The Synthesis and characterization of a BIS(4-(3-(4-Phenoxy)Propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV), Zr(Nitrile)2 and the attempted synthesis of Zr(Amine)2 and coordination polymers containing Zr(dspOH)2

Kathy-Jo Brodsky
THE SYNTHESIS AND CHARACTERIZATION OF
BIS(4-(3-(4-PHENOXY)PROPIONITRILE))-N,N'-DISALICYLIDENE-
1,2-PHENYLENEDIAMINO)ZIRCONIUM(IV), Zr(NITRILE)2 AND THE
ATTEMPTED SYNTHESIS OF Zr(AMINE)2 AND COORDINATION
POLYMERS CONTAINING Zr(dspOH)2

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REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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THE SYNTHESIS AND CHARACTERIZATION OF BIS(4-(3-(4-PHENOXY)PROPIONITRILE))-N,N'-DISALICYLIDENE-1,2-PHENYLENEDIAMINO)ZIRCONIUM(IV), ZR(NITRILE)₂ AND THE ATTEMPTED SYNTHESIS OF ZR(AMINE)₂ AND COORDINATION POLYMERS CONTAINING ZR(dspOH)₂

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August 19, 1994
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ABSTRACT

The synthesis of a series of bis(quadridenate)zirconium(IV) complexes, that can be considered as derivatives of the model complex, bis(N,N'-disalicylidene-1,2-phenylenediaminozirconium (IV), Zr(dsp)₂, was conducted in order to produce zirconium coordination complexes with reactive terminal groups that would undergo ligand centered polymerization reactions. The previously reported Zr(dspOH)₂ complex and the previously unreported Zr(nitrile)₂ (shown below) and Zr(amide)₂ complexes were synthesized, purified and characterized by FTIR, ¹H NMR and elemental analysis. The attempted polymerization reactions of Zr(dspOH)₂ with diacid chlorides did not yield the desired linear coordination polymers. The attempted reduction of Zr(nitrile)₂ to Zr(amine)₂ was not successful via catalytic hydrogenation or chemical reduction methods. The synthesis of these complexes will be discussed.

![Chemical structures](image-url)
# TABLE OF CONTENTS

Acknowledgements ........................................................................................................ i

Abstract .......................................................................................................................... ii

List of Tables .................................................................................................................. iv

List of Figures .................................................................................................................. v

List of Abbreviations ...................................................................................................... ix

Introduction ................................................................................................................... 1

Overall Synthetic Scheme: Nitrile Complex ................................................................. 30

Overall Synthetic Scheme: Diol Complex ..................................................................... 35

Experimental: Nitrile Complex ..................................................................................... 40

Results: Nitrile Complex
  Characterization ......................................................................................................... 54

Experimental: Diol Complex ......................................................................................... 62

Results: Diol Complex
  Characterization ......................................................................................................... 69

Discussion
  Synthesis and Characterization .................................................................................. 73
  Conclusions ................................................................................................................... 100

Appendix ...................................................................................................................... 113

References .................................................................................................................... 136
LIST OF TABLES

Table I. Elemental Analyses and Physical Characterization Data for Ligands and Complexes (Nitrile) .......... 55

Table II. Infrared Spectral Characterization Data for the Ligands and Complexes (Nitrile) .......... 56

Table III. $^1$H NMR Spectral Characterization Data for Ligands and Complexes (Nitrile) .......... 57

Table IV. Summary of Reduction of the Nitrile Complex by Catalytic Hydrogenation .......... 58

Table V. Summary of All Reduction Reactions .......... 61

Table VI. Elemental Analyses and Physical Characterization Data for Ligands and Complexes (Diol) .......... 70

Table VII. Infrared Spectral Characterization Data for the Ligands and Complexes (Diol) .......... 71

Table VIII. $^1$H NMR Spectral Characterization Data for the Ligands and Complexes (Diol) .......... 72
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthesis of Polyphenylsilsesquioxane</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Synthesis of Polyphosphazenes</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Carborane Unit</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>Synthesis of m-Carborane-Siloxane polymer</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>Synthesis of Polyamides with a Crown Ether Moiety</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>Synthesis of Polymer by Metal Ligand Exchange</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>Synthesis of Polymer by Ligand Centered Reaction</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>Synthesis of Beryllium containing Polymer by Ligand Centered Reaction</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>Eight Coordinate Zr Polymer By Ligand Centered Polymerization Reaction</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>Coordination Polymer formed by Coordination of M to Poly(Schiff base)</td>
<td>18</td>
</tr>
<tr>
<td>11</td>
<td>Synthesis of Zr(dsp)2</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>Zr(cedsp)2</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure 13. Synthesis and Polymerization of Zr(adsp)2 .................................. 23
Figure 14. Synthesis and Polymerization of Zr(madsp)2 .................................. 25
Figure 15. Outline of Synthetic Approach Diol ................................................. 28
Figure 16. Outline of Synthetic Approach Nitrile .............................................. 29
Figure 17. Aromatic Nucleophilic Substitution Mechanism .................................. 78
Figure 18. Outline of Synthetic Results (Diol) ................................................... 101
Figure 19. Outline of Synthetic Results (Nitrile) ................................................. 102
Figure 20. Nitrile and Imine Bonding Considerations .......................................... 105
Figure 21. Introducing Terminal Carboxylate Groups ....................................... 110
Figure 22. Introducing Terminal Vinyl Groups into the Complex ......................... 111
Figure 23. Terminal Vinyl Groups in the Complex .............................................. 112
Figure 24. FTIR spectrum of 3-(4-(3-amino-4-nitrophenoxy)phenyl)propionitrile: purified by recrystallization ................................................. 114
Figure 25. FTIR spectrum of 3-(4-(3-amino-4-nitrophenox)-phenyl)propionitrile: purified by column chromatography

Figure 26. FTIR spectrum of ortho diamine ether intermediate

Figure 27. FTIR spectrum of H2(nitrile)

Figure 28. FTIR spectrum of Zr(nitrile)2

Figure 29. FTIR spectrum of hydrogenation product (31193)

Figure 30. FTIR spectrum of hydrogenation product (42893)

Figure 31. FTIR spectrum of complex agitated with NH3 (51493)

Figure 32. FTIR spectrum of hydrogenation product (5593)

Figure 33. FTIR spectrum of Zr(amide)2

Figure 34. 1H NMR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by recrystallization

Figure 35. 1H NMR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by column chromatography
Figure 36. $^1$H NMR spectrum of H$_2$(nitrile) .................................. 126

Figure 37. $^1$H NMR spectrum of Zr(nitrile)$_2$ .................................. 127

Figure 38. $^1$H NMR spectrum of Zr(amide)$_2$ .................................. 128

Figure 39. IR spectrum of H$_2$(dspCO) .................................................. 129

Figure 40. FTIR spectrum of Zr(dspCO)$_2$ ............................................ 130

Figure 41. FTIR spectrum of Zr(dspOH)$_2$ ............................................ 131

Figure 42. FTIR spectrum of Zr(dspOH)$_2$ reacted with acetyl chloride .......... 132

Figure 43. FTIR spectrum of recrystallized Zr(dspOH)$_2$ reacted with acetyl chloride .................................................. 133

Figure 44. $^1$H NMR spectrum of Zr(dspCO)$_2$ ........................................ 134

Figure 45. $^1$H NMR spectrum of Zr(dspOH)$_2$ ........................................ 135
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$(nitrile)</td>
<td>4-(3-(4-phenoxy)propionitrile)-N,N'-disalicylidene-1,2-phenylenediamine</td>
</tr>
<tr>
<td>Zr(nitrile)$_2$</td>
<td>Bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino) zirconium(IV)</td>
</tr>
<tr>
<td>Zr(amine)$_2$</td>
<td>Bis(4-(4-(3-aminopropyl)phenoxy))-N,N'-disalicylidene-1,2-phenylenediamino) zirconium(IV)</td>
</tr>
<tr>
<td>Zr(amide)$_2$</td>
<td>Bis(4-(N-(3-(4-phenoxy)propyl)ethanamide))-N,N'-disalicylidene-1,2-phenylenediamino) zirconium(IV)</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Zr(O-n-Bu)$_4$·n-BuOH</td>
<td>Tetra-n-butoxyzirconium(IV) butanol solvate</td>
</tr>
<tr>
<td>superhydride</td>
<td>Lithium triethylborohydride</td>
</tr>
<tr>
<td>H$_2$(dspCO)</td>
<td>4-(phenylmethanone)-N,N'-disalicylidene-1,2-phenylenediamine</td>
</tr>
<tr>
<td>Zr(dspCO)$_2$</td>
<td>Bis(4-(phenylmethanone))-N,N'-disalicylidene-1,2-phenylenediamino) zirconium(IV)</td>
</tr>
<tr>
<td>Zr(dspOH)$_2$</td>
<td>Bis(4-(phenylmethanol))-N,N'-disalicylidene-1,2-phenylenediamino) zirconium(IV)</td>
</tr>
</tbody>
</table>
$\text{Zr(dsp)}_2$ \hspace{1cm} $\text{Bis}(\text{N,N}'-\text{disalicylidene-1,2-phenylenediaminato})\text{zirconium(IV)}$

$\text{Zr(cedsp)}_2$ \hspace{1cm} $\text{Bis}(4-(\text{carboxyethyl})-\text{N,N}'-\text{disalicylidene-1,2-phenylenediaminato})\text{zirconium(IV)}$

$\text{Zr(adsp)}_2$ \hspace{1cm} $\text{Bis}(4\text{-amino-N,N}'-\text{disalicylidene-1,2-phenylenediaminato})\text{zirconium(IV)}$

$\text{Zr(cdsp)}_2$ \hspace{1cm} $\text{Bis}(4\text{-cyano-N,N}'-\text{disalicylidene-1,2-phenylenediamino})\text{zirconium(IV)}$

$\text{Zr(madsp)}_2$ \hspace{1cm} $\text{Bis}(4\text{-methyleneamino-N,N}'-\text{disalicylidene-1,2-phenylenediamino})\text{zirconium(IV)}$

$\text{Zr(ndsp)}_2$ \hspace{1cm} $\text{Bis}(4\text{-nitro-N,N}'-\text{disalicylidene-1,2-phenylenediaminato})\text{zirconium(IV)}$

x
INTRODUCTION

Organic polymers have widespread importance as evidenced by their incorporation into many aspects of modern life. One indication of the great versatility of traditional macrocyclic materials is seen in the fact that they have been processed into elastomers, oils, hydraulic fluids, lubricants, rubber, adhesives, gaskets, coatings, resins and surfactants among other things. However these substances have limitations that render them unacceptable materials in various engineering applications and these limitations have prompted the research for new materials capable of functioning in severe operating conditions. The areas in which the wholly organic polymers are most lacking are high temperature stability and oxidative resistance to atmospheric oxygen. Many organic backbone polymers react with oxygen or ozone losing their desirable properties in the process. In addition many organic polymers degrade with exposure to ultraviolet light, swell or dissolve in organic fluids, burn, and have restricted usable temperature ranges. The requirements of space vehicles, rockets, and aircraft demand resilient materials that maintain their properties at temperatures of 500-800 C. (1)

Organic polymers fail because ordinary C-C and C-H bonds are too weak and too reactive to confer the required stability on polymers to withstand high operating temperatures and oxidative degradation. In recent years considerable research in the
development of inorganic or partially inorganic polymers has occurred. It is theorized that incorporation of metallic elements into the polymer structure will lead to improved thermal properties, conducting or semiconducting materials and better oxidative resistance among other things. When trying to design innovative synthetic polymeric materials it is useful to bear in mind that the strongest and most inert chemical bonds that can be incorporated into the framework of a macromolecule are sought. It is known that the oxides of metals have extremely high heats of formation implying stable bonds and therefore metal-oxygen linkages are deemed desirable as basic framework components. (2) A framework composed entirely of such bonds leads to glass, ceramic or porcelain materials therefore it is desirable to incorporate stable organic groups like phenyl rings which derive stability from their high degree of resonance. It is also predicted that because of the many and varied metal atom valencies different numbers of side groups can be considered in the framework. The large number of geometrical configurations observed in coordination compounds leads to the speculation of incorporating some of that diversity into polymer structures. The longer metal bonds (relative to C-C bonds) should produce effects on bond angles which in turn will affect properties such as elasticity. Multiple bonding through lone electron pairs (such as on nitrogen) with vacant metal d orbitals can be expected to strengthen links.(1), (2)
There are many types of metal containing or inorganic polymers that are of commercial interest. It is useful to examine the synthetic routes to these semiorganic polymers in order to build on their insights and apply them to future endeavors. It is also useful to note the desirable or improved properties these materials exhibit over traditional macromolecular ones and determine to what structural component they are attributed. By correlating polymer molecular structure to macroscopic material properties the polymer structure can then be designed to enhance particular material properties. By way of introduction to this thesis work the following examples of semiorganic polymers will be briefly discussed: polysiloxanes, \((\text{CH}_3)_2\text{Si-O-}\); polycarborane siloxanes, \(-\text{C(B}_{10}\text{H}_{10})\text{C-Si(}\text{CH}_3)_2\text{-O-}\); polyphosphazenes, \(\text{N=P(OR)}_2\-\); and those types of coordination polymers which specifically contain coordinate covalent bonds to metal ions in the repeat unit. Another type of coordination polymer, polyamides containing crown ether moieties (18-crown-6 rings) in the backbone is also included. A brief review including a depiction of the principal structural unit of these examples follows. The discussion here is necessarily limited to a select few metal-containing polymers but one should bear in mind that under the broad topic of metal-containing polymers there are the subtopics of the wholly inorganic polymers (such as polymeric silicates, or glasses), organometallic polymers and various other types of semi-organic polymers such as phthalocyanine polymers.
The properties of silicon and carbon are considerably different even though they are situated in the same group. The normal oxidation state of both elements is 4 but Si can expand its valence shell by using available 3d orbitals for bonding. Stevens (3) states that Si-O bonds have some double bond character arising from overlap of oxygen p orbitals with silicon vacant d orbitals. Si-O bonds therefore are more stable than C-O bond (it is noted that the Si-Si bond is less stable than C-C bond). (3) Polysiloxanes have very low glass transition temperatures, (Tg), (-127 °C) stemming from the greater flexibility due to increased bond angles and bond lengths of the Si-O bond. (3) These materials have the advantage of increased conformational variability or elasticity at use temperatures. Other desirable properties are good thermal and oxidative stability, unchanging viscosity with temperature (up to a point), excellent chemical resistance and dielectric properties. One interesting example of a polysiloxane is a soluble (in CH2Cl2, THF, and benzene) ladder or double chain polymer, polyphenylsilsesquioxane, demonstrating a very symmetric arrangement of fused rings. (4) See FIGURE 1. This linear network structure has Si and O atoms present in the polymer main chain and approximately 11 units repeated per chain. The structure accommodates the tetrahedral bond angles on silicon and 155 degree angles on the oxygen. The Si-O bonds are very stable covalent bonds that are inert to reaction conditions.
Deprotection chemistry may be done on the terminal groups without affecting the backbone structure.\(^{(5)}\)

