination of a low-coordination geometry and positive charge may have increased the Lewis acidity in a complex, it does not appear to be the most appropriate strategy for the ROP of cyclic esters. Thus, the development of neutral 3-coordinate Al complexes has come to the attention of some research groups.

Moreover, there is an assumption that neutral species without charge transfer to the monomer should inhibit the tendency of the catalysis to proceed by cationic polymerizations, thus directing the catalysis to the desired coordination-insertion route for the ROP of cyclic esters. Only a few groups reported the syntheses and applications of 3-coordinate neutral Al complexes.

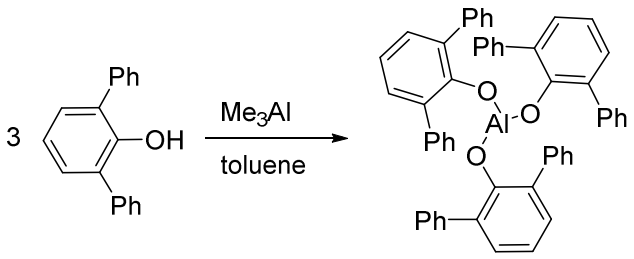
Power *et al.* reported the first monomeric, 3-coordinate aluminum thiolate compound in 1991.[3] The complex was prepared by the reaction of aluminum halide with LiSMes* (Mes* = 2,4,6-$^{t}Bu_3C_6H_2$) in a 1:2 ratio to give $Al(SMes^*)_3$, **15**, through a disproportion mechanism that was not clarified (eq 1.1). The structure of **15** in a monomeric and 3-coordinate form was confirmed by X-ray crystallography.

$$2AlBr_3 + 4LiSMes^* \xrightarrow{\text{toluene}} \underset{\mathbf{15}}{Al(SMes^*)_3} + Br_2Al(SMes^*) + 4LiBr \quad \text{..... (1.1)}$$

The formation of the 3-coordinate neutral complex **15** is preserved by the high degree of bulkiness of the thiolate ligands. No subsequent applications of **15** were reported in addition to structure elucidations. Although the supermesitylthiolate (SMes*) groups contributed greatly to the stability of **15**, the high steric bulk of supermesityl groups decreased the nucleophilicity of an otherwise thiolate group. In addition, the extremely sterically hindered groups may inhibit the access of monomers to coordinate to the metal center. Therefore, it is anticipated that **15** will be inactive in the ROP of cyclic esters based on the mechanistic explanation (Scheme 1-2) in which a good nucleophile is required to attack the acyl carbon prior to ring-opening.

Yamamoto *et al.* reported that the reaction of trimethylaluminum with the bulky ligand tri(2,6-diphenylphenoxide) led to a neutral, 3-coordinate complex **16** (Scheme 1-8).[29] The tendency of Al to form a 4-coordinate species was apparently inhibited by the sterically hindered ligands.[29] The very high steric hindrance of 2,6-diphenylphenoxide groups in **16** may prevent the coordination of monomers in the initial step; therefore, it was not anticipated that **16** be active in the ROP of cyclic esters. However, the 3-coordinate environment renders **16** highly Lewis acidic, and the complex has been proven to be effective as a Lewis acid catalyst in Diels-Alder type reactions. For example, **16** can discriminate between structural difference of aldehydes possessing similar reactivity, thereby facilitating the selective functionalization of the less hindered aldehyde carbonyl.

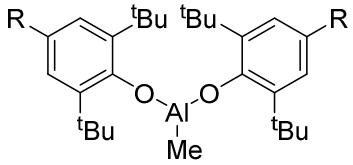
Scheme 1-8. Aluminum tris(2,6-diphenylphenoxide) complex.[29]



16

Wu *et al.* showed that tuning the electronic and steric properties of the ligands can improve the reactivity of Al complexes in polymerizations.[30] The neutral 3-coordinate $(phenoxy)_2AlMe$ complex **17** (Figure 1-10) was investigated in the polymerization of acrylates. As the author concluded, **17c** showed a higher activity level than did **17a** and **17b**, indicating that

the electron-withdrawing Br in R position increased the Lewis acidity of the metal center. As postulated by Wu, **17** functions as a radical initiator by the homolytic cleavage of the Al-Me bond. This process is facilitated in the presence of acrylate at elevated temperatures. Therefore, **17** may not be appropriate to initiate coordination-insertion mechanism for the ROP of cyclic esters.



17

17a: R = H
17b: R = CH_3
17c: R = Br

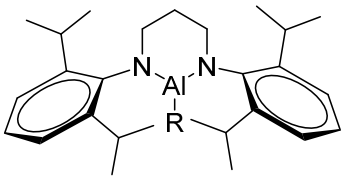
Figure 1-10. A diphenoxy aluminum methyl complex.[30]

It can be concluded that the stability of a low-coordinate Al complex is offered by the steric bulk of the substituents, and that the reactivity of metal complexes in polymerizations is determined by the Lewis acidity of the metal center as well as by the nucleophilicity of the substituents. Although **12** – **14** show a low-coordinate environment around the Al center, the associated positive charge possibly directs the catalysis towards a cationic mechanism other than the coordination-insertion by which the ROP of lactones proceeds.

Complexes **15** – **17** were prepared in a 3-coordinate neutral form, but there has been no reports regarding any of these complexes in the ring-opening polymerization of lactones. A possible reason might be an inhibition of coordination between monomers and acyl oxygens by the highly bulky substituents on Al center.

Consequently, an introduction of a bidentate ligand and nucleophilic substituent to the complex offers a strategy worth pursuit. A bidentate ligand is expected to enhance the stability of the complex during catalysis, and a nucleophilic substituent may attack the acyl carbon of lactones to promote the ring-opening process.

It was not until 2002 that Chen *et al.* reported the first example of an aluminum complex employing diamido chelating ligands to stabilize the metal centers in a single-component, neutral and 3-coordinate form, **18** (Figure 1-11).[31]



18

18a: R = Me; **18b**: R = ^{i}Bu; **18c**: R = C_6F_5

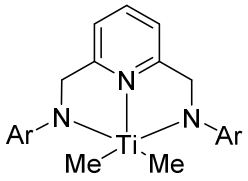
Figure 1-11. A neutral, 3-coordinate, chelating (diamido)AlR complex.[31]

In the ring-opening polymerization of ε-caprolactone, the isobutyl derivative **18b** exhibited the highest activity, followed by **18a** and **18c**. This polymerization was carried out at

room temperature, and an isolated yield of 74% was obtained in 1.5 hours with **18b**. It can be reasoned that the nucleophilicity and steric bulk of R groups may have played an important role in the ring-opening polymerization of ε-caprolactone.

The successful ROP of cyclic esters catalyzed by **18** suggests that a bulky, chelating, and bidentate ligand is able to maintain the aluminum center in a 3-coordinate form, as well as to stabilize the complex during catalytic reactions. More importantly, as shown in Scheme 1-2 (step b), a nucleophilic R group, such as the isobutyl group in **18b**, could coordinate to the carbonyl carbon of the cyclic ester and substantially increase the activity of the complex in the ROP of cyclic esters.

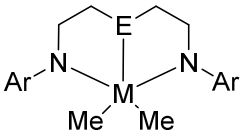
The application of chelating diamido ligands in aluminum chemistry such as **18** has been rarely reported. The prevalent use of diamido ligands was found mostly in early transition metal complexes, such as those of Ti, Zr, and Hf.[32] The most representative examples are McConville and Shrock catalysts, **19** and **20** (Figure 1-12), respectively.[33] Subsequent applications of **19** and **20** were exclusively present in olefin polymerization, and none was found in the ROP of cyclic esters.



19

McConville catalyst

Ar = 2,6-diisopropylphenyl



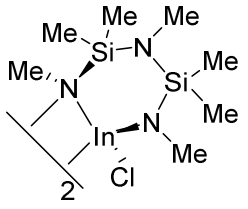
20

Shrock catalyst

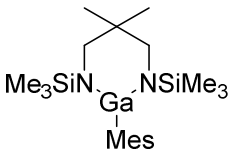
M = Ti, Zr, Hf
E = O, S

Figure 1-12. McConville and Shrock catalysts with diamido ligand.

Some reports on the use of chelating diamido ligands in Group 13 main group metals were apparent mainly in Ga and In chemistry.[34] The (diamido)InCl complex **21** exists as a dimeric species, and the gallium analogue **22** shows a 3-coordinate configuration (Figure 1-13). There has been no application of either complexes reported up to date.



21



22

Mes: mesityl group

Figure 1-13. (Diamido)In and Ga complexes.[34]

As a conclusion, the successful application of the neutral 3-coordinate **18b** (Figure 1-11) in the polymerization of ε-caprolactone highlights the importance of chelating diamido ligands in stabilizing a low-coordinate aluminum complex. This opens a wide field of exploration for preparing catalysts of higher activities.

1.3 Novel Diamine-functionalized Phosphines as Ligands

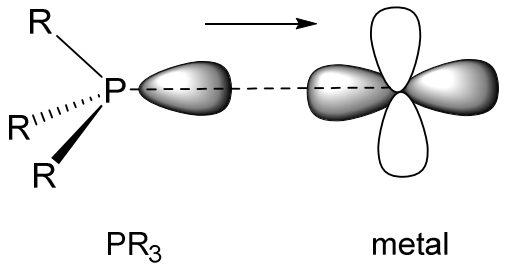
1.3.1 General Considerations of Phosphine Ligands

Tertiary phosphines, PR_3, were brought to the attention of many research groups because by varying R, electronic and steric properties, these compounds can be tuned for desired applications. Therefore, the most studied properties were focused on electronic and steric considerations.

1.3.1.1 Electronic Considerations:

Phosphines as ligands behave like NR_3 as σ-donors by donating the lone pair to a metal (Scheme 1-9). But unlike NR_3, phosphines are also π-acceptors to receive electrons from a filled metal d orbital (Scheme 1-10). The combined donor-acceptor property situates phosphines among the most important ligands in coordination chemistry.

Scheme 1-9. The σ-donating property of phosphine PR_3 to a metal.

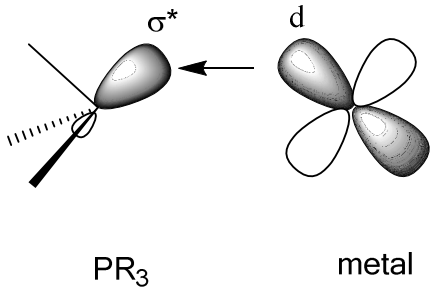


As σ-donors, phosphines donate a lone pair of electrons in an available orbital to the metal. The empty 3d orbitals on P were originally thought responsible as π-acceptor orbitals for back donation of electrons from the metals. Orpen *et al.* in 1985 stated that the important

acceptor orbital of the phosphine is not a pure 3d orbital, but rather a hyibridization of 3d and σ* orbitals on the phosphorus atom.[35] It was not until 1990 that the same research group proposed a revised view of backbonding interaction in M-P complexes, through which the involvement of antibonding orbital σ*, in comprising the π-acceptor orbital on a phosphine, is more likely than that of its 3d orbitals.[36]

Gilheany *et al.* in 1994 further clarified that the participation of phosphorus d orbital in constituting the acceptor orbital can be ruled out based on the high-lying energy of the d orbitals. It is the more accessible P-R σ* orbital that receives electron density from the metal d orbitals (Scheme 1-10).[37] This updated view has since been widely accepted by research groups engaging in phosphine chemistry.

Scheme 1-10. Pi (π) backbonding orbital of phosphines through P-R σ* orbital.[37]



The π-acceptor property separates phosphines from nitrogen ligands because the π-acceptor strength can be tuned by varying the R groups around the phosphorus atom. Usually, more electronegative R groups result in more accessible σ* for backbonding.[37] The combined accepting-donating property is the major contributing factor in the popularity of phosphines for coordination chemistry.

1.3.1.2 Steric Considerations:

In addition to the electronic effects, the steric effect constitutes an important parameter in determining the properties of phosphines. Tolman's parameter θ (theta) is most commonly used to measure the steric bulk of a phosphine. Using a CPK model (space-filling model), Tolman proposed to measure θ from the metal center, located at a distance of 2.28 Å from the phosphorus atom in the appropriate direction, a cone is constructed which embraces all atoms of the substituents on the phosphorus atom (Figure 1-14).[38] The cone angle is particularly useful when the electronic effect of ligands becomes insignificant. Sterically more bulky ligands (larger θ values) result in a higher dissociation rate and produce a less stable complex.[39]

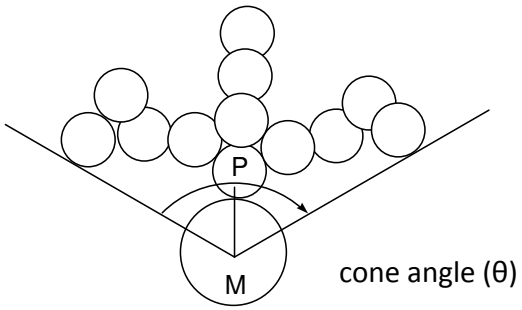


Figure 1-14. Tolman's cone angle, θ.[38]

Also shown by Tolman, more hindered phosphines (with larger R groups) reduce the orbital overlap between M and P atoms due to their steric repulsion effects. This steric effect was demonstrated by the increased dissociation rates (k_d).[40]

Chelating Bidentate Phosphines:

Although Tolman's cone angle has been widely accepted for monodentate ligands, that

for bidentate ligands is less straightforward. In bidentate ligands, the two phosphorus donor atoms are separated by a bridging element and the distance between the two phosphorus atoms is kept at a fixed value (Figure 1-15). The major difference of bidentate phosphines over their monodentate counterparts is that they offer the advantage of the chelate effect, which enhances the stability of the complex. The bite angle, referred to as the chelation angle, is determined more by ligand backbone constraints and less by metal valence angles.[41]

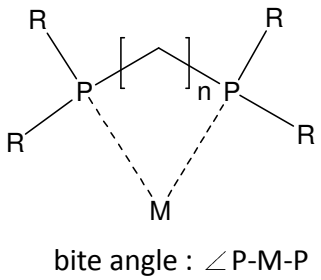
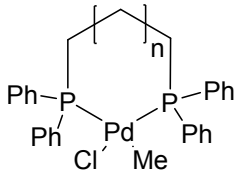


Figure 1-15. Bite angle of a bidentate diphosphine ligand-metal complex.[41]

Parameters such as the number of atoms (n) and chemical entity, whether aliphatic or aromatic, in the linker (Figure 1-15) result in a different ring size, rigidity, and reactivity of the complexes. Usually, larger bite angles, as a result of a greater n value, increase the reactivity of the complex. However, when n becomes greater than optimal, the lone pair on the phosphorus atom lies in a wrong orientation, and the rigidity of the complex decreases.

As in the example of carbonylation of Pt-CH_3 bond in Pt(CH_3)F(CO)(PH_3) complex, with complex **23** (Figure 1-16) as the catalyst, the reaction rate was found to increase in the order **23a** < **23b** = **23c**.[42] This reaction rate increases as the number of carbons in the backbone increases, indicating that the reactivity is proportional to the bite angle of the complex. When carbonylation was performed with **23a** (n = 2, the complex with the smallest bite angle), the rate of reaction

was much slower than that obtained with larger bite angles **23b** (n = 3) and **23c** (n =4). However, complexes **23b** and **23c** in carbonylation have shown similar reaction rates, suggesting that the optimal bite angle occurs when n = 3 in the diphosphine palladium complex **23**. When n > 3, the rigidity of the complex was lost, and the rate of reaction no longer increased.



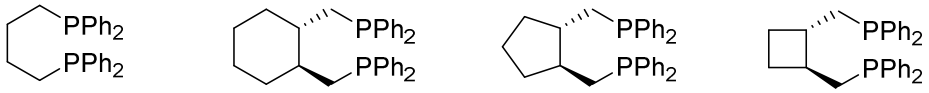
23

23a: n = 2, (dppe)Pd(CH_3)Cl
23b: n = 3, (dppp)Pd(CH_3)Cl
23c: n = 4, (dppb)Pd(CH_3)Cl

Figure 1-16.(Diphosphine)Pd(Me)Cl complex.[42]

Consequently, the bite angle and rigidity of diphosphine metal complexes appears closely related to their performance and selectivity in catalysis. In hydrofomylation of 1-pentene catalyzed by $(PhCN)_2PtCl_2$-$SnCl_2 \cdot 2H_2O$ with $Ph_2P(CH_2)_nPPh_2$ as the ligand, it was found that **24a** (Figure 1-17), n = 4, became particularly effective. When n exceeded four, the reactivity was reduced abruptly, and it gradually vanished. Evidently, the 7-member chelate ring resulted in the optimal P-Pd-P bite angle.[43]

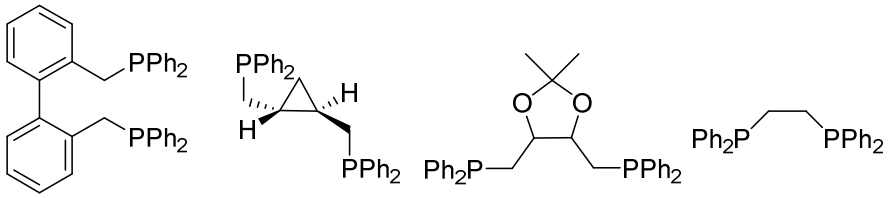
Ligands **24a** through **24d** were made to further evaluate the effect of structural rigidity of different 7-member Pd complexes in the catalysis of hydroformylation reactions. The most strained linker in **24d** produced the most rigid chelate ring with Pd, followed by **24c**, **24b**, and **24a**. As a result, the highest activity was observed with **24d** as the ligand, then followed by **24c**, **24b** and **24a**.[43] This positive proportionality between structural rigidity and reactivity was well demonstrated.



24a **24b** **24c** **24d**

Figure 1-17. Ligands added to $PtCl_2(PhCN)_2$-$SnCl_2 \cdot 2H_2O$ for hydroformylation of 1-pentene.[43]

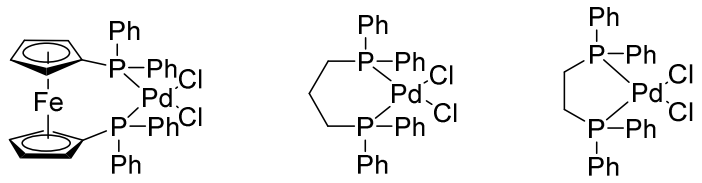
In rhodium-catalyzed hydroformylation of 1-hexene, a bite angle θ (P-Rh-P) of close to 120° in $[Rh(CO)_2H(diphosphine)]$ gave the highest selectivity and reactivity. A trend of decreasing reactivity follows the order when using BISBI, T-BDCP, DIOP, and DIPHOS (Figure 1-18) as the diphosphine ligands. Bite angles formed by the diphosphine ligands with Rh exhibited the same decreasing order as that of the reactivity. Although reactivity is proportional to the bite angle, the chelating character will be lost if the bite angle becomes larger than 120°.[41]



	BISBI	**T-BDCP**	**DIOP**	**DIPHOS**
θ (P-Rh-P)	112.6°	106.6°	102.2°	84.5°

Figure 1-18. Diphosphine ligands with Rh complexes in hydroformylation of 1-hexene.

In palladium catalyzed cross coupling reactions of Grignard reagents with organic halides, $[(dppf)PdCl_2]$ **25** displayed a higher efficiency than $[(dppp)PdCl_2]$ **26** and $[(dppe)PdCl_2]$ **27**, which can be ascribed to its large P-Pd-P bite angle and small Cl-Pd-Cl angle (Figure 1-19).[44]

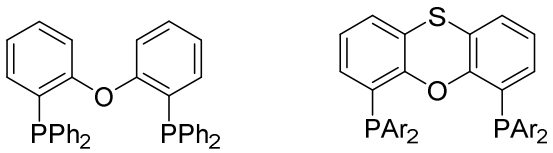


25 **26** **27**

θ (P-Pd-P) 99.07° 90.60° 85.8°

Figure 1-19. Bite angles of various (diphosphine)$PdCl_2$ compounds.[44]

In nickel-catalysed hydrocyanation of terminal alkene and ω-unsaturated fatty acid esters, it was the optimized bite angle that gave the highest selectivity. The order of reactivity and selectivity was found to be reduced as the bite angle (P-Ni-P) in the complex decreased from **30**, **29** to **28** (Figure 1-20) as the ligand.[45]



28 : θ = 105°

29 : Ar = Ph, θ = 113°
30 : Ar = $C_6H_3(CF_3)_2$-3,5, θ = 115°

θ : calculated bite angle of P-Ni-P

Figure 1-20. Calculated bite angles of (diphosphine)[Ni] complexes.[45]

In summary, ring size and structural rigidity play important roles in determining the reactivity of a complex. As evaluated by applying the 6-member complex **26** in C-C coupling reactions, it performed much better than its 5-member analog **27** (Figure 1-19). By keeping the ring size constant for two similar complexes, bite angles were determined by the backbone constraints. The more rigid complexes **30** and **29** resulted in larger bite angles than did the less

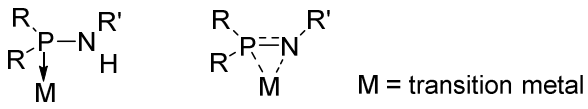
rigid analog **28** (Figure 1-20). Tuning the ring size and rigidity of the backbone in a diphosphine-metal complex shall offer more insight into the structural-reactivity relationship.

1.3.1.3 Bidentate Amidophosphine Ligands

Phosphorus-nitrogen compounds display a wide variety of structural diversity because of their many bonding possibilities. Compounds containing phosphorus-nitrogen (P-N) bonds have received significant attention due to their readily available synthetic preparations.

Compounds containing P-N single bonds have been well established and are called aminophosphines or phosphazanes. One of the stability concerns for species containing P-N bonds is ascribed to nitrogen and phosphorus inversions, resulting in unstable compounds. Moreover, this instability property can be inhibited by π interaction between P and N, as well as by incorporation of steric hindered substituents, R and R' (Figure 1-21), on either or both atoms. The other instability of the P-N compounds arises from the ease of oxidation from P(III) to P(V) oxidation states, accompanied with a change of coordination number around P from 3 to 5. The aminophosphines described herein were presented as P(III) in a three-valent environment.

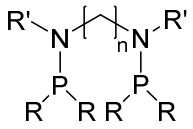
An aminophosphine coordinates to a transition metal in at least two possible modes, through the phosphorus atom **31**, and through both phosphorus and nitrogen atoms **32** (Figure 1-21).[46] The application of bidentate complex **32** is widely studied, whereas that of the monodentate complex **31** remains less thoroughly explored.



31 32

Figure 1-21. Possible coordination modes of an aminophosphine to a transition metal, monodentate **31**, and bidentate **32**.[46]

Coordinating through phosphorus atoms in a bidentate aminophosphine ligand became a great interest for chemists engaging in coordination chemistry because the stronger donating capability of phosphorus can be employed to the best extent. Ligands such as ($NR'PR_2$)-(linker)-($NR'PR_2$) **33** (Figure 1-22) can be prepared from diamines and chlorophosphines in a relatively simple route.

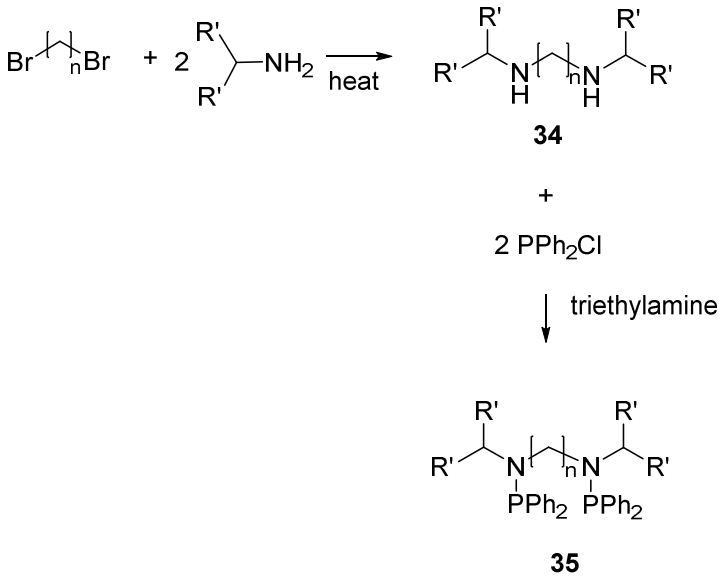


33

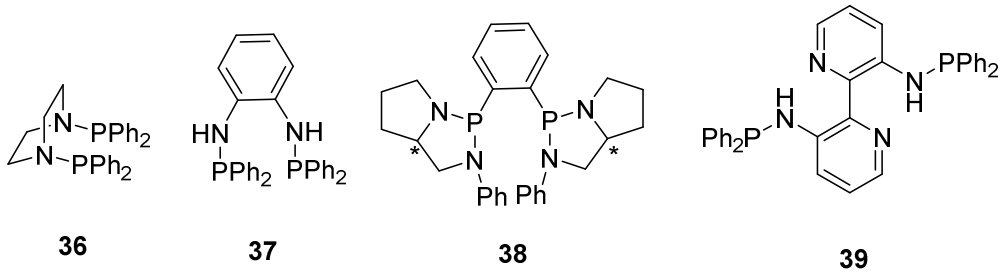
Figure 1-22. Aminophosphine, (R_2PNR')-(linker)-($NR'PR_2$).

The preparation of **35** (Scheme 1-11) represents the general synthetic preparation for most aminophosphines.[47] The diamine precursor **34** was made through Sn2 nucleophilic substitution of the dihaloalkyl (or dihaloaryl) with two equivalents of amine. By reacting with two equivalents of Ph_2PCl (or other halophosphines) in the presence of an appropriate base, such as triethylamine, **35** can be prepared under relatively facile conditions.[47]

Scheme 1-11. A general synthetic route for aminophosphine.[47]



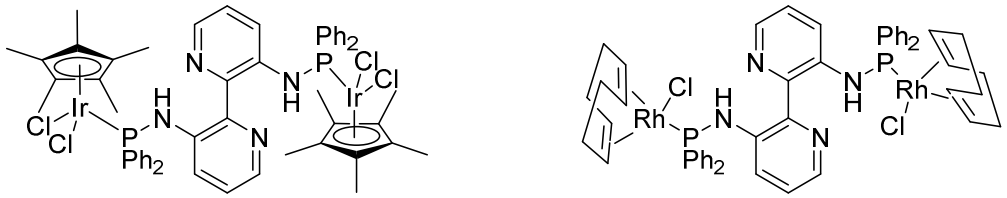
Woollins *et al.* reported the synthesis of piperazine phosphine **36** (Figure 1-23), of which various bidentate complexes can be formed with Ni, Pd, and Pt.[48] With an aromatic linker, the same research group reported the preparation and coordination chemistry of 1,2-diaminophosphine **37**.[49] It was shown that **37** formed a 7-member bidentate chelate with Pd and Mo exclusively through phosphorus donors. Wills *et al.* synthesized ESPHOS **38**, and showed that it was active in asymmetric allylic substitution reactions when it was added *in situ* with palladium pre-catalysts.[50] Although there was no detailed structural elucidation about the complexation of **38** to a metal as a well-defined complex, results of ^{31}P NMR study were consistent with phosphorus being the coordinating element when the ligand was added *in situ* to a Pd source.



36 **37** **38** **39**

Figure 1-23. Representative examples of bidentate aminophosphine ligands, piperazine **36**, 1,2-diaminophonsphine **37**, ESPHOS **38** and pyridinyl aminophosphine **39**.[48-51]

Ligand **39** was synthesized and coordinated to Ir and Rh in order to form **40** and **41** (Figure 1-24) as bridging complexes, and both were active as catalysts in the hydrogenation of ketones.[51] It is worth noting that both complexes utilize phosphorus as the coordinating atom.



40 **41**

Figure 1-24. Diaminophosphine with Ir, **40**, and Rh, **41** complexes.[51]

As concluded from above examples, **36** with an aliphatic linker forms a bidentate complex with Ni, Pd, and Pt, and **37** with an aromatic linker forms a bidentate complex with Pd and Mo. It would be of greater interest to investigate the coordination chemistry of **36** and **37** with early transition metals.

Ligand **38** presents a more interesting structure in that the phosphorus atoms are positioned closer to the linker moiety than the nitrogens. The coordination of **38** to a metal may

result in either a 7-member ring with the nitrogen donors, or a 5-member ring with the phosphorus atoms. In addition, the resulting product could form a bridging complex coordinated through either or both the donor atoms (P and N), or through other coordination modes. The stereogenic centers, marked by * (Figure 1-23), may also have significant effect in the coordination of **38** to metals.

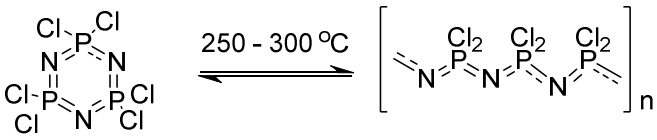
The coordination of **39** (Figure 1-23) is limited to Ir and Rh, resulting in **40** and **41**(Figure 1-24), respectively. Both complexes are bridged by the phosphorus atoms as a dinuclear species. Coordination study of **39** to other transition metals may provide additional insight into other possible coordination modes than those shown by the bridging complexes **40** and **41**.[51] The possibility of **39** to form a bidentate complex with early or first-row transition metals is worth investigating.

Consequently, ligands containing two P-N bonds were being investigated by a few research groups, but the variety of such compounds is limited. Because P and N are both donors, the application of these compounds as a ligand through only the phosphorus atoms is scarce. An opportune research direction for chemists may be exploring to gain insight into the chemistry of bis-aminophosphines in coordination chemistry and in subsequent applications.

1.3.2 *N*-Heterocyclic Phosphines (NHPs) and Phosphenium Cations

Heterocyclic compounds containing both phosphorus and nitrogen atoms have caught the attention of chemists due to their wide structural diversity. Several heterocyclic P-N compounds have found practical applications in inorganic synthesis, in which a classical example would be the synthesis of polyphosphazenes **43** from chlorophazenes **42** (Scheme 1-12).[52]

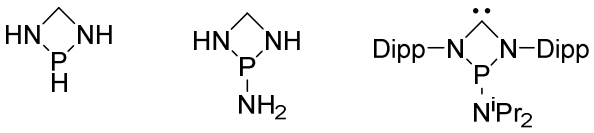
Scheme 1-12. Formation of polyphosphazene **43** from chlorophosphazene **42**.[52]



42 **43**

Structures such as **42**, comprising only P-N bonds, belong to the oldest inorganic framework known. However, the application of compounds similar to **42** is limited to polymerization. Only a little development has occurred to enhance the chemical and physical properties of the resulting polymers by varying the side groups, with means such as replacing Cl with other groups. No application of **42** can be found in coordination chemistry.

The incorporation of carbon(s) into the P-N compounds as an organic backbone may have extended their applications to coordination chemistry. The simplest structures belong to 4-member heterocycles with one carbon between the two nitrogens, as shown in **44**, **45**, and **46** (Figure 1-25).[53]



44 **45** **46**

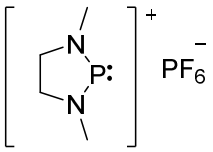
Dipp: 2,6-diisopropylphenyl
^{i}Pr: isopropyl

Figure 1-25. 4-Member ring *N*-heterocyclic compound.[53]

There have not been many practical applications of 4-member heterocycles utilizing P as the donor atom. The simplest structures, **44** and **45**, have found no application in coordination

chemistry.[53a, 53b] Although **46** consists of a phosphorus atom in between the two nitrogens, it is actually an *N*-heterocyclic carbene (NHC) with the carbon as the donor atom.[53c] The effort to confer reactivity to phosphorus atom in a 4-member cyclic compound has been never reported in coordination chemistry up to date.

Expanding the ring size to a five-member heterocyclic species is more interesting and practical because of their relatively uncomplicated synthesis. Phosphenium cation species **47** (Figure 1-26) resembles the popular NHC ligands with the phosphorus in place for the carbene carbon.[54] Despite the fact that NHPs were discovered at least two decades before the emergence of NHCs, NHPs received much less attention in coordination chemistry. Although the donor ability of a phosphorus atom is attenuated by the positive charge in **47**, some π-acceptor character may be increased. This increase of the π-acceptor property perhaps offers effective utility in coordination chemistry prior to catalytic applications.

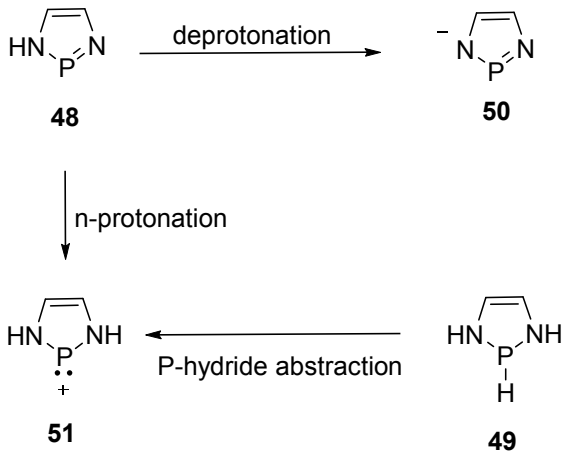


47

Figure 1-26. A *N*-heterocyclic phosphenium cation.[54]

Synthetically, the five-member heterocycles are derivatives of 1,3,2-diazaphosphole **48** (Scheme 1-13).[55] The *N*-heterocyclic phosphenium cation **51** can be prepared by *N*-protonation of **48** or *P*-hydride abstraction of **49**. Deprotonation of **48** results in the anionic species **50**.

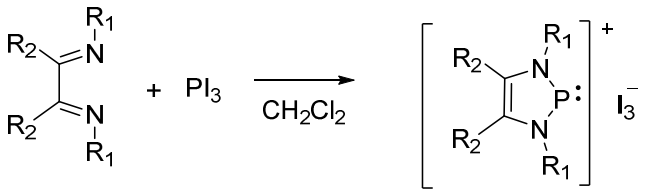
Scheme 1-13. Five-member heterocycles.[55]



48 50 51 49

Compound **52** represents the substituted analogue of **51** and can be prepared by two-electron reduction of α-diimine with trihalophosphine, such as PI_3 (Scheme 1-14).[56]

Scheme 1-14. Synthesis of 5-member NHPs.[56]

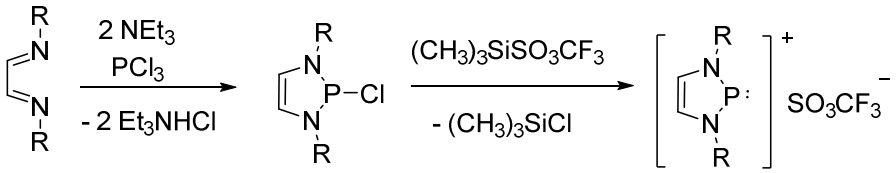


52

R_1 = ^{t}Bu, p-tolyl, Mes, Dipp, Cy
R_2 = H, Me

The precursor **53** leading to the cationic species **54**, an analogue of **52**, can be prepared via a direct base-promoted reaction with PCl_3 (Scheme 1-15).[57] Subsequent abstractions of chloride with a halide scavenger such as $(CH_3)_3SiSO_3CF_3$ (TMS triflate) afford the formation of the desired NHP cationic species **54**.

Scheme 1-15. Synthesis of neutral and cationic NHPs.[57]

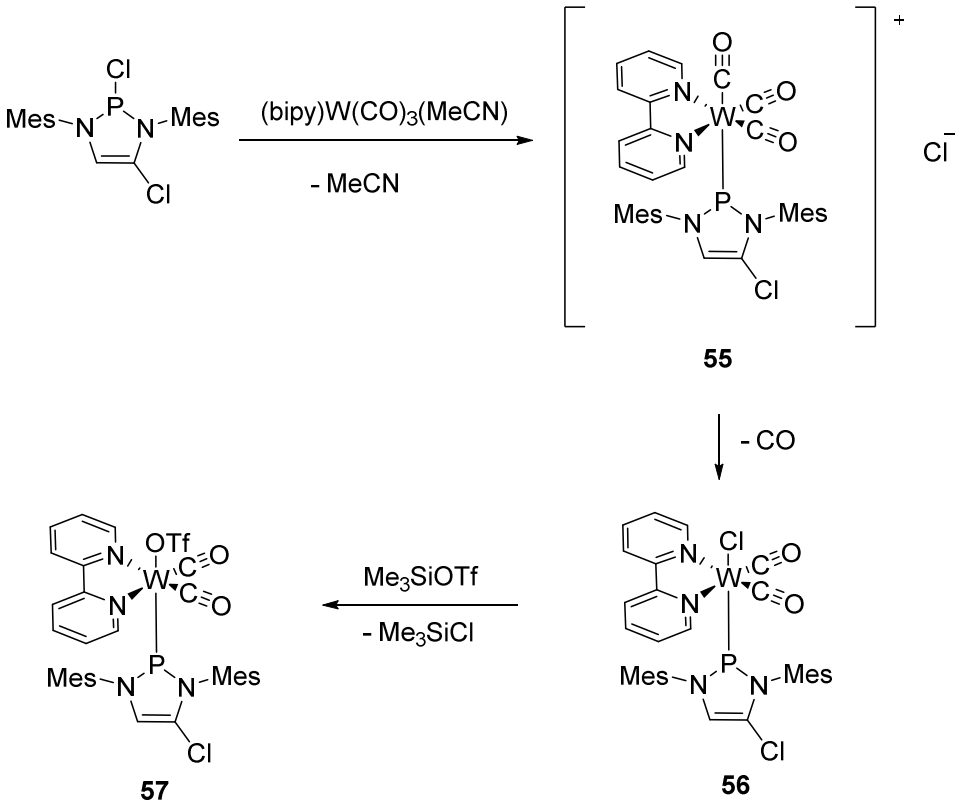


53 **54**

R = alkyl, aryl groups

The early investigation of 5-member neutral phosphines and cationic phosphenium salts was reported as a complex with tungsten by the reaction of [(bipy)W(CO)$_3$(MeCN)] with P-chloro-NHP, producing an unstable cationic complex **55**, which then underwent decarbonylation to give **56** at room temperature (Scheme 1-16).[58] Further reaction of **56** with Me_3SiOTf afforded **57**. The formation of W-P bond in **55** was due to the π-basicity of the metal as well as the π-accepting property of the NHP.

Scheme 1-16. Complexation of NHP with tungsten, cationic **55** and neutral complexes **56** and **57**.[58]



Complexations of NHPs to other transition metals have been also reported, such as NHP-Rh **58**, NHP-Pt **59**, and **60** (Figure 1-27).[59] It is thought that the formation of these complexes was driven by the π-accepting property of the NHPs.[59-60] A successful synthesis of NHPs coordinated to Group 6 transition metals was also reported as stable complex **61** (Figure 1-27).[60-61]

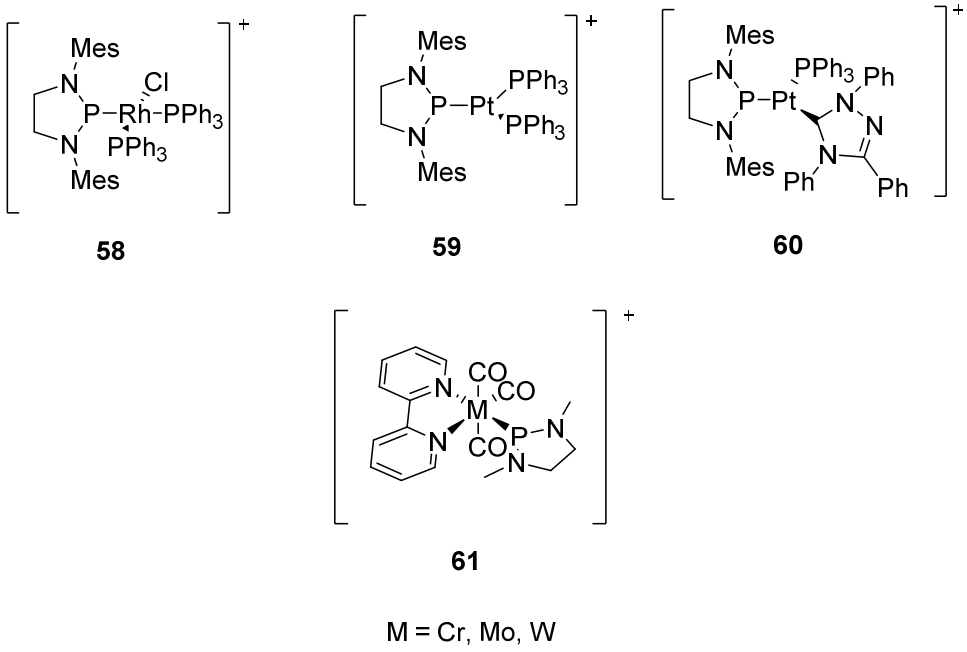
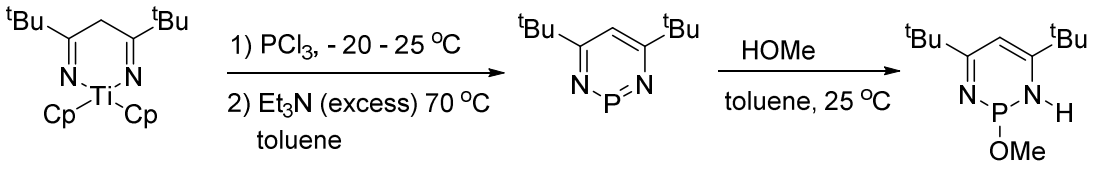


Figure 1-27. NHP-metal complexes.[59-60]

Compared to 4-member NHPs, the 5-member cyclic NHPs exhibited a wider variety of applications in coordination with various metals. If the trend seems to hold, then there is a high potential that 6-member NHPs could also serve as a ligand to form metal complexes.

