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UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

THE SYNTHESIS OF GROUP IV METALLOCENE DICHLORIDES WITH VARIABLE STERICS, CONFORMATIONAL MOBILITY AND GEOMETRIC SHAPES

A Dissertation
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

By
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Norman, Oklahoma
1997

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THE SYNTHESIS OF GROUP IV METALLOCENE DICHLORIDES WITH VARIABLE STERICS, CONFORMATIONAL MOBILITY AND GEOMETRIC SHAPES

A Dissertation APPROVED FOR THE
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

BY

Ronald L Halterman

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Kenneth M. Nicholas

Lance Lobban

ACKNOWLEDGMENTS

Without the support of family and friends, the work contained within this dissertation thesis would not have been possible. I would like to begin by thanking my parents Jim Combs and Cai Combs, and my special friend ThanhTruc "Nikki" Pham for their never ending support and love.

There is no other way to describe Dr. Ronald L. Halterman other than incredible. Over the last five years he contributed to my development as a chemist as, in addition to becoming a friend.

All the past members whom I have not had the pleasure to work with deserve recognition for paving the way for myself, current and future members of the working group. I am also grateful to Shyi-Tai Jan, Joann Kihega, David Standlee, Heike Friedrichs, Bret Behrens, Eric Bailly, Dorothee Kowalski, Oleg Stenzel, Frank Dübner, Dirk Karasiak, Dan Mei, Jaing Chang, Jason Shipman, Junfu Huang, Vladimir Marin, Casandra McDaniel, Flawn Benjamin, Amy Gerken, Aric Coffman, Nathan Pailes, Dale Rudolph, Aldamash Abdulwali, Qian Pan, April Smith, Bill Pandor, Chad Seljeseth, Becky L. and Patrick Foster for their friendship.

Tim Ramsey and Alex Tretryakov deserve special recognition for giving me the technical skills to survive in the laboratory as well as being friends.

Finally, I would like to show my appreciation to Sumita Singh who has become a close friend over the last few years, and for sacrificing so much of her time over the past three months.

TABLE OF CONTENTS

Page

Chapter 1 Cyclopentadienes, Indenes, and Their Metallocenes

Chapter 2 Synthetic Applications for Zirconocenes and Titanocenes

Chapter 3 Steric Modification of a Chiral Metallocene

Chapter 4 The Synthesis and Structural Determination of Zirconocene Dichlorides Having Conformationally Rigid Structures and Geometrically *Closed* Shapes

Chapter 5 The Synthesis of Geometrically Very Open Metallocene Dichlorides and Their Cp_{cent}-Metal-Cp_{cent} Bond Angles

LIST OF FIGURES

Page

Page

LIST OF TABLES

Page

THE SYNTHESIS OF GROUP IV METALLOCENE DICHLORIDES WITH VARIABLE STERICS, CONFORMATIONAL MOBILITY AND GEOMETRIC SHAPES

ABSTRACT

2,2'-Bis[1-(4,7-dimethyl-indenylmethyl)]-1,1'-binaphthyltitanium and -zirconium dichlorides have been synthesized from 2,2'-bis(bromomethyl)-1,1'-binaphthalene **221**. 2,2'-Bis(bromomethyl)-1,1'-binaphthalene **221** was alkylated with 4,7-dimethylindene **229** to yield 2,2'-bis[1-(4,7-dimethyl-indenylmethyl)]-1,1'-binaphthalene **(S)-(-)-212**. The dilithio salts were formed and metallated with titanium trichloride and zirconium tetrachloride to give *ansa*-bis[1-(4,7-dimethyl-indenylmethyl)]-1,1'-binaphthyltitanium dichloride **(S)-(+)-232** and -zirconium dichloride **233**.

New chiral doubly bridged bis(tetrahydroindenyl)zirconium dichloride **285** has been synthesized from chiral doubly bridged **284** in excellent yield. These complexes give access to rigid *ansa*-bis(indenyl)- and *ansa*-bis(tetrahydroindenyl)zirconium dichlorides. The structures of **284** and **285** were determined by X-ray diffraction and have confirmed the *closed* shape of these metallocene dichlorides.

We have prepared several novel metallocene dichlorides bridged at the 7,7' position of the indenyl moiety. The new metal complexes include the methylene bridged *dl*-bis(4,6-dimethylinden-7-yl)methylidenetitanium dichloride **349**, and *dl*-bis(4,6-dimethylinden-7-yl)]methylidenezirconium dichloride **348** which were prepared from *m*-xylene. In addition, *dl*-1,2-bis(4-methylinden-7-yl)]ethylidene, *dl*-1,2-bis(4-isopropylinden-7-yl)]ethylidenezirconium dichlorides (***dl*-339**) and (***dl*-340**) and *dl*-1,2-bis(4-isopropylinden-7-yl)]ethylidenetitanium dichloride (***dl*-341**) were synthesized from *p*-cymene and *p*-xylene, respectively. The structure of metallocene dichlorides ***dl*-339**, ***dl*-340**, and ***dl*-341** were determined by X-ray crystallography and found to have C_1-symmetry in the solid state, but in solution exhibit C_2-symmetry as seen in their ^1H NMR

spectra at room temperature. The synthesis of these new titanocene and zirconocene dichlorides will be discussed.

Chapter 1

CYCLOPENTADIENES, INDENES, AND THEIR METALLOCENES

1.1 Introduction

The pharmaceutical industry continues to be a major contributor to the growing demand for enantiomerically pure compounds. However, synthetic methodology which begins with the addition of an achiral reagent to a prochiral substrate results in the formation of an equal amount of both enantiomers **A** and **B** since the enantiomers have equal energy (Figure 1-1). As a result, specialized technology for obtaining single enantiomers has steadily increased.

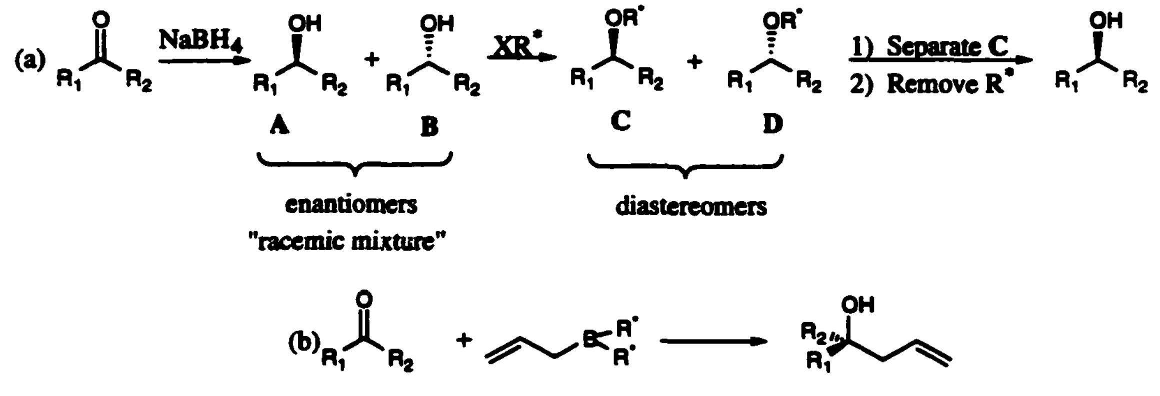
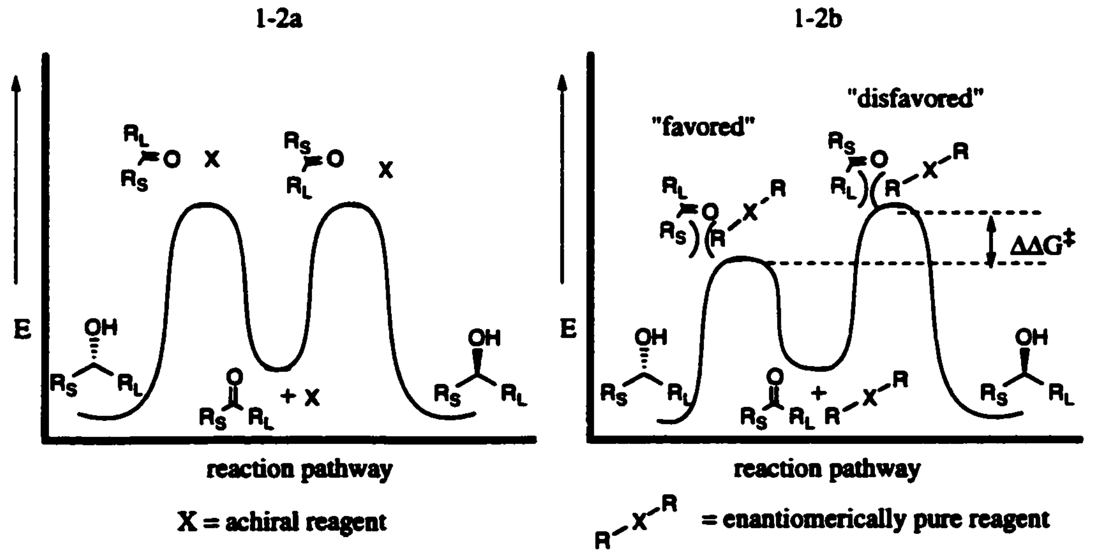


Figure 1-1. (a) Resolution R* = enantiomerically pure group (b) Stoichiometric asymmetric synthesis.

One of the techniques for acquiring enantiomerically enriched compounds involves the reaction of two enantiomers, known as a racemic mixture, with a chiral reagent to produce two diastereomers which can be separated (Figure 1-1a). A second route for acquiring single enantiomers involves the addition of a chiral reagent to a prochiral substrate (Figure 1-1b). This selectivity is achieved through the formation of diastereomeric transition states which have different energies (Figure 1-2). These transition states result from the steric interactions between the source of chirality and the incoming substrate, and if one transition state is kinetically favored over another the enantiomer

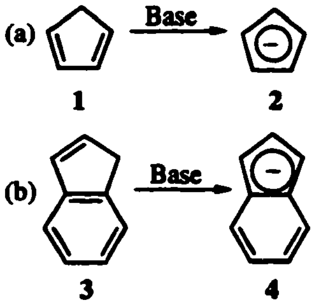
Figure 1-2. Reaction coordinate energy diagrams a) achiral reaction b) enantioselective reaction.



arising from the kinetically "favored" transition state is formed. Hence, high selectivity can be achieved if this energy difference is sufficient (generally $\Delta\Delta G^{\ddagger} > 3.0$ Kcal/mol). However, a disadvantage of resolution and stiochiometric enantioselective synthesis is the use of an equimolar amount of the chiral reagent to starting material. Because of this, the two processes can be costly if the chiral reagent is not recycled, so finding alternative methods are desirable.

Recent developments in catalytic processes and the availability of numerous enantiomerically pure ligands have led to several catalytic enantioselective reactions. In contrast to the stoichiometric enantioselective process, the source of chiral induction is found at the catalyst, thus precluding stoichiometric amounts of chiral reagent. Like the stoichiometric analogs, the selectivity arises from steric interactions between the source of chirality and the incoming substrate. To accomplish this, many research groups have focused their attention on the synthetic utility presented by catalytic cycles containing group 4 transition metals. This interest has been spurred by the variety of processes these transition metals catalyze which will be discussed in chapter 2.

Figure 1-3. (a) Cyclopentadienyl ligand
(b) Indenyl ligand



In addition to their utility, group 4 transition metals have two highly variable classes of carbon π-ligands available. These ligands are the cyclopentadienyl (Cp) ligand (**2**) and the indenyl (In) ligand (**4**) which can be formed from cyclopentadiene (**1**) and indene (**3**), respectively (Figure 1-3). Chiral ligands of this class are often chosen because they provide the qualities for a good chiral ligand. The necessities that make a good chiral ligand which are stereoselective have been outlined by Kagan and are listed below.[1]

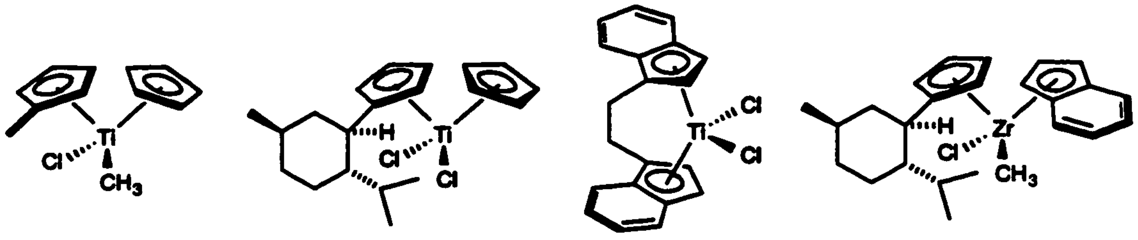
1) The ligand must stay coordinated to the metal during the stereochemical defining step.
2) The catalytic activity when using the chiral ligand should be comparable to that of the achiral ligand.
3) The ligand should be easily modified to allow chemical variations to enable a match between substrate and chiral ligand.
4) The ligand synthesis should be short, simple and begin with inexpensive starting materials.
5) It should be possible to synthesize both enantiomers.

Chiral Cp's and In's meet the needs listed above, therefore, the objective is to design chiral metallocenes with the appropriate steric environment for enantioselective reactions. This chapter will focus on the relevant background and discuss previous work done in an attempt to accomplish the objective.

1.2 Sources of chirality

The synthesis of metallocenes has taken large steps over the last few decades. Much of the improvement is due to the development of synthetic methodology and its application toward the synthesis of chiral metallocenes. This chirality in metal complexes can be introduced by several methods (Figure 1-4).[2] The first method introduces chirality by arranging four different groups around the metal center as shown by complex **5**[3] and is defined as *metal centered chirality*. Chiral metallocenes can also be formed through the coordination of a chiral ligand or a prochiral ligand to a non-stereogenic metal center as shown with structures **6**[4] and **7**,[5] respectively, and is termed *ligand derived chirality*. The third and final method for creating a chiral metal complex combines the first two methods as shown in the final complex.

Figure 1-4. Sources of chirality.

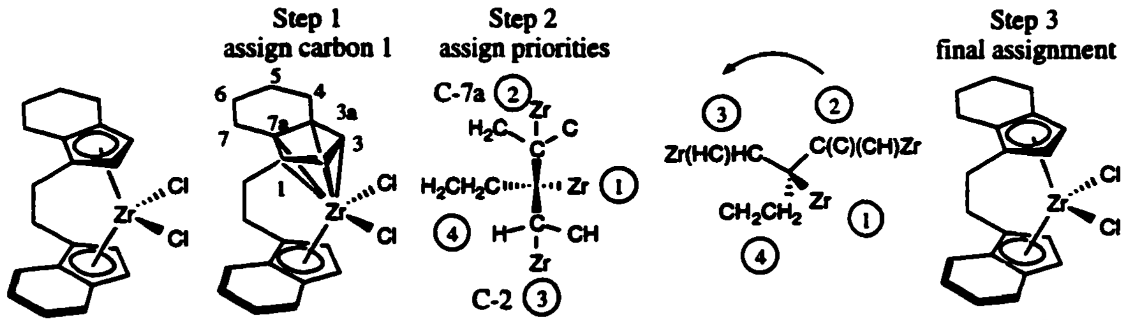


5 **6** **7** **Combination**

1.3 Nomenclature

The assignment of *R/S* nomenclature can be applied to the π-faces of the Cp and indenyl ligands due to the "planar" chirality of the Cp ring when bound to the metal.[6a] To assign the *R/S* nomenclature to the π-faces, the three steps outlined below can be taken.

Figure 1-5. Assignment of planar chirality in metallocenes.



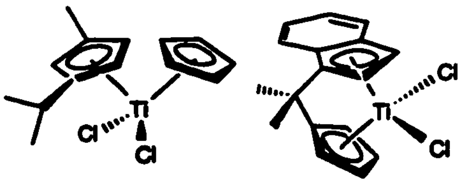
8

(1*S*,1*S*)-**8** or
(p-*S*,p-*S*)-**8**

First, carbon 1 on the Cp moiety must be found as seen for metal complex **8**[7] in step 1 of Figure 1-5. Step 2 will be the prioritization of the atoms attached to carbon 1. This is done by treating the π-atoms of the Cp moiety as if they are each bound to the metal center. Priority 1 is then given to the metal, and the exocyclic carbon from the bridging unit is assigned priority 4 since it is the only carbon atom not attached to the metal. The remaining carbons are designated as follows, carbon 7a priority 2 and carbon 2 priority 3 based on the higher degree of substitution at carbon 7a. The final step to the assignment requires the rotation of carbon 1 so that the lowest priority group is pointed back thus revealing the 1*S* stereochemical designation.

The same process is done on the remaining Cp moiety leaving a 1*S*, 1*S* assignment. Erker has further elaborated the naming process by using the designation of "p" to denote planar chirality at carbon 1 on each π-face which would give a p-*S*, p-*S* assignment for structure **8**.[6b] Additional assignments have been made for metal complexes **9**[8] and **10**[9] depicted in Figure 1-6.

Figure 1-6. Two additional examples.



(1*S*)-**9** or
(p-*S*)-**9**

(1*S*)-**10** or
(p-*S*)-**10**

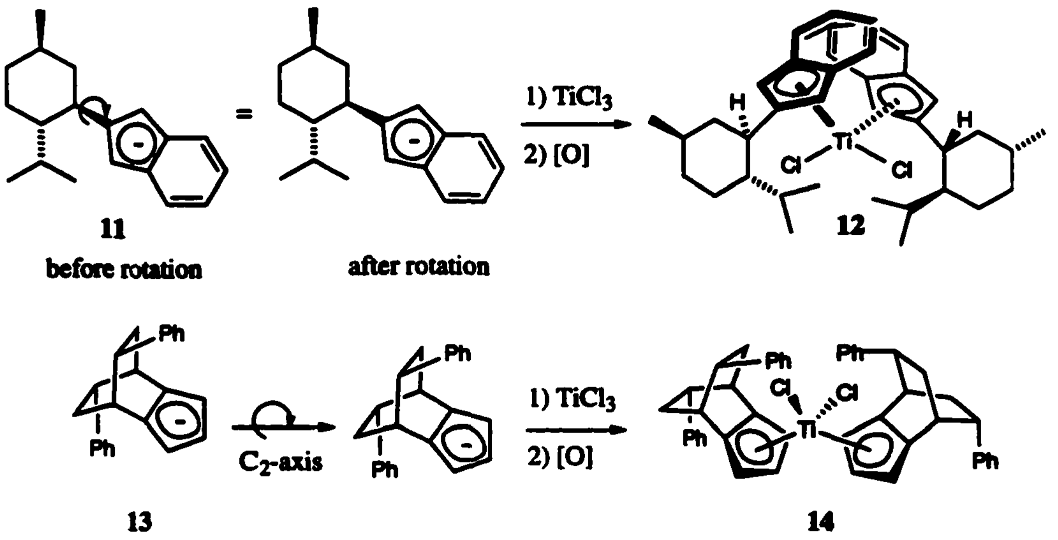
As a note, the method used above for determining the *R*/*S* nomenclature for complex **8** and **10** contradicts in some cases the method used by Schlögle since this method would require planar chirality to be assigned to the highest priority carbon.[6a] This is relatively simple in the cases of unbridged Cp complexes, such as titanocene dichloride **9**, because the highest priority π-carbon is usually the 1-position while Brintzinger has used the 1-position to denote the R/S nomenclature of planar chirality in *ansa*-bis(indenyl)metallocenes. Either method can be used, and for future reference the 1-position will carry the *R*/*S* designation with a "1" appearing before the designation.

1.4 Faces of cyclopentadienyls and indenyls

In addition to the before-mentioned planar chirality, cyclopentadienyl and indenyl ligand π-faces can be described as homotopic, enantiotopic, or diastereotopic.[2] The difference between these types of faces can be seen through various operations and by the products formed upon metalation.

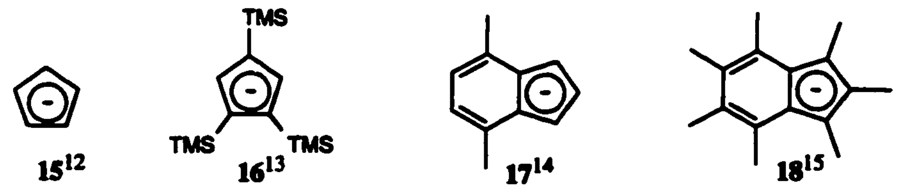
Homotopic faces can be interconverted by rotation about a carbon-carbon bond as shown with indenyl ligand **11** (Figure 1-7).[10] Homotopic faces can also be interconverted

Figure 1-7. Metalation of ligands with homotopic π-faces gives a single metal complex.



by a C_2-symmetry operation as shown with Cp ligand **17**.[11] In addition, metalation of ligands with homotopic π-faces lead to formation of a single metal complex due to their inherent selectivity. Examples of ligands falling into this category include unsubstituted Cp, monosubstituted Cp's, symmetrically polysubstituted Cp's, indenyl ligands substituted in the 2-position , and symmetrically substituted indenyl ligands (Figure 1-8).

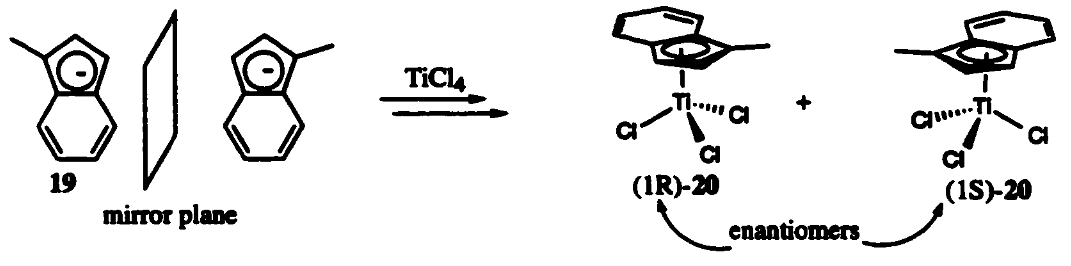
Figure 1-8. Other ligands with homotopic π-faces.