This represents an example of a polymer with silicon and oxygen linkages incorporated into the backbone with organic side groups framing the Si-O backbone. The organic side groups are substituted with hydroxyl groups to promote solubility in polar organic solvents. This material shows promise as a microlithographic resist material because of its ability to be cast from the solution state, its ability to form an SiO\(_2\) layer in a plasma environment and its solubility in polar organic solvents. The material properties which cause it to act as a resist material were deliberately designed into the polymer structure.
Phosphazene polymers, also called phosphonitrilic polymers form amorphous, colorless films with elastomeric properties. They also exhibit improved chemical resistance and thermal stability. See FIGURE 2. The high conformational mobility (which determines elastomeric properties) can be explained in terms of
the nitrogen to phosphorus bond. Here (p - d) pi bond overlap occurs due to the availability of the five phosphorus d orbitals. This is considerably less restrictive than (p p) pi bonding which composes C-C double bonds. Stevens (3) uses bonding to explain why the phosphorus-nitrogen backbone has minimal electron delocalization. The bonding involves overlap of nitrogen 2p and phosphorus 3d pi orbitals that results in an orbital node located at every third atom in the backbone.

\[
\begin{array}{c}
\text{Cl} \\
N = P \\
\text{Cl}
\end{array}
\]

\[
\text{RO}^+ \text{Na}^+ \xrightarrow{\text{THF/reflux}} \left[\begin{array}{c}
N = P \\
\text{OR}
\end{array}\right]_n
\]

\[
\text{R}_2\text{NH} \xrightarrow{\text{THF/reflux}} \left[\begin{array}{c}
N = P \\
\text{NR}_2
\end{array}\right]_n
\]

Polyphosphazenes

FIGURE 2. Synthesis of Polyphosphazenes

The P-Cl bond has fairly high reactivity in nucleophilic substitution and the poly(organophosphazene) synthetic route makes use of a chemically unstable polymeric species as an intermediate for the preparation of stable derivatives. This represents an example of chemical modification after the backbone of the polymeric structure has been constructed.(6)
In typical organic chemistry the option of modification of existing polymers by substitution is rarely a viable synthetic route, necessitating that each polymer be made by polymerization of the corresponding monomer. (7)

Boron containing polymers have been synthesized by incorporation of carborane units (cluster with a cage structure, see FIGURE 3) into the polymer. Carborane, $\text{C}_2\text{B}_{10}\text{H}_{12}$, is an icosahedral structure, extremely stable and having a pseudoaromatic character attributed to complete electron delocalization. The hydrogens attached to the carbons are more acidic than those attached to boron and they can be replaced with lithium by reaction with butyllithium to prepare carborane derivatives. The m-carborane-siloxane polymers exhibit elastomeric properties with excellent thermal and oxidative stability. The unique properties of these polymers are due to the presence of the carborane cluster. (8)(9) See FIGURE 4.

FIGURE 3. Carborane Unit
\[
\begin{align*}
n \text{C}_2\text{B}_{10}\text{H}_{12} + 2n \text{BuLi} & \rightarrow \text{Li-C-(B}_{10}\text{H}_{10})\text{-C-Li} + 2n \text{Cl(}\text{CH}_3)_2\text{Si-O-Si(}\text{CH}_3)_2\text{Cl} \\
-2n \text{BuOH} & \rightarrow \text{Cl(}\text{CH}_3)_2\text{Si-O-Si(}\text{CH}_3)_2\text{-C-(B}_{10}\text{H}_{10})\text{-C-Si(}\text{CH}_3)_2\text{-O-Si(}\text{CH}_3)_2\text{Cl} \\
-2n \text{HCl} & \rightarrow [\text{Si(}\text{CH}_3)_2\text{-O-Si(}\text{CH}_3)_2\text{-C-(B}_{10}\text{H}_{10})\text{-C-Si(}\text{CH}_3)_2\text{-O-Si(}\text{CH}_3)_2\text{-O}]_n \\
\text{H}_2\text{O} & \rightarrow \text{m-carborane-siloxane polymer}
\end{align*}
\]

FIGURE 4. Synthesis of m-Carborane-Siloxane Polymer

These examples represent some of the earliest successful semi-organic polymers. Going to even more electropositive centers such as transition metal centers should lead to a host of new material properties. Transition metals have been incorporated into coordination polymers which are another class of semiorganic polymers.
Coordination polymers can be broadly defined to include any macromolecular entity containing coordinate covalent bonds. Coordination polymers are usually classified as inorganic polymers but it is probably more accurate to describe them as semiorganic polymers in recognition of the fact that most of the ligands used are organic. For this discussion the definition will be limited to those polymers which contain a metallic element in the coordinate covalent bond. Furthermore the discussion will be limited to examples from the literature dealing for the most part with transition metal centers of coordination. There are a few novel examples of polymers involving main group metals that will also be discussed.

One novel polymeric material that was found in the literature describes a family of macrocyclic ethers which complex the cations of alkali metals. Intermediates such as dibenzo-18-crown-6 were prepared, then nitrated followed by reduction to diamine compounds. Condensation reactions of the diamine with aromatic diacid chlorides were used to incorporate the complexing properties into the backbone of a polymer. See FIGURE 5.

Complexation of the metal occurs after the polymer is constructed. (10) (11) (12)
It has been pointed out that although many interesting coordination polymers have been prepared, the thermal properties frequently prove not to be as good as the wholly aromatic polymers. According to Bailar, coordination of a transition metal with organic ligands alters various properties of both. The organic ligand can be rendered more stable toward hydrolysis, oxidation, chemical reagents and high temperature. By extension it was thought that coordination might give extremely
stable polymers. Research conducted during W.W. II found only short chains formed and the monomers lost much of their stability when linked into polymeric units. Bailar (13) concludes that the breakdown of the organic groups probably occurs. Bailar (13) has compiled a list of design considerations and has concluded that chelation of ligands enhances stability but that stability is rendered only to the bonds of the ligand in the immediate vicinity of the metal ion. Therefore the organic links should be short and strong. One difficulty encountered here is that with short (but stable) connecting chains flexibility is usually lost. This can lead to a lack of solubility in various solvents. (13)

The literature describes three different ways metal coordination polymers can be formed. (14) One method by which the polymer can form involves metal-ligand exchange. This is the scheme used to prepare polymers from Bis(8-hydroxy-5quinolyl) and metal acetylacetonates. (15) See FIGURE 6.

$$\text{HO} - \begin{array}{c} \text{N} \\ \text{N} \end{array} - \text{OH} + \text{M(acac)}_2 \rightarrow \begin{array}{c} \text{O} \\ \text{N} \\ \text{N} \end{array} - \text{O} \rightarrow \text{M} \rightarrow \text{n} \rightarrow + 2\text{Hacac}$$

FIGURE 6. Synthesis of Polymer by Metal Ligand Exchange
The bis-chelating ligand, which forms both N and O bonds to M, attaches itself simultaneously to two different metal ions. The substances isolated are highly colored, insoluble rigid materials that are thermally stable up to 500 C. Bailar also indicates that because of partial ionic character in the coordinate bonds, they tend to rearrange more readily than ordinary covalent bonds. (13)

The second method involves use of coordination compounds that have on its periphery groups which can be used in polymer formation. Condensation polymerization requires the existence of the appropriate monomers from which small molecules can be split without affecting the coordination sphere. Polymerizations of the condensation type should be strictly analogous to organic condensation polymerizations. (16) These reactions are termed ligand centered reactions. An example involves the dihydroxy derivative of Schiff bases being converted to polycarbonates by a condensation reaction with phosgene. (3) See FIGURE 7.
Another example involves the main group metal beryllium. The beryllium-diketone polymers were found to be soluble in nonpolar solvents or were insoluble powders that did not exhibit heat stability above 200 C. (17) (18) See FIGURE 8.
A final example of this method of metal-containing polymer synthesis involves chain growth of an inert metal center through ligand-centered Schiff-base condensation reactions. One scheme reported in the literature involves the use of the labile complex Zr(sal)₄ condensed with 1,2,4,5-tetraaminobenzene or alternatively 3,3',4,4'-tetraaminobiphenyl. This method of metal-containing polymer synthesis utilizes ligand synthesis during the polymerization reaction to overcome low solubility of the aromatic Schiff base ligand. An in situ condensation reaction was utilized to convert a labile zirconium (IV) complex to an inert polymeric product where the double-headed quadridentate...
ligands are much more inert to substitution. (20) The reaction takes place in DMSO, a strongly polar aprotic solvent capable of such strong interactions with water molecules that it promotes the forward reaction by preventing hydrolysis of the zirconium. Gel permeation estimates a number average molecular weight of 10,000. The zirconium chelate polymer exhibits a decomposition temperature of 600 °C indicating high thermal stability. The scheme relies on increasing the ligand dentate number to render the labile metal ion inert in the polymer, in this case by going from four bidentate ligands to two quadridentate ligands. See FIGURE 9.

![Chemical structures](image)

FIGURE 9. Eight Coordinate Zr Polymer by Ligand Centered Polymerization Reaction
The third method of forming coordination polymers involves use of a preformed organic or inorganic polymer to which a metal atom or ion can be chemically bound. (3) The metallic element is coordinated to a polymer repeat unit containing donor groups. Marvel examined poly (Schiff bases). (21) The polymeric ligands were made from a dialdehyde which was then treated with a diamine, o-phenylenediamine, to give the polymeric Schiff base. Metal acetate in THF reacted to incorporate the metal ion into the polymer. See FIGURE 10. The heat stability of the polymeric chelates did not prove to be as stable as the monomeric chelates. (21) (22) Enhanced stability over the methylene series was found if the dialdehyde used contained the SO₂ group. The polymer produced was slightly more thermally stable. It was postulated that the greater electron withdrawing power of the SO₂ group caused an increase in phenol acidity, improving the strength of the metal to oxygen bond. (23)
Polymeric Schiff base

polymeric chelate

monomeric chelate

FIGURE 10. Coordination Polymer Formed by Coordination of M to Poly(Schiff base)
Zirconium is an interesting transition metal center to incorporate into a coordination polymer. Since it can have eight ligand donor atoms covalently bound to it, the zirconium metal atom is said to possess eight coordination. For a metal to attain eight coordination the covalent radius (effective radius) of the metal must be large enough to accommodate the ligand donor atoms in the inner coordination sphere with minimal steric and electronic repulsions.\(^{(24)}\) The metal must also be able to accept the electron density from the eight ligand donor atoms by counter balancing the build-up of negative charge. This is best accomplished with metal ions which attain high formal oxidation states such as +3, +4, +5, and +6. Zirconium has a stable high formal oxidation state of +4. \(^{(24)}\)

Chelation, the possession of more than one donor atom per ligand makes possible multiple bonds to the same metal ion. This leads to the formation of chelate rings upon coordination to the metal atom, the 5 and 6 member rings being quite stable. By virtue of its high formal oxidation state and its ability to complex eight donor atoms, zirconium is capable of forming coordination complexes with two quadridentate ligands. These ligands form cages around the zirconium metal ion that are orthogonal to one another in three dimensional space. When a high organic content is present in the ligands these coordination complexes show good solubility in organic solvents such as benzene and dichloromethane. It has been reported that the solubility
properties are due in part to the three dimensional structure of the complex which prevents stacking. (19) (25)

An eight coordinate zirconium complex, Zr(dsp)2, was reported in the literature in 1979 as a model compound from which to form soluble, thermally stable coordination polymers. (25) The synthesis of this compound is shown in FIGURE 11.

\[
\text{Zr(dsp)}_2
\]

FIGURE 11. Synthesis of Zr(dsp)2
It was previously established that Zr alkoxides such as Zr(O-n-Bu)₄·n-BuOH (and as opposed to Zr(sal)₄) could be used to obtain bis(quadridentate Schiff base)zirconium(IV) products where ethylenediamine condensed with salicylaldehyde was the Schiff base ligand. (26)

Building on that synthetic method, Schiff base ligands were synthesized based on the condensation of 1,2-phenylenediamine with salicylaldehyde and then complexed with Zr alkoxides. In 1982 the first known zirconium complex containing eight coordination through bis quadridentate chelation and having two uncoordinated terminal functional groups, Zr(cedsp)₂ was prepared and reported. (27) See FIGURE 12. The diester derivative of Zr(dsp)₂ was found to have good solubility in benzene and dichloromethane. This complex failed to produce polymers by ligand centered reactions of the diester with aromatic diamines because the metal coordination complex decomposed under the high temperature polymerization conditions. The polymerization reactions were run at temperatures greater than 300°C.
FIGURE 12. Zr(cedsp)$_2$

In 1987, a zirconium eight coordinate chelate complex was prepared and successfully subjected to catalytic hydrogenation (Pd/C, H$_2$) to convert the terminal nitro groups to terminal (uncoordinated) amine groups that were capable of polymerization. (28) Reaction of the complex with pyromellitic dianhydride led to formation of short chain oligomers of soluble polyamic acid. A degree of polymerization of 80 was reported based on gel permeation chromatography and viscosity experiments. The product was produced by solution polymerization and these materials offered the potential of processability in the solution state. See FIGURE 13.
FIGURE 13. Synthesis and Polymerization of Zr(adsp)₂

The next step in the evolution of the project involved creating longer organic segments between the complex and the terminal reactive groups. It was hypothesized that increased...
solubility in organic solvents would result with an increased amount of structural flexibility. This increased solubility would lead to the formation of higher molecular weight polymers then previously obtained. (28) Another important reason to incorporate longer organic segment involved moving the reactive end groups from the vicinity of the transition metal coordination sphere. It was thought that reactivity at the periphery of the molecule was affected by conjugation and was interfering with both the reactions to functionalize the terminal groups and with subsequent polymerization reactions.