The synthesis of trivalent NHPs, though, is still limited. One of the routes to forming **64** (Scheme 1-17) started with the very reactive precursor diazaphosphinine **63**, which was prepared with the (diimino)$TiCp_2$ complex **62** (Scheme 1-17).[62] Moreover, **63** can be transiently isolated only with the bulkier *tert*-butyl group as the substituent in 4 and 6 positions. The formation of any cationic species subsequent to **64** has not been reported.

Scheme 1-17. Synthesis of a six-member NHP.[62-63]

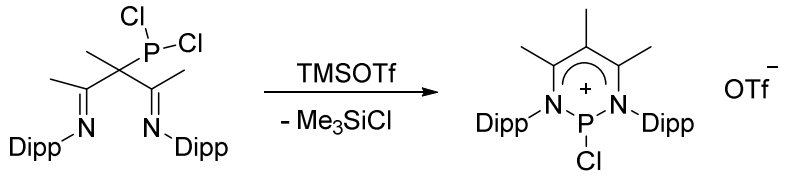


62 **63** **64**

Cp = cyclopentadienyl

Prior attempts at synthesizing 2-coordinate 6-member NHPs in a cationic state have been unsuccessful by using β-diketiminate ligands.[64] The phosphorus containing species **65** treated with TMSOTf (trimethylsilyl triflate) affords the formation of **66**, which is a cationic chlorophosphenium salt supported by a β-diketiminate ligand in a 3-coordinate geometry (Scheme 1-18).

Scheme 1-18. Three-coordinate NHP cationic species **66**.[64]



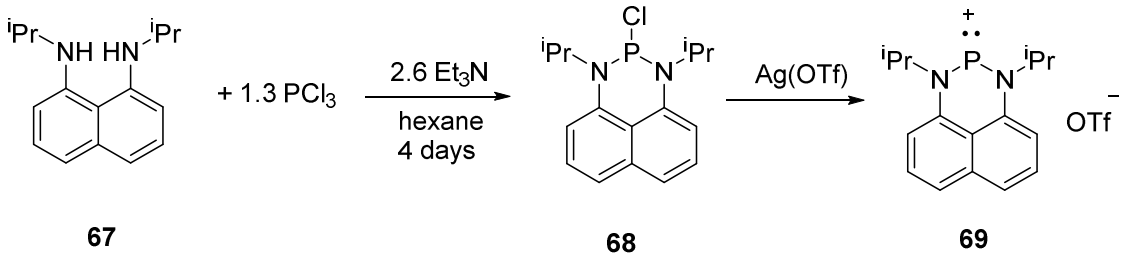
65 **66**

Dipp = 2,6-diisopropylphenyl
TMSOTf = trimethylsilyl triflate

The interest in applying the analogous scaffold of β-diketiminate to form 2-coordinate NHPs still remains. Perhaps diamido ligands, as shown for the 5-member species (Figure 1-27), may provide a better supporting system for the formation of 6-member NHP species in a 3-

coordinate neutral or 2-coordinate cationic form. Employing 1,8-bis(alkylamino)naphthalene ligand **67** (Scheme 1-19), followed by acid abstraction with triethylamine, allows the neutral (diamido)PCl **68** to form, but a longer reaction time of 4 days is required. Removal of the halide with Ag(OTf) results in the formation of **69** as a cationic species in a 2-coordinate gometry.[65] The ability of diamido ligands in supporting the formation of a 3-coordinate neutral NHP and 2-coordinate cationic NHP^+ species was well demonstrated in such experiments. Species **69** was the first NHP^+ to be reported as 2-coordinate supported by a diamido ligand in a 6-member form. No application of **69** in coordinating to metals has been reported.

Scheme 1-19. Synthesis of a six-member 2-coordinate NHP^+, **69**.[65]

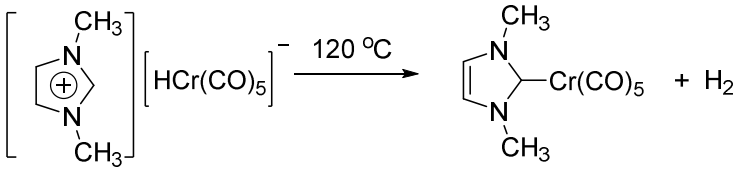


67 **68** **69**

1.4 Tri(*N*-heterocyclic) Carbene Palladium Complexes

The first examples of *N*-heterocyclic carbene (NHC) metal complexes were reported by Öfele and Wanzlick in 1968.[66] Öfele treated the imidazolium salt **70** in the hope of synthesizing a dihydrido chromium complex; instead, the metal carbene complex **71** (Scheme 1-20) was generated as the product. Öfele later characterized **71** and discovered that it was a metal carbene complex.[66a]

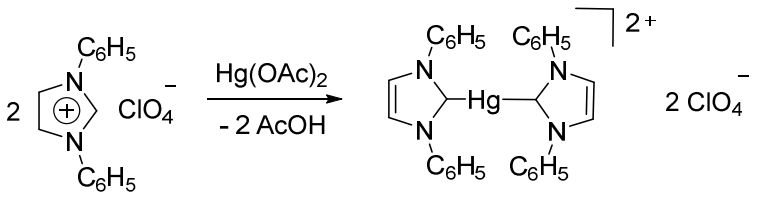
Scheme 1-20. Öfele's (NHC)$Cr(CO)_5$ complex.



70 **71**

A separate group led by Wanzlick developed a different route to synthesize the NHC metal complex **73** (Scheme 1-21) by treating the imidazolium salt **72** with $Hg(OAc)_2$. The synthesis was more facile than that of Öfele, for applying heat or adding base to the reaction became unnecessary. This scenario that avoids the use of heat and base has been adopted by most chemists ever since.

Scheme 1-21. Wanzlick's (diNHC)Hg complex.[66b]



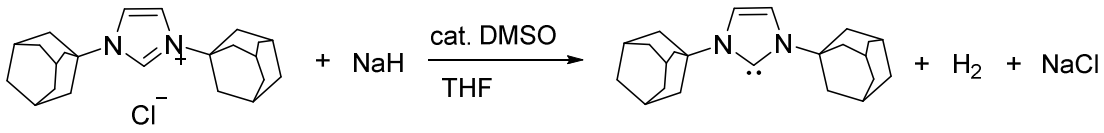
72 **73**

Nevertheless, there has been no literature report regarding the application of **71** and **73**. Therefore, NHCs had not received considerable attention until 1991 when a free NHC was reported by Arduengo *et al*.

1.4.1 *N*-Heterocyclic Carbene (NHC) Ligands

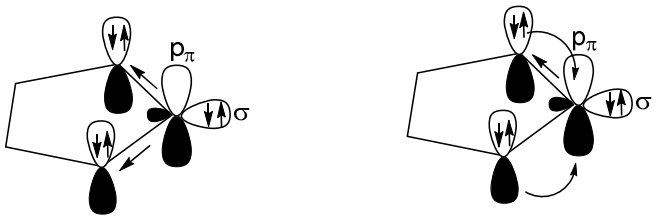
N-heterocyclic carbenes (NHCs) have become the most studied heterocyclic carbenes since Arduengo *et al.* isolated the first isolable free imidazol-2-ylidene **74** (Scheme 1-22) in 1991.[67] The exceptional stability of **74** is provided by both electronic and steric effects.

Scheme 1-22. The first example of free *N*-heterocyclic carbene by Arduengo.[67]



74

In electronic effects, the nitrogens contribute to the stability of carbene **74** in two ways.[68] Mesomeric (resonance) effects (Figure 1-28(b)) given by the donation of the lone pairs on nitrogens to the empty *p*-orbital of the carbene carbon lift the energy of p_π orbital (LUMO). Meanwhile, the nitrogens being more electronegative (inductive) can stabilize and lower the σ-nonbonding orbital (HOMO) (Figure 1-28(a)). As a result, the combination of mesomeric and inductive effects increases the HOMO-LUMO (σ-p_π) energy gap and favors the carbene in a singlet state.[69]



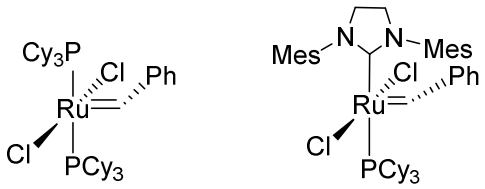
(a) Inductive effect (b) Mesomeric effect

Figure 1-28. Electronic stabilization of NHC.

In parallel to the electronic effects, bulky *N*-substituents (adamantyl groups in **74**) protect the carbene lone pair from self-dimerizing, as well as deterring other side reactions.

Primarily, the steric and electronic effects act to provide **74** with an exceptional stability. As a result, the lone pair on the carbene carbon is available as a donor pair, making NHCs a strong σ-donating ligand.

The property of stronger σ-donating ability of NHCs than phosphines was best demonstrated by Grubbs *et al.*[70] The ruthenium alkylidene complex **75** (Figure 1-29) for olefin metathesis was first prepared with PCy_3 (tricyclohexyl phosphine) in the axial positions, and the complex was referred to as Grubbs first generation catalyst. A dramatic improvement of performance for the metathesis of olefins was obtained with **76**, known as Grubbs second generation catalyst. The increased catalytic activity of **76** relative to **75** was attributed to the replacement of PCy_3 with NHC in one of the axial positions.



75 **76**

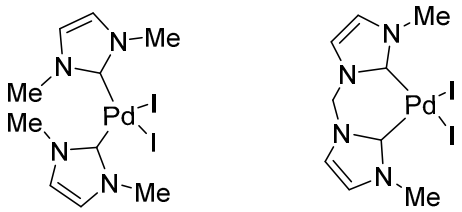
Figure 1-29. Grubbs first and second generation catalysts **75** and **76**, respectively.

Additionally, the superior performance of **76** to **75** in olefin metathesis demonstrated that NHCs proved to be better in stabilizing metal centers than phosphines under catalytic conditions, all features attributed to the stronger σ-donating properties of NHCs. Thereafter, NHC ligands have become the popular substitute for phosphines in palladium chemistry.

1.4.2 Synthesis and Application of Monodentate NHC Palladium Complexes

The application of NHCs as ligands for transition metals has led to significant advances in several important catalytic reactions. In addition to olefin metathesis, Pd-catalyzed coupling reactions are among the most notable applications.

The first application of (NHC)Pd catalyzed coupling reaction was reported by Herrmann *et al.* in 1995.[68] Applying **77** and **78** (Figure 1-30) in the Mizoroki-Heck reaction for the coupling of bromoarenes and n-butylacrylates resulted in a satisfactory activity, in that both catalysts achieved a turnover number of greater than 99 at 130 ^{o}C for 10 hours. This enhanced activity was ascribed to the enrichment of electron density imparted by the strong σ-donating NHC ligands. Thereafter, chemists started extensive studies of applying (NHC)Pd complexes in improving the proficiency of C-C coupling reactions.

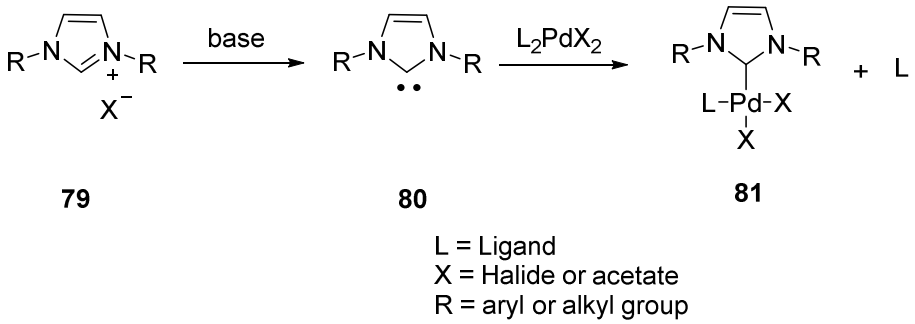


77 **78**

Figure 1-30. First NHC complexes in the Mizoroki-Heck reaction.[68]

In general, the (NHC)Pd complex **81** (Scheme 1-22) can be formed by heating their precursor imidazolium salt **79** with L_2PdX_2 (X = halide or acetate) in the presence of a base. The free NHC **80** can be isolated if the R group is sufficiently bulky to prevent the carbene carbon from self-dimerization or other side reactions.

Scheme 1-22. General scheme for the synthesis of (NHC)Pd complexes.



79 **80** **81**

A number of monodentate (NHC)Pd complexes have been prepared, exhibiting high levels of catalytic activity, as reported by various groups. Some representative complexes active in coupling reactions are shown in Figure 1-31.[71]

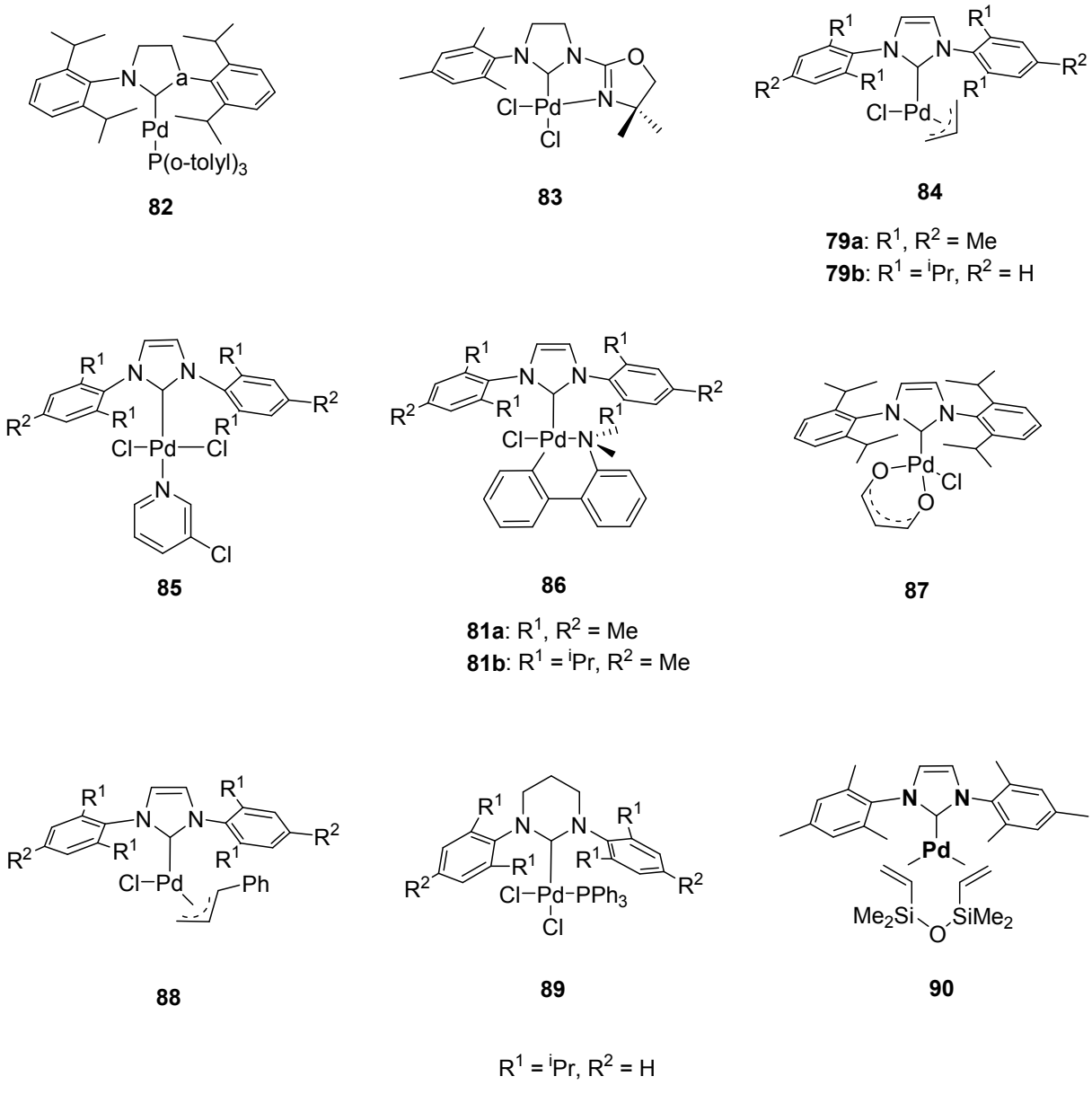


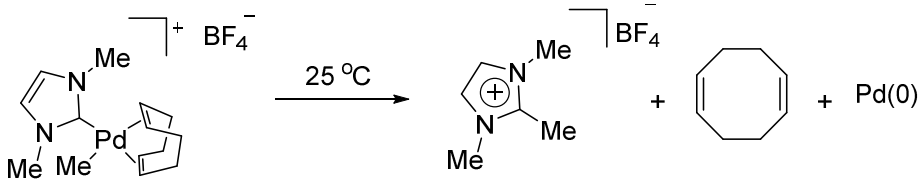
Figure 1-31. Representative examples of monodentate (NHC)Pd complexes.

Complexes **82** – **89** (Figure 1-31) have been proven to be active in C-C and/or C-N coupling reactions. Complex **90** was claimed to be the first (monoNHC)Pd(olefin) complex in which the oxidation state of palladium is Pd(0). It has been also shown that **90** was active in telomerization of 1,3-dienes with alcohols. The common reactivity feature of complexes **82** - **90** has been attributed to the steric environment around Pd. A trend of reactivity versus steric bulk revealed that usually sterically hindered NHCs led to higher activities.[72]

In general, *N*-2,6-diisopropylphenyl (Dipp) NHCs perform better than *N*-2,4,6-trimethylphenyl (mesityl) substituted NHCs. It was demosntrated by Organ *et al.* that an increase in steric bulk close to the metal center can offer advantages in promoting transmetalation, which is viewed as the rate-limiting step for some C-C coupling reactions., e.g. using bulkier Dipp groups instead of mesityl as the *N*-substituent.[72]

Although NHCs confer higher stability to the metal complexes by their strong σ-donating ability than the corresponding phosphines, there are potential decomposition pathways to which NHC complexes are prone. A number of cases have been reported wherein NHC complexes suffer from reductive elimination reactions between NHCs and *cis*-ligands. The first report to identify this stability issue was published in 1998 by Carvell *et al.*[73] The ionic complex **91** was observed to decompose at 25 ^{o}C to **92** through reductive elimination of the cis methyl and NHC. Inactive Pd(0) was isolated as precipitates, and free COD (cyclooctadiene) was observed (Scheme 1-23) as a result of the decompostion reaction.

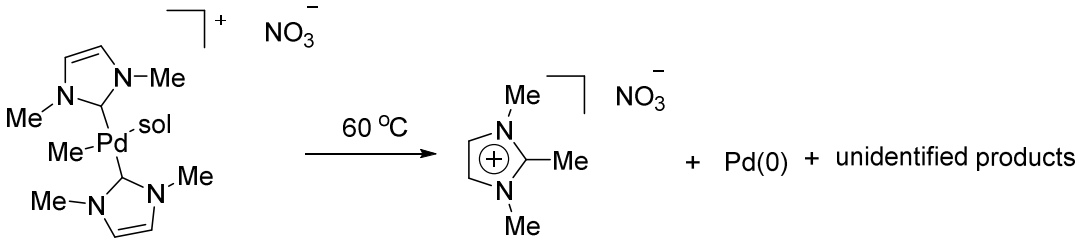
Scheme 1-23. Reductive elimination of (NHC)Pd complex.[73]



91 **92**

To further investigate the effects of NHCs and the stability of their resulting complexes, **93** with two NHCs was synthesized to gain more insight into the decomposition pattern (Scheme 1-24). A decomposition pathway similar to **91** was observed for **93.** The reductive-elimination product **94** and Pd(0) were then isolated from the reaction. Some unidentified organic products were also discovered in the reaction, probably from the second NHC. It was observed that **91** decomposed at a lower temperature than **93**, 25 °C vs 60 °C respectively. Probably, the additional NHC in **93** further stabilizes the complex to a certain extent.

Scheme 1-24. Reductive elimination of (diNHC)Pd complex.[73b]



sol = DMSO

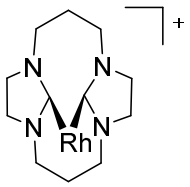
93 **94**

In summary, the breakage of NHC-Pd bond can occur under appropriate conditions. The decomposition study becomes significant because the introduction of an additional NHC increases the stability of (NHC)Pd complexes, as judged by the thermal decompositions of **91** and **93**. In addition, it seems promising that chelating multidentate (NHC)Pd complexes should possess higher stabilities than their monodentate analogues as described.

1.4.3 Synthesis and Application of Chelating diNHC Palladium Complexes.

Metal complexes containing multidentate ligands usually show higher entropic stability as compared to their monodentate analogues; this property is likely due to chelate effects. As seen in the stability difference between **91** and **93**, the higher thermal stability was attributed to the additional NHC incorporated into the complex. Therefore, it will be of great interest to explore the presence or absence of stability improvement when multiple NHCs can be transformed into a multidentate chelating NHC ligand.

The first metal complexes incorporating chelating diNHC ligands were reported by Lappert *et al.* as early as 1980.[74] The Rh(cod)(diNHC) ionic complex **95** (Figure 1-32) was reported to elucidate its structure, but no application of it has yet been presented.

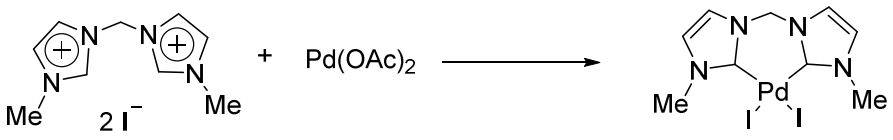


95

Figure 1-32. First example of chelating diNHC and metal complex by Lappert *et al.*,

Complex **78** (Figure 1-30) was the first chelating bidentate (diNHC)Pd complex applied in C-C coupling reactions, specifically the Mizoroki-Heck reaction.[68] The synthesis was relatively simple in that **78** was formed by treating the *bis*-imidazolium salt **96** with $Pd(OAc)_2$ via *in situ* deprotonation (Scheme 1-25).

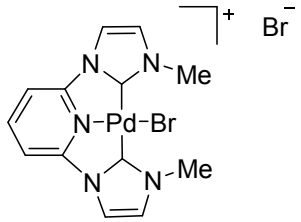
Scheme 1-25. Synthesis of (diNHC)Pd complex through *in situ* deprotonation.



96 OAc = acetate **78**

As shown above, relative to monodentate (NHC)Pd complexes, bidentate (diNHC)Pd complexes are less prone to decomposition because of the higher stability created by chelate effects.[73b, 75] Numerous publications have demonstrated the high thermal stability of (diNHC)Pd complexes. A representative example was shown by Crabtree *et al.*, **97** (Figure 1-33), maintained its activity in the Heck coupling of aryl bromides at 184 ^{o}C in air.[76] The coordination pattern

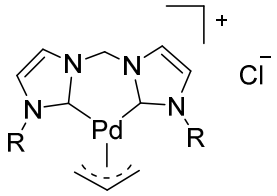
around palladium in **78** and **97** maintains square planar geometry in spite of the different bridging moieties between the two NHC ligands.



97

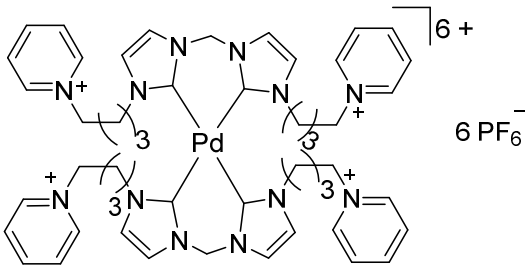
Figure 1-33. A pincer type CNC (diNHC)Pd(II) complex.[76]

Although the synthesis of chelating (diNHC)Pd(II) complexes as demonstrated is relatively simple (Scheme 1-25), their application and synthesis have been under-explored.

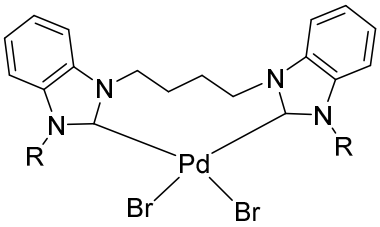


98

R = Methyl, n-Butyl, Mesityl



99



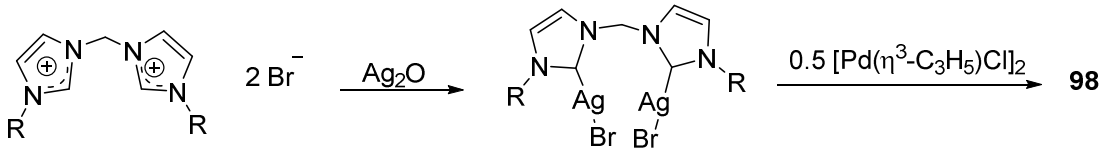
100

R = alkyl, aryl groups

Figure 1-34. Examples of (diNHC)Pd(II) complexes.

Complexes **98**, **99**, and **100** (Figure 1-34) were recently reported in the form of chelating bidentate (diNHC)Pd(II) species. Complex **98** was reported to elucidate an alternative route of forming the complex through transmetalation reactions (Scheme 1-26).[77] As reported by Elsevier *et al.*, the bis-imidalozlium salt **101** can be easily transformed into a silver carbene complex **102**, (diNHC)Ag_2Br_2, and the subsequent transmetalation reaction with palladium sources leading to **98** required no further purification.

Scheme 1-26. Synthesis of (diNHC)Pd complex via transmetalation.



Complex **99** was prepared through the same transmetallation route as **98** adopted, and it was one of the few bidentate (diNHC)Pd(II) complexes proven to be active in an olefination of aryl halides with styrenes.[78] The synthesis of **100** proceeds by *in situ* deprotonation, and it has been shown to be a rare Pd-based catalyst active for direct arylation of benzothiazole and arylbromides.[79]

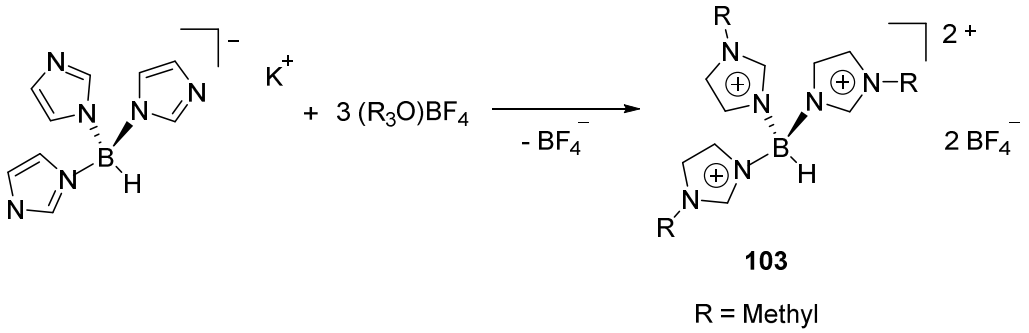
Although only a handful of studies have been focused on the synthesis and application of chelating bidentate (diNHC)Pd(II) complexes, selected examples (as described) presented a high potential of application in catalysis. The coordination environment around Pd maintains square planar as predicted for Pd(II) species.

Finally, it is primarily the chelate effects of the multiple NHCs that result in a higher stability for the bidentate (diNHC)Pd complexes to withstand the harsh conditions during catalytic reactions. The longevity of the Pd catalysts can be extended during catalyses for higher catalytic performance.

1.4.4 Application of triNHC Ligands in the Formation of Metal Complexes.

There have been very few examples concerning the synthesis of triNHC species, and none of them were reported to display a coordination in which all NHCs were bound to a single palladium center in a mononuclear pattern. Fehlhammer *et al.* reported the first triNHC precursor tri-imidazolium salt **103** (Scheme 1-27).[80]

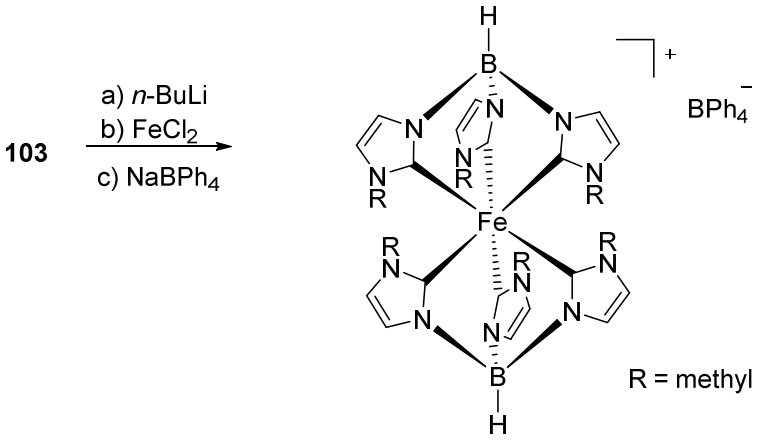
Scheme 1-27. Synthesis of the first triNHC precursor, tri-imidazolium salt.[80]



103

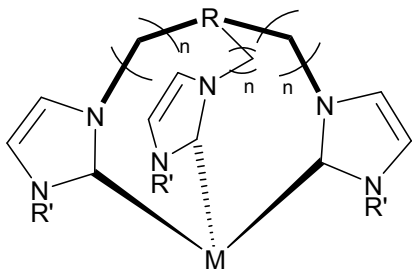
Although **103** was employed to coordinate with iron to form tripodal $[(triNHC)_2Fe(III)]^+$ cationic complex **104** in a pseudo-facial geometry (Scheme 1-28), no attempts have been made to coordinate with palladium sources.

Scheme 1-28. Synthesis of the first triNHC(metal) complex.[80]



104

The developments of triNHC ligands were all focused on building molecules in a tripodal geometry. In addition to the Fe(III) complex **104**, the coordination of triNHC ligand **103** and its derivatives to transition metals (Figure 1-35), such as **105a** for Co and **105b** for Tl, all concluded in a pseudo-facial coordinated complex as reported by Meyer *et al.*[81]



105

105a: R' = 2,6-dimethylphenyl, R = N, M = Co, n = 2
105b: R' = ^{t}Bu, R = C_6Me_3, M = Tl, n = 1

Figure 1-35. Examples of triNHC-metal complexes.[81a]

Whittlesey and Pascu reported the application of tripodal NHC ligands in the formation of trinuclear complexes, **106a**, **106b**, and **106c** with each NHC bound to a different palladium center (Figure 1-36).[82] A preliminary investigation of **106** in the Suzuki reaction was conducted. As a result, **106b** and **106c** were found active for the coupling of aryliodide and arylbromide with phenylboronic acid.

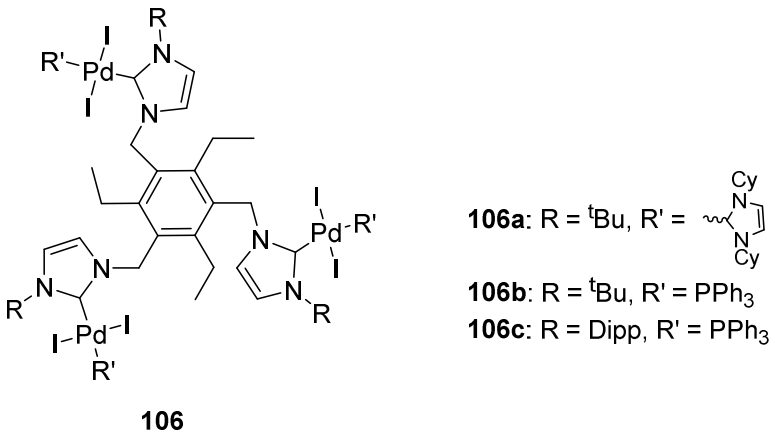


Figure 1-36. (triNHC)Pd_3 complexes.[82]

In summary, transition metal complexes of Fe, Co and Tl incorporating triNHC ligands all display a pseudo-facial coordination mode as demonstrated in **104** and **105**. Subsequent catalytic applications of these mononuclear complexes have not been reported up to date. Complex **106** is a result of a triNHC ligand coordinated to palladium as a trinuclear species in a monodentate pattern. Although the variants of **106**, such as **106b** and **106c**, exhibited a satisfactory result in the Suzuki coupling of aryliodides and arylbromides with phenylboronic acid, 99% yield at 120 ^{o}C for 2 hours, the stability of a multidentate NHC-Pd complex under catalytic conditions was not addressed.

1.5 Research Objectives

The research detailed in this thesis falls under the general heading of rare coordination environments for either transition metal or main group elements, or for the ligands that bind to them and subsequently gain additional insight into coordination chemistry. Catalytic studies are investigated with the resulting species where possible. The three specific objectives are as follows: i) design of neutral 3-coordinate aluminum alkyl complexes incorporating chelating diamido ligands for applications as single-component catalysts in the ROP of cyclic esters, ii) design of 2-coordinate phosphenium cations incorporating diamido ligands for applications in transition metal coordination chemistry and iii) design of chelating tridentate triNHC ligands for applications in group 10 chemistry. The environment around aluminum will be tuned to induce a 3-coordinate environment for higher Lewis acidity, and that for phosphorus will be focused on NHPs with expanded ring sizes. The preparation of a novel (triNHC)Pd(II) complex will strive to discover the possibility of forming the first chelating κ^3–triNHC ligand that can coordinate in a meridional fashion.

i) 3-Coordinate Neutral Aluminum Complexes

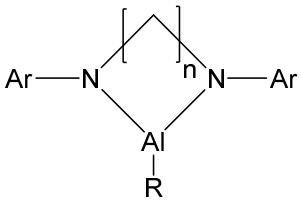
One objective of this thesis focuses on synthesizing highly active aluminum catalysts that meet the criteria of being 3-coordinate, neutral, and single-component for the ROP of cyclic esters. Aluminum species in the ROP of cyclic esters proceed by the commonly accepted coordination-insertion mechanism (Scheme 1-8), and it is the low-coordinate neutral aluminum complex that is best adopted by this mechanism. As demonstrated by Chen *et al.*, the 3-coordinate and single-component Al complex **18** (Figure 1-11) led to a high activity level for the

ring-opening polymerization of ε-caprolactone under facile reaction conditions, such as room temperature and short reaction time.[31] Based on the structure of **18** consisting of a 6-member ring, it would be of great value to gain insight into the synthesis and applications of analogous complexes with varying ring sizes. We hypothesize that (diamido)Al complexes comprising different bite angles (N-Al-N) are fundamental to the investigation of the structure-reactivity relationship. Different bite angles can be obtained by preparing (diamido)Al complexes in different ring sizes.

The strategy to synthesize 3-coordinate aluminum complexes consists of incorporating bulky ligands to inhibit the formation of 4-coordinate or higher configurations about aluminum. Diamido ligands with tunable *N*-substituents and linker lengths offer an obvious ligand of choice for making aluminum complexes of different ring sizes. The chelating and sterically hindered diamido ligands (provided bulky *N*-substituent is incorporated) are expected to overcome the electronic effect that aluminum species tend to be 4-coordinate. A proposed structure **107** (Figure 1-37) is presented, in which the diamido chelating ligand forms a metallacyclic structure with aluminum through the nitrogen donors with a linker that determines the ring size.

In addition, the introduction of an appropriate substituent R to **107** is important for subsequent catalytic applications of the complex. It is expected that a nucleophilic R group can attack the carbonyl carbon of the lactone after coordination of the acyl oxygen to the monomers (Scheme 1-2). Then, subsequent insertions and ring-openings of the monomers into the Al-R bond can proceed in a more facile condition through the effect given by the sterically hindered ligands. It is expected that the polymerization process can proceed at room temperature in shorter reaction times without the addition of initiators provided with a sterically hindered system that

contains a highly Lewis acidic metal center. Moreover, the R group should not only be a nucleophile, but also a leaving group, as the departure of R from Al center should take place under mild conditions. Preparation of a single-component system is imperative in that it provides a single-site catalyst, coordination of one monomer at a time, which minimizes the interference that is commonly seen in a multiple-site coordination system. As a result, it is expected that homogeneous polymer chain lengths can be obtained with a polydispersity index (PDI) close to one.



107

Ar = a bulky aromatic group
R = substituent group
[ ]$_n$ = a linker group, aromatic or aliphatic

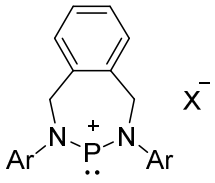
Figure 1-37. Proposed 3-coordinate diamido aluminum complex.

Combining the criteria of being 3-coordinate and single-component, a highly active aluminum catalyst in the ROP of cyclic esters can be anticipated. By varying the linker length in **107**, different ring sizes can be formed in order to study the structural-reactivity relationship of the resulting complexes.

ii) 7-Member *N*-heterocyclic Phosphines

The successful synthesis of 5-member divalent NHPs and their coordination to metals leads to further investigations in exploring NHPs with larger ring sizes. Although the recent efforts in making 6-member divalent NHP^+ cationic species have been successful to some extent, as demonstrated by **69** (Scheme 1-19), there was no further coordination chemistry that followed. Various ring sizes of monodentate NHPs were expected to offer different bite angles (N-P-N) and lead to different reactivity levels in coordination chemistry and catalysis.

My first research objective was to investigate the synthesis of monodentate divalent 7-member heterocycles by utilizing diamidophosphines as the precursors. The rigidity of the molecule was enhanced by using an aromatic backbone, which should provide the molecule with a larger bite angle. Synthetic challenges were expected because there was no precedent literature existed regarding the synthesis of 7-member ring *N*-heterocyclic phosphine compounds. Compound **108** (Figure 1-38) was proposed by applying 1,4-diamido ligands with sterically tunable *N*-substituents (Ar in **108**).



108

Ar = bulky aromatic groups
X = counterion

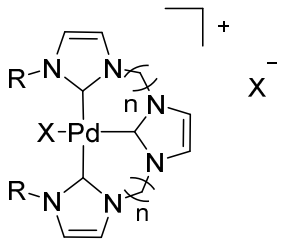
Figure 1-38. Proposed 7-member NHP.

Different Ar groups in **108** were investigated for the effect of steric hindrance in the

preparation of desired species.

iii) Novel Chelating Mononuclear (triNHC)Pd(II) Complexes

To better understand the stability of chelate effects given by triNHC ligands to palladium centers as a mononuclear species, it is of great interest to develop a novel triNHC ligand that can coordinate to palladium in a meridional κ^3-C,C,C mode, thus promoting the formation of a square planar geometry with palladium. A novel (triNHC)Pd(II) complex **109** (Figure 1-39) is proposed.



109

R = alkyl, aryl group
X = halide or acetate

Figure 1-39. Proposed (triNHC)Pd complex.

Although the donor ability of multiple NHCs is expected to stabilize the Pd center to an exceptional extent, the linker lengths (values of n in **109**) remain to be determined for the formation of a square planar geometry. Distortions of molecular geometry may occur if a proper linker length is not provided. Synthetic challenges include the search of appropriate R and X

groups. The chemical entity of R being aryl or alkyl, as well as the steric bulk of R, may require novel synthetic considerations. Furthermore, the X group in **109** is initially proposed to be either a halide or acetate, as these options have been commonly incorporated in cationic palladium complexes. Subsequent investigations into the stability-reactivity relationship of **109** in C-C coupling reactions were carried out.