15[12] **16**[13] **17**[14] **18**[15]

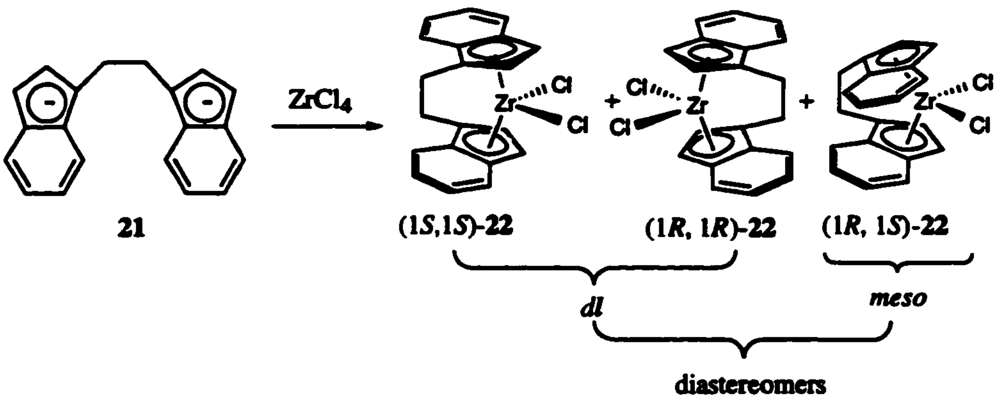
Enantiotopic π-faces are interconverted through a mirror plane (Figure 1-9). Unlike metalation of ligands with equivalent or homotopic π-faces, the metalation of a single Cp or indenyl ligand with enantiotopic π-faces leads to a racemic mixture of enantiomeric metal complexes as seen with the formation of (1*R*)-**20** and (1*S*)-**20** from indenyl **19**.[16] The picture becomes a bit more complicated if two equivalents of a ligand with enantiotopic faces are used. This is conveniently illustrated with bis(indenyl) **21** (Figure 1-10).[7] Metalation of this ligand leads to the formation of the racemic *dl*-metal complexes (1*R*,1*R*)-**22** and (1*S*,1*S*)-**22**, and the diastereomeric *meso*-complex (1*R*,1*S*)-**22**. The ratio of the diastereomeric complexes need not be 1:1 since the diastereomeric complexes arise from diastereomeric transition states which could have different energy barriers to formation.

Figure 1-9. Metalation of a Cp ligand with enantiotopic π-faces.



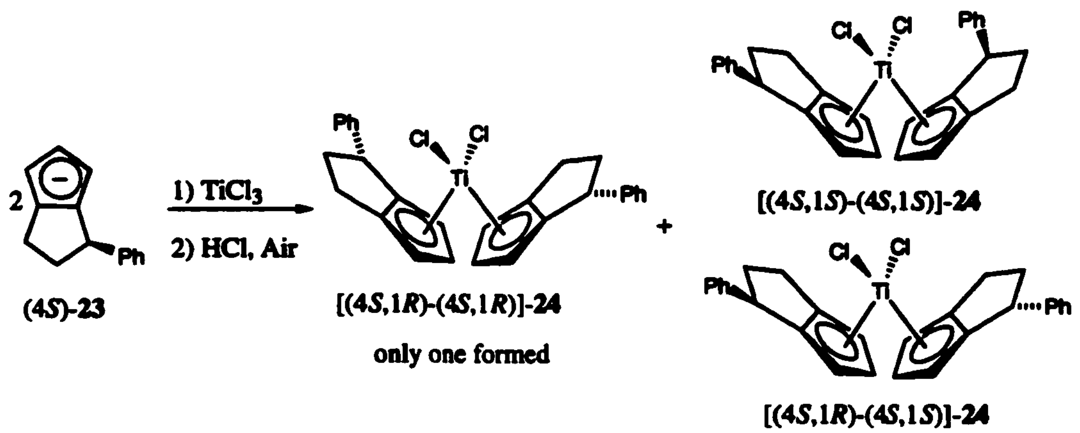
Ligands belonging to this class are unsymmetrically substituted Cp's and indenyls in which the substituents are achiral.

Figure 1-10. Metalation with a ligand with two enantiotopic π-faces.



Lastly, ligands with π-faces that are diastereotopic cannot be interconverted by rotation, a C_2-symmetry operation, or reflection through a mirror plane. Ligands belonging to this class have at least one atom with a *R*- or *S*-configuration and one *R*- or *S*-stereochemical designation for the π-face. The metalation of ligands in this class has a theoretical possibility of forming three diastereomeric metal complexes as pictured with the metalation of Cp ligand **23** (Figure 1-11).[17] However, inherent steric biases existing in some Cp ligands with diastereotopic faces can lead to excellent selectivity upon metalation. Examples of these will be seen in later sections.

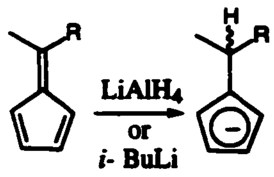
Figure 1-11. Metalation of a Cp ligand with diastereotopic π-faces.



The previous examples illustrate simple models for the different types of π-faces. It also demonstrates having ligands with homotopic faces reduces the number of products formed, hence, simplifying isolation. Therefore, it is advantageous to have ligands with homotopic faces or highly selective diastereotopic faces when possible.

1.5 Nonbridged cyclopentadienes, indenes and their metallocene dichlorides

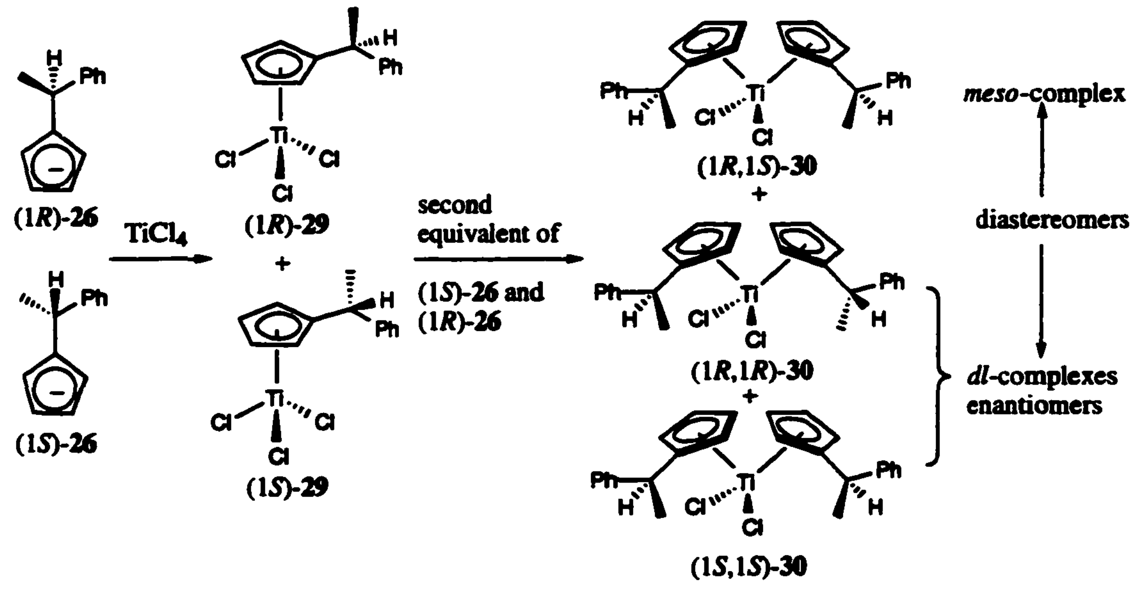
Figure 1-12. Reduction of fulvene to give racemic monosubstituted Cp's.



25 R = Ph
27 R = cyclohexyl
26 R = Ph
28 R = cyclohexyl

The first chiral, racemic monosubstituted Cp's were readily synthesized from the reduction of unsymmetrically substituted fulvenes like **25** with $LiAlH_4$.[18] It was later found by Erker that **25** and **27** could be reduced with *iso*-butyllithium to give chiral Cp's (Figure 1-12).[19] However, metalation of the racemic ligand revealed a serious problem. To illustrate this problem imagine adding racemic Cp to titanium tetrachloride (Figure 1-13). This initial metalation forms a racemic mixture of (1*R*)-**29** and (1*S*)-**29**. Now a second addition of racemic Cp would give rise to 3 metallocene complexes since (1*R*)-**29** can react with either (1*R*)-**26** or (1*S*)-**26**, and (1*S*)-**29** can metallate with (1*S*)-**26** or (1*S*)-**26**. The final mixture could consist of the *meso*-complex (1*R*,1*S*)-**30**, and the racemic *dl*-complexes (1*R*,1*R*)-**30** and (1*S*,1*S*)-**30** with the first being a diastereomer of the later two.[20] However, because the formation of these complexes results from diastereomeric transition states, the *meso*-complex can be in a greater or lower quantity than the *dl*-complexes depending on the relative energies of the corresponding transition states.

Figure 1-13. Metalation of chiral racemic Cp.



This problem of diastereomeric complexes arising from racemic Cp was later lessened with the synthesis of chiral, non-racemic Cp ligands. The first reported Cp ligand of this type was synthesized from the reduction of fulvene **25** with LiAlH$_4$ in the presence of (-)-quinine to give modest enantioselectivity (~17% enantiomeric excess).[21] This was a significant step toward the synthesis of chiral Cp's, but the presence of a substantial amount of the second enantiomer (~40% of the undesired enantiomer) led to the same problem that plagued the racemic mixture.

In 1978, the first enantiomerically pure natural product derived ligand and metallocene was published by Kagan and Cesarotti.[4] This synthesis of the (-)-menthol derived ligand strategically displaced the tosylate with cyclopentadienylsodium to afford **33** (Figure 1-14). Although simple, the synthesis provided enantiomerically enriched ligand with homotopic π-faces which, upon metalation, gave a single metallocene complex **34**. A number of analogous monosubstituted cyclopentadienes are pictured in Figure 1-15.

Figure 1-14. Synthesis of (-)-menthol derived titanocene dichloride.

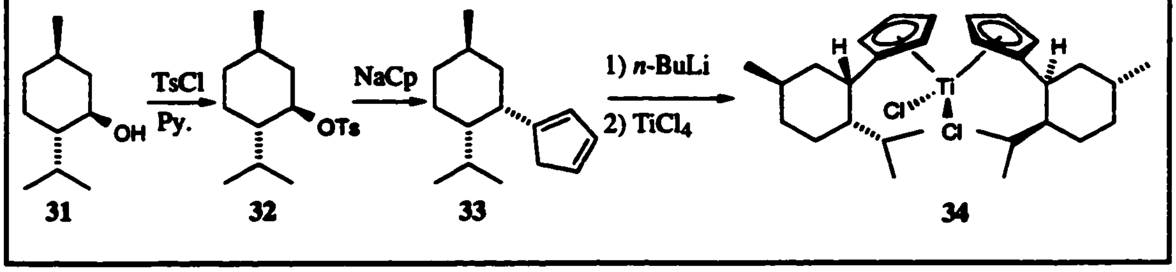
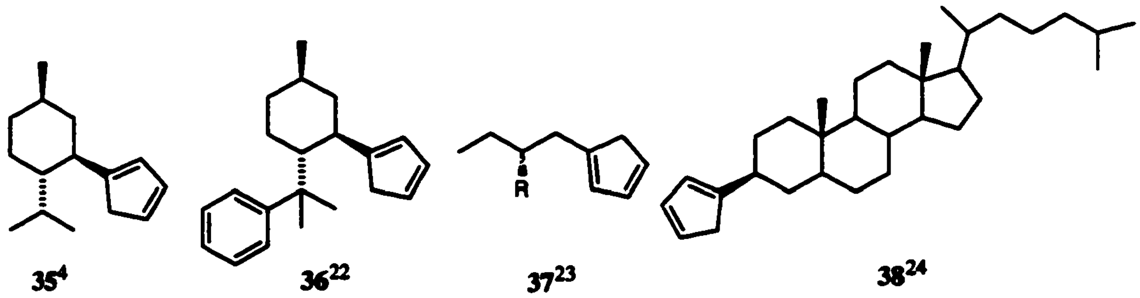


Figure 1-15. Examples of enantiomerically pure monosubstituted cyclopentadienes.



Recently Erker has synthesized a number of monosubstituted ligands derived from enantiomerically pure menthol derivatives to give enantiomerically pure 1-indenyl ligand **39** through a similar synthetic strategy (Figure 1-16).[25] In contrast to the monosubstituted Cp faces, the 1-indenyl ligand faces are diastereotopic and lead to a mixture of diastereomeric metallocene complexes of **40** when metallated. Several modifications of indene **39** have been synthesized by Erker and are shown in Figure 1-17.

Figure 1-16. Synthesis of the (-)-menthol derived indenyl ligand and zirconocene dichloride.

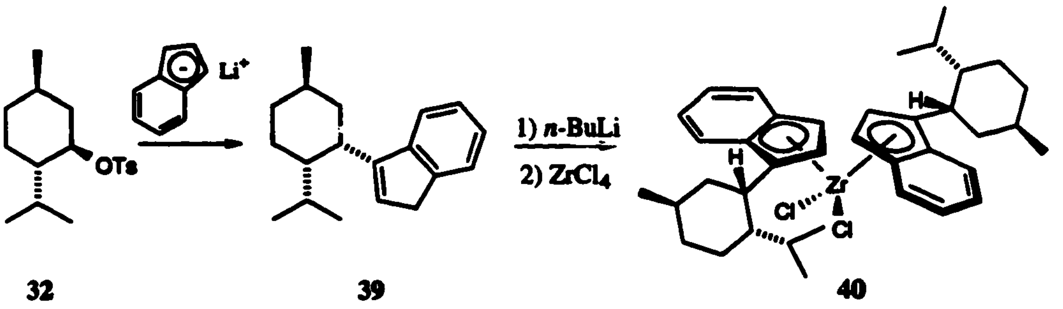
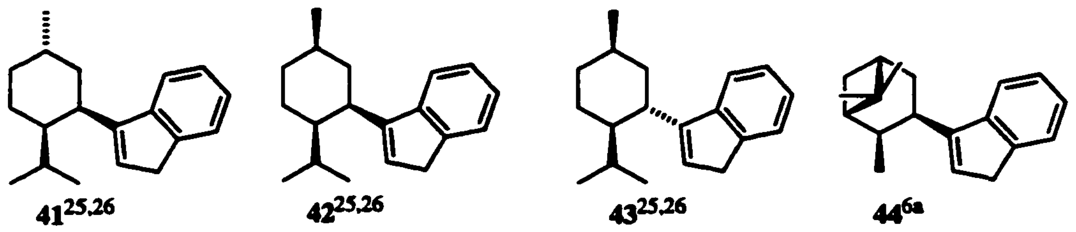


Figure 1-17. Chiral 1-indenyls.



Although somewhat more difficult to synthesize, fused Cp ligands were made to inhibit the rotation between the Cp moiety and chiral unit. The elimination of this rotation could create a more defined chiral pocket around the metal center. The first of these fused Cp ligands was synthesized by Halterman and Vollhardt[22,27] from enantiomerically pure camphor through a stepwise cycloannulation and later by Paquette[28] through an alternate methodology. Figure 1-18 pictures the original route to cyclopentadiene **49**. A drawback to the metalation of cyclopentadiene **49** is the possibility of forming three distinct diastereomeric metallocenes due to the diastereotopic Cp faces. However, the steric environment around the π-faces resulted in a fairly selective metalation. This is seen with the formation of [(4*R*,7*S*,1*R*)-(4*R*,7*S*,1*R*)]-**50** and [(4*R*,7*S*,1*R*)-(4*R*,7*S*,1*S*)]-**50** in a 95:5 ratio while the third [(4*R*,7*S*,1*S*)-(4*R*,7*S*,1*S*)]-**50** was not observed. This mixture was subsequently separated to give pure C_2-symmetric metallocene dichloride [(4*R*,7*S*,1*R*)-(4*R*,7*S*,1*R*)]-**50**. Several examples of fused cyclopentadienes are given in

Figure 1-18. Camphor derived cyclopentadiene via the Halterman and Vollhardt route.

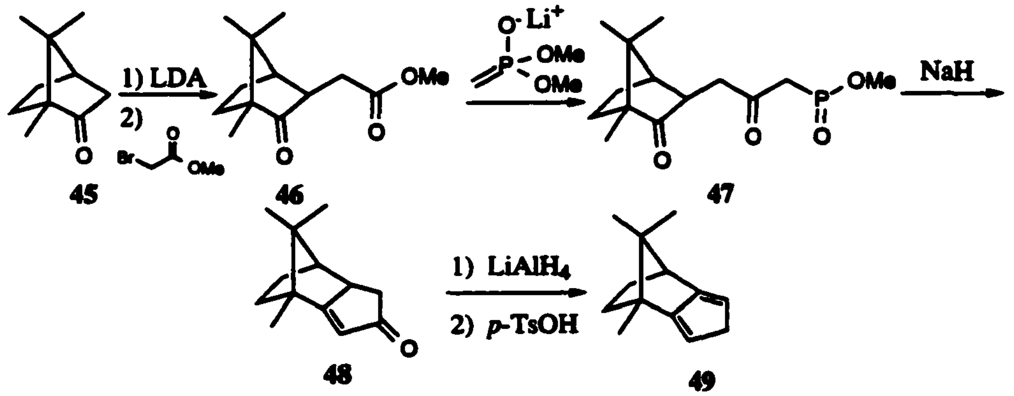
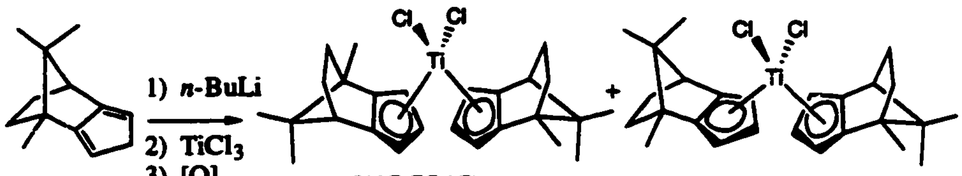


Figure 1-20 with **52** being the only fused Cp shown with diatereotopic faces which is achiral.

Figure 1-19. Metalation of the camphor derived Cp.

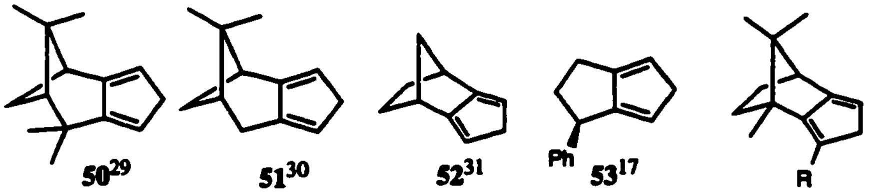


(4*R*,7*S*)-**49**

[(4*R*,7*S*,1*R*)-(4*R*,7*S*,1*R*)]-**50**

[(4*R*,7*S*,1*R*)-(4*R*,7*S*,1*S*)]-**50**

Figure 1-20. Notable fused cyclopentadienes.

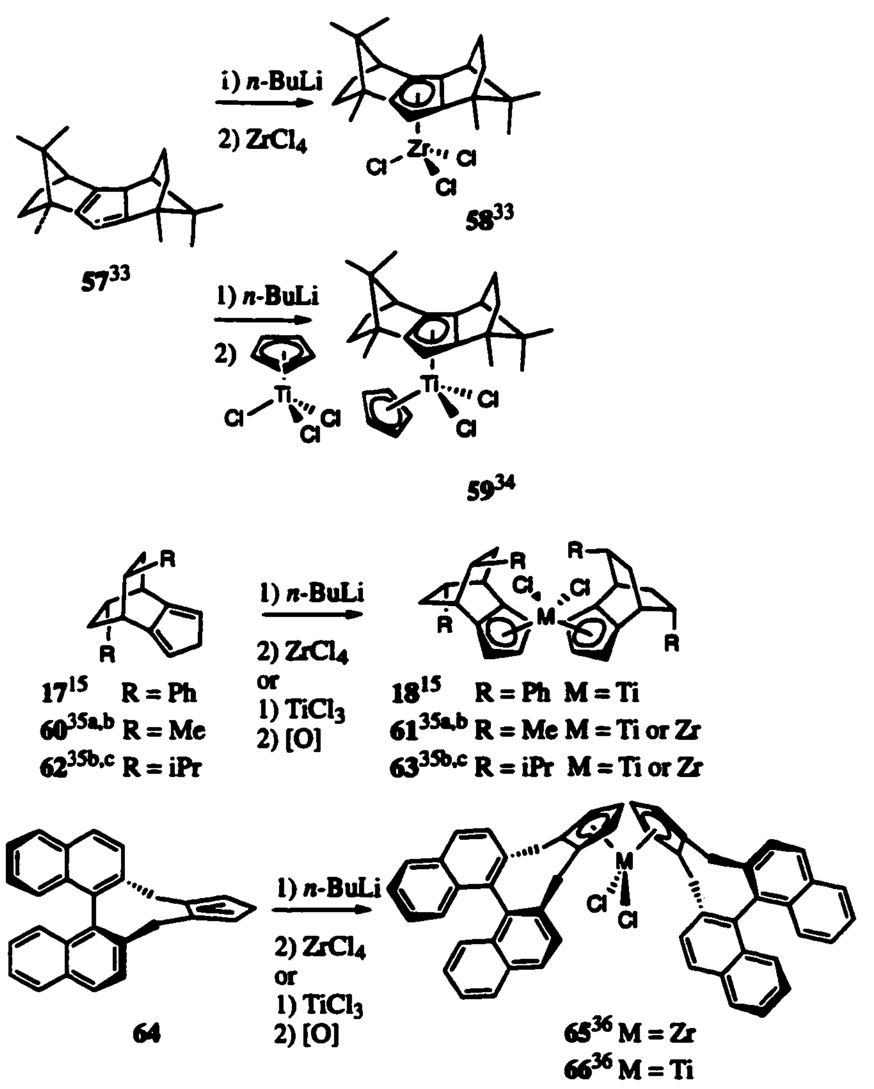


50[29] **51**[30] **52**[31] **53**[17]

54 R = Me
55 R = Ph
56 R = tBu
ref. 32

An interesting class of fused ligands has been synthesized by Erker,[33] Halterman and Vollhardt,[15] Halterman and Chen,[35] and Halterman and Colleti[36] (Figure 1-21). These ligands are unique because they have homotopic π-faces which was made possible through the introduction of C_2-symmetry into the ligand. This symmetry inherently makes the metalation selective.