In 1988 a chelated metal complex with two terminal free amino groups was reported. (29) This complex, Zr(madsp)2 had been designed so that a methylene unit separated the amine end groups from the aromatic system of the ligand. The starting benzonitrile complex was reported to have been reduced to a benzyl amine via catalytic hydrogenation using the conditions of Raney nickel, sodium hydroxide and H2 for five hours. A preliminary reaction of that complex with a cyclic dianhydride was also reported as successful due to the observation that the starting material was consumed within 10 minutes at 0°C. The trial polymerization reaction was run using 0.02 g (0.26 mmol) of the Zr(madsp)2 complex. See FIGURE 14.
A general problem encountered in many polymerization systems has been a difficulty in obtaining polymers of sufficiently high molecular weight (at least 10,000) to have reasonable
strength properties. The cause of this difficulty has been due in large part to general insolubility of the polymers. Low molecular weight polymers often precipitate from the reaction mixture and prevent the achievement of high molecular weights. (30) It was hypothesized that because of the high solubility of the zirconium complexes, long polymer chains with improved solubility in organic solvents could be produced. (28)

Therefore the objective of this research was the synthesis of several new bis(quadridentate)zirconium(IV) complexes in order to produce polymerizable complexes capable of undergoing ligand centered polymerization reactions to produce soluble coordination polymers. The bis(quadridentate zirconium(IV) complexes, Zr(dspCO)₂ and Zr(dspOH)₂, previously reported were synthesized and purified and both model reactions and polymerization reactions were attempted. The previously unreported complexes Zr(nitrile)₂ and Zr(amide)₂ were synthesized via a multistep synthetic route. The attempted synthesis of Zr(amine)₂ was conducted as well. In addition several other new compounds (a diarylether, and Schiff base ligand) were made as intermediates along the synthetic route. The compounds were characterized by FTIR, NMR and elemental analysis.

The research reported herein describes several routes for the preparation of metalorganic monomers for use in the synthesis of soluble coordination polymers. The routes focus on
the synthesis of zirconium coordination complexes with polymerization capacity through the terminal groups of the ligands chelated to the transition metal. The salicylaldimine ligands (formed by the condensation of salicylaldehyde and a primary amine and containing the azomethine group RHC=N-) involve polychelation to the zirconium ion through its oxygen and nitrogen donor atoms in a manner similar to the parent compound Zr(dsp)2. What is new in the current research is that additional side groups were introduced into the salicylaldimine Schiff base ligands by either an ether link with a terminal aliphatic nitrile group, or a carbonyl group, to form Zr(nitrile)2 and Zr(dspCO)2 respectively. Next the ligands were modified by reduction reactions to produce reactive terminal functional groups and thus produce reactive coordination complexes that would act as monomers in polymerization reactions with diacid chlorides.

Zr(dspCO)2 was reduced with superhydride to the diol Zr(dspOH)2 and Zr(nitrile)2 was catalytically reduced to the amide Zr(amide)2 after unsuccessfully trying to reduce it (via both catalytic hydrogenation and chemical reduction) to Zr(amine)2.

FIGURES 15 and 16 summarize and outline the synthetic approach to linear and soluble coordination polymers.
Zr\textsubscript{2}CrCH_{2}LiB[C_{2}H_{5}]_{3}H

Polymerization with diacid chlorides

Linear Coordination Polymers

FIGURE 15. Outline of Synthetic Approach: Diol
FIGURE 16. Outline of Synthetic Approach: Nitrile
N≡C-(CH₂)₂

\[
\begin{align*}
\text{OH} & \quad \text{Cl} \\
\text{NO}_2 & \quad \text{NH}_2
\end{align*}
\]

\[
\text{N≡C-(CH₂)₂} + \text{Cl-} \quad \text{NH}_2 \\
\text{NO}_2
\]

\[
\Delta \quad \text{K}_2\text{CO}_3 \\
\text{DMF}
\]

\[
\text{REACTION 1}
\]

N≡C-(CH₂)₂

\[
\text{O} \\
\text{NH}_2 \\
\text{NO}_2
\]

\[
\text{1} \\
3-(4-(3-amino-4-nitrophenoxy)phenyl)propionitrile
\]

\[
\quad \text{+ KCl + KHCO}_3
\]

Pd/C

\[
\text{H}_2
\]

\[
\text{REACTION 2}
\]

N≡C-(CH₂)₂

\[
\text{O} \\
\text{NH}_2 \\
\text{NH}_2
\]

\[
\text{2} \\
3-(4-(3,4-diaminophenoxy)phenyl)propionitrile
\]

Synthetic Scheme Nitrile: Overall 1
4-(3-(4-phenoxy)propionitrile)-N,N'-disalicylidene-1,2-phenylenediamine

H₂(nitrile)

Synthetic Scheme Nitrile: Overall 2
Synthetic Scheme Nitrile: Overall 3
Bis(4-(4-(3-aminopropyl)phenoxy))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV)

Zr(amine)$_2$

Synthetic Scheme Nitrile: Overall 4
Bis(4-(N-(3-(4-phenoxy)propyl)ethanamide)\text{-}N,N'\text{-}disalicylidene\text{-}1,2-phenylenediamino)zirconium(IV)  

\[ \text{Zr(amide)}_2 \]  

Synthetic Scheme Nitrile: Overall 5
Synthetic Scheme Diol: Overall 1
Synthetic Scheme Diol: Overall 2
REACTION 3

1) $2 \text{LiB}[\text{C}_2\text{H}_5]_3\text{H}$ (Superhydride)

2) Hydrolysis

Bis(4-phenylmethanol)-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV)

$\text{Zr(dspOH)}_2$

Synthetic Scheme Diol: Overall 3
Synthetic Scheme Diol: Overall 4
Synthetic Scheme Diol: Overall 5
EXPERIMENTAL: NITRILE COMPLEX

Reagent grade solvents and chemicals were used. Salicyladehyde (Aldrich) and tetra-n-butoxyzirconium(IV) butanol solvate (Zr(O-n-Bu)4·n-BuOH) (Alfa), were purified by reduced pressure distillation. N,N-dimethylformamide (DMF), (Aldrich) and acetic anhydride (Aldrich) were vacuum distilled from calcium hydride (Aldrich) prior to use. Tetrahydrofuran, THF (Aldrich) was dried over calcium hydride prior to distillation. The other reagents, 5-chloro-2-nitroaniline (Aldrich), 3-(4-hydroxyphenyl)propionitrile (Lancaster or Trans World Chemicals), sodium acetate (Baker), anhydrous ammonia (Aldrich) and petroleum ether (20-40 °C boiling fraction) were used without further purification. The dinitrogen gas (Air Products) used with the glovebag operations was dried over calcium sulfate. All thin layer chromatograms were obtained on silica gel with fluorescent indicator (Kodak).

3-(4-(3-amino-4-nitrophenoxy)phenyl)propionitrile (1)

The identities of the starting materials, 5-chloro-2-nitroaniline, (Aldrich), and 3-(4-hydroxyphenyl) propionitrile, (Lancaster or Trans World Chemicals) were confirmed by FTIR,
melting point, $^1$H and $^{13}$C NMR and elemental analysis. A 250 ml round bottom flask equipped with a N$_2$ inlet, magnetic stirrer and a condenser was charged with a solution of 10.0 g (0.0680 mol) of 3-(4-hydroxyphenyl)propionitrile in 75 ml of DMF, an excess of anhydrous potassium carbonate, K$_2$CO$_3$, 11.0 g (0.0800 mol), and a solution of 11.7 g (0.0680 mol) of 5-chloro-2-nitroaniline in 75 ml of DMF. The contents were stirred and maintained at reflux for 24 hours under a positive dinitrogen pressure. Progress of the reaction was followed by thin layer chromatography, TLC, using either 1:1 THF:pet ether or 1:1 dichloromethane:pet ether eluent. The yellow spot due to the 5-chloro-2-nitroaniline starting material (R$_f$=0.6) disappeared and a darker yellow spot representing the Williamson ether product appeared with a lower R$_f$ value (R$_f$=0.4).

Upon cooling, the contents of the reaction flask were suction filtered and washed several times with portions of DMF to separate out the KCl and KHCO$_3$ salt biproducts. The DMF was removed by reduced pressure distillation. The resulting dark brown oily residue was extracted with portions of diethyl ether until the ether layers failed to pick up a yellow color. After rotary evaporation of the solvent, a brown solid was isolated. This was recrystallized six or more times from 2-propanol and pet ether to give a yield of 7.51 g (39%) of an orange-yellow solid. The melting point was 118-121 °C. Prior to characterization the substance was dried under vacuum at 100 °C for 2 days. Analysis: Calculated
for C₁₅H₁₃N₃O₃: C, 63.6; H, 4.70; N, 14.9%. Found: C, 62.8; H, 4.70; N, 15.1%.

The reaction was repeated omitting the successive recrystallization steps. Purification was accomplished by flash column chromatography using 230-400 mesh (60 Å) silica gel, (Aldrich). The impure product was eluted with acetone under a positive N₂ pressure. A bright orange-yellow colored solid, 11.63 g, 61% yield, was isolated after rotary evaporation of the solvent. Gas chromatography (5890 Series II Hewlett Packard) confirms the presence of only one peak. Analysis: Found: C, 63.0; H, 4.83; N, 14.4%. The product was further characterized by FTIR and ¹H NMR. The characterization data was consistent with the expected structure.

3-[(4-(3,4-diaminophenoxy)phenyl)propionitrile (2)

A Paar bottle was charged with a solution of 3.00 g (0.0106 mol) of recrystallized 3-(4-(3-amino-4-nitrophenoxy)phenyl)propionitrile in 50 ml of dichloromethane and the catalyst, 1.00g Pd/C (10%). This mixture was subjected to 60 psi H₂ (gauge pressure) with agitation for 2.5 hours in the pressure reaction apparatus. A liquid nitrogen trap was placed before the water aspirator that was used to exhaust the reaction chamber to prevent moisture contamination. Progress of the reaction was followed by TLC using 1:1 THF:pet ether eluent. The
disappearance of the yellow ether starting material spot (Rf=0.44) and the appearance of a dark spot (visible under UV light) with a slightly lower Rf value (Rf=0.25) indicated completion of the reaction. It was observed that this spot discolored in air. The contents of the reaction were filtered through a Celite pad and rinsed with dichloromethane. Rotary evaporation of the solvent yielded a light yellow oily residue. This product was characterized by FTIR and the spectral data was consistent with the expected structure. The product was immediately used in a Schiff base synthesis because of its sensitivity to atmospheric degradation. (Note: special precautions are needed for the handling and disposal of hydrogen saturated palladium/carbon catalysts.)

4-(3-(4-phenoxy)propionitrile)-N,N'-disalicylidene-1,2-phenylene diamine, H2(nitrile) (3)

A solution of 2.50g (0.0205mol) of salicylaldehyde in 100 ml absolute ethanol was added to the oily residue isolated from the above hydrogenation reaction 3-(4-(3,4-diaminophenoxy) phenyl)propionitrile. The amount of freshly distilled salicylaldehyde used was exactly twice the calculated theoretical yield of the diamine. The mixture was heated to reflux at which time the solution turned orange and a precipitate formed. Reflux was continued overnight. Progress of the reaction was followed
by TLC where the appearance of a yellow spot, Rf=0.60 signaled the formation of the desired product. The contents were vacuum filtered while still hot and then washed with additional absolute ethanol. The product was vacuum dried in a desiccator with an attached vacuum pump for 3 days. A yield of 2.93 g (62%) of the Schiff base product, an orange colored solid was obtained with a melting point of 128-130 °C. Analysis: Calculated for C_{29}H_{23}N_{3}O_{3}: C, 75.5; H, 5.10; N, 9.20%. Found: C, 75.7; H, 5.01; N, 9.14%. The product was also characterized by ^1H NMR and FTIR. The characterization data was consistent with the expected structure.

\[
\text{Bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV), } \quad \text{Zr(nitrile)2 (4)}
\]

Under a dry dinitrogen atmosphere (glovebag), a round bottom flask equipped with a stirbar was charged with 0.44 g (0.0011 mol) of freshly distilled Zr(O-n-Bu)4-n-BuOH. A solution of 1.05 g (.00220 mol) of 4-(3-(4-phenoxy)propionitrile)-N,N'-disalicylidene-1,2-phenylenediamine in 100 ml of absolute ethanol was added and the flask equipped with a condenser fitted with a calcium sulfate drying tube. Immediately the formation of a bright yellow precipitate was observed. The reaction was stirred 24 hours at reflux temperature. Progress of
the reaction was followed by TLC using 1:1 THF:pet ether eluent. Both the filtrate (containing the starting materials) and the precipitate (product dissolved in acetone, Rf=0.55) were spotted onto the TLC plate to monitor reaction progress. Suction filtration of the hot mixture led to the isolation of a canary yellow solid 0.89 g, 80% yield. Decomposition occurred at 320-321 °C. Analysis: Calculated for C58H42N6O6Zr: C, 69.0; H, 4.19; N, 8.32%. Found: C, 69.5; H, 4.23; N, 8.38%. The product was also characterized by 1H NMR and FTIR. The characterization data was consistent with the expected structure.

**Attempted Synthesis of Bis(4-(4-(3-aminopropyl)phenoxy))-N,N' disalicylidene-1,2-phenylenediamino)zirconium(IV), Zr(amine)₂**

**Method A**

A Paar flask was charged with a solution of 1.00 g (9.89x10⁻⁴ mol) of bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV) in 25 ml of freshly distilled THF, 2.00 g (wet weight) Raney nickel catalyst which was washed repeatedly with absolute ethanol prior to use, and 0.10 g (0.0025 mol) of crushed NaOH in 25 ml of absolute ethanol. This mixture was subjected to 60 psi H₂ with agitation for 20 hours. TLC's were taken every half hour for the first 10
hours. The original yellow spot disappeared and no new yellow spot was observed on the TLC's.

Method B

A Paar flask was charged with a solution of 1.00 g (9.89 x 10^-4 mol) of bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV) in 100 ml of freshly distilled THF. The flask was cooled to -70 °C, saturated with anhydrous ammonia and charged with 0.7 g of rhodium on alumina catalyst. The flask was pressurized to 60 psi H2 and agitated at room temperature for three days. There was no apparent reaction as progress of the reaction was followed by TLC and there was no change in either Rf or appearance of the starting spots.

Method C

A Paar flask was charged with a solution of 1.00 g (9.89 x 10^-4 mol) of bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-3,4-phenylenediamino)zirconium(IV) in 100 ml of freshly distilled THF and 2.44 g of thoroughly washed Raney nickel catalyst. The flask was pressurized with 60 psi H2 and agitated for 30 hours at room temperature. TLC showed no yellow spot only a colorless spot that appeared as a fluorescent blue spot under ultra-violet light. After removal of the catalyst the starting material was not recovered.

