2002

Synthesis and characterization of group IV metal complexes featuring tridentate diamidoamine ligands

Alicia R. Morgan
West Virginia University

Follow this and additional works at: <https://researchrepository.wvu.edu/etd>

Recommended Citation

Morgan, Alicia R., "Synthesis and characterization of group IV metal complexes featuring tridentate diamidoamine ligands" (2002). *Graduate Theses, Dissertations, and Problem Reports*. 1559.
<https://researchrepository.wvu.edu/etd/1559>

This Thesis is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Thesis in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Thesis has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

Synthesis and Characterization of
Group IV Metal Complexes
Featuring Tridentate Diamidoamine Ligands

Alicia R. Morgan

Thesis submitted to the Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements for the degree of

Master of Science
in
Chemistry

Jeffrey L. Petersen, Ph.D., Chair
Robert S. Nakon, Ph.D.
Alan M. Stolzenberg, Ph. D.

Department of Chemistry

Morgantown, West Virginia
2002

Keywords: Group IV Metals, Diamidoamine Ligands, Amine Elimination, Arene Elimination
Copyright 2002 Alicia R. Morgan

ABSTRACT

Synthesis and Characterization of Group IV Metal Complexes Featuring Tridentate Diamidoamine Ligands

Alicia R. Morgan

New synthetic routes for the preparation of five-coordinate zirconium and titanium complexes featuring tridentate diamidoamine ligands were developed. Zirconium dichloride complexes, $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$ ($\text{R} = \text{H}, \text{SiMe}_3$), were synthesized via a one-step toluene elimination reaction. Analogous titanium dichloride complexes, $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$ ($\text{R} = \text{H}, \text{SiMe}_3$), were prepared using a one-step amine elimination reaction.

The NMR data for all four of the $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{MCl}_2$ -type complexes demonstrated that they exhibit C_s symmetry in solution, as indicated by the observation of six carbon resonances for the aryl carbons and three ^1H and ^{13}C NMR resonances for the methyl groups of the mesityl substituents. Molecular structures obtained from crystals of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$ and $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Ti}$) confirmed the identity of the five-coordinate zirconium and titanium dichloride complexes. The bond angles about the zirconium or titanium atom in the respective complexes indicate that they adopt a geometry that is consistent with the *fac* structure.

Acknowledgements

I would like to thank my advisor Dr. Petersen for his expertise and patience in helping me to perform my research and write my thesis.

Table of Contents

Title Page	i
Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Tables	vi
List of Figures	vii
Chapter 1. Introduction	1
Chapter 2. Results and Discussion	14
2.1. Preparation and Characterization of Triamines (Mes)NH(CH ₂) ₂ NR(CH ₂) ₂ NH(Mes), R = H, SiMe ₃	14
2.2. Preparation and Characterization of Five-Coordinate Zirconium Complexes	16
2.3. Preparation and Characterization of Five-Coordinate Titanium Complexes	19
2.4. Description of the Crystal Structures of 10 , 11 , and 13	20
Chapter 3. Concluding Remarks	30
Chapter 4. Experimental Section	31
4.1. Reagents	31
4.2. General Considerations	31
4.3. Preparation of Starting Materials	32
4.3.1. Preparation of Zr(NMe ₂) ₄ , 1	32
4.3.2. Preparation of Ti(NMe ₂) ₄ , 2	32
4.3.3. Preparation of Ti(NMe ₂) ₂ Cl ₂ , 3	33
4.3.4. Preparation of LiNEt ₂ , 4	33
4.3.5. Preparation of Ti(NEt ₂) ₄ , 5	33
4.3.6. Preparation of Ti(NEt ₂) ₂ Cl ₂ , 6	34
4.4. Preparation of Triamines (Mes)NH(CH ₂) ₂ NR(CH ₂) ₂ NH(Mes), R = H, SiMe ₃	35
4.4.1. Preparation of (Mes)NH(CH ₂) ₂ NH(CH ₂) ₂ NH(Mes), Mes = Mesityl, 7	35
4.4.2. Preparation of (Mes)NH(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ NH(Mes), Mes = Mesityl, 8	35
4.5. Preparation of Five-Coordinate Zirconium Bis(dimethylamido) Complexes	36

4.5.1. Preparation of [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]Zr(NMe ₂) ₂ , Mes = Mesityl, 9	36
4.6. Preparation of Five-Coordinate Zirconium Dichloride Complexes	37
4.6.1. Preparation of [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]ZrCl ₂ , Mes = Mesityl, 10	37
4.6.1.1. Reaction of 9 with SiMe ₃ Cl	37
4.6.1.2. Toluene Elimination Reaction	37
4.6.2. Preparation of [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]ZrCl ₂ , Mes = Mesityl, 11	38
4.7. Preparation of Five-Coordinate Titanium Dichloride Complexes	39
4.7.1. Preparation of [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]TiCl ₂ , Mes = Mesityl, 12	39
4.7.1.1. Amine Elimination Reaction with 3	39
4.7.1.2. Amine Elimination Reaction with 6	40
4.7.2. Preparation of [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]TiCl ₂ , Mes = Mesityl, 13	40
4.8. Description of the X-ray Structural Analyses	41
Chapter 5. References	45
Vita	48

List of Tables

Table 1.1. Polymerization Properties of McConville's Catalysts	8
Table 1.2. Polymerization Properties for [Mes ₂ N ₂ NH]ZrMe ₂ /[Ph ₃ C][B(C ₆ F ₅) ₄]	9
Table 2.1. Selected Bond Angles (°) About the Central Metal Atom in [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]ZrCl ₂ (10), and [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]MCl ₂ (M = Zr (11) and Ti (13))	28
Table 2.2. Selected Interatomic Distances (Å) for [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]MCl ₂ (M = Zr (11) and Ti (13))	28
Table 4.1. Frame Scan Parameters	41
Table 4.2. Crystal Data and Structural Information for [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]ZrCl ₂ (10) and [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]MCl ₂ (M = Zr (11) and Ti (13))	43
Table 4.3. Selected Interatomic Distances (Å) and Bond Angles (°) for [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]ZrCl ₂ (10) and [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]MCl ₂ (M = Zr (11) and Ti (13))	44

List of Figures

Figure 1.1. Activation of Metallocenes by Alkylaluminumchlorides	1
Figure 1.2. General Mechanism for Polymer Chain Formation	2
Figure 1.3. Polypropylene Microstructures	2
Figure 1.4. One of Brintzinger's C_2 -Symmetric Catalysts	3
Figure 1.5. Bercaw's Doubly-Bridged Zirconocenes	4
Figure 1.6. Catalyst Precursor Developed at Exxon and Dow	5
Figure 2.1. Catalytic Cycle for Aryl Amination Reaction	14
Figure 2.2. Perspective view of the molecular structure and the atom labeling scheme for [(Mes)N(CH ₂) ₂ NH(CH ₂) ₂ N(Mes)]ZrCl ₂ , 10 .	21
Figure 2.3. Perspective view of the molecular structure and the atom labeling scheme for [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]ZrCl ₂ , 11 .	22
Figure 2.4. Perspective view of the molecular structure and the atom labeling scheme for [(Mes)N(CH ₂) ₂ N(SiMe ₃)(CH ₂) ₂ N(Mes)]TiCl ₂ , 13 .	23
Figure 2.5. Configurations of Five-Coordinate Complexes	26
Figure 2.6. Perspective view of the molecular structure of 10 looking parallel to the ZrCl ₂ plane.	27

Chapter 1. Introduction

Polymers are used for a vast variety of applications. Over the past fifty years, the production of polyolefins has grown to a multibillion-dollar industry, with worldwide production approaching 200 billion pounds per year. The earliest Ziegler-type catalyst systems used for the polymerization of olefins were heterogeneous and relied on mixtures of TiCl_3 or TiCl_4 and various alkyl aluminum halides. A major breakthrough came in 1957 when Natta¹ and Breslow,² working independently, found that Cp_2TiCl_2 could be activated with Et_3Al or Et_2AlCl to produce an effective homogeneous polymerization catalyst for ethylene. Their discovery marked the beginning of the development of homogeneous polymerization catalysts for ethylene and α -olefins. The polydispersity indexes ($\text{PDI} = M_w/M_n$) for the atactic polymers produced by the metallocenes were ~ 2 ,³ indicating that, unlike their heterogeneous predecessors, these homogeneous catalysts had a single active site. This feature meant that, for the first time, detailed mechanistic studies could be performed.

The activation of metallocenes by alkylaluminum chlorides is presumed to proceed via the mechanism shown in Figure 1.1.⁴ Alkylation of the metallocene by the alkylaluminum chloride is followed by halide abstraction to give the 14-electron alkyl cation, Cp_2MR^+ . This coordinatively and electronically unsaturated species allows for coordination of the olefin and its subsequent migratory insertion into the metal-carbon bond. The importance of the metal-alkyl cation Cp_2MR^+ is underscored by the extensive efforts that have been expended to synthesize and study metal complexes that can be activated to produce this catalytically active species.⁵⁻¹²

Figure 1.1. Activation of Metallocenes by Alkylaluminum chlorides

Once the cationic active site has been generated from catalyst precursors, the polymer chain grows by the migratory insertion mechanism shown in Figure 1.2.¹³ This mechanism contains three basic steps: initiation, in which the active site is generated; propagation, in which

the olefin molecules (in this case ethylene) undergo rapid migratory insertion into the metal-alkyl bond; and termination or chain transfer, which can occur via several pathways, including β -elimination and hydrogenolysis.

Figure 1.2. General Mechanism for Polymer Chain Formation

The insertion mechanism shown in Figure 1.2 generates polymers of varying stereoregularity, with the three most common being isotactic, syndiotactic, and atactic. Polypropylene chains depicting examples of each of these polymer microstructures are shown in Figure 1.3.

Figure 1.3. Polypropylene Microstructures

In isotactic polypropylene, each methyl substituent on the carbon backbone is oriented in the same direction. In syndiotactic polypropylene, the orientations of the methyl groups alternate along the carbon backbone. In atactic polypropylene, the methyl groups are oriented in random directions.

Sinn and Kaminsky, the first people to study polymerization of alkenes other than ethylene, discovered that group IV metallocenes could be activated with methylalumoxane (MAO) to produce effective catalysts for the polymerization of both ethylene and α -olefins.^{14,15} However, these homogeneous metallocene catalysts were less active and produced polymers of lower molecular weight than the heterogeneous Ziegler-Natta catalysts. During the 1980's, many modifications were made to metallocene-based compounds in a quest to improve their catalytic properties. The primary goals were to increase their catalytic activities and to allow for control of the molecular weight and microstructure of the resultant polymer.^{16,17} Brintzinger and Wild^{18,19} used an interannular ethylene bridge to impose chirality on the metallocenes. These C_2 -symmetric complexes (Figure 1.4), which have decreased steric congestion and increased Lewis acidity of the metal centers,²⁰ produce highly isotactic polymer when activated with MAO.^{21,22} In some cases, the level of isotacticity was comparable to that obtained with heterogeneous Ziegler-Natta catalysts. In addition, studies of propene polymerization have established that the catalytic activities for some of these *ansa*-zirconocenes, including the one shown in Figure 1.4, are higher than for the stereochemically unselective, unsubstituted Cp_2ZrCl_2 .

Figure 1.4. One of Brintzinger's C_2 -Symmetric Catalysts

Zirconocenes with a one-atom $SiMe_2$ bridge exhibit even higher activities than those analogues with a two-atom ethylene bridge.^{23,24} The shorter bridge increases the angle between the planes

of the Cp or Cp-based rings,^{25,26} thereby increasing the accessibility of the catalytically active metal center to the incoming α -olefin. The shorter bridge also prevents substituents in the 5 position (labeled in Figure 1.4) of the ligand from hindering access of the α -olefin to the active site, an effect that has been observed in catalysts containing three- and four-atom bridges.¹⁶

Bercaw and coworkers developed a series of C_s -symmetric zirconocenes with two silylated bridges (Figure 1.5) that, when activated with MAO, produce polypropylene that ranges from moderately to highly syndiotactic.²⁷⁻³⁰

Figure 1.5. Bercaw's Doubly-Bridged Zirconocenes

His group also developed a series of bridged and unbridged neutral scandocene alkyl complexes (Cp_2ScR) that are isoelectronic to the cationic group IV metallocenes (Cp_2MR^+). They then replaced the two cyclopentadienyl groups with the dianionic bifunctional chelating ligand $[(C_5Me_4)SiMe_2(N-t-Bu)]^{2-}$. The replacement of the two 6-electron cyclopentadienyl groups with a ligand containing one 6-electron cyclopentadienyl group and a 4-electron amido group reduced the formal electron count from fourteen to twelve, thus increasing the Lewis acidity of the metal center.³¹⁻³³ Although these modified scandocene complexes displayed fairly low polymerization rates, they did display lower chain transfer (i.e., termination) rates than the original scandocene alkyl complexes. Therefore, appropriate ligand modifications can influence the reactivity and improve the catalytic performance of these highly electrophilic organoscandocene complexes.