Figure 1-21. Fused C_2-symmetric cyclopentadienes and their metallocene dichlorides.

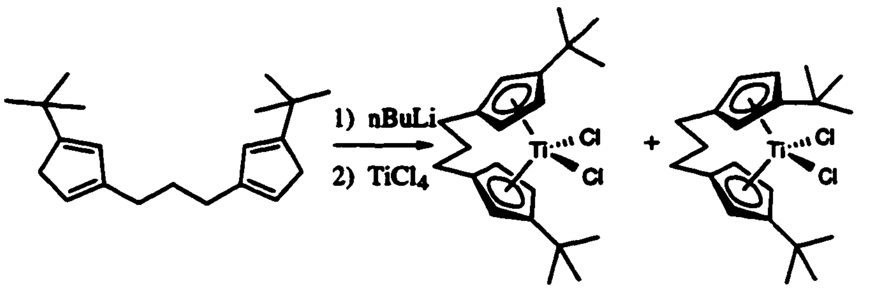


1.6 Bridged cyclopentadienes and *ansa*-bis(Cp)metallocene dichlorides

Numerous chiral Cp ligands were covered in the previous section. Several introduced chirality while further defining the chiral pocket. This was seen with the fused Cp ligands which have an additional bond to prevent rotation about the carbon-carbon bond between the Cp moiety and the source of chirality.

In 1978, Brintzinger reported the synthesis, metalation, and resolution of bridged bis(Cp) **66** and metallocene *dl*-**67**.[37] This work demonstrated that a chiral C_2-symmetric

Figure 1-22. The first reported bridged metallocene dichloride.



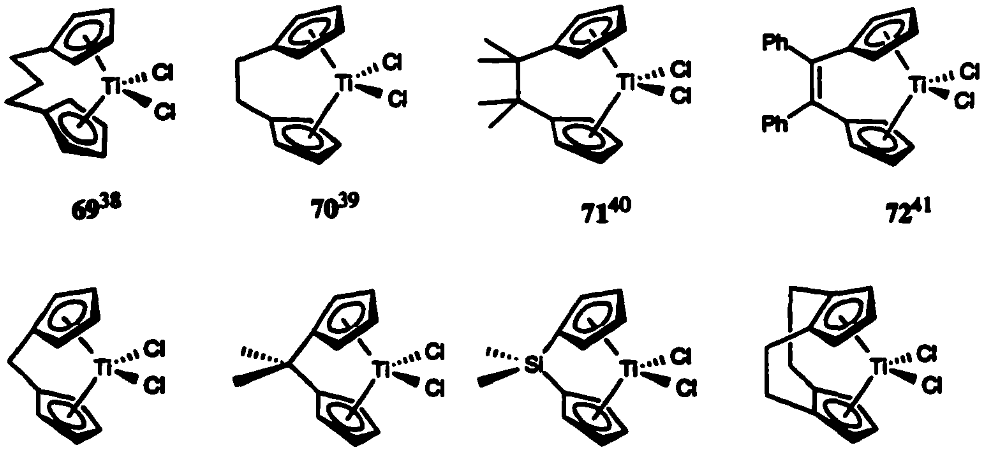
67 *dl*-**68** *meso*-**68**

complex could be formed with a well defined chiral pocket through a bridging unit as seen in Figure 1-22. The bridging unit restricted the rotation of the Cp about the Cp-metal bond which had not been solved by the unbridged fused Cp ligands. This bridging system opened the door to several areas of manipulation. The bridging unit provided a potential site for modification in addition to the four open sites on the Cp moiety. Several groups have developed methodologies to take advantage of these two areas.

1.6.1 Modifications to bridged Cp's

Researchers have synthesized a number of achiral bridged metallocene dichlorides. These achiral bridged metallocenes illustrate the many modifications which exist for the

Figure 1-23. Illustration of bridge modifications in achiral metallocene dichlorides.

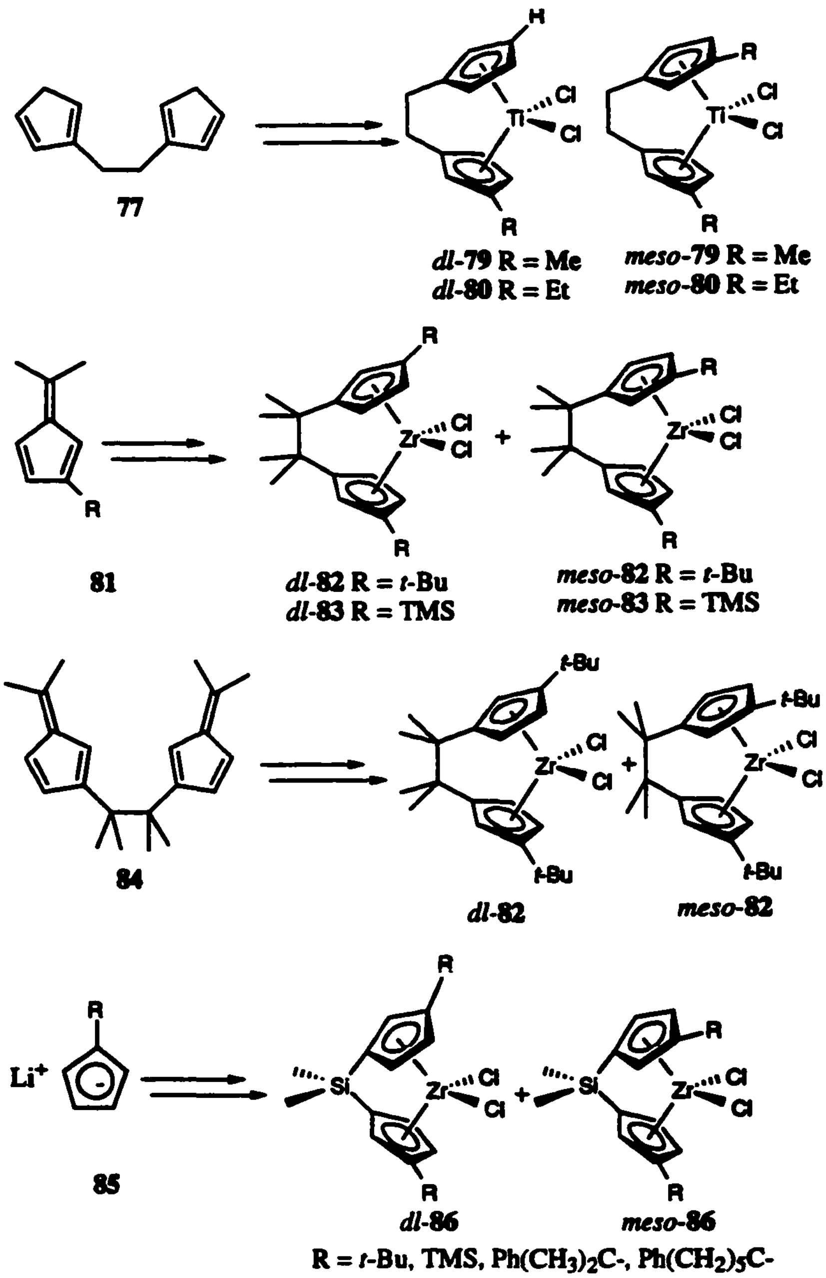


69[38] **70**[39] **71**[40] **72**[41]

73[42] **74**[43] **75**[44] **76**[45] bridging unit (Figure 1-23). Over the last two decades methodologies for the synthesis of sterically modified versions of the achiral derivatives, seen below, have been reported.

Collins and coworkers have done considerable work in this area and have reported the synthesis of several sterically modified version of **70** from ethylene bridged bis(cyclopentadiene) **77** (Figure 1-24).[46] Other research groups developed routes to

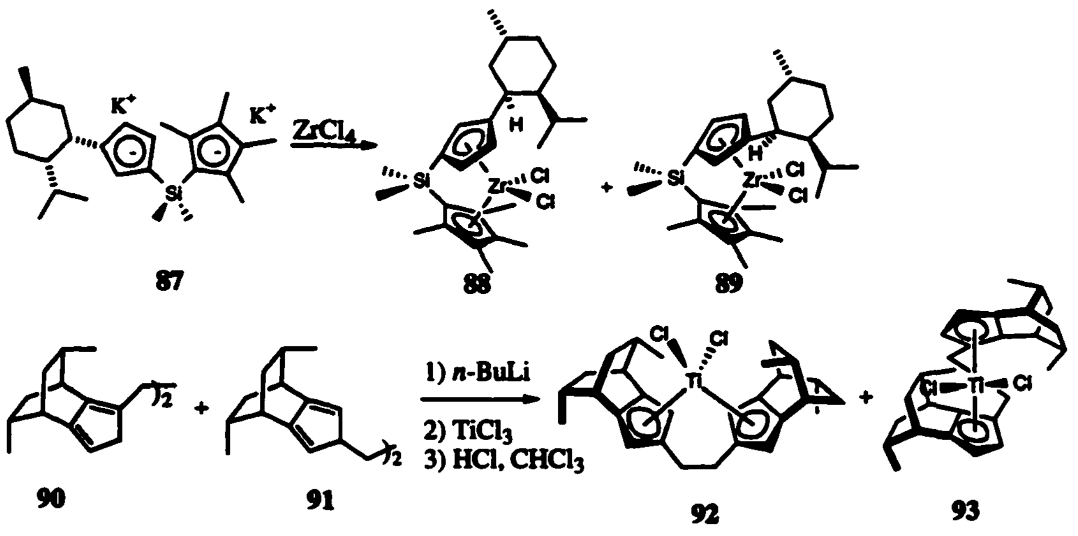
Figure 1-24. Routes to one and two atom bridged metallocene dichlorides.



bridged cyclopentadienes and chiral *ansa*-metallocene dichlorides have been developed from 6,6-dimethylfulvenes **81**,[47] bridged fulvene **84**,[48] and substituted cyclopentadienyllithium **85**.[49]

Metallocene complexes prepared from chiral Cp's with achiral bridges have been reported. These have the potential for selective metalation because the chiral Cp could act as a directing group to selectively form a single diastereomeric metallocene complex over another. An example of this is cyclopentadiene **87** shown in Figure 1-25 but this bis(Cp) has diastereotopic faces, and in this case metalation led to the formation of the diastereotopic metallocenes **88** and **89** in a 2:1 ratio.[50] An enantiomerically enriched metallocene **92** with an achiral bridge and homotopic π-faces was published by Halterman and Chen.[51] This solved the problem seen in the previous example by placing the bridge at the 2-position which kept the Cp faces homotopic and resulted in the formation metallocene dichloride **92**.

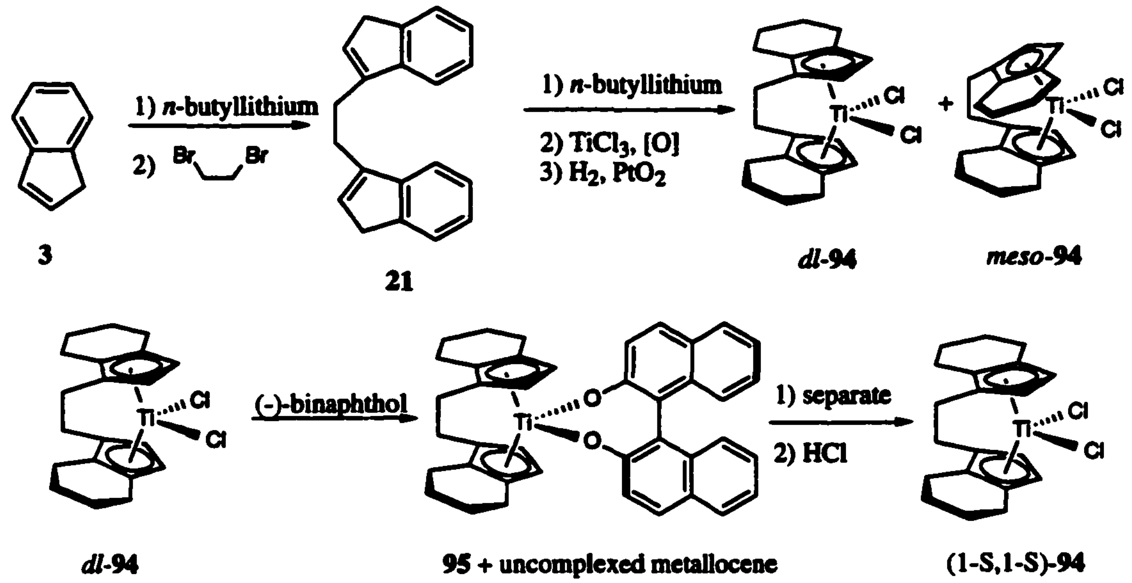
Figure 1-25. Chiral Cp's with an achiral bridge.



1.7 Bridged bis(indenes) and *ansa*-bis(indenyl)metal complexes

A second significant contribution by Brintzinger to metallocene synthesis came with the publication of the first isolated *ansa*-bis(tetrahydroindenyl)titanium dichloride **94**, and its resolution starting from commercially available indene and dibromoethane (Figure 1-26).[5] These complexes had the bridging unit which could be, like the cyclopentadienyls, modified but the indenyl group provided significant advantages when it came to introducing steric and electronic modifications.

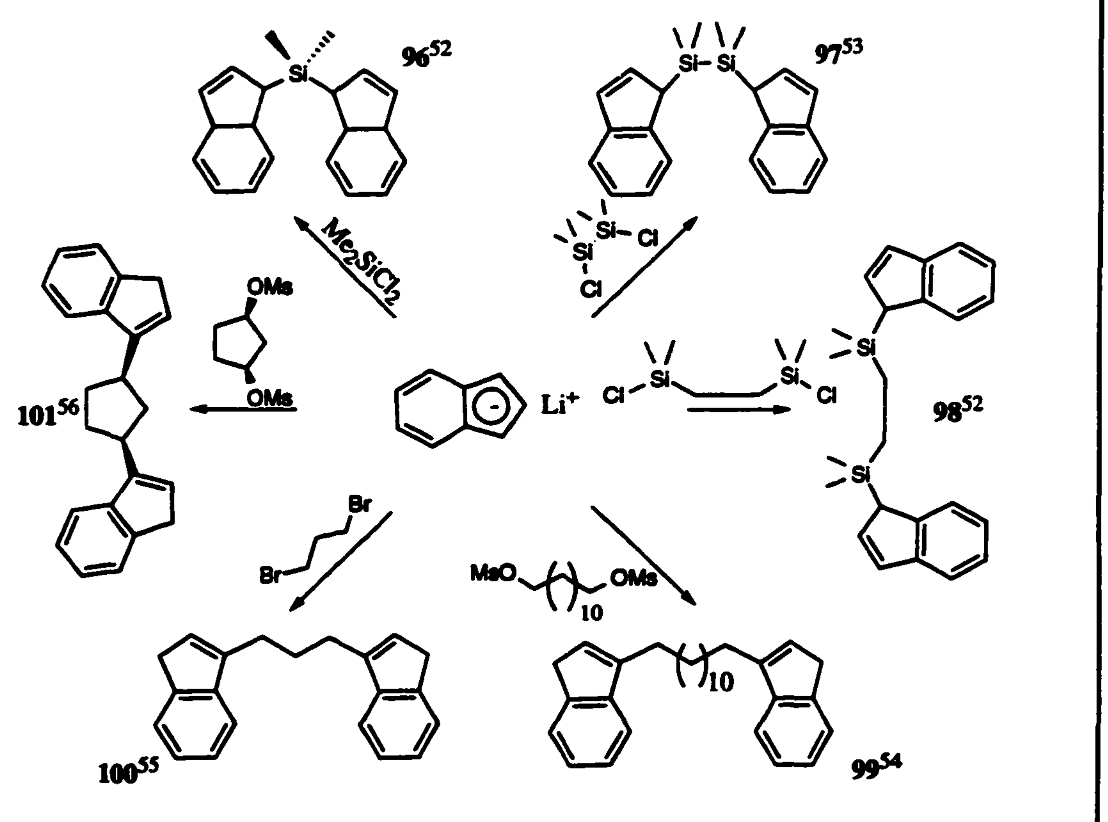
Figure 1-26. Synthesis of Brintzinger's ethylene bis(tetrahydroindenyl)titanium dichloride.



1.7.1 Achiral bridges

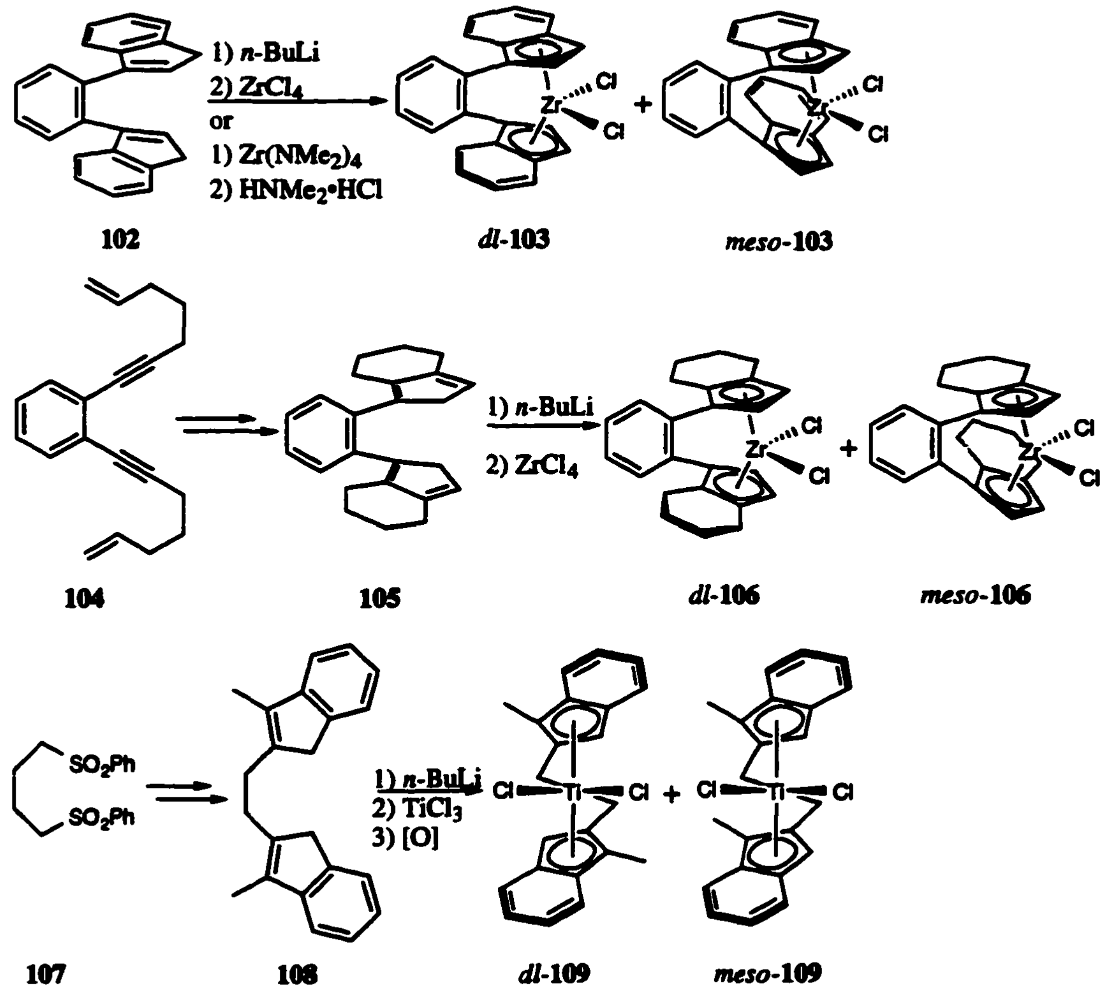
The bridging of indenes has been found to be much easier when compared to cyclopentadienes due to the chemical reactivity of the 1- and 3-positions. Owing to this chemical reactivity, selective alkylation of the indenyl anion at the 1- and 3-positions remains a popular method for introducing countless bridging elements (Figure 1-27).

Figure 1-27. Achiral bridged bis(indenes) via alkylation with indenyllithium.