Method D
A Paar flask was charged with a solution of 0.16 g (1.6x10^-4 mol) of bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV) in 70 ml of freshly distilled THF and 6.00 g (wet weight) of active Raney Nickel catalyst. The catalyst was thoroughly washed prior to its addition to the Paar flask by rinsing it seven times with THF. This was to ensure that absolutely no water was present and therefore could not be a possible cause of interference in the desired hydrogenation reaction. The Paar flask was cooled to -70 °C in a large dry ice-acetone bath. Anhydrous ammonia (Aldrich) was bubbled into the flask which was connected to a series of water and aqueous acid traps. When the solution was saturated with liquified ammonia the Paar flask was attached to the pressure hydrogenator apparatus and pressurized to 60-65 psi H2 (gauge pressure) and allowed to agitate for 48 hours. The gauge pressure increased to 90 psi as the solution warmed to room temperature. Progress of the reaction was followed by TLC using a 1:1 mixture of THF:dichloromethane eluent. The solution containing the product was filtered through a Celite pad using suction filtration and washed several times with portions of THF. Rotary evaporation of the solution produced an oily residue. Pet ether was used to extract out impurities and side products. Gravity filtration leads to the isolation of a yellow-brown solid in exceedingly low yield. The TLC of this material produces a single yellow spot at the origin. The eluent was changed to 1:1
THF:acetone to move the spot off the origin. In this chromatography system the product was a single yellow spot at Rf=0.3. This product was characterized by FTIR. The characterization data was not consistent with the expected structure.

\[ \text{Bis(4-(N-(3-(4-phenoxy)propyl)ethanamide)-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV), Zr(amide)2} \ (6) \]

A Paar flask was charged with a solution of 0.16 g, \((1.6 \times 10^{-4} \text{ mol})\) of bis(4-(3-(4-phenoxy)propionitrile))-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV) in 100 ml of freshly distilled THF, 120 ml of freshly distilled acetic anhydride, 12 g of anhydrous sodium acetate and 17 g of washed Raney Nickel catalyst. The Paar flask was agitated in the pressure reaction apparatus at 60 psi H\(_2\) (gauge pressure) for 1 hour. The reaction was monitored by TLC. The initial yellow spot with R\(_f\)=0.55 disappeared and a yellow spot just above the origin appeared. The chromatography system consisted of 1:1 THF : pet ether eluent. The product TLC also showed a fluorescent blue spot with R\(_f\)=0.8. The Raney nickel catalyst and excess solid sodium acetate were removed by suction filtration through a Celite pad using additional portions of THF to wash the catalyst. Rotary evaporation removed the solvent leaving an orange oil. This was
dissolved in dichloromethane and washed with several portions of water. The dichloromethane portions were dried with magnesium sulfate. Decolorizing carbon was added and the contents filtered through a Celite pad. The solvent was removed by rotary evaporation. Additional solvent removal was affected by leaving the sample under a vacuum overnight. Pet ether was used to triturate the resulting oil to obtain a yellow crystalline solid, 39% yield. Analysis: Calculated for C$_{62}$H$_{54}$N$_6$O$_8$Zr: C, 67.55; H, 4.94; N, 7.62%. Found: C, 66.08; H, 4.92; N, 7.42%. The product was also characterized by FTIR and $^1$H NMR. The characterization data was consistent with the expected structure.

After repeated recrystallizations from dichloromethane and pet ether it was observed that the sample had darkened, possibly suggesting decomposition of the complex. This observation was confirmed by the results of an elemental analysis on the resubmitted sample. Analysis: Found: C, 64.80; H, 5.16; N, 6.91%.

**Attempted Synthesis of 1,6-hexanediamine from adiponitrile**

**Method A**

A four neck round bottom flask equipped with a magnetic stirrer and a reflux condenser fitted with a drying tube was charged with a solution of 2.71 g (0.0250 mol) of adiponitrile (1,4-dicyanobutane) (Aldrich) dissolved in 100 ml of freshly distilled THF. An addition funnel charged with (0.100 mol) 100ml of 1 M superhydride, (LiB[C$_2$H$_5$]$_3$H), under a dinitrogen atmosphere was
used to add portions of the reducing agent to the reaction flask over 20 minutes. The reaction solution was stirred for five hours and periodically monitored for any signs of reaction by TLC. The starting material, observed as a blue spot that was apparent under UV light remained present throughout the entire time period. A reaction between the reaction solution and the silica gel of the TLC plate was observed when spotting the plate. After stirring an additional hour 47.6 g (0.200 mol) of cobalt(II)chloride hexahydrate (Baker) was added in portions (according to the method of reference 31) during which time violent gas evolution occurred. The resultant bright blue mixture was stirred for two hours at room temperature. It was observed that there was no reaction between the reaction mixture and the silica gel of the TLC plate. The presence of the starting material was still observed. An additional 100 mls (0.100 mol) of superhydride was added to the reaction mixture. Further gas evolution was observed but no change in the TLC was registered. FTIR of the crude solution did not indicate the presence of an aliphatic amine.

Method B

A Paar bottle was charged with a solution of 5.41 g (0.0500 mol) of adiponitrile in 50 mls of absolute ethanol, 2.00 g (wet weight) Raney nickel catalyst which was washed repeatedly with absolute ethanol prior to use, and 0.10 g (0.0025 mol) of crushed NaOH. This mixture was subjected to 60 psi H2 (gauge pressure) with agitation for five hours. TLC results indicate the presence of
the starting material. The reaction was allowed to continue for 48 hours with TLC's taken every two hours during the working day. The contents of the reaction were filtered through a cellite pad and rinsed with dichloromethane. The solution was treated with decolorizing carbon to remove any impurities. The purple solution was concentrated by rotary evaporation of the solvent and 200 ml of deionized water added. The aqueous layer had a beige color and cloudy appearance. The aqueous layer was concentrated down by rotary evaporation. A reference solution of 1,6-hexanediamine in benzene was spotted along side of the reaction product. The TLC indicated the reaction product did not correspond to the desired product.
Method C

A two neck round bottom flask equipped with a magnetic stirrer and a reflux condenser fitted with a drying tube was charged with 1.1 g (0.010 mol) of adiponitrile (also called 1,4-dicyanobutane). An addition funnel was charged with 40 ml (0.040mol) of the reducing agent LiAl[OC(CH3)3]3H under a dinitrogen atmosphere. The reducing agent was added slowly to the reaction flask with stirring. The progress of the reaction was followed by TLC where the eluent was 1:1 THF:pet ether. A solution of the expected product, 1,6-hexanediamine in benzene, and a solution of the starting material, 1,4-dicyanobutane in THF were spotted along side of the reaction solution as reference points. No changes were detected in the Rf values of the components of the reaction solution. The solution was stirred 5 hours and periodically checked for reaction progress. A reaction was observed to take place on the surface of the TLC plate indicating the continued reactivity of the reducing agent. The reaction was allowed to stir an additional 5 hours.
Characterization

All IR spectra were obtained as KBr mulls using a Perkin-Elmer 1760X FTIR spectrometer equipped with a He-Ne 633 nm laser. All spectra were calibrated against polystyrene. $^1$H NMR spectra were obtained using a 200 MHz Bruker NMR spectrometer. All NMR samples were dissolved in deuterated dichloromethane with TMS as the internal reference. Melting points were determined using a Mel-Temp apparatus. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a 240 XA CEC instrument.
RESULTS: NITRILE COMPLEX

Characterization

Table I contains physical data and the results of elemental analyses for the intermediates, the Schiff base ligand and the bis(quadridendate)zirconium(IV) complexes. The infrared and $^1$H NMR spectral data are collected in Tables II and III respectively for same compounds. The spectra are collected in the Appendix. Table IV summarizes all the conditions and results for the many attempts to reduce the complex via catalytic hydrogenation. Table V is a summary of all reduction reactions to convert an aliphatic nitrile to a primary amine (results include attempts on an organic model compound, adiponitrile, and on the complex Zr(nitrile)$_2$).
<table>
<thead>
<tr>
<th></th>
<th>ETHER</th>
<th>H₂(nitrile)</th>
<th>Zr(nitrile)₂</th>
<th>Zr(amide)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₁₅H₁₃N₃O₃</td>
<td>C₂₉H₂₃N₃O₃</td>
<td>C₅₈H₴₂N₆O₆Zr</td>
<td>C₆₂H₵₴N₆O₈Zr</td>
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<tr>
<td><strong>Mol. Wt.</strong></td>
<td>283.3</td>
<td>461.00</td>
<td>1010.2</td>
<td>1102.4</td>
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<tr>
<td><strong>melt. pt. (C)</strong></td>
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<td>128-130</td>
<td>320 (dec.)</td>
<td>150 (darkens)</td>
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<td></td>
<td></td>
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<td>180 (dec)</td>
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<tr>
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<tr>
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Table II. Infrared Spectral Characterization Data for the Ligands and Complexes

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<th>Assignmenta (cm⁻¹)</th>
<th>Ether</th>
<th>H₂(nitrile)</th>
<th>Zr(nitrile)₂</th>
<th>Zr(amide)₂</th>
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<tbody>
<tr>
<td>Ph-(OH)</td>
<td></td>
<td>3544 W</td>
<td></td>
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<tr>
<td>N-H primary amine str</td>
<td>3467 S</td>
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<td>-</td>
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<tr>
<td>N-H sub. amide</td>
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<td></td>
<td></td>
<td>3369 S</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3177 M</td>
</tr>
<tr>
<td>H-C aromatic</td>
<td>3042 W</td>
<td>3067 W</td>
<td>3062 W</td>
<td>3043 W</td>
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<td>H-C aliphatic</td>
<td>2964 W</td>
<td>2929 W</td>
<td>2934 W</td>
<td>2926 S</td>
</tr>
<tr>
<td>CN nitrile unconjugated</td>
<td>2255 M</td>
<td>2241 W</td>
<td>2246 W</td>
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<tr>
<td>C=O amide</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1656 S</td>
</tr>
<tr>
<td>C=N imine</td>
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<td>1616 S</td>
<td>1609 S</td>
<td>1608 S</td>
</tr>
<tr>
<td>NH₂ primary amine (bnd)</td>
<td>1625 S</td>
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<tr>
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<td>1575 S</td>
<td>1543 S</td>
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<tr>
<td>Ph nucleus</td>
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<td>1480 S</td>
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<td></td>
<td></td>
<td>1448 S</td>
<td>1447 S</td>
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<tr>
<td>NO₂ coupled str bands</td>
<td>1509 S</td>
<td>-</td>
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<tr>
<td>(Ph-O)-Zr</td>
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<td>1316 S</td>
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<td>1277 M</td>
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<td>Ph-O-Ph</td>
<td>1240 S</td>
<td>1252 S</td>
<td>1245 M</td>
<td>1244 M</td>
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<td></td>
<td>1220 S</td>
<td>1224 M</td>
<td>1201 M</td>
<td>1202 M</td>
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<td>1197 M</td>
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</table>

a Conditions: KBr mulls, polystyrene as external calibration; abbreviations S= strong, M= medium, W= weak, B= broad.
Table III. $^1$H NMR Spectral Characterization Data for Ligands, Complexes.a

<table>
<thead>
<tr>
<th>Assignment (ppm)</th>
<th>Ether</th>
<th>$H_2$(nitrile)</th>
<th>Zr(nitrile)$_2$</th>
<th>Zr(amide)$_2$</th>
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<tr>
<td>Phenol H</td>
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<td></td>
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<tr>
<td>H</td>
<td>13.2 S (1)</td>
<td>8.5 S (1)</td>
<td>8.5 S (1)</td>
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<tr>
<td></td>
<td>12.9 S (1)</td>
<td>8.4 S (1)</td>
<td>8.4 S (1)</td>
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<td>Imine</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>8.65 S (1)</td>
<td>8.5 S (1)</td>
<td>8.5 S (1)</td>
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<tr>
<td></td>
<td>8.55 S (1)</td>
<td>8.4 S (1)</td>
<td>8.4 S (1)</td>
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</tr>
<tr>
<td>Aromatic H</td>
<td>8.10 D (1)</td>
<td>7.5-7.4 M (4)</td>
<td>7.4-7.3 M (3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.33 D (2)</td>
<td>7.4-7.3 M (3)</td>
<td>7.0-6.9 M (8)</td>
<td>7.2-6.9 M (11)</td>
</tr>
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<td></td>
<td>7.28</td>
<td></td>
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<tr>
<td></td>
<td>7.10 D (2)</td>
<td>7.1-6.9 M (8)</td>
<td>6.5-6.4 M (2)</td>
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</tr>
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<td></td>
<td>7.02</td>
<td></td>
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<tr>
<td></td>
<td>6.35 Q (1)</td>
<td>6.0-5.9 M (2)</td>
<td></td>
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</tr>
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<td></td>
<td>6.34</td>
<td></td>
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<td>6.32</td>
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<td></td>
<td>6.31</td>
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<td>6.21 D (1)</td>
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<tr>
<td>Aliphatic C-H</td>
<td>3.01 T (2)</td>
<td>2.9 T (2)</td>
<td>3.0 T (2)</td>
<td>3.2 Q (2)</td>
</tr>
<tr>
<td></td>
<td>2.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.69 T (2)</td>
<td>2.65 T (2)</td>
<td>2.7 T (2)</td>
<td>2.7 T (2)</td>
</tr>
<tr>
<td></td>
<td>2.66</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2.62</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>2.0 S (3)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>1.9 T (2)</td>
</tr>
<tr>
<td>Amine</td>
<td>2.12 S (2)</td>
<td>-</td>
<td>-</td>
<td>1.0 T (1)</td>
</tr>
</tbody>
</table>

a Conditions: All spectra obtained in dichloromethane-d$_2$ with TMS as internal reference. Peak integration given in parentheses. S= singlet, D=doublet, T=triplet, Q=quartet, M=multiplet, Br=broad.
Table IV. Summary of Reduction of the Nitrile complex by Catalytic Hydrogenation