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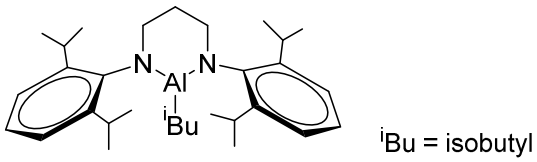
CHAPTER 2. LOW-COORDINATE DIAMIDO ALUMINUM COMPLEXES FOR APPLICATIONS IN LACTONE POLYMERIZATIONS

2.1 Introduction

The first chelating 3-coordinate diamido aluminum alkyl complex **1** (Figure 2-1) reported by Chen *et al.* incorporates a 6-member ring. It was postulated that the stabilizing ability of **1** to retain 3-coordinate geometry is contributed by the 6-member ring which allows for the formation of a relatively large bite angle (N-Al-N). A large bite angle is thought to effectively bring the bulky *N*-groups, such as Dipp (2,6-diisopropylphenyl) in **1**, closer to the metal center and protect the metal center from further reactions, such as dimerizations that most aluminum complexes have been prone to.[31] Nevertheless, **1** remains as the only neutral 3-coordinate diamido aluminum complex that is highly active in the polymerization of ε-caprolactone.



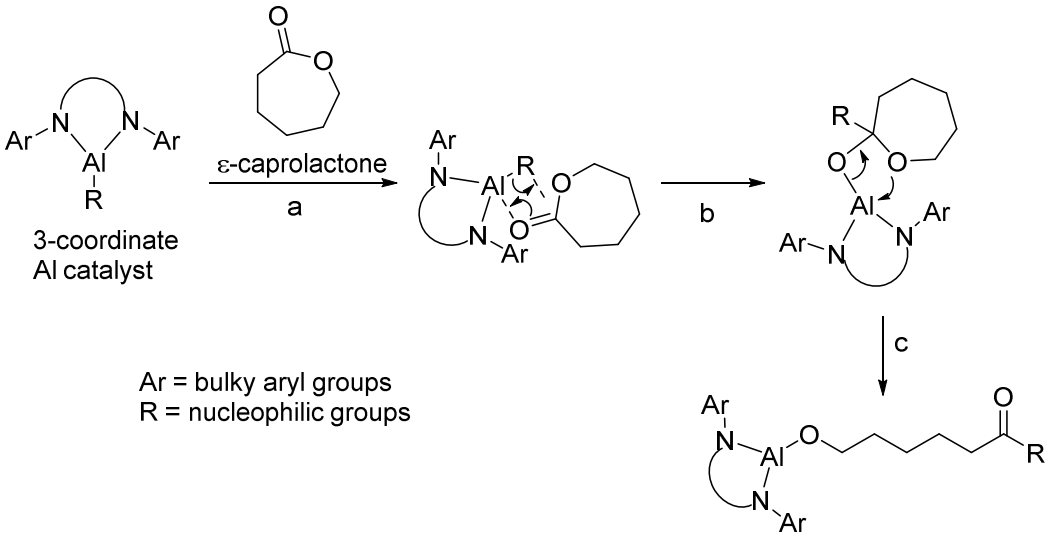
1

Figure 2-1. The first neutral 3-coordinate diamido aluminum complex.[31]

When the ring-opening polymerization (ROP) of ε-caprolactone with **1** was investigated, a high reactivity was found at room temperature in 1.5 hour without any addition of initiators (such as alcohol). It was postulated that aluminum complexes similar to **1** were more Lewis acidic due to their relatively low coordination environment, a 3-coordinate geometry around the metal center. Combined with suitable initiating groups (such as isobutyl in **1**), 3-coordinate

aluminum complexes as single component catalysts were able to permit a high reactivity in the ROP of cyclic esters by promoting a facile coordination between the monomers and the aluminum center via formations of σ-bonds. As generalized in Scheme 2-1, the highly Lewis acidic 3-coordinate Al complex allows for the formation of a coordinated intermediate through a facile coordination process (step a). The intermediate constituted σ-bonds that were formed between the acyl carbon and R group, as well as between the carbonyl oxygen and Al. Then, the σ-bond complex rearranged (step b) and led to the formation of an insertion product (step c), in which the monomer was inserted into Al and R group of the aluminum catalyst (Scheme 2-1).

Scheme 2-1. Proposed coordination-insertion mechanism of ROP of ε-caprolactone.



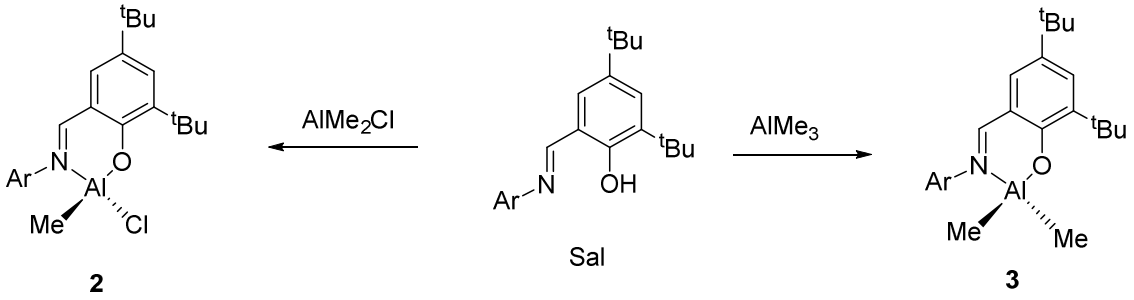
As suggested by the commonly accepted mechanism (Scheme 2-1), a high activity in the ROP of ε-caprolactone is not only attributed to the high Lewis acidity of the 3-coordinate aluminum center but also the nucleophilic group on the metal.[9a, 10, 21] A nucleophilic R group (Scheme 2-1) can coordinate to the carbonyl carbon more easily, thereby encouraging the

subsequent ring-opening (steps b and c in Scheme 2-1) of the cyclic esters.

It was my goal to explore more insights into the synthesis of different neutral aluminum complexes, including 4- and 3-coordinate species. My objectives extended to the investigation of structure-reactivity relationships of the resulting complexes in catalyzing the ROP of cyclic esters. Prior work in the Foley group included the synthesis and catalytic performance of Al complexes with ligands carrying different donor atoms.

Prior study in the group started with the synthesis of 6-member ring Al complexes incorporating salicylaldiminato (sal = 2-[CH═N(2,6-$^{i}Pr_2$-C_6H_3)]-4,6-$^{t}Bu_2$-phenoxide) ligands containing an imino-phenoxy moiety (Scheme 2-2).[83] The resulting complexes **2** and **3** were supported by a nitrogen and an oxygen as the donor elements.

Scheme 2-2. (sal)AlMeCl, **2** and (sal)$AlMe_2$, **3.**

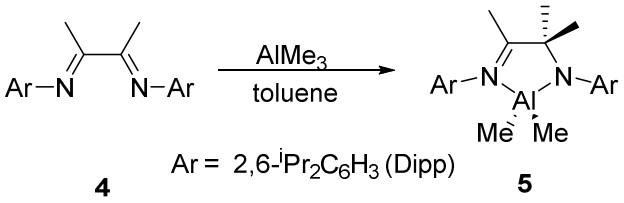


Although complexes **2** and **3** mimic the ring size of **1** (a 3-coordinate, 6-member complex), the environment around aluminum center remains a 4-coordinate geometry.[84] The resulting complexes are mononuclear species.

Synthesis of complexes with reduced ring size was carried out in the prior work of Foley's group. The α-diimine ligand **4** with $AlMe_3$ to form (α-diimine)AlMe as a 5-member

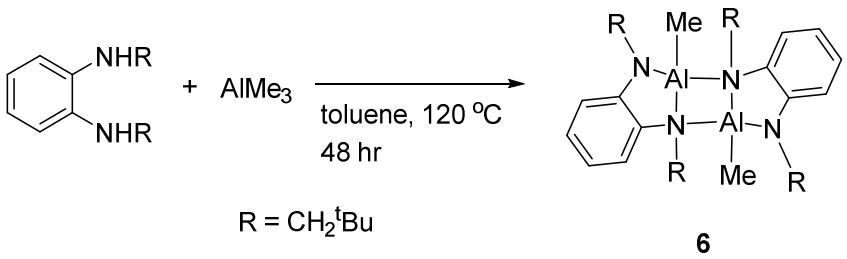
complex was attempted. Nevertheless, a methyl shift from the aluminum center to one of the bridging carbons took place, and the complex (imino-amido)$AlMe_2$ **5** was formed as a result (Scheme 2-3). Complex **5** features two nitrogens as the donor elements and is a 5-member mononuclear Al species in a 4-coordinate geometry.[84]

Scheme 2-3. Synthesis of 5-member (imino-amido)$AlMe_2$.



The reported synthesis of 5-member diamido aluminum complexes has been rare. One representative example was given by Lappert *et al.* (Scheme 2-4).[85] As demonstrated in the synthesis of **6** (Scheme 2-4), although the relatively bulky *N*-substituent ($CH_2{}^tBu$) was employed, a 3-coordinate complex was not obtained. Instead, **6** showed a distinctive 4-coordinate geometry as a dinuclear species.

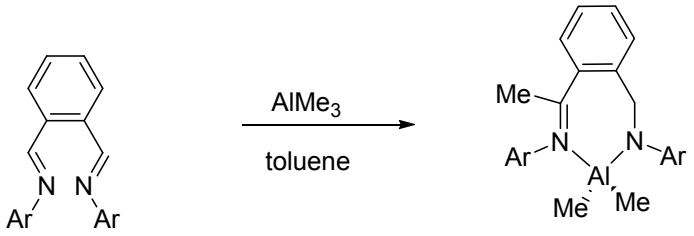
Scheme 2-4. $[(1,2\text{-diamido})AlMe]_2$.[85]



There was no explanation as to why **6** was formed in a 4-coordinate geometry. Despite the relatively large bite angle (N-Al-N = 121.90^{o}), I postulated that a large bite angle must be accompanied with a *N*-substituent R that was bulky to a certain degree so as to inhibit the dimerization reactions and promote the formation of 3-coordinate products. Changing the R groups to a bulkier substituent, such as 2,6-diisopropylphenyl or mesityl, could have protected the Al center from dimerization reactions and maintained the complexes in a 3-coordinate environment.

The combined effect of a wider bite angle (N-Al-N) produced by a larger ring size and a high steric bulk of *N*-substituents allows for the formation of a 3-coordinate diamido-aluminum complex. A high catalytic activity can be obtained through the high Lewis acidity of the resulting 3-coordinate complex. Therefore, ring size effect was brought to my attention for further investigation. Complexes **2** and **3** comprise a 6-member ring moiety and **5** belongs to a 5-member category. It will be of interest if a complex with expanded ring size to 7-member can be prepared for catalytic comparison. The γ-diimine ligand **7** has been employed in coordinating with palladium, cobalt, iron and chromium, but the use of it in aluminum chemistry has not been investigated.[86] Therefore, γ-diimine ligand **7** was employed to prepare a 7-member Al complex, and the synthesis resembled that of **5** in that a methyl shift resulted in a 7-member (imino-amido)$AlMe_2$ complex **8** (Scheme 2-5).[83, 87]

Scheme 2-5. Synthesis of 7-member (imino-amido)$AlMe_2$ complex.



7 **8**

Ar = 2,6-diisopropylphenyl

Catalytic results of **2**, **3**, **5** and **8** in ε-caprolactone polymerization showed the following order, arranged in descending polymerization yield: **5** (96%) > **8** (78%) > **2** (70%) > **3** (63%). Reaction conditions were kept at 60 ^{o}C with 1 equivalent of *tert*-butanol as the initiator.

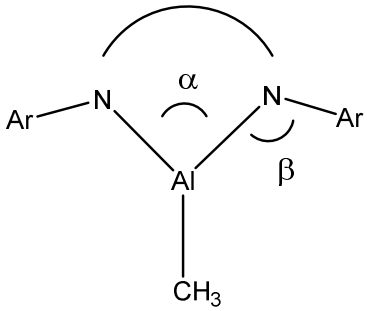
Examining the previous work in Foley's group, the highest reactivity in ROP of ε-caprolactone exhibited by **5** was likely due to the imino-amido ligand that carried two nitrogen donor atoms being superior to **2** and **3**, which incorporated only one nitrogen donor atom. The difference in catalytic performance of **2** and **3** was thought to be insignificant. Conversely, the reason that the 5-member ring complex **5** performed better than the 7-member analog **8** could be twofold. Firstly, the linker that connects the two nitrogen donors in **5** is aliphatic and that in **8** is aromatic, which may have some influence in stabilizing the catalyst. Secondly, the bite angle between N-Al-N in **5** is significantly smaller than that in **8**, and it is possible that neither of them was optimal. Moreover, the difference in ROP reactivity of **5** and **8** is not considered substantial as they must be all subjected to a relatively harsh reaction condition, namely 60 ^{o}C in toluene for at least 12 hours.

As a result of the ROP of ε-caprolactone, complexes **2**, **3**, **5** and **8** all fall into the category of low reactivity compared to our expectation of being highly active under facile reaction

conditions. The reason for the low reactivity of our complexes versus **1** could be mainly attributed to the molecular conformation, in that **1** was constructed based on a 3-coordinate geometry, and that of **2**, **3**, **5** and **8** were 4-coordinate with attenuating Lewis acidity.

Although very few examples, except for Chen's catalyst **1**, have demonstrated the use of chelating diamido ligand to synthesize neutral 3-coordinate Al complexes, it is thought that diamido ligands with bulky *N*-substituents encompass the ability to arrive at that purpose. Following the analogous project design as in the prior work for **2**, **3**, **5** and **8**, further investigation was devised to clarify the effect of varying ring size relative to the activity in ROP reactions for the resulting complexes.

As expressed in the research goals in section **1.5**, the application of diamido ligands in the formation of aluminum complexes was proposed for high activities in the ROP of ε-caprolactone. The ideal complex is depicted as **9** (Figure 2-2). The linker in **9** can be adjusted to accommodate 5- and 7-member ring moieties with varying bite angle α to explore structure-reactivity relationships. As can be seen in Figure 2-2, the β angle between Al-N-Ar decreases as the bite angle α increases. The decreased β angle compresses Ar groups towards the metal center and protects Al from side reactions, such as dimerizations. As well, the bulky *N*-substituent Ar will be chosen to stabilize the metal center from further reactions and help maintain the complex in a 3-coordinate geometry.



9

Figure 2-2. Proposed structure of 3-coordinate, neutral, (diamido)Al complex.

Herein, a detailed synthesis and catalysis of the resulting (diamido)Al complexes in the ROP of lactones is provided.

2.2 Results and Discussion

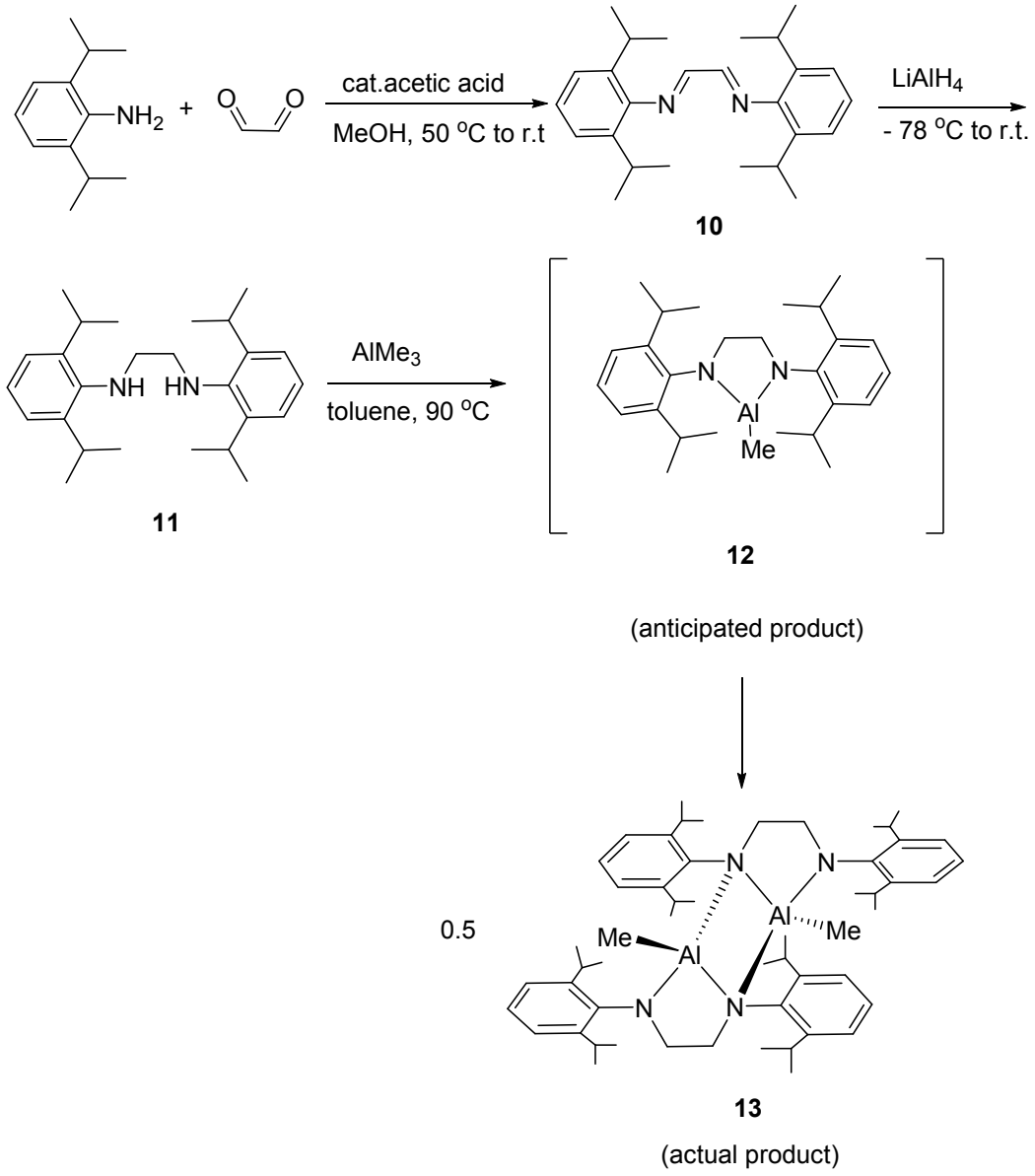
2.2.1 5-Member 1,2-Diamido Aluminum Complexes

To investigate the synthesis and reactivity of 5-member (diamido)Al complexes in the ROP of lactones, I employed the use of a α-diimine for the formation of a (1,2-diamido)AlR (R = alkyl) complex.

The α-diimine **10** was prepared according to a published procedure (Scheme 2-6).[88] The corresponding 2,6-diisopropylaniline was chosen due to its large steric bulk provided by the isopropyl groups for the protection of the aluminum center as the complex formed. In order to transform the 1,2-diimine **10** to its corresponding diamine **11**, a reduction reaction was performed with $LiAlH_4$ as the reducing agent in diethyl ether. The reaction was quenched by the addition of KOH until $Al(OH)_3$ was observed. The mixture was subjected to aqueous extraction with three equal portions of water to remove $Al(OH)_3$, and organic layer was collected. Subsequent filtration and drying of the organic layer afforded **11** as white solids at 83% yield.

The 1,2-diamine **11** was treated with one equivalent of $AlMe_3$ at 90 ^oC in toluene. The progression of the reaction was indicated by the evolution of gas. Upon completion of the reaction after 24 hours, the reaction mixture was subjected to high vacuum until a constant weight was obtained. Compound **13** (anticipated **12**) was obtained as white solid at 90% yield.[88] Complex **13** is different from **6** (Scheme 2-4) in that the linker bridging the two amino nitrogens in the anticipated product **12** (Scheme 2-6) has been changed to an aliphatic ethylene group.

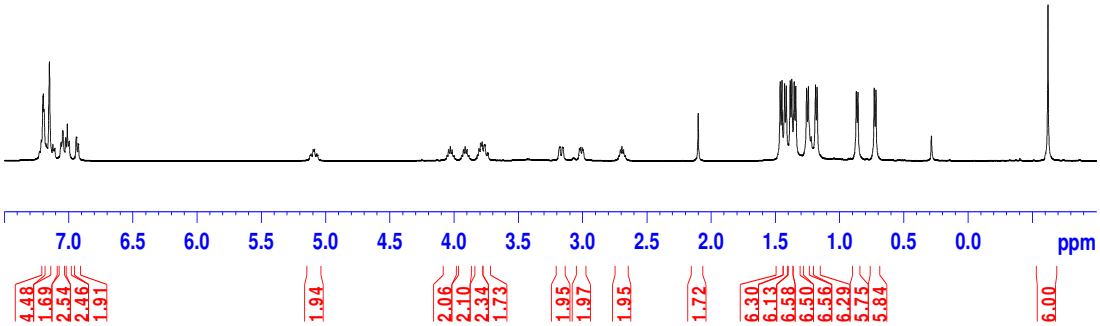
Scheme 2-6. Synthesis scheme of 5-member (1,2-diamido)Al complex.



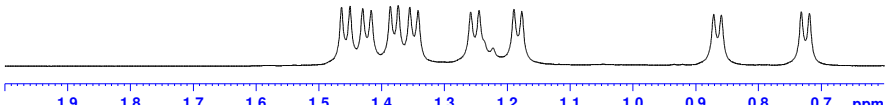
Several attempts were made to crystallize the final product **12**, but it was unsuccessful in obtaining a single crystal suitable for X-ray diffraction. However, ^{1}H NMR results suggested that it was in fact a dinuclear species **13** (Figure 2-3). As evidenced by the ^{1}H NMR spectrum in Figure 2-3(b), the methyl protons appeared as eight doublets, and Figure 2-2(c) showed that

bridging and 3^{o} protons (^{i}Pr) were all in different chemical environment. The NMR spectra is consistent with the C*i* symmetry of **13**. If **12** had been formed in solution, a NMR spectrum consistent with C_{2v} symmetry would be expected, wherein the bridging protons should appear as a singlet signal integrated for four and that for isopropyl methyls should appear as two doublets, each integrated for 12 protons.

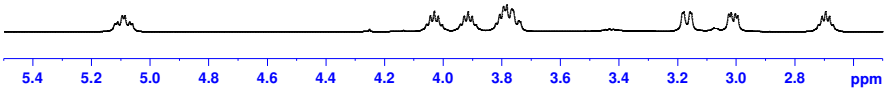
a. ^{1}H NMR spectrum of **13**.

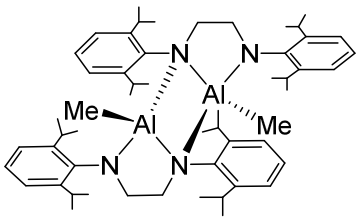


b. ^{i}Pr-methyl protons chemical shifts of **13.**



c. Bridging and 3^{o} proton chemical shifts of **13.**





13

Figure 2-3. ^{1}H NMR spectra of complex **13** in C_6D_6.

As a result of the synthesis, the reason that the formation of 3-coordinate neutral (1,2-diamido)AlMe complex **12** was inhibited was possibly due to the smaller ring size as compared with **1** (Figure 2-1). It is postulated that the bite angle α of a 5-member ring is not large enough to drive the 2,6-diisopropylphenyl groups toward the metal center from further dimerizations. Therefore, the synthesis resulted in the formation of **13** as a dinuclear complex.

Although the expected 3-coordinate species **12** did not form, the resulting product **13** retained the ring size of interest as a 5-member complex. Anticipated effects of higher Lewis acidity provided by a 3-coordinate geometry cannot be assessed, however the effect of a smaller bite angle as a result of a reduced ring size relative to catalytic activities should provide some insights into the ROP activity of lactones.

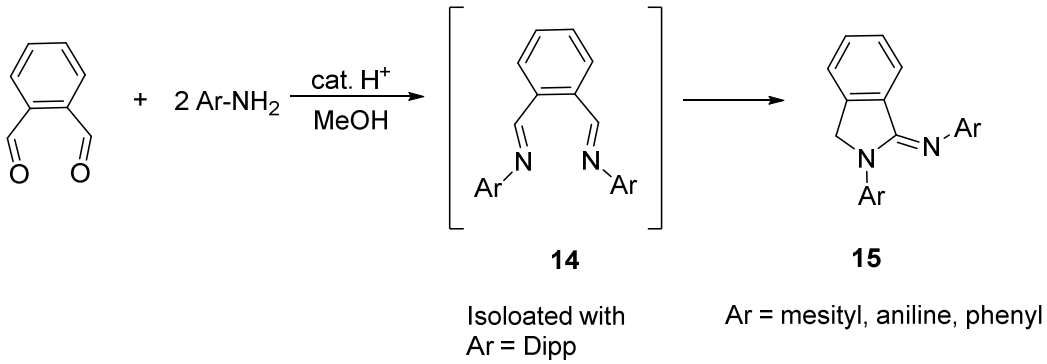
2.2.2 7-Member 1,4-Diamido Aluminum Complexes

It has been shown that the attempt of synthesizing a 3-coordinate neutral Al complex by employing a 1,2-diamido ligand was unsuccessful (Scheme 2-6). It is the 5-member ring not large enough to provide a bite angle α in **13** as does the 6-member ring complex **1**. I postulated that further expansion of the ring size to a 7-member moiety should retain a 3-coordinate geometry as a mononuclear species for the resulting complex. Therefore, a 1,4-diamine (γ-diamine) became the ligand of choice as it should form a 7-member aluminum complex if the synthesis were successful.

There has been no literature precedent regarding the application of 1,4-diamido ligands in aluminum chemistry. The most apparent approach to synthesize γ-diamine is through the reduction of γ-diimine as shown similar to that of **11** from **10** via reduction with $LiAlH_4$ (Scheme 2-6). As evidenced by Foley *et al.*,[7] double condensations of *o*-phthalaldehyde with two

equivalents of substituted aniline was shown to form γ-diimine **14**; however, **14** can only be isolated and characterized with X-ray structure provided Ar being 2,6-diisopropylphenyl (Dipp) group. It was later found that any Ar group with a steric bulk smaller than Dipp was unable to render **14** isolable but led to the formation of iminoisoindolines **15** via subsequent cyclizations (Scheme 2-7).[89]

Scheme 2-7. Condensation of substituted anilines and *o*-phthalaldehyde.[87, 89]

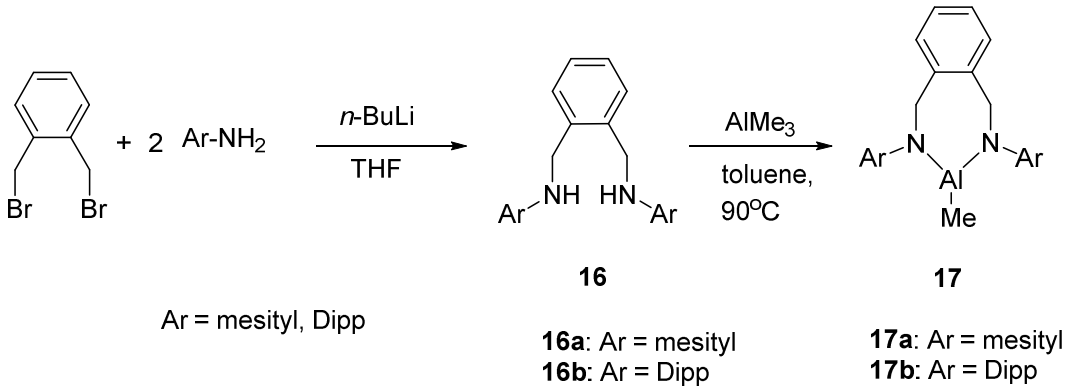


Although the synthesis of the 5-member [(1,2-diamido)AlMe]$_2$ **13** (Scheme 2-6) was successful through diimine route, the same preparation was not applicable to forming the analogous (1,4-diamido)AlMe complex due to cyclization reactions that inevitably followed (Scheme 2-7). Therefore, I proposed another synthetic route (Scheme 2-8) to arrive at the complex of interest **17**. The advantage of using dibromo-*o*-xylene was that the formation of 1,4-diamines (precursors to diamido ligands) **16** avoided the diimine intermediates.

Deprotonations of a substituted aniline were performed by treating two equivalents of substituted aniline with slight excess of n-butyllithium in THF at -78 ^{o}C. A white precipitate was observed upon warming of the solution to room temperature. One equivalent of dibromo-*o*-xylene was added to the reaction mixture, which was stirred for additional 12 hours. The reaction

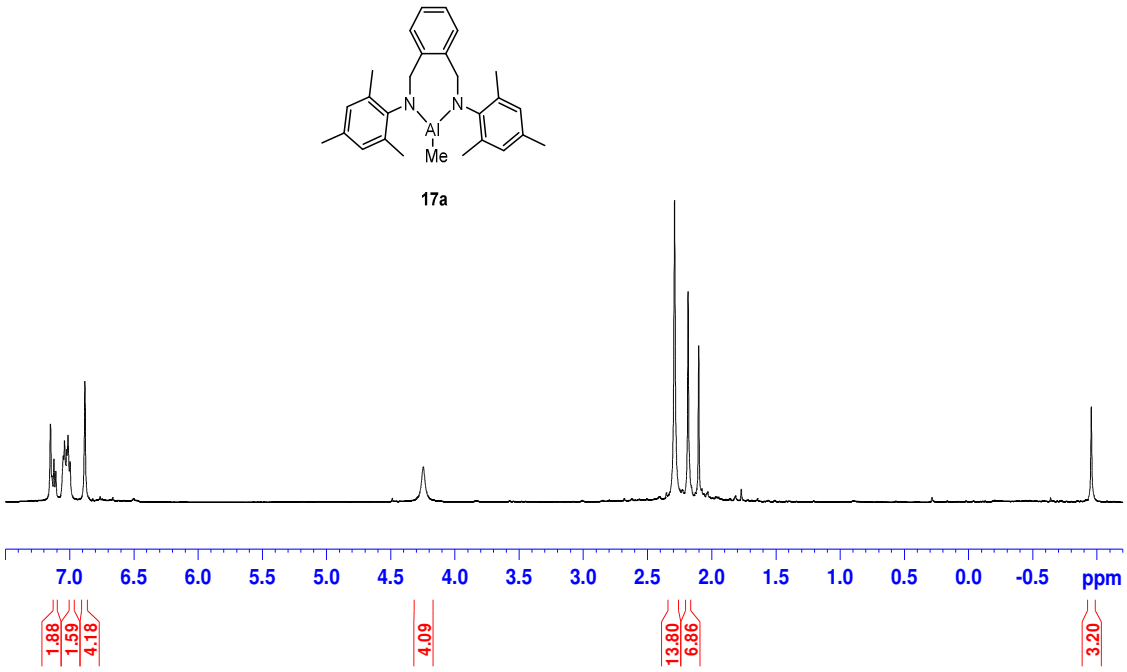
was then quenched with water and the product **16** was obtained by extraction with diethyl ether. After removal of residual solvents under vacuum, white solid product **16a** can be obtained at 86% yield, and **16b** at 74% yield. Subsequent complexations of **16** with trimethylaluminum proceeded by the route similar to that for **13**. Trimethylaluminum was added at 1:1 ratio to **16** in toluene and the evolution of vapors was observed. After stirring at 90 ^{o}C for 12 hours in a sealed container, the reaction mixture was vacuum-dried to afford **17a** at 90% yield, and **17b** at 84% yield.[90] Crystals suitable for X-ray diffraction analysis were obtained from slow recrystallization of **17a** and **17b** from toluene at -20 ^{o}C.

Scheme 2-8. Synthesis of (1,4-diamido)AlMe.



The ^{1}H NMR spectrum of **17a** (Figure 2-4) showed that the methyl protons appear at -0.95 ppm integrating for three protons, whereas the benzylic protons appear at 4.26 ppm as one singlet suggest a C_{2v} symmetry for the molecule. The ^{1}H NMR spectrum **17b** showed the same characteristic signal at 4.32 ppm, which was consistent with a 3-coordinate C_{2v} symmetry complex.

a. ^{1}H NMR spectrum of **17a**



b. ^{1}H NMR spectrum of **17b**

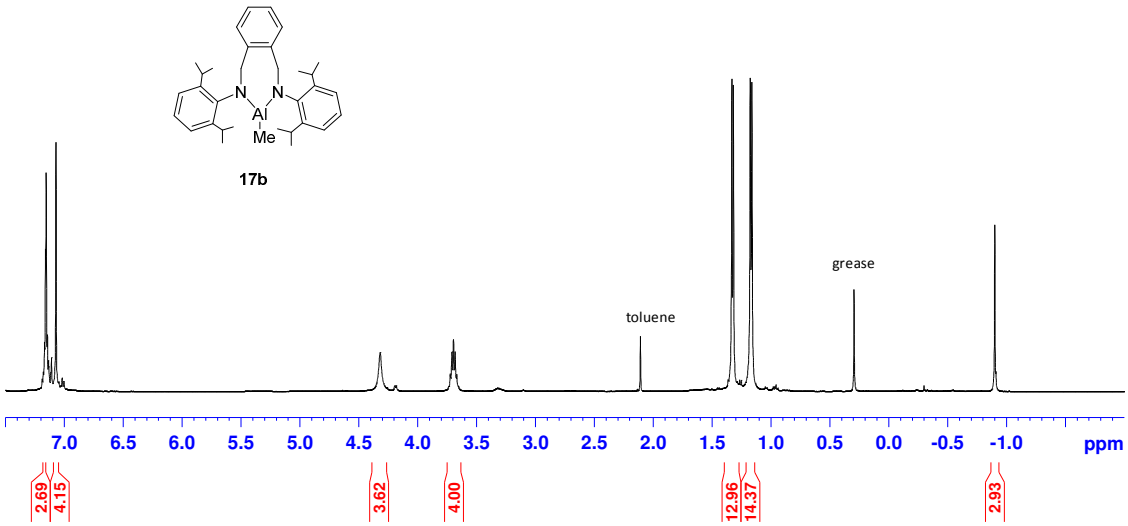


Figure 2-4. ^{1}H NMR spectrum of **17**.

The crystal structure of **17a** (Figure 2-5) assumed a trigonal planar geometry around Al center as determined by the sum of the bond angles to 360°. The bond angle (bite angle) between N(1)-Al(1)-N(2) is 113.58°. The angle between N(1)-Al(1)-C(27) is 120.85° and that for N(2)-Al(1)-C(27) is 125.46°. The bond length between Al-C (methyl) in **17a** is measured 193 pm, which is significantly shorter than 198 pm for non-bridging Al-C bond in $AlMe_3$.[91]

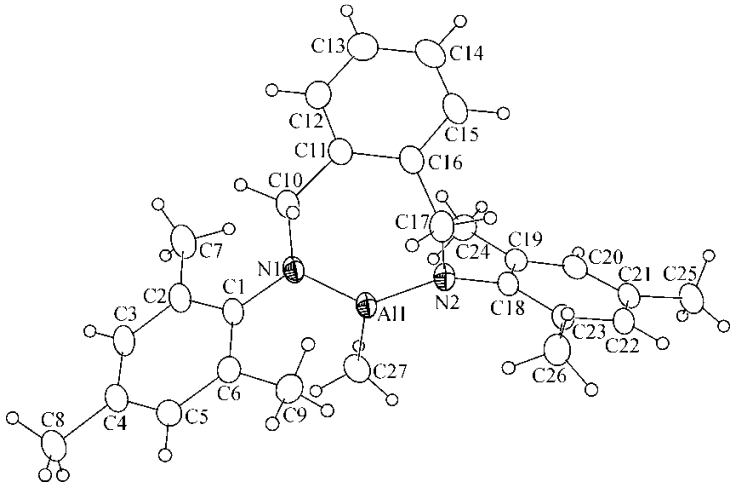
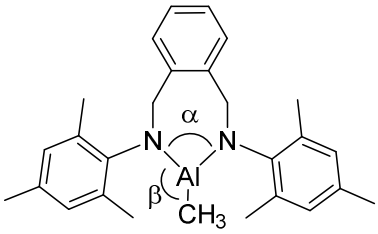


Figure 2-5. Crystal structure of **17a** (1,4-diamido)^{mes}AlMe.

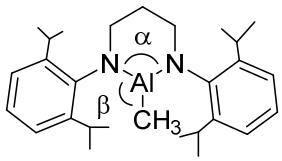
A structure comparison of the 7-member ring **17a** and the 6-member ring analog prepared by Chen[11] is shown in Table 2-1. The α-bond angle of **17a** measures 113.6° and is significantly larger than the value 109.2° as shown in Chen's 6-member ring analog. It is evident that the larger α-bond angle is a result of ring expansion from 6- to 7-member ring. In addition, the bond length of Al-C in **17a** is 191 pm, which is shorter than 193 pm as shown in Chen's catalyst. The longer Al-C bond length in **17a** suggests a weaker bond strength than the 6-member ring analog. As a result, the methyl group is more likely to dissociate from the metal center as a better leaving group in **17a** than that in Chen's catalyst. The combined effect of larger α-bond angle and

weaker Al-C bond is expected to increase the activity of **17a** when applied as a catalyst in PCL reactions.

Table 2-1. Structure comparison of **17a** and Chen's catalyst.[11]



17a



Chen's catalyst

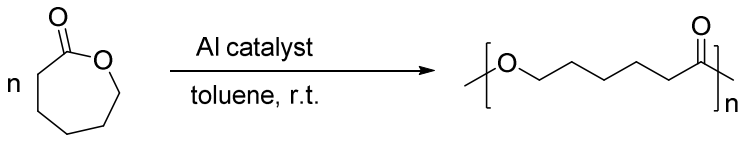
	17a	Chen's catalyst
Al - C bond length (pm)	193	191
α - bond angle	113.6°	109.2°
β - bond angle	120.9°	125.2 °

2.2.3 Application of Aluminum Complexes in the ROP of Lactones

Our research goal was to investigate the structural-reactivity relationship of (diamido)AlR complexes in the ring-opening polymerization of lactones. The most commonly used polylactone material is polycaprolactone, which has been widely used in biomedical applications, such as suture and drug delivery, owing to its biodegradable properties. The reaction condition for the ROP of ε-caprolactone was based on that used for **1** in order to compare the effect in activity with Al complexes of different ring sizes. Therefore, the reaction condition for the polymerization reactions was set at room temperature without addition of any

initiator. The polymerization reactions were carried out in toluene and the completion of reactions was monitored by ^{1}H NMR experiments at different time intervals (Table 2-2).

Table 2-2. ROP results of ε-caprolactone with (diamido)AlR complex.



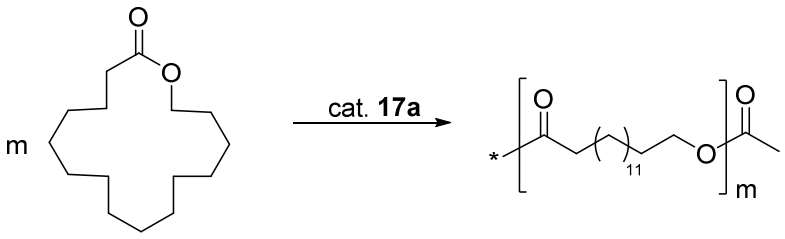
Monomer: cat. ratio	Al catalyst	Reaction time (hour)*	Yield
100:1	**13**	24	0%
	17a	0.50	quantitative
	17b	0.50	quantitative
200:1	**13**	24	0%
	17a	0.50	quantitative
	17b	0.50	quantitative
400:1	**13**	24	0%
	17a	0.75	quantitative
	17b	0.75	quantitative
1000:1	**13**	24	0%
	17a	0.92	quantitative
	17b	0.92	quantitative

*Reaction times were optimized with ^{1}H NMR experiments by taking aliquots of the reaction mixtures at different time intervals.

As a result, the 4-coordinate **13** was inactive under the condition specified (Table 2-2), but **17a** and **17b** completed the polymerization reaction in one hour at quantitative yield with equivalent (n) of ε-caprolactone ranging from 100 to 1000. The inactivity of **13** in the ROP of ε-caprolactone polymerizations was anticipated due to the low Lewis acidity resulted from its 4-coordinate geometry. In contrast, **17** differs from **13** in that the higher steric bulk resulted from its larger ring size (7-member) afforded the formation of a mononuclear 3-coordinate complex. The high activity in the ROP of ε-caprolactone of **17a** and **17b** could be attributed to their high Lewis acidity that allowed for a facile coordination of substrates to the metal complex. The exceptional performance of **17a** and **17b** was thought to possess the potential to catalyze lactones with a larger ring size.