Synthetic methodologies other than direct nucleophilic displacement of a leaving group with indenyl anion have been devised. One clever route has been reported by Halterman and Tretyakov.[57] They demonstrated that the formation of complexes **103** could be done in two convenient steps from commercially available starting materials (Figure 1-28). A similar complex was reported by Halterman and Ramsey which was generated from bis(enyne) **104**.[58] Achiral bridging elements at the 2-position on the indenyl moiety are much rarer due to the difference in reactivity at the 2-indenyl positions. Because of this difference, great length must be traveled to obtain bis(indenyl) ligands bridged at the 2-position. Nantz has developed a unique synthetic methodology which enables the synthesis of 1,2-bis(2-indenyl)ethane **117** from tethered phenyl sulfone **116**.[59]

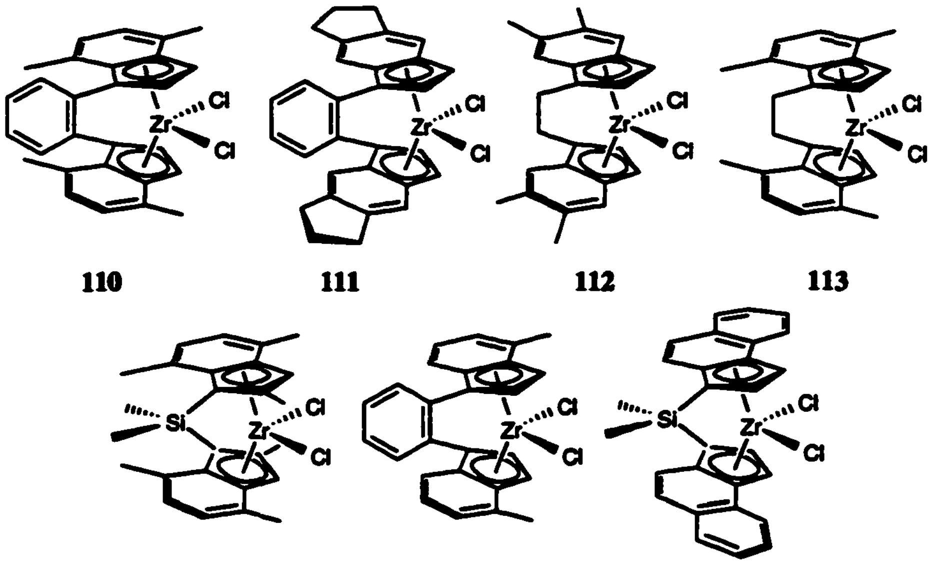
Figure 1-28. Synthesis of bis(indenyl)metal complexes via non-nucleophilic strategies.



1.7.2 Steric modifications

Steric modifications have been introduced through the use of symmetrically substituted indenes as seen with complexes **110**,[57] **111**,[57] **112**,[60] **113**,[60] and **114** (Figure 1-29).[61] With careful planning incorporation of unsymmetrically substituted indenes has been reported. In these cases the bridging element is introduced on the less sterically hindered indenyl position as shown by complexes **115**[57] and **116**.[62]

Figure 1-29. Bridged bis(indenyl)metal complexes of symmetrically substituted bis(indenes) and unsymmetrically substituted bis(indenes).



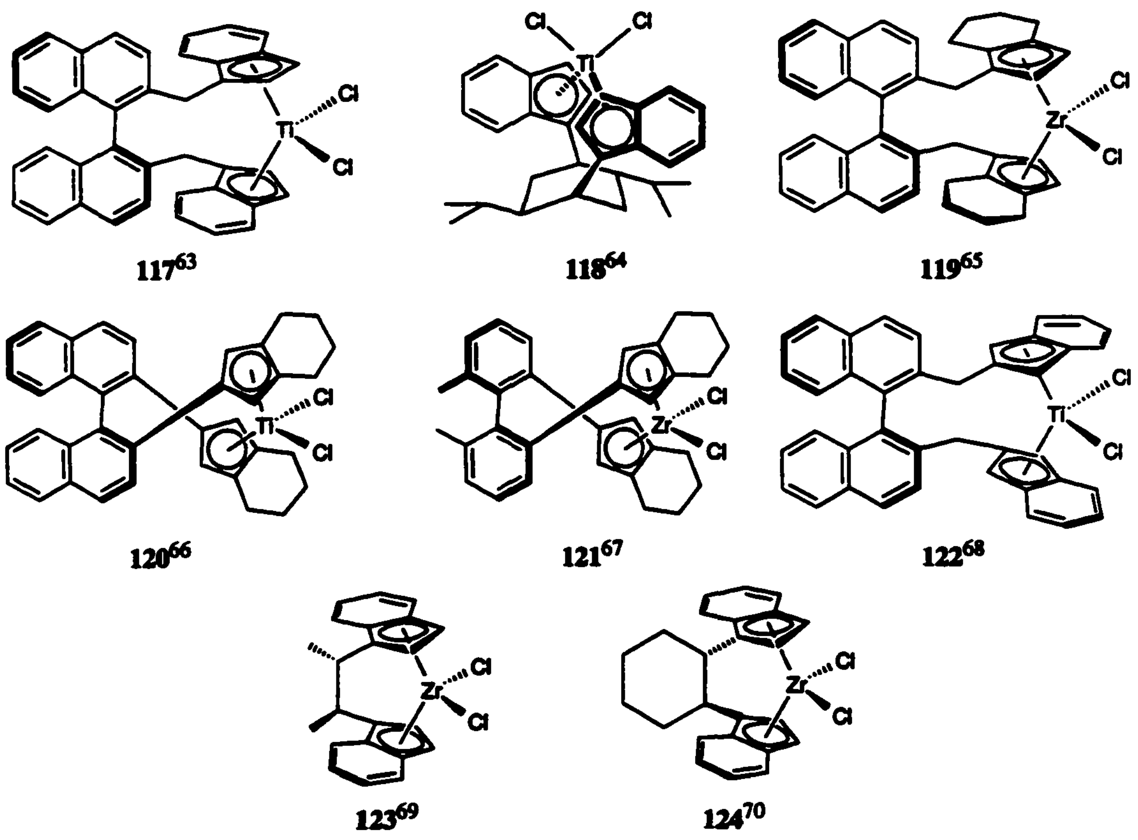
110 111 112 113

114 115 116

1.7.3 Chiral bridges

Work continues to be aimed toward the synthesis of chiral bridging bis(indenyls). These chiral bridges could potentially lead to formation of enantiomerically pure metallocene dichlorides. A number of groups have published the use of chiral bridges ranging from a chiral ethylene to binaphthylene units (Figure 1-30).

Figure 1-30. Bis(indenyl)metal complexes with chiral bridges.



117[63] 118[64] 119[65]

120[66] 121[67] 122[68]

123[69] 124[70]

1.8 Conclusion

This section briefly covered background information about sources of chirality, nomenclature, types of π-faces, and presents numerous ligands and metallocenes. If the number of group 4 metallocene dichlorides continues to grow, as they have over the last 20 years, a better understanding of the effects of the steric and electronic environment should result from their use in enantioselective reactions. From this, their potential as powerful tools in organic synthesis should be fulfilled.

Chapter 2

SYNTHETIC APPLICATIONS FOR ZIRCONOCENES AND TITANOCENES

2.1 Introduction

There are numerous reasons to use titanocene and zirconocene complexes in organic transformations. Like other transition metals, zirconium and titanium are capable of coordinating many organic functional groups. This coordination could cause a labile species to become reactive, a reactive species to become more reactive, or reverse the reactivity of certain functional groups. As a result, reactions which are unattainable through conventional organic methodologies become possible. In addition, the availability of a wide range of structurally well defined catalysts make zirconocene and titanocene complexes especially attractive for stereoselective organic transformations. This chapter will briefly cover several organic applications for these metallocenes.

2.2 Olefin Polymerization

In 1976 Kaminsky reported the activation of Cp_2ZrCl_2 with methylalumoxane(MAO) to give a zirconium species capable of polymerizing ethylene.[71] Soon after, Kaminsky and Brintzinger published the production of isotactic polypropylene using zirconocene dichloride **8** in the presence of MAO (Figure 2-1).[72]

As these zirconocene dichlorides were developed and applied to the polymerization process, a correlation between catalyst structure and polypropylene composition was found.[73] In general C_2-symmetrical zirconocene dichlorides give isotactic polypropylene, C_1-symmetrical metallocenes give hemiisotactic polypropylene, C_s-symmetrical metallocenes give syndiotactic polypropylene, and metallocenes such as **125**[72] give atactic polypropylene (Figure 2-2).

Figure 2-1. Polymerization of propylene with Brintzinger's complex.

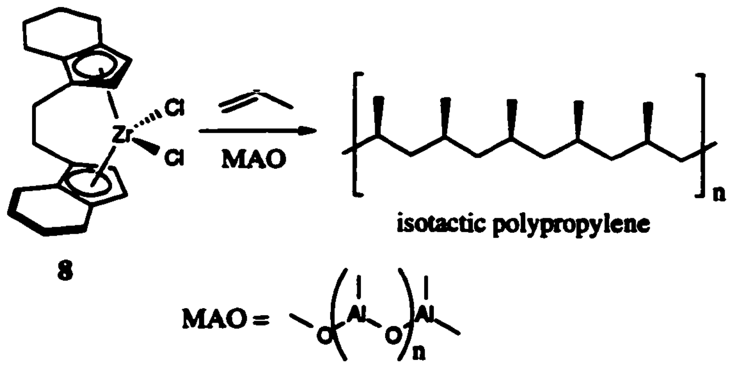


Figure 2-2. Correlation between metallocene dichloride structure and polymer composition.

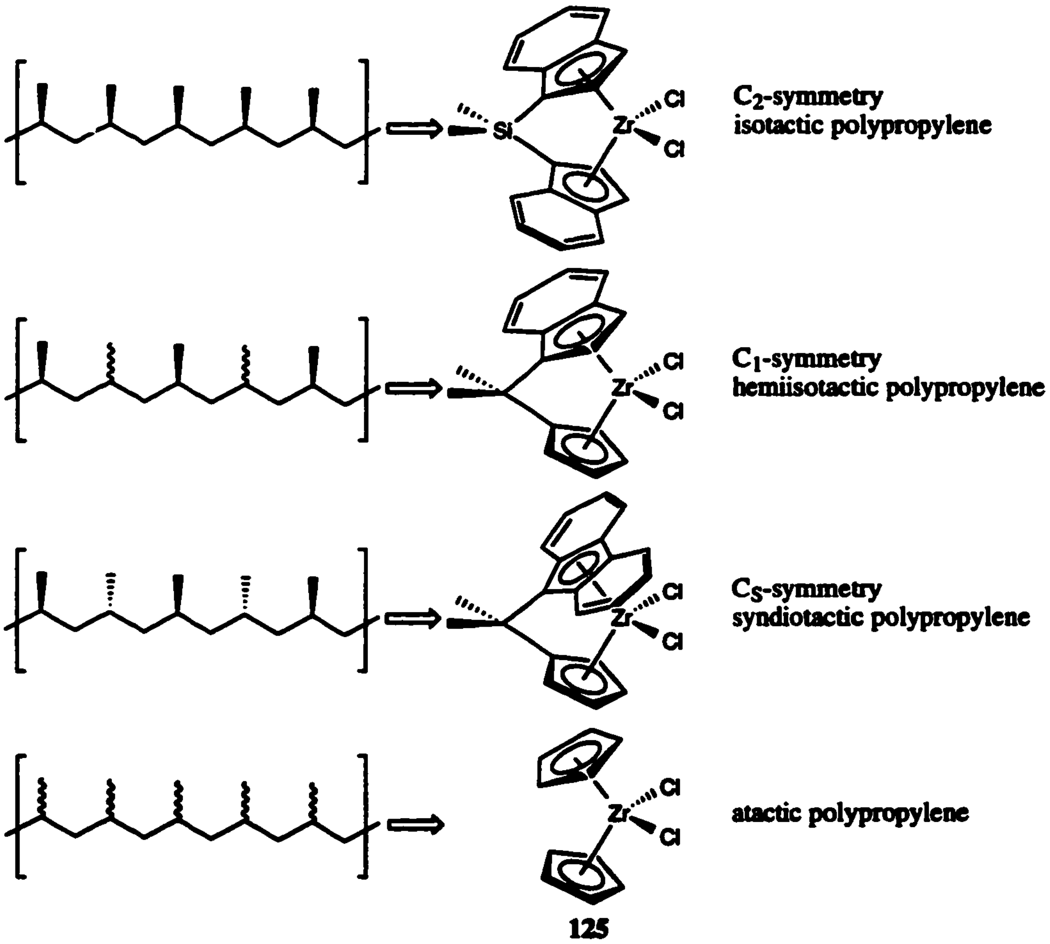
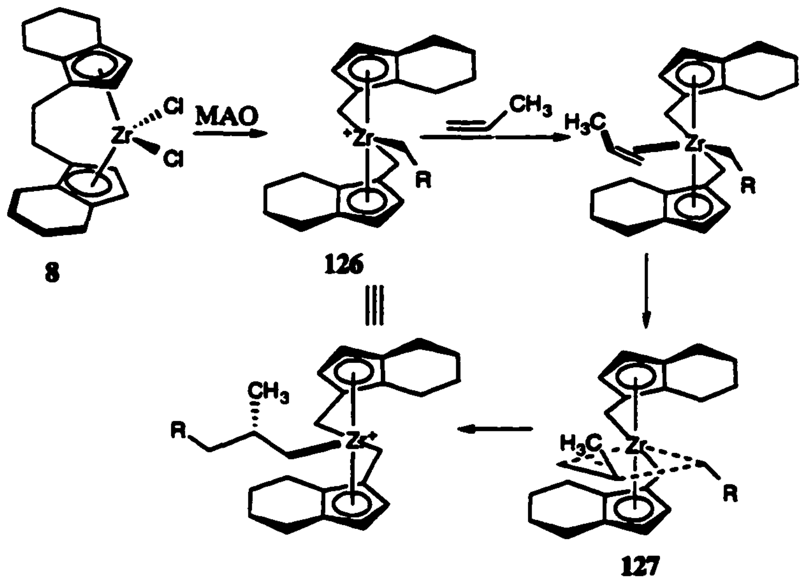
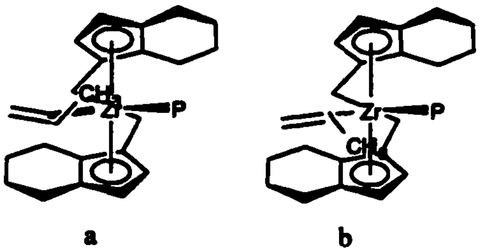


Figure 2-3. A polymerization mechanism.



R = H or polymer chain

Figure 2-4. (a) Favored approach
(b) Less favored approach.



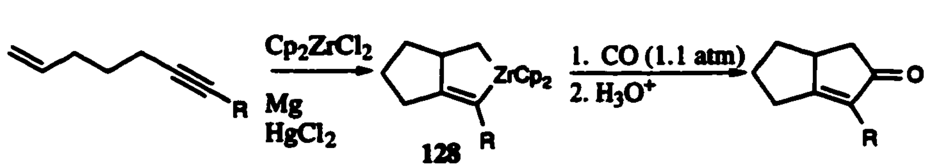
P = growing polymer chain

Intensive mechanistic studies are continuing to be made to determine the true nature of the active species. To date these studies have led to a general catalytic cycle for the polymerization of olefins. A simple picture of the catalytic process is illustrated in Figure 2-3.[74] The activation of the zirconocene dichloride with MAO gives an alkyl cationic zirconium species **126**. The olefin then coordinates the cationic zirconium so that the least amount of steric interaction is involved during the approach which has been found to occur with high facial selectivity (Figure 2-4).[75] Finally, the olefin inserts into the existing zirconium carbon bond regenerating the cationic species and the process continues until a terminating step occurs.

2.3 Cyclization reactions

Intramolecular enyne cyclizations can be done using stoichiometric amounts of zirconium dichloride to give functionalized cyclic products. As seen in Table 2-1, treatment of enynes with Cp_2ZrCl_2, magnesium, and mercury(II) chloride gives rise to zirconocycle **128**. The zirconocycle can then be treated with CO to give a stoichiometric Pauson-Khand type reaction that affords cyclopentenones.[76]

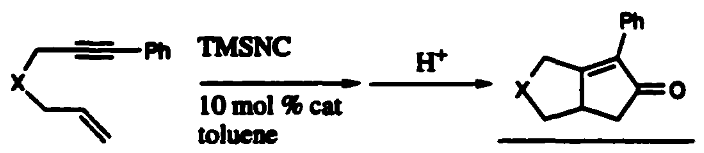
Table 2-1. Enyne cyclization with zirconocene dichloride.



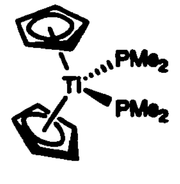
R	Product (% Yield)
TMS	65
$SnMe_3$	63
Me	65
Ph	55
CH=CH-Hex-(E)	50

In 1994 Buchwald developed a titanocene version of the zirconocene cyclization that is catalytic (Table 2-2).[77] He accomplished this with various enynes in the presence of titanocene **129** (10 mol%) and TMSNC followed by workup to give the corresponding

Table 2-2. Catalytic enyne cyclization with titanocene complex **129** and TMSNC.



cat =



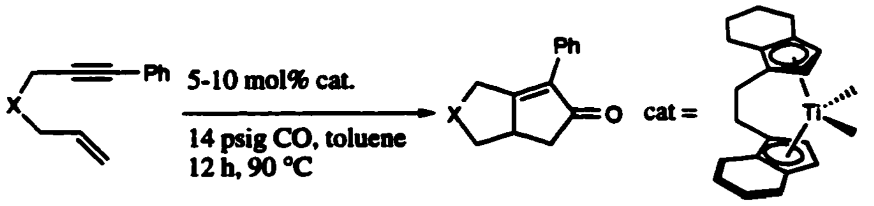
129

X	Yield
O	80
CH_2	44
PhN	55

cyclic enones in moderate to excellent yields. Recently Buchwald published a catalytic enantioselective version of the above with metallocene complex **130** in the presence of CO (Table 2-3).[78]

A tentative catalytic cycle has been proposed by Buchwald for the above processes which is shown in Figure 2-5.[77,78] Initially, titanocene dicarbonyl **131** is generated *in situ*

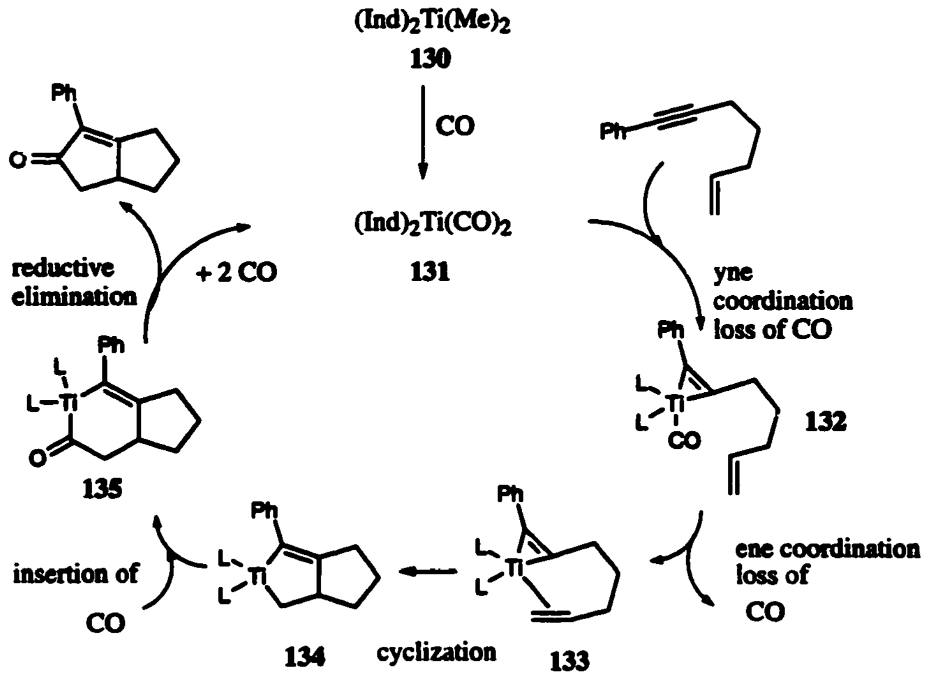
Table 2-3. Enantioselective catalytic Pauson-Khand type reaction.



130

X	yield (%)	ee (%)
O	85	96
CH_2	70	87
BOC-N	84	74

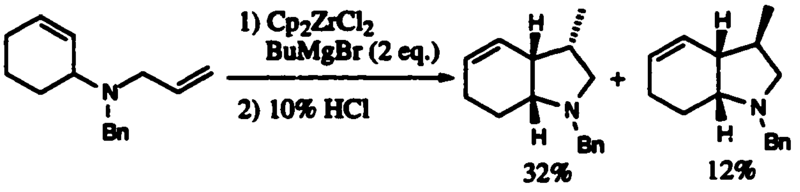
Figure 2-5. Buchwald's mechanism for the titanium catalyzed Pauson-Khand reaction.



from titanocene **130** in the presence of CO. One of the carbonyl groups is then replaced when the yne coordinates the titanocene, and the second carbonyl group is lost when the ene coordinates. Cyclization affords titanocyclopentene **134** which is followed by insertion of CO and reductive elimination to afford the corresponding enone.