<table>
<thead>
<tr>
<th>ATTEMPTa</th>
<th>CONDITIONS</th>
<th>RESULT</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (13093)</td>
<td>Raney nickel; NaOH; 60 psi H₂; 0-20 hr</td>
<td>No yellow spot on the TLC</td>
<td>Puchebner,B Report on Olin Grant RIT 1988</td>
</tr>
<tr>
<td>2 (21693)</td>
<td>Rh/Al₂O₃; NH₃; 60 psi H₂; 0-3 days</td>
<td>No reaction</td>
<td>Freifelder, M.; J. Am. Chem. Soc. 1960, 82, 2386</td>
</tr>
<tr>
<td>3 (21893)</td>
<td>Raney nickel; No NH₃; 60 psi H₂; 0-30 hrs.</td>
<td>Possibly coupled products; TLC: No yellow spot; blue spot visible under UV light</td>
<td>Huber,W. J. Am. Chem. Soc. 1944, 66, 876</td>
</tr>
<tr>
<td>4 (22593)</td>
<td>Raney nickel; NH₃; 60 psi H₂; 0-24 hrs.</td>
<td>TLC shows new yellow spot and disappearance of original spot; Isolate only a few drops of oil</td>
<td>Rylander, P.N. Hydrogenation Methods; Academic: N.Y., 1985; p97</td>
</tr>
<tr>
<td>5 (3293)</td>
<td>Raney Ni; NH₃; 65 psi H₂; 0-48 hr.</td>
<td>orange-yellow oil; very low yield</td>
<td></td>
</tr>
<tr>
<td>6 (31193)</td>
<td>Raney Ni; NH₃; 65 psi H₂; 0-48 hr.</td>
<td>orange-yellow oil/solid; FTIR inconclusive: small NH stretch; low yield</td>
<td></td>
</tr>
<tr>
<td>ATTEMPT</td>
<td>CONDITIONS</td>
<td>RESULT</td>
<td>REFERENCE</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>--------</td>
<td>-----------</td>
</tr>
<tr>
<td>7 (42893)</td>
<td>Raney Ni; NH₃; 65 psi H₂; 0-7 hr.</td>
<td>yellow solution turns black suddenly during rotary evap of solvent FTIR shows no resolution</td>
<td></td>
</tr>
<tr>
<td>8 (5593)</td>
<td>Raney Ni; NH₃; 60 psi H₂; 0-7 hr</td>
<td>fine dark yellow solid isolated; FTIR shows no resolution; complex destroyed</td>
<td></td>
</tr>
<tr>
<td>9 (51393)</td>
<td>Raney Ni only</td>
<td>solution turns from bright yellow to greenish color; 75% of the starting mat'l isolated</td>
<td></td>
</tr>
<tr>
<td>10 (51493)</td>
<td>NH₃ only</td>
<td>fine dark yellow powder isolated; FTIR indicated no resolution; complex destroyed</td>
<td></td>
</tr>
<tr>
<td>ATTEMPT</td>
<td>CONDITIONS</td>
<td>RESULT</td>
<td>REFERENCE</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>--------</td>
<td>-----------</td>
</tr>
<tr>
<td>11 (92393)</td>
<td>Raney Ni; sodium acetate; acetic anhydride; 60 psi H₂; 1 hr</td>
<td>TLC: appearance of blue spot visible under UV and a new yellow spot; disappearance of original yellow spot; orange-brown oil; low yield; FTIR, NMR</td>
<td>Gould, F.E.; Johnson, G.S. Ferris, A.F. J. Org. Chem. 1960, 25, 1658</td>
</tr>
<tr>
<td>12 (12094)</td>
<td>same as above; 30 min.</td>
<td>40% yield of yellow solid; elemental anal low by 1% in C only; FTIR, NMR; complex disintegrates upon repeated recrystallization.</td>
<td></td>
</tr>
<tr>
<td>13 (71594)</td>
<td>Model dinitrile used: adiponitrile; Raney Ni; 60 psi H₂, NaOH, EtOH; 0-20 hr</td>
<td>No reaction by 10 hr; product isolated neither starting material or expected product</td>
<td>Bergeron, R.J.; Garlich, J.R.; Stolowich, N.J. J. Org. Chem. 1984, 49, 2997</td>
</tr>
</tbody>
</table>

a These numbers refer to notebook pages.
Table V. **SUMMARY OF ALL REDUCTION REACTIONS**

I. **COMPLEX**

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Acetylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(NITRILE)$_2$</td>
<td>ZR(AMINE)$_2$</td>
</tr>
</tbody>
</table>

**Catalytic Hydrogenation**

I. Raney Nickel
   1. Ammonia; THF
   2. NaOH; Abs. EtOH

II. Rhodium/Al$_2$O$_3$
   1. NH$_3$; THF

II. **MODEL ORGANIC REACTION**

<table>
<thead>
<tr>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-(CH$_2$)$_4$-CN</td>
</tr>
<tr>
<td>ADIPONITRILE</td>
</tr>
</tbody>
</table>

**Catalytic Hydrogenation**

I. Raney Nickel
   1. NaOH; EtOH

**Chemical Reduction**

I. LiB(C$_2$H$_5$)$_3$H
II. LiB(C$_2$H$_5$)$_3$H; Co(II)Cl$_2$
III. LiAl[OC(CH$_3$)$_3$]H
EXPERIMENTAL: DIOL COMPLEX

Reagent grade solvents and chemicals were used. Absolute ethanol, diethyl ether and petroleum ether 20-40 °C boiling fraction were used without further purification. Tetrahydrofuran (THF) was dried over calcium hydride and distilled prior to use. Tetra-n-butoxyzirconium(IV) butanol solvate (Zr(O-n-Bu)4.n-BuOH, (Alpha), and salicylaldehyde (Aldrich) were distilled at reduced pressure prior to use. Acetyl chloride (Aldrich) was fractionally distilled prior to its use. The other reagents, 3,4-aminobenzophenone, lithium triethylborohydride (1M solution in THF from Aldrich; also called super hydride), and piperonyloyl chloride (Aldrich) were used without further purification. The dinitrogen gas (Air Products) used with the glovebag operations was dried over calcium hydride. All thin layer chromatograms were obtained on silica gel with fluorescent indicator (Kodak).

4-(phenylmethanone)-N,N′-disalicylidene-1,2-phenylenediamine, H2(dspCO) (Z)

A one liter three neck round bottom flask equipped with a magnetic stirrer, and a reflux condenser fitted with a calcium sulfate drying tube was charged with a solution of 10.1 g (0.0470 mol) of 3,4-diaminobenzophenone in 450 ml of absolute ethanol
(according to the method of reference 32). The stirred solution was charged with 40.0 g, (0.328 mol) of freshly distilled salicylaldehyde and gently heated. A catalytic amount of glacial acetic acid was added. Reaction occurs within minutes; the orange solution changes to a yellow precipitate. An additional 300 ml of absolute ethanol were added. Progress of the reaction was monitored by TLC. The appearance of a yellow spot with an Rf=0.7 when eluted in 17:3 carbon tetrachloride: methanol, indicated completion of the reaction. The yellow product was isolated with a yield of 15.9 g (80.4%). The material exhibited a sharp melting point at164-165 C. The product was characterized by FTIR. The spectral data was consistent with the proposed structure.

\[
\text{Bis(4-(phenylmethanone)-N,N'-disalicylidene-1,2-phenylenediamino)zirconium(IV), } \text{Zr(dspCO)}_2 \quad (8)
\]

The zirconium alkoxide (Zr(O-n-Bu)4·n-BuOH, used as the starting material, was freshly distilled according to the following method: A single neck 250 ml round bottom flask, equipped with a magnetic stir bar and placed in a sand filled heating mantle, was charged with tetra-n-butoxyszirconium(IV) butanol solvate (Zr(O-n-Bu)4·n-BuOH) while under a dinitrogen atmosphere. A short U-tube was used to attach the receiver flask to the distillation pot. The entire setup was wrapped in heat tape with a dedicated
variac control. The temperature was monitored in three different places: a thermometer was placed directly into the sand bath, and two thermometers were fitted into the heat tape next to the receiver pot and the distillation pot. The vacuum pump (0.5 mm Hg) was initially operated at room temperature to evaporate the butanol. After the vigorous bubbling subsided, the variac controlled heating mantle was used to heat the sand to 276 °C in order to melt the Zr(OBu)4. The variac controlled heat tape was turned on when the temperature in the sand reached 320 °C. The distillate was a clear liquid that tended to solidify near the mouth of the flask. A heat gun was used to re-liquify the substance by mounting and aiming it at the neck of the receiver pot. Shut down operations required that the distillation pot cool off first while maintaining the heat to the U tube and receiver pot. Next the other heat sources were shut off. After cooling to room temperature the entire glassware setup was moved to a glovebag where it could be disassembled and capped without exposure to the atmosphere.

A one liter three neck round bottom flask equipped with a condenser fitted with a magnesium sulfate drying tube, magnetic stir bar and a heating mantle was charged with 18.8 g (0.0447 mol) H2dspCO in 750 ml of absolute ethanol (according to the method of reference 32). In a dinitrogen atmosphere (glovebag), 8.59 g (0.0224 mol) of Zr(OBu)4 was added to the flask. The
reaction was stirred at reflux temperature overnight. Progress of the reaction was followed by TLC using 17:3 carbon tetrachloride:methanol with several drops of glacial acetic acid as the eluent. TLC showed one yellow spot, Rf=0.5. Deionized water was added to induce precipitation and the product was collected by vacuum filtration. The fine yellow solid collected in 91% yield, 37.8 g darkened at 250 °C and decomposed at 315 °C when heated. This material was characterized by FTIR and ¹H NMR. The characterization data was consistent with the proposed structure.

\[ \text{Bis(4-(phenylmethanol)-N,N'-disalicylidene-1,2-phenylene diamino)zirconium(IV), Zr(dspOH)2 (9)} \]

A three neck 250 ml round bottom flask equipped with a reflux condenser fitted with a calcium sulfate drying tube, magnetic stirrer, nitrogen inlet,bubbler and a septum was purged, flamed out, and blanketed with a dry dinitrogen atmosphere then charged with 5.0 g (0.0054 mol) Zr(dspCO)2 in 100 ml of freshly distilled THF (according to the method of reference 32). A syringe was used to add 10.8 ml (1.08x10⁻² mol) of lithium triethylborohydride to the reaction flask dropwise. An additional 5 ml of super hydride was added then the reaction was quenched by the addition of 40 ml of absolute methanol and 0.5 ml of glacial acetic acid. The contents of the flask changed from red colored solution to yellow. A yellow precipitate was collected by suction
filtration. Ice cubes were added to the filtrate to induce further precipitation of a bright yellow solid with R_f=0.43. Progress of the reaction was followed by TLC using 17:3 carbon tetrachloride:methanol as the eluent. This product was recrystallized three times from benzene/pet ether with a yield of 2.51 g (49.8% yield). Further recrystallization of the Zr(dspOH)_2 complex involved dissolving it into hot absolute ethanol, cooling and then precipitating it with the addition of pet ether. The product which was dried under vacuum at 100 °C for three days was observed to decompose at 174 °C. Analysis: Calculated for C_{54}H_{36}N_{4}O_{6}Zr: C, 69.6; H, 4.33; N, 6.01%. Found: C, 68.07; H, 4.47; N, 5.76%. The product was further characterized by FTIR and ^1H NMR. The characterization data was consistent with the proposed structure.

*Reaction of Zr(dspOH)_2 with acetyl chloride*

A 100 ml 3 neck round bottom flask equipped with an icebath, and a magnetic stirrer was charged with a solution of 2.00 g (0.00215mol) of Zr(dspOH)_2 in 80 ml of freshly distilled THF. A syringe was used to add 0.40 ml (0.0056 mol) of freshly distilled acetyl chloride to the flask. TLC immediately shows the loss of the yellow spot corresponding to the starting diol (R_f=0.4 ) and the appearance of a brown spot slightly above the origin. Several other colorless spots (apparent as fluorescent spots under UV
light) were also present. An yellow-orange precipitate which has limited solubility in methanol was isolated. The product was characterized by FTIR. The spectral data was not consistent with the proposed structure.

*Attempted reaction of piperonyloyl chloride with Zr(dspOH)$_2$*

A three neck 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser fitted with a calcium sulfate drying tube was placed into a dinitrogen glovebag and charged with a solution of 1.03 g (0.00599 mol) of piperonyloyl chloride in 50 ml of freshly distilled THF. The flask was equipped with a dinitrogen inlet and bubbler and charged with a solution of 2.00 g (0.00215 mol) of recrystallized Zr(dspOH)$_2$ in 40 ml of dry THF. A comparison of the TLC's taken initially and after one hour of mixing indicated that no change had occurred. The flask was heated to reflux for several hours. The final TLC indicated no changes from the initial one.

*Zr(dspOH)$_2$ refluxed in THF*

A 100 ml 2 neck round bottom flask equipped with a reflux condenser fitted with a calcium sulfate drying tube, heating mantle and a magnetic stirrer was charged with 2.00 g (0.00215 mol) of...
mol) of recrystallized Zr(dspOH)₂ in 55 ml of freshly distilled THF and heated at reflux temperatures for two days. TLC indicates the presence of 2 yellow spots and two colorless (fluorescent under UV) spots as opposed to the initial TLC which had only a single yellow spot.
RESULTS: DIOL COMPLEX

*Characterization*

Table VI contains physical data and the results of elemental analyses for the Schiff base ligand and the bis(quadridentate)-zirconium (IV) complexes. The infrared and $^1$H NMR spectral data are collected in Tables VII and VIII respectively for the same compounds. The spectra are collected in the Appendix.
Table VI. Elemental Analyses and Physical Characterization Data for Ligands and Complexes.

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<thead>
<tr>
<th></th>
<th>H₂(dspCO)</th>
<th>Zr(dspCO)₂</th>
<th>Zr(dspOH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₂₇H₂₀N₂O₃</td>
<td>C₅₄H₃₆N₄O₆Zr</td>
<td>C₅₄H₄₀N₄O₆Zr</td>
</tr>
<tr>
<td>Mol. Wt.</td>
<td>420.47</td>
<td>928.13</td>
<td>932.16</td>
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<tr>
<td>Melt. Pt. (C)</td>
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<td>315 (dec.)</td>
<td>174 (dec.)</td>
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<td></td>
<td></td>
<td>250 (darken)</td>
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<tr>
<td>Elem. Anal.</td>
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<tr>
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<tr>
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<tr>
<td>Exp</td>
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<td>6.01</td>
<td>5.68</td>
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</tbody>
</table>
Table VII. Infrared Spectral Characterization Data for the Ligands and Complexes

<table>
<thead>
<tr>
<th>Assignmenta (cm⁻¹)</th>
<th>H₂(dspCO)</th>
<th>Zr(dspCO)₂</th>
<th>Zr(dspOH)₂</th>
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</thead>
<tbody>
<tr>
<td>Ph-OH</td>
<td>3300 B</td>
<td>-</td>
<td>3544 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3351 B</td>
</tr>
<tr>
<td>Ar C-H</td>
<td>3060 M</td>
<td>3059 M</td>
<td>3061 M</td>
</tr>
<tr>
<td>C=O</td>
<td>1655 S</td>
<td>1657 S</td>
<td>-</td>
</tr>
<tr>
<td>C=N</td>
<td>1614 S</td>
<td>1610 S</td>
<td>1614 S</td>
</tr>
<tr>
<td>Ph nucleus conjugated</td>
<td>1583 S</td>
<td>1583 S</td>
<td>1543 S</td>
</tr>
<tr>
<td>Ph-O</td>
<td>1280 S</td>
<td>1317 S</td>
<td>1316 S</td>
</tr>
<tr>
<td>Ph-O-Zr</td>
<td>-</td>
<td>-</td>
<td>1381 M</td>
</tr>
</tbody>
</table>

a Conditions: KBr mulls, polystyrene as external calibration; abbreviations S=strong, M=medium, W=weak, B=broad.
Table VIII. 