On the basis of Bercaw's results, researchers at both Exxon Corporation³⁴⁻³⁶ and Dow Chemical Co.³⁷ independently developed group IV metal polymerization catalysts of the form $[(\eta^5\text{-C}_5\text{R}_4)\text{SiR}'_2(\eta^1\text{-NR}'')] \text{MCl}_2$ ($\text{M} = \text{Ti, Zr, Hf}$; $\text{R} = \text{alkyl}$; $\text{R}', \text{R}'' = \text{alkyl or aryl}$) (Figure 1.6). These catalyst precursors, upon activation with MAO, produce highly active catalysts for the copolymerization of ethylene and 1-alkenes. They produce high molecular weight polymer due to two factors. First, migratory insertion of the olefin is made more facile by the decreased steric crowding and the electron deficiency of the metal center. Second, the constrained geometry of the active site creates more space in which the polymer chain can grow, thereby decreasing the polymer's tendency to undergo chain transfer.

Figure 1.6. Catalyst Precursor Developed at Exxon and Dow

The increase in Lewis acidity that results from replacement of two bridged or unbridged cyclopentadienyl ligands with a bifunctional monocyclopentadienyl amido ligand improved the catalytic properties of the metallocenes. To further increase the Lewis acidity of the catalyst precursors, group IV metal complexes that incorporated a chelating diamido ligand were prepared. Many early examples of these compounds, such as the titanium dibenzyl complex $[\text{MeNSiMe}_2\text{XSiMe}_2\text{NMe}]\text{Ti}(\text{CH}_2\text{Ph})_2$, $\text{X} = \text{NMe}, \text{CH}_2$,³⁸ contained either silylated chelate rings or silyl substituents at the amide nitrogens. However, McConville and coworkers prepared several zirconium complexes featuring the bulky 2,6-diisopropylphenyl group.^{39,40} The use of bulky substituents minimizes dimerization and potentially provides control of polymer microstructure by directing the approach of the olefin to the electrophilic metal center.

Prior to preparing the zirconium complexes, McConville's group used the metathetical reaction of the lithium salt LiNHAr ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) with 1,3-dibromopropane to generate the ligand precursor $(\text{Ar})\text{NH}(\text{CH}_2)_3\text{NH}(\text{Ar})$, designated $(\text{BDAP})\text{H}_2$ (Eq. 1.1).

The diamine $(\text{BDAP})\text{H}_2$ was then reacted with $\text{Zr}(\text{NMe}_2)_4$ to produce the zirconium bis(dimethylamido) complex $(\text{BDAP})\text{Zr}(\text{NMe}_2)_2$ (Eq. 1.2).

This mixed-amide zirconium complex was then treated with two equivalents of $[\text{Me}_2\text{NH}_2]\text{Cl}$ to produce the octahedral dimethylamine adduct $(\text{BDAP})\text{ZrCl}_2(\text{NHMe}_2)_2$, which was found to be unstable to loss of dimethylamine. The related zirconium complex $(\text{BDAP})\text{ZrCl}_2\text{py}_2$ was formed via reaction of $(\text{BDAP})\text{Zr}(\text{NMe}_2)_2$ with two equivalents of $[\text{Me}_2\text{NH}_2]\text{Cl}$ in the presence of excess pyridine (Eq. 1.3).

The McConville group subsequently reacted $(\text{BDAP})\text{ZrCl}_2\text{py}_2$ with a series of alkylating agents in an effort to generate zirconium alkyl derivatives. The reaction of $(\text{BDAP})\text{ZrCl}_2\text{py}_2$ with two equivalents of MeMgCl afforded the dimethyl compound $(\text{BDAP})\text{ZrMe}_2$ (Eq. 1.4).

McConville and his coworkers studied the 1-hexene polymerization chemistry of $(\text{BDAP})\text{ZrMe}_2$ with the co-catalysts MAO, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, and $\text{B}(\text{C}_6\text{F}_5)_3$.⁴¹ They found that activation with MAO at 68°C afforded a catalyst that yielded both poly(1-hexene) ($M_w = 26,000$; $M_n = 15,100$; $\text{PDI} = 1.72$) and oligomers. Activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ at 23°C produced only oligomer. The third system, $(\text{BDAP})\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$, was found to be inactive at 23°C .

The relative lack of activity displayed by $(\text{BDAP})\text{ZrMe}_2$ for the polymerization of 1-hexene prompted McConville and coworkers to examine the ability of chelating diamide complexes of titanium to polymerize 1-hexene.⁴² Alkyl derivatives of titanium complexes featuring two different chelating diamides of the form $[\text{ArNH}(\text{CH}_2)_3\text{NHA}r]^{2-}$, where $\text{Ar} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$ and $2,6\text{-Me}_2\text{C}_6\text{H}_3$, were prepared. The silylated diamines were reacted with TiCl_4 to give the dichloride adduct, which was then reacted with two equivalents of MeMgCl to give the respective dimethyl complexes (Eq. 1.5).

Polymerization experiments were performed with each of the alkyl derivatives using different co-catalysts, including MAO, $\text{B}(\text{C}_6\text{F}_5)_3$, and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. The catalyst systems generated poly(1-hexene) with high molecular weight and low PDI. For the dimethyl complex with $\text{Ar} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$, designated as $(\text{BDAP})\text{TiMe}_2$, M_w ranged from 29,600 with $\text{B}(\text{C}_6\text{F}_5)_3$ to 81,500 with MAO, M_n ranged from 16,100 with $\text{B}(\text{C}_6\text{F}_5)_3$ to 47,000 with MAO, and the PDI ranged from 1.35 with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to 1.84 with $\text{B}(\text{C}_6\text{F}_5)_3$. The lowest activity for this

titanium dimethyl catalyst precursor was with $\text{B}(\text{C}_6\text{F}_5)_3$ (2,000 g of poly(1-hexene)/mmol of catalyst · h), the highest with MAO (350,000 g of poly(1-hexene)/mmol of catalyst · h). For the dimethyl complex with $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, designated as $(\text{BDMP})\text{TiMe}_2$, the maximum and minimum values for M_w , M_n , PDI, and activity were all lower than for $\text{Ar} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$.

The polymerization properties for the alkyl derivatives of McConville's group IV metal complexes featuring chelating diamide ligands are summarized in Table 1.1.

Table 1.1. Polymerization Properties of McConville's Catalysts

Complex	Co-catalyst	M_w	M_n	M_w/M_n	Activity
$(\text{BDAP})\text{ZrMe}_2$	MAO	26,000	15,100	1.72	150
	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	produces only oligomer			
	$\text{B}(\text{C}_6\text{F}_5)_3$	inactive for polymerization			
$(\text{BDAP})\text{TiMe}_2$, $\text{Ar} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$	MAO	81,500	47,000	1.73	350,000
	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	239,100	177,500	1.35	104,000
	$\text{B}(\text{C}_6\text{F}_5)_3$	29,600	16,100	1.84	2,000
$(\text{BDMP})\text{TiMe}_2$, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$	MAO	54,000	30,400	1.78	290,000
	$\text{B}(\text{C}_6\text{F}_5)_3$	26,200	14,500	1.81	2,000

The above data indicate that the homogeneous catalysts derived from the titanium alkyls are superior to those based on the zirconium alkyls. Only the $(\text{BDAP})\text{ZrMe}_2/\text{MAO}$ system produced poly(1-hexene). However, it exhibited much lower activity than the $(\text{BDAP})\text{TiMe}_2/\text{MAO}$ and $(\text{BDMP})\text{TiMe}_2/\text{MAO}$ systems, which were the first ones to demonstrate the living polymerization of 1-hexene.

In addition to these chelating diamido ligands, Schrock and McConville⁴³ began to prepare five-coordinate complexes that incorporate tridentate chelating diamidoamine ligands. The triamine $\text{HN}(\text{CH}_2\text{CH}_2\text{NHMe})_2$, designated as $\text{H}_2[\text{Mes}_2\text{N}_2\text{NH}]$, is readily generated by using Buchwald's catalyst⁴⁴ to arylate diethylenetriamine using mesityl bromide. Reaction with $\text{Zr}(\text{NMe}_2)_4$ forms the bis(dimethylamido) zirconium complex, which can then be reacted with SiMe_3Cl to afford the dichloride adduct $[\text{Mes}_2\text{N}_2\text{NH}]\text{ZrCl}_2$ (Eq. 1.6).

Treatment of this dichloride with excess MeMgI affords the dimethyl adduct, $[\text{Mes}_2\text{N}_2\text{NH}]\text{ZrMe}_2$, in high yields. The co-catalyst $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was then added to this dimethyl complex in order to examine the system's ability to polymerize 1-hexene. The polymerization results for this catalyst system are summarized in Table 1.2.

Table 1.2. Polymerization Properties for $[\text{Mes}_2\text{N}_2\text{NH}]\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$

Equivalents of $[\text{Mes}_2\text{N}_2\text{NH}]\text{ZrMe}_2$	M_n	M_w	PDI
134	12,500	16,200	1.3
313	17,000	20,900	1.2
626	12,700	17,200	1.4

The results indicate that M_w and M_n for this system are of the same order of magnitude as for $(\text{BDAP})\text{ZrMe}_2/\text{MAO}$, $(\text{BDAP})\text{TiMe}_2/\text{MAO}$, $(\text{BDAP})\text{TiMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$, $(\text{BDMP})\text{TiMe}_2/\text{MAO}$, and $(\text{BDMP})\text{TiMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$. They are, however, an order of magnitude lower than for $(\text{BDAP})\text{TiMe}_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.

During the past two years, a synthetic effort was undertaken at West Virginia University to develop more efficient synthetic routes for the preparation of group IV metal complexes featuring a tridentate chelating diamidoamine ligand. Two different ligand precursors, $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{NH}(\text{Mes})$, $\text{R} = \text{H}, \text{SiMe}_3$, were used for this purpose. The triamine $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{Mes})$, first introduced by Schrock and McConville, was prepared by the arylamination of diethylenetriamine with mesitylene bromide in the presence of Buchwald's catalyst.⁴³ The trimethylsilyl-substituted amine $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{NH}(\text{Mes})$ was subsequently generated by the slow addition of

(Mes)NH(CH₂)₂NH(CH₂)₂NH(Mes) to an ether solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and SiMe₃Cl (Eq. 1.7).

Although Schrock and McConville successfully developed a two-step reaction sequence to prepare [Mes₂N₂NH]ZrCl₂ (Eq. 1.8), their reaction sequence relied on the use of SiMe₃Cl to convert [Mes₂N₂NH]Zr(NMe₂)₂ to the desired dichloride derivative.⁴³

However, previous experience had shown that the reaction of metal-amido complexes such as [(C₅H₄SiMe₂(NPh)]Zr(NMe₂)₂ with SiMe₃Cl is not as effective in the presence of a coordinated arylamido ligand (Eq. 1.9).^{45,46}

Consequently, alternative synthetic methodologies avoiding the use of SiMe₃Cl were pursued for the preparation of [(Mes)N(CH₂)₂NR(CH₂)₂N(Mes)]MCl₂-type complexes (R = H, SiMe₃; M = Ti, Zr).

Reactivity studies performed by Lückert and Petersen⁴⁵ have shown that the thermally induced amine elimination reaction of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ with $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2\text{N}(\text{H})\text{R}$ provides a simple one-step route leading directly to $[(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{NR}]\text{TiCl}_2$ ($\text{R} = t\text{-Bu}, ^i\text{Pr}, \text{Ph}$) (Eq. 1.10).