Further investigation into the activity of the promising complex **17** was conducted in the polymerization of ω-pentadecalactone (ω-PDL), which belongs to the macrolactone family constituted of a 16-member ring (Scheme 2-9).

Scheme 2-9. ROP of ω-pentadecalactone.



Consequently, the ROP of ω-PDL has not been successful in following the same conditions that polymerization of ε-caprolactone employed. Further optimization of reaction conditions lead to quantitative yield of polypentadecalactone (PPDL) at 100 ^{o}C in the absence of solvent (neat reaction) for 30 minutes (Table 2-3).

Table 2-3. Polymerization result of ω-pentadecalactone with **17a**.

Monomer: cat.	Reaction Time (mins)	Temperature (°C)	Polymerization Yield (%)	Melting Point (°C)
200:1	30	100	Quantitative	85
100:1	30	100	Quantitative	90
400:1	30	100	Quantitative	90

2.3 Conclusion

The original hypothesis that the structure-reactivity relationship in the ring-opening polymerization of lactones heavily depended on the Lewis acidity of the aluminum center was demonstrated through this research work by two different lactones, ε-caprolactone and ω-pentadecalactone.

Of the first, the 3-coordinate complexes **17a** and **17b** with a 7-member ring moiety presented a superior performance in catalyzing the polymerization of ε-caprolactone to that with the reported 6-member ring complex **1**. Along with the 5-member ring complex **13**, a reasonable comparison can be made to elucidate the difference.

Table 2-4. Reactivity comparison of complexes **13, 1** and **17** in ROP of ε-CL**.**

Cat.	Reaction Time (hour)	Temperature (°C)	Polymerization Yield (%)	Coordination number of catalyst
13	24	r.t.	0	4
1[a]	1.5	r.t.	74	3
17a	0.92	r.t.	Quantitative	3
17b	0.92	r.t.	Quantitative	3

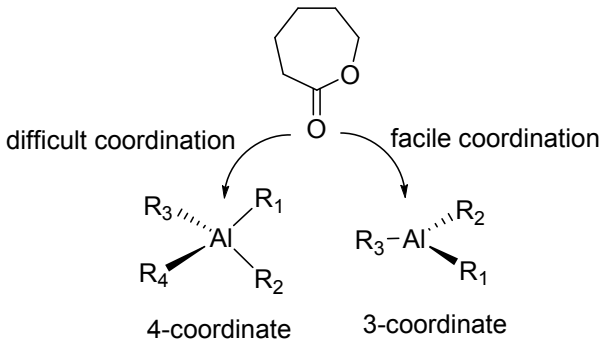
[a] Synthesis and catalysis study conducted by Chen *et al.*[31]

By confining the reaction condition to room temperature in toluene without addition of any initiator, the catalysis result as summarized in Table 2-4 reveals that the catalyst performance first relied on the coordination around the metal center. As can be seen that **13** in a 4-coordinate

geometry show no activity under the reaction condition specified. Complex **1** as reported by Chen *et al.* concluded in 74% of yield in 1.5 hour. The highest activity was displayed by complexes **17a** and **17b** at a quantitative yield in one hour.

It has become apparent that the high Lewis acidity plays a role in increasing the reactivity in the ROP of lactones, as exemplified by the polymerization of ε-caprolactone (Table 2-4). The low-coordinate **1**, **17a** and **17b** with high Lewis acidity resulted in a higher catalytic activity. Complex **13** with a 4-coordinate geometry was unable to provide more accessible sites for monomers to coordinate, therefore the initiation process of the catalysis cannot proceed as facile as those with 3-coordinate geometry. As illustrated in Scheme 2-10, the saturated 4-coordinate Al complex assuming a tetrahedral geometry is unable to offer available coordination sites as in the 3-coordinate complex in a trigonal planar geometry.

Scheme 2-10. Comparison of coordination of ε-caprolactone to 3- and 4-coordinate complexes.



The difference between **1** and **17** is mostly attributed to the ring size of the complexes, 6- and 7-member ring, respectively. A typical bite angle α, as shown in **9** (Figure 2-2), of the 6-member complex **1** is 109.87°, which assumes a trignonal planar geometry (sum of angles to 360.66°). The bite angle α for the 7-member complex **17a** is 113.58°, which is significant larger

than the 6-member complex **1**. However, **17a** also shows a trigonal planar geometry as the sum of all angles around aluminum is 359.89^{o}.

As a result of a larger α angle, β angle between Al-N-Ar (Figure 2-2) will be reduced accordingly and thereby push the bulky Ar groups toward aluminum center so as to protect the metal center from further reactions. Consequently, it is the steric hindrance that warrants the formation of 3-coordinate complexes **1** and **17** despite the use of the same bulky Ar groups. Based on the same analogy, **13** cannot be isolated as a mononuclear 3-coordinate species for the lack of sufficient bite angle due to its relatively small ring size. Therefore, it has been clear that the synthesis of a 3-coordinate (diamido)AlR complex is largely dependent upon both the ring size and the bulkiness of the *N*-substituent groups. In contrast, the superior performance of **17** to **1** in the ROP of ε-caprolactone was not as clear, and there has been little literature precedent to investigate the structure-reactivity relationship of (diamido)AlR complexes in that regard.

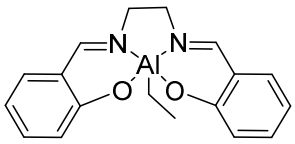
I postulated that it is reasonable that the larger ring size accompanied with a larger α angle further away from tetrahedral geometry ideal for aluminum complexes encourages the departure of the nucleophilic group (^{i}Bu in **1** and Me in **17**) after the coordination of monomers to the acyl oxygen of the catalyst. It is also possible that the bulky environment results in increased ring strain in the monomer upon coordination to Al. However, further investigations into the root cause of the difference in catalytic activity between **1** and **17** will be of great interest for subsequent research.

To advance the application of **17** in ring-opening polymerization of lactones, I was interested in searching for a polymer potentially applicable to our catalyst and more of industry use. The most prevalent polymer in industry has been polyethylene (PE) constituting long aliphatic chains. The polylactone that displays similar physical property to PE is

polypentadecalactone (PPDL) which also consists of long aliphatic chains with added biodegradability. It owes its PE-like properties to the high crystallinity of the methylene units, giving it a melting point around 95 °C and a glass transition temperature (T_g) of -27 °C (LDPE: T_m = 97-117 °C; T_g = -25 °C). PPDL also possesses similar elasticity and ductility to PE, thus PPDL can be considered as a degradable PE mimic. Due to the fact that PPDL has been mainly produced through enzyme catalysis, such as lipase, it will be of great value if one metal-based catalyst could be prepared to perform the same task, even at higher efficientcy.[92] In addition to enzymatic ring-opening polymerization, Kunioka *et al.* reported the use of aluminum triflate and achieved a yield of 49% at 100 ^{o}C in toluene for 6 hours. However, glycerol must be added as the initiator.[93]

Some rare earth metal catalysts have been tested for the formation of PPDL, and a representative example of which was demonstrated by the use of a neodymium alkyl complex, $Nd(O^{i}Pr)_3$. The neodymium complex completed the polymerization at a quantitative yield in 4 hours at 60 ^{o}C and was considered one of the most active systems.[94] Moreover, the relatively inaccessible and pricey nature of rare earth is not as attractive as aluminum-based catalysts.

It was not until 2011 that Duchateau *et al.* reported the first application of ROP of PDL with salen-aluminum complexes.[95] The 5-coordinate salen-aluminum complex **18** as the catalyst was able achieve a quantitative yield of PPDL in one hour at 100 ^{o}C in toluene. Complex **18** represents the only aluminum system that is active in the ROP of macrolactones. However, benzyl alcohol as the initiator must be added to the mixture for the reaction to proceed.



18

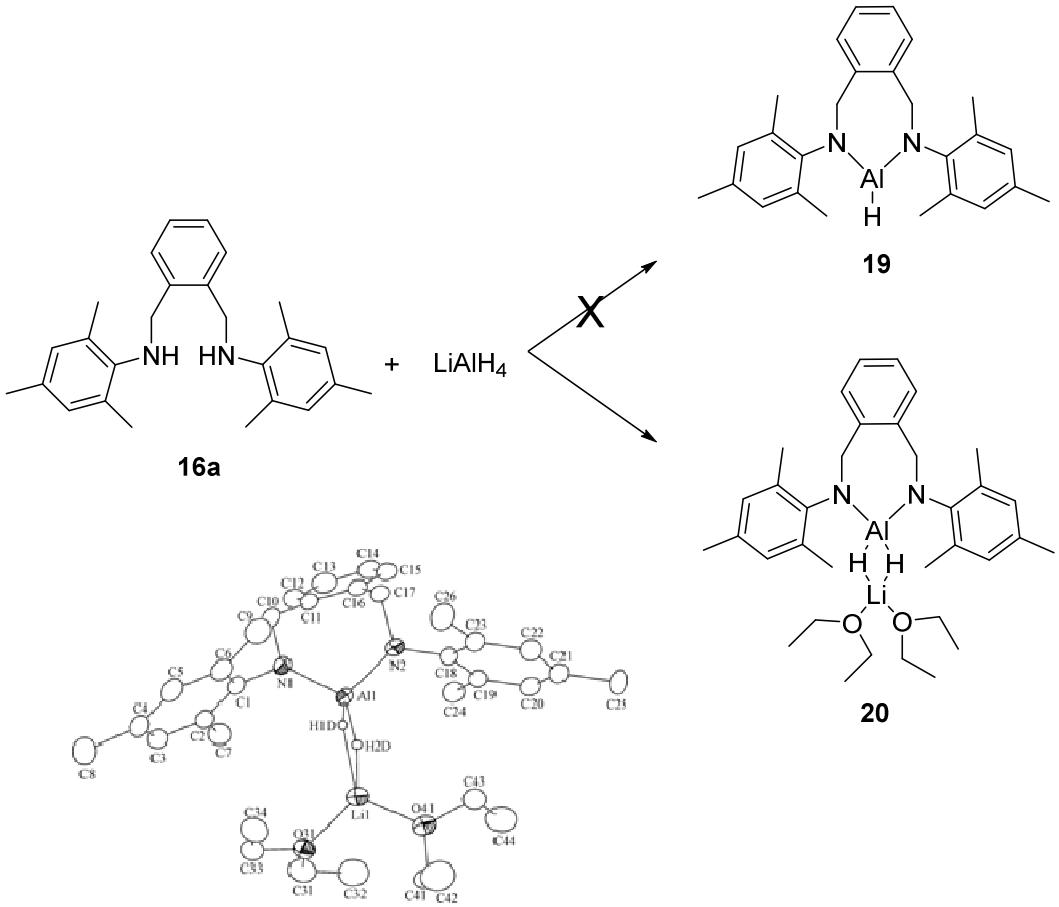
Figure 2-6. The salen-aluminum complex active in the ROP of PDL.

With **17a** as the catalyst, the ROP reaction of polymerization of ω-PDL (Scheme 2-9) initially followed the exact same condition as that for ε-CL, at room temperature in toluene. However, there was no activity found in the preliminary study. It was suggested that it might be the reduced ring strain of a larger ring that was unable to provide a favorable thermodynamic condition to ring open the monomer. Subsequent optimizations of reaction conditions concluded in heating the solid monomer at 100 ^{o}C beyond the melting point of polypentadecalacone (m.p. 90 - 95 ^{o}C) in the presence of **17a**. Careful monitoring of the reaction progress found that 100% product was obtained in 30 minutes. It is worth noting that ROP of ω-PDL was conducted in the absence of solvent, referred to as neat reaction.

It has been evident that the 1,4-diamido moiety was proven a superior ligand system to support the formation of 7-member Al complexes in 3-coordinate geometry. However, it was not clear what role the methyl group (Al-Me) played in maintaining the 3-coordinate geometry as well as in forming the desired coordination. To further clarify this point, I devised an alternative synthesis by employing the same diamido ligand to prepare a hydride (H) substituted variant **19**. A hydride group has been considered sharing similar properties with methyl, but having a smaller size. The synthesis was attempted (Scheme 2-11) by treating equimolar of **16a** and $LiAlH_4/Et_2O$ solution in diethyl ether (Et_2O) at room temperature. The progression of the reaction can be observed by the generation of H_2 gas upon the addition of $LiAlH_4$ to the mixture.

Consequently, the desired product **19** was not formed after removal of solvent; instead, **20** was concluded as the final product. Although **20** comprised a 7-member ring moiety, the coordination environment was the commonly seen 4-coordinate geometry for aluminum complexes. It is clear that the R substituent in (1,4-diamido)AlR species with a size less than a methyl is not able to sustain the 3-coordinate geometry.

Scheme 2-11. Synthesis of (1,4-diamido)^{Mes}Al(μ-H)$_2$Li(Et$_2$O)$_2$.



crystal structure of **20**

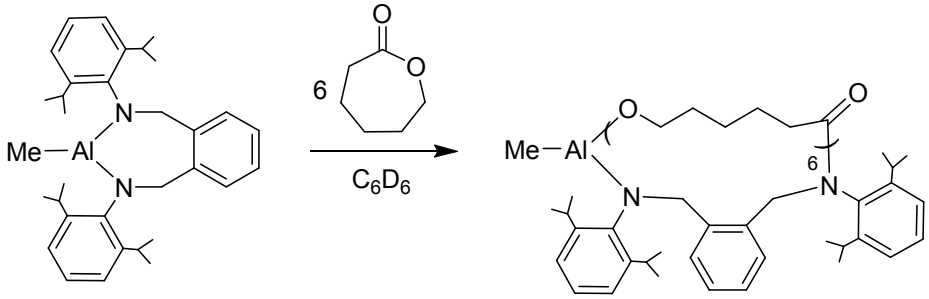
The crystal structure of **20** revealed that the coordination environment around Al assumed

a tetrahedral geometry. Although the coordination pattern of **20** was not up to the expectation as a more Lewis acidic 3-coordinate environment, the role of hydride (Al-H) in catalysis is worth exploring.

The catalytic performance of **20** for the ROP of ε-caprolactone was tested under the identical condition that **17a** was subjected to. It was found no product yield and complex **20** was proven inactive under the conditions specified. The inactivity of [(1,2-diamido)^{Dipp}Al(μ-Me)]$_2$ **13** and [(1,4-diamido)^{Mes}Al(μ-H)$_2$ · Li(Et$_2$O)$_2$] **20** in the ROP of ε-caprolactone suggests that the coordination environment around Al center plays an important role in the ROP of ε-caprolactones. This is consistent with my results (Table 2-2) that the high Lewis acidity resulted from a 3-coordinate complex is the contributing factor leading to high catalytic activities.

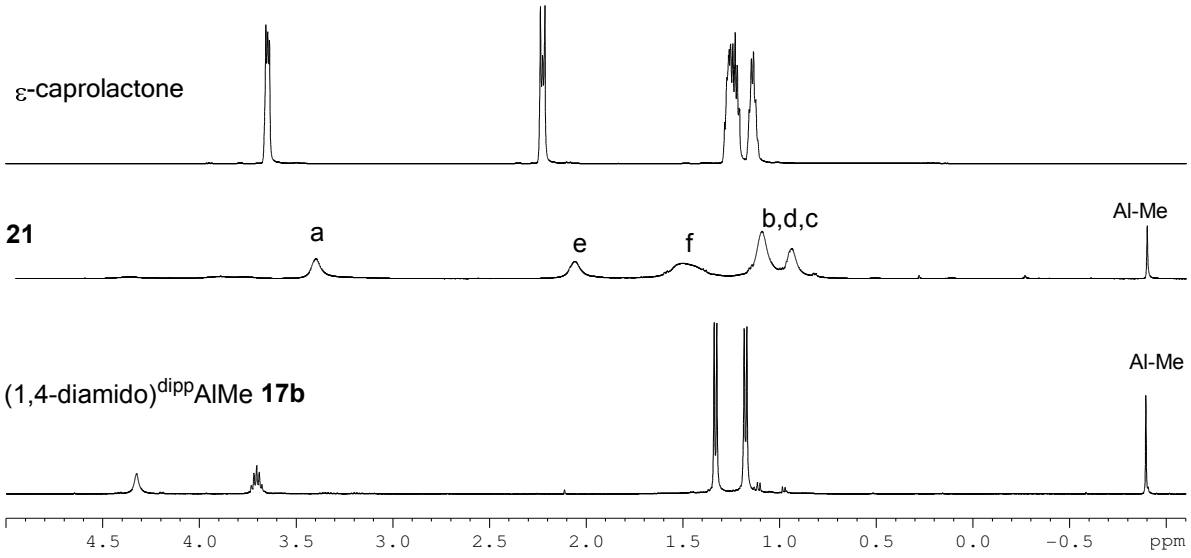
To gain more mechanistic insights into the ROP of ε-caprolactone with the 3-coordinate complexes, **17b** was treated with ε-caprolactone at 1:6 molar ratio in C_6D_6 (Scheme 2-12). According to the resulting ^{1}H NMR spectra (Figure 2-7), the product was concluded as **21** from the reaction.

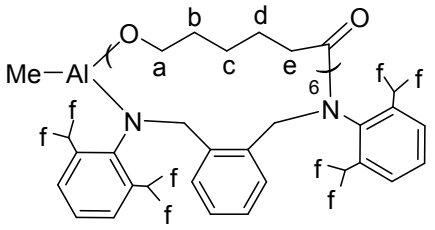
Scheme 2-12. Reaction of **17b** with 6 equivalents of ε-caprolactone in C_6D_6.



17b **21**

From the resulting ^{1}H NMR spectrum (Figure 2-7) of **17b** and ε-caprolactone, it was found that the methyl group still attached to aluminum (Al-Me) as evidenced by its chemical shift at -0.9 ppm. In addition, the isopropyl methyl groups that are two distinct doublets in the NMR spectrum of **17b** have merged to a broad singlet in the NMR spectrum of the oligomer, which suggests that the structure of **21** is as shown in Scheme 2-12. This result is interesting in that the insertion of ε-caprolactone actually takes place into Al-N bond instead of Al-Me bond that I originally hypothesized based on the proposed mechanism in Scheme 2-1. Although the reasons for this unexpected insertion mechanism were still unclear, it was reasonable that the methyl group in **17b** was not a good leaving group due to the stronger Al-C bond, as evidenced by its shorter bond length than free Al-C bonds.





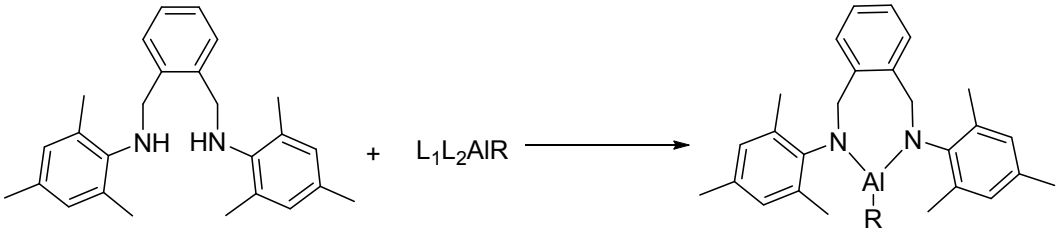
21

Figure 2-7. ^{1}H NMR spectra of **21** (in C_6D_6).

To drive the insertion mechanism of the 3-coordinate complex **17** in the ROP of ε-caprolactone toward the proposed pattern in Scheme 2-1, wherein the R group in Al-R was the nucleophilic group, it was necessary to devise syntheses that led to the formation of (1,4-diamido)AlR, with R being halides or alkoxyides. A preliminary screening of Al sources to react with the 1,4-diamine **16a** did not afford any product of interest, such as **22a** ~ **22c**. The reaction of **16a** with Me_2AlCl, targeted for **22a** yielded only the starting material. Reactions of **16a** with $AlCl_3$ for **22b**, either in the presence of a strong base (n-BuLi or t-BuLi) or not, showed no

product yield. The same results were obtained in treating **16a** with $Al(OiPr)_3$ for **22c**. Future explorations to synthesize **22** with other strategies are deemed necessary.

Scheme 2-13. Attempted synthesis of (1,4-diamido)AlR, R = Cl, O^{i}Pr.



16a **22**

22a: $L_1 = L_2$ = Me, R = Cl
22b: $L_1 = L_2 = R$ = Cl
22c: $L_1 = L_2 = R = O^iPr$

In summary, the 1,4-diamido ligand system was shown to be successful in the preparation of 3-coordinate neutral aluminum complexes. The ligand system allows for a simple manipulation of the steric bulk by tuning the *N*-substituents and of the chelate angle by varying the ring size. Aside from the 4-coordinate geometry that most aluminum complexes assume, the diamido ligand system has been proven to be a superior supporting ligand to afford a relatively rare 3-coordinate aluminum species under facile reaction conditions. Catalytic studies revealed that it was the high Lewis acidity of the metal center that leads to the highest catalytic activity. As shown in this study, the 3-coordinate aluminum complex **17** in the ROP of ε-caprolactone was concluded in the highest reactivity ever reported for Al complexes. The exceptional performance of **17** can be attributed to its large bite angle as compared to the reported complex **1**. Evidently, the bite angle of aluminum species is one of the critical factors that dictates the catalytic performance. In addition to the rare coordination environment about the metal center, in search

of an optimal bite angle of a diamido aluminum complex has become the determining parameter in designing a highly active catalyst in ROP of lactones.

2.4 Experimental

General Information. Unless otherwise stated, all reactions were performed under N_2 or vacuum using standard Schlenk techniques or in a N_2-filled drybox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated oil or sand baths. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.24) and C_6D_6 (^1H: δ 7.16; ^{13}C: δ 128.06). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR data was collected by Diffuse Reflectance Spectroscopy. Reagents such as 2,6-diisopropylaniline (Dipp-NH_2), 2,4,6-trimethylaniline (mesityl-NH_2), lithium aluminum hydride ($LiAlH_4$) and trimethylaluminum ($AlMe_3$) were purchased from Sigma-Aldrich Chemical Company and used as received except for 2,6-diisopropylaniline which was distilled prior to use. Compounds **10**, **11** and **16** were prepared according to a published procedure with minor modifications.[88, 96] Polymerization monomers ε-caprolactone and ω-pentadecalactone were purchased from Sigma-Aldrich Chemical Company, wherein ε-caprolactone was purified with a reduced pressure distillation under nitrogen before use and ω-pentadecalactone was used as received.

Polymerization of ε-caprolactone

Polymerization reactions were carried out in an nitrogen-filled glovebox and the reaction vessel was an ACE pressure reaction tube containing a stir bar. In a typical experiment, **17a** (10.0 mg, 23.8 μmol) or **17b** (12.0 mg, 23.8 μmol) was dissolved in 3 mL of toluene and ε-caprolactone monomer was added (0.26 mL, [M]/[I] = 100). The solution was stirred at room temperature for 30 minutes to produce a gel-like polymer. The reaction vessel was taken out of

the box, and methylene chloride was added to dissolve the polymer gel. The solution was then precipitated into cold methanol (50 mL), filtered, washed with methanol, and dried under high vacuum to a constant weight. Yield: > 99%.

^{1}H NMR (C_6D_6): δ = 3.99 (t, 2H), 2.12 (t, 2H), 1.53 (dd, 2H), 1.42 (dd, 2H), 1.18 (dd, 2H) . Additions of ε-caprolactone monomer 0.52 mL, 1.04 mL and 2.60 were performed for [M]/[I] = 200, 400 and 1000, respectively, by following the above procedures.

Polymerization of ω-pentadecalactone (ω-PDL)

In a nitrogen-filled glovebox, **17a** (10.0 mg, 23.8 μmol) and ω-PDL (57.2 mg, 2.38 mmol, [M]/[I] = 100) were added in an ACE pressure reaction tube containing a stir bar. The reaction tube was sealed with a teflon cap and transferred outside the glove box to a oil bath preset at 100 ^{o}C for 30 minutes. The gel-like polymer crude was then precipitated into cold methanol (50 mL), filtered, washed with methanol, and dried under high vacuum to a constant weight. Melting point: 89 ^{o}C. Yield: > 99%. ^{1}H NMR ($CDCl_3$): δ = 4.03 (dd, 2H), 2.27 (dd, 2H), 1.58 (m, 4H), 1.56 (m, 2H), 1.29 (m, 18H) .

Additions of ω-PDL monomer 114.4 mg and 228.8 mg were performed for [M]/[I] = 200 and 400, respectively, by following the above procedures.

2.4.1 Synthesis of Ligands

2.4.1.1 *N*^{1},*N*^{2}-bis(Dipp)ethane-1,2-diimine (**10**)[88]

This reaction was carried out at ambient atmosphere. A 500-mL round bottom flask was charged with 2,6-diisopropylaniline (9.5 mL, 45.2 mmol), methanol (100 mL) and acetic acid (0.1 mL). Refluxed at 50 ^{o}C for 20 minutes while stirring. Glyoxal (2.5 mL, 22.0 mmol) in 50

mL of methanol was slowly added to the mixture through the opening of the condenser. The reaction mixture was refluxing at 50 ^{o}C for 1 hour, and then stirring for 12 hours at room temperature. The oil bath was removed to allow the reaction mixture to equilibrate to room temperature. The resulting precipitate was filtered and collected. The filtrate was collected in a 500-mL round bottom flask and stored at -20 ^{o}C for further precipitation. The precipitate was dried under vacuum to afford the yellow solid (7.54 g, 91%). ^{1}H NMR ($CDCl_3$): δ = 8.09 (s, 2H), 7.44 (d, *J* = 7.5Hz, 1H), 7.38 (m, 3H), 7.31 (m, 2H), 7.04 (m, 3H), 6.99 (d, *J* = 6.7Hz, 2H), 7.12 ~ 7.21 (m, 6H), 2.93 (sept, J = 7.0 Hz, 4H), 1.19 (d, J = 6.5 Hz, 12H).

2.4.1.2 *N*^{1},*N*^{2}-bis(Dipp)ethane-1,2-diamine (**11**)[16]

A Schlenk flask was charged with **10** (1.71g, 4.5 mmol) in diethyl ether (10 mL) under nitrogen atmosphere. $LiAlH_4$ (1M in THF, 11.4 mL, 11.4 mmol) was slowly added to the mixture at -78 ^{o}C and stirred for 1 hour. The cold bath was removed and the mixture was stirred at room temperature for 12 hours. The reaction was quenched by adding 1% KOH aqueous in dropwise until white precipitate of $Al(OH)_3$ was formed. The mixture was extracted with water (10 mL x 3) and the organic layer was collected and dried with $MgSO_4$.The organic layer was dried under vacuum to afford the white solid product (1.4 g, 83%). ^{1}H NMR (C_6D_6): δ = 7.14 (m, 6H), 3.45 (sept, *J* = 7.0 Hz, 4H), 3.39 (s, 2H), 3.08 (s, 4H), 1.24 (d, J = 6.5 Hz, 24H).

2.4.1.3 *N,N'*-bis(mesityl)-1,4-diamine (**16a**)[16]

In a Schlenk flask capped with a rubber septum, a mixture of 2,4,6-trimethylaniline (4.2 mL, 30.0 mmol) in tetrahydrofuran (50 mL) was dropwise added with n-butyl lithium (33.0 mmol) at -78 ˚C through a needle syringe under a constant flow of N_2. After stirring for 1 hour at

this temperature, the solution became cloudy orange with a white precipitate forming. The cold bath was removed and the solution was allowed to stir for an additional hour at room temperature, during which the solution became a clear orange color. Next, dibromo-*o*-xylene (4.0 g, 15.0 mmol) in 5 mL of THF was added to the reaction solution through the septum with a needle syringe. The resulting solution was left to stir overnight. The reaction was quenched with an addition of 200 mL distilled water and extracted with diethyl ether (3 × 100 mL). The combined organic layer was dried over magnesium sulfate, and the residual solvent was removed in vacuum. The orange solid was then re-dissolved in a minimal amount of diethyl ether and re-crystallized from an ice bath. The white crystals were filtered, washed with ice cold methanol and dried under vacuum to yield the air and moisture stable product (4.8 g, 86%). ^{1}H NMR (C_6D_6): δ = 7.27 (m, 2H), 7.09 (m, 2H), 6.78 (s, 4H) 4.08 (s, 4H), 3.12 (br. s, 2H), 2.17 (s, 6H), 2.13 (s,12H). ^{13}C NMR (C_6D_6): δ = 143.8, 138.9, 131.3, 130.1, 129.6, 129.5, 50.6, 20.5, 8.2.

2.4.1.4 *N,N′*-bis(Dipp)-1,4-diamine (**16b**)[16]

In a Schlenk flask capped with a rubber septum, a mixture of 2,6-diisopropylaniline (5.7 mL, 21.0 mmol) in tetrahydrofuran (50 mL) was dropwise added with n-butyl lithium (33.0 mmol) at -78 °C through a needle syringe under a constant flow of N_2. Dibromo-*o*-xylene (2.7 g, 10.0 mmol) was added to the mixture by following the procedures for the synthesis of **16a**. By following the same procedures for **16a** yielded air and moisture stable white solid **16b** (5.1 g, 74%). ^{1}H NMR (C_6D_6): δ = 7.53 (m, 2H), 7.13 (m, 4H), 4.19 (s, 4H), 3.33 (sept, J = 7 Hz, 4H), 3.28 (br. s, 2H),1.17 (d, J = 7 Hz, 24H). ^{13}C NMR (C_6D_6): δ = 143.4, 142.7, 138.3, 128.5, 124.4, 123.7, 53.6, 27.9, 24.1.

2.4.2 Synthesis of Aluminum Methyl Complexes

2.4.2.1 5-Member (1,2-diamido)^{Dipp}AlMe (**13**)

In a drybox under N_2 atmosphere **11** (1.0 g, 2.6 mmol) was added to 20 mL of toluene in an ACE pressure reaction tube containing a stir bar. The reaction mixture was added with 2.0 M $AlMe_3$/toluene solution (1.24 mL, 2.48 mmol) in a dropwise manner over a course of 10 minutes. During the addition of $AlMe_3$ solution, the vapor of CH_4 was observed. The reaction tube was capped after the vapor diminished. The tightly capped reaction mixture was transferred outside the drybox to an oil bath preheated to 90 ^oC. The reaction mixture was allowed to stir for additional 24 hours at 90 ^oC. The oil bath was removed and the reaction mixture was allowed to equilibrate to room temperature. The reaction mixture was transferred to a drybox and the solution was dried under vacuum in a round bottom flask. The white solid was isolated to yield air and moisture sensitive product (0.99 g, 90%). ^1H NMR (C_6D_6): δ = 7.19 (m, 4H), 7.12 (m, 2H), 7.06 ~ 6.99 (m, 4H), 6.91 ~ 6.94 (m, 2H), 5.09 (dd, J = 5.0 Hz, 2H), 4.03 (sept, J = 6.0 Hz, 2H), 3.92 (sept, J = 6.0 Hz, 2H), 3.79 (sept, J = 6.0 Hz, 2H), 3.76 (dd, J = 5.0 Hz, 2H), 3.17 (dd, J = 5.0 Hz, 2H), 3.01 (dd, J = 5.0 Hz, 2H), 2.69 (sept, J = 6.0 Hz, 2H), 1.45 (d, J = 7.0 Hz, 6H), 1.42 (d, J = 7.0 Hz, 6H), 1.38 (d, J = 7.0 Hz, 6H), 1.34 (d, J = 7.0 Hz, 6H), 1.25 (d, J = 7.0 Hz, 6H), 1.18 (d, J = 7.0 Hz, 6H), 0.86 (d, J = 7.0 Hz, 6H), 0.73 (d, J = 7.0 Hz, 6H), -0.62 (s, 6H). ^{13}C NMR (C_6D_6): δ = 148.2, 147.6, 146.9, 146.7, 146.6, 144.7, 126.1, 125.4, 125.3, 124.7, 124.7, 124.2, 123.8, 58.6, 54.3, 30.9, 30.6, 30.2, 29.6, 29.1, 28.4, 27.8, 27.7, 24.9, 24.4, 23.3, 22.7. TOF-MS (*m/z*): calcd for $C_{54}H_{82}Al_2N_4$ $[M - C_{27}H_{41}AlN_2]^+$: 420.3035, found: 420.3081.

2.4.2.2 7-Member (1,4-Diamido)^{Mes}AlMe (**17a**)

In a drybox under N_2 atmosphere, a 100-mL ACE pressure reaction tube was charged with a stir bar and **16** (0.49 g, 1.3 mmol) in toluene (10 mL). The reaction mixture was added dropwise with 2.0 M $AlMe_3$/toluene solution (0.66 mL, 1.3 mmol) through needle syringe. The reaction tube was sealed with teflon cap and transferred outside the drybox for heating at 90◦C for 24 h. The solution was cooled to room temperature and transferred to the drybox. The solvent was removed under high vacuum to yield the white solid product (0.49 g, 90%). ^{1}H NMR (C_6D_6): δ = 7.06 (s, 4H), 6.91 (s, 4H), 4.26 (br. s, 4H), 2.36 (s, 12H), -0.97 (s, 3H), 2.19 (s, 6H), -0.95 (s, 3H). ^{13}C NMR (C_6D_6): δ = 142.1, 135.4, 132.7, 130.1, 129.4, 56.7, 20.6, 19.3, 1.1.

2.4.2.3 7-Member (1,4-Diamido)^{Dipp}AlMe (**17b**)

A 100 mL teflon-capped high pressure reaction vessel was charged with**16b** (0.46 g, 1.0 mmol) and dissolved in 5 mL of toluene. The same procedure was used as for **17a** to yield colourless crystals of **17b** (0.42 g, 84 %). ^{1}H NMR (C_6D_6): δ = 7.15 (m, 6H), 7.07 (s, 4H), 4.32 (br s, 4H), 3.70 (sept, J =7 Hz, 4H), 1.32 (d, J =7 Hz, 12H), 1.17 (d, J = 7 Hz, 12H), -0.90 (s, 3H). ^{13}C NMR (C_6D_6): δ = 146.8, 141.5, 130.4, 125.6, 123.8, 59.16, 4.46, 24.9, 24.7, 1.1.

2.4.2.4 Synthesis of (1,4-diamido)^{Mes}Al(μ-H)$_2$Li(Et_2O)$_2$ (**20**)

In a drybox, a 20-mL teflon-capped reaction vial pre-filled with 5.0 mL of diethyl ether was charged with **16a** (300.0 mg, 0.8 mmol), a stir bar and 1M $LiAlH_4$/THF solution (0.98 mL, 0.98 mmol). The mixture was stirred for 12 hours at room temperature in the drybox. The mixture was dried under vacuum to afford the white solid product (396.8 mg, 89%). ^{1}H NMR

(C_6D_6): δ = 7.09 ~ 7.20 (m, 4H), 6.78 (m, 4H), 4.28 (s, 4H), 4.18 (br s, 2H), 3.28 (q, 8H), 2.23 (s, 12H), 2.22 (s, 6H), 1.05 (t, 12H). ^{13}C NMR (C_6D_6): δ = 150.7, 142.9, 137.6, 131.3, 130.0, 129.4, 127.0, 65.7, 57.5, 21.0, 20.1, 14.7.

2.5 References

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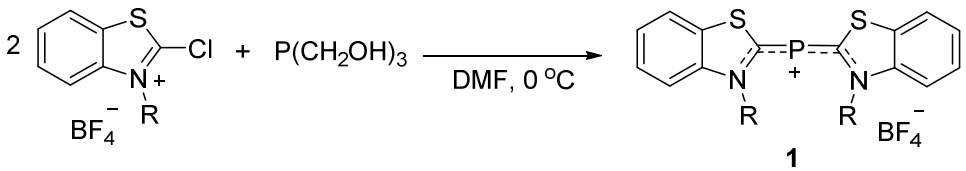
CHAPTER 3. APPLICATION OF 1,4-DIAMINES IN THE FORMATION OF NOVEL 1,4-DIAMIDO PHOSPHINES AND THEIR CORRESPONDING PHOSPHENIUM CATIONS

3.1 Introduction

A phosphenium cation (R_2P^+) is a two 2-coordinate phosphorus center with a lone pair, wherein the phosphorus center carries a positive charge. The first reported synthesis of stable phosphenium cations (Scheme 3-1) dates back as early as 1964 by Hoffmann *et al.*[97] The phosphenium species **1** (Scheme 3-1) was prepared through a relatively simple synthesis by treating two equivalents of *N*-ethyl-2-chlorobenzothiazolium fluoroborate with one equivalent of tris-(hydroxymethy1)phosphine at 0 ^oC. Thereafter, some varieties of molecular structures were studied with the most significant one utilizing chelating diamido ligands to form a new class of cyclic cationic species **2b** (Figure 3-1), known as *N*-heterocyclic phosphenium cation (NHP^+) in which the phosphorus centers were coordinated by two nitrogens.[98]

Scheme 3-1. Synthesis of the first stable phosphenium cation.[97]



1

R = C_2H_5

A phosphine is a neutral 3-coordinate phosphorus species with a lone pair residing on the phosphorus atom. A *N*-heterocylic phosphine (NHP), such as **2a** (Figure 3-1), is a phosphine

species with the phosphorus atom coordinated by the two nitrogens of a diamido ligand in a bidentate form. The first *N*-heterocyclic phosphine (NHP) compound was reported in the form of a substituted phosphine **2c** (Figure 3-1) in 1965 by Kemenater *et al.*[99] However, the simple structure of **2c** did not receive much attention until whether the reactivity of the hydrogen connected to phosphorus (analogous R_2PH) being protonic or hydridic was investigated by Gudat *et al.*[100]

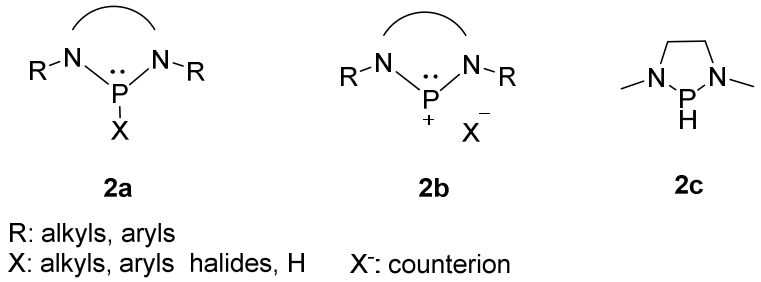
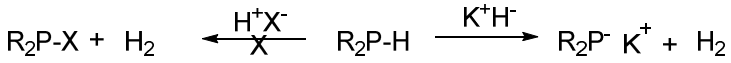


Figure 3-1. Structural examples of NHP and NHP^+ species.

It was later confirmed by a simple experiment that the hydrogen in a R_2P-H bond was actually protonic (Scheme 3-2), unlike that of a silane which showed both properties provided with the same conditions. The general interest of manipulating P-H bond has arisen from the low bond polarity in view of electronegativities ($\chi^{AR}(H) = 2.20$, $\chi^{AR}(P) = 2.06$). Measures to increase the bond polarity in order to encourage the dissociation of the P-X bond for the formation of P^+ cationic species seemed conceivable through substituent effects. Replacements of the hydrogen with a more eletronegative group, e.g. a halide, as well incorporating aromaticity to the ring system should result in an umpolung effect.[101]

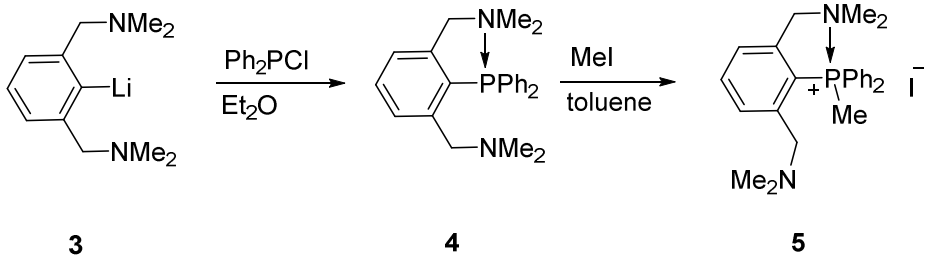
Scheme 3-2. Protonic reactivity of a phosphane hydrogen.