Zirconium promoted stoichiometric diene cyclizations have been reported by Mori (Figure 2-6).[79] The active species was generated from the treatment of Cp_2ZrCl_2 with 2 equivalents of *n*-butyl Grignard. The active catalyst could then cyclize diene **136** to afford cyclic products **137** and **138**, respectively.

Figure 2-6. Zirconocene promoted diene cyclization.



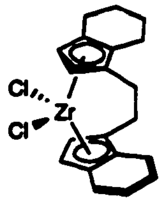
136 **137** **138**

2.4 Carbomagnesations and related reactions

A variation of the Dzhemilev[80] reaction has been developed by Hoveyda.[81] He has demonstrated that nonracemic zirconocene **8** could catalyze the addition of alkylmagnesium chloride to five-, six-, and seven-membered unsaturated heterocycles to give the corresponding alcohols and amines under mild conditions. In addition, these conditions afforded excellent enantioselectivity over the entire range of substrates tested. Table 2-4 pictures three examples.

Hoveyda has proposed the catalytic cycle shown in Figure 2-7.[81] The zirconocene dichloride **8** is activated with two equivalents of alkylgrignard to give active species **139**. The unsaturated olefin then approaches the zirconium in such a way as to minimize steric

Table 2-4. Carbomagnesation of cyclic ethers.

Cyclic Olefin $\xrightarrow[\text{5 equiv. RMgCl}]{\text{10 mol\% cat.}}$ Alcohol cat =  8

THF

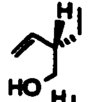
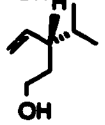
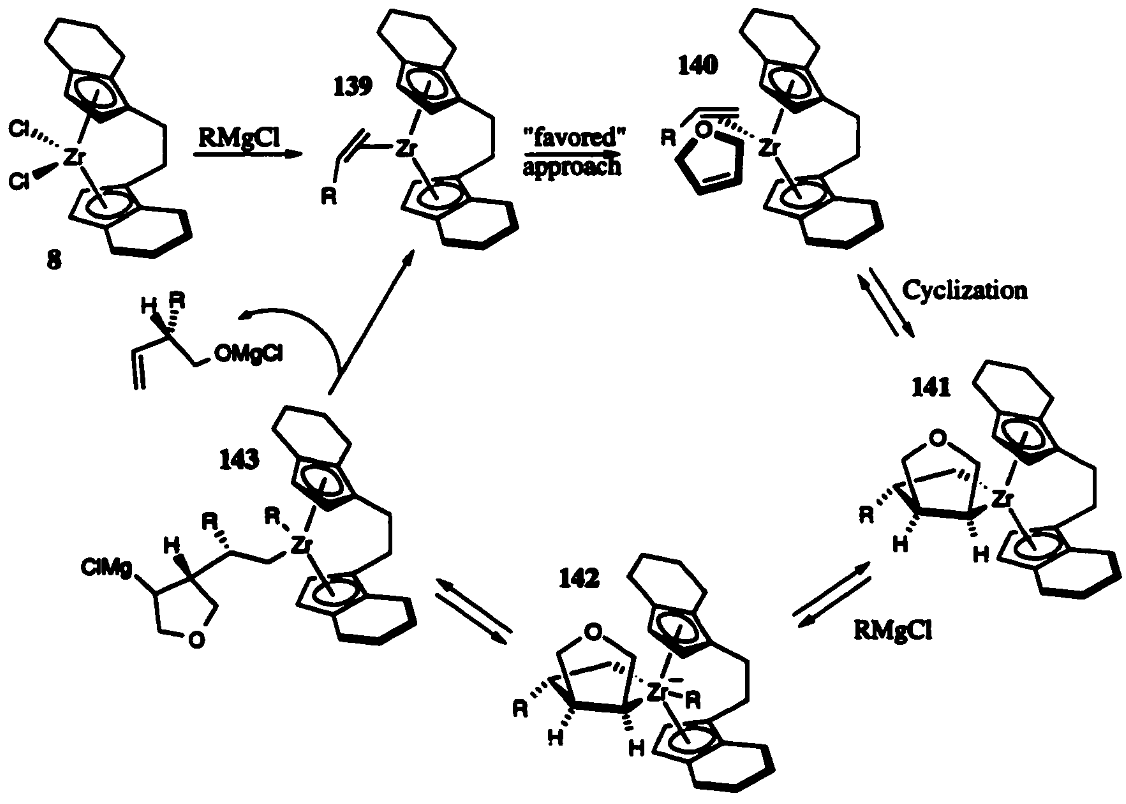
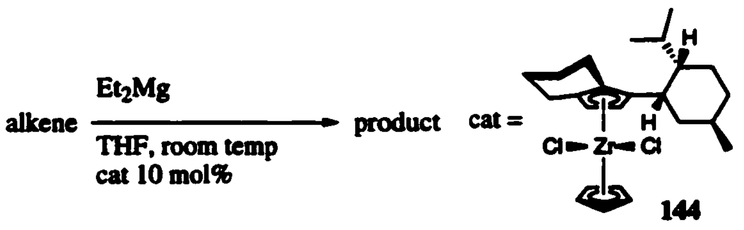
Cyclic Olefin	RMgCl	Alcohol	ee %	yield (%)
	EtMgCl		>97	65
	EtMgCl		95	73
	n-PrMgCl		98	40

Figure 2-7. Carbomagnesation mechanism proposed by Hoveyda.

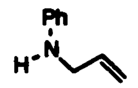
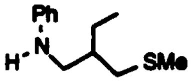
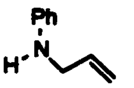
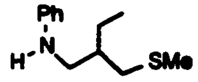
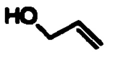
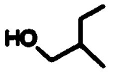


repulsion between the substrate and metallocene ligands and forms a zirconocyclopentane intermediate **141**. Another equivalent of alkyl-Grignard coordinates to the zirconium and opens the zirconocycle. Eventually β-hydride transfer and alkoxide elimination occurs to yield the product and regenerate the catalyst.

Table 2-5. Carbomagnesation using a menthyl substituted indenyl complex.



144

alkene	electrophile	product	ee (%)	yield (%)
	(MeS)$_2$		75	95
	(MeS)$_2$		52	61
			56	75

Whitby has also done extensive work in the area of carbomagnesation and has found that other zirconocene dichlorides can be used to add ethylmagnesium chloride across unactivated olefins (Table 2-5).[82] Two factors control the stereoselectivity in this system (Figure 2-8). One, the wall must effectively block one half of the zirconium so that the olefin cannot approach from that side. Two, the roof directs the approach of the incoming olefin. Whitby has proposed a different catalytic cycle for the carbomagnesation of olefins (Figure 2-9).[83] Nonetheless, both cycles can account for the observed products in each case.

Figure 2-8. Roof and wall effect.

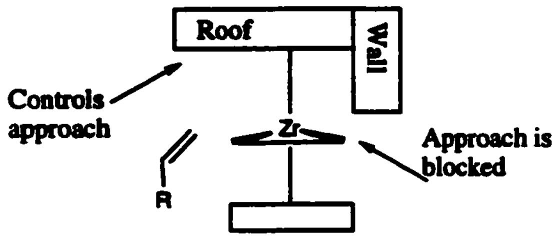
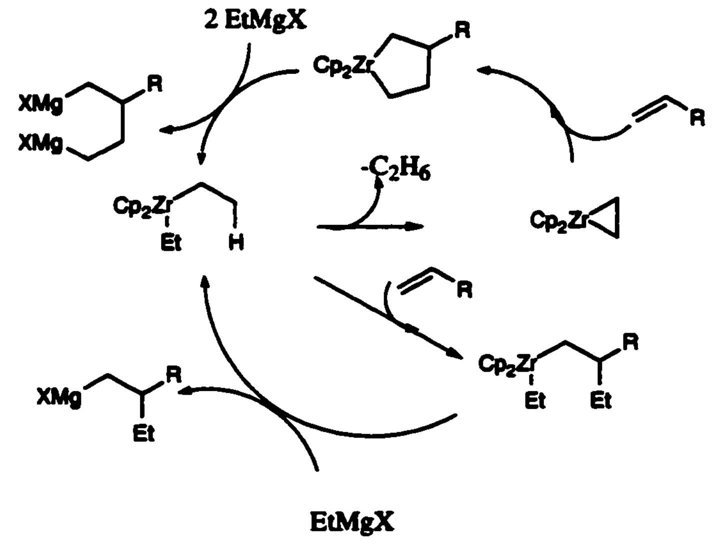
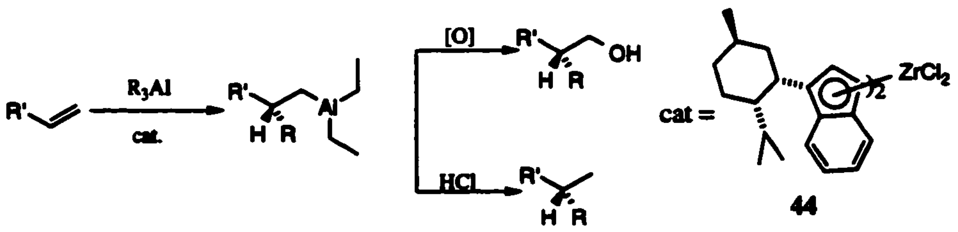


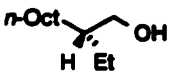
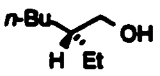
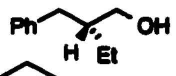
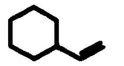
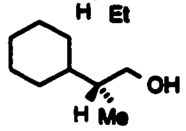
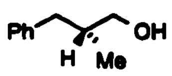
Figure 2-9. Whitby's proposed catalytic cycle for the carbomagnesation of olefins.



Negishi has reported a similar alkyl addition to olefins that uses trialkylaluminums in the presence of catalyst **44** (Table 2-6).[84] Subsequent workup yielded the corresponding alcohol or hydrocarbon with excellent enantioselectivity.

Table 2-6. Enantioselective carboalumination of monosubstituted olefins.

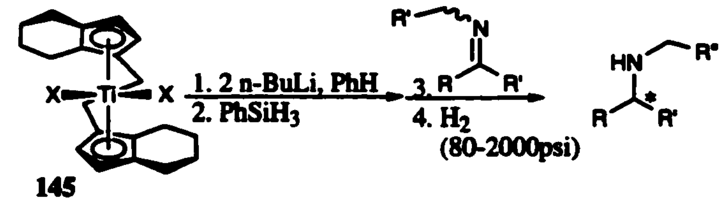


olefin	R of R_3Al	product	ee %	yield %
	Et		92	64
	Et		92	63
	Et		93	69
	Me		65	80
	Me		70	77

2.5 Reduction of imines and carbonyls

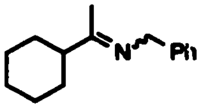
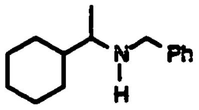
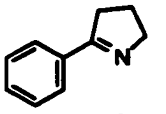
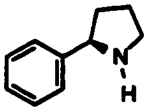
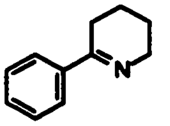
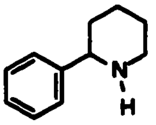
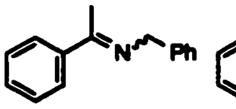
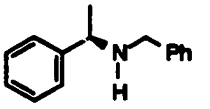
Buchwald has published a considerable amount of work on asymmetric hydrogenation of imines using enantiomerically enriched titanocene complex **145** (Table 2-7).[85] He has found that treatment of **145** with *n*-butyllithium and phenylsilane followed by subsequent treatment with hydrogen (80-2000 psi) produced the necessary conditions for the reduction of acyclic and cyclic imines. Of interest is the more facile reduction of cyclic imines verses acyclic amines. This reactivity difference is believed to be due to the N-alkyl group being tied down, thus, increasing the availability of the nitrogen to coordinate to the metal.

Table 2-7. Catalytic asymmetric reduction of imines.



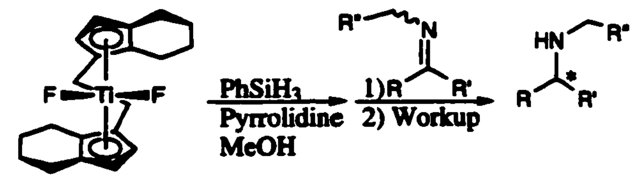
145

X_2 = 1,2'-binaphth-2,2'-diolate

imine	amine	ee (%)	yield (%)
		76	93
		98	77
		97	70
		85	93

Buchwald has further advanced the enantioselective hydrogenation of imines through the application of titanocene **146** to afford cyclic and acyclic amines under mild conditions with high stereoselectivity (Table 2-8).[86] It was found that **146** could be transformed into the active species upon treatment with $PhSiH_3$ (Figure 2-10). Species

Table 2-8. Enantioselective hydrosilylation of imines.



146

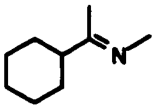
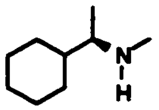
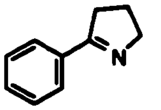
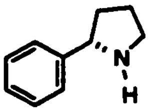
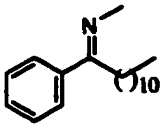
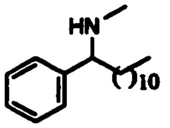
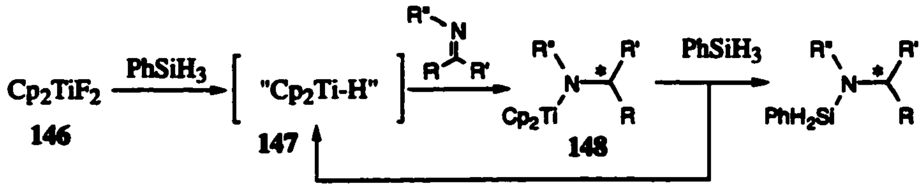
imine	amine	ee (%)	yield (%)
		99	95
		98	96
		95	88

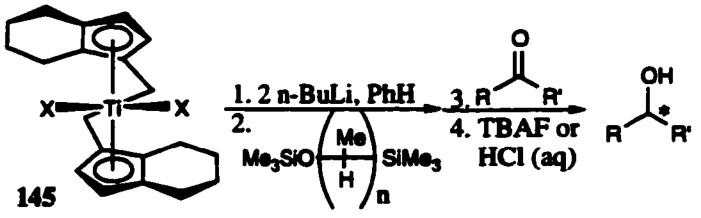
Figure 2-10. Proposed catalytic cycle for hydrosilylation of imines.



147 was then capable of transferring the hydride to the imine while $PhSiH_3$ regenerated the catalyst and afforded the silylated amine.

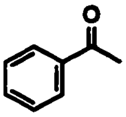
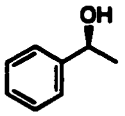
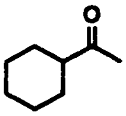
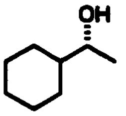
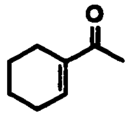
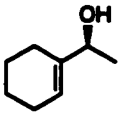
Buchwald has also developed the use of **145** as a precatalyst for the reduction of ketones (Table 2-9).[87] He has found that **145** could react with *n*-butyllithium and polymethylhydrosilane to generate a catalyst which would then reduce ketones with fair to excellent enantioselectivity. Other notable attempts at catalytic enantioselective reduction of aryl alkyl ketones with C_2-symmetric chiral bridged and unbridged metallocenes have been reported with some success.[88]

Table 2-9. Enantioselective hydrosilylation of ketones.



145

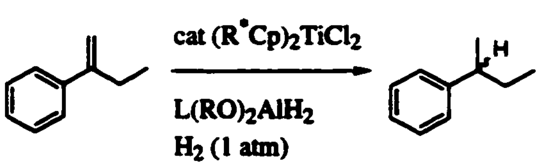
X_2-1,2'-binaphth-2,2'-diolate

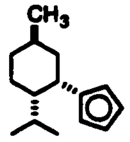
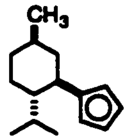
ketone	alcohol	time (d)	ee (%)	yield (%)
		0.9	97	73
		4	24	67
		1	90	72

2.6 Hydrogenation of olefins

The stereoselective hydrogenation of simple unfunctionalized olefins has been known since 1979.[89] In these example the hydrogenations were done using nonbridged bis(neomenthylCp) and bis(menthylCp)titanium dichlorides which were reduced with aluminum hydride derivatives (Table 2-10). The resulting species could then be used to hydrogenate 2-phenyl-1-butene in the presence of 1 atm of hydrogen at temperatures ranging from -5 to 35 °C. Under optimal conditions they could obtain (S)-2-phenylbutane in 28% ee with 75 turnovers at 5 °C.

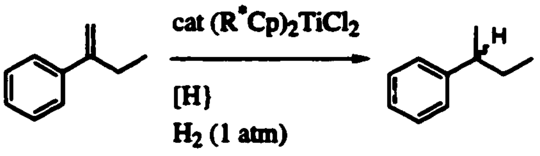
Table 2-10. The first stereoselective hydrogenation using titanocene dichlorides.

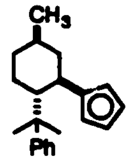


R*Cp	temp (°C)	ee (%)
	20	7
	5 20	28 15

Several classes of monosubstituted and annulated titanocene dichloride precatalysts have been used for the hydrogenation of 2-phenyl-1-butene with a slight advantage going to the annulated complexes (Table 2-11). [15,22,23] To date the most selective of the

Table 2-11. Other titanocene dichlorides used for the hydrogenation of unfunctionalized olefins.



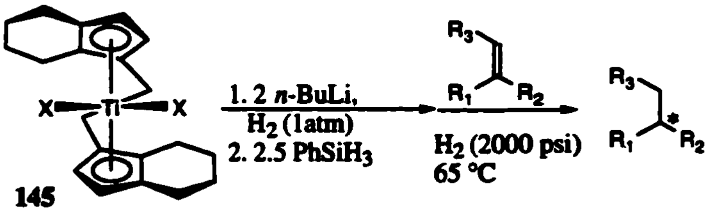
R*Cp	temp (°C)	ee (%)[a]
	23	33
	-20	34
	-78 25	95 68

a = ee % given in literature

metallocene dichloride precursor has been the titanocene dichloride with an annulated C_2-symmetric ligand.[15]

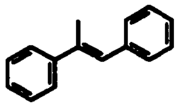
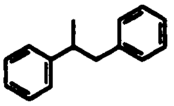
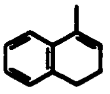
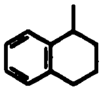
Buchwald has demonstrated that *ansa*-bis(indenyl)titanium complex **145** could reduce unfunctionalized olefins if activated with *n*-butyllithium, and phenylsilane (Table 2-12).[90] This species could then hydrogenate trisubstituted olefins in the presence of hydrogen (2000 psi) at 65 °C for 9-184 h with moderate to high enantioselectivity.

Table 2-12. Hydrogenation of trisubstituted olefins.



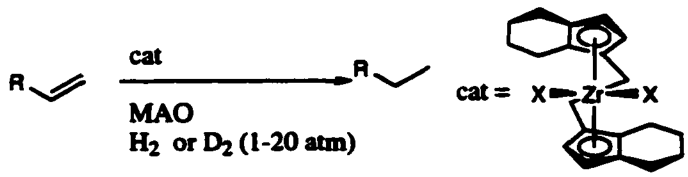
145

X_2-1,2'-binaphth-2,2'-diolate

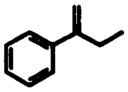
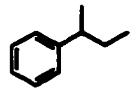
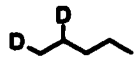
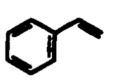
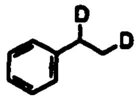
olefin	product	time (h)	ee (%)	yield (%)
		9	>99	94
		184	83	74

Waymouth and Pino demonstrated that a cationic zirconium species was capable of catalyzing the hydrogenation of simple unfunctionalized olefins (Table 2-13).[75] They demonstrated a zirconocene complex could be activated with MAO and be used to hydrogenate or deuterate 2-phenyl-1-butene, 1-pentene and styrene at reasonable temperatures and pressures. They also determined that the enantioface which is hydrogenated/deuterated is the opposite of the facial selectivity for the polymerization of propene.

Table 2-13. Zirconium catalyzed hydrogenation/deuteration of unfunctionalized olefins.



X_2-1,2'-binaphth-2,2'-diolate

olefin	product	ee (%)
		36
		23
		65

2.7 Conclusion

This chapter provided a small sampling of the applications for zirconocenes and titanocenes in organic synthesis. Other applications for zirconocenes and titanocenes that were not covered include asymmetric Diels-Alder reactions,[91] diastereoselective[92] and enantioselective formation of homoallylic alcohols,[92b] hydrozirconation of alkenes and alkynes,[93] alkene isomerization,[64] and catalytic asymmetric epoxidation of unfunctionalized olefins.[63b,c,66] To further develop these processes, metallocenes varying in structural composition must be synthesized which may lead to higher selectivity and reactivity. The synthetic strategies for varying the conformational shape and mobility of old and new metallocenes will be covered in the following chapters.