<table>
<thead>
<tr>
<th>Assignment</th>
<th>(\text{H}_2(\text{dspCO}))(^b)</th>
<th>(\text{Zr}(\text{dspCO})_2)</th>
<th>(\text{Zr}(\text{dspOH})_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{OH})</td>
<td>12.8 D 12.6 10.8 D 10.3</td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>(\text{C=N})</td>
<td>9.1 S 8.9 S</td>
<td>8.6 S (1) 8.5 S (1)</td>
<td>8.6 S (1) 8.5 S (1)</td>
</tr>
<tr>
<td>(\text{Ar C})</td>
<td>7.3-7.9 M 7.3-8.1 M 6.1-7.2 M</td>
<td>7.9 M (4) 7.7-7.5 M (4) 7.3-7.2 M</td>
<td>7.5-7.3 M (10) 7.2-7.1 M 6.9 M (4) 6.5-6.4 M (2) 5.9-5.8 M (2)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: All spectra obtained in dichloromethane-d\(_2\) with TMS as internal reference. Peak integration given in parentheses. S=singlet, D=doublet, T=triplet, Q=quartet, M=multiplet, B=broad. 

\(^b\) Reference 33
DISCUSSION

Synthesis and Characterization

The previously unreported bis(quadridentate Schiff base) zirconium(IV) complex, Zr(nitrile)\textsubscript{2} was prepared by reaction of the appropriate Schiff base ligand, H\textsubscript{2}(nitrile) with Zr(O-n-Bu)\textsubscript{4}
\cdot n-BuOH according to the scheme:

\[
\text{Zr}(O-n-Bu)\textsubscript{4}
\cdot n-BuOH + 2\text{H}_2\textsubscript{(nitrile)} \rightarrow \text{Zr(nitrile)}\textsubscript{2} + 5n-BuOH
\]

The previously unreported bis(quadridentate Schiff base) zirconium(IV) complex, Zr(amide)\textsubscript{2} was prepared by catalytic hydrogenation of Zr(nitrile)\textsubscript{2} in the presence of acetic anhydride and sodium acetate according to the scheme:

\[
\text{Zr(nitrile)}\textsubscript{2} + \text{Raney Ni / H}_2 \rightarrow \text{Zr(amide)}\textsubscript{2}
\]

The previously reported bis(quadridentate Schiff base)zirconium(IV) complex, Zr(dspOH)\textsubscript{2} was prepared from the precursor Zr(dspCO)\textsubscript{2} by chemical reduction of the carbonyl to the alcohol using superhydride reagent (which leads to a boron adduct intermediate that requires a hydrolysis reaction) according to the scheme: (32)
The purified $\text{Zr(dspOH)}_2$ complex was reacted with several mono and diacid chlorides and an anhydride to investigate its polymerization behavior. (33)

The following discussion presents the evidence used to support the conclusion that each target molecule was isolated with the expected structure. Each intermediate was isolated, purified to a single spot on thin layer chromatograms and characterized by the TCL, elemental analysis and FTIR and $^1\text{H}$ NMR spectra prior to its use in succeeding reactions. Spectral data from FTIR and $^1\text{H}$ NMR provided evidence of the structure. TLCs were used to monitor reaction progress as well as determine the purity of the substance isolated. Elemental analyses showed that the elements were present in the expected proportions.

The synthetic routes for preparation of $\text{Zr(amide)}_2$ and $\text{Zr(dspOH)}_2$ herein described were based on similar past syntheses involving salicylidene phenylenediamine Schiff base ligands and zirconium ion.

The multiple step synthetic sequence depicted in Synthetic Scheme Nitrile: Overall 1-5 (pg 30-34) was devised for the preparation of the bis(quadridentate Schiff base)zirconium(IV)
complex, Zr(nitrile)$_2$. Subsequently a series of reduction reactions, both catalytic hydrogenation and chemical reduction were attempted to try to convert the terminal nitrile groups to primary amines. The following comments and observations examine this synthetic design.

The synthesis of the diaryl ether was based on the Williamson ether synthesis, however it is noted that this synthesis usually involves the reaction of a metal alkoxide or phenoxide with an alkyl halide via an $S_N2$ pathway to produce ethers. The best results are obtained when methyl or primary alkyl halides are used in these reactions. (34) In order to synthesize a diaryl ether an aryl halide must be used. The diaryl ether that was the target molecule in the present synthesis, product reaction 1, Scheme I, depended on a nucleophilic aromatic substitution reaction of the aryl halide. Aryl halides are usually inert to substitution reactions by the $S_N1$ or $S_N2$ pathways. Aryl halides do not undergo $S_N1$ reactions because the formation of an unstable aryl cation is required. Since aryl cations are unstable, the energetics of the reaction do not favor its formation. Aryl halides also don't undergo $S_N2$ reactions because the ring geometry and steric hindrance prevent backside attack.(35) Instead substitution reactions of aryl halides proceed by an aromatic nucleophilic substitution mechanism involving a two step addition-elimination pathway. The incoming nucleophile adds to the aryl halide to form a negatively charged complex then the
halide ion is eliminated. A further influence complicating this reaction is the fact that aryl halides are deactivated towards substitution reactions. The low reactivity of aryl halides is attributed to the delocalization of electrons by resonance. Therefore, this reaction requires the aryl halide have electron withdrawing substituents in the ortho or para positions that serve to activate it to reactions. (35) FIGURE 17 depicts the mechanism of this reaction. In the addition step of nucleophilic aromatic substitution, a nucleophile attaches itself to the carbon bearing the halide, making that carbon tetrahedral and the ring acquires a negative charge. The presence of electron withdrawing groups at ortho and para positions of the ring markedly activate the halogen of the aryl halide toward displacement because of the groups ability to stabilize the carbanion by dispersing the charge. An electron donating group intensifies the negative charge and destabilizes the carbanion, slowing down the reaction. Deactivation by an electron releasing group such as NH$_2$ will be strongest when it is ortho or para to the halogen. An electron donating substituent in the meta position will deactivate the ring to a lesser extent. (36) The aryl halide used in the present synthesis, 2-nitro-5-chloroaniline has an electron withdrawing substituent, NO$_2$ ortho to the halogen atom and an electron donating group, NH$_2$ meta to it. The NO$_2$ group has inductive effects as well as resonance which activates the ring to an even greater extent. The combined effects of these substituents will
control the overall reactivity of the aryl halide and the tendency towards side reactions.

Intermediate carbanion stabilized by resonance and induction

Aromatic Nucleophilic Substitution Mechanism

FIGURE 17. Aromatic Nucleophilic Substitution Mechanism
Several references discuss the use of copper catalysts in the preparation of substituted diaryl ethers (ArOAr') by the reaction of alkali phenoxides and aryl halides. Studies have shown that yields vary considerably with different copper catalyst preparations. (37) The present synthesis did not use any catalyst and some reaction times exceeded 48 hours.

The first evidence that the Williamson ether synthesis of 3-(4-(3-amino-4-nitrophenoxy)phenyl)propionitrile, 1, had been accomplished was seen in the TLC results collected while the reaction was in progress. The starting materials (consisting of a fluorescent blue spot corresponding to the phenol, and a yellow spot due to the substituted aniline, Rf=0.6) and the reaction mixture were spotted side by side on a silica gel plate and eluted in 1:1 THF:pet ether. Appearance of a new yellow spot of lower Rf, (Rf=0.4), and the disappearance of the original yellow spot was taken as confirmation that the reaction had progressed and was nearly complete. A brown spot that appeared slightly above the origin was thought to be a product from a competing side reaction. Further supporting evidence came from the FTIR spectral data of the many times (6-8) recrystallized product. Most of the absorption bands in the spectrum could be assigned to one or another functional group in the molecule. The product shows the typical absorption bands for an aromatic ether (1240 cm⁻¹), aromatic primary amine (NH₂ asymmetrical and symmetrical stretches, 3467 and 3339 cm⁻¹ respectively, as well as NH₂
bending at 1622 cm\(^{-1}\) and aromatic C to N stretching at 1221 cm\(^{-1}\), aromatic nitro group (asymmetrical and symmetrical NO\(_2\) stretchings at 1574 and 1333 cm\(^{-1}\) respectively) and an aliphatic nitrile (stretching vibration at 2256 cm\(^{-1}\)). (38) (39) Additional supporting evidence was seen in the elemental analysis which indicated it was low by 0.8% in the carbon content, 0.2% high in its nitrogen content and correct in the hydrogen content relative to the theoretical values.

The \(^1\)H NMR was difficult to interpret because it appeared that another compound was giving rise to additional chemical shifts and causing interference. It was deemed necessary to further purify the ether product, obtain a one spot TLC, verify the purity of the sample by gas chromatography and resubmit for both elemental analysis and NMR. Successive recrystallizations of the isolated product did not fully remove the faint spot just above the origin that plagued this purification. Flash column chromatography and evaporation of the eluent provided a much more satisfactory method of purification. TLCs of the isolated product showed only the single yellow spot that corresponded to the product. Also the gas chromatogram indicated only a single peak. The elemental analysis indicated the carbon content was 0.6% low, hydrogen was high by 0.13%, and nitrogen was low by 0.5% relative to theoretical values. The \(^1\)H NMR was now interpretable and an assignment of every proton could be made. The protons on the carbons of the imine groups were observed
downfield at 8.1 and 7.9 ppm. Chemical shifts for the two aromatic rings and the aliphatic protons of the molecule integrated correctly.

The product, 2, of the hydrogenation reaction of the nitro aromatic ether to an ortho diamine aromatic ether, was not isolated but was used immediately with salicylaldehyde to form the Schiff base product. This strategy was employed to avoid the problem of rapid oxidative decomposition of ortho diamine aromatic compounds. However a drop of the oily product was placed between sodium chloride salt plates and an FTIR spectrum obtained immediately. The spectrum showed strong primary amine stretches, the continued presence of the nitrile band and other characteristic complex bands but now lacked the nitro group bands. The TLC plates discolored upon sitting in air at the spot assigned to the diamine. This was taken as further evidence that the desired product had been isolated since ortho diamine compounds are noted for rapid oxidation/decomposition in air.

The strongest evidence supporting the formation of the Schiff base product, 3, was found in the results of the elemental analysis and the $^1$H NMR spectrum. The elemental analysis results for carbon, hydrogen and nitrogen are all within 0.3% of the theoretical values. All the chemical shifts can be assigned to the various protons and the integrations are correct. The two phenolic protons have downfield chemical shifts at 13 ppm, the imine
protons appear at 8.5 ppm and the upfield chemical shifts at 2-3 ppm are assigned to the aliphatics attached to the nitrile.

The FTIR spectrum shows the disappearance of the primary amine stretches (asymmetrical and symmetrical at 3400-3200 cm\(^{-1}\)) and the appearance of a broad weak hydroxyl band at 3544 cm\(^{-1}\). The disappearance in the 1650-1600 cm\(^{-1}\) region of the NH\(_2\) scissor band is masked by the appearance of the imine stretch in the same region, just as disappearance of the aromatic carbon to nitrogen (of the NH\(_2\)) stretch is masked by continued presence of the aromatic ether in the 1240 cm\(^{-1}\) region of the spectrum.

The complexation reaction, reaction 4 of Scheme I, of the zirconium alkoxide, Zr(O-n-Bu)\(_4\)-n-BuOH and the Schiff base ligand, H\(_2\)(nitrile) can be explained as an acid-base reaction based on Bronsted-Lowry theory of acids and bases. The Schiff base ligand acts as the proton donor, donating the phenoxy protons to the proton acceptor. The coordinated butoxide ligands of the zirconium alkoxide act as the proton acceptor or base. The reaction can be depicted in the following way:

\[
2 \text{(Schiff Base) ligands} + \text{Zr(O-n-Bu)}_4\text{-n-BuOH} \rightarrow \text{bis(quadridentate) Zr(IV) complex} + \text{BuOH}
\]

\[\text{stronger acid} \quad \text{stronger base} \quad \text{weaker conj. base} \quad \text{weaker conj. acid}\]
Acid-base reactions are reversible with the equilibrium displaced in the direction of the weaker acid base combination. (40)

The solvent choice for the complexation reaction was important because it could promote the desired reaction in several ways. Boiling absolute ethanol dissolves both the zirconium alkoxide and the free Schiff base ligand, H2(nitrile) starting materials but the product generated, the Zr(nitrile)2 complex, is insoluble in the reaction medium thereby driving the reaction towards completion. Additionally, absolute ethanol, as an anhydrous solvent, was suitable for use with zirconium alkoxide because Zr(O-n-Bu)4·n-BuOH is rapidly hydrolyzed to a less reactive [Zr4(OH)8(H2O)16]8+ complex cation. (41) Other precautions to prevent moisture contamination of the reaction involved the use of dinitrogen gas dried over calcium hydride and a glovebag and calcium sulfate drying tube attached to the reflux condenser.

Another driving force favoring the products of the reaction is the entropy increase caused by the forward reaction. The displacement of butanol by the Schiff base ligands leads to the presence of three additional particles on the right side of the reaction equation relative to the left side. Typically chelation leads to stabilized complexes because of this entropy factor. (42) The chelate effect contributes to the favorable product formation in
other ways as well. The high stability of chelates is related to the nature of the organic chelating agent which combines with the metal cation. The size and number of rings formed with the metal and stabilizing or interfering resonance interactions are all governed by the structure of the chelating agent. It is noted that 5 or 6 membered rings are most stable and an increase in the number of rings within a particular chelate structure results in greater stability of the chelate.\(^{(42)}\)\(^{(43)}\) The starting material in this reaction Zr(O-n-Bu)\(_4\)-n-BuOH has no chelation associated with its structure. The bis quadridentate complex that results from this reaction has each Schiff base ligand chelated to the metal through four donor atoms; two oxygen and two nitrogen atoms. Chelation between the metal ion and the organic ligands causes the formation of two six membered rings and a five membered ring per ligand.

Evidence that supports the conclusion that the complexation reaction product, Zr(nitrile)\(_2\), was produced was seen in the TLC data. Initial spotting of the reaction solution produced a yellow spot that represented the soluble Schiff base product. As the reaction proceeds, an insoluble canary yellow solid forms and spotting the reaction mixture showed only a faint yellow spot indicating the presence of residual starting material. Dissolving the bright yellow substance formed into THF or acetone, and spotting on silica gel plates produces a darker yellow spot of similar \(R_f\).
Additional evidence was seen in the $^1$H NMR spectrum where the disappearance of the downfield hydroxyl shifts and the upfield shift of several aromatic protons (protons are shifted out of the aromatic multiplet and appear at 6.5 and 6.0 ppm) can be attributed to the complexation by the zirconium metal ion. It was observed that upon complexation electronic interactions between the central metal ion and the ligands significantly influences the chemical environment of particular ligand atoms. This can be attributed to effects caused by covalent bonding of the ligand donor atoms to the zirconium cation. If that is the case then complexation reactions should exert similar consistent effects on the spectral behavior of other similar previously made schiff base ligands. A comparison of FTIR and $^1$H NMR data of the ligand before and after the complexation reaction of eight coordinate zirconium complexes previously reported in the literature exhibit the characteristic spectral shifts. (25) (28) In the FTIR spectrum the phenolic C-O stretch was observed to shift from 1280 cm$^{-1}$ to greater than 1300 cm$^{-1}$ upon complexation to the zirconium(IV) cation. The imine stretch near 1610 cm$^{-1}$ remained in about the same place before and after complexation. The chelated complex exhibits a strong zirconium to oxygen bond as well as a zirconium to aldimine nitrogen bond. In the $^1$H NMR spectrum, the metal-chelated aldimine resonances appear as sharp singlets shifted upfield from the free ligand aldimine chemical shifts. The phenolic hydroxyl ligand resonance is absent in the metal chelated
spectrum. It is noted that aromatic protons ortho to either the phenolic group or the imine group are shifted upfield out of the other aromatic signals. (28)

The results of the elemental analysis provide additional evidence to support the conclusion that the zirconium ion and the ligands have formed a complex. Relative to the theoretical values it was found that the carbon content was high by 0.5 %, the hydrogen content was low by 0.01 % and the nitrogen content was high by 0.06 %.