A dialkyldiamine ligand was applied to look into the possibility of forming a cyclic cationic species (Scheme 3-3).[102] Treating the diamine **3** and diphenylphosphine chloride resulted in the formation of **4**, which can be methylated to form the cation **5** with a positive charge on phosphorus. As show in **4** and **5** (Scheme 3-3), The monoanionic ligand **3** stabilized **4** and **5** through its neutral nitrogen donors. Although **5** was not considered as a NHP^+ species for the lack of 2-coordination around phosphorus, the role of the nitrogen atoms in the ligand moiety to stabilize the phosphorus center presented an interesting property. It was later found that transforming a diamine to a diamido ligand [($^-$:NR_2(linker)R_2N:$^-$] can be used to form NHPs by best utilizing the strong donor ability of the anionic nitrogens. In addition, the chelate effect of the diamido ligands further adds stability to the resulting NHPs.[98]

However, with the emergence and growing popularity of *N*-heterocyclic carbene (NHC) as a ligand in coordination chemistry, the syntheses and applications of NHPs seemed to be under-explored.

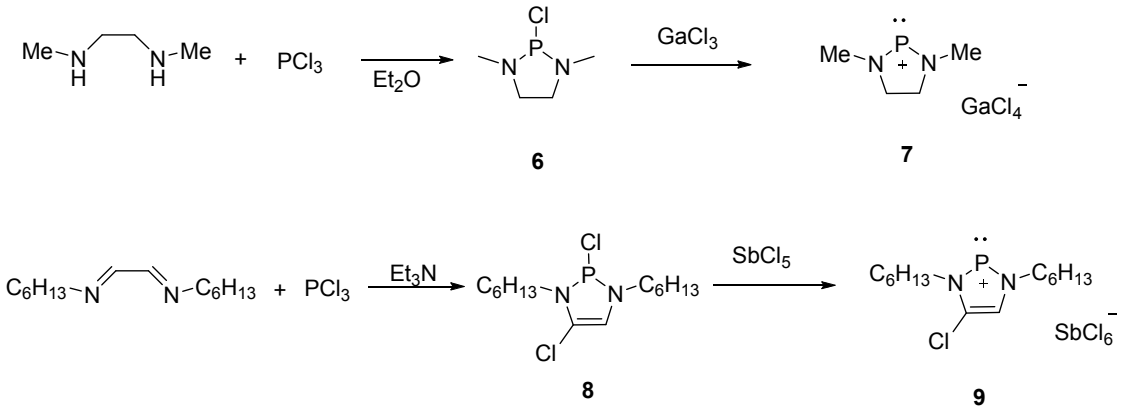
Scheme 3-3. Formation of phosphenium cation.



3 **4** **5**

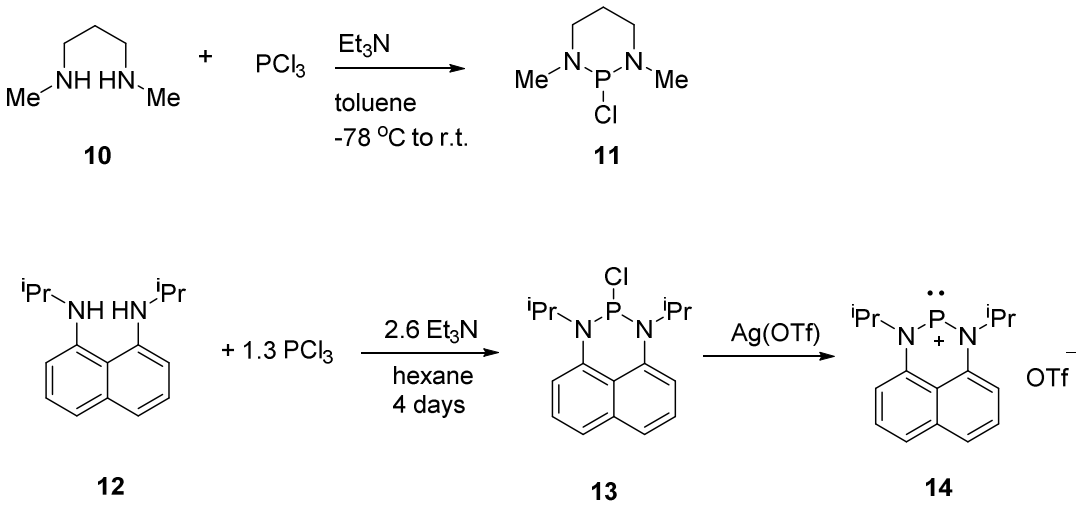
Although the applications of diamido ligands to form NHPs have been somewhat investigated, more in-depth research was much less than that of *N*-heterocyclic carbenes (NHCs). While some varieties of NHP and NHP^+ have been reported, they were dominated by 5-member species, structurally similar to **6** and **8** (Scheme 3-4).[98, 103] Compounds **7** and **9** represented NHP^+ species in that the phosphorus centers were supported by the diamido ligands in a 2-coordinate geometry.[104] It is worth noting that the formation of **7** and **9** was through a simple halide abstraction with Lewis acids from their corresponding NHPs.

Scheme 3-4. Examples of 5-member NHP^+.

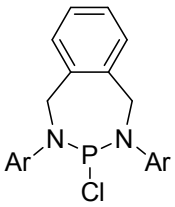


Although 6-member NHPs were known, examples have been rare. The neutral 3-coordinate species **11** and **13** (Scheme 3-5) were prepared in a single step reaction from their corresponding 1,3-diamines **10** and **12**, respectively, with trichlorophosphine.[105] Analogous to their 5-member ring counterpart **8**, the diamine precursors **10** and **12** were transformed *in situ* into diamido ligands in the presence of triethylamine (Et_3N) which deprotonated the amines and precipitated as a salt ($Et_3N^+Cl^-$). NHPs with an aromatic linker in **8** and **13** seemed to encompass the capacity to stabilize the rare 2-coordinate NHP^+ after halide abstraction, shown as **9** and **14** respectively.

Scheme 3-5. Examples of 6-member NHPs.[105a, 105e]



To further extend the synthesis and potential applications of NHPs, I was interested in expanding the ring size to a 7-member conformation proposed as **15** (Figure 3-2). The synthesis was based on utilizing 1,4-diamine with an aromatic backbone, which I expected to maintain a rigid structure so as to ensure a larger bite angle (N-P-N) than its 5- and 6-member counterparts. The large bite angle could be potentially of advantage to forming a larger Tolman's angle as described in section **1.3.1.2** for future applications in coordination chemistry. As demonstrated by multiple studies, an optimal Tolman's angle, usually a large angle, encouraged the dissociation of coordinated phosphine ligands from their metal complexes, and thus increased the catalytic activities that they were designed for. Examples of higher catalytic activities as a result of optimal Tolmans' angles include (phosphine)Rh complexes in hydroformylation[106], (diphosphane)Pd complexes in allylic alkylation[107], (diphosphine)Ni complexes in hydrocyanation[108] and (diphosphine)Pd complexes in amination of arylhalides.



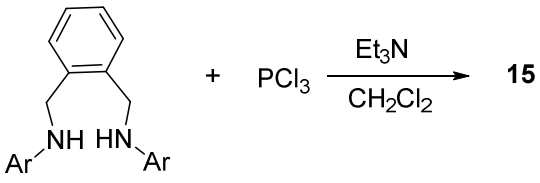
15

15a: Ar = Dipp
15b: Ar = mesityl

Figure 3-2. Proposed neutral 7-member (1,4-diamido)^{Ar}PCl.

Based on the successful application of 1,4-diamido ligands in forming neutral aluminum complexes (Chapter 2), I was interested in widening the scope of applying such ligand system to prepare novel NHP species. To arrive at the proposed structure **15** (Figure 3-2), a synthetic strategy (Scheme 3-6) was devised in a simplest route possible by referencing to that leading to **11** and **13**.

Scheme 3-6. Synthetic scheme of 7-member NHPs.



Ar = Dipp, Mes

3.2 Results and Discussion

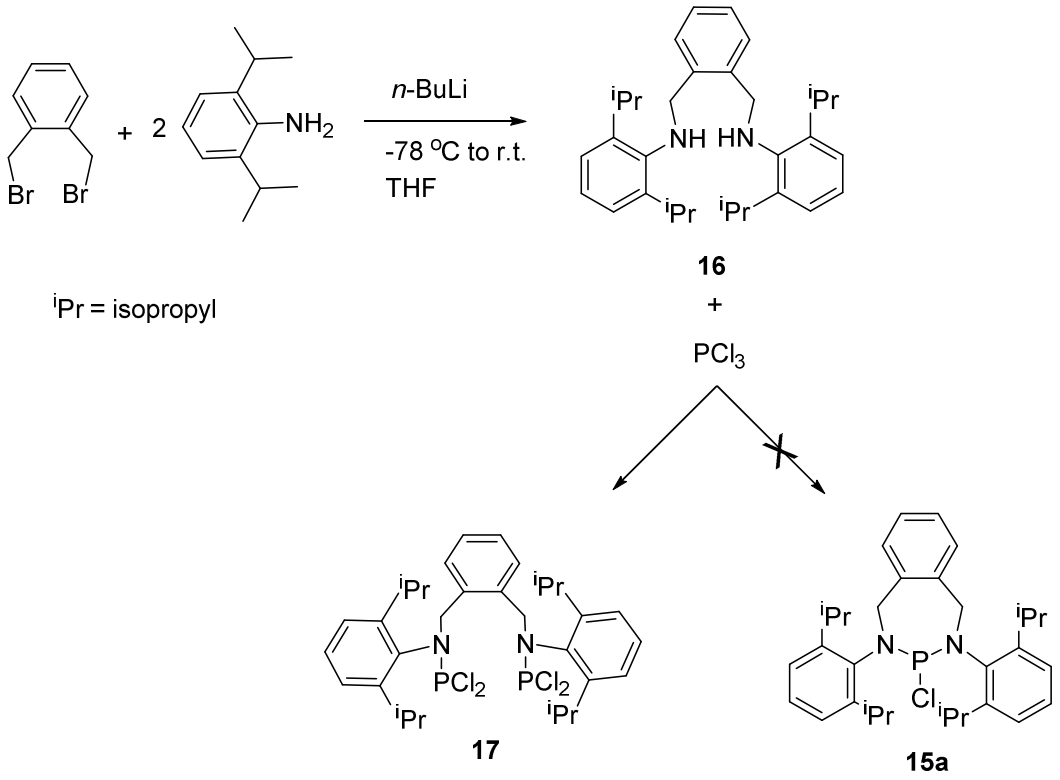
It has been shown by many groups that the steric bulk and basicity of a phosphine ligand increased the reactivity of the metal-phosphine complex.[109] Although the steric-reactivity relationship was rarely addressed for NHP species, I believed that the same principle was applicable and should be adopted in the preparation of 7-member NHPs.

Therefore, I started the synthesis by employing 2,6-diisopropylphenyl (Dipp) as the *N*-substituent since it was commonly known as a bulky group and often used in coordination chemistry. Groups other than Dipp were investigated until the optimal steric property was found to yield successful NHP species. Subsequent investigations included the conversion of neutral 3-coordinate NHP into NHP^+ species as well as attempted replacement of Cl in **15** (Figure 3-2) with other groups.

3.2.1 Attempted Synthesis of (1,4-Diamido)^{Dipp}PCl.

The 1,4-diamine with 2,6-diisopropylphenyl group as the *N*-substituent was prepared from the reaction of 2,6-diisopropylphenyl amine and *o*-dibromoxylene. The reaction afforded the formation of **16** (Scheme 3-7). Further cyclic addition of **16** with PCl_3 did not afford the expected product **15a** but the acyclic bridging species **17** [μ-(1,4-diamido)$^{Dipp}P_2Cl_4$]. Later confirmative reactions indicated that even in the excess of **16**, compound **17** was consistently yielded as the major product.

Scheme 3-7. Attempted synthesis of (1,4-diamido)^{Dipp}PCl.



Although similar preparations demonstrated by other groups have been shown successful in synthesizing 5- and 6-member NHPs, the same synthetic strategy did not afford the formation of the expected 7-member **15a**.[110] The unsuccessful cyclization of **16** with PCl_3 was possibly due to the excessive large bite angle θ (Figure 3-3) in a 7-member NHP, which was unable to accommodate the sterically hindered 2,6-diisopropylphenyl groups in **16**. The combination of an excessive large bite angle and steric bulk of *N*-groups gives rise to an unavoidable steric repulsion between the isopropyl group and P-Cl bond (Figure 3-3). As θ becomes larger, the isopropyl group will be pushed further inward closed to P-Cl bond, and the steric repulsion thus

generated inhibits the cyclization process. Instead, each of the N donor in the 1,4-diamido ligand forms a P-N bond with PCl_3 in favor of the formation of the bridging species **17** (Scheme 3-7).

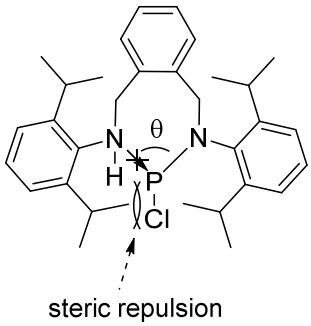


Figure 3-3. Possible inhibition of cyclization.

Spectroscopic characterization has shown that the resulting structure has a high symmetry C_{2v} as opposed to the expected C_s symmetry.

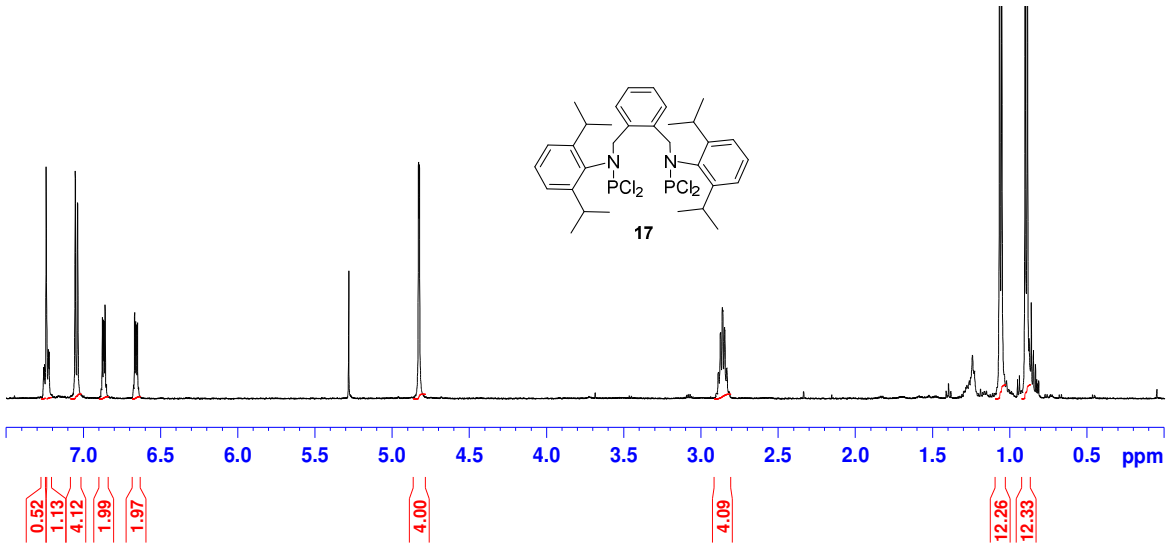


Figure 3-4. ^1H NMR (C_6D_6) spectrum of **17**.

As shown in the ^{1}H NMR spectrum (Figure 3-4), the four benzylic protons appeared as surrounded in the same chemical environment and resulted in one singlet at 4.80 ppm, which is consistent with a C_{2v} symmetry. Other supporting evidence on the spectrum included the septet at 2.85 ppm for the four tertiary-isopropyl (methanetriyl) protons, again due to the high symmetry of the molecule.

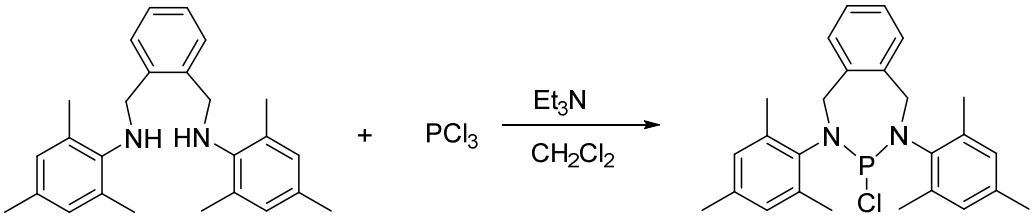
It has become clear that steric hindrance played a determining role in the formation of 7-member NHPs as demonstrated by **17** with the bulky 2,6-diisopropylphenyl group as the *N*-substituent. Further continuation of the project was proceeded by reducing the steric bulk of *N*-substituent to a less hindered group, such as a mesityl, to reach the goal of obtaining a neutral 3-coordinate NHP species.

3.2.2 (1,4-Diamido) ^{Mes}PCl.

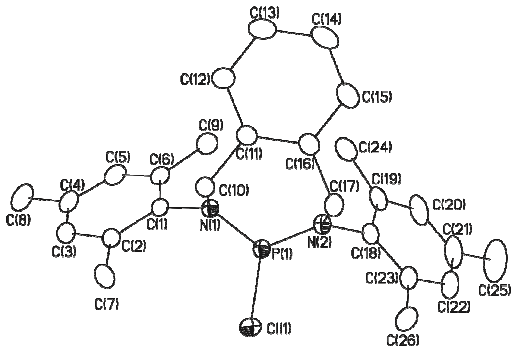
Due to the postulation that the unsuccessful preparation of **15a** was caused by the high steric bulk of the Dipp group (Figure 3-3), I continued the synthesis with mesityl as the *N*-substituent, which has been recognized having a steric bulk second to Dipp.

To investigate the steric effect in the cyclization prior to forming a 7-member NHP as proposed in this project, the synthetic conditions for **15b** were kept unchanged as that for **17**, except for the change of the 1,4-diamine precursor to 2,4,6-trimethylaniline (mesitylamine) (Scheme 3-8). Addition of mesitylamine and PCl_3 was prepared in equimolar amount and reacted in dichloromethane with an excessive amount of triethylamine (Et_3N). The resulting product was analyzed by ^{1}H NMR and shown to be the monophosphine product **15b**.

Scheme 3-8. Synthesis of (1,4-diamido)^{Mes}PCl, **15b**.



15b



X-ray crystal structure of **15b**

Analysis of the ^{1}H NMR NMR (Figure 3-5) revealed that the benzylic protons appeared as two doublet of doublets at 5.80 and 3.65 ppm, each integrating for 2 protons, indicating a diastereotopic characteristic. Each benzylic proton *H* (C-C*H*H'-N-P) is coupled to its geminal proton H' and then to P, resulting in the observed doublet of doublets. In addition, the six aromatic methyl groups appear at two different chemical shifts, 2.10 ppm for *ortho* and 2.60 ppm for *para* methyls due to the ring strain that resulted in the methyls surrounded by different chemical environments. The combined ^{1}H NMR information is consistent with a C_s symmetry of **15b**. The crystal structure of **15b** measures a bite angle (N-P-N) of 105.33^{o}. The molecular geometry around phosphorus is a trigonal pyramidal arrangement. The measured P-Cl bond

length is 2.204 Å. Even though the P-Cl bond length is much longer than a normal single bond (< 2.18 Å), it remains in a range suggesting significant covalent interaction.[111] The P-N bond length of **15b** 1.487 Å is significant shorter than a normal P-N(sp^3) value of 1.683 Å.[112] The lengthening of P-Cl bond and shortening of P-N bond suggests a strong (N) → σ*(P-Cl) hyperconjugation.

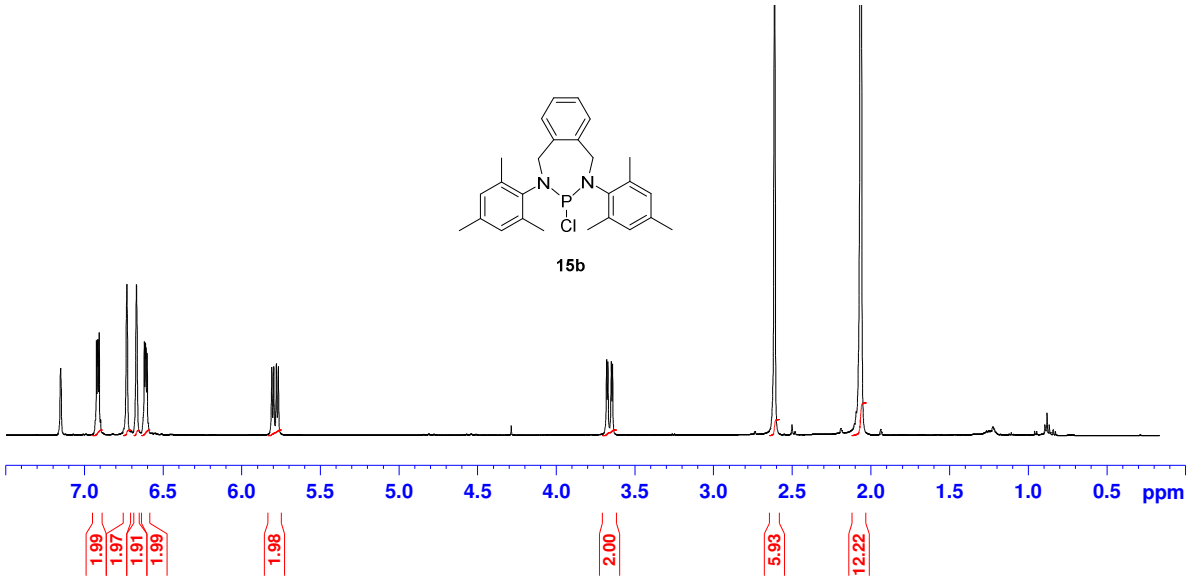
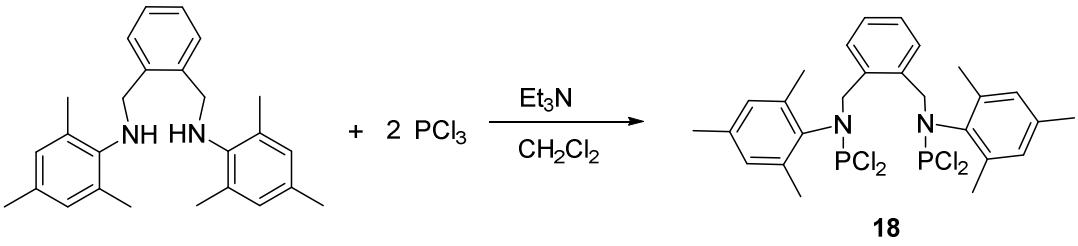


Figure 3-5. ^{1}H NMR (C_6D_6) spectrum of **15b**.

The successful synthesis of **15b** at room temperature demonstrated that the cyclization of 1,4-diamine with PCl_3 can proceed at a facile route as proposed (Scheme 3-8). The result was in support of the postulation that the steric bulk of *N*-substituent played an important role in the cyclization process. The unsuccessful synthesis of **15a** was indeed due to the large steric hindrance of the Dipp group as the less bulky mesityl counterpart led to the formation of **15b** in a 3-coordinate geometry.

In addition, I carried out a synthesis (Scheme 3-9) to confirm that by controlling the stoichiometric ratio of 1,4-diamine to PCl_3 at 1:2, whether a bridging diphosphine species **18** (similar to **17**) can be formed under the same reaction conditions.

Scheme 3-9. Synthesis of (μ-1,4-diamido)$^{Mes}(PCl_2)_2$.



The ^{1}H NMR spectrum of **18** (Figure 3-6) indicates that the four benzylic protons appears at 4.20 ppm as a singlet. The chemical equivalency of the benzylic protons is consistent with a C_{2v} symmetry and is in agreement with that displayed by **17** (Figure 3-4).

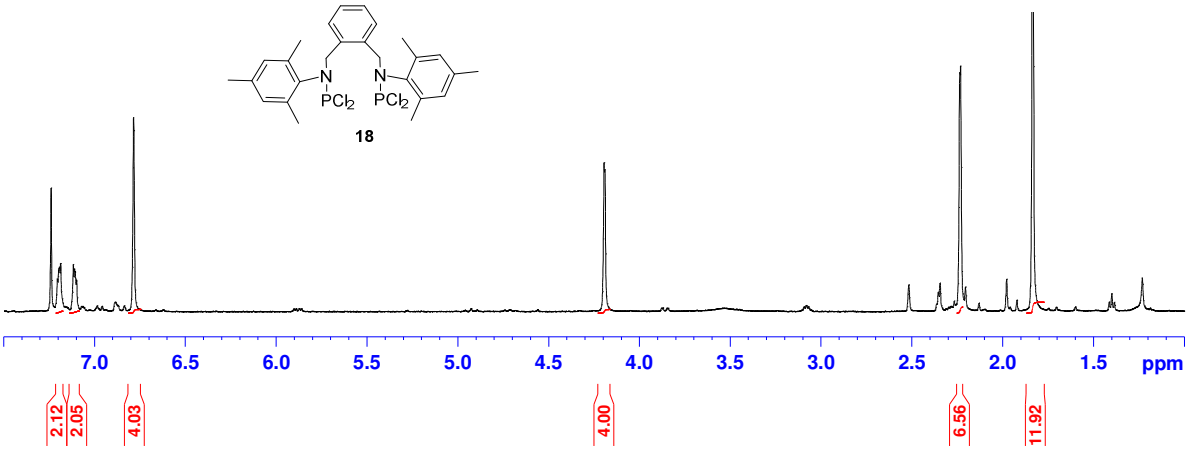


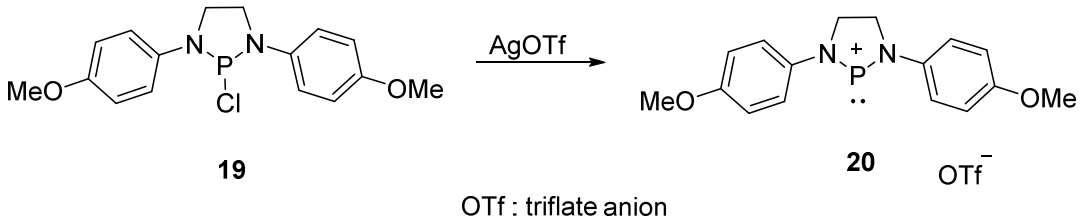
Figure 3-6. ^{1}H NMR (C_6D_6) spectrum of **18**.

In conclusion, the successful synthesis of the 3-coordinate neutral NHP **15b** represented the first 7-member species ever reported. The 1,4-diamido ligand has been proven to be very useful in the formation of NHPs with an expanded ring size. Mesityl as the *N*-substituent was shown to encompass a higher versatility than Dipp to afford the formation of NHP and bridging diphosphine species, conclusively attributed to the steric effect.

3.2.3 [(1,4-Diamido)^{Mes}P]$^+$

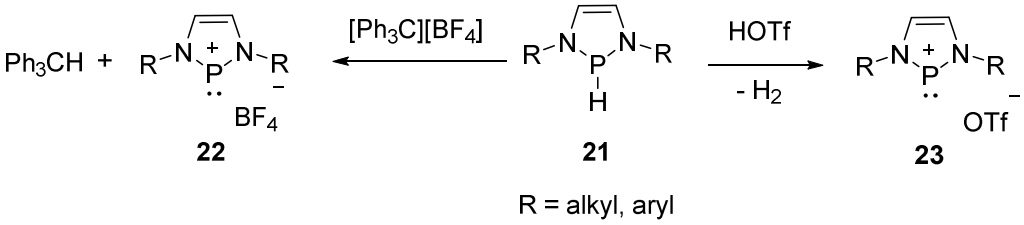
While neutral *N*-heterocyclic carbenes have been predominately applied as strong σ-donors in coordination chemistry, their isoelectronic counterpart divalent phosphenium cations (NHP^+) may possess both σ-donating and π-accepting properties. However, the synthesis of divalent phosphenium species has been rare. One of the examples was by halide abstraction of a neutral NHP to form a 5-member NHP^+ through the use of silver triflate (AgOTf), exemplified as **20** (Scheme 3-10) .[113] The reaction seemed simple with silver as the halide abstracting reagent. As shown for the synthesis of the divalent cationic NHP^+ **20**, a single step of halide abstraction led to the formation of the product (Scheme 3-10).

Scheme 3-10. An example of formation of 5-member NHP^+ species with AgOTf.[113a]



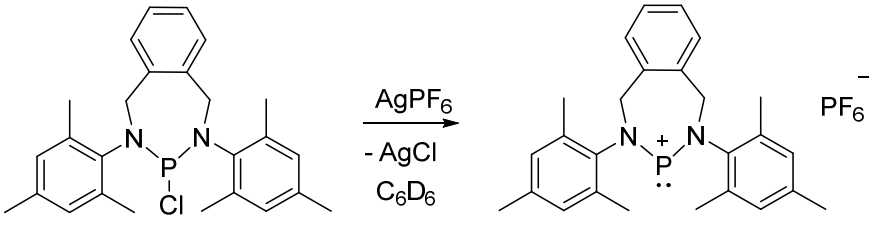
Other examples of yielding divalent NHP^+ cations from (1,2-diamido)PH **21** included removing the hydrogen with $[Ph_3C][BF_4]$ (triphenylcarbenium tetrafluoroborate) and HOTf (trifluoromethanesulfonic acid), resulting in products **22** and **23** with BF_4^- and OTf^- as the counterions, respectively (Scheme 3-11).[55]

Scheme 3-11. Formation of 5-member NHP^+ species with HOTf and $[Ph_3][BF_4]$.[55]



On a trial basis, attempts into the forming a divalent NHP^+ cation were carried out by halide abstractions of **15b** with an alternative silver source $AgPF_6$ (silver hexafluorophosphate) (Scheme 3-12).

Scheme 3-12. Attempted synthesis of $[(1,4\text{-diamido})^{Mes}P]^+ [PF6]^-$.



The ^{1}H NMR spectrum of the expected product **24** was examined. The change of coordination environment around phosphorus was evidenced by the broad signal of benzylic protons between 4.28 ~ 4.76 ppm (Figure 3-7) compared to that of **15b** at 5.80 and 3.65 ppm (Figure 3-5). The mergence of benzylic protons is consistent with a C_{2v} symmetry as expected for the expected product **24**. Moreover, I was unable to obtain **24** in a purified solid form but only as an oily liquid. For a reason not clear, it may be attributed to the counterion PF_6^- in the final product that resulted in the observed physical state.

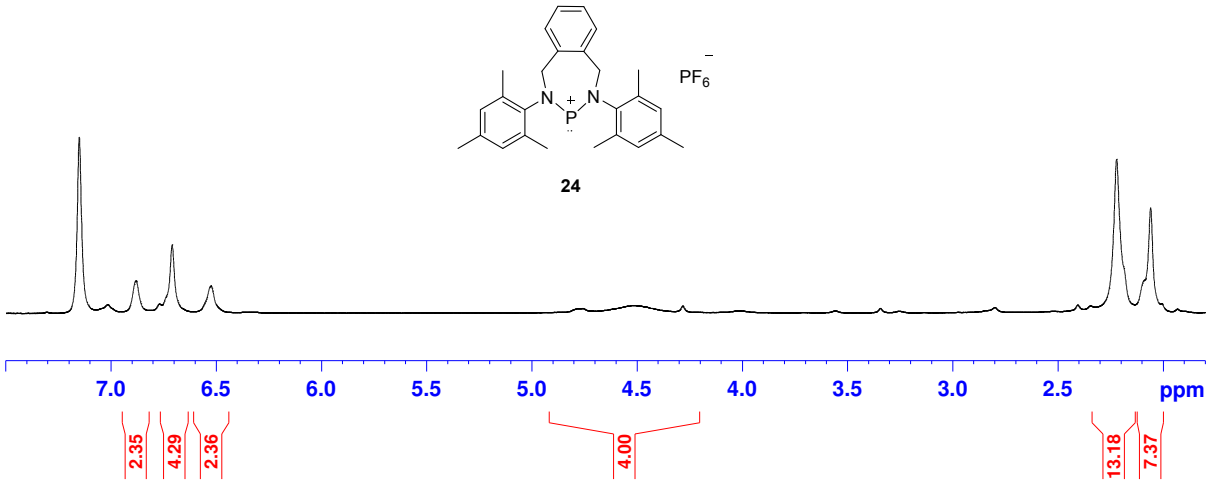
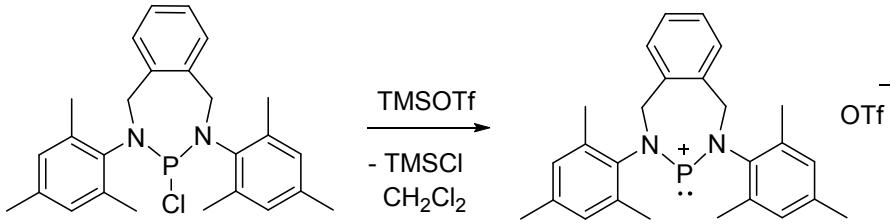


Figure 3-7. ^{1}H NMR (C_6D_6) spectrum of [(1,4-diamido)$^{Mes}P^{+}$] [$PF6^{-}$].

Alternatively, another halide abstracting reagent TMSOTf (trimethylsilyl trifluoromethanesulfonate) was used to look into the effect of changing the counterion to triflate (Scheme 3-13). The advantage of the reaction was the relatively volatile side product (b.p. ~ 57 ^{o}C), TMSCl (trimethylsilyl chloride), which can be removed along with the reaction solvent without further purification.

Scheme 3-13. Synthesis of [(1,4-diamido)^{Mes}P]$^{+}$ [OTf]$^{-}$.



The product **25** can only be isolated as highly hygroscopic solids, and I was unable to obtain a crystal suitable for X-ray analysis. The ^{1}H NMR spectrum (Figure 3-8) showed the characteristics of the formation of **25**. Similar to its PF_6^- counterpart **24** (Figure 3-7), the chemical shifts of benzylic protons were broadened bewteen 4.20 ~ 4.80 ppm from the two signals at 5.80 and 3.65 ppm (Figure 3-5) for **15b**. The six methyl groups on the mesityls appeared as 2 singlets, of one integrating for 12 and the other integrating for 6 protons. The combined ^{1}HNMR result is consistent with the formation of the desired product in a C_{2v} symmetry.

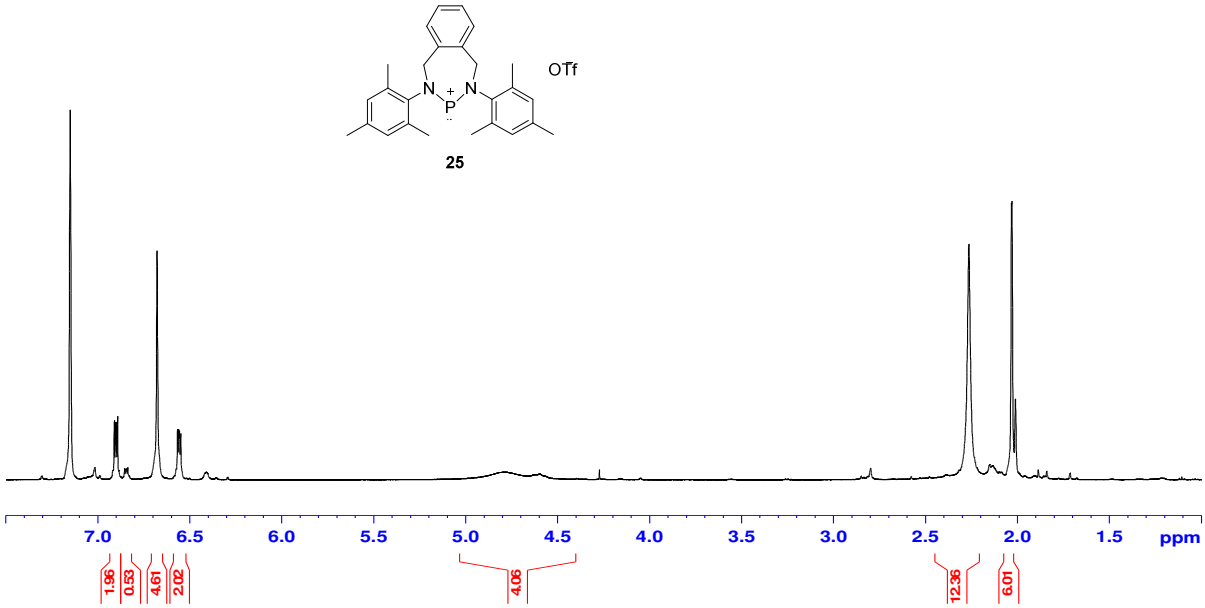


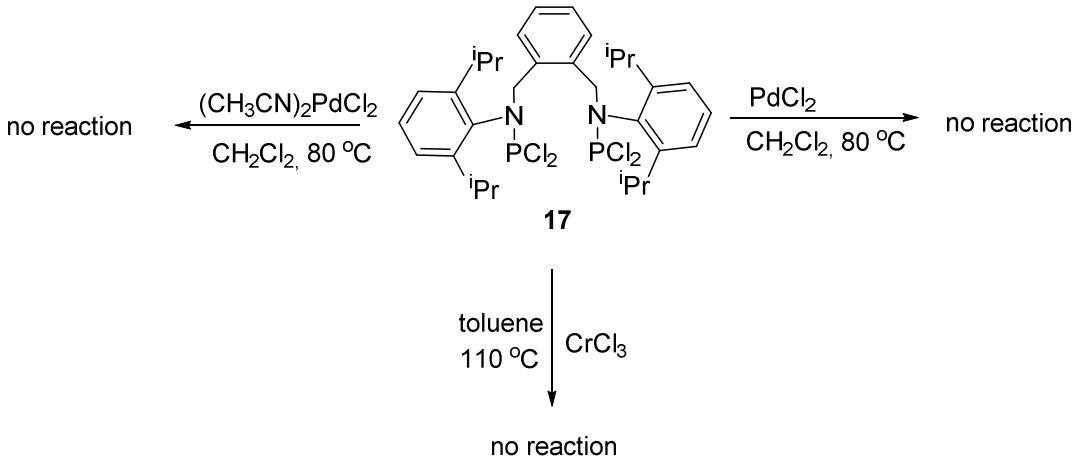
Figure 3-8. ^{1}H NMR (C_6D_6) spectrum of $[(1,4\text{-diamido})^{Mes}P]^{+}$ $[OTf]^{-}$.

3.3 Conclusion

This project was an extended application of 1,4-diamido ligands in the formation of 7-member low-coordinate phosphorus species. The capability of 1,4-diamido ligand in forming low-coordinate aluminum complexes was proven successful as demonstrated in Chapter 2 of this thesis.

The chelating 1,4-diamido ligand with tunable *N*-substituents investigated in this research project started with *N*-Dipp group, and the result showed that the cyclization was inhibited by the steric bulk arisen from the isopropyl groups. As postulated in Figure 3-3, the steric repulsion between isopropyl groups and P-Cl bond could be responsible for the inhibition of cyclization reactions. As a result, a bridging diphosphine species (μ-1,4-diamido)$^{Dipp}(PCl_2)_2$ **17** was formed (Scheme 3-7). Subsequent exploration into the potential applications of **17** was conducted by coordinating with Pd(II) and Cr(III). As summarized from various reactions depicted in Scheme 3-14, species **17** was unable to form coordinated complex with either Pd or Cr. It is possible that the electron-withdrawing chloride groups on phosphorus largely decreased the donor ability of phosphorus. Further exploration of coordinating **17** to other transition metals are being investigated.

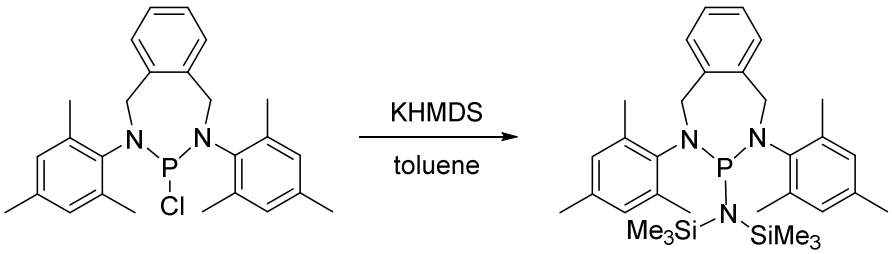
Scheme 3-14. Attempted coordination of **17** to transition metals.