Chapter 3

STERIC MODIFICATION OF A CHIRAL METALLOCENE

3.1 Introduction

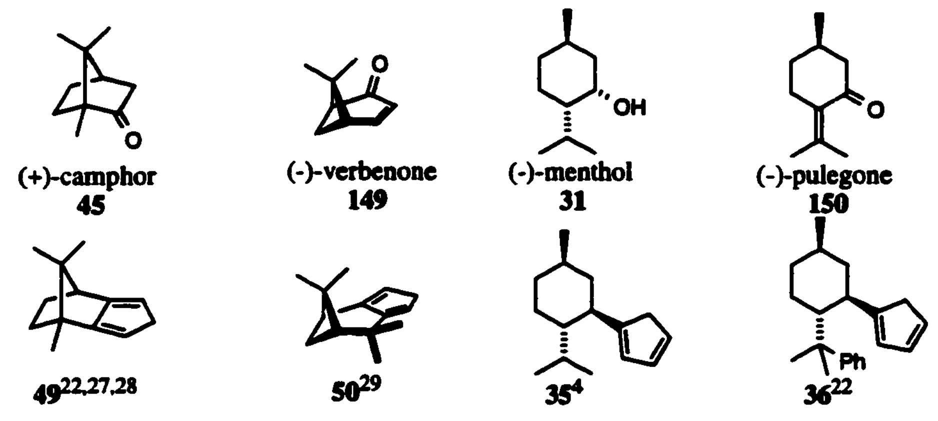
The previous chapters provided background information about Cp and indenyl ligands, and several applications for zirconocene and titanocene complexes. To date a majority of the attention has been focused on the often-successful application of Brintzinger's complex. Nonetheless, there is still room for improvement. To acquire more information on the effects of metallocene structure on reaction outcome, a systematic study of various features of the metallocene complex can be done. Of the possible methods for varying the metallocene dichloride this chapter will focus on the methodologies for synthesizing sterically modified Cp's and indenyls, and the design and synthesis of new sterically modified metallocene dichlorides.

3.2 Strategies for the synthesis of enantiomerically pure sterically modified nonbridged Cp complexes

Numerous research groups have incorporated enantiomerically enriched starting materials from naturally occurring compounds to form enantiomerically pure Cp's (Figure 3-1). The Cp's depicted in Figure 3-1 could be considered steric modifications of one another, but little work has been done toward the systematic synthesis of sterically modified Cp's within the framework of a single carbon skeleton.

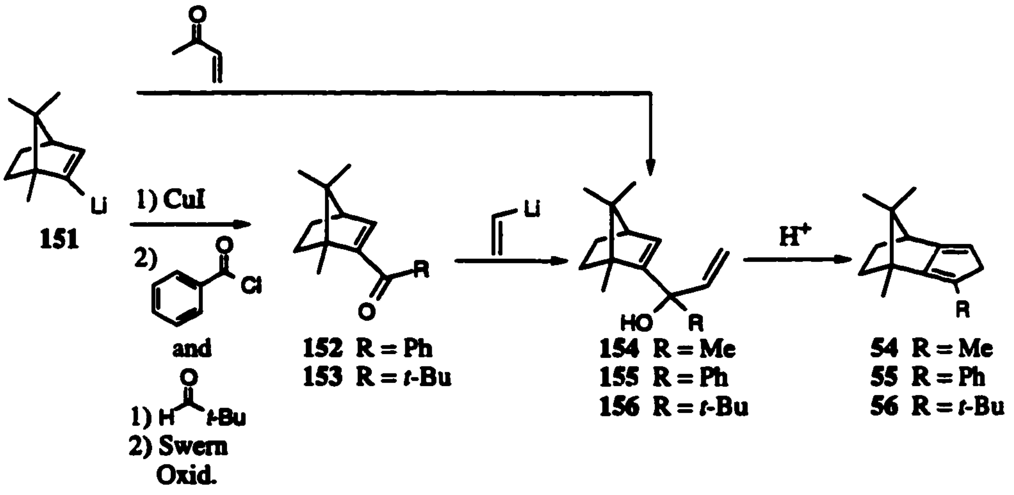
Recently, steric modifications of (+)-camphor derived Cp **49**[22,27,28] were published by Halterman and Tretyakov (Figure 3-2).[32] This was accomplished through the addition of vinyllithium **151** to 2,2-dimethylpropanal, methylvinyl ketone, and benzoyl chloride to afford the corresponding alcohols, and ketone. The alcohol from 2,2-dimethylpropanal was oxidized to ketone **153**. Subsequent addition of vinyllithium to ketones **152** and

Figure 3-1. Natural products and their Cp's.



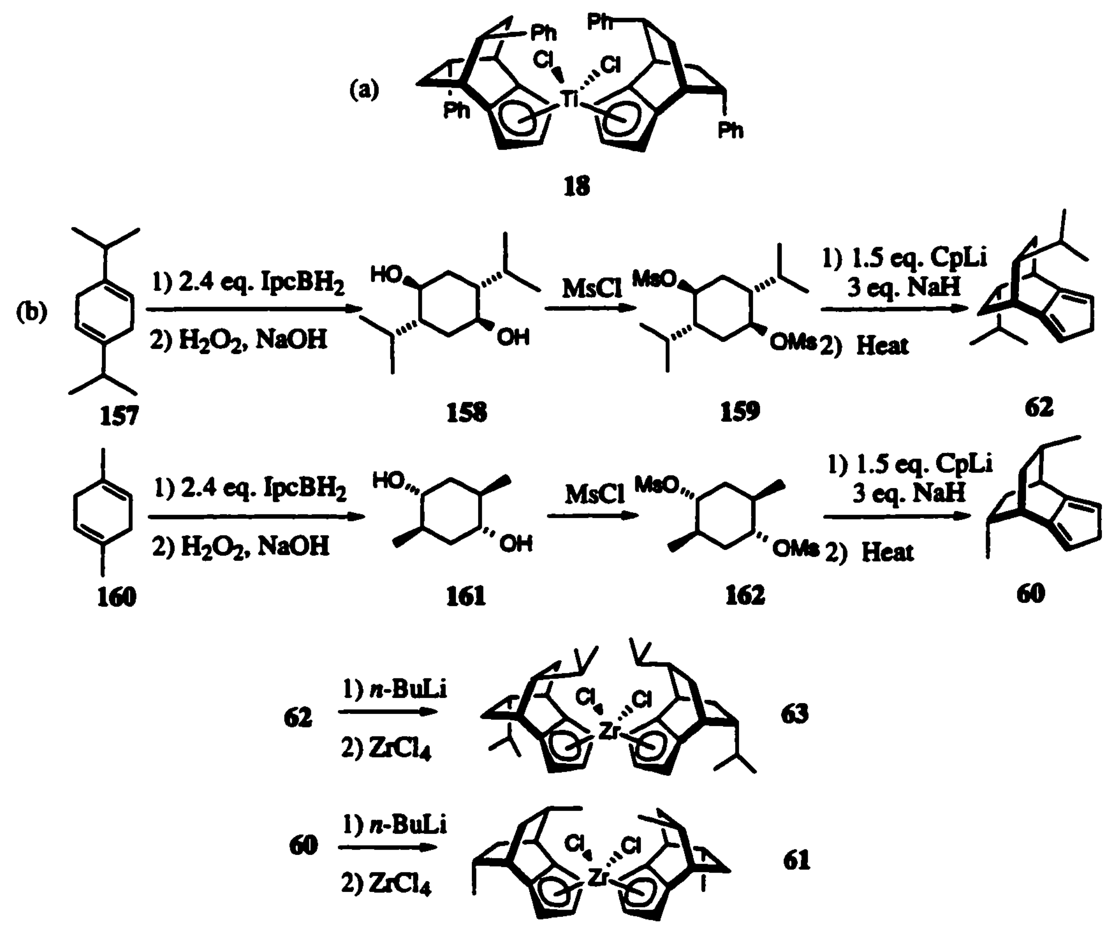
153 resulted in the formation of the bis(allylic)alcohols **155** and **156**. The substituted Cp's were then formed through acid catalyzed Nazarov cyclization from the respective bis(allylic)alcohols.

Figure 3-2. Sterically modified (+)-camphor derived Cp via Nazarov cyclization.



Steric variations of enantiomerically enriched metal complex **18**[15] via asymmetric synthesis have been reported by Halterman and Chen (Figure 3-3).[35] The preparation of two variations began with the treatment of achiral alkenes **157** and **160** with enantiomerically enriched (+)- or (-)-α-isopinocamphenylborane to afford diols **158** and **161**. The diols were then converted to the dimesylates **159** and **162** with methylsulfonylchloride. Treatment of the mesylates with cyclopentadienyllithium in the

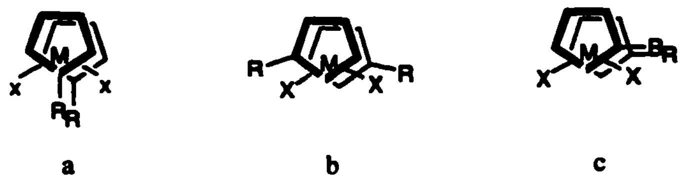
Figure 3-3. (a) Origninal titanocene dichloride
(b) Asymmetric synethesis of sterically modified Cp's and metallocene dichlorides.



presence of excess sodium hydride, preceded by heating afforded the fused ligands **60** and **62**. Subsequent metalation yielded the corresponding zirconocene dichlorides **61** and **63**.

A drawback of metallocene dichlorides with unbridged ligands comes from the rotation of the Cp around the metal (Figure 3-4). If more than one rotational isomer is reactive then it becomes difficult to correlate stereochemical outcome with catalyst structure.

Figure 3-4. Rotation of a Cp around the Cp-metal bond.

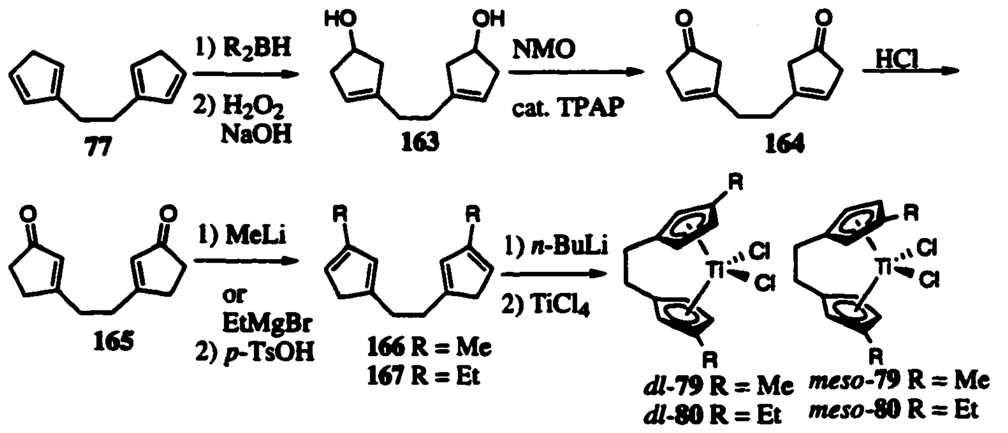


In addition, the possiblity of having reduced stereoselectivity through the reactions involving less selective conformations does exist.

3.3 Strategies for the synthesis of chiral sterically modified bridged Cp complexes

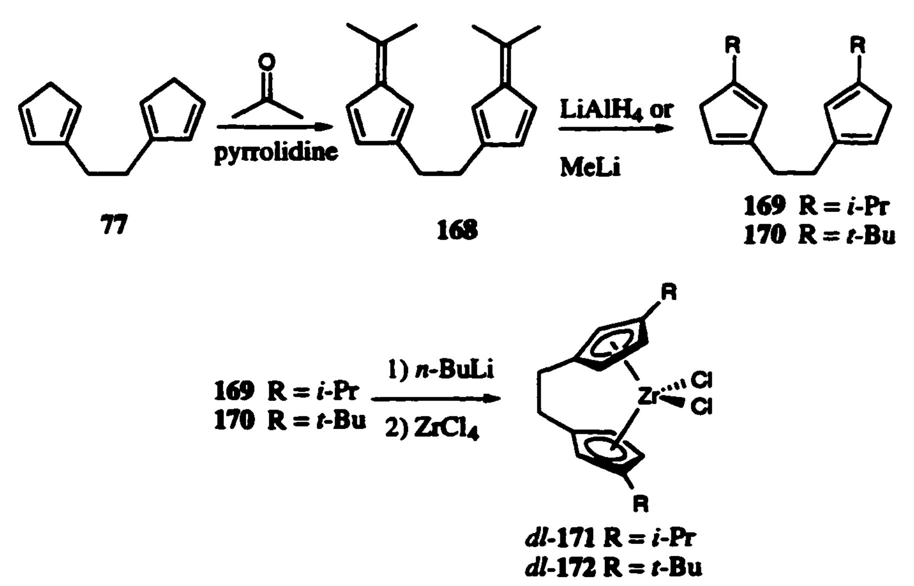
Methods for preparing sterically modified *ansa*-bis(Cp)metal dichlorides with achiral bridging elements have been reported, but since selective alkylation of the Cp anion is difficult to control, elaborate routes to these ligands have been developed.

Figure 3-5. Synthesis of sterically modified ethylene bridged bis(Cp)titanium dichlorides.



Collins and coworkers have devised a clever pathway to substituted ethylene bridged Cp's from bridged bis(Cp) **77** (Figure 3-5).[46] A crucial step involved the selective oxidation of bis(Cp) **77** to diol **163** as single regioisomer. The diol was then oxidized to diketone **164**. The diketone was then treated with acid to promote alkene isomerization to give α,β–unsaturated ketone **165**. Subsequent addition of methyllithium or ethylmagnesiumbromide followed by acid catalyzed dehydration provided the desired bis(Cp)'s **166** and **167** which could then be metallated.

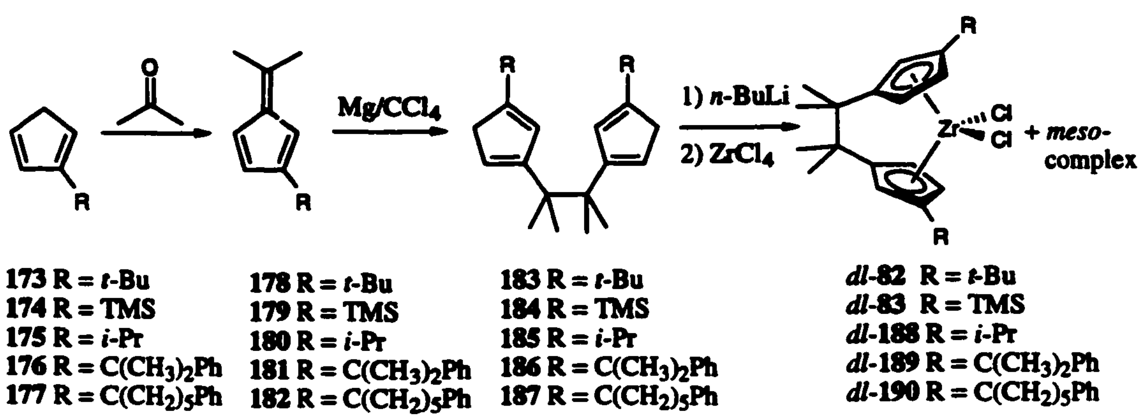
Figure 3-6. Isopropyl and *tert*-butyl substituted ethylene bridged Cp's and their metal dichlorides.



The isopropyl and *tert*-butyl substituted ethylene bridged bis(Cp)'s were conveniently synthesized from the condensation of acetone and parent bis(Cp) **77** to give ethylene bridged fulvene **168** (Figure 3-6).[46] Addition of methyllithium or $LiAlH_4$ followed by dehydration resulted in the formation of bis(Cp)'s **169** and **170**, respectively. Metalation of the bridged bis(Cp)'s gave the corresponding metal dichlorides **171** and **172**.

Brintzinger has published a direct route to a number of ethylene bridged bis(Cp)'s using a magnesium/carbon tetrachloride promoted coupling of substituted fulvenes (Figure

Figure 3-7. Fulvene coupling to bridged bis(Cp)metal dichlorides.

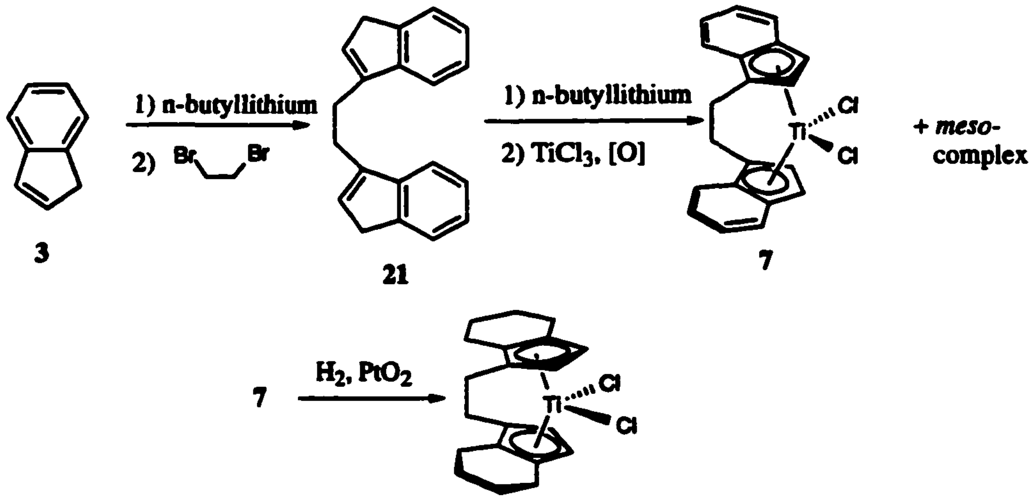


3-7).[47] This synthesis and the others mentioned previously are significant because the ligands once complexed afford the titanium and zirconium dichlorides with well-defined chiral pockets. This is due to the bridging unit which inhibits the rotation of the Cp ligands around the metal center. The major disadvantages are that the ligands are limited due to the relative difficulty of introducing modifications as seen with Collin's long route to sterically modified Cp's **166** and **167**, and the faces of these ligands are enantiotopic and can lead to *dl/meso* mixtures of the metallocene dichlorides.

3.4 Strategies for the synthesis of chiral sterically modified bridged indenyl complexes

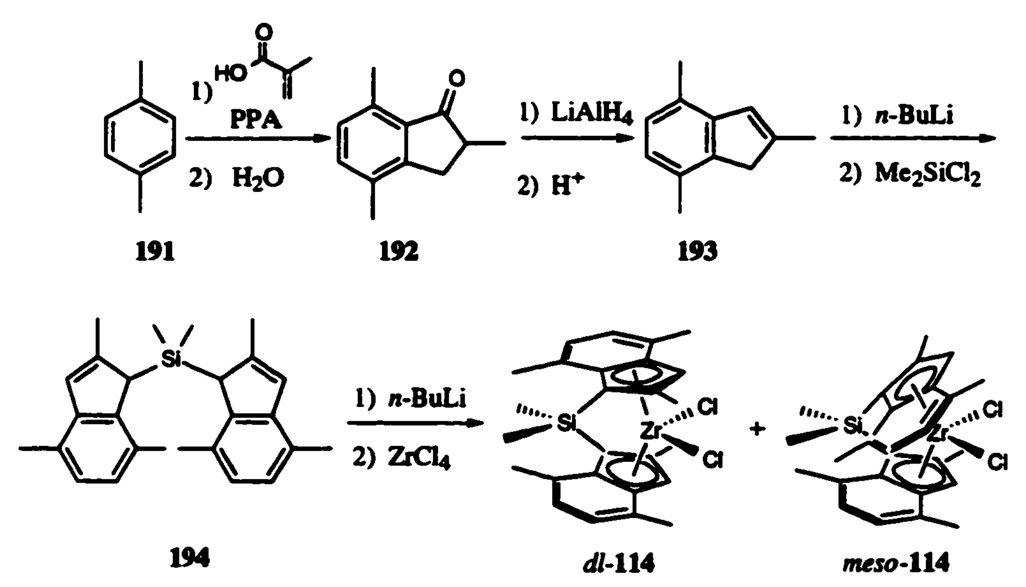
Since the initial report of the ethylene bridged bis(indenyl)titanium complex **7** and (tetrahydroindenyl)titanium complex **94**, numerous sterically modified metallocenes have been synthesized (Figure 3-8).[5] One approach often employed for increasing the steric size around the metal center has come from the hydrogenation of the indenyl complex **7** to give the tetrahydroindenyl complex **94**, which is also electronically different.

Figure 3-8. Brintzinger's synthesis of the first *ansa*-bis(indenyl)titanium dichloride.



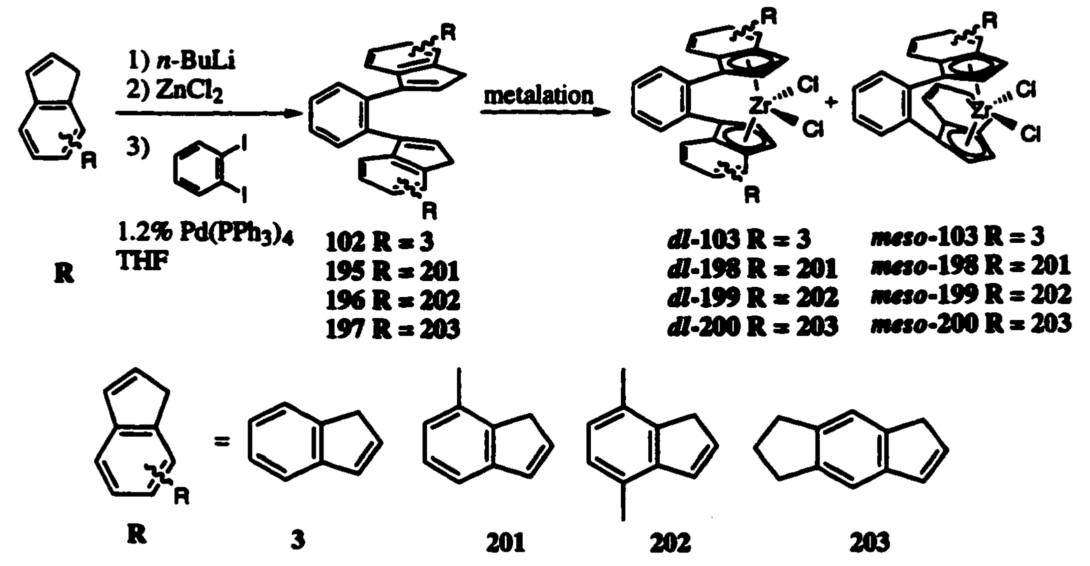
dl-**94**

Figure 3-9. Use of symmetrically substituted indenes.