The FTIR spectral data showed the disappearance of the hydroxyl band at 3500 cm\(^{-1}\) and the appearance at 1316 cm\(^{-1}\) of the metal to phenoxide (Zr-O-phenyl) stretch.

Further evidence of reaction is exhibited in the melting behavior of the ligand before and after complexation. The free Schiff base ligand, H\(_2\)(nitrile) was observed to melt between 128-130 °C. After the complexation reaction, the bis(quadridentate Schiff base)zirconium(IV) complex had a decomposition temperature of 320 °C.

The next reaction required conversion of the Zr(nitrile)\(_2\) complex via reduction reactions to the primary amine, Zr(amine)\(_2\). Catalytic hydrogenation, the reaction of a compound with hydrogen in the presence of a catalyst, is a powerful synthetic method because most functional groups can be reduced and at the end of the reduction the heterogeneous catalyst can be separated from the solution by filtration leaving a contaminant
free solution. An alternative reduction method involves homogeneous catalysis. The need to remove the catalyst during workup is considered a major disadvantage of homogeneous catalysis. Catalytic hydrogenation was the preferred method and was investigated first and most thoroughly as a means to the Zr(amine)₂ complex. Chemical reduction was explored only when many catalytic hydrogenation attempts failed to produce satisfactory results.

An empirical approach is usually taken in the selection of a heterogeneous catalyst. The catalyst is treated as if it were an organic reagent showing characteristic properties in its catalytic behavior toward each functionality. By a search of the literature one can determine what type of metal has proved active and selective previously. (44) Complications can arise when a selective reduction of bifunctional molecules is desired. For a function to be reduced, it must undergo an activated adsorption on a catalytic site and to be reduced selectively it must occupy preferentially most of the active catalyst sites. Regardless of how easily a function can be reduced, no reduction of that functional group will occur if all of the sites are occupied by something else (a poison, solvent or other function). (44) Selectivity can be influenced by reaction environment, solvent and steric hindrance associated with the molecular structure. Hydrogenation reactions can fail due to poisoning, interaction with the solvent, coupling, poor selectivity or over hydrogenation. (44)
Prereduction of a catalyst involves agitating the catalyst, solvent and hydrogen without the substrate. This procedure is done if the catalyst is to be used under mild conditions. It is also suggested that one prereduce the catalyst when a system fails which the literature suggests should work. A disadvantage associated with this technique is that it is time consuming. (45) The use of solvents in hydrogenations is necessary when the substrate is a solid. It helps to moderate the heat of hydrogenation as well but it should be borne in mind that solvents influence rate as well as selectivity. Solvents can compete for catalyst sites with the reacting substrates and alter hydrogen availability at the catalyst surface. (45) In any case as a practical consideration Paar bottles should not be more than half full to ensure good mixing.

The nitrile hydrogenation scheme and the tendency towards formation of secondary amines can be depicted as below: (46)
Nitrile Hydrogenation Scheme

Nitriles are reduced to an imine intermediate which is further reduced to an amine, equation (1). The production of secondary amines as byproducts occurs when the amine and the imine intermediate form an addition product, equation (2). This addition product can eliminate ammonia and add hydrogen to become saturated, equations (2) and (4). Or it can undergo direct hydrogenolysis, the cleavage by hydrogen, to produce secondary amine byproducts, equation (3).

Some clever methods to overcome the byproduct problem involve interrupting the equilibrium conditions. Strongly acidic solvents prevent further reaction of the initially formed primary amine by formation of an ammonium salt. (47) This technique
requires the substrate have the ability to survive in an acidic medium. The zirconium complexes under investigation are known to be destroyed in acidic (and basic) media. (48)

Another effective way to prevent coupling reactions is to acetylate the primary amine as formed by carrying out the reduction in an anhydride solvent. When acetic anhydride is used under these conditions, the acetamide derivative is produced. Another common technique for minimizing secondary amine formation is to carry out the hydrogenation in the presence of ammonia. (49) Ammonia is thought to compete with the primary amine in attack on the intermediate imine, equations (5) and (6). Anhydrous ammonia should be used to prevent hydrolysis reactions. (47)

\[
\begin{align*}
R-\text{C}≡\text{N} & \xrightarrow{\text{H}_2} R-\text{C}≡\text{N} & R-\text{CH}≡\text{NH} & \xrightarrow{\text{NH}_3} R-\text{CH}-\text{NH}_2 \\
\text{NH}_3 & & \text{NH}_2
\end{align*}
\]

(5)

\[
\begin{align*}
R-\text{CH}-\text{NH}_2 & \text{NH}_2 \xrightarrow{\text{H}_2} R\text{CH}_2\text{NH}_2 & + \text{NH}_3
\end{align*}
\]

(6)

If water (moisture) is present the intermediate imine can undergo a reductive hydrolysis, equation 7. The aldehyde intermediate may also be a source of secondary amine as well, equation 8. (47) (51)
\[
\begin{align*}
R-\text{CH}=\text{NH} + \text{H}_2\text{O} & \quad \xrightarrow{\text{O}} \quad R\text{CH} + \text{NH}_3 + \text{H}_2 \quad \rightarrow \quad R\text{CH}_2\text{OH} \quad (7) \\
\quad + \text{RCH}_2\text{NH}_2 & \quad \downarrow \quad \text{H}_2 \quad \rightarrow \quad \text{(RCH}_2)_2\text{NH} + \text{H}_2\text{O} \\
\end{align*}
\]

Reduction of the \(\text{Zr(nitrile)}_2\) complex to \(\text{Zr(amine)}_2\) proved to be a difficult reaction. The first attempt at catalytic hydrogenation of the \(\text{Zr(nitrile)}_2\) complex to \(\text{Zr(amine)}_2\) sought to reproduce conditions used in Dr. Illingsworth's laboratory in 1988. The complex \(\text{Zr(cdsp)}_2\) (containing a benzonitrile), was reported to have been converted to \(\text{Zr(madsp)}_2\), (a complex containing a benzylic primary amine), in 54% yield by using Raney nickel and sodium hydroxide in 95% ethanol and laboratory grade THF. (29) Later undergraduate attempts of this same reaction had less consistent results reported. (50)(33)

In the current synthesis, similar conditions failed to produce the desired product, \(\text{Zr(amine)}_2\). The procedure differed in that absolute ethanol and dried solvents were used in the current synthesis but not in the reactions done in 1988. The main difference in the two complexes was that aliphatic dinitriles as opposed to benzonitriles were now the subject of the reduction reaction. TLC results indicated the loss of the yellow spot of the complex without the appearance of a new yellow spot. The lack of a yellow spot in the TLC was thought to indicate the destruction of
the complex. Isolation from the catalyst and rotary evaporation of
the solvent did not produce enough product even to do an FTIR
with.

When this set of conditions failed as a means to the
Zr(amine)₂ complex, alternative catalytic hydrogenation
techniques were sought out. Raney nickel in the presence of
ammonia has been reported to successfully reduce nitriles to
primary amines. Typically the reductions were done at elevated
temperatures and pressures (approximately 100 °C, 1000 psig)
unless massive amounts of nickel were used. Cobalt has been used
similarly but requires even more vigorous conditions. The
literature provides examples where platinum, palladium and
rhodium catalysts are used under mild conditions in conjunction
with ammonia to reduce nitrile compounds especially those that
are sensitive to extensive hydrogenolysis. It was thought that
the method of catalytic hydrogenation would work in this
situation if a mild enough reducing agent could be found that
would reduce the nitrile without reaction at other sites on the
complex.

Freifelder reported catalytic hydrogenation of
aliphatic nitriles under mild conditions (2-3 atmospheres H₂
pressure at room temperatures) using a rhodium catalyst in
ethanolic ammonia. He recommended using a 10 to 20% ratio of
5% rhodium on alumina in 10% ethanolic ammonia however other
strong bases could be substituted for the ammonia. In the
current synthesis this mild catalytic system failed to cause any change in the nitrile complex. It appeared that the catalyst although used from a new and unopened bottle was not active. Prereduction failed to activate the catalyst and this method was discarded. Its entirely possible that the ammonia present acted as a poison to the rhodium catalyst thereby rendering it non functional.

Catalytic hydrogenation was next attempted using a Raney nickel catalyst without ammonia or NaOH present. Changes in the TLC indicated that reaction was occurring, i.e., the characteristic yellow spot associated with the complex disappeared. However no product was isolated during the workup. It was thought that coupled products may have formed and been insoluble in the THF solvent hence thrown away with the catalyst. Alternatively the conditions may have been deleterious to the structural integrity of the complex.

Next, the reduction was attempted with anhydrous ammonia present to prevent coupling reactions. The TLC indicated reaction was occurring and a characteristic yellow spot was observed. After workup only a few drops of an oily substance was isolated. These were deemed to be encouraging results so the reaction was repeated varying the reaction times to both longer and shorter reaction times. Each time yields were exceedingly low and usually an impure oil. The fifth attempt produced a small quantity of an orange-yellow solid along with the oil. The resulting FTIR showed
the characteristic signals for the complex but was inconclusive with regards to the primary/secondary amine regions. It was speculated that the presence of ammonia was having an adverse affect on the complex. Zirconium complexes are not stable under strongly basic conditions which tend to destroy the inner coordination sphere. Although ammonia is a weak base it may have a similar effect on these types of complexes. The complex was mixed with ammonia and allowed to agitate for several hours. A small amount of a fluffy brown-yellow precipitate was isolated. The lack of resolution in the FTIR spectrum indicated that destruction of the complex had occurred. To establish that Raney nickel alone did not destroy the complex, the Zr(nitrile)\(_2\) complex was agitated for 8 hours with washed Raney nickel without hydrogen or ammonia present. 75% of the complex was recovered and the solution which originally was a bright yellow now had a green-yellow color. This result seems to indicate that some interaction (chemisorption) of the catalyst and the complex occurs but that it is not the source of the destruction of the complex.

Gould et. al. reported catalytic hydrogenation of nitriles to acetylated primary amines by the use of acetic anhydride in the presence of Raney nickel and a basic cocatalyst such as sodium acetate. (53) They reported that some nitriles like benzonitrile were more easily reduced and required no basic cocatalyst. This reduction method when applied to the Zr(nitrile)\(_2\) complex which has aliphatic nitriles, produced a small quantity of an orange-
brown oil, enough for an FTIR and a $^1$H NMR. The next attempt of the same reaction produced a 40 % yield of a dark yellow solid that was characterized as the Zr(amide)$_2$ complex. Attempts to improve the yield failed. Furthermore, repeated recrystallizations of the previously isolated material led to darkening and apparent destruction of the complex possibly due to side group rearrangements or labilization of the ligands coordinated to the transition metal. This is a preliminary conclusion, again based on the FTIR which showed a loss of the resolution characteristically seen for the zirconium complexes.

Acid or base hydrolysis of the acetylated product allows isolation of the amine as the salt or as the free base respectively. However, typical hydrolysis conditions involve a large excess of the concentrated acid or base (the acid or base is a reactant not a catalyst) and long reflux times. Under these conditions, the Zr(amide)$_2$ complex is likely to decompose prior to removal of the acetyl group. This reaction was not attempted as the recrystallization process had an adverse effect on the complex.

It is important to note that the formation and isolation of the substituted amide provides evidence that the primary amine had formed because the acetylation reaction is a nucleophilic substitution reaction of the amine with the anhydride. The fact that the acetylated product was produced after 30 minutes of reaction means that the primary amine must also have formed in the previous catalytic reduction reactions but not been detected.
by the TLC system. Additionally this means that the long reaction times were unnecessary and most probably harmful to the complex.

A model dinitrile compound was selected to be used in further experiments involving reduction reactions to primary diamines. This would allow the determination of the proper conditions to obtain the desired product without consuming the zirconium complex whose production required such a lengthy synthetic procedure. The model dinitrile selected for these preliminary reductions was 1,4-dicyanobutane also known as adiponitrile. 1,6-hexanediameine was the expected diamine product from the catalytic hydrogenation reaction.

Upon further searching of the literature for additional methods of reducing nitriles to amines a reference was discovered that described the catalytic hydrogenation of aliphatic nitriles using Raney nickel and sodium hydroxide in ethanol for 28 hours with 95% yield. (54) When the above conditions were utilized with the adiponitrile, no reaction was observed after 10 hours and when the reaction continued overnight neither the starting material nor the desired product was isolated. This reaction should work according to the literature. This reaction was only attempted once on the aliphatic dinitrile. It is possible by altering one or more of the conditions of this reaction that it could be made to work in the expected way.
The method of catalytic hydrogenation of the terminal nitriles group of the zirconium complex to primary amines appeared to have some problems associated with it. The inability to reduce selectively one functional group over another, the possible poisoning of the catalyst by certain compounds as well as the complications resulting from equilibria that lead to secondary amines are all possible sources of difficulty in this reaction and eventually led to the investigation of other reduction methods.

Chemical reduction by use of complex metal hydrides such as lithium aluminum hydride and sodium borohydride was investigated as an alternative method. Lithium aluminum hydride is a strong reducing agent that is known to reduce nitriles. (55) But it had previously been determined that lithium aluminum hydride destroyed the zirconium complexes. (56) It was also determined that the less reactive reducing agent, sodium borohydride reacted with zirconium complexes to produce insoluble bridged clusters or polymeric materials. (32) Even more selective (and therefore less reactive) reducing agents were sought in order to investigate whether they could successfully reduce the terminal nitrile groups without side reactions or destruction of the zirconium complex.