This reaction is attractive for two reasons. Firstly, $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ is a red-orange semi-crystalline solid that can be readily prepared from the stoichiometric addition of two equivalents of SiMe_3Cl to $\text{Ti}(\text{NMe}_2)_4$ (Eq. 1.11).

More importantly, the amine elimination reaction of $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2(\text{NHR})$ with $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ proceeds cleanly to afford a single product. In contrast, the reaction of $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2(\text{NHR})$ with $\text{Ti}(\text{NMe}_2)_4$ yields a complicated mixture rather than $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{NR})]\text{Ti}(\text{NMe}_2)_2$. Therefore, a synthetic effort was undertaken to determine if the corresponding reactions of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ with $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{NH}(\text{Mes})$ ($\text{R} = \text{H}, \text{SiMe}_3$) could be used to prepare five-coordinate $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$ complexes in one step (Eq. 1.12).

Although $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ was readily prepared from $\text{Ti}(\text{NMe}_2)_4$,⁴⁵ the corresponding reaction of $\text{Zr}(\text{NMe}_2)_4$ with two equivalents of SiMe_3Cl afforded a trinuclear zirconium complex, $\text{Zr}_3(\text{NMe}_2)_8\text{Cl}_4$, rather than $\text{Zr}(\text{NMe}_2)_2\text{Cl}_2$ (Eq. 1.13).⁴⁶

This is a consequence of the greater tendency of zirconium to form oligomeric structures linked by bridging ligands. Further, the smaller size of Ti(IV) is better suited for structures of lower coordination number than is the larger Zr(IV). As a result, an alternative reaction scheme for the preparation of the corresponding $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$ -type complexes had to be developed.

A potentially viable alternative to the amine elimination reaction involves the elimination of an arene. The reaction of metal-benzyl complexes with an amine is known to proceed with loss of toluene and the formation of a M-N(amido) bond.^{47,48} Preliminary studies demonstrate that the reaction of $\text{M}(\text{benzyl})_4$ ($\text{M} = \text{Zr}, \text{Hf}$) with $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{Mes})$ eliminates two equivalents of toluene to produce $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{M}(\text{benzyl})_2$ in nearly quantitative yields (Eq. 1.14).⁴⁹

In order to prepare the metal dichloride derivatives via a similar arene elimination reaction, the corresponding $\text{M}(\text{benzyl})_2\text{Cl}_2$ complex would be required. Zucchini and coworkers reported that treatment of $\text{Zr}(\text{benzyl})_4$ with two equivalents of gaseous HCl in diethyl ether produces the ether adduct $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{ether})_x$, which was reported to be thermally unstable and light sensitive.⁵⁰ Despite these difficulties, it was felt that $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{ether})_x$, when prepared in the absence of

light at reduced temperature, may provide a suitable reagent for the preparation of the desired diamidoamine zirconium dichloride complexes. Instead of corrosive HCl gas, the crystalline solid $[\text{NEt}_3\text{H}]\text{Cl}$ was used to prepare $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{ether})_x$, thus simplifying the quantitative protonation of $\text{Zr}(\text{benzyl})_4$. In addition, the triethylamine formed by this reaction can be readily removed under vacuo, leaving $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{ether})_x$ for subsequent reaction with $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{NH}(\text{Mes})$, $\text{R} = \text{H}, \text{SiMe}_3$ (Eq. 1.15).

The results of these investigations have led to the development of two complementary synthetic routes for the preparation of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$ and $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$ complexes. Specific details of the preparation and characterization of these five-coordinate diamidoamine group IV metal complexes are described in this thesis.

Chapter 2. Results and Discussion

2.1 Preparation and Characterization of Triamines (Mes)NH(CH₂)₂NR(CH₂)₂NH(Mes), R = H, SiMe₃

The preparation of (Mes)NH(CH₂)₂NH(CH₂)₂NH(Mes), **7**, was accomplished by the arylation of diethylenetriamine with two equivalents of bromomesitylene using a palladium-catalyzed reaction (Eq. 2.1). A catalytic cycle for a generic palladium-catalyzed arylation reaction is shown in Figure 2.1.⁴⁴ The first step in the synthesis of the amine involves the oxidative addition of bromomesitylene to a (BINAP)Pd-complex. Addition of the amine to the oxidative addition product affords the intermediate (BINAP)Pd(Ar)Br-amine complex, which upon deprotonation with sodium *t*-butoxide gives (BINAP)Pd(Mes)[NHR]. Finally, the arylated amine and the catalyst (BINAP)Pd are generated in step 4 via reductive elimination.

Figure 2.1. Catalytic Cycle for Aryl Amination

The triamine was isolated as a dark reddish solid and characterized by NMR measurements. In the ^1H NMR spectrum, the two equivalent hydrogens bonded to each of the mesityl rings produced a singlet at δ 6.94. The coupling of the two equivalent outer N-H protons to the methylene protons resulted in a triplet at δ 3.38. The methylene protons of the $(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$ bridge were observed as two distinct multiplets of equal intensity at δ 3.02 and 2.88. The twelve protons of the *ortho* methyl substituents of the mesityl groups produced a singlet at δ 2.26; the six protons attached to the *para* methyl substituents afforded a singlet at δ 2.21. The resonance for the internal N-H proton was not resolved and may have been obscured by the other peaks.

The ^{13}C NMR spectrum exhibited eight distinct resonances. The four inequivalent carbons comprising each of the mesityl rings produced resonances in the aromatic region at δ 143.6, 131.2, 129.7, and 129.4. The methylene groups of the $(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$ bridge gave two signals at δ 50.0 and 48.4. The *para* and *ortho* methyl substituents of the mesityl groups appeared at δ 20.5 and 18.3, respectively.

Preparation of the trimethylsilyl-substituted amine $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{NH}(\text{Mes})$, **8**, was accomplished by reacting the triamine **7** with an ether solution containing an equimolar amount of DBU and an excess of SiMe_3Cl (Eq. 2.2). The ^1H NMR spectrum indicated the desired product was formed in a fairly clean reaction. The four equivalent protons bound to the two mesityl rings produced a singlet at δ 6.79. The eight methylene protons of the $(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2$ linkage displayed a single multiplet at δ 2.97. The *ortho* and *para* methyl substituents of the mesityl rings afforded singlets at δ 2.22 and 2.21, respectively. The nine methyl protons of the trimethylsilyl group presented a sharp singlet at δ 0.11.

The ^{13}C APT (Attached Proton Test) NMR spectrum of **8** displayed nine distinct peaks. Four of them were found in the aromatic region at δ 143.6, 130.9, 129.4, and 129.1, corresponding to the *ipso*, *para*, *meta*, and *ortho* carbons of the mesityl rings, respectively. The methylene carbons produced resonances at δ 47.1 and 46.5. The *para* and *ortho* methyl substituents of the aromatic rings gave resonances at δ 20.5 and 18.4, respectively. The peak for the methyl carbons of the trimethylsilyl group was found at δ 0.14.

2.2 Preparation and Characterization of Five-Coordinate Zirconium Complexes via Two Complementary Routes

The efficacy of the alternative synthetic routes developed by this investigation could best be judged if their resultant products could be compared to known compounds. With this in mind, **9** and **10**, the first five-coordinate complexes made, were synthesized via Schrock's amine elimination procedure.⁴³ The preparation of the bis(dimethylamido) zirconium complex $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{Zr}(\text{NMe}_2)_2$, **9**, was accomplished by heating a toluene solution containing equimolar amounts of **7** and $\text{Zr}(\text{NMe}_2)_4$, **1** (Eq. 2.3). The temperature of the reaction mixture was maintained at 100 °C overnight. The ^1H NMR spectrum of the product residue indicated that this reaction proceeded with the formation of only the desired compound. The four protons in the *meta* positions of the mesityl rings appeared as a singlet at δ 6.94. Three multiplets corresponding to the internal N-H proton and the two chemically inequivalent methylene groups were found at δ 3.35, 3.00, and 2.55. The methyl protons of the two dimethylamido ligands afforded two singlets at δ 3.05 and 2.28. Three singlets for the inequivalent methyl substituents of the mesityl substituents appeared at δ 2.47, 2.44, and 2.21.

The ^{13}C NMR spectrum of **9** featured eleven distinct resonances. The four inequivalent quaternary carbons of the mesityl groups produced resonances in the aromatic region at δ 150.1, 134.1, 134.0, and 131.7, with the signal furthest downfield corresponding to the *ipso* carbon.

The chemical shifts for the two inequivalent *meta* carbons were virtually the same, with only partial resolution of their respective singlets at δ 129.7. This assignment was further confirmed in the gated non-decoupled ^{13}C NMR spectrum by the appearance of a doublet due to the coupling of each *meta* carbon with a single proton. This spectrum also gave information about the other protonated carbons. The methylene carbons appeared as two 1:2:1 triplets at δ 55.2 and 48.8, with coupling constants of $^1J_{\text{C-H}} = 133$ and 135 Hz, respectively. The inequivalent NMe carbons produced 1:3:3:1 quartets at δ 44.3 ($^1J_{\text{C-H}} = 131$ Hz) and δ 40.9 ($^1J_{\text{C-H}} = 132$ Hz). The three inequivalent methyl carbons of the mesityl rings exhibited a singlet at δ 21.0 ($^1J_{\text{C-H}} = 122$ Hz) and a pair of overlapping signals centered at δ 19.2 ($^1J_{\text{C-H}} = 122$ Hz).

Two complementary routes were found to be suitable for the preparation of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$, **10**. Treatment of **9** with excess SiMe_3Cl in toluene at 100 °C proceeds with the formation of **10** in good yield (86.7%) (Eq. 2.4). The ^1H NMR spectrum of the isolated product showed that this reaction proceeded with the formation of only one compound. The four *meta* protons on the mesityl substituents produced a singlet at δ 6.88. The N-H proton and the two inequivalent methylene groups of the $(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$ linkage gave multiplets at δ 3.87, 3.54, and 3.45. The methyl resonances for the three inequivalent methyl groups of the mesityl substituents appeared as three separate singlets at δ 2.37, 2.33, and 2.22.

The ^{13}C NMR spectrum of **10** contained eleven distinct resonances. The six different aromatic carbons of the mesityl groups afforded six resonances at δ 145.0, 135.3, 134.1, 133.7, 129.6, and 129.5, with the *ipso* carbon being the furthest downfield. In the gated non-decoupled ^{13}C NMR spectrum, the *meta* carbons appeared as separate doublets δ 129.6 and 129.5 with $^1J_{\text{C-H}} = 161$ Hz. The methylene carbons appeared as two triplets at δ 56.8 and 49.2 with $^1J_{\text{C-H}} = 137$ and 134 Hz, respectively. The three methyl substituents on the mesityl groups appeared as separate 1:3:3:1 quartets at δ 20.9 ($^1J_{\text{C-H}} = 126$ Hz), 18.8 ($^1J_{\text{C-H}} = 125$ Hz), and 18.7 ($^1J_{\text{C-H}} = 125$ Hz).

Alternatively, the zirconium complex **10** may also be prepared in one step by the reaction of $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{Et}_2\text{O})_x$ —initially generated in diethyl ether by the reaction of $\text{Zr}(\text{benzyl})_4$ and $[\text{NEt}_3\text{H}]\text{Cl}$ —with **7** in toluene. This reaction proceeds cleanly and avoids the use of SiMe_3Cl . The ^1H NMR data of the isolated product are identical to those obtained from the product of the reaction of the bis(dimethylamido) zirconium complex **9** with SiMe_3Cl used in Schrock's published procedure.⁴³ An X-ray structural analysis of **10** confirmed its identity.

The corresponding five-coordinate zirconium complex $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$, **11**, was also prepared by the elimination of two equivalents of toluene from the reaction of $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{Et}_2\text{O})_x$ and a triamine, in this case **8**. The ^1H NMR spectrum of **11** is consistent with the presence of mirror symmetry. The two *meta* protons of the mesityl rings are inequivalent, as evidenced by the appearance of two resonances at δ 6.90 and 6.80. The methylene protons produced multiplets at δ 3.63, 3.03, 2.84, and 2.68. The three methyl substituents of each of the aromatic rings were inequivalent, affording singlets at δ 2.57, 2.48, and 2.12. The singlet at δ 0.27 corresponded to the protons of the trimethylsilyl group.