After changing the *N*-Dipp groups to *N*-mesityl, the steric repulsion between *N*-group and P-Cl bond was presumably reduced (Figure 3-3) and the 3-coordinate **15b** was formed under a mild condition, room temperature in the presence of triethylamine, as a neutral 7-member NHP. The species **15b** is the first example of 7-member NHP ever presented.

It was thought that electronic property of **15b** could be tuned by changing the electron-withdrawing Cl to other groups. A trimethylsilyl amide moiety has been regarded as an electron-donating group and was applied in preparing variant species of **15b** (Scheme 3-15). KHMDS ($K[N(SiMe_3)_2]$) was reacted with **15b** in an attempt to change the Cl to an amide group, as well as reversing the electronic property of the species by imposing higher electron density to phosphorus.

Scheme 3-15. Attempted synthesis of (1,4-diamido)^{Mes}P(NSiMe$_3$)$_2$.



15b **26**

KHMDS = K[N(SiMe$_3$)$_2$]

The attempted synthesis of **26** (Scheme 3-15) was examined for the change of benzylic protons as compared with the starting compound **15b**. Chemical shifts of benzylic protons of **26** were evidently different from its starting compound **15b**. Two doublet of doublets due to coupling of H_AH_BC with each other and with P at 5.05 and 4.55 ppm indicated that the molecular symmetry was retained as compared to its starting compound **15b** at 5.80 and 3.65 ppm (Figure 3-5). However, the change of chemical shifts for benzylic protons revealed that the coordination environment around phosphorus has been greatly varied likely due to the trimethylsilyl amide group. Due to the observation that the benzylic protons remained in two separate chemical shifts, I assumed that a P-N bond was formed and the possibility of trimethylsilyl amide being counterion can be ruled out.

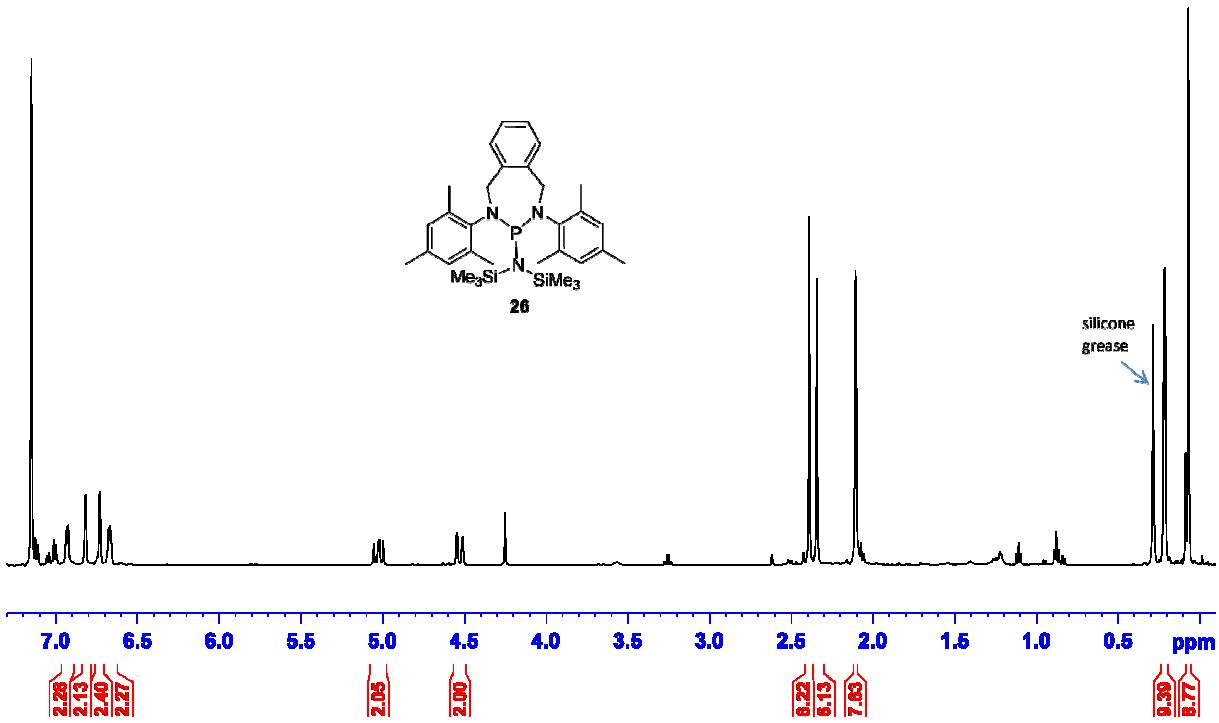


Figure 3-9. ^{1}H NMR (C_6D_6) spectrum of (1,4-diamido)^{Mes}PN($SiMe_3$)$_2$.

In summary, investigations into preparing novel NHP species have been proven successful with the use of 1,4-diamido ligands to yield 7-member ring moieties. The 7-member neutral and cationic ionic NHPs can be prepared in relatively facile routes. Although continuing efforts to changing the electronic property of **15b** by substituting Cl with other electron-donating groups have not been clear thus far, the change of electronic environment around phosphorus center can be realized as demonstrated by **26** (Figure 3-9) versus **15b** (Figure 3-5) based on ^{1}H NMR interpretations. The novel NHP and NHP^{+} species presented in this project encompass the potential for future applications in coordination chemistry by utilizing their σ-donor and π-acceptor properties.

3.4 Experimental

General Information. Unless otherwise stated, all reactions were performed under N_2 or vacuum using standard Schlenk techniques or in a N_2-filled drybox. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.24) and C_6D_6 (^1H: δ 7.16; ^{13}C: δ 128.06). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR data was collected by Diffuse Reflectance Spectroscopy. Reagents such as 2,6-diisopropylaniline (Dipp), 2,4,6-trimethylaniline (mesityl), KHMDS ($K[N(SiMe_3)_2]$), PCl_3, and triethylamine (Et_3N) were purchased from Sigma-Aldrich Chemical Company and used as received except for 2,6-diisopropylaniline which was distilled prior to use. 1,4-Diamines, such as *N,N′*-1,4-bis(mesityl) benzyl-diamine and *N,N′*-1,4-bis(Dipp) benzyl-diamine, were prepared according to the procedures described in Chapter 2 of this thesis.

3.4.1 Synthesis of (μ-1,4-Diamido)$^{Dipp}(PCl_2)_2$ **(17)**

In a drybox, *N,N′*-1,4-bis(Dipp) benzyl-diamine (0.50 g, 1.09 mmol) in dichloromethane (10 mL) was added with PCl_3 (188 μL, 2.20 mmol) and stirred for 0.5 hour at room temperature. Triethylamine (608 μL, 4.40 mmol) was added to the mixture and the solution became cloudy with a white precipitate forming after 20 minutes. The mixture was stirred for additional 12 hours and vacuumed to dryness. The resulting white solid was added with 15 mL of hexane and stirred for 1.0 hour. The suspension was filtered. The filtrate was collected and dried under vacuum to yield moisture sensitive product (0.60 g, 83%). Crystals were obtained from slow

evaporation of **17** in dichloromethane. ^{1}H NMR (C_6D_6): δ = 6.99 (m, 2H), 6.87 (m, 4H), 6.80 (t, J = 2 Hz, 2H), 6.61 (t, J = 2 Hz, 2H), 5.07 (s, 4H), 3.05 (sept, J = 6.5 Hz, 4H), 1.08 (d, J = 7.0 Hz, 12H), 0.89 (d, J = 7.0 Hz, 12H). ^{13}C NMR (C_6D_6): δ = 149.8, 135.5, 135.3, 133.8, 133.36, 132.4, 129.5, 129.4,127.6, 124.4, 124.4, 50.9, 50.9, 28.8, 26.9, 26.9, 22.7, 22.6. EI-MS (*m/z*): calcd for $C_{32}H_{42}Cl_4N_2P_2$: 656.1577, found: 656.1601. ^{31}P NMR (C_6D_6): δ = 155 ppm.

3.4.2 (1,4-Diamido)^{Mes}PCl **(15b)**

In a drybox, *N,N'*-1,4-bis(mesityl) benzyl-diamine (0.6 g, 1.61 mmol) in dichloromethane (5 mL) was added with PCl_3 (140 μL, 1.61 mmol) and stirred for 0.5 hour at room temperature. Triethylamine (900 μL, 6.44 mmol) was added to the mixture and the solution became cloudy with a white precipitate forming after 30 minutes. The mixture was stirred for additional 12 hours and vacuumed to dryness. The resulting white solid was added with 15 mL of hexane and stirred for 1.0 hour. The suspension was filtered. The filtrate was collected and dried under vacuum to yield moisture sensitive product (0.61g, 87%). Crystals were obtained from slow evaporation of **15b** in dichloromethane. ^{1}H NMR (C_6D_6): δ = 6.91 (m, 2H), 6.90 (s, 2H), 6.73 (s, 2H), 6.61 (m, 2H), 5.80 (dd, J = 6.0 Hz, 2H), 3.65 (dd, J = 6.0 Hz, 2H), 2.61 (s, 6H), 2.07 (s, 6H), 2.05 (s, 6H). ^{13}C NMR (C_6D_6): δ = 139.3, 136.9, 136.9, 136.4, 136.4, 130.7, 130.7, 129.3, 129.27, 128.6, 127.7, 127.5, 126.9, 55.9, 20.4, 20.2. EI-MS (*m/z*): calcd for $C_{26}H_{30}ClN_2P$: 436.1835, found: 436.1835. ^{31}P NMR (C_6D_6): δ = 149 ppm.

3.4.3 Synthesis of (μ-1,4-Diamido)^{Mes}(PCl_2)$_2$ (**18**)

In a drybox, *N,N'*-1,4-bis(mesityl) benzyl-diamine (0.20 g, 0.53 mmol) in dichloromethane (5 mL) was added with PCl_3 (460 μL, 5.30 mmol) and stirred for 0.5 hour at

room temperature. Triethylamine (0.3 mL, 2.10 mmol) was added to the mixture and the solution became cloudy with a white precipitate forming after 40 minutes. The mixture was stirred for additional 12 hours and vacuumed to dryness. The resulting white solid was added with 15 mL of hexane and stirred for 1.0 hour. The suspension was filtered. The filtrate was collected and dried under vacuum to yield moisture sensitive product (0.28 g, 89%). ^{1}H NMR (C_6D_6): δ = 7.20 (m, 2H), 7.11 (m, 2H), 6.78 (s, 4H), 4.19 (s, 4H), 2.23 (s, 6H), 1.23 (s, 12H). ^{13}C NMR (C_6D_6): δ = 138.8, 138.7, 138.4, 134.8 132.5, 129.9, 129.8, 49.1, 29.8, 20.5, 20.4, 18.8, 18.7. EI-MS (*m/z*): calcd for $C_{26}H_{30}Cl_4N_2P_2$: 572.0638, found: 572.0638. ^{31}P NMR (C_6D_6): δ = 154 ppm.

3.4.4 [(1,4-Diamido)^{Mes}P]$^{+}$ [OTf]$^{-}$ (**25**)

In a drybox, **15b** (0.33 g, 0.74 mmol) in toluene (5 mL) was added with TMSOTf (trimethylsilyl trifluoromethanesulfonate) (162 μL, 0.89 mmol) and stirred for 2.0 hours at room temperature. The mixture was vacuumed to dryness to afford the air and moisture sensitive product (368.0 mg, 90%). ^{1}H NMR (C_6D_6): δ = 6.91 (m, 2H), 6.67 (s, 4H), 6.55 (m, 2H), 4.80 (br. s, 4H), 2.26 (s, 12H), 2.03 (s, 6H). ^{13}C NMR (C_6D_6): δ = 138.1, 136.8, 136.7, 128.8, 128.2, 121.6, 119.9, 119.1, 115.8, 114.1, 112.9, 57.7, 20.4, 19.7. EI-MS (*m/z*): calcd for $C_{27}H_{30}F_3N_2O_3PS$ [M - OTf + H_2O]: 401.2141, found: 419.2190. ^{31}P NMR (C_6D_6): δ = 244 ppm.

3.5 References

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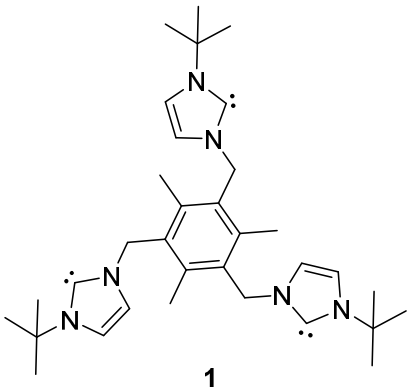
CHAPTER 4. TRI(*N*-HETEROCYCLIC CARBENE) PALLADIUM COMPLEXES

The project regarding (triNHC)Pd(II) (tri(*N*-heterocyclic carbene) palladium(II)) complexes was originally initiated by Tressia Paulose in the Foley group, and I have been involved in the continuation of the project after Tressia finished her assigned work. The continuing effort included reproducing and optimizing the synthesis of triNHC ligands, carrying out C-C coupling reactions with the resulting (triNHC)Pd(II) complexes and investigating into other variants of triNHC ligands.

4.1 Introduction

The structural characterization of isolable *N*-heterocyclic carbenes (NHCs) in 1991 laid the foundation for vigorous research in the design and applications of these ligands in organometallic chemistry.[67] The strong σ-donating property of the carbene carbons has made NHCs an excellent utility in coordination chemistry, especially as a ligand with transition metals. Over the last two decades, a wide variety of NHC ligands has been prepared resulting in a fast development of new catalysts for a wide variety of organic transformations.[114] Many of these catalysts exhibit among the highest activities known in their field.[115] While the majority of NHC complexes have involved monodentate NHCs, bidentate chelating NHC ligands (diNHCs) have also been widely researched, especially with regards to the formation of palladium complexes.[116] With respect to the research of triNHCs, it was shortly after Arduengo reported his stabilized NHC, Dias and Jin synthesized and isolated the first free triNHC **1** (Figure 4-1) wherein all NHCs were connected by a common aromatic linker. But, no metal complexation could be achieved with **1** as a ligand by the group.[117] Up to date, ligands containing three or more carbene units are still rare.



1

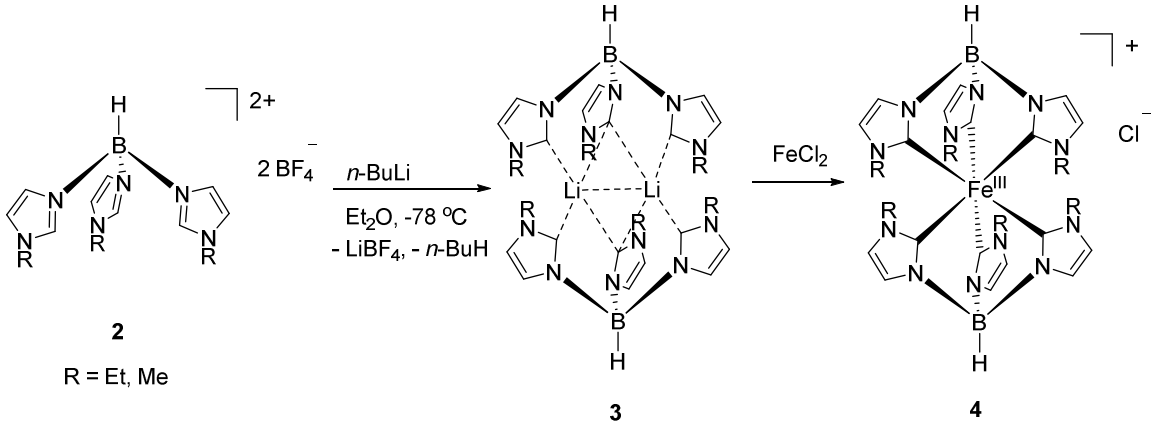
Figure 4-1. The first example of free triNHC.

While there have been some research groups searching for the possibility of using triNHCs as ligands, all of them are designed to coordinate in a pseudo-facial or tripodal mode and are better suited for tetrahedral or octahedral geometries. With regards to tripodal NHCs, representative examples were reported by the groups of Fehlhammer, Smith and Meyer.[80, 118]

Fehlhammer *et al.* introduced the carbene analogues of the tris(imidazolyl)borate ligands **2** (Scheme 4-1) in which the boron center was coordinated to three imidazoles as neutral donors.[80] Upon reacting with metal halides via *in situ* deprotonations with n-butyllithium, the triNHC ligand coordinated to various metals in a κ^3-coordination mode forming distorted octahedral complexes, such as the iron complex **4**. The free carbenes pertaining to **4** were unable to be isolated. It was shown by Fehlhammer that a carbene lithium complex was actually formed as an intermediate in the reaction. The presence of the intermediate was later confirmed by an isolation of the (triNHC-borate)$_2$Li$_2$ **3** (Scheme 4-1).[119] It was clear that the formation of complex **4** proceeded through salt metathesis of the lithium complexes with metal halides. Complex **4** showed a molecular structure of distorted octahedral geometry comprising two triNHC units in a mononuclear hexacarbene-metal complex. This is likely due to a lack of steric

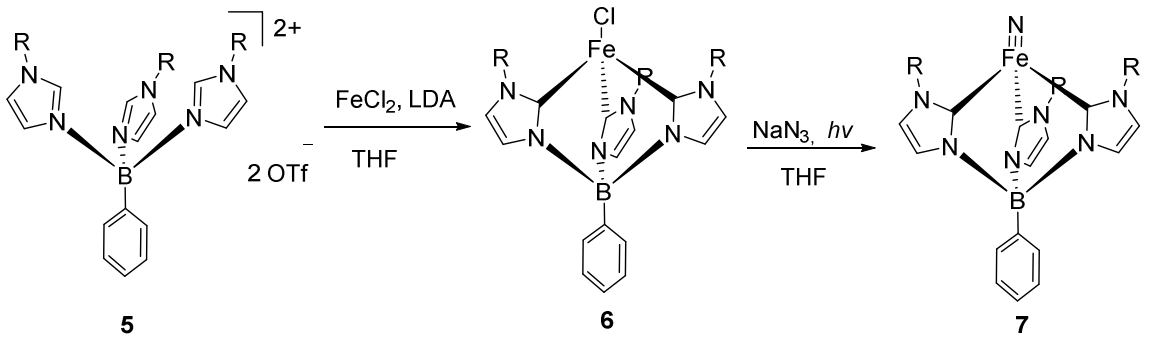
hindrance provided by the R groups (methyl or ethyl in Scheme 4-1) at the nitrogens (3-position) of the imidazol-2-ylidene rings. No further catalytic study has been reported with **4** as a catalyst possibly due to the lack of available coordination sites in the metal center.[119]

Scheme 4-1. Example of the synthesis of [(triNHC-borate)$_2$Fe^{III}]Cl complex.[119]



It was later demonstrated by Smith *et al.* that **2** can be tuned to its variant species **5** (Scheme 4-2) by introducing bulkier groups to the *N*-positions of the imdazolyl moieties and replacing the hydrido (H) group at the boron center with a phenyl. The sterically hindered **4** can then be complexed to iron as a 4-coordinate complex **6**. The formation of **6** versus **4** demonstrated the role of steric bulk in inhibiting the coordination of additional ligands. With respect to the application of a lower-coordination complex, Smith *et al.* has further shown that a (nitrido)Fe(IV) complex can be formed by treating **6** with sodium azide, and the resulting complex **7** was demonstrated to be a good catalyst for the formation of ammonia.[118b]

Scheme 4-2. Examples of mononuclear (triNHC)borate-metal complexes.[80, 118b]



5 **6** **7**

5a: R = mesityl
5b: R = tert-butyl

Pascu and Whittlesey *et al.* looked into the possibilities of modifying ligand **1** to complex with palladium precursors. The resulting complex **8** (Figure 4-2) was applied in C-C coupling reactions. Complex **8** is a trinuclear species with each NHC bound to a different palladium center.[82] Results of the Suzuki reactions showed that the highest catalytic activity can be obtained in a quantitative yield at 120 ^{o}C for 2 hour with **8b** as the pre-catalyst for the coupling of aryliodide and phenylboronic acid. Although Whittlesey has presented an example by applying a triNHC ligand in the formation of (triNHC)Pd_3 **8**, the utility of using a triNHC chelating ligand to form a tridentate palladium complex in a mononulcear form was not demonstrated.

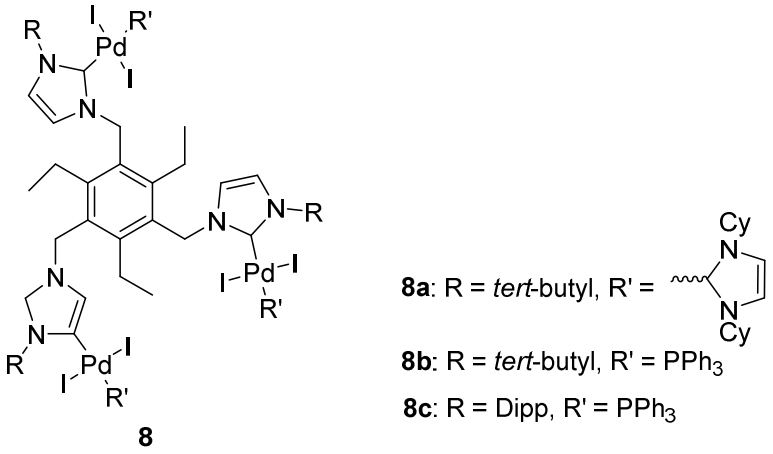


Figure 4-2. Tripodal [(NHC)Pd(II)]$_3$ complexes.

Meyer *et al.* further searched for the possibility of forming a mononuclear metal complex with **1** as the ligand. As a result, the relatively large cavity and rigid structure generated by this ligand can only accommodate very large metal ions, such as the thallium(I) cation.[81c] Complex **9** (Figure 4-3) displayed the coordination pattern of the resulting (triNHC)Tl(I) species.

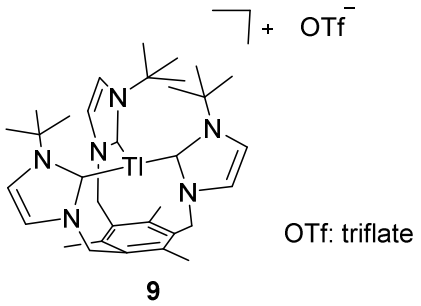


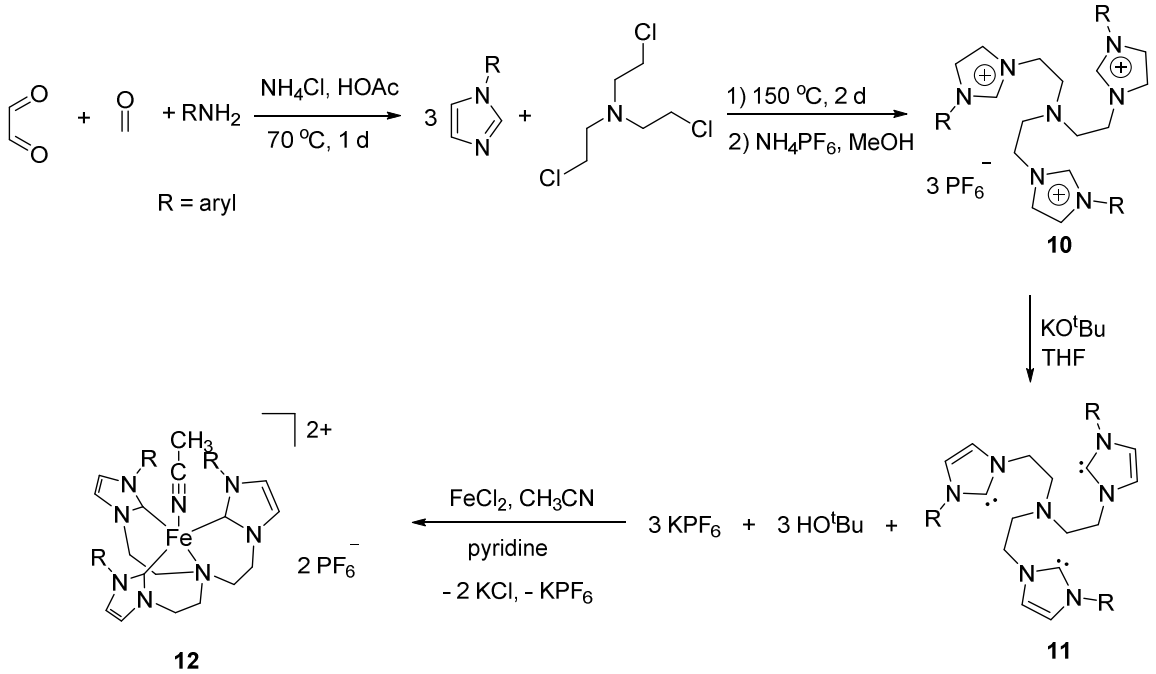
Figure 4-3. A mononuclear tripodal (triNHC)Tl(I) complex.

To expand the versatility of the ligand system structurally based on **1**, Meyer *et al.* reduced the size of the anchor element by replacing the mesityl linker group with a nitrogen and increased the linker length between the anchoring nitrogen and the carbenes. This modification

was aimed at forming a smaller cavity and a less rigid structure for coordination with transition metals of smaller sizes. As a result, the triNHC ligand **11** was formed and its corresponding mononuclear iron complex **12** (Scheme 4-3) can be prepared.

The synthesis of tridentate NHC ligands adopted by Meyer followed the similar routes leading to mono- and diNHC ligands. According to the synthesis scheme (Scheme 4-3), the most stable intermediate prior to the formation of triNHC ligands was the triimidazolium salt **10**, which can be stored over a prolonged period of time, and the synthesis as reported represented the typical route. Followed by a simple deprotonation step, a triNHC moiety **11** can be formed.[81a, 118d]

Scheme 4-3. Synthesis example of a triNHC-metal complex.



As detailed in Scheme 4-3, the synthesis of substituted imidazoles proceeded by a relatively simple route in which the formation of products was carried out in a one-pot reaction.

Although there are many substituted imidazoles commercially available, the synthesis as depicted (Scheme 4-3) is nevertheless the typical route when an in-house preparation is needed. Treatment of the resulting imidazoles in methanol with ammonium hexafluorophosphate results in a complete substitution of chloride and the formation of the triimidazolium salt **10**. Deprotonation of **10** with a strong base, e.g. potassium *tert*-butoxide, yields the free triNHC ligand **11**. It is difficult to remove the deprotonation by-product *tert*-butanol. However, this deprotonation step can be replaced by a transmetallaton route as will be described later in this chapter. Consequently, the coordination of **11** to $FeCl_2$ afforded the formation of the cationic complex **12**, $[(triNHC)Fe(II)(MeCN)]^{2+}$, which displays a geometry in that all carbene units coordinated to the metal center in a pseudo-facial mode.

In order to make the best use of the stabilizing ability of a triNHC ligand, it is preferred that a (triNHC)Pd(II) complex can be formed as a mononuclear species wherein all three NHC moieties coordinate to the metal center in a κ^3-*C,C,C* mode. Due to the fact that palladium accounts for about 1/4 of all complexes incorporating diNHC ligands, further investigations into the possibility of complexing triNHC ligands with palladium have been of interest in our group.

In summary, the predominant use of (NHC)Pd(II) complexes in catalyzing coupling reactions, especially C-C couplings, has attracted the attention of various groups to explore more insights into applying multidentate NHCs as a ligand. Although mono- and di(NHC)Pd(II) complexes have been extensively studied, the only triNHCs were all designed in a tripodal form and were not suited for the formation of tridentate mononuclear (triNHC)Pd(II) complexes. To further address the stabilization effects of multiple NHCs to their complexes with palladium, our goal was to synthesize an easily accessible tridentate chelating NHC ligand that could coordinate

to Pd in a meridional fashion, and thus making a triNHC ligand that is ideal for square planar geometries.[73a, 120]

4.2 Results and Discussion

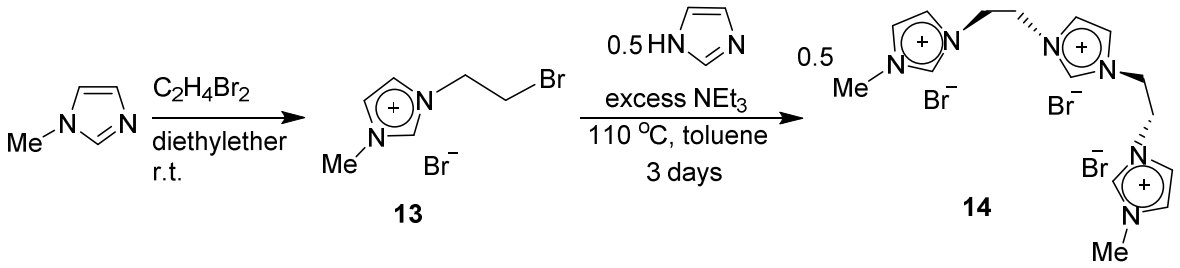
The synthesis and characterization of an air and moisture stable (triNHC) palladium(II) complex is described in this section. The commercially available *N*-methylimidazole was used to initiate the project by Tressia Paulose, and she has been successful in the preparation of the [(triNHC)^{Me}PdCl]Cl complex. I have been involved in the continuing investigations to apply the resulting complex in C-C coupling reactions and attempting to synthesize analogs of the complex with different *N*-substituents or counterions.

4.2.1 triNHC Ligands

The synthesis of triimidazolium salts has been previously reported by Dupont and Eberlin to study multiply charged radicals; however, the synthesis resulted in a yield of only 16% and it has never been used as a NHC ligand precursor.[120] The original preparation was carried out by treating **13** and imidazole at 2:1 stoichiometric ratio in acetonitrile at 60 ^{o}C for 2 days. Another procedure developed by Lee *et al.* produced a much higher yield of 79% for the synthesis of ethylene bridged diimidazolium salts.[121] The synthesis was a simple reflux in THF wherein 2 equivalents of *N*-methylimidazole and 1 equivalent of 1,2-dibromoethane were treated. Although the preparation reported by Lee was not for a triimidazolium salt, the method they developed afforded a much cleaner product that required no further purification, except a filtration step to isolate the solid product in the reaction mixture.[121]

By evaluating the synthesis routes provided by Lee and Dupont, I adopted a simple two-step process that optimized the yield and simplified the synthesis of the ethylene-bridged triimidazolium salt **14** as depicted in Scheme 4-4.

Scheme 4-4. Synthesis of an ethylene-bridged triimidazolium salt.



The synthesis was able to afford a yield of 80% for **14**. The first step involves the synthesis of 1-(2-bromoethyl)-3-methylimidazolium bromide **13** by the reaction of *N*-methylimidazole with dibromoethane in diethyl ether at room temperature. The formation of **13** was indicated by the gradual formation of precipitates in solution. In the second step, two equivalents of **13** were reacted with one equivalent of imidazole in the presence of excess triethylamine at 110°C for 3 days. The ethylene-bridged triimidazolium tribromide **14** slowly precipitates over the course of the reaction as a white solid in high purity after washing with THF (Scheme 4-4).

Although Dupont and Eberlin have synthesized and well characterized the triimidazolium salt **14** with spectroscopic evidences, I have further advanced the characterization by crystallographic methods.[120] Crystals of **14** suitable for single crystal X-ray analysis were obtained by slow diffusion of diethyl ether into a concentrated solution in DMF (Figure 4-4). The triimidazolium salt co-crystallized with one molecule of water in the unit cell due to wet DMF being used in the crystallization. In the crystal structure, one of the terminal imidazolium rings is in an *anti* configuration with respect to the bridging imidazolium ring, while the other terminal imidazolium ring has a *syn* relationship with the bridging ring. The three bromide ions form hydrogen bonds with the three carbenic hydrogen atoms on the C2 positions of the imidazolium

rings with an average H···Br distance of 2.868 Å. The *syn* configuration of the two imidazolium rings likely arises from the incorporation of the water molecule which engages in hydrogen bonding with only the two bromides that are hydrogen bonding to the *syn*-oriented imidazolium rings (average OH···Br distance is 2.605 Å). A *syn*-orientation of imidazolium rings due to the presence of water was also observed in the reported structure of an ethylene-bridged bisimidazolium salt.

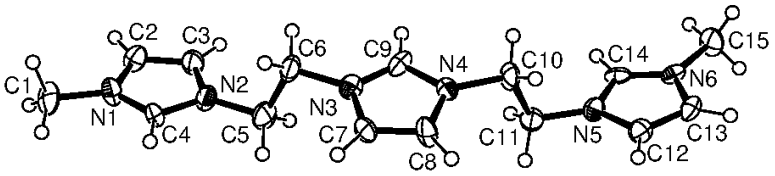


Figure 4-4. ORTEP plot **14**·H_2O at the 50% probability level. The bromide anions and water molecule are omitted for clarity.

4.2.2 Dimethyl triNHC Palladium Complex, [(triNHC)^{Me}PdCl]Cl

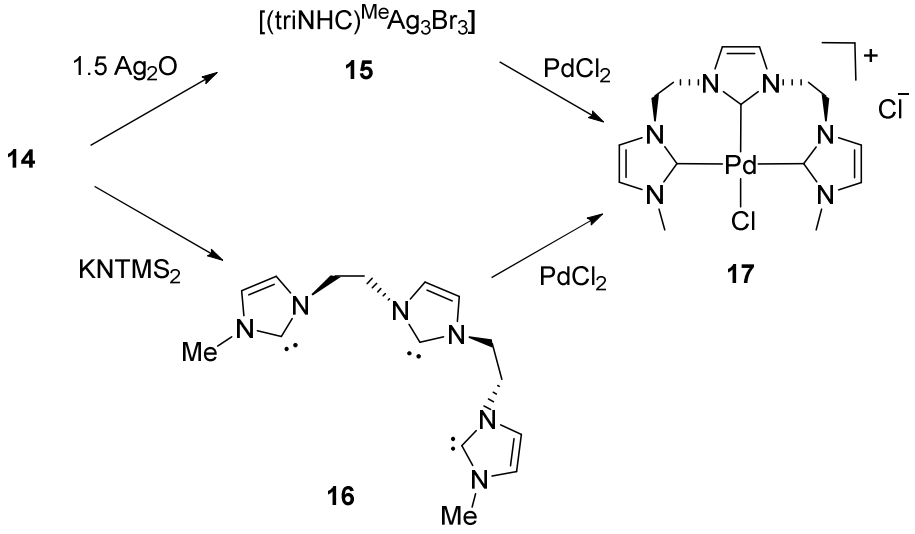
In general, there are two common routes that lead to the formation of NHC-metal complexes. These are free carbene and silver transmetallation routes as illustrated in Scheme 4-5. The free carbene route proceeds through **16** as a free carbene after deprotonation of **14** with a strong base, such as $KNTMS_2$ (potassium bis(trimethylsilyl)amide). Following a coordination with a Pd(II) source $PdCl_2$, complex **17** is anticipated. On the other hand, literature precedents have suggested a silver transmetallation route, in which a stable silver carbene complex **15** is formed and can be stored over an extended period of time.[122]

Upon evaluation of the two alternative routes in Scheme 4-5, the silver transmetallation route was chosen. As expected, the [(triNHC)^{Me}PdCl]Cl complex **17** was successfully

synthesized via the transmetallation route using (triNHC)$^{Me}Ag_3Br_3$ complex **15** as the transmetallating reagent (Scheme 4-5) The advantage of using the sliver carbene **15** as the carbene transfer reagent is its simple preparation and ease of handling due to its high stability in air.

The silver carbene (triNHC)$^{Me}Ag_3Br_3$ (**15)** can be formed by reacting **14** with 1.5 equivalent of Ag_2O in the absence of light at room temperature, based on literature procedures for mono and diNHC complexes of silver.[122b]

Scheme 4-5. Synthesis of [(triNHC)^{Me}PdCl]Cl.



The silver complex **15** is sparingly soluble in highly polar solvents such as DMF and DMSO and displays remarkable stability towards heat, light, air and moisture. The ^{1}H NMR spectra of **15** show the absence of any signal between 8-10 ppm indicating the successful deprotonation of triimidazolium salt **14** (Figure 4-5). The bridging ethylene protons in **15** now appear as two multiplets at 4.55 and 4.40 ppm, each integrating for four protons as compared to

the singlet obtained for **14** at 4.75 ppm for 8 protons. No further structural characterization of the silver salt was carried out and it was used as is to form a (triNHC)^{Me}Pd(II) complex.

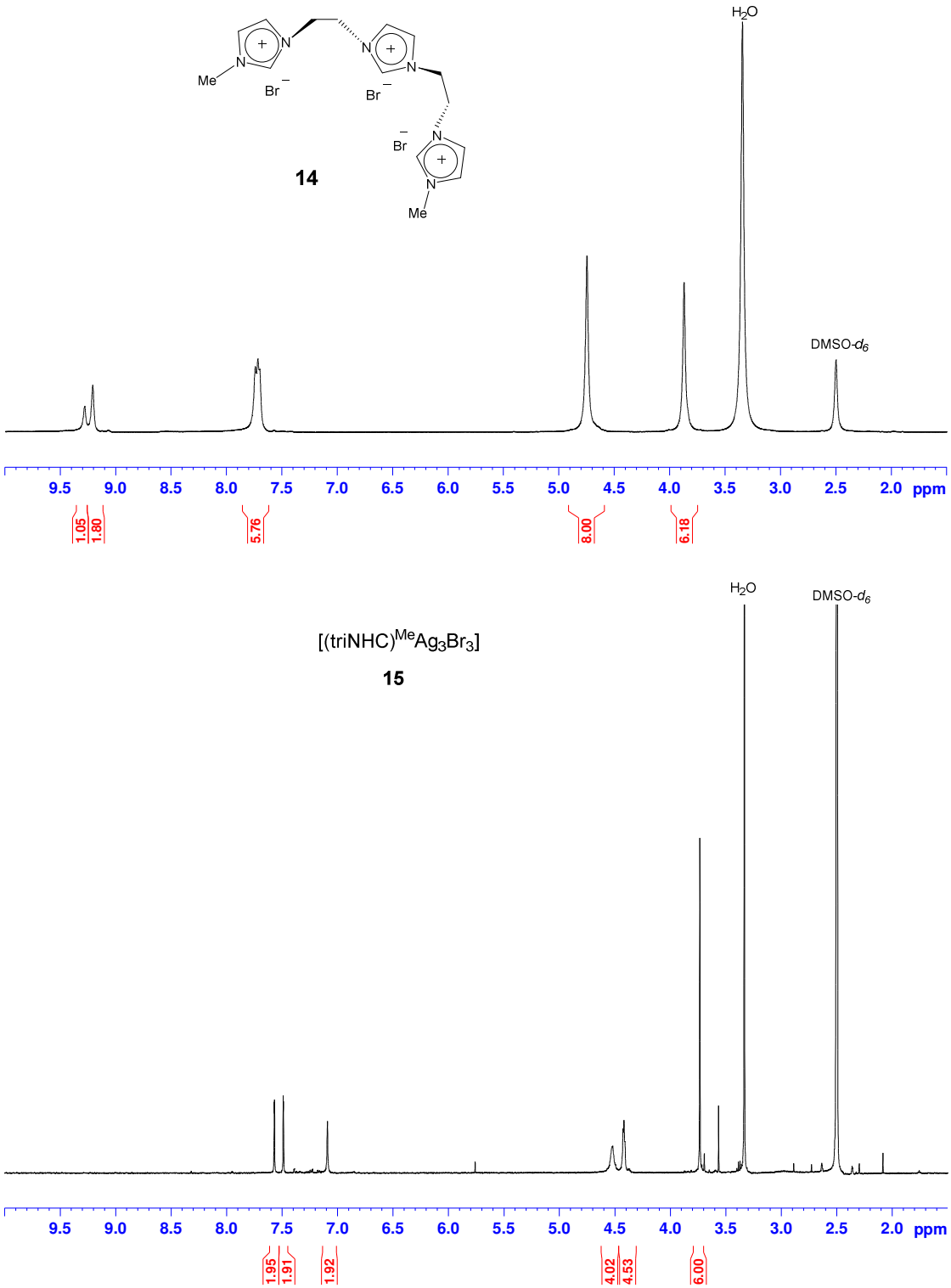
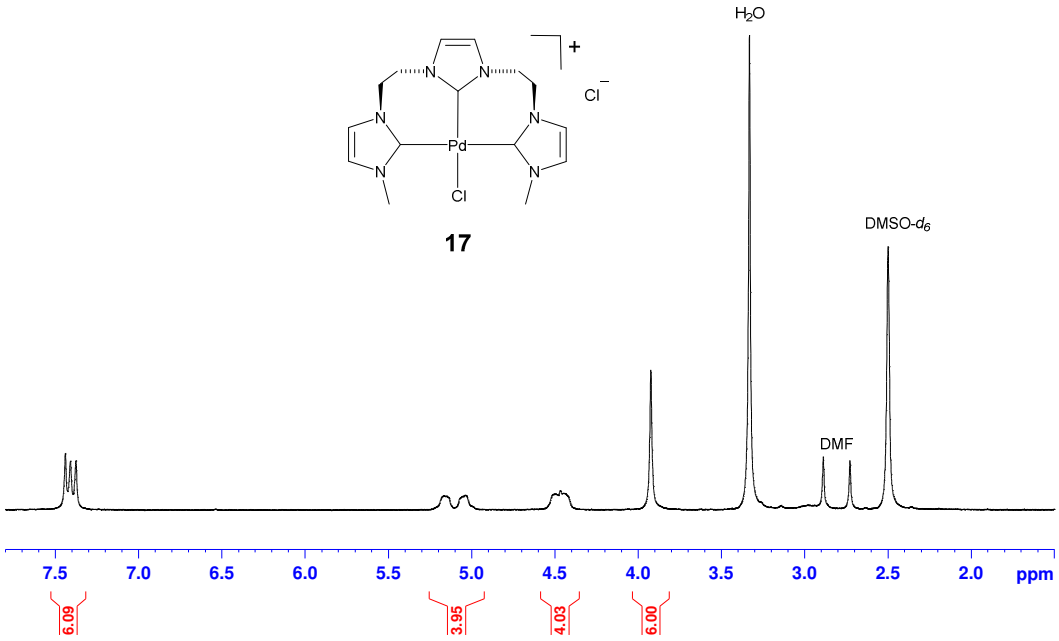


Figure 4-5. ^{1}H NMR spectra of **14** and **15** in DMSO-d_6.