Another popular approach for introducing steric bulk employs readily synthesized symmetrically substituted indenes (Figure 3-9).[61] In most cases these indenes are bridged via alkylation to give 1 or 2 atom bridged indenes and metallocene dichlorides. Another advantage of this method has been found in the enhanced *dl/meso* ratio of the metal complexes.

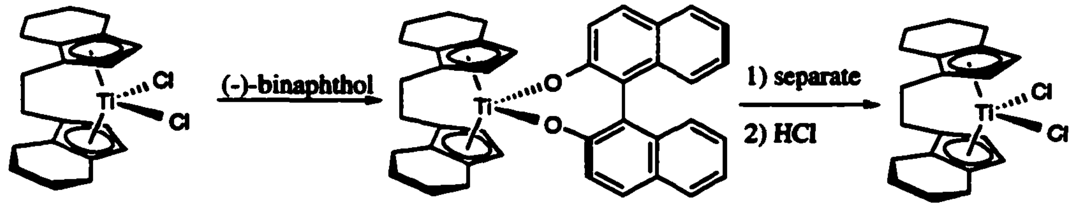
Figure 3-10. Synthesis of phenyl bridged *ansa*-bis(indenyl)zirconium dichlorides.



Recently Halterman and Tretyakov have synthesized a variety of metallocene complexes in two convenient steps (Figure 3-10).[57] The ligands were prepared from their respective indenyllithiums. The indenyllithiums were initially treated with zinc chloride to give indenylzinc chloride. The indenylzinc chlorides were then coupled with 1,2-diiodobenzene in the presence of palladium(0) to afford several phenyl bridged bis(indenes). Interestingly metalation of these compounds resulted in a mixture of *meso*- and *dl*-complexes ranging from a 1:1 to a 1:10 *meso:dl* ratio depending upon metalation conditions and the indenyl ligand.

In the above cases the metal complexes obtained from direct metalation were racemic. To acquire the enantiomerically pure/enriched form a resolution has to be done at the metal dichloride stage (Figure 3-11).[5] This method has been widely used by researchers for bridged Cp's and tetrahydroindenyls, but has not been reported for the resolution of *ansa*-bis(indenyl)metal dichlorides. Therefore, chiral bridging units have been used to procure "self-resolving" enantiomerically enriched *ansa*-bis(indenyl)metal complexes.

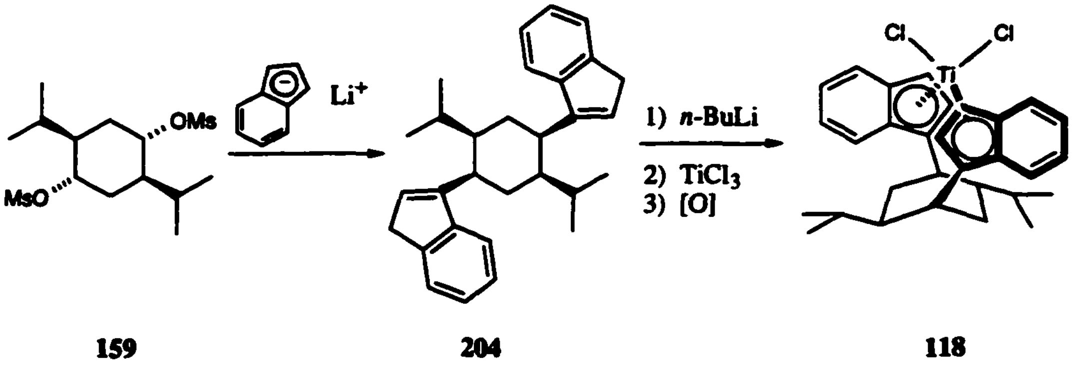
Figure 3-11. Resolution of racemic metallocene dichlorides.



dl-94 95 + uncomplexed metallocene (1S,1S)-94

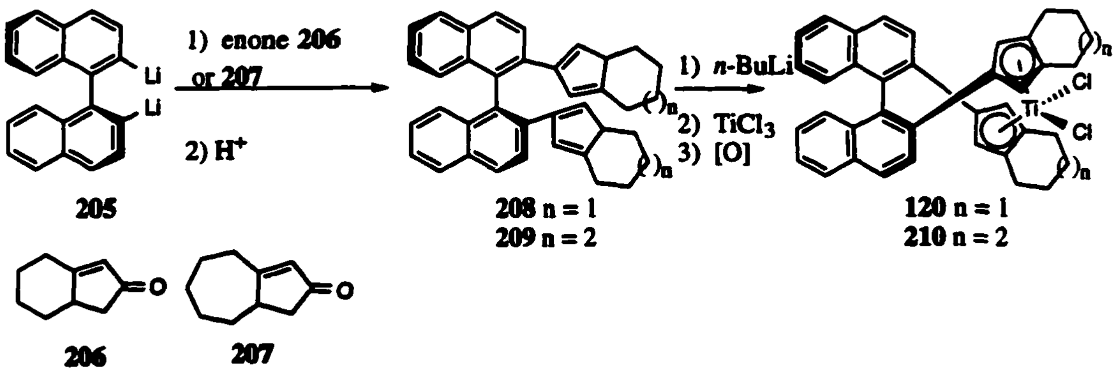
Like the achiral versions, the introduction of indene to enantiomerically enriched bridging units can be done by alkylating with the indenyl anion as seen with the example published by Halterman and Chen (Figure 3-12).[64]

Figure 3-12. Enantiomerically enriched cyclohexane *ansa*-bis(indenyl)titanium dichloride.



One of the methodologies used to increase the steric size around the metal center has been through the hydrogenation of the indenyl double bonds at the metal complex which was previously illustrated in Figure 3-8. Another method was demonstrated by Halterman and Ramsey (Figure 3-13).[66,94] In their synthetic pathway the nucleophile was the bridging unit **205** and the electrophile was enone **206** or **207** which could be converted to the bridged Cp's **208** and **209** via acid catalyzed dehydration after the addition.

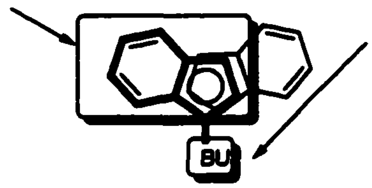
Figure 3-13. Steric modifications via enone addition.



3.5 Rationale for the design and synthesis of sterically modified *ansa*-bis(indenyls)zirconium and -titanium dichlorides

From the limitations and advantages described above it was determined that the synthetic design of sterically modified group 4 metallocene dichlorides should include the following (Figure 3-14).

Figure 3-14. Requirements for the design of sterically modified bis(indenyl)metal complexes with a chiral bridging unit.



Use of indenyl moiety allows for easy introduction of steric modifications

Bridging unit
enantiomerically pure to avoid resolution

should allow easy addition of indenyl anion

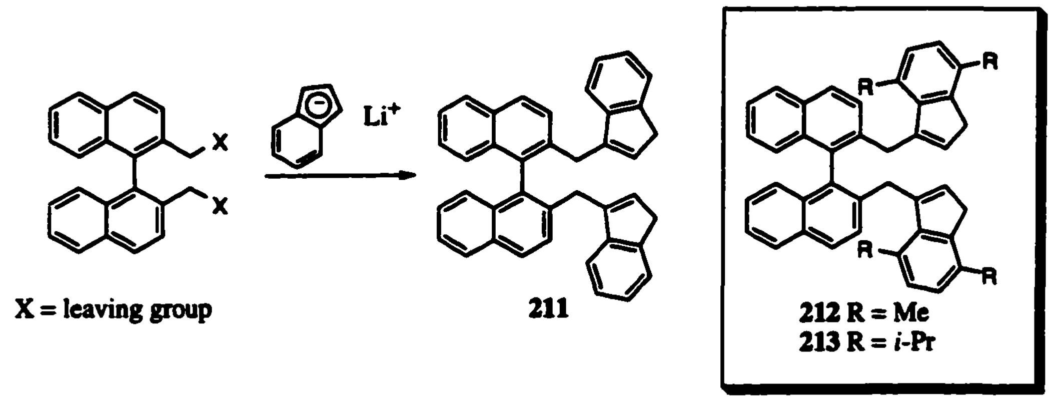
prevents rotation of indenyl moiety around the metal

1) C_2-symmetry needed to be incorporated into the design to limit the number of possible approaches for the incoming substrate.
2) Include a bridging unit to limit the possible conformations of the indenyl moiety. In addition, the bridging unit should be chiral and easily obtained enantiomerically enriched since the resolution of the bis(indenyl) metallocene dichlorides is not yet known. The bridging unit should allow introduction of an indenyl unit.
3) Use the indenyl moiety to introduce subtle changes to the steric size of the substituents at C4 and C7 on the indenyl moiety which has not yet been applied toward chiral bridging units.

3.6 Application of methodology for achiral bridges to the chiral binaphthalene bridge

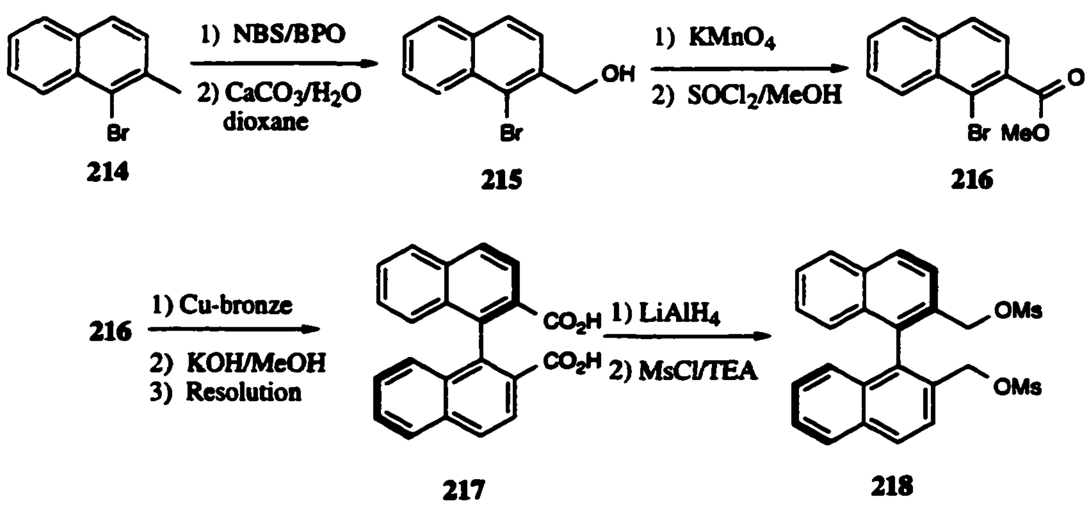
With the guidelines outlined above, we set out to synthesize sterically modified versions of ligand **211**^{63a} previously synthesized in our group (Figure 3-15). The synthetic strategy was based on the alkylation of a binaphthalene moiety because the bridging unit could be resolved. In addition, the synthetic methodology developed previously showed promise for the introduction of the indenyl moiety. We therefore set our objective on the synthesis of ligands **212** and **213**.

Figure 3-15. Previously synthesized bis(indenyl) and targets.



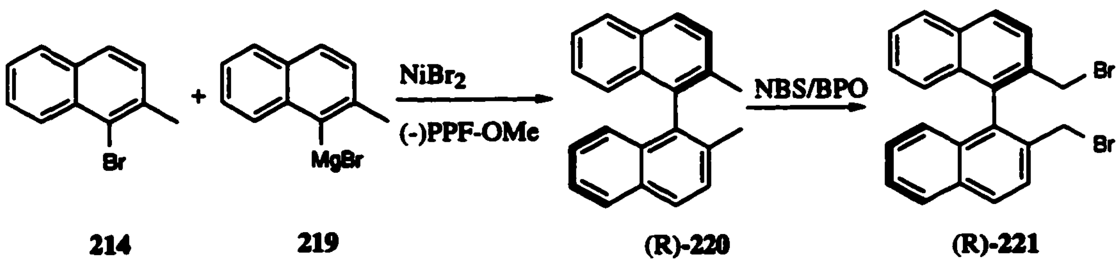
Fortunately a number of methods for synthesizing the binaphthalene moiety existed. Previously Halterman and Colletti had published the improved synthesis and resolution of diacid **217** (Figure 3-16).^{36b} This synthesis began with the oxidation of 1-bromo-2-methylnaphthalene **214** to yield alcohol **215**. The alcohol was then oxidized to the carboxylic acid with KMnO$_4$ and converted to ester **216**. The binaphthalene moiety was formed via a copper-mediated Ullmann coupling of ester **216** and then saponified to diacid **217**. The diacid was resolved with brucine to afford both enantiomers of **217**. Binaphthalene **218** was prepared by LiAlH$_4$ reduction to give the corresponding alcohol. The reduction was followed by esterification with methylsulfonyl chloride to afford the desired binaphthalene moiety.

Figure 3-16. Synthesis of the binaphthalene moiety.



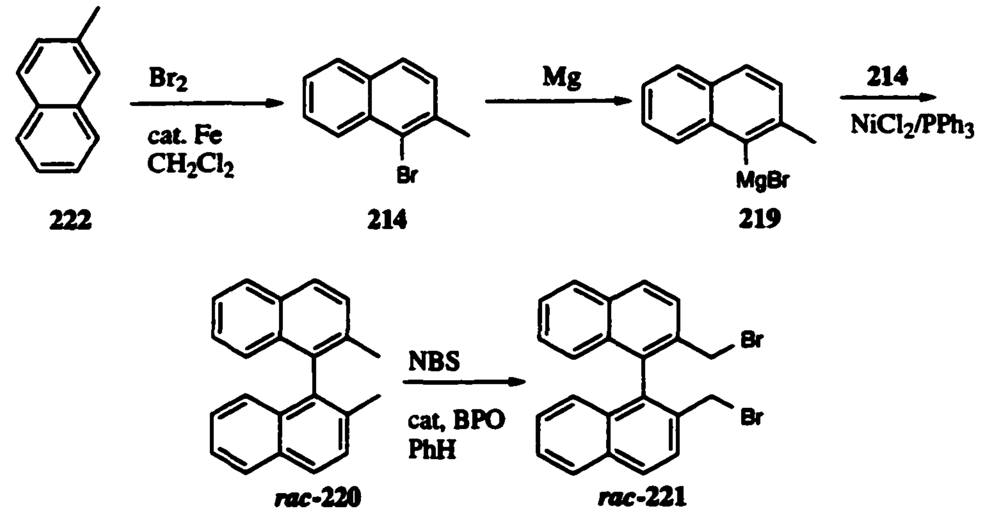
A second direct route to the desired binaphthalene moiety was reported by Ito and coworkers via an enantioselective coupling of 1-bromo-methylnaphthalene **214** with Grignard reagent **219** in the presence of $NiBr_2$ and 1-(diphenylphosphino)-2-(1-methoxyethyl)ferrocene (Figure 3-17).[95] The resulting 2,2'-dimethyl-1,1'-binaphthalene **220** was then brominated with NBS to afford the desired binaphthalene unit **221**.

Figure 3-17. Asymmetric synthesis of the binaphthalene moiety.



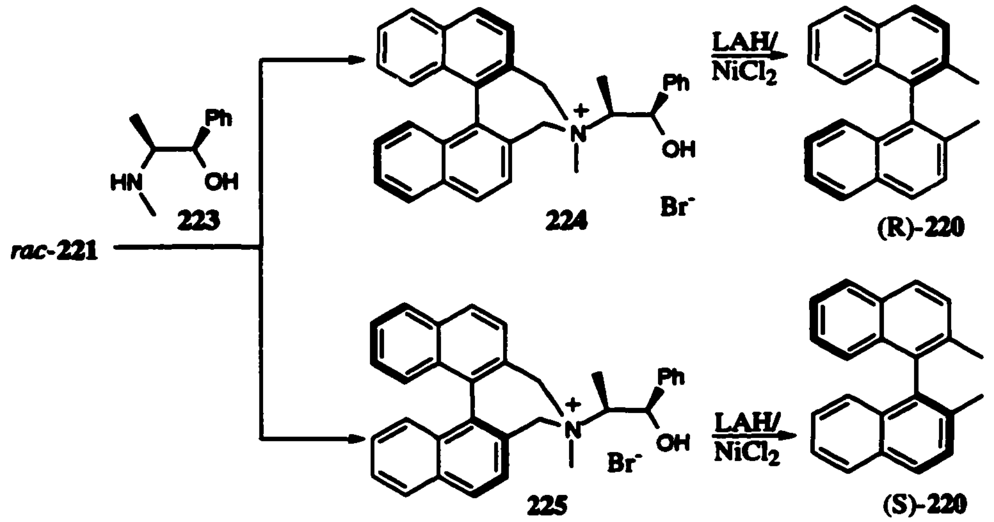
Because of the length of the first method and the inconsistent results obtained when repeating the asymmetric synthesis of **220**, we turned our attention toward the synthesis of racemic dibromide **221** and an alternate resolution (Figure 3-18).[96] Racemic **221** could be obtained from the bromination of 2-methylnaphthalene **222** to give bromide **214**. Grignard reagent **219** was then prepared and coupled with bromide **214** in the presence of $NiCl_2$ and triphenylphosphine. NBS bromination afforded racemic dibromide **221**.

Figure 3-18. Synthesis of racemic dibromide **221**.



Racemic **221** was resolved conveniently and reliably on large scale according to a procedure by Maigrot and Mazaleyrat in three steps with at least 95% enantiomeric excess (Figure 3-19).[96] Racemic **221** was treated with *l*-ephedrine **223** to afford the quaternary ammonium salts **224** and **225**. These salts were easily separated by recrystallization and then reduced with lithium aluminum hydride in the presence of NiCl$_2$ to give enantiomerically enriched 2,2'-dimethyl-1,1'-binaphthalene **220**. Enantiomerically

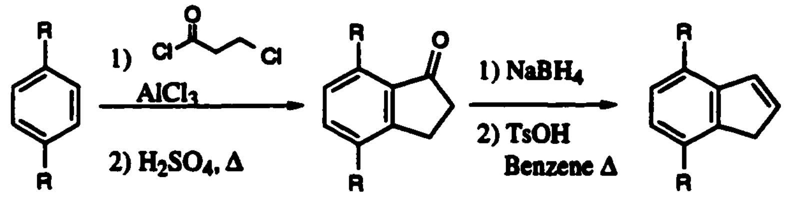
Figure 3-19. Maigrot and Mazaleyrat resolution.



enriched **220** was again subjected to NBS bromination yielding the enantiomerically enriched bromides (R)-**221** and (S)-**221**.

The desired C4 and C7 alkyl substituted indenes were synthesized according to the procedure outlined by Piccolrovazzi and coworkers (Figure 3-20).[13] Para-substituted arenes **191** and **226** were treated with aluminum trichloride and 3-chloropropionylchloride. The reaction mixture was quickly worked-up and treated with sulfuric acid and heat to give the corresponding ketones. Reduction and acid catalyzed dehydration gave 4,7-diisopropylindene (**229**) and 4,7-dimethylindene (**230**) from their respective ketones.

Figure 3-20. Synthesis of 4,7-substituted indenes.



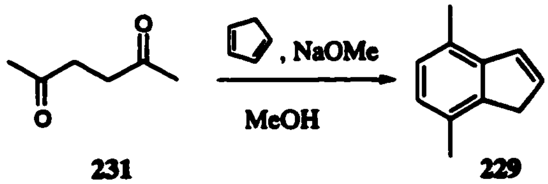
191 R = Me
226 R = *i*-Pr

227 R = Me
228 R = *i*-Pr

229 R = Me
230 R = *i*-Pr

Recently, a convenient one pot synthesis of 4,7-dimethylindene (**229**) had been published by Erker from 2,5-hexadione (**231**), cyclopentadiene, and sodium methoxide (Figure 3-21).[97] We have repeated the condensation on multigram scale to afford indene **229** in 65-80% yield.

Figure 3-21. One pot synthesis of 4,7-dimethylindene.

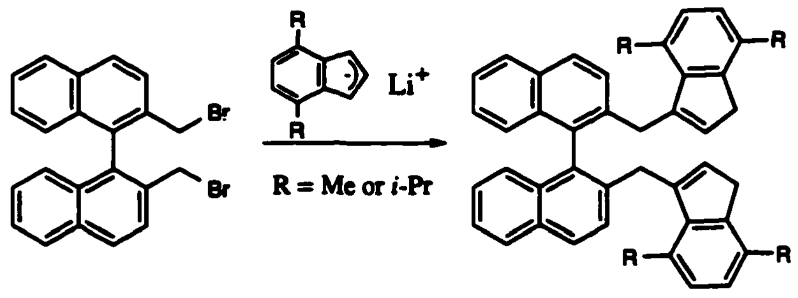


231

229

Treating racemic or enantiomerically pure 2,2'-bis(bromomethyl)-1,1'-binaphthalene with lithiated 4,7-dimethylindene **229** at -78 °C gave the desired bis(indene) **212** in 70% yield as a white solid after purification (Figure 3-22). The desired bis(indene) **212** was identified by the appearance of two doublets at 2.98 and 2.68 ppm which corresponded to the two diastereotopic protons of the methylene group between the indenyl and binaphthalene moiety, in addition to the appearance of two methyl singlets at 2.25 and 2.24 ppm and two indenyl signals at 6.38 and 5.28 ppm in the ^{1}H NMR spectrum of **212** (Figure 3-23). Attempts to alkylate the lithio salt of 4,7-diisopropylindene **230** with dibromide **221** under a range of conditions resulted in the recovery of starting material. The inability to alkylate the indenyllithium of **230** is believed to be due the unfavorable steric interactions of the isopropyl group at the C4 and C7 position with the binaphthalene alkylating reagent.