A total of twelve peaks were found in the ^{13}C APT NMR spectrum of **11**, six of them in the aromatic region. Four of these six resonances corresponded to the four quaternary carbons of each mesityl ring: the *ipso*-carbon appeared at δ 148.6, and the *ortho*- and *para*-carbons at δ 134.7, 133.3, and 132.8. In the gated non-decoupled ^{13}C NMR spectrum, the *meta* carbons appeared as separate doublets δ 130.3 and 129.8 with $^1\text{J}_{\text{C-H}} = 162$ and 157 Hz, respectively. The methylene carbons appeared as two triplets at δ 56.8 and 52.3 with $^1\text{J}_{\text{C-H}} = 137$ and 135 Hz, respectively. The three methyl substituents on the mesityl groups appeared as separate 1:3:3:1 quartets at δ 20.9 ($^1\text{J}_{\text{C-H}} = 121$ Hz), 20.1 ($^1\text{J}_{\text{C-H}} = 125$ Hz), and 19.4 ($^1\text{J}_{\text{C-H}} = 125$ Hz). The three

equivalent methyl protons of the trimethylsilyl substituent displayed a quartet at δ 0.0 with $^1J_{\text{C-H}} = 119$ Hz. An X-ray structural analysis of **11** confirmed its identity.

2.3 Preparation and Characterization of Five-Coordinate Titanium Complexes

The analogous five-coordinate titanium dichloride complexes $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$, **12**, and $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$, **13**, were prepared in excellent yields ($\geq 90\%$) by heating a toluene solution of **7** and **8**, respectively, with $\text{Ti}(\text{NR}'_2)_2\text{Cl}_2$ ($\text{R}' = \text{Me}$ (**3**), Et (**6**)) under a nitrogen flush (Eq. 2.6). Both compounds were isolated as reddish-orange solids that were only moderately soluble in chloroform.

The titanium complex **12** was initially prepared using $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$, **3**. The alternative titanium reagent $\text{Ti}(\text{NEt}_2)_2\text{Cl}_2$, **6**, was used due to complications encountered in the preparation of **3**. Initial attempts to prepare **3**, a solid, gave a mixture of products. The titanium reagent **6** was easier to prepare, but it was an oil, making it more difficult to store and handle. It was eventually found that by using at least 2.5 equivalents of SiMe_3Cl , **3** could be obtained as a reasonably pure semicrystalline solid. Yields and NMR data are comparable for the reactions of both **3** (93.9% yield) and **6** (98.6% yield) with **7**.

The ^1H NMR spectrum of **12** in chloroform- d_1 displayed the expected number of resonances. The *meta* protons of the mesityl substituents appeared as singlets at δ 6.85 and 6.84. The protons of the methyl substituents of the aryl groups displayed singlets at δ 2.36, 2.27, and 2.22. The N-H proton appeared as a pseudo-quartet at δ 3.75 due to coupling with methylene protons. The protons of the methylene carbon adjacent to the amine nitrogen appeared as a doublet of triplets at δ 3.55; the protons of the methylene carbon adjacent to the amido nitrogen appeared as a doublet of triplets at δ 4.18.

The ^{13}C NMR spectrum of **12** also displayed the expected number of resonances. The four inequivalent quaternary aromatic carbons produced peaks at δ 135.7, 131.9, 129.7, and 129.2. The resonances for the *meta* carbons were found at δ 129.3 and 129.2. The *ortho* and *para* methyl substituents produced peaks at δ 20.8, 18.9, and 18.8. The resonances for the methylene carbons adjacent to the amine and to the amido nitrogens appeared at δ 49.2 and 60.7, respectively.

The titanium dichloride complex **13** was prepared by heating a toluene solution of **8** with **6** under a nitrogen flush. The ^1H NMR data indicated the desired product was formed. The inequivalent *meta* protons of the mesityl rings produced singlets at δ 6.85 and 6.83. The methylene protons produced three distinct multiplets at δ 4.19, 3.75, and 3.57. The expected fourth multiplet was not observed, probably because other peaks obscured it. The three methyl substituents of the aromatic rings were inequivalent, affording singlets at δ 2.36, 2.27, and 2.22. The nine equivalent protons of the trimethylsilyl group produced a singlet at δ 0.52. The ^{13}C APT NMR spectrum did not display the expected number of peaks. The *ipso*-carbon and the *meta*-carbons of the mesityl groups gave resonances at δ 146.9 and δ 129.3 and 129.2, respectively. The remaining carbons of the aryl rings were not observed. The methylene carbon resonances were found at δ 61.3 and 52.7. The methyl substituents on the aromatic rings produced peaks at δ 20.8, 19.5, and 18.8, while the methyl carbons of the trimethylsilyl group produced a peak at δ 0.5. An X-ray structural analysis of **13** confirmed its identity.

2.4 Description of the Molecular Structures of **10**, **11**, and **13**

Crystals of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$ (**10**) and $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{MCl}_2$ (M = Zr (**11**) and Ti (**13**)) were obtained by slow removal of diethyl ether from saturated solutions of the respective complexes. The five-coordinate zirconium complex **10** crystallized in the centrosymmetric monoclinic space group $\text{P}2_1/\text{c}$, whereas the zirconium and titanium complexes **11** and **13** crystallized in the non-centrosymmetric orthorhombic space group $\text{P}2_12_12_1$. Each crystal lattice has four independent molecules per unit cell. Perspective views of **10**, **11**, and **13** are depicted in Figures 2.2, 2.3, and 2.4, respectively; the atom numbering schemes are provided for the non-hydrogen atoms.

Figure 2.2. Perspective view of the molecular structure and the atom labeling scheme for $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$, **10**. The thermal ellipsoids are scaled to enclose 30% probability.

Figure 2.3. Perspective view of the molecular structure and the atom labeling scheme for $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$, **11**. The thermal ellipsoids are scaled to enclose 30% probability.

Figure 2.4. Perspective view of the molecular structure and the atom labeling scheme for $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$, **13**. The thermal ellipsoids are scaled to enclose 30% probability.

In each complex, the coordination environment of the metal consists of two sp^2 amido nitrogen donors, the central sp^3 amine nitrogen donor of the tridentate ligand, and two σ -bonded chloride ligands. The Zr-N(amido) distances of 2.055(5) and 2.048(6) Å for **10** and 2.038(3) and 2.042(3) Å for **11** are somewhat shorter than the Zr-N(amido) distances in other five-coordinate d^0 Zr(IV) amido complexes (such as 2.104(5) and 2.101(4) Å in $[(Ar)NCH_2(NC_5H_3)CH_2N(Ar)]ZrCl_2$, where Ar = 2,6-di-isopropylphenyl;⁵¹ 2.070(4) and 2.077(4) Å in $[(Ar)NCH_2(NC_5H_3)CH_2N(Ar)]ZrCl_2$, where Ar = 2,6-dimethylphenyl;⁵² and 2.095(4) Å in $[(Mes)N(CH_2)_2NMe(CH_2)_2N(Mes)]ZrMe_2$ ⁴³) that also feature appreciable N(p_π)-Zr(d_π) π -bonding. The shorter Zr-N(amido) bond distances observed for **10** and **11** compared to those for the latter three zirconium complexes is a consequence of the relative positions of the two amido π -donors. The N(amido)-Zr-N(amido) bond angles in **10** and **11** are *ca.* 120°, whereas those in $[(Ar)NCH_2(NC_5H_3)CH_2N(Ar)]ZrCl_2$ and $[(Mes)N(CH_2)_2NMe(CH_2)_2N(Mes)]ZrMe_2$ are *ca.* 140°, indicating that the amido nitrogen atoms are positioned more nearly *trans* to each other in the latter complexes. This arrangement places each filled nitrogen p_π -orbital in direct competition because their respective electron pairs are interacting with the same zirconium d_π -orbital. Consequently, the longer Zr-N(amido) bond distances reflect a decrease in the N(p_π)-Zr(d_π) contribution to these bonds in these three complexes. These zirconium complexes all display Zr-N(amido) distances typical for electrophilic Zr(IV) complexes containing two or more amido nitrogen donors, such as 2.07 ± 0.01 Å for $Zr(NMe_2)_4$.⁵³

The corresponding Ti-N(amido) distances of 1.892(2) and 1.905(2) Å for **13** are appreciably shorter than the two Ti-N(amido) distances of 1.979(5) and 1.977(6) Å in $[(Ar)NCH_2(NC_5H_3)CH_2N(Ar)]Ti(CH_2CMe_2Ph)Br$, where Ar = 2,6-dimethylphenyl,⁵⁴ but are comparable to the Ti-N(amido) distances of 1.905(2) and 1.910(2) Å in the related five-coordinate d^0 titanium complex, $[N(SiMe_3)(CH_2)_2N(SiMe_3)(CH_2)_2N(SiMe_3)]TiMe_2$.⁵⁵ The observed variation for these Ti-N(amido) bonds can also be attributed to the relative positions of the amido nitrogen π -donors in these five-coordinate titanium complexes. The N(amido)-Ti-N(amido) bond angles in **13** and $[N(SiMe_3)(CH_2)_2N(SiMe_3)(CH_2)_2N(SiMe_3)]TiMe_2$ of 121.45(9) and 124.67(9)°, ⁵⁵ respectively, are appreciably smaller than the corresponding angle of 142.1(2)° in $[(Ar)NCH_2(NC_5H_3)CH_2N(Ar)]Ti(CH_2CMe_2Ph)Br$.⁵⁴

Whereas the amido nitrogen donors have two lone pairs for π -bonding to the electron deficient group IV metal, the central amine nitrogen donor of the tridentate diamidoamine ligand has only one lone pair, which is utilized to form a dative $N \rightarrow Zr$ or $N \rightarrow Ti$ bond. As a result, the central M-N(amino) distances of 2.361(6), 2.475(3), and 2.438(2) Å for **10**, **11**, and **13**, respectively, are significantly longer than the corresponding M-N(amido) distances. The 0.11 Å increase in the Zr-N(amine) bond distance upon replacement of the hydrogen on the central nitrogen of **10** with the trimethylsilyl substituent in **11** is a consequence of the decrease in the nitrogen donor strength due to the greater electron withdrawing character of the trimethylsilyl substituent relative to hydrogen. An even more substantial elongation of the central Zr-N(amino) distance was observed for $[N(Me_3Si)(CH_2)_2N(SiMe_3)(CH_2)_2N(SiMe_3)]ZrCl(CH(SiMe_3)_2)$.⁵⁶ In this case, the corresponding Zr-N(amino) interatomic separation of 2.770(5) Å is 0.73 Å longer than the two Zr-N(amido) distances of 2.035(5) and 2.041(5) Å.