Subsequent reaction of the silver complex **15** with one equivalent $PdCl_2$ in DMF at 90 °C for 24 h afforded [(triNHC)^{Me}PdCl]Cl (**17**) as a yellow solid at 55% yield. The triNHC ligand coordinates to the Pd center in a chelating κ^3-*C,C,C* mode as determined by NMR spectroscopy, with all data consistent with **17** being a C_s symmetric species where the two terminal imidazolylidenes are symmetry-related. For example, there was only one singlet at 3.9 ppm in the ^{1}H NMR spectra in DMSO-d_6 for the two methyl groups integrating for six protons and three singlets at 7.35, 7.40 and 7.45 ppm, each integrating for two protons, for the remaining imidazolylidene protons (Figure 4-6). In the ^{13}C NMR spectra there are two signals for the carbenic carbons (N*C*N) at 167 and 154 ppm consistent with the two terminal and one bridging imidazolylidenes. The ethylene protons show up as four discrete doublet of doublet of doublets in the ^{1}H NMR spectrum at 5.16, 5.04, 4.50 and 4.46 ppm, each integrating for two protons, which is indicative of limited fluxionality in the ligand backbone on the NMR timescale.



17

Figure 4-6. ^{1}H NMR spectra of **17** in DMSO-d_6.

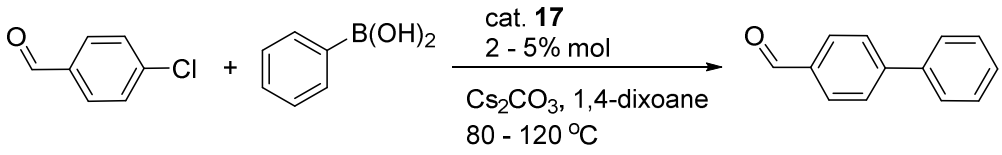
The elemental analysis is consistent with the proposed formula, [(trisNHC) ^{me}PdCl]Cl, and the mass spectra of **17** show an intense molecular ion peak at m/e 425, consistent with formation of the monocationic [(trisNHC)^{Me}PdCl]$^{+}$ ion. The thermal stability of **17** was evaluated using thermogravimetric analysis. The (triNHC) ^{me}Pd complex showed exceptional thermal stability with decomposition occurring at 260°C. A common problem with alkyl-bridged diNHC complexes is their poor solubility with crystals typically needing to be grown from hot DMSO or DMF layered with a less-polar solvent. [(triNHC) ^{me}PdCl]Cl complex **17** is no exception as it is sparingly soluble only in DMF and DMSO with no observable solubility in toluene, ether, THF, acetonitrile or CH_2Cl_2. I was unable to grow crystals suitable for X-ray analysis.

4.2.3 [(triNHC)^{Me}Pd]Cl Complex in C-C Coupling Reactions

The Heck or Suzuki coupling of aryl bromides with olefins or phenylboronic acid is relatively trivial, with TONs often reported in the hundred thousand or even million range.[123] The analogous coupling with aryl chlorides is much more difficult with turnover numbers (TONs) usually in the hundreds.[124] Monodentate NHC complexes of palladium are much more active than reported alkyl-bridged diNHCs, with one of the most active systems developed by Nolan and capable of coupling deactivated aryl chlorides with arylboronic acids at room temperature in 1-24 hours with TONs up to 1000.[125] Alkyl-bridged (diNHC)Pd complexes have reported TONs anywhere from 0 to 35 for aryl chlorides, significantly lower than their monoNHC counterparts.[126] The decreased activity of diNHC complexes is presumably due to the entropic stability afforded by the chelating NHC ligand. Consistent with this trend, attempts to use

[(triNHC)^{Me}PdCl]Cl complex **17** to couple *para*-chlorobenzaldehyde with phenylboronic acid at 80°C over 24 hours using Cs_2CO_3 as base in DMSO or 1,4-dioxane as solvent resulted in no coupled product (Scheme 4-6). Further optimizations in the reaction conditions by varying catalyst loadings to 5% mol as well as increasing reaction temperatures to 120°C did not afford any product.

Scheme 4-6. Conditions for the Suzuki coupling reactions.



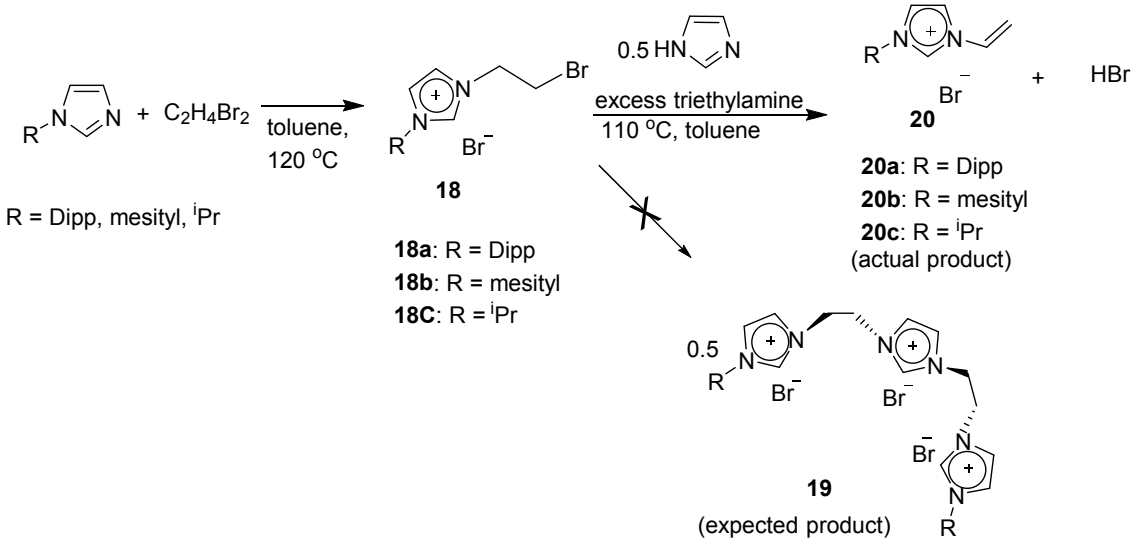
4.2.4 Attempts to Synthesize Variants of Complex **17**.

The initial goal of achieving a complex in a chelating κ^3-*C,C,C* mode of coordination as presented by **17** in a square planar geometry was successful in that methyls being the *N*-substituents and Cl being the counterion for the ionic complex. However, in the actual application of the resulting complex in the Suzuki and Heck coupling reactions, **17** showed no activity. Apart from the most possible reason of being the high thermal stability that **17** demonstrated, another probable reason could be the poor solubility that I have observed when **17** was subjected to various reaction conditions. Therefore, I devised alternative strategies by changing the *N*-methyl substituents to other groups or the Cl counterion to an acetate in an attempt to increase the solubility of the resulting complexes in common organic solvents.

The proposed synthesis of *N*-substituted triimidazolium salts was depicted in Scheme 4-7. The synthesis was commenced by using Dipp (2,6-diisopropylphenyl) and mesityl (2,4,6-trimethylphenyl) as the R groups because *N*-Dipp- and *N*-mesitylimidazoles have been employed

as common NHC precursors for their high steric bulk and solubility. An alternative alkyl substituted imidazole *N*-isopropylimidazole was also employed to substitute for the *N*-methyl analogue. The synthesis route followed that leading to the formation of **14**.

Scheme 4-7. Attempted synthesis of *N*-substituted triimidazolium salt.

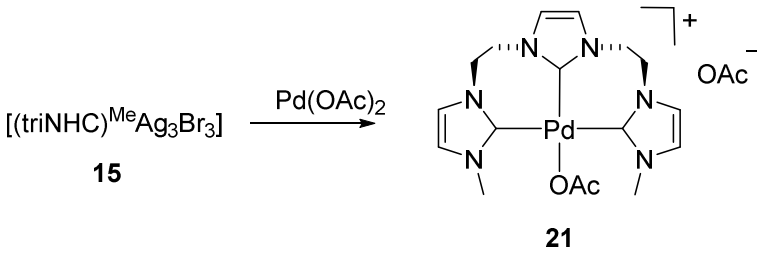


As a result of the proposed synthesis (Scheme 4-7), I was unable to obtain the expected product **19** because it consistently resulted in **20** as the major product. Supported by ^{1}H NMR spectra (in $CDCl_3$) of the resulting products, e.g. **20a**, the terminal olefinic protons appeared as two doublet-of-doublets at 5.45 and 5.95 ppm, whereas the olefinic proton connected to the alpha-carbon appeared at 8.13 ppm as another doublet-of-doublets. Coupled with a mass spectrum of the resulting products, it showed an intense molecular ion peak at m/e 255, the spectral evidences were consistent with the formation of **20a**. Some unidentifiable side products from the reaction were observed. None of the continuing efforts made to remedy the synthesis based on Scheme 4-7 in favor of **19** formation has been successful, such as changing the reaction

solvents, using different bases or varying the reaction temperatures. As the results suggested, it was postulated that elimination reactions dominated over the expected substitution routes, and favored the formation of terminal alkenes.

It has been known that $Pd(OAc)_2$ exhibits a better solubility than $PdCl_2$ in most organic solvents. Changing the counterion from Cl to acetate for the (triNHC)Pd(II) complex could be another strategy to increase the solubility of **17**. A structure was proposed as $[(triNHC)^{Me}Pd(OAc)](OAc)$ **21** (Scheme 4-8) and the synthesis followed that for **17** through silver transmetallation route.

Scheme 4-8. Synthesis of $[(triNHC)^{Me}Pd(OAc)]OAc$ complex.

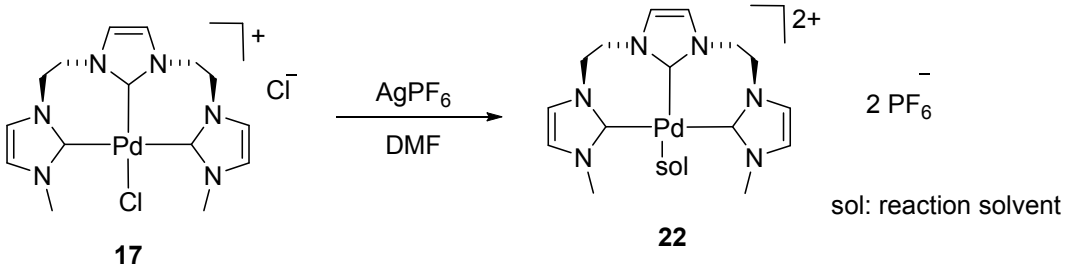


As a result, spectroscopic evidences (Figure 4-7) were consistent with the formation of **21.** The two *N*-methyl groups appeared as one singlet integrating for six protons at 3.80 ppm in the ^{1}H NMR spectra in DMSO-d_6. Two singlets at 1.70 and 1.66 ppm each integrating for three protons for the coordinated and free acetate methyls. The bridging ethylene protons are two multiplets at 5.17 and 4.46 ppm, each integrating for four protons. Imidazolylidene protons appeared as three discrete singlets at 7.32, 7.39 and 7.43 ppm, each integrating for two protons (Figure 4-7a). In the ^{13}C NMR spectra for **21**, there are two signals for the carbenic carbons (N*C*N) at 167 and 154 ppm representing the two terminal and one bridging imidazolylidenes

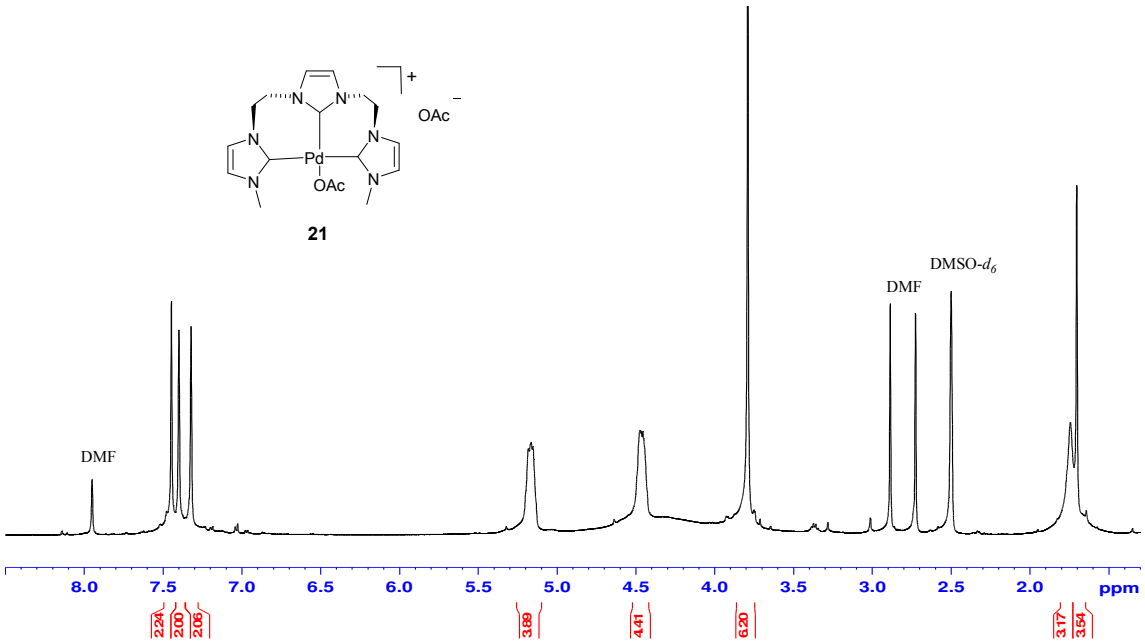
(Figure 4-7b). The mass spectra of **21** showed a major molecular ion peak at m/e 449, consistent with formation of the monocationic [(trisNHC) ^{me}Pd(OAc)]$^{+}$ ion. Compared to **17**, the solubility of **21** in organic solvents was slightly improved by visual observations.

Additional experiments (Scheme 4-9) were attempted to change the counterion from Cl to PF_6, which is known for its non-coordinating and solubility enhancing properties to a metal complex. Consequently, I was unable to characterize the anticipated product **22** by obtaining unambiguous NMR spectra, and the reaction products appeared as oily liquid.

Scheme 4-9. Attempted synthesis of [(triNHC)Pd] $(PF_6)_2$.



a. ^{1}H NMR spectra of **21.**



b. ^{13}C NMR spectra of **18.**

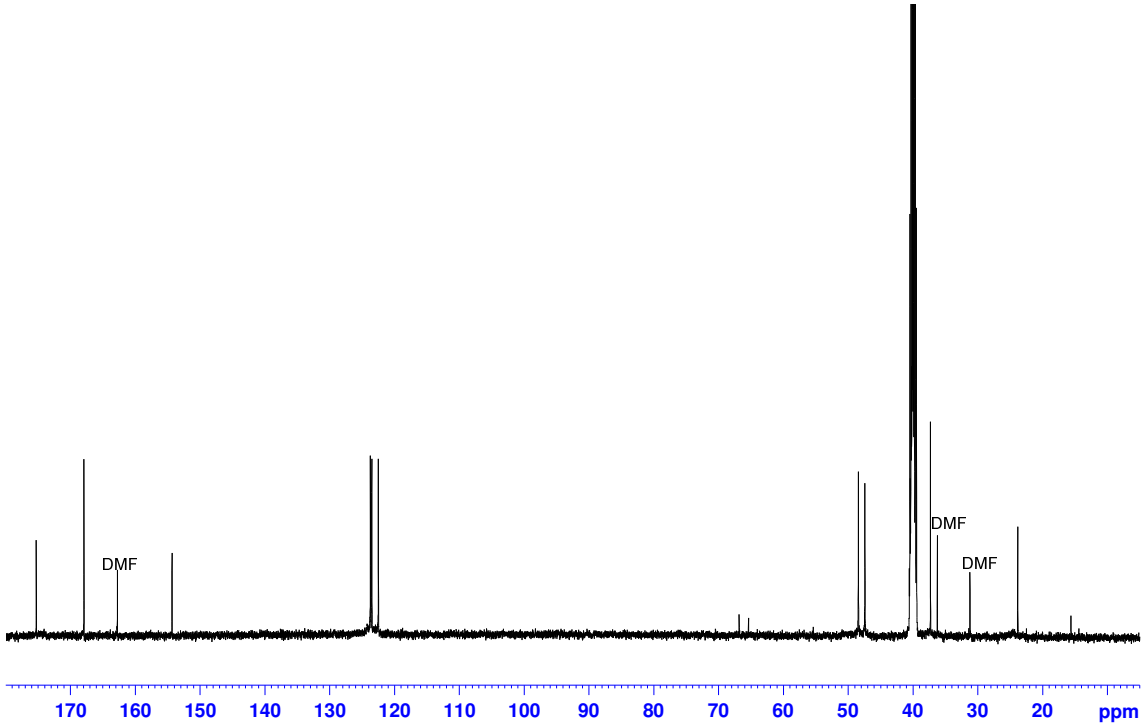


Figure 4-7. NMR spectra of **18** in DMSO-d_6.

Subsequent applications of **21** as a pre-catalyst in the Suzuki and Heck coupling reactions afforded no product yields. Unlike **17** in catalytic reactions, **21** was observed more soluble in the reaction mixtures; therefore, the solubility issue that inhibited the reactivity of the resulting complexes, **17** and **21**, as a pre-catalyst is not the only contributing factor. Obviously, the exceptional stability of the complexes conferred by the triNHC ligand plays an important role that afforded no catalytic activity in C-C coupling reactions.

4.3 Summary and Conclusion

In summary, I have synthesized ethylene-bridged triNHC complexes of palladium wherein all three NHC moieties coordinate meridionally in a chelating fashion. The resulting [(triNHC)PdCl]Cl **17** and [(triNHC)Pd(OAc)](OAc) **21** complexes are thermally robust and show no activity in Suzuki and Heck coupling chemistry for the coupling of aryl chlorides with phenylboronic acid. The main problems with the complexes are their very poor solubility properties and high structural stabilities.

Further attempts to change the *N*-substituents were unsuccessful due to synthetic issues (Scheme 4-7). The main possible reason could be attributed to the competition between substitution and elimination reactions. For a reason not clear, when the *N*-substituent was replaced with a group other than a methyl, elimination dominated over substitution reaction and afforded terminal alkenes **20** as the major product. It was once assumed that the addition of base, such as triethylamine, promoted the elimination route; however, a trial experiment without adding any base still led to the same results. Additional work to replace the counterion Cl in **17** to OAc (acetate) was conducted and concluded in the formation of **21**. Although **21** was slightly more soluble than **17** in common organic solvents, it showed no activity in C-C coupling reactions.

In conclusion, **17** and **21** were the first mononuclear (triNHC)Pd(II) complexes that showed a meridional pattern in a square planar geometry with all three carbenic carbons coordinated to Pd.[127]

4.4 Experimental

General Information. Unless otherwise stated, all reactions were performed under N_2 or vacuum using standard Schlenk techniques or in a N_2-filled drybox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated oil or sand baths. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.24), C_6D_6 (^1H: δ 7.16; ^{13}C: δ 128.06) and DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.52). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR data was collected by Diffuse Reflectance Spectroscopy. Triethylamine was dried by treating with calcium hydride and distilling prior to use. Ag_2O was purchased from Alfa-Aesar Chemical Companny and used as received. Reagents such as imidazole, 2,6-diisopropylaniline (Dipp), 2,4,6-trimethylaniline (mesityl), *N*-methylimidazole and 1,2-dibromoethane, were purchased from Sigma-Aldrich Chemical Company and used as received except for 2,6-diisopropylaniline which was distilled prior to use. $PdCl_2$ and $Pd(OAc)_2$ were purchased from PMO Pty Ltd, Australia and used as received.

4.4.1 Synthesis of 1-(2-Bromoethyl)-3-methyl-1*H*-imidazol-3-ium bromide (**13**)

A 250-mL round bottom flask was charged with a stir bar, *N*-methylimidazole (1.10 mg, 24.4 mmol), 30 mL diethyl ethter and 1,2-dibromoethane (12.7 mL, 146.0 mmol) at ambient conditions. The mixture was stirred for 2 days and white precipitates were formed. The collection of product was by filtering the reaction mixture and isolation of the solid. The collected solid was washed with diethyl ether (15 mL x 3) and vacuumed to dryness to yield air and moisture stable product. The filtrate was transferred to another 250-mL round bottom flask

and stirred for another day. Collection of product was repeated for the subsequent 2 days to yield combined product **13** (2.5 g, 39%). ^{1}H NMR (DMSO-d_6): δ = 9.21 (s, 1H, NC*H*N)), 7.83 (s, 1H, CC*H*N), 7.76 (s, 1H, NC*H*C), 4.62 (dd, J = 5.5 Hz, 2H, NCH_2C), 4.03 (dd, J = 5.5 Hz, 2H, CCH_2Br), 3.94 (s, 3H, CH_3).

4.4.2 Synthesis of (triNHC)^{Me} Ligand (**14**)

A Schlenk flask was charged with a mixture of imidazole (0.1 g, 1.47 mmol), **13** (0.8 g, 2.94 mmol), NEt_3 (0.5 mL) and toluene (20 mL) and was stirred at 110 ^{o}C for 3 d under dinitrogen. A white precipitate was isolated, washed with THF (3x15 mL) and dried under vacuum to yield **14** as a white powder (0.62 g, 80%). ^{1}H NMR (DMSO-d_6): δ = 9.31 (s, 1H, NC*H*N), 9.23 (s, 2H, NC*H*N), 7.74 (s, 2H, CH_{imid}), 7.71 (s, 2H, CH_{imid}), 7.69 (s, 2H, CH_{imid}), 4.74 (s, 8H, NCH_2CH_2N), 3.87 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): δ = 137.2 (3C, N*C*HN), 123.9 (2C, *C*H_{imid}), 122.8 (2C, *C*H_{imid}), 122.4 (2C, *C*H_{imid}), 48.6 (2C, N*C*H_2*C*H_2N), 48.1 (2C, N*C*H_2*C*H_2N), 36.1 (2C, *C*H_3). ESI-MS (*m/z*): calcd for $C_{15}H_{23}Br_3N_6$ $[M\text{-}Br]^+$: 447.0332, found: 447.0461.

Crystal data for **14**·H_2O: $C_{15}H_{25}Br_3N_6O$, FW = 545.14, colorless, triclinic, space group *P*-1, a = 7.2455(4) Å, b = 9.0825(5) Å, c = 16.1017(9) Å, α = 87.026(3)^{o}, β = 83.576(4)^{o}, γ = 86.089(5)^{o}, Z = 2, ρ_{calc}: 1.725 Mg/m^3, 12303 collected reflections, 3699 unique (R_{int} = 0.1003), Final R indices [I > 2σ(I)] were R1 = 0.0731, wR2 = 0.2019. Data was collected at -100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program. Cell refinement and data reductions used the programs DENZO and SCALEPACK. SHELXS-97 was used to solve the structures and SHELXL-97 was used to refine the structures. ORTEP-3 for Windows was used for molecular graphics and PLATON was used to prepare material for publication. H atoms

were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

4.4.3 Synthesis of (triNHC)^{Me} Ag_3Br_3 (**15**)

A suspension of **14** (0.6 g, 1.08 mmol) and 1.5 equivalent of Ag_2O (0.38 g, 1.62 mmol) in dichloromethane (5 mL) was stirred at room temperature for 1 day under dinitrogen in the absence of light. The color of the suspension gradually changed from black to light brown. The precipitate was isolated, washed with dichloromethane (5 mL x 3) and dried under vacuum to yield **15** as a light brown powder (0.84 g, 91%) ^{1}H NMR (DMSO-d_6): δ = 7.57 (s, 2H, CH_{imid}), 7.49 (s, 2H, CH_{imid}), 7.09 (s, 2H, CH_{imid}), 4.52 - 4.47 (m, 4H, NCH_2CH_2N), 4.57 - 4.48 (m, 4H, NCH_2CH_2N), 3.73 (s, 6H, CH_3).

4.4.4 Synthesis of [(triNHC)^{Me}PdCl]Cl (**17**)

A suspension of **15** (0.18 g, 0.21 mmol) and $PdCl_2$ (0.04 g, 0.21 mmol) in DMF (5 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a pale yellow precipitate was obtained which was filtered and dried under vacuum to yield **17** as a yellow powder (0.06 g, 56%). ^{1}H NMR (DMSO-d_6): δ = 7.44 (s, 2H, CH_{imid}), 7.41 (s, 2H, CH_{imid}), 7.37 (s, 2H, CH_{imid}), 5.16 (ddd, J = 15 Hz, 7.1 Hz, 3.5 Hz, 2H, NCH_2CH_2N), 5.04 (ddd, J = 15 Hz, 7.1 Hz, 3.5 Hz, 2H, NCH_2CH_2N), 4.50 (ddd, J = 15 Hz, 7.1 Hz, 3.5 Hz, 2H, NCH_2CH_2N), 4.46 (ddd, J = 15 Hz, 7.1 Hz, 3.5 Hz, 2H, NCH_2CH_2N), 3.92 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): δ = 167.1 (N*C*N), 154.8 (N*C*N), 124.1, 123.8, 122.5 (*C*H$_{imid}$), 48.5 (N*C*H$_2$CH$_2$N), 47.3 (NCH$_2$*C*H$_2$N), 38.8 (*C*H$_3$). HRMS

(*m/z*): calcd for $C_{15}H_{20}Cl_2N_6Pd$ $[M\text{-}Cl]^+$: 425.0473, found: 425.0485. Anal. Calcd for $C_{15}H_{20}N_6PdCl_2$: C 39.02; H 4.37; N 18.20. Found: C 38.77; H 4.59; N 17.87.

4.4.5 Synthesis of $[(triNHC)^{Me}Pd(OAc)](OAc)$ (**18**)

A suspension of **15** (1.5 g, 1.77 mmol) and $Pd(OAc)_2$ (0.4 g, 1.77 mmol) in DMF (25 mL) was stirred at 90 ^oC for 24 h under dinitrogen. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a pale yellow precipitate was obtained which was filtered and dried under vacuum to yield **18** as a yellow powder (0.48 g, 51%). ^1H NMR (DMSO-d_6): δ = 7.43 (s, 2H, CH_{imid}), 7.39 (s, 2H, CH_{imid}), 7.32 (s, 2H, CH_{imid}), 5.17 (dd, J = 15 Hz, 6.0, 2H, NCH_2CH_2N), 4.46 (dd, *J* = 15 Hz, 6.0 Hz, 2H, NCH_2CH_2N), 3.79 (s, 6H, CH_3), 1.70 (s, 3H, CH_3CO), 1.66 (s, 3H, CH_3CO). ^{13}C NMR (DMSO-d_6): δ = 174.8 (C*C*O),167.4 (N*C*N), 153.9 (N*C*N), 123.3, 123.1, 122.0 (*C*H$_{imid}$), 47.9 (N*C*H$_2$CH$_2$N), 46.9 (NCH$_2$*C*H$_2$N), 36.8 (*C*H$_3$), 23.4 (*C*CO). HRMS (*m/z*): calcd for $C_{19}H_{29}N_6O_4Pd$ $[M\text{-}OAc]^+$: 449.0895, found: 449.0920.

4.4.6 Attempted synthesis of $[(triNHC)^{Me}Pd(PF_6)](PF_6)$ (**22**)

A suspension of **17** (0.50 g, 1.08 mmol) and $AgPF_6$ (0.55 g, 2.16 mmol) in DMF (5 mL) was stirred at room temperature for one hour under dinitrogen. The solution was then filtered to remove the AgCl precipitate. The filtrate was collected and vacuumed to a constant weight. The product **22** was an oily liquid (0.76 g, 93%). ^1H NMR (DMSO-d_6): δ = 7.95 (s, 1H), 7.50 (s, 2H), 7.46 (s, 2H), 7.40 (s, 2H), 5.50 - 4.30 (br. s, 8H), 3.95 (s, 6H), 2.92 (s, 3H), 2.80 (s, 3H).

4.5 References

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CHAPTER 5. SUMMARY, CONCLUSIONS AND FUTURE WORK

The research concluded in this thesis consists of results from three areas: i) successful applications of 1,2-diamido- and 1,4-diamido ligands in forming aluminum complexes, of which the latter displays a 3-coordinate geometry and shows exceptional activities in the ROP of ε-caprolactone when used as a single component catalyst, ii) extending the application of chelating diamido ligands to form novel 7-member 3-coordinate NHP (*N*-heterocyclic phosphine) and 2-coordinate NHP^+ cations (phosphenium cations) for their potential applications in coordination chemistry, iii) successful synthesis of the first chelating κ^3–triNHC ligand that can coordinate to palladium to form a novel (triNHC)Pd(II) complex in a meridional fashion, which shows extraordinary stability provided by the triNHC ligands.

Included in this chapter are brief summaries, conclusions and recommended future works for the three areas of research described above.

5.1 Low-coordinate (Diamido)aluminum Complexes for Applications in Lactone Polymerizations

5.1.1 Summary and Conclusions

The goal of this aluminum-related project was composed of two parts. First, I sought to design neutral 3-coordinate aluminum complexes because there has not been many 3-coordinate aluminum complexes reported active in the ROP of cyclic esters. In addition, the high abundance and low cost of aluminum is of great advantage if an aluminum complex could be made active in the ROP of cyclic esters to be used as biodegradable polymers. Although 3-coordinate aluminum ionic complexes had been reported and investigated for their catalytic activities, none were reported active in the ROP of cyclic esters.[27-28, 128]

Complex **1** (Figure 5-1) presented by Chen *et al.* was the first and only neutral 3-coordinate aluminum species highly active in the ROP of ε-caprolactone.[31]

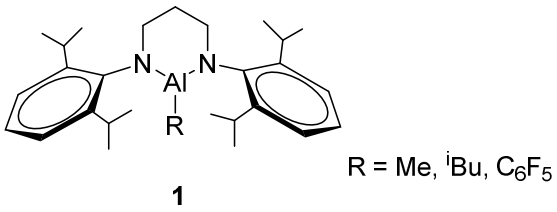


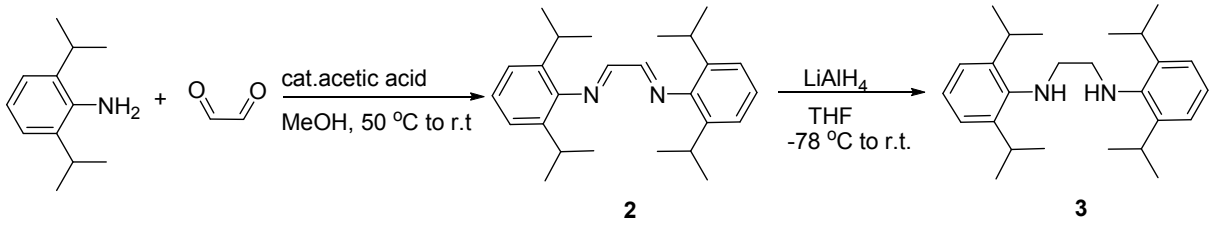
Figure 5-1. The first neutral 3-coordinate (diamido)AlR complex

I was interested in exploring more insights into the structure-reactivity of Al complexes in the ROP of cyclic esters based on the effects of different ring sizes that comprise the compelxes. In addition to the 3-coordinate geometry around Al center, which was thought to contribute significantly to its high activity in the ROP of ε-caprolactone, the bite angle (N-Al-N)

of the complex could be of great influence as larger bite angles may increase the dissociation rate of R groups from Al center, and thus increase the catalytic activity. The strategy to changing the bite angle is to prepare analogous Al complexes in different ring sizes, such as 5- and 7-member rings through different ligand designs. With the existing 6-member Al complex **1**, I devised to prepare 5-member and 7-member complexes with 1,2- and 1,4-diamido ligands, respectively.

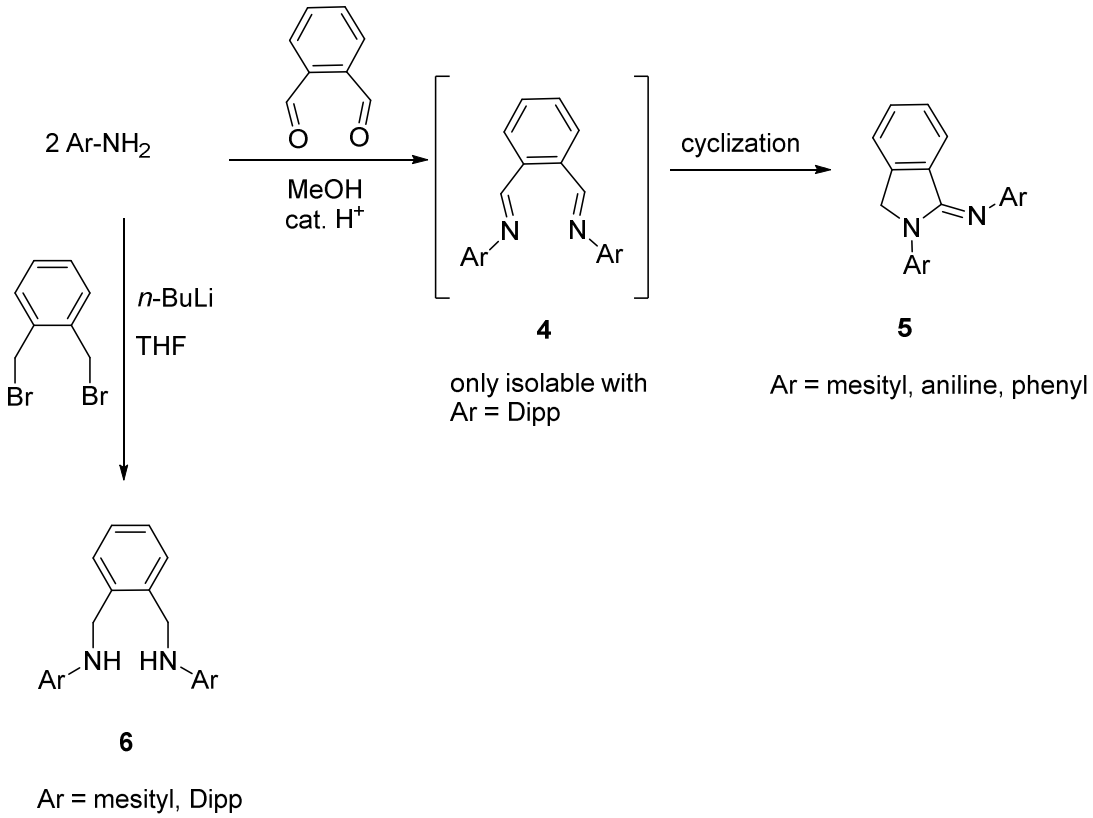
The 1,2-diamine can be formed through an isolable 1,2-diimine intermediate **2**, which was then reduced to afford the formation of 1,2-diamine **3** (Scheme 5-1).

Scheme 5-1. Synthesis of 1,2-diamines.



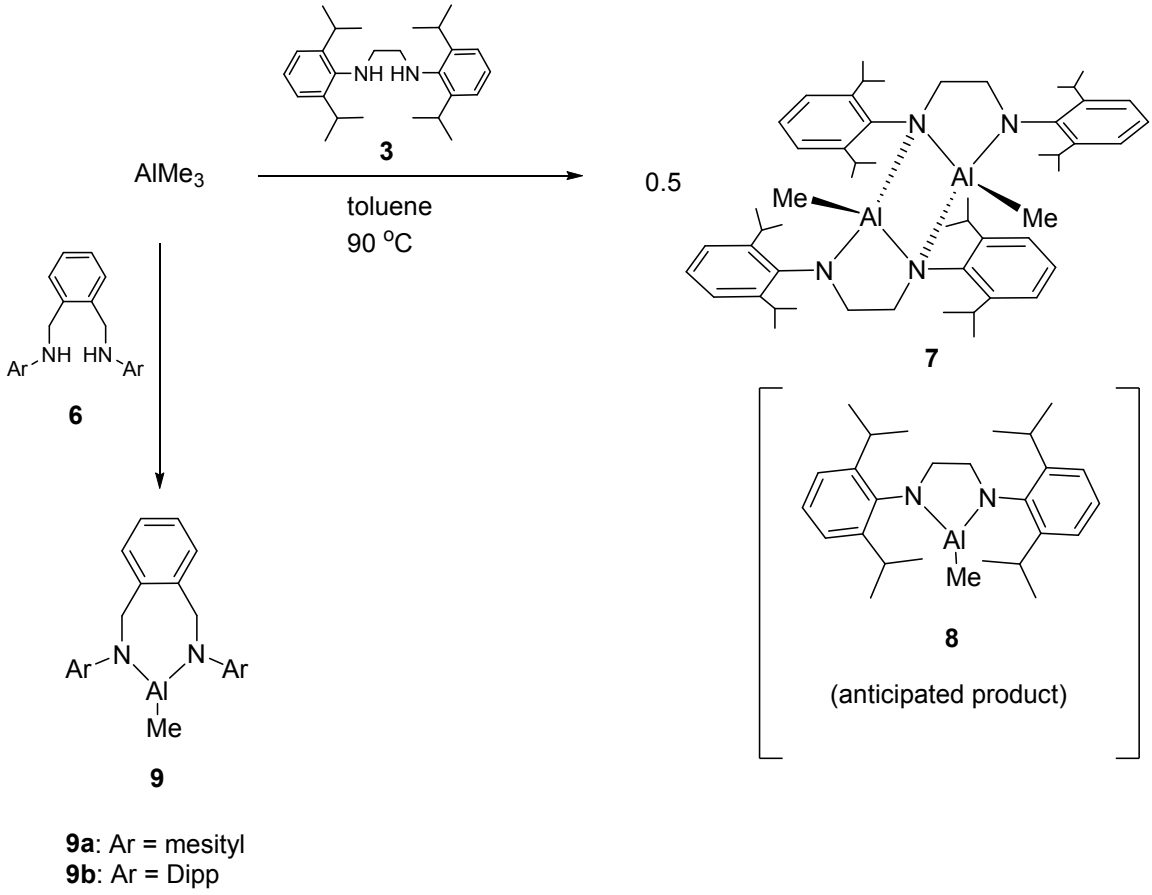
However, the simple preparation of 1,2-diamines (Scheme 5-1) cannot be applied to the synthesis of 1,4-diamines. The resulting 1,4-diimines were shown prone to rapid intramolecular cyclization to the corresponding iminoisoindolines **5** (Scheme 5-2). Although increasing the steric bulk by incorporating 2,6- diisopropylphenyl (Dipp) groups on the nitrogen positions allowed for the isolation of bis(*N*-Dipp)-1,4-dimine **4**, the product was not stable under ambient conditions (Scheme 5-2). In all cases, the 1,4-diimines **4** underwent intramolecular cyclizations to form iminoisoindolines **5**.[89] Consequently, another synthetic route was adopted by treating dibromo-*o*-xylene with arylamines in the presence of n-butyllithium. As a result, the 1,4-diamines **6** can be formed after a simple workup procedure.