More selective reducing agents have been made by substituting one or more of the hydride ions with alkyl or alkoxy groups. (55) The next attempts to reduce the Zr(nitrile)\(_2\) focused on the use of such milder chemical reducing agents.
Superhydride, LiB[C₂H₅]₃H was used in conjunction with cobalt(II) in an attempt to chemically reduce the adiponitrile by modifying a method described in the literature. (31) The literature reported successful reduction of dinitriles to primary amines using cobalt(II)/sodium borohydride. In the current synthesis the procedure was adapted by substituting superhydride for the sodium borohydride. This reaction failed to consume the starting material and it was concluded that superhydride was too mild a reducing agent to be successful with aliphatic nitriles. Superhydride was first tried alone with adiponitrile and when it failed to reduce the adiponitrile, the cobalt(II) was added along with additional superhydride. Continued presence of the starting material signaled the failure of this method.

The final chemical reduction method involved the use of LiAl[OC(CH₃)₃]H, a reducing agent that has only one active hydride and bulky substituents groups which it was thought would prevent bridging reactions from occurring. It was not known if this reducing agent was reactive enough to reduce the nitrile functional group. The reaction was attempted using the model aliphatic dinitrile. No reaction was observed to have taken place after 10 hours. The progress of the reaction was followed by TLC. A reaction was observed to take place when the silica gel surface was spotted with the reaction solution. This was taken as evidence that the reducing agent was active and reacted with the
silica gel. Reference solutions of the expected product 1,6-hexane diamine and the starting material were prepared and spotted alongside the reaction mixture to assist in the interpretation of the TLC results. In each TLC the starting material was observed in the reaction solution.

The multiple step synthetic sequence depicted in Synthetic Scheme Diol: overall 1-5, (pgs 35-39) was previously used for the preparation of the bis(quadridentate Schiff base)zirconium(IV) complex, Zr(dspOH)₂.(32) This synthesis was repeated in order to further purify the complex before polymerization reactions were attempted.

The first reaction was a straight forward Schiff base reaction between salicylaldehyde and 3,4-diaminobenzophenone catalyzed by a minute amount of glacial acetic acid. This reaction was completed within two hours.

The complexation reaction to produce Zr(dspCO)₂, (8), proceeded smoothly so long as care was exercised to prevent the hydrolysis of Zr(O-n-Bu)₄·n-BuOH. A dinitrogen atmosphere in conjunction with a glove bag was sufficient to prevent hydrolysis reactions. The Rf values of the Zr dspCO₂ complex and H₂(dspCO) are identical however the addition of a few drops of glacial acetic acid to the eluent caused protonation of the imine bond of H₂(dspCO) and changed its Rf value.(32) In this way the extent of reaction could be followed by monitoring residual starting material.
Chemical reduction of the carbonyl functional group to the alcohol, (2), was achieved using superhydride. Complexation of zirconium to the nitrogen of the imine group must be done prior to this reaction to protect the imine from being reduced in the subsequent reduction reaction of the carbonyl group.

Purification of the Zr(dspOH)2 complex consisted of recrystallization from ethanol/pet ether followed by dichloromethane/pet ether, followed by repeated recrystallizations from benzene/pet ether. This was followed by one week of vacuum drying at room temperature and three more days of drying under vacuum at 100 °C. A large number of recrystallizations were required in order to obtain a sample that was within 0.3% of the theoretical values of carbon, hydrogen and nitrogen. This was considered necessary before polymerization reactions could be attempted. The melting point of the Zr(dspOH)2 complex was 174 °C. This represented a significant departure from the behavior of the Zr(dspCO)2 complex which has a decomposition temperature of 315 °C.

Once an adequately pure Zr(dspOH)2 complex was obtained model reactions were conducted with acetyl chloride, 4-methyl-phthalic anhydride and piperonyloyl chloride to investigate the reactivity of the diol. The reaction of Zr(dspOH)2 with acetyl chloride produced an orange-yellow precipitate with limited solubility in methanol. The FTIR indicated a broad strong band at 3529-2799 cm⁻¹ as well as characteristic strong bands at 1611,
1546 and 1300 representing the imine, aromatic carbons and the phenyl to oxygen vibrations respectively. The expected band for an ester functional group did not appear. Zr(dspOH)$_2$ failed to react with piperonyloyl chloride as evidenced by the TLC data which indicated that the starting material was still present. Heat was increased on the flask until reflux temperatures were reached but no reaction was observed to occur.

Polymerization reactions were attempted but the Zr(dspOH)$_2$ complex was unreactive towards aromatic diacid chlorides and longer chain aliphatic diacid chlorides. The attempts to react the purified Zr(dspOH)$_2$ complex with terephthaloyl chloride and sebacoyl chloride failed. (33)

Heating the Zr(dspOH)$_2$ complex alone in THF at the reflux temperature indicated that it was unstable as evidenced by the appearance of four new spots on the TLC.

Conclusions

Two different synthetic routes were investigated to try to produce coordination complexes that could serve as difunctional monomers in linear polymerization reactions. The results are summarized in Figures 18 and 19.
FIGURE 18 Outline of Synthetic Results
OUTLINE OF SYNTHETIC RESULTS

FIGURE 19 Outline of Synthetic Results
Although the two routes led to different terminal groups in the complexes, the same underlying strategy was employed in the construction of each complex. The design strategy relied on introducing latent functionality into the organic portion of the ligand, i.e., the functional group was present but in a precursor form. The nitrile was the precursor to the primary amine of the Zr(amine)$_2$ and Zr(amide)$_2$ complexes and the ketone was the precursor to the alcohol of the Zr(dspOH)$_2$ complex. The strategy depends on the ability of the complex to survive intact the final set of conditions required to convert those terminal functional groups from unreactive to reactive sites for polymerization.

The primary amine desired as a terminal functional group can not be present in the organic portion of the molecule until after the Schiff base condensation reaction because primary amines are one of the reactants in that reaction along with an aldehyde. Its presence would lead to mixtures of products. Therefore the terminal primary amine must either be present as a latent functionality, or alternatively added into the structure by later reactions or else be present in a protected form.

The nitrile functional group has a triple bond consisting of one sigma bond and two pi bonds. Nitrogen has its unshared electron pair in an sp orbital. The 50% s character in the sp orbital means the electrons are closer to the nucleus and more tightly held. The electrons are less available and make the nitrile group an extremely weak base. Because of its stability strong
conditions are required to reduce it. The imine bond of the Schiff base ligand is more easily reduced than the nitrile. The imine nitrogen has its unshared electron pair in an sp² orbital which has 33% s character. (57)

Many restrictions are placed on the design of the synthetic route when imine bonds are present in the complex. The strategy of the design involved introduction of the nitrile group into the organic ligand prior to the Schiff base reaction. Next the design strategy involved the protection of the imine bond by complexing the Schiff base ligand with the zirconium ion thereby forming a stable complex. The nitrogen of the imine donates its unshared electron pair to the zirconium ion to form a stable bond that is further stabilized as part of a chelate ring. See FIGURE 20.
more readily reduced
$N$ is $sp^2$ hybridized

stronger bond
$N$ is $sp$ hybridized

convert to complex

coordinate covalent bond
stabilizes the imine $N$

FIGURE 20. Nitrile and Imine Bonding Considerations
The next step involved the conversion of the latent functionality of the nitrile to primary amines. Success here depended on the use of strong reducing conditions to alter the end groups while the rest of the complex remains unchanged. After repeated attempts to produce the diamine endcapped complex one possible conclusion reached was that the strong reducing conditions required to reduce the nitrile had overcome the stability of the coordination bond between zirconium and the nitrogen and labilized the ligand from the inner coordination sphere of the metal. Once labilized, it was unprotected and subject to the reducing conditions. This would also explain the low yields of products that were consistently obtained for hydrogenation reactions. In many cases the product isolated indicated the complex had been destroyed. Like other heterogeneous catalysts, Raney nickel catalysts functions via surface reactions. The highly symmetrical complex with its many electronic environments could be absorbed in such a way that other sites on the complex are exposed and undergo reaction faster than the nitriles do. This effect may be enhanced because the end group nitriles are present in fairly low concentration relative to other electronic sites on the complex. The ability to convert the nitrile to the substituted amide means that the primary amine is formed and should be able to be isolated. Short reaction times and a different detection system are suggested to improve the results.
The carbonyl reduction to the alcohol to produce Zr(dspOH)₂ was accomplished by selection of a reducing agent strong enough to reduce the carbonyl group without reducing the imine in the complex. It is more difficult to explain the lack of reactivity of the purified Zr(dspOH)₂ complex in typical organic reactions. The large number of recrystallizations required to purify the diol indicated a tenacious impurity that might have interfered with the reactivity of the end groups. A boron adduct may have been the contaminant if the hydrolysis reaction was incomplete. Column chromatography is suggested as an alternative method of purification.

It's a good idea to use a model compound to explore hydrogenation and other reaction conditions. The model compound used to explore the reduction reactions should have been selected much earlier in the project so that the complexes which require long synthetic procedures were not unnecessarily wasted. In retrospect a different model compound, one that bears a closer resemblance to the organic portion of the zirconium complex would make a better choice for the preliminary experiments. The diamine chosen for study 1,6-hexanediamine, is a liquid-low melting solid which has very high solubility in water and therefore its isolation during workup differs from that of the complex. 3-phenylpropionitrile is suggested as an additional choice for a model compound with which to explore reduction methods in the future however it is not a dinitrile compound. The
best choice of a model compound would be a dinitrile compound with organic portions similar to those of the ligands. One problem is that one might find conditions that successfully reduce aliphatic nitriles but that may not leave the zirconium complex intact.

Future work that continues the thorough exploration of heterogeneous hydrogenation catalysts might focus on the use of platinum metal catalysts with LiOH present to promote the desired reaction. Alphatic nitriles were reported to have been reduced in very short times periods under these conditions.(59)

In the future, another possibility is to seek alternative synthetic designs, ones which do not subject the complexes to harsh conditions. Different synthetic routes can be devised that ensure the complex remains intact during the conversion of the end groups.

For instance, although it is possible to produce Zr(amide)$_2$ and convert it to the free amine Zr(amine)$_2$ harsh hydrolysis conditions are required that probably would decompose the complex. An alternative synthetic route depicted in FIGURE 21 involves the use of a cyclic dianhydride rather than acetic anhydride. The product of this reduction reaction forms both the amide linkage as well as generating free carboxylate groups through which polymerization reactions could take place. A possible scenario is where phthalic anhydride, a common cyclic dianhydride is used as the acylating agent. The reaction of this complex with a diamine of choice would yield a polyamide. The
condensation reaction to produce a polyamide typically involves heat and the driving off of the water byproduct. It is not certain how heat stable the complexes are when large organic side chains are involved. It was observed that the final complexes isolated had different physical properties such as considerably lower decomposition points. Zr(dspOH)₂ was observed to decompose at 174 °C and Zr(amide)₂ decomposed at 180 °C. It can be hypothesized that the organic portions of the ligands might have lost the advantage of increased stability by association with the zirconium ion. They might be thermally weak links in the polymer.

An alternative reaction of the Zr(dspCO)₂ complex could be as a reactant in a Wittig reaction. (58) See FIGURES 22 and 23 for two possible examples that introduce a double bond into the complex. Wittig reactions typically take place under mild conditions. The monomer, a coordination complex with terminal vinyl groups can then be polymerized via a free radical mechanism to form a linear polymer with the zirconium ion in the backbone. This avoids the reduction reaction all together in this case.
Proposed synthesis of a Zr complex with bis terminal carboxyl groups available for polymerization

FIGURE 21. Introducing Terminal Carboxylate Groups
Proposed synthesis of a Zr complex with bis terminal vinyl groups polymerizable via free radical mechanism.
Alternative Wittig reaction to introduce bis terminal vinyl groups into the complex

FIGURE 23. Terminal Vinyl Groups in the Complex
APPENDIX

The collected infrared and 1H NMR spectra of the complexes and ligands of the nitrile and diol syntheses.
List of Spectra

FTIR spectrum of 3-(4-(3-amino-4-nitrophenoxy)phenyl)propionitrile: purified by recrystallization 114

FTIR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by column chromatography 115

FTIR spectrum of ortho diamine ether intermediate 116

FTIR spectrum of H2(nitrile) 117

FTIR spectrum of Zr(nitrile)2 118

FTIR spectrum of hydrogenation product (31193) 119

FTIR spectrum of hydrogenation product (42893) 120

FTIR spectrum of complex agitated with NH3 (51493) 121

FTIR spectrum of hydrogenation product (5593) 122

FTIR spectrum of Zr(amide)2 123

1H NMR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by recrystallization 124

1H NMR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by column chromatography 125

1H NMR spectrum of H2(nitrile) 126

1H NMR spectrum of Zr(nitrile)2 127

1H NMR spectrum of Zr(amide)2 128

IR spectrum of H2(dspCO) 129
FTIR spectrum of Zr(dspCO)2

FTIR spectrum of Zr(dspOH)2

FTIR spectrum of Zr(dspOH)2 reacted with acetyl chloride

FTIR spectrum of recrystallized Zr(dspOH)2 reacted with acetyl chloride

1H NMR spectrum of Zr(dspCO)2

1H NMR spectrum of Zr(dspOH)2
Figure 24. FTIR spectrum of 3-(4-(3-amino-4-nitrophenoxo)phenyl)propionitrile: (1) purified by recrystallization
Figure 25. FTIR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: (1) purified by column chromatography.
Figure 26. FTIR spectrum of ortho diamine ether intermediate (2)
Figure 28. FTIR spectrum of Zr(nitrile)2 (4)
Figure 29. FTIR spectrum of hydrogenation product (31193)
Figure 30. FTIR spectrum of hydrogenation product (42893)
Figure 31. FTIR spectrum of hydrogenation product (51493)
Figure 32. FTIR spectrum of hydrogenation product (5593)
Figure 34. 1H NMR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by recrystallization
Figure 35. $^1$H NMR spectrum of 3-(4-(3-amino-4-nitrophenoxy)-phenyl)propionitrile: purified by column chromatography (1) in CH$_2$Cl$_2$-d$_2$
Figure 36. $^1$H NMR spectrum of H$_2$(nitrile) (3) in CH$_2$Cl$_2$-d$_2$
Figure 37. $^1$H NMR spectrum of Zr(nitrite)$_2$ (4) in CH$_2$Cl$_2$-d$_2$
Figure 38. $^1$H NMR spectrum of Zr(amide)$_2$ (6) in CH$_2$Cl$_2$-d$_2$
Figure 40. FTIR spectrum of Zr(dspCO)2 (8)
Figure 41. FTIR spectrum of Zr(dspOH)2 (Ω)
Figure 42. FTIR spectrum of Zr(dpOH)2 (2) reacted with acetyl chloride.
Figure 43. FTIR spectrum of recrystallized Zr(dspOH)2 (9)
reacted with acetyl chloride
Figure 44. $^1$H NMR spectrum of Zr(dspCO)2 in CH2Cl2-d2 (8)
Figure 45. $^1$H NMR spectrum of Zr dspOH)2 in CH2Cl2-d2 (2)
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