X-ray structural analyses performed on five-coordinate group IV metal complexes featuring a dianionic tridentate diamido ligand indicate that these compounds may adopt two different molecular configurations within a trigonal bipyramidal framework. These two configurations are designated as meridonal (*mer*) and facial (*fac*). In the *mer* structure (Figure 2.5), the two terminal amido nitrogen donors occupy the two axial sites and the central donor atom (X) lies in the equatorial plane. The three donor atoms of the tridentate ligand in this C_{2v} -symmetric structure further define a plane that bisects the L-M-L bond angle. This structural arrangement was reported by Schrock and his co-workers for $[(Ar)N(CH_2)_2O(CH_2)_2N(Ar)]MR_2$ -type complexes, where M = Zr or Hf, R = alkyl, Ar = 2,6-dimethylphenyl or 2,6-diisopropylphenyl;^{57,58} $[(t-BuN-o-C_6H_4)_2O]MMe_2$, where M = Ti or Zr;⁵⁹ and $[(Mes)N(CH_2)_2NMe(CH_2)_2N(Mes)]ZrMe_2$.⁴³ The corresponding $[(Ar)NCH_2(NC_5H_3)CH_2N(Ar)]ZrCl_2$ complexes^{51,52} that feature a planar pyridyl nitrogen donor also conform to the *mer* configuration. In contrast, in the C_s -symmetric *fac* structure (Figure 2.5), the two amido nitrogen donors occupy two equatorial positions and the central donor atom (X) resides in an axial position. This alternative ligand arrangement was observed for $[N(Me_3Si)(CH_2)_2N(SiMe_3)(CH_2)_2N(SiMe_3)]ZrCl(CH(SiMe_3)_2)$ ⁵⁶ as well as $[(Ar)N(CH_2)_2O(CH_2)_2N(Ar)]Ti(benzyl)_2$ and $[(Ar)N(CH_2)_2S(CH_2)_2N(Ar)]ZrMe_2$, where Ar = 2,6-dimethylphenyl.⁵⁸

Figure 2.5. Configurations of Five-Coordinate Complexes

A careful examination of the bond angles about the zirconium (**10** and **11**) or titanium (**13**) atom provided in Table 2.1 indicates that these three five-coordinate complexes adopt a geometry that is consistent with the *fac* structure. One of the two chloride ligands (i.e., Cl(2)) lies *trans* to the central amino nitrogen of the tridentate diamidoamine ligand. The equatorial positions of the distorted trigonal bipyramid are defined by the two amide nitrogen donor atoms and Cl(1). The respective Cl(2)-M-N(2) and Cl(1)-M-N(2) bond angles (169.54(16) and 87.41(16)° for **10**, 166.41(7) and 93.06(7)° for **11**, and 170.23(6) and 91.99(6)° for **13**) are consistent with Cl(2) lying *trans* to N(2) and Cl(1) occupying an equatorial position of a distorted trigonal bipyramid. The obtuse dihedral angles between the corresponding planes containing N(1), M, N(2) and N(2), M, N(3) of 131.4, 130.6, and 128.0° in **10**, **11**, and **13**, respectively, deviate substantially from the corresponding idealized dihedral angle of 180° expected for the C_{2v} -symmetric *mer* structure but are more similar to the 120° dihedral angle expected for the C_s -symmetric *fac* structure. Chelation of the diamidoamine ligand in these complexes produces two puckered five-membered rings with an S-shaped backbone (Figure 2.6). To reduce steric congestion about the M atom, the two mesityl substituents on the amido nitrogen donors of **10**, **11**, and **13** are directed toward the side opposite from the equatorial chloride ligand, Cl(1), and away from the hydrogen or trimethylsilyl group at N(2). This feature is readily seen in Figure 2.6, which provides a view parallel to the Zr(1), Cl(1), and Cl(2) plane in **10**.

Figure 2.6. Perspective view of the molecular structure of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$, **10**, looking parallel to the ZrCl_2 plane.

Table 2.1. Selected Bond Angles (°) About the Central Metal Atom in [(Mes)N(CH₂)₂NH(CH₂)₂N(Mes)]ZrCl₂ (**10**) and [(Mes)N(CH₂)₂N(SiMe₃)(CH₂)₂N(Mes)]MCl₂ (M = Zr (**11**) and Ti (**13**))

Bond Angle	10	11	13	Ideal
Cl(1)-M-Cl(2)	103.05(8)	100.52(4)	97.79(4)	90
Cl(1)-M-N(1)	110.04(16)	114.82(9)	116.41(7)	120
Cl(1)-M-N(2)	87.41(16)	93.06(7)	91.99(6)	90
Cl(1)-M-N(3)	114.29(17)	115.24(9)	115.03(7)	120
Cl(2)-M-N(1)	104.15(17)	100.61(10)	99.20(7)	90
Cl(2)-M-N(2)	169.54(16)	166.41(7)	170.23(6)	180
Cl(2)-M-N(3)	102.82(17)	99.56(9)	99.73(7)	90
N(1)-M-N(3)	120.1(2)	120.67(14)	121.45(9)	90
N(1)-M-N(2)	71.7(2)	72.95(11)	76.24(8)	120
N(2)-M-N(3)	72.3(2)	74.64(11)	75.96(8)	90

The covalent radius of zirconium (1.45 Å) and the ionic radius of Zr⁴⁺ (0.80 Å) are *ca.* 0.12 – 0.13 Å larger than those of titanium (1.32 Å) and Ti⁴⁺ (0.68 Å).⁶⁰ Consequently, the larger size of zirconium is expected to produce longer M-Cl and M-N bonds than titanium in similar ligand environments. A comparison of the structural data in Table 2.2 shows that the observed differences between the M-Cl and M-N(amido) distances for **11** and **13** are consistent with this expectation. However, the corresponding M-N(amino) bonds are more similar in magnitude. Although these long M-N(amino) bonds reflect the weaker amine nitrogen donor strength due to the trimethylsilyl substituent, an additional lengthening of the Ti-N(2) bond in **13** arises from the more sterically crowded coordination environment about the smaller titanium metal center.

Table 2.2. Selected Interatomic Distances (Å) for [(Mes)N(CH₂)₂N(SiMe₃)(CH₂)₂N(Mes)]MCl₂ (M = Zr (**11**) and Ti (**13**))

Bond Distance	11 (M = Zr)	13 (M = Ti)	Difference
M-Cl(1)	2.415(1)	2.2885(9)	0.126
M-Cl(2)	2.402(1)	2.2563(10)	0.145
M-N(1)	2.038(3)	1.892(2)	0.146
M-N(2)	2.475(3)	2.438(2)	0.037
M-N(3)	2.042(3)	1.905(2)	0.137

Finally, the M-Cl(2) bond *trans* to the M-N(2) bond in both **11** and **13** is consistently shorter than the M-Cl(1) bond that lies perpendicular to the M-N(2) bond. The weaker dative bonding interaction of the neutral amino nitrogen donor in these complexes is compensated for

by enhanced π -donation from Cl(2) to the electrophilic metal. The noticeably larger difference, $\Delta_{\text{M-Cl}}$, between the two M-Cl distances of 0.032 Å in **13** compared to 0.013 Å in **11** provides another indication of a weaker N(2)→M dative interaction in **13** compared to **11**.

The results of the X-ray structural analyses of **10**, **11**, and **13** clearly show that these three mononuclear complexes adopt analogous five-coordinate facial structures. The NMR data for these complexes demonstrate that they exhibit C_s symmetry in solution, as indicated by the observation of six distinct carbon resonances for the aryl carbons and three different ^1H and ^{13}C NMR resonances for the three methyl groups of the mirror-related mesityl substituents. The S-shaped backbone of the $\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2\text{N}$ unit introduces an element of chirality in the solid state structures of **10**, **11**, and **13**. However, the appearance of two rather than four distinct methylene carbon resonances indicates that the chemical environments of the α and β methylene carbons (relative to the central amino nitrogen) are equivalent on the NMR time scale.

Chapter 3. Concluding Remarks

New synthetic routes for the preparation of five-coordinate zirconium and titanium complexes featuring tridentate diamidoamine ligands were developed during the course of the investigations described in this thesis. The zirconium dichloride complexes $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{ZrCl}_2$, $\text{R} = \text{H}$ (**10**) and SiMe_3 (**11**), were synthesized via a one-step toluene elimination reaction. This toluene elimination involved the reaction of $\text{Zr}(\text{benzyl})_4$ with two equivalents of $[\text{NEt}_3\text{H}]\text{Cl}$ to produce a thermally and photochemically unstable intermediate, $\text{Zr}(\text{benzyl})_2\text{Cl}_2(\text{Et}_2\text{O})_x$, that was reacted with one of two triamines, $(\text{Mes})\text{NH}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{NH}(\text{Mes})$, $\text{R} = \text{H}$ (**7**), SiMe_3 (**8**), as it was generated. This reaction offered multiple advantages over the route used by Schrock and McConville.⁴³ It did not require heat, the use of SiMe_3Cl , or the isolation and purification of an intermediate bis(dimethylamido) zirconium complex. Analogous titanium dichloride complexes $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NR}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$, $\text{R} = \text{H}$ (**12**) and SiMe_3 (**13**), were prepared using a one-step amine elimination reaction that employed the reaction of **7** or **8** with the titanium reagent $\text{Ti}(\text{NR}_2)_2\text{Cl}_2$, $\text{R} = \text{Me}$ (**3**) or Et (**6**).

The NMR data for complexes **10**, **11**, **12**, and **13** demonstrated that they exhibit C_s symmetry in solution, as indicated by the fact that six distinct carbon resonances for the aryl carbons and three different ^1H and ^{13}C NMR resonances for the three methyl groups of the mirror-related mesityl substituents are observed. Molecular structures obtained from crystals of **10**, **11**, and **13** confirmed that the one-step toluene and amine elimination reactions successfully prepared five-coordinate zirconium and titanium dichloride complexes. In each case, the coordination environment of the metal consists of two sp^2 amido nitrogen donors, the central sp^3 amine nitrogen donor of the tridentate ligand, and two σ -bonded chloride ligands. The bond angles about the zirconium (**10** and **11**) or titanium (**13**) atom indicate that these three complexes adopt a geometry that is consistent with the *fac* structure, in which one of the two chloride ligands (i.e., $\text{Cl}(2)$) lies *trans* to the central amino nitrogen of the tridentate diamidoamine ligand and the equatorial positions are defined by the two amide nitrogen donor atoms and $\text{Cl}(1)$.

Chapter 4. Experimental Section

4.1 Reagents

Reagent grade hydrocarbon and ethereal solvents were purified using standard methods.⁶¹ Pentane, toluene, and THF were refluxed under nitrogen over Na/K and then transferred to storage flasks containing $[(C_5H_5)_2Ti(\mu-Cl)_2]_2Zn$.⁶² The deuterated solvents C_6D_6 (Aldrich, 99.5%) and $CDCl_3$ (Aldrich, 99.8%) were dried over activated 4Å molecular sieves prior to use, as were diethylenetriamine (Aldrich) and Et_2NH (Aldrich). $TiCl_4(THF)_2$ ⁶³ and $Zr(benzyl)_4$ ⁵⁰ were prepared by literature procedures. $[NEt_3H]Cl$ was prepared by the stoichiometric addition of HCl to a pentane solution of NEt_3 . $TiCl_4$ (Aldrich), *n*-BuLi (Aldrich, 1.6 M in hexanes), HCl (Matheson), $LiNMe_2$ (Aldrich), NEt_3 (Aldrich), $SiMe_3Cl$ (Aldrich), 2-bromomesitylene (Aldrich), Na-O-*t*Bu (Acrös), $Pd_2(dba)_3 \cdot CHCl_3$ (Strem Chemicals), *rac*-BINAP (Strem Chemicals), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich) were used without further purification.

4.2 General Considerations

All syntheses and manipulations were carried out on a double-manifold, high-vacuum line or in a Vacuum Atmospheres glovebox equipped with an HE-493 Dri-Train. Reactions were typically carried out in pressure-equalizing filter-frits equipped with high-vacuum Teflon stopcocks and solv-seal joints. Nitrogen was purified by passage over reduced BTS catalysts and activated 4Å molecular sieves. All glassware was thoroughly oven-dried and/or flame-dried under vacuum prior to use. NMR sample tubes were sealed under approximately 500 Torr of nitrogen. 1H and ^{13}C NMR spectra were measured on a JEOL GX-270 or Eclipse 270 FT-NMR spectrometer operating in the FT mode at 270 (1H) and 67.5 MHz (^{13}C). The 1H chemical shifts are referenced to the residual proton peak of benzene- d_6 (δ 7.15) or chloroform- d_1 (δ 7.24); the ^{13}C resonances are referenced to the central carbon peak of benzene- d_6 (δ 128.0) or chloroform- d_1 (δ 77.0). Elemental analyses were performed by Complete Analysis Laboratories Inc. of Parsippany, NJ.

4.3 Preparation of Starting Materials

4.3.1 Preparation of $\text{Zr}(\text{NMe}_2)_4$, 1

To a 100-mL solv-seal flask equipped with a side arm was added 5.70 g (111.7 mmol) of LiNMe_2 . To the side arm was added 6.00 g (25.7 mmol) of ZrCl_4 . Toluene (*ca.* 40 mL) was added via vacuum distillation. The reaction mixture was stirred overnight at room temperature. The toluene was removed and replaced by *ca.* 50 mL of pentane. The product was extracted and the solvent removed, leaving a semi-crystalline residue. The product was sublimed, giving a white crystalline solid.

Yield: 66.0 % (4.53 g, 16.9 mmol)

^1H NMR data (C_6D_6): δ 3.04 (s, CH_3).