Scheme 5-2. Synthesis of 1,4-diamines.



Complexations of the resulting diamines with aluminum were performed by reacting 1,2- and 1,4-diamines with $AlMe_3$ for 5-member and 7-member complexes, respectively (Scheme 5-3). The complexation reactions took place at elevated temperatures in toluene, and the resulting complexes were purified by a simple evaporation of solvent under high vacuum.

Scheme 5-3. Preparation of (diamido)^{Ar}AlMe complexes.



With respect to the synthesis of 5-member complexes, I found that α-diamido ligands were unable to yield the anticipated product **8**. The actual resulting complex **7** (Scheme 5-3) was a 4-coordinate dimeric species. An apparent cause that inhibits the formation of a mononuclear 3-coordinate species is that the 1,2-diamido ligand is insufficient in providing enough steric bulk for the stabilization of a 3-coordinate geometry possibly due to the relatively small bite angle (N-Al-N). The small bite angle is not able to adequately compress the *N*-Dipp groups towards the metal center to protect the metal from dimerizations. Therefore, not only a bulky *N*-substituent is required, but also a large ring size is necessary in tuning the steric bulk for the protection of the

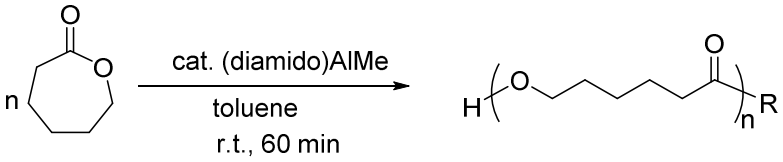
metal center.

Continuing investigations were focused on the application of 1,4-diamido ligands to prepare 7-member (1,4-diamido)^{Ar}AlMe **9** (Scheme 5-3). Due to the expected larger bite angle (N-Al-N) in a 7-member ring, the formation of a neutral monomeric 3-coordinate aluminum complex **9** (Scheme 5-3) was formed. The stability of Al to maintain a 3-coordinate geometry in **9** was attributed to the additional steric protection provided by the Ar groups that were brought closer to the metal center through the compression of a larger bite angle in a 7-member ring system.

The formation of **9** has exemplified that the effect of a pronounced steric protection resulted from a large bite angle (N-Al-N) and bulky *N*-Ar groups plays a crucial role in stabilizing a 3-coordinate aluminum complex.

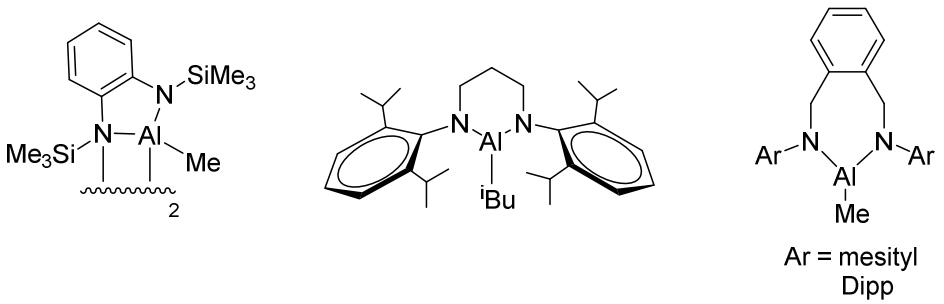
The performance of the Al complexes that I have developed was evaluated in the ROP of ε-caprolactone under specified reaction conditions (Scheme 5-4), using the complexes as single-component catalysts at room temperature for one hour in toluene. The 4-coordinate complex **7** in the ROP of ε-caprolactone concluded in no activity. This result agreed with the assumption that a 4-coordinate aluminum complex was unable to offer Lewis acidity high enough for the polymerization to proceed at facile reaction conditions. The results of the 7-member complex **9** in the ROP of ε-caprolactone under the same conditions showed catalytic activities superior to that of the reported 6-member complex **1**. The yield of polycaprolactone is 100% in one hour at room temperature.

Scheme 5-4. Reactions of ROP of ε-caprolactone.



n = 100 ~ 1000

The structure-reactivity relationships were studied based on bite angles of the complexes versus catalytic activities of the complexes in the ROP of ε-caprolactone (Figure 5-2).



ring size	5	6	7
bite angle (N-Al-N)	91°	109°	114°
activity (ROP of cyclic esters)	inactive	high	highest

Figure 5-2. Structure-activity relationship of (diamido)AR complexes of varying ring sizes.[31, 85]

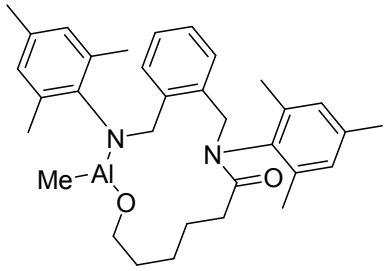
As concluded in Figure 5-2, the activity of diamido aluminum complexes in the ROP of cyclic esters first follows the coordination patterns around Al centers, in which the 4-coordinate complex is inactive under the specified conditions due to the lack of Lewis acidity. Although the lowest bite angle between N-Al-N to generate enough steric protections for the formation of a 3-coordinate species has not been identified, the value 91° in a typical 5-member ring is believed to

be below the critical angle. On the other hand, the 6-member 3-coordinate (1,3-diamido)^{Dipp}Al^{i}Bu **1** with a bite angle (N-Al-N) of 109^{o} shows a high activity.[31] Moreover, the activity of **1**was exceeded by the most active 7-member (1,4-diamido)^{Ar}AlMe that we have developed with a bite angle of 114^{o}.

In summary, the project regarding aluminum-based complexes has concluded in the successful synthesis of novel 3-coordinate (1,4-diamido)^{Ar}AlMe complexes, which demonstrated exceptional catalytic activities–in the ROP of ε-caprolactone. More importantly, we have demonstrated that diamido moieties are good supporting ligands in the formation of 3-coordinate neutral aluminum complexes because the ligand system can be easily tuned for an appropriate steric bulk and ring size in the final complex.

5.1.2 Future Work

Our preliminary mechanistic study in the ROP of ε-caprolactone suggested that the monomer actually inserted into Al-N instead of Al-Me, and the insertion product was shown as **10** (Figure 5-3). Although this result was consistent with the 6-member complex **1** reported by Chen *et al.*, it was our interest to modify **9** by changing the Me group to a different moiety such that the insertion can take place into Al-R, where R ≠ alkyl.[31]

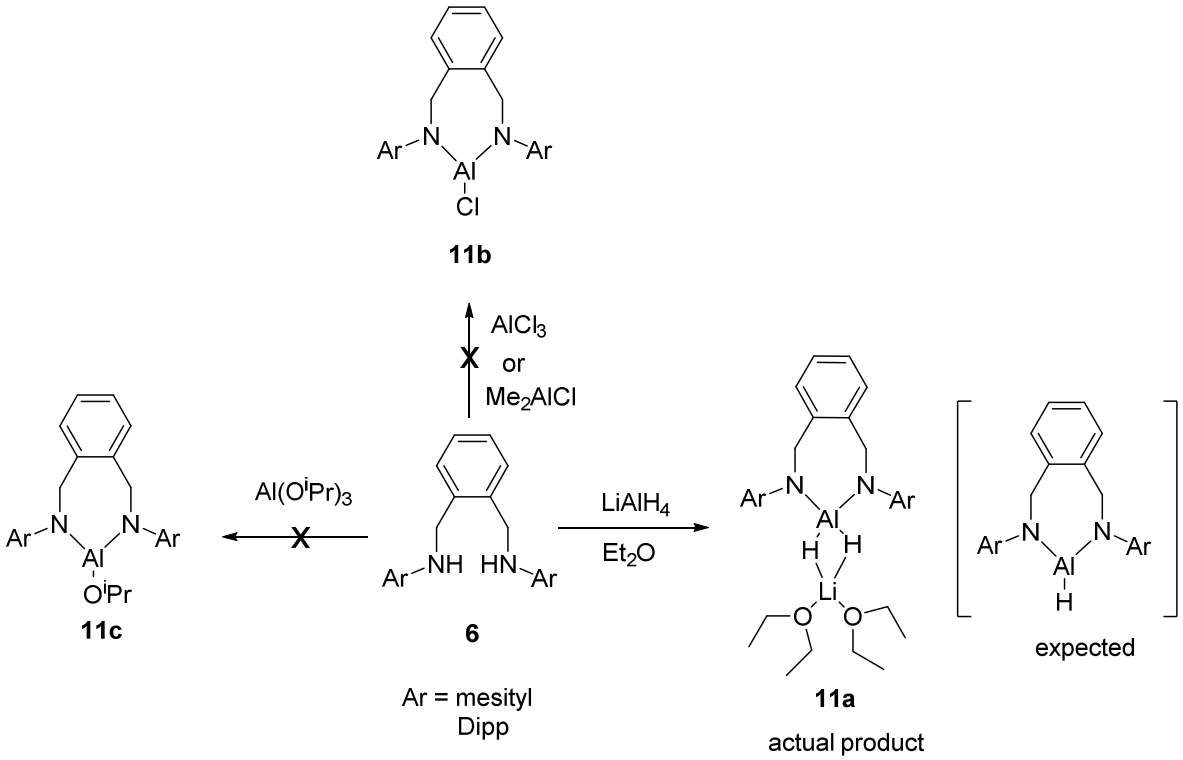


10

Figure 5-3.Insertion product of ε-caprolactone monomer into **9**.

Choices of R groups would include halides, hydrides and alkoxides, as suggested in Scheme 5-5.

Scheme 5-5. Attempted synthesis of (1,4-diamido)^{Ar}AlR complexes where R ≠ alkyl.

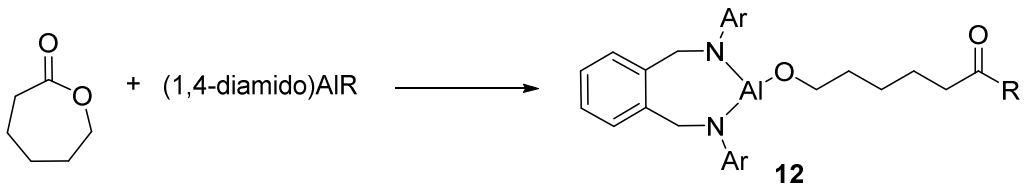


Initial attempts to synthesize the suggested complexes **11** have been unsuccessful. Direct treatments of 1,4-diamine **6** with $LiAlH_4$ did not yield the expected 3-coordionate product (the expected product in the bracket in Scheme 5-5); in turn, the reactions concluded in the formation of (1,4-diamido)^{Ar}Al (μ-H)$_2$(Et_2O) **11a** as a 4-coordinate complex.

Attempts of treating the 1,4-diamine **6** with $AlCl_3$ (or Me_2AlCl), either at room or elevated temperatures (e.g., 90 ^oC and 110 ^oC) in toluene, did not yield the expected product **11b**. There was no observable reaction from these attempts. Additional reactions attempted for the formation of (1,4-diamido)^{Ar}AlO^iPr **11c** by treating **6** with Al(O^iPr)$_3$ also concluded in no observable reactions. An investigation into the cause of the inability to form **11** is being carried out.

Our future work in the project will be focused on directing the insertion mechanism of the ROP of ε-caprolactone to that expressed as **12** (Scheme 5-6), in which the insertion of monomers takes place into Al-R bond. Therefore, the search for alternative routes to arrive at the formation of **11** has become the priority for the continuation of this project.

Scheme 5-6. Expected insertion product of ε-caprolactone monomer into **12**.



12

5.2 Synthesis of Novel NHP and Cationic NHP^+ Species

The project regarding *N*-heterocyclic phosphine (NHP) chemistry originated from the lack of investigations into π-acceptor properties of the species as compared to the abundant research already existed for their use as σ-donors in coordination chemistry. Therefore, we focused first on the synthesis of phosphine species that bear more π-accepting properties by utilizing the diamido ligands.

Up to date, most NHPs were made with diamido moieties as the supporting ligands. The most significant examples were given as 5-member NHPs, such as **12a** and **12b** (Figure 5-4), whereas the properties of 1,2-diamido ligands being bidentate and chelating were employed.[100] Applications of 1,3-diamido ligands were also used to synthesize 6-member NHPs, such as **12c** and **12d** (Figure 5-4).[103, 105a, 105e]

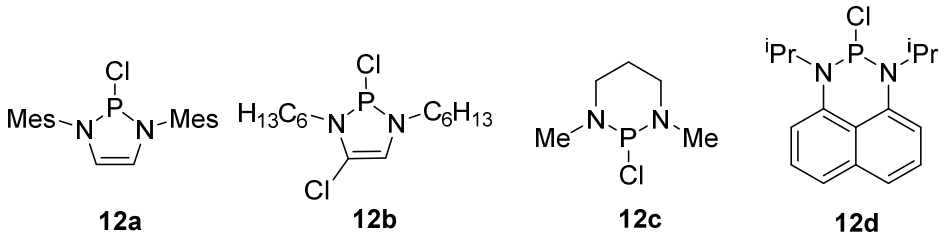


Figure 5-4. Examples of 5- and 6-member neutral NHPs.

In addition to the neutral 3-coordinate NHPs (Figure 5-4), further manipulations leading to the formation of their divalent cationic analogues, *N*-heterocyclic phosphenium cations (NHP^+), were through a simple halide abstraction reaction. For example, treating **12a** with Me_3SiOTf (OTf = triflate) led to the formation of the divalent cationic phosphenium species **13a** (Figure 5-5). The same halide abstraction applied to **12d** afforded the formation of **13b**. The

significance of a divalent NHP^+ is that a positive charge is imposed on the phosphorus atom to further increase the π-accepting strength of the species.

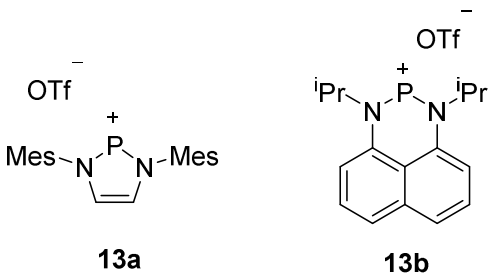


Figure 5-5.Examples of divalent phosphenium cationic NHP^+ species.

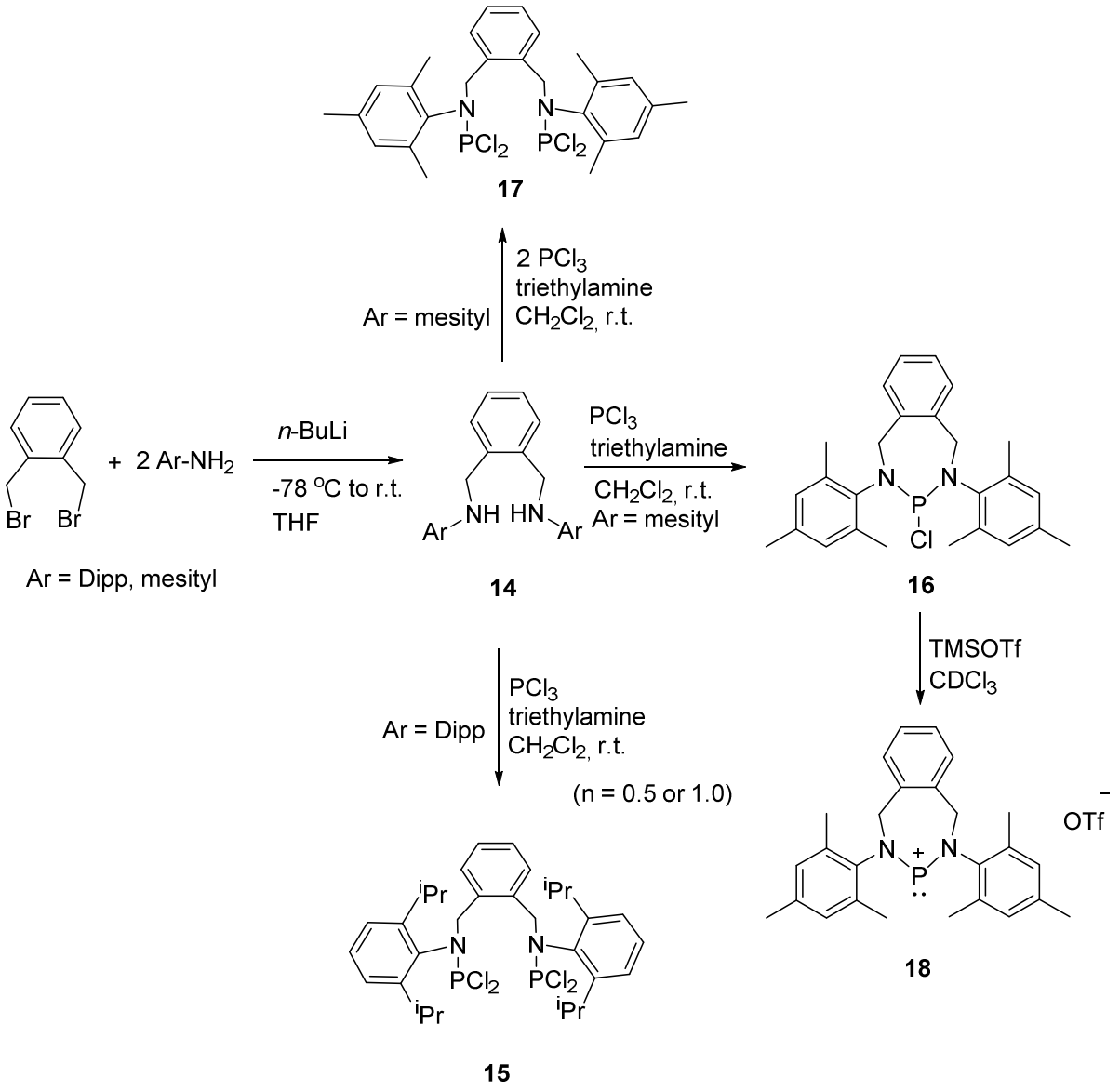
Tolman's cone angle has been commonly used to evaluate the performance of monodentate phosphines in coordination chemistry and catalysis.[38] Phosphines (PR_3) with larger Tolman's angles, resulted from bulkier R groups, usually led to a higher activity when their resulting complexes with transition metals were used in various catalytic applications.[39] We postulated that the bite angles between N-P-N in NHP species resembled Tolman's cone angles and they may have an impact on future applications in coordinating with transition metals. The values of bite angles for 3-coordinate neutral NHPs were proportional to ring sizes, such as 90° for 5-member[129] and 99° for 6-member NHPs.[65, 130] Therefore, I was interested in expanding the ring size of NHPs to 7-member for its effects on bite angles and π-accepting properties. A preliminary result was concluded in the successful synthesis of a novel 7-member NHP and its corresponding cationic NHP^+ species.

5.2.1 Summary and Conclusions

Our project started by employing 2,6-diisopropylphenyl (Dipp) and 2,4,6-trimethylaniline (mesityl) as the *N*-substituents to prepare 1,4-diamines **14** as the precursors to 1,4-diamido

ligands (Scheme 5-7). It was found that regardless of the stoichiometric ratios of the 1,4-diamines to trichlorophosphine being 1:1 or 2:1, the *N*-Dipp group yielded the bridging diphosphine species **15** as the major product. The formation of **15** was due to the excessive steric bulk of the *N*-Dipp groups that inhibited the desired cyclization reaction. Whereas, when treating 1,4-diamine with mesityl as the *N*-group in 1:1 ratio to PCl_3 under the same reaction condition, (1,4-diamido)^{Mes}PCl **16** was formed as a 7-member NHP. Similar to the *N*-Dipp analogues, when the *N*-mesityl substituted 1,4-diamines were treated with two equivalents of PCl_3, the bridging product **17** can be formed.

Scheme 5-7. Synthesis of 1,4-diamidophosphines.



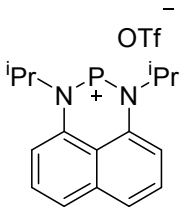
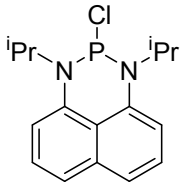
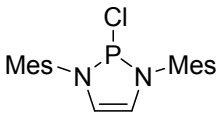
With the demonstrated higher versatility of mesityl than Dipp groups as the *N*-substituents in the 1,4-diamio moiety, we then focused on applying the resulting neutral (1,4-diamido)^{Mes}PCl **11** for further formations of divalent cationic NHP^{+} species. The abstraction of Cl in **16** with $AgPF_6$ did not afford the product [(1,4-diamido)^{Mes}P]$^{+}PF_6^{-}$ in a solid form, possibly due to counterion effects. Treating **16** with TMSOTf (trimethylsilyl trifluoromethanesulfonate)

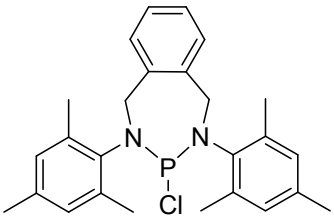
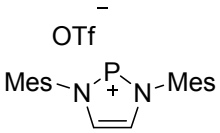
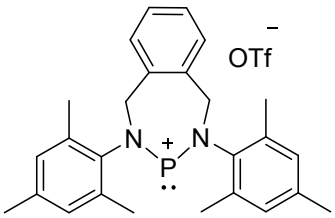
afforded the formation of **18** (Scheme 5-7) as a divalent NHP^+cationic species. Species **16** and **18** are the first successful examples of 7-member NHP and NHP^+ species, respectively.

The bite angle between N-P-N in the neutral NHP **16** was measured 105.33^o based on a crystallographic analysis. Compared to the reported bond angles for 5- and 6-member NHPs, the 7-member NHP we developed showed a significant larger value. As expected, a trend can be found in increasing bond angles with respect to ring sizes: 5-member (90^o) < 6-member (99^o) < 7-member (105^o).[129-130]

Analysis of ^{31}P NMR spectroscopy (Table 5-1) showed that the chemical shifts of neutral 5-member **12a**[98] and 7-member **16** both appeared at 149 ppm, indicating a similar de-shielding effect imposed by the 1,2- and 1,4-diamido ligands and Cl group on the phosphorus atom.[131] The 6-member NHP **12d** was reported at a chemical shift of 102 ppm on ^{31}P NMR timescale, possibly due to the *N*-isopropyl groups that reduced the de-shielding effect.[105a] The cationic NHP^+ **13b** is the ionic counterpart of **12d**, and the ^{31}P NMR chemical shift of **13b** appeared at 142 ppm. The significant more downfield chemical shift of **13b** than **12d** represents a pronounced de-shielding effect of imposing a positive charge on the phosphorus atom in **13b**. The ^{31}P NMR chemical shift of **18** was 244 ppm, and that for **13a** (Figure 5-5) was 200 ppm.[129] Since **18** and **13a** were built based on the identical chemical moiety except the ring sizes, this result suggests that the stronger de-shielding effect was conferred by the larger ring size of **18** that we have developed in this project.

Table 5-1. ^{31}P NMR chemical shifts of various NHP and NHP^{+} compounds**.**

Compounds	 **13b**	 **12d**	 **12a**
^{31}P, δ	142 ppm (CD_2Cl_2)	102 ppm (CD_2Cl_2)	149 ppm ($CDCl_3$)

Compounds	 **16**	 **13a**	 **18**
^{31}P, δ	149 ppm (C_6D_6)	200 ppm ($CDCl_3$)	244 ppm (C_6D_6)

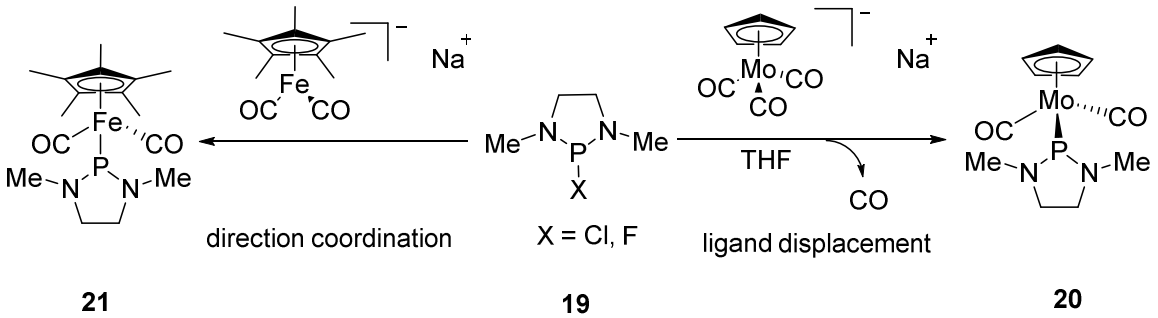
As result, we have demonstrated that by utilizing 1,4-diamido ligands, novel 7-member *N*-heterocyclic phosphines can be prepared. Furthermore, the neutral NHPs can be derivatized to their corresponding divalent NHP^{+} species via a simple halide abstraction with a potential in coordination chemistry as a new class of σ-donor/π-acceptor ligands.[58] The structural effects of different ring sizes to the π-acidity of the resulting NHP and NHP^{+} species can be postulated from their ^{31}P NMR chemical shifts.[131] As concluded in Table 5-1, the de-shielding effects were observed most pronounced by transforming the neutral NHPs to their cationic NHP^{+}s, whereas a larger ring size, such as a 7-member ring species as we have demonstrated in this project, also plays a critical role in increasing the π-acidity of the species.

5.2.2 Future Work

The future work of this project will be focused on the application of the novel NHP **16** and NHP^+ **18** in coordination chemistry. A preliminary screening of transition metals to complex with **18** was carried out with CuCl, $Pd(dba)_2$ and $(PPh_3)_3CuBr$. Up to date, the screening reactions were unable to deliver characterizable products. The search for a suitable metal source and synthetic methodologies is an on-going task.

Another proposed application of **16** and **18** in coordination chemistry will be the direct coordination and ligand displacement of existing metal complexes. Representative examples of NHPs in coordination chemistry were given in a 5-member NHP **19** with an anionic oranomolybdenum complex to form $(NHP)CpMo(CO)_2$ **20** through ligand displacements, and with an anionic iron complex to form $(NHP)Cp^*Fe(CO)_2$ **21** through direct coordination (Scheme 5-8).[132] In search of electron rich transition metals, preferably anionic metal complexes as demonstrated in Scheme 5-8, as the coordinating centers to complex with **16** and **18** is the immediate future work of this project.

Scheme 5-8. Examples of NHP in direct coordination and ligand displacement of a metal complex.



21 **19** **20**

5.3 Tri(*N*-heterocyclic carbene) Palladium Complexes.

Multiple NHCs have been proven more effective than monoNHCs in adding stability to a metal complex. Due to the abundant research already existed for mono- and diNHC palladium complexes, I was interested in developing novel (triNHC)Pd complexes and applying them in C-C coupling reactions.[116a, 116c, 116d]

The project regarding (triNHC)Pd(II)X complexes was a continuation from the previous work initiated by Tressia Paulose in the Foley group. The continuing project attached to the original research was focused on further characterizations of the resulting $[(triNHC)^{Me}PdCl]^{+}Cl^{-}$ complex by reiterating on the synthetic routes that were developed in the research group.[127, 133]

In addition to the original results, the goal of this thesis work was of two-fold. Firstly, the potential of $[(triNHC)^{Me}PdCl]^{+}Cl^{-}$ complex in C-C coupling reactions was evaluated. Secondly, the syntheses of variant complexes based on the same skeleton with varying *N*-substituents and/or counterions were carried out to resolve the solubility issues inherited in the complex.

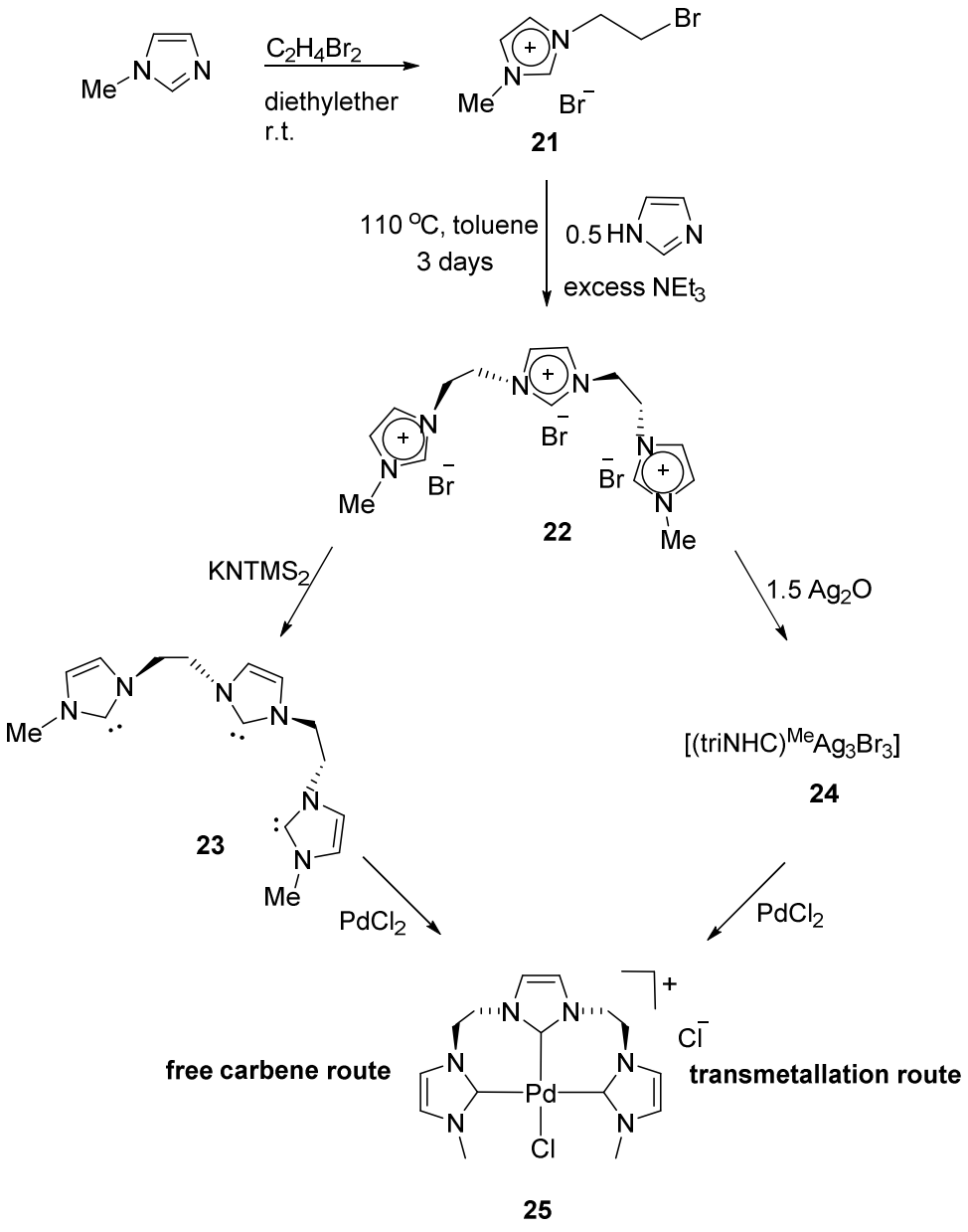
5.3.1 Summary and Conclusions

The synthetic strategy (Scheme 5-9) developed in the Foley group led to the formation of a novel complex **25** $[(triNHC)^{Me}PdCl]^{+}Cl^{-}$, wherein all three NHC moieties have been shown coordinated to the metal center in a κ^3-*C,C,C* mode. Complex **25** is the first example of a triNHC ligand coordinated to Pd center in a square planar geometry.

The imidazolium salt **21** (Scheme 5-9) was synthesized by treating *N*-methyl imidzaole with excess dibromoethane in diethyl ether at room temperature. The product slowly precipitated out of the solution and can be obtained by a simple filtration.[78, 121] The air and moisture stable **21** was used for the next step without further purifications. Although the triimidazolium salt **22** was

previously studied by Eberlin and Dupont for multiply charged di-radicals, their reported yield was only 16%.[120] We optimized the synthesis by treating **21** with 0.5 equivalent of imidazole in the presence of excessive triethylamine at 110 °C.[134] As a result, the yield of **22** reached as high as 80%.

Scheme 5-9. Synthesis of $[(triNHC)^{Me}PdCl]^{+}Cl^{-}$.

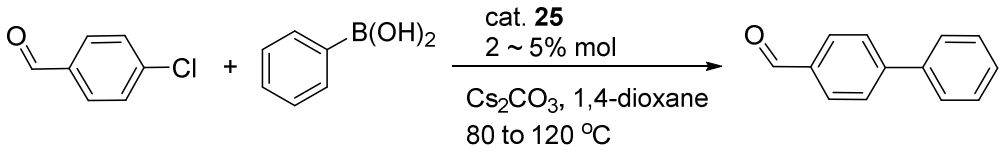


In order to convert the triimidazolium salt **22** to a carbene entity, two scenarios were formulated in search of a better route. The most common preparation known as "free carbene route" was through deprotonations of a imidazolium salt by a strong base to obtain its corresponding NHC ligand, as presented by Arduengo.[67] In the case of our triNHC system, we proceeded by reacting **22** with $KNTMS_2$ (or KHMDS, potassium bis(trimethylsilyl)amide) to yield the free carbene triNHC **23** (Scheme 5-9). However, the free carbene **23** is not stable against air and moisture, nor can it be stored overtime without decompositions. It was postulated that the instability of **23** was contributed by the lack of steric protection for the carbenic carbons, as the *N*-methyl groups do not offer enough steric hindrance. Another proposed "transmetallation route" was conducted by treating **22** with 1.5 equivalent of Ag_2O in dichloromethane at room temperature in the absence of light. The resulting product **24** $[(triNHC)^{Me}Ag_3Br_3]$ already carries a carbene entity and shows a high stability under ambient conditions. The major advantage of using **24** as the triNHC transferring reagent is that it can be bottled for an extended period of time due to its high stability. Followed by a transmetallation reaction by reacting **24** with $PdCl_2$, the $[(triNHC)^{Me}PdCl]^+Cl^-$ complex **25** was formed. Various crystallization measures attempted to grow crystals of **24** for X-ray analysis were unsuccessful due to the exceptionally low solubility of the complex in most organic solvents. However, spectroscopic evidence has supported the molecular structure of **25** in a square planar geometry, wherein all the NHCs were coordinated to the metal center as illustrated in Scheme 5-9. In addition to the low solubility in organic solvents, **25** showed an extraordinary stability against air, moisture and heat.

In the application of C-C coupling reactions, the Suzuki reaction to couple arylchlorides and phenylboronic acid was performed with **25** as the catalyst under standard conditions

(Scheme 5-10).

Scheme 5-10. The Suzuki coupling reaction for (triNHC)Pd(II) complexes.

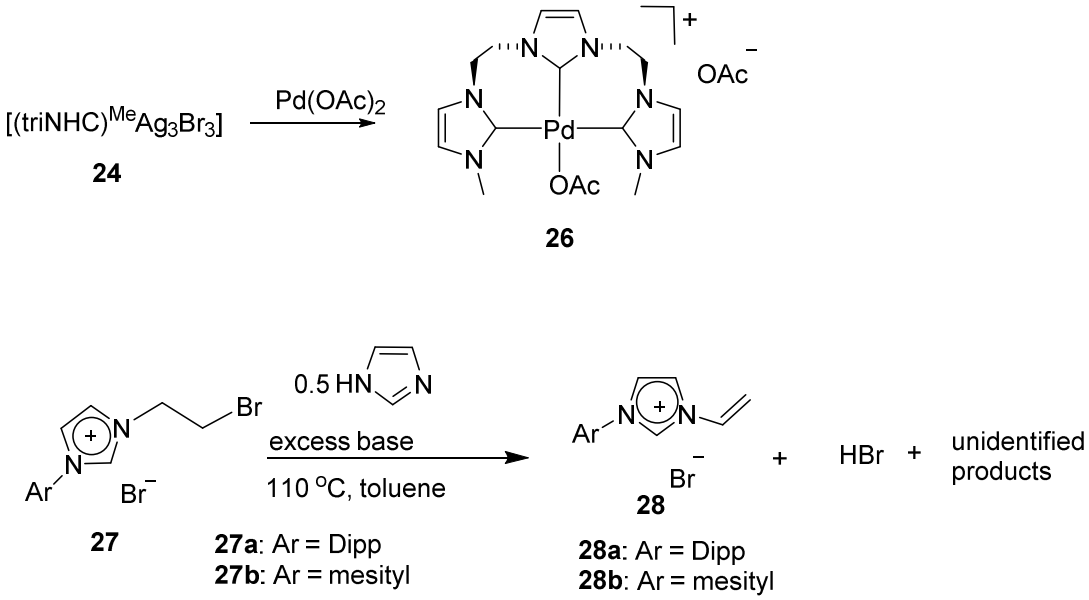


Multiple attempts for the Suzuki coupling reaction were carried out with *p*-chlorobenzaldehyde and phenylboronic acid as the substrates (Scheme 5-10). Using **25** as the catalyst by varying the reaction temperatures from 80 to 120 ^{o}C in combination with catalyst loadings from 2 to 5%, all attempts concluded in no coupled product. It was thought that the inactivity of **25** in C-C coupling reactions was attributed to its poor solubility properties.

Two strategies were devised to increase the solubility of **25** in most organic solvents: changing the counterion from Cl to acetate and incorporating *N*-aryl to replace the *N*-methyl group. It is commonly known that a palladium(II) species with an acetate substituent possesses a higher solubility than its chloride analogue in organic solvents, e.g., $Pd(II)(OAc)_2$ is more soluble than $Pd(II)Cl_2$. The formation of $[(triNHC)^{Me}OAc]^{+}OAc^{-}$ **26** was carried out via transmetallation route by using **24** as the carbene transfer reagent to react with $Pd(OAc)_2$ (Scheme 5-11). Moreover, there was no improvement of solubility observed, and the Suzuki coupling (Scheme 5-10) afforded no product yield with **26** as the catalyst. Additional attempts by treating **27** with half equivalent of imidazole were performed to change the *N*-methyl to *N*-Ar groups (Ar = mesityl or Dipp) in the triNHC moiety (Scheme 5-11). For a reason not yet clear, elimination reactions dominated over the expected substitution reactions, and **28** was concluded as the major product. Remedy reactions conducted by using different bases, such as Et_3N, NaH

and Cs_2CO_3, all favored the elimination product **28**.

Scheme 5-11. Synthesis of [(triNHC)^{Me}PdOAc] OAc and triimidazolium salt with *N*-Ar groups.



In summary, this project concluded in the synthesis of the first ethylene-bridged triNHC complexes of palladium wherein all three NHC moieties coordinate meridionally in a chelating fashion. It is the triNHC ligand that gives an exceptional stability against air and heat (stable until 278 ^{o}C) to the resulting [(triNHC)^{Me}PdCl]Cl and [(triNHC)^{Me}PdOAc]OAc complexes. Moreover, it is the thermal robustness and poor solubility that cause the complexes inactive in the Suzuki coupling of aryl chlorides and phenylboronic acid.

5.3.2 Future Work

The modifications (Scheme 5-11) to complex **25** were unsuccessful in changing the *N*-methyl groups to other aryl groups due to inherent synthetic difficulties, in which the synthesis

route designed for *N*-aryl triimidazolium salts favored the elimination products. On the other hand, the change of counterions afforded the formation of **26** with acetate as the counterion. Although **26** showed no activity as that for **25** in coupling (Scheme 5-10) reactions, the change with different counterions presented a promising modification route. Therefore, a screening of various counterions, such as triflate, BF_4^-, BPh_4^-, etc, will be the immediate future work with respect to the continuation of this project.

5.4 References

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