4.3.2 Preparation of $\text{Ti}(\text{NMe}_2)_4$, 2

To a 100-mL solv-seal flask equipped with a side arm was added 2.0 g (39.2 mmol) of LiNMe_2 . To the side arm was added 3.0 g (9.0 mmol) of $\text{TiCl}_4(\text{THF})_2$. Toluene (*ca.* 30 mL) was added via vacuum distillation. The $\text{TiCl}_4(\text{THF})_2$ was added in small increments over the course of several hours. The reaction mixture was allowed to stir for 24 hours, resulting in a yellow solution. The toluene was then removed and replaced by pentane. The solution was filtered and the product extracted. The pentane was removed, leaving a bright yellow liquid.

Yield: 90.7 % (1.83 g, 5.75 mmol)

^1H NMR data (C_6D_6): δ 3.11 (s, CH_3).

4.3.3 Preparation of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$, **3**

Toluene (*ca.* 20 mL) and 2.10 mL (16.5 mmol) of SiMe_3Cl were added via vacuum distillation to a flask containing 1.83 g (5.75 mmol) of **1**. The reaction mixture was stirred at room temperature for several hours and then heated to 60 °C for 10 hours, producing a reddish-orange solution. The solvent was removed. The product was then washed with *ca.* 30 mL of pentane. The reddish-orange solid was dried *in vacuo*. The ^1H NMR spectrum, measured in C_6D_6 , showed the product was clean.

Yield: 92.2 % (1.56 g, 7.59 mmol)

^1H NMR data (C_6D_6): δ 2.95 (s, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR data (C_6D_6): δ 45.3 (CH_3).

4.3.4 Preparation of LiNEt_2 , **4**

Pentane (50 – 60 mL) and 11.7 mL (113.1 mmol) of Et_2NH were added to a 250-mL round-bottom flask via vacuum distillation. While the reaction mixture was stirring under a liquid nitrogen/isopropyl alcohol bath, a disposable syringe was used to add 71 mL (113.6 mmol) of 1.6 M *n*-BuLi in hexane. The reaction mixture was slowly warmed to room temperature and then stirred overnight. The solution was filtered and the pentane removed. The resultant white, powdery solid was washed repeatedly with several mL of pentane and then dried *in vacuo*.

Yield: 92.6 % (8.28 g, 104.8 mmol)

4.3.5 Preparation of $\text{Ti}(\text{NEt}_2)_4$, **5**

To a 100-mL solv-seal flask equipped with a side arm was added 1.4703 g (18.6 mmol) of **4**. To the side arm was added 1.5152 g (4.54 mmol) of $\text{TiCl}_4(\text{THF})_2$. Toluene (*ca.* 35 mL) was added via vacuum distillation. The $\text{TiCl}_4(\text{THF})_2$ was then added in small increments. The reaction

mixture was stirred overnight at room temperature. The reaction was then heated at 100 °C under a nitrogen atmosphere for several hours. The toluene was replaced by *ca.* 40 mL pentane. The solution was filtered and the product extracted before the solvent was removed. The brownish-red oily product was dried *in vacuo*. The ^1H NMR spectrum, measured in C_6D_6 , indicated the product was clean.

Yield: 92.6 % (1.42 g, 4.32 mmol)

^1H NMR data (C_6D_6): δ 3.57 (q, CH_2), 1.10 (t, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR data (C_6D_6): δ 45.3 (CH_3), 15.6 (CH_2).

4.3.6 Preparation of $\text{Ti}(\text{NEt}_2)_2\text{Cl}_2$, **6**

Toluene (*ca.* 30 mL) and 1.10 mL (8.67 mmol) of SiMe_3Cl were vacuum transferred into a 100-mL solv-seal flask containing 1.3486 g (4.01 mmol) of **5**. The reaction was placed under a nitrogen atmosphere and stirred overnight at room temperature; it was then heated to 60 °C for 60 hours. The toluene was removed and *ca.* 40 mL of pentane added. The solution was filtered and the product extracted before the solvent was removed. The deep red oily product was then dried *in vacuo*. The ^1H NMR spectrum, measured in C_6D_6 , indicated the clean formation of the desired product.

Yield: 92.6 % (0.977 g, 3.71 mmol)

^1H NMR data (C_6D_6): δ 3.55 (q, CH_2), 0.87 (t, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR data (C_6D_6): δ 47.1 (CH_3), 14.1 (CH_2).

4.4 Preparation of Triamines (Mes)NH(CH₂)₂NR(CH₂)₂NH(Mes), R = H, SiMe₃

4.4.1 Preparation of (Mes)NH(CH₂)₂NH(CH₂)₂NH(Mes), Mes = Mesityl, **7**

To a 100-mL solv-seal flask were added 1.03 g (9.98 mmol) of diethylenetriamine, 4.00 g (20.1 mmol) of 2-bromomesitylene, 2.50 g (26.0 mmol) of Na-O-tBu, 0.0211 g (0.0204 mmol) of Pd₂(dba)₃·CHCl₃, and 0.0379 g (0.0608 mmol) of *rac*-BINAP. Toluene (*ca.* 40 mL) was added via vacuum distillation. The reaction mixture was placed under a nitrogen atmosphere and heated to 100 – 120 °C for 40 hours. The reaction mixture was cooled to room temperature and filtered. The product was extracted and the toluene removed, leaving a dark reddish solid. Pentane (*ca.* 30 mL) was added via vacuum distillation. The solution was filtered and the solvent removed, leaving a dark oily product. The oil was frozen using liquid nitrogen. The product remained a solid after the liquid nitrogen was removed and the flask warmed to ambient temperature. The product was dried *in vacuo*.

Yield: 91.7% (3.11 g, 9.16 mmol)

¹H NMR data (CDCl₃): δ 6.81 (s, Mes*H*), 3.38 (t, NH), 3.03 (m, CH₂), 2.83 (m, CH₂), 2.26 (s, *o*-MesMe), 2.21 (s, *p*-MesMe).

Gated non-decoupled ¹³C NMR data (CDCl₃): δ 143.6 (s, *ipso*-C), 131.2 (s, *p*-MesMe), 129.7 (s, *o*-MesMe), 129.4 (d, MesCH, 145.8), 50.0 (t, CH₂, 132.5), 48.4 (t, CH₂, 135.6), 20.5 (q, *p*-MesMe, 125.1), 18.3 (q, *o*-MesMe, 125.6).

4.4.2 Preparation of (Mes)NH(CH₂)₂N(SiMe₃)(CH₂)₂NH(Mes), Mes = Mesityl, **8**

To a 100-mL solv-seal flask equipped with a side arm was added 1.2358 g (8.12 mmol) of DBU. To the side arm was added 2.7693 g (8.16 mmol) of **7**. Diethyl ether (*ca.* 35 mL) and 1.1 mL (8.67 mmol) of SiMe₃Cl were added via vacuum distillation. The DBU/SiMe₃Cl/Et₂O solution was placed under a nitrogen atmosphere and stirred at room temperature for 1 hour, immediately forming a white solid. The triamine was added in small increments. The reaction mixture was

stirred overnight at room temperature. The solution was filtered, the product extracted with pentane, and the solvent removed. The brown oily product was dried *in vacuo*. The ^1H and ^{13}C APT NMR spectra, measured in CDCl_3 , indicated the desired product was fairly pure.

Yield: 92.6 % (3.11 g, 7.55 mmol)

^1H NMR data (CDCl_3): δ 6.79 (s, MesCH), 2.97 (m, CH_2), 2.22 (s, *o*-MesMe), 2.21 (s, *p*-MesMe), 0.11 (s, SiMe_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR data (CDCl_3): δ 143.6 (*ipso*-C), 130.9 (*p*-MesCMe), 129.4 (*m*-MesCH), 129.1 (*o*-MesCMe), 47.1 (CH_2), 46.5 (CH_2), 20.5 (*p*-MesMe), 18.4 (*o*-MesMe), 0.14 (SiMe_3).

4.5 Preparation of Five-Coordinate Zirconium Bis(dimethylamido) Complexes

4.5.1 Preparation of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{Mes})]\text{Zr}(\text{NMe}_2)_2$, Mes = Mesityl, **9**

To a 100-mL solv-seal flask were added 0.500 g (1.87 mmol) of **1** and 0.635 g (1.87 mmol) of **7**. Toluene (*ca.* 35 mL) was added in the glove box. The toluene solution was heated to 100 °C overnight, using nitrogen to periodically flush the NMe_2H produced during the reaction. The toluene was removed, leaving a semi-crystalline residue. The product was extracted with pentane, the solution filtered, and the solvent removed.

Yield: 97.9 % (0.745 g, 1.44 mmol)

^1H NMR data (C_6D_6): δ 6.94 (s, MesCH), 3.35 (m, NH), 3.05 (s, NMe_2), 3.00 (m, NHCH_2CH_2), 2.55 (m, NHCH_2), 2.47 (s, *o*-Mes CH_3), 2.44 (s, *o*-Mes CH_3), 2.28 (s, NMe_2), 2.21 (s, *p*-Mes CH_3).

Gated non-decoupled ^{13}C NMR data (C_6D_6), (mult, $^1\text{J}_{\text{C-H}}$ in Hz): δ 150.1 (s, *ipso*-C), 134.1 (s, *o*-MesC), 134.0 (s, *o*-MesC), 131.7 (s, *p*-MesC), 129.7 (d, *m*-MesCH, 160), 55.2 (t,

NCH₂CH₂, 133), 48.8 (t, NCH₂, 135), 44.3 (q, NMe, 131), 40.9 (q, NMe, 132), 30.0 (q, *p*-MesCH₃, 122), 19.2 (*o*-MesCH₃, 122).

4.6 Preparation of Five-Coordinate Zirconium Dichloride Complexes

4.6.1 Preparation of [(Mes)N(CH₂)₂NH(CH₂)₂N(Mes)]ZrCl₂, Mes = Mesityl, **10**

4.6.1.1 Reaction of **9** with SiMe₃Cl

To a 100-mL solv-seal flask were added 1.8544 g (3.59 mmol) of **9** and *ca.* 15 mL of toluene. A 1.0-mL (7.88 mmol) volume of SiMe₃Cl (roughly 50% excess) was added to the toluene solution via vacuum distillation. The reaction mixture was heated to 60 °C and stirred overnight under nitrogen. The solvent was then removed. The resultant compound was washed in pentane, in which it was only slightly soluble. The solvent was removed and the product residue was dried *in vacuo*. The ¹H NMR spectrum of the finely divided solid showed that **10** was produced in a clean reaction.

Yield: 86.7 % (1.55 g, 3.11 mmol)

¹H NMR data (CDCl₃): δ 6.88 (s, MesCH), 3.87 (m, NH), 3.54 (m, NCH₂CH₂), 3.45 (m, NCH₂), 2.37 (s, *o*-MesCH₃), 2.33 (s, *o*-MesCH₃), 2.22 (s, *p*-MesCH₃).

Gated non-decoupled ¹³C NMR data (CDCl₃), (mult, ¹J_{C-H} in Hz): δ 145.0 (s, *ipso*-C), 135.3 (s, *p*-MesC), 134.1 (s, *o*-MesC), 133.7 (s, *o*-MesC), 129.6 (d, *m*-MesCH, 161), 129.5 (d, *m*-MesCH, 161), 56.8 (t, NHCH₂CH₂, 137), 49.2 (t, NHCH₂, 134), 20.9 (q, *p*-MesCH₃, 126), 18.8 (q, *o*-MesCH₃, 125), 18.7 (q, *o*-MesCH₃, 125).

4.6.1.2 Toluene Elimination Reaction

To a 250-mL round-bottom flask equipped with two side arms was added 3.8871 g (8.53 mmol) of Zr(benzyl)₄. To one side arm was added 2.3481 g (17.06 mmol) of [NEt₃H]Cl. To the other

side arm was added 2.8958 g (8.53 mmol) of **7**. Diethyl ether (*ca.* 60 mL) was added via vacuum distillation. The reaction was stirred at 0 °C while the [NEt₃H]Cl was added in small increments. The volatiles were then removed. Toluene (*ca.* 75 mL) was added. The reaction was stirred at 0 °C while **7** was added in small increments. The reaction was then warmed to room temperature and stirred overnight. The solution was filtered and the product extracted before the toluene was removed. The product was then washed in *ca.* 45 mL of pentane. Soluble impurities were extracted before the pentane was removed. The light tan solid was dried *in vacuo*. The ¹H NMR spectrum, measured in CDCl₃, confirmed the formation of **10** as the only product.

Yield: 87.9 % (3.75 g, 7.50 mmol)

¹H NMR data (CDCl₃): δ 6.87 (s, MesCH), 3.87 (m, NH), 3.55 (m, NCH₂CH₂), 3.45 (m, NCH₂), 2.37 (s, *o*-MesCH₃), 2.32 (s, *o*-MesCH₃), 2.22 (s, *p*-MesCH₃).

Chemical Analysis: Calculated for C₂₂H₃₁N₃Cl₂Zr: C, 52.89; H, 6.25; N, 8.41. Found: C, 51.79; H, 6.40; N, 7.96.

4.6.2 Preparation of [(Mes)N(CH₂)₂N(SiMe₃)(CH₂)₂N(Mes)]ZrCl₂, Mes = Mesityl, **11**

To a 250-mL round-bottom flask equipped with two side arms was added 3.6524 g (8.01 mmol) of Zr(benzyl)₄. To one side arm was added 2.2063 g (16.03 mmol) of [NEt₃H]Cl. To the other side arm was added 3.2994 g (8.01 mmol) of **8**. Diethyl ether (*ca.* 60 mL) was added via vacuum distillation. The reaction was stirred at 0 °C while the [NEt₃H]Cl was added in small increments. The volatiles were then removed. Toluene (*ca.* 65 mL) was added. The reaction was stirred at 0 °C while **8** was added in small increments. The reaction was then warmed to room temperature and stirred overnight. The solution was filtered and the toluene removed. The product was then washed in *ca.* 40 mL of pentane. The off-white solid was dried *in vacuo*. The ¹H NMR spectrum, measured in C₆D₆, confirmed the formation of **11** as the only product.

Yield: 74.2 % (3.39 g, 5.94 mmol)

^1H NMR data (C_6D_6): δ 6.90 (s, MesH), 6.80 (s, MesH), 3.63 (m, CH_2), 3.03 (m, CH_2), 2.84 (m, CH_2), 2.68 (m, CH_2), 2.57 (s, MesCH₃), 2.48 (s, MesCH₃), 2.12 (s, MesCH₃), 0.27 (s, Si(CH₃)₃).

Gated non-decoupled ^{13}C NMR data (C_6D_6), (mult, $^1\text{J}_{\text{C-H}}$ in Hz): δ 148.6 (s, *ipso-C*), 134.7 (s, MesCCH₃), 133.3 (s, MesCCH₃), 132.8 (s, MesCCH₃), 130.3 (d, MesCH, 162), 129.8 (d, MesCH, 157), 56.8 (t, CH_2 , 137), 52.3 (t, CH_2 , 135), 20.9 (q, MesCH₃, 121), 20.1 (q, MesCH₃, 125), 19.4 (q, MesCH₃, 125), 0.0 (q, Si(CH₃)₃, 119).

Chemical Analysis: Calculated for $\text{C}_{25}\text{H}_{39}\text{N}_3\text{Cl}_2\text{SiZr}$: C, 52.51; H, 6.87; N, 7.35. Found: C, 52.29; H, 6.87; N, 7.27.

4.7 Preparation of Five-Coordinate Titanium Dichloride Complexes

4.7.1 Preparation of [(Mes)N(CH₂)₂NH(CH₂)₂N(Mes)]TiCl₂, Mes = Mesityl, 12

4.7.1.1 Amine Elimination Reaction with 3

To a 100-mL solv-seal flask were added 0.305 g (1.47 mmol) of **3**, 0.500 g (1.47 mmol) of **7**, and *ca.* 30 mL of toluene. The reaction mixture was heated at 100 °C overnight under a nitrogen flush. The toluene was removed. Pentane (*ca.* 35 mL) was added via vacuum distillation. The solvent was decanted off the product and removed. The powdery, reddish-orange product was dried *in vacuo*.

Yield: 93.9% (0.631 g, 1.38 mmol)

^1H NMR data (CDCl_3): δ 6.85 (s, MesH), 6.83 (s, MesH), 4.19 (m, CH_2), 3.75 (m, CH_2), 3.55 (m, CH_2), 3.39 (bs, NH), 2.36 (s, MesMe), 2.27 (s, MesMe), 2.21 (s, MesMe).

$^{13}\text{C}\{^1\text{H}\}$ NMR data (CDCl_3): δ 135.7 (*ipso-C*), 131.9 (*p*-MesCMe), 129.7 (*o*-MesCMe), 129.3 (*o*-MesCMe), 129.2 (MesCH), 129.2 (MesCH), 60.7 (CH_2), 49.2 (CH_2), 20.8 (*p*-MesMe), 18.9 (*o*-MesMe), 18.8 (*o*-MesMe).

Chemical Analysis: Calculated for $\text{C}_{22}\text{H}_{31}\text{N}_3\text{Cl}_2\text{Ti}$: C, 57.91; H, 6.85; N, 9.21. Found: C, 56.98; H, 6.96; N, 8.92.

4.7.1.2 Amine Elimination Reaction with **6**

To a 100-mL solv-seal flask containing 0.9769 g (3.71 mmol) of **6** were added 1.6184 g (4.77 mmol) of **7** and *ca.* 35 mL of toluene. The reaction mixture was heated to 100 °C under a nitrogen flush for 48 hours. The toluene was then replaced by *ca.* 30 mL pentane. The solvent was decanted off the product and then removed. The product was dried *in vacuo*. The ^1H NMR spectrum of the product, measured in CDCl_3 , indicated **12** was formed in a fairly clean reaction. The product was washed several times with pentane and then dried *in vacuo*.

Yield: 98.6 % (1.67 g, 3.66 mmol)

^1H NMR data (CDCl_3): δ 6.85 (s, MesH), 6.84 (s, MesH), 4.18 (m, CH_2), 3.75 (m, CH_2), 3.55 (m, CH_2), 3.34 (m, NH), 2.36 (s, MesMe), 2.27 (s, MesMe), 2.22 (s, MesMe).

4.7.2 Preparation of $[(\text{Mes})\text{N}(\text{CH}_2)_2\text{N}(\text{SiMe}_3)(\text{CH}_2)_2\text{N}(\text{Mes})]\text{TiCl}_2$, Mes = Mesityl, **13**

To a 100-mL solv-seal flask containing 1.0488 g (3.99 mmol) of **6** and 1.4994 g (3.64 mmol) of **8** was added *ca.* 40 mL of toluene. The reaction was stirred overnight while heating to 100 °C under a nitrogen flush. The solvent was then removed and the product dried *in vacuo*. Pentane (*ca.* 30 mL) was added. The solvent was decanted off the solid and the impurities extracted. The pentane was then removed and the product dried *in vacuo*.

^1H NMR data (CDCl_3): δ 6.85 (s, MesH), 6.83 (s, MesH), 4.19 (m, CH_2), 3.75 (m, CH_2), 3.57 (m, CH_2), 2.36 (s, MesMe), 2.27 (s, MesMe), 2.22 (s, MesMe), 0.52 (s, SiMe_3).

^{13}C APT NMR data (CDCl_3): δ 146.9 (*ipso-C*), 129.3 (MesCH), 129.2 (MesCH), 61.3 (CH_2), 52.7 (CH_2), 20.8 (MesCH₃), 19.5 (MesCH₃), 18.8 (MesCH₃), 0.5 ($\text{Si}(\text{CH}_3)_3$).

Chemical Analysis: Calculated for $\text{C}_{25}\text{H}_{39}\text{N}_3\text{Cl}_2\text{SiTi}$: C, 56.82; H, 7.44; N, 7.95. Found: C, 56.74; H, 7.60; N, 8.16.

4.8 Description of the X-ray Structural Analyses

The X-ray structural analyses of **10**, **11**, and **13** were performed by following the same general procedures. Each crystal was coated with the perfluoropolyether PFO-XR75 (Lancaster) and sealed under nitrogen in a glass capillary. Each sample was optically aligned on the four-circle of a Siemens P4 diffractometer equipped with a graphite monochromatic crystal, a $\text{MoK}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$), and a SMART CCD detector held at 5.054 cm from the crystal. The samples of the two zirconium compounds were cooled to -50°C by the nitrogen cold stream provided by a LT-2 low temperature attachment.

Four sets of 20 frames each were collected using the ω scan method with a ten second exposure time. Integration of these frames followed by reflection indexing and least squares refinement produced a crystal orientation matrix and preliminary lattice parameters. Data collection consisted of the measurement of a total of 1650 frames in five different runs covering a hemisphere of data. Frame scan parameters are summarized in Table 4.1.

Table 4.1. Frame Scan Parameters

Run	2θ	ω	ϕ	χ	Scan axis	Scan width ($^\circ$)	Frames (#)	Exposure time (s)
1	28	43.00	0.00	280.00	2	-0.3	100	30
2	28	43.00	90.00	280.00	2	-0.3	100	30
3	28	43.00	180.00	280.00	2	-0.3	100	30
4	28	43.00	270.00	280.00	2	-0.3	100	30
5	28	28.00	0.00	30.00	3	0.3	1250	30

The program SMART (version 5.6)⁶⁴ was used for diffractometer control, frame scans, indexing, orientation matrix calculations, least squares refinement of cell parameters, and the data collection.

All 1650 crystallographic raw data frames were read by program SAINT (version 5/6.0)⁶⁴ and integrated using 3D profiling algorithms. An absorption correction was applied using the SADABS routine available in SAINT.⁶⁴ The data were corrected for Lorentz and polarization effects as well as any crystal decay. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values from the International Tables for X-ray Crystallography.⁶⁵

Initial coordinates for all of the non-hydrogen atoms were determined by a combination of direct methods and difference Fourier methods with the use of SHELXTL 6.1.⁶⁶ Idealized positions for the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 (aromatic protons) or 1.5 (methyl protons) times that of the adjacent carbon. The positions of the methyl hydrogen atoms were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i |F_o^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2 (F_o^2) + (a P)^2 + b P]$, where $P = (\text{Max}(F_o^2, 0) + 2 F_c^2)/3$, converged to give final discrepancy indices⁶⁷ tabulated in Table 4.2.

Table 4.2. Crystal Data and Structural Information for [(Mes)N(CH₂)₂NH(CH₂)₂N(Mes)]ZrCl₂ (**10**) and [(Mes)N(CH₂)₂N(SiMe₃)(CH₂)₂N(Mes)]MCl₂ (M = Zr (**11**) and Ti (**13**))

Empirical Formula	C ₂₁ H ₃₁ Cl ₂ N ₃ Zr	C ₂₅ H ₃₉ Cl ₂ N ₃ SiZr	C ₂₅ H ₃₉ Cl ₂ N ₃ SiTi
Formula Weight	499.62	571.80	528.48
Temperature, K	223(2)	223(2)	295(2)
Wavelength, λ	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	orthorhombic	orthorhombic
Space Group	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a, Å	15.537(3)	8.9109(6)	7.6772(3)
b, Å	11.263(2)	16.1975(12)	14.3292(6)
c, Å	14.829(2)	19.4837(13)	25.8800(11)
β , deg	109.589(3)		
Volume, Z	2444.8(7) Å ³ , 4	2812.2 Å ³ , 4	2847.0(2) Å ³ , 4
Density (calc.), g/cm ³	1.357	1.351	1.233
Abs. Coefficient, cm ⁻¹	6.80	6.41	5.47
F(0 0 0)	1032	1192	1120
Crystal Dimensions	0.10 x 0.16 x 0.36 mm	0.12 x 0.14 x 0.20 mm	0.09 x 0.20 x 0.41 mm
θ Range for Data Collection	2.28 to 27.52°	1.63 to 27.55°	1.57 to 27.54°
Limiting Indices	-20 $\leq h \leq$ 20 -14 $\leq k \leq$ 13 -19 $\leq l \leq$ 18	-10 $\leq h \leq$ 11 -21 $\leq k \leq$ 19 -24 $\leq l \leq$ 25	-9 $\leq h \leq$ 9 -18 $\leq k \leq$ 18 -33 $\leq l \leq$ 33
Reflections Collected	16863	20341	20337
Independent Reflections	5563 ($R_{\text{int}} = 0.1156$)	6393 ($R_{\text{int}} = 0.0621$)	6493 ($R_{\text{int}} = 0.0465$)
Completeness	98.9 %	99.4 %	99.4 %
Refinement Method	full-matrix on F_o^2	full-matrix on F_o^2	full-matrix on F_o^2
Restraints/Parameters	0/263	0/298	0/298
GOF on F^2	0.968	1.010	1.020
R indices [$I > 2\sigma(I)$]	R1 = 0.0664 wR2 = 0.1371	R1 = 0.0438 wR2 = 0.0757	R1 = 0.0420 wR2 = 0.0960
R indices (all data)	R1 = 0.1866 wR2 = 0.1821	R1 = 0.0733 wR2 = 0.0837	R1 = 0.0658 wR2 = 0.1047
Largest Difference Peak and Hole	0.724, -0.636 e/Å ³	0.379, -0.327 e/Å ³	0.227, -0.195 e/Å ³

Table 4.3. Selected Interatomic Distances (Å) and Bond Angles (°) for [(Mes)N(CH₂)₂NH(CH₂)₂N(Mes)]ZrCl₂ (**10**) and [(Mes)N(CH₂)₂N(SiMe₃)(CH₂)₂N(Mes)]MCl₂ (M = Zr (**11**) and Ti (**13**))

A. Interatomic Distances

	10	11	13
M-Cl(1)	2.417(2)	2.415(1)	2.2885(9)
M-Cl(2)	2.411(2)	2.402(1)	2.2563(10)
M-N(1)	2.055(5)	2.038(3)	1.892(2)
M-N(2)	2.361(6)	2.475(3)	2.438(2)
M-N(3)	2.048(6)	2.042(3)	1.905(2)
N(1)-Cl(1)	1.472(8)	1.463(5)	1.473(3)
N(1)-C(5)	1.456(9)	1.449(5)	1.450(3)
N(2)-C(2)	1.475(9)	1.514(4)	1.498(3)
N(2)-C(3)	1.469(9)	1.503(4)	1.491(3)
N(3)-C(4)	1.470(8)	1.463(4)	1.473(3)
N(3)-C(14)	1.449(8)		
N(3)-C(17)		1.449(4)	1.448(3)
N(2)-Si(1)		1.820(3)	1.823(2)

B. Bond Angles

	10	11	13
Cl(1)-M-Cl(2)	103.05(8)	100.52(4)	97.79(4)
Cl(1)-M-N(1)	110.04(16)	114.82(9)	116.41(7)
Cl(1)-M-N(2)	87.41(16)	93.06(7)	91.99(6)
Cl(1)-M-N(3)	114.29(17)	115.24(9)	115.03(7)
Cl(2)-M-N(1)	104.15(17)	100.61(10)	99.20(7)
Cl(2)-M-N(2)	169.54(16)	166.41(7)	170.23(6)
Cl(2)-M-N(3)	102.82(17)	99.56(9)	99.73(7)
N(1)-M-N(2)	71.7(2)	72.95(11)	76.24(8)
N(1)-M-N(3)	120.1(2)	120.67(14)	121.45(9)
N(2)-M-N(3)	72.3(2)	74.64(11)	75.96(8)

Chapter 5. References

1. Natta, G.; Pino, P.; Mazzanti, G.; Giannini, U. *J. Am. Chem. Soc.* **1957**, *79*, 2975.
2. Breslow, D.S.; Newburg, N.R. *J. Am. Chem. Soc.* **1957**, *79*, 5072.
3. Herwig, J.; Kaminsky, W. *Polym. Bull. (Berlin)* **1983**, *9*, 464.
4. Dyachkovski, F.S.; Shilova, A.K.; Shilov, A.E. *J. Polym. Sci., Part C* **1967**, *16*, 2333.
5. Eisch, J.J.; Piotrowski, A.M.; Brownstein, S.K.; Gabe, E.J.; Lee, F.L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.
6. Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *C9*, 347.
7. Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T.J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.
8. Eshuis, J.J.W.; Tan, Y.Y.; Teuben, J.H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277.
9. Bochmann, M.; Jagger, A.J.; Wilson, L.M.; Hursthouse, M.B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838.
10. Jordan, R.F.; Dasher, W.E.; Echols, S.F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.
11. Jordan, R.F.; LaPointe, R.E.; Bajgur, C.S.; Echols, S.F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.
12. Amorose, D.M.; Lee, R.A.; Petersen, J.L. *Organometallics* **1991**, *10*, 2191.
13. Jordan, R.F. *Symp. on Cat. and Organomet. Chem.* **1988**, *65*, 285.
14. Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.
15. Sinn, H.; Kaminsky, W.; Vollmer, H.J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390.
16. Brintzinger, H.H.; Fisher, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143 and references cited therein.
17. Guram, A.S.; Jordan, R.F. In *Comprehensive, Organometallic Chemistry*; 2nd ed.; M.F. Lappert, Ed.; Pergamon: Oxford, **1995**; Vol. 4; pp 589 – 925.
18. Wild, F.W.R.P.; Zsolnai, L.; Huttner, G.; Brintzinger, H.H. *J. Organomet. Chem.* **1982**, *232*, 233.
19. Wild, F.W.R.P.; Wasiucionek, G.; Huttner, G.; Brintzinger, H.H. *J. Organomet. Chem.* **1985**, *288*, 63.
20. Carpenetti, D.W.; Kloppenburg, L.; Kupec, J.T.; Petersen, J.L. *Organometallics* **1996**, *15*, 1572.
21. Ewen, J.A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
22. Kaminsky, W.; Külper, K.; Brintzinger, H.H.; Wild, F.W.R.P. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507.

23. Ewen, J.A.; Elder, M.J.; Jones, R.L.; Haspeslagh, L.; Atwood, J.L.; Bott, S.G.; Robinson, K. *Makromol. Chem. Macromol. Symp.* **1991**, 48/49, 253.
24. Kaminsky, W.; Engehausen, R.; Zoumis, K.; Spaleck, W.; Rohrmann, J. *Makromol. Chem.* **1992**, 193, 1643.
25. Hortmann, K.; Brintzinger, H.H. *New J. Chem.* **1992**, 16, 51.
26. Burger, P.; Hortmann, K.; Brintzinger, H.H. *Makromol. Chem. Macromol. Symp.* **1993**, 66, 127.
27. Herzog, T.A.; Zubris, D.L.; Bercaw, J.E. *J. Am. Chem. Soc.* **1996**, 118, 11988.
28. Miyake, S.; Bercaw, J.E. *J. Mol. Catal. A: Chem.* **1998**, 128, 29.
29. Veghini, D.; Day, M.W.; Bercaw, J.E. *Inorg. Chim. Acta.* **1998**, 280, 226.
30. Veghini, D.; Henling, L.M.; Burkhardt, T.J.; Bercaw, J.E. *J. Am. Chem. Soc.* **1999**, 121, 564.
31. Shapiro, P.J.; Cotter, W.D.; Schaefer, W.P.; Labinger, J.A.; Bercaw, J.E. *J. Am. Chem. Soc.* **1994**, 116, 4623.
32. Piers, W.E.; Shapiro, P.J.; Bunel, E.E.; Bercaw, J.E. *Synlett* **1990**, 2, 74.
33. Shapiro, P.J.; Bunel, E.E.; Schaefer, W.P.; Bercaw, J.E. *Organometallics* **1990**, 9, 867.
34. Canich, J.M. Eur. Patent Appl. EP-420-436-A1, 1991.
35. Canich, J.M. U.S. Patent Appl. 5,026,798, 1991.
36. Canich, J.M.; Hlatky, C.G.; Turner, H.W. PCT Appl. WO92-00333, 1992.
37. Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G. F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S. Eur. Patent Appl. EP-416-815-A2, 1991.
38. Brauer, D.J.; Bürger, H.; Wiegel, K. *J. Organomet. Chem.* **1978**, 150, 215.
39. Guérin, F.; McConville, D.H.; Vittal, J.J. *Organometallics* **1995**, 14, 3154.
40. Scollard, J.D.; McConville, D.H.; Vittal, J.J. *Organometallics* **1995**, 14, 5478.
41. Scollard, J.D.; McConville, D.H.; Vittal, J.J. *Organometallics* **1997**, 16, 4415.
42. Scollard, J.D.; McConville, D.H.; Payne, N.C.; Vittal, J.J. *Macromolecules* **1996**, 29, 5241.
43. Liang, L.C.; Schrock, R.R.; Davis, W.M.; McConville, D.H. *J. Am. Chem. Soc.* **1999**, 121, 5797.
44. Wolfe, J.P.; Wagaw, S.; Buchwald, S.L. *J. Am. Chem. Soc.* **1996**, 118, 7215.
45. Lückert, J., unpublished research report, West Virginia University, 1998.
46. Petersen, J.L.; Ritchie, H.; Richardson, B.; Christy, M., unpublished results.
47. Cloke, F.G.N.; Geldbach, T.J.; Hitchcock, P.B.; Love, J.B. *J. Organomet. Chem.* **1996**, 506, 343.
48. Chen, Y.X.; Marks, T.J. *Organometallics* **1997**, 16, 3649.
49. Kloskowski, M., unpublished research report, West Virginia University, 2002.

50. Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organometal. Chem.* **1971**, 26, 357.
51. Guérin, F.; McConville, D.H.; Vittal, J.J. *Organometallics* **1996**, 15, 5586.
52. Merkel, M.; Petersen, J.L., unpublished results.
53. Hagen, K.; Holwill, C.J.; Rice, D.A.; Runnacles, J.D. *Inorg. Chem.* **1988**, 27, 2032.
54. Guérin, F.; McConville, D.H.; Payne, N.C. *Organometallics* **1996**, 15, 5085.
55. Clark, H.C.S.; Cloke, F.G.N.; Hitchcock, P.B.; Love, J.B.; Wainwright, A.P. *J. Organometal. Chem.* **1995**, 501, 333.
56. Cloke, F.G.N.; Hitchcock, P.B.; Love, J.B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.
57. Schrock, R.R.; Schattenmann, F.; Aizenberg, M.; Davis, W.M. *Chem. Commun.* **1998**, 199.
58. Aizenberg, M.; Turculet, L.; Davis, W.M.; Schattenmann, F.; Schrock, R.R. *Organometallics* **1998**, 17, 4795.
59. Baumann, R.; Davis, W.M.; Schrock, R.R. *J. Am. Chem. Soc.* **1997**, 119, 3830.
60. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY **1960**.
61. Gordon, A.J.; Ford, R.A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972.
62. Setokowski, D.G.; Stucky, G.D. *Inorg. Chem.* **1975**, 14, 2192.
63. Manzer, L.E. *Inorg. Synth.* **1982**, 21, 134.
64. SMART, SAINT and XPREP programs are part of the Bruker crystallographic software package for single crystal data collection, reduction, and preparation.
65. International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.).
66. Sheldrick, G. M., SHELXTL6.1 (2000), Crystallographic software package, Bruker AXS, Inc. Madison, Wisconsin, USA.
67. The equations for the R-factors are $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ and $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[wF_o^2]]^{1/2}$. The expression for the “goodness-of-fit” is $GOF = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters which were varied during the last refinement cycle.

Vita

Alicia R. Morgan

The author is the daughter of Mr. Paul Morgan and Mrs. Jo Ann Morgan and was born on February 10, 1979 in Glen Dale, West Virginia. She was raised in McMechen, West Virginia and graduated from John Marshall High School in 1997. She received a Bachelor of Science degree in chemistry from West Virginia University in Morgantown, West Virginia, in May 2001. She is currently a chemistry graduate student at West Virginia University, where she is a candidate for the degree of Master of Science.

Poster Presentation

A.R. Morgan, M. Merkel, M. Kloskowski, and J.L. Petersen, "Explorations of Alternative Routes for the Preparation of Electrophilic Group 4 Metal Complexes Featuring Chelating Diamido Ligands," presented by JLP at the Organometallics Gordon Research Conferences held from July 21 – 26, 2002 at Salve Regina University, Newport, RI.