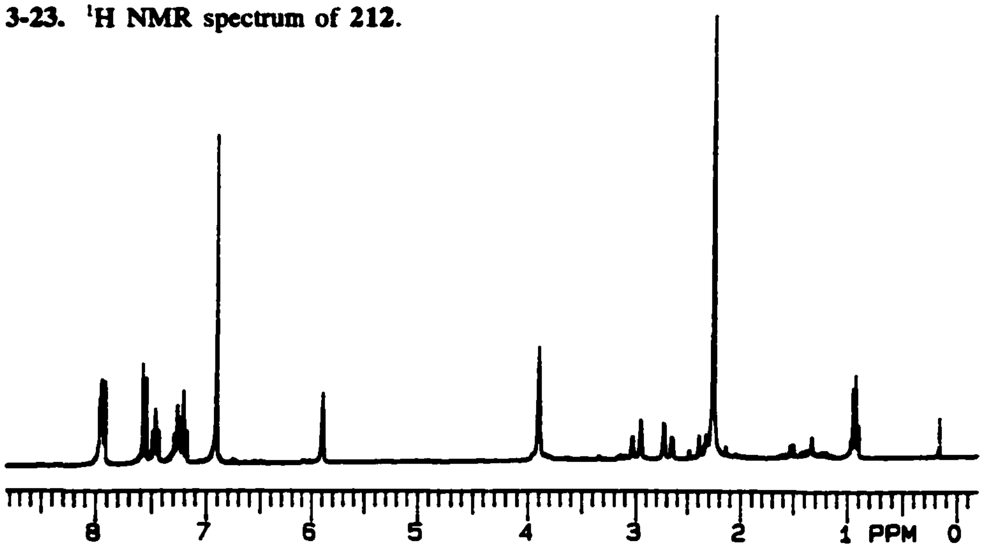
Figure 3-22. Synthesis of the binaphthylene bridged bis(indenes).



rac-**221**, or (S)-**221**

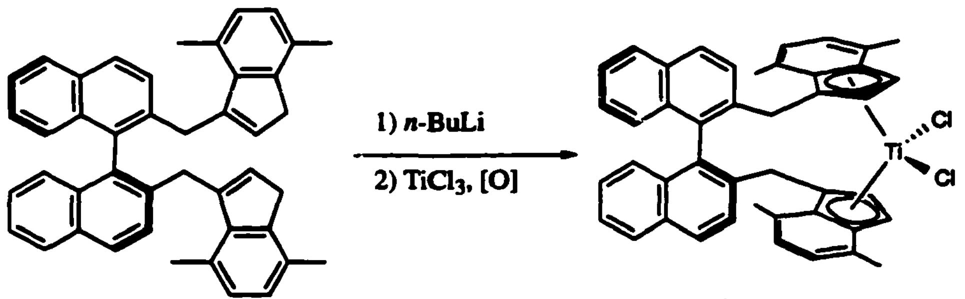
212 R = Me 70%
213 R = *i*-Pr 0%

Figure 3-23. ^1H NMR spectrum of **212**.



Metalation of (S)-(-)-**212** was done by forming the dilithiosalt of **212** with *n*-butyllithium in THF (Figure 3-24). The solution of the dilithio salt was then added to a slurry of titanium trichloride[63a] in THF at -78 °C then refluxed for 5 h. Air oxidation[94] in the presence of 2 N HCl and chloroform afforded crude titanocene (S)-(+)-**232**. Purification of the crude mixture afforded titanocene dichloride (S)-(+)-**232** in 24% yield as a dark green solid. Evidence for the formation of the C_2-symmetrical titanocene dichloride included a characteristic spreading of the ^1H NMR signals for methylene groups on the indenyl moiety from 2.25 and 2.24 ppm to 2.05 and 2.35 ppm, in addition to the simplified ^1H NMR spectrum which ruled out the C_1-symmetrical titanocene dichloride (Figure 3-25).

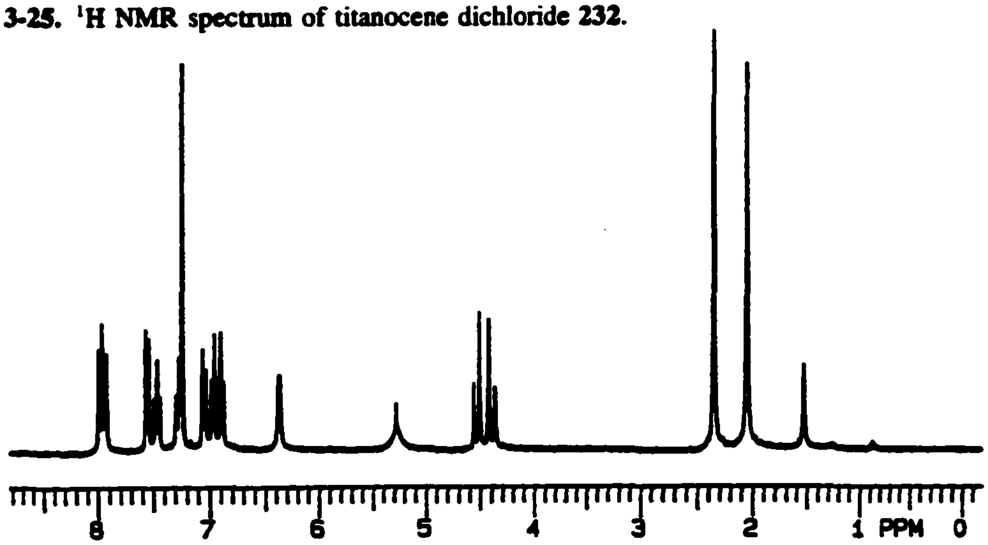
Figure 3-24. Formation of titanocene dichloride **232**.



(S)-(-)-212

(S)-(+)-232
24%

Figure 3-25. ^{1}H NMR spectrum of titanocene dichloride **232**.



Previously metallocene dichlorides containing the binaphthalene bridge were found to be conformationally mobile.[63a] Therefore, titanocene dichloride **232** was expected to be conformationally mobile. Low temperature ^{1}H NMR experiments were done with apparent coalescence occurring at 220 K. However, without the appearance of the signals belonging to the C1-symmetrical conformations the calculation of the energy barrier was not possible (Figure 3-26). Nevertheless, the additional methyl groups on the ligand apparently lowered the activation barrier for the interconversion between the different conformations.

Figure 3-26. Variable temperature ^{1}H NMR spectra of **232**.

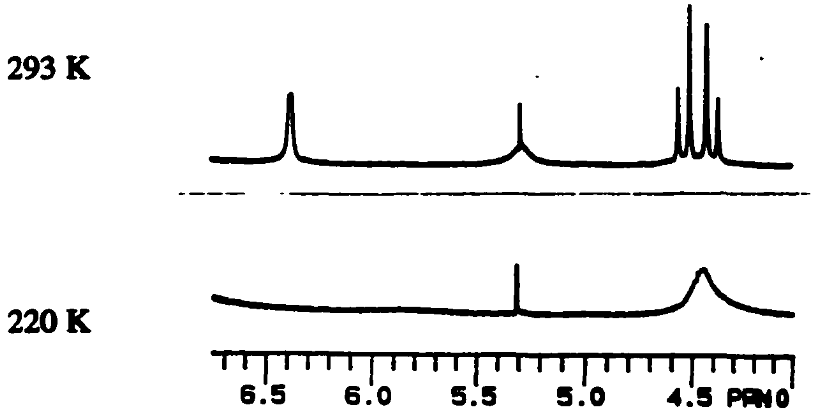
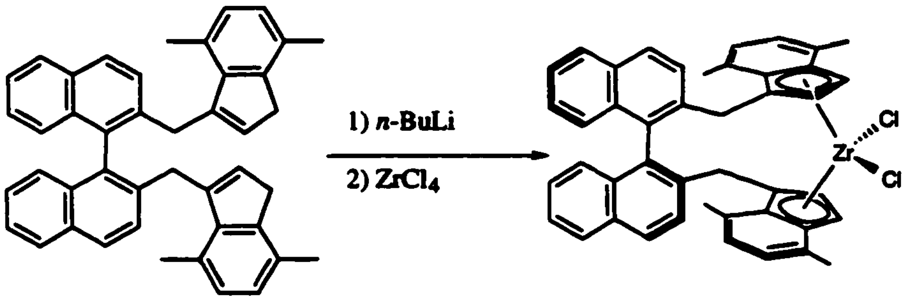


Figure 3-27. Formation of zirconocene dichloride **233**.

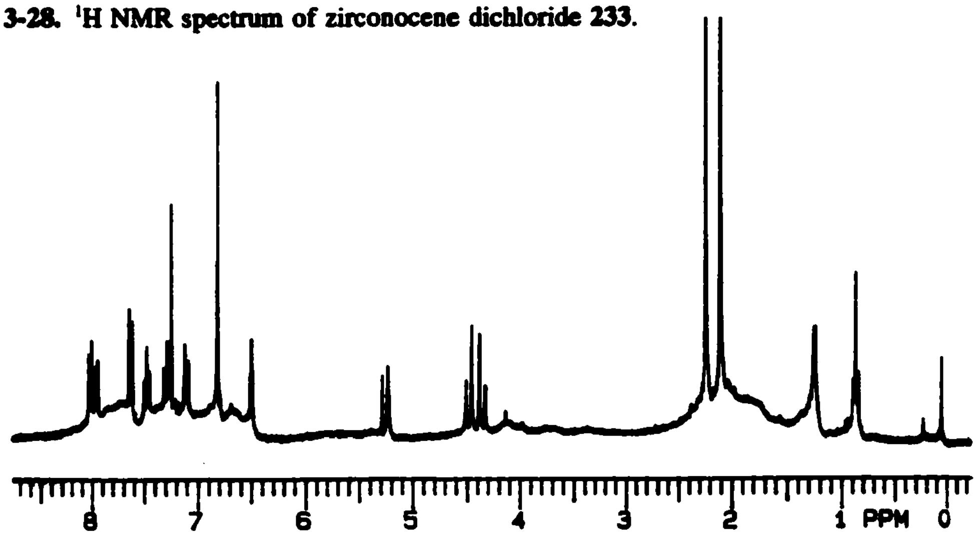


rac-**212**

233
21%

Metalation of the racemic dilithio salt of **212** with zirconium tetrachloride[94] in ether produced a bright yellow zirconocene dichloride **233** (Figure 3-27). Purification of zirconocene **233** afforded the pure product in 21% yield. The product could be identified by the expected shift of the indenyl methyl groups from 2.25 and 2.24 ppm to 2.23 and 2.10 ppm, and appearance of the H-1 and H-2 indenyl signals at 6.49 and 5.23 ppm, respectively (Figure 3-28).

Figure 3-28. ^{1}H NMR spectrum of zirconocene dichloride **233**.



3.7 Conclusion

A convenient synthesis of two new binaphthalene bridged metallocene dichlorides was presented. As shown, methodology currently being used for the introduction of steric bulk to metallocenes with achiral bridges can be applied toward the synthesis of sterically modified *ansa*-bis(indenyl)metal dichlorides with chiral bridging units. This was accomplished through the alkylation of a binaphthalene moiety with dimethylindene. With the two new complexes there are now a number of metallocene complexes covering a range of steric modifications with the same carbon skeleton which can be compared in enantioselective syntheses in the future.

Chapter 4

THE SYNTHESIS AND STRUCTURAL DETERMINATION OF ZIRCONOCENE DICHLORIDES HAVING CONFORMATIONALLY RIGID STRUCTURES AND GEOMETRICALLY *CLOSED* SHAPES

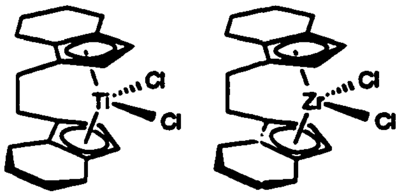
4.1 Introduction

Extensive research continues in an effort to develop metallocene dichlorides with favorable geometric features for stereoselective reactions while maintaining overall reactivity. Chapter 3 discussed the synthetic methodology for obtaining sterically modified *ansa*-metallocene complexes with chiral and achiral bridges. In addition to steric modifications, the modifications of conformational mobility and geometric shape are concerns when developing new metallocene dichlorides. This chapter will concentrate on the strategies used to control the mobility and shape, the synthesis of a new chiral zirconocene dichloride that is conformationally constrained with a closed shape and the structural determination of two zirconocene dichlorides in this class.

4.2 Conformational mobility: Synthesis of conformationally constrained systems

One feature common in most catalysts is the ability to correlate the catalyst structure to the stereochemical outcome of a reaction. However, this is only possible if the catalyst ligands are conformationally restricted. Zirconocene and titanocene dichloride catalysts are no exception. Because of this, semi-rigid and rigid metallocene complexes are desirable and conformationally mobile complexes are undesirable which, as previously discussed, is a drawback of nonbridged Cp and indenyl complexes. However, *ansa*-metallocene dichlorides provide the conformational restraints which make them attractive as potential catalysts.

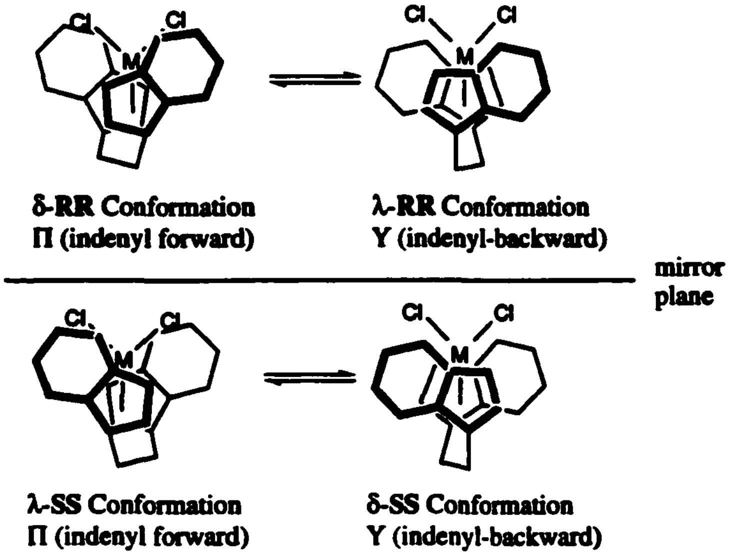
Figure 4-1. Brintzinger's complexes.



94 **8**

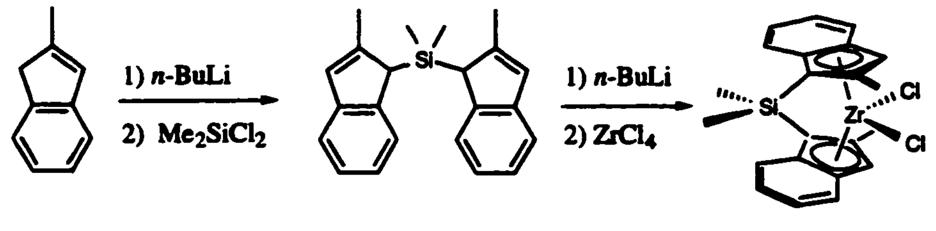
Brintzinger's ethylene bridged bis(tetrahydroindenyl)metal complexes **94**[5] and **8**[7] continue to be intensively tested because these complexes provide defined chiral pockets in addition to the short synthetic pathway to the ligands and metallocenes (Figure 4-1). Although these complexes are bridged, it is known that they are not conformationally constrained as they have been found to fluctuate rapidly between the two conformations through a twisting of the ethano bridge (Figure 4-2).[98] These two conformations have been described by Brintzinger and a number of groups as δ-**RR** and λ-**RR** or δ-**SS** and λ-**SS** in which the δ and λ correspond to the twist in the bridging unit. However, confusion can arise when describing the two conformations since the reflection through a mirror plane reverses the δ and λ designation while the position of the indenyl moieties remains constant. Piccolrovazzi and coworkers have described these conformations with the Greek symbols Π (in front) and Y (behind) to describe the forward or backward positioning of the indenyl moieties.[99]

Figure 4-2. Fluctuation of Brintzinger's complexes.



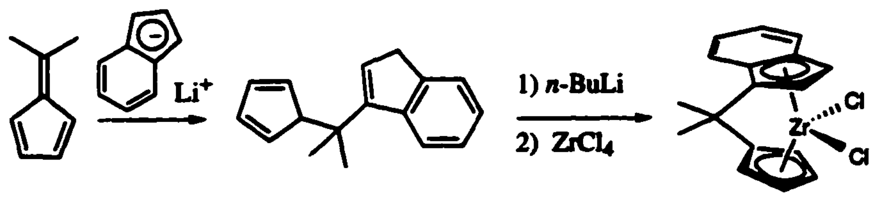
The most common method to further restrict the conformational mobility seen in Brintzinger's complexes has been through the use of single atom bridges. This single atom bridge is often introduced through the alkylation of Me_2SiCl_2 with unsubstituted and substituted indenes and cyclopentadienes (Figure 4-3).[100]

Figure 4-3. Application of dimethylsilane as a bridging unit.



234 **235** **236**

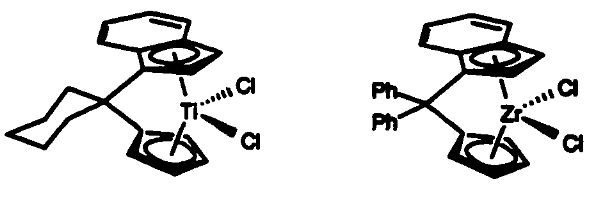
Figure 4-4. Synthesis of an *ansa*-metallocene dichloride with a one carbon bridge.



237 **238** **239**

Another popular approach for synthesizing single atom bridged metallocenes has been used by Green (Figure 4-4).[9] The single carbon bridged metallocene complex **239** was prepared in two steps from indenyllithium and 6,6-dimethylfulvene **237**. A number of groups have used this methodology to synthesize countless metallocene dichlorides with two Cp ligands or a combination of a Cp ligand with a indenyl or fluorenyl ligand. Two

Figure 4-5. Additional examples from fulvene methodology.

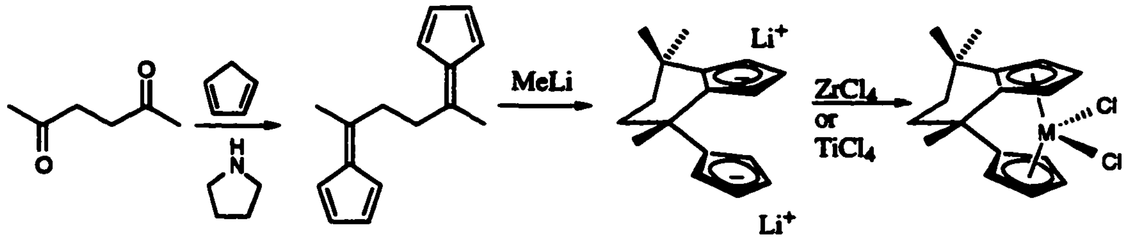


240[101] **241**[9]

additional examples which were synthesized via nucleophilic addition of an anion to a fulvene moiety are shown in Figure 4-5.[9,101]

Two novel routes to rigid *ansa*-bis(Cp)metal complexes were developed using the fulvene strategies. Erker synthesized the first annulated C_1-symmetrical *ansa*-metallocene system seen in Figure 4-6.[97,102] This was accomplished via condensation of two equivalents of Cp with 2,5-hexadione (**231**) to give bis(fulvene) **242**. Fulvene **242** was then treated with 2 equivalents of methyllithium which resulted in the formation of an annulated Cp anion **243**. Dilithio salt **243** could then be metallated with zirconium tetrachloride or titanium tetrachloride to afford the corresponding zirconocene and titanocene dichlorides.

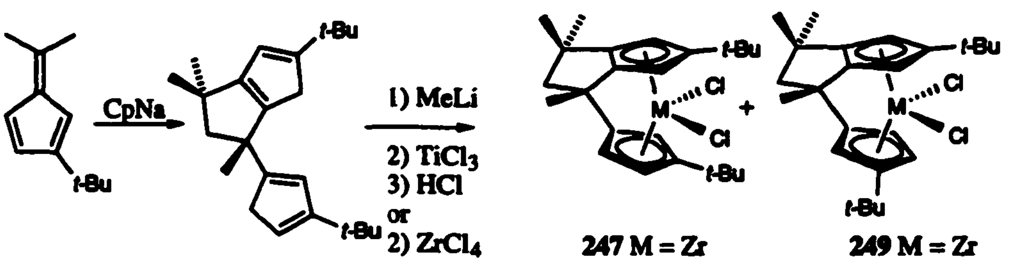
Figure 4-6. The first annulated C_1-bridged *ansa*-bis(Cp)metal dichlorides.



231 **242** **243** **244** M = Zr **245** M = Ti

A similar complex was prepared in one step by Gautheron and Urazowski (Figure 4-7).[103] They demonstrated that substituted fulvene **178** could be condensed with itself in the presence of a catalytic amount of cyclopentadienylsodium to give bridged bis(Cp) **246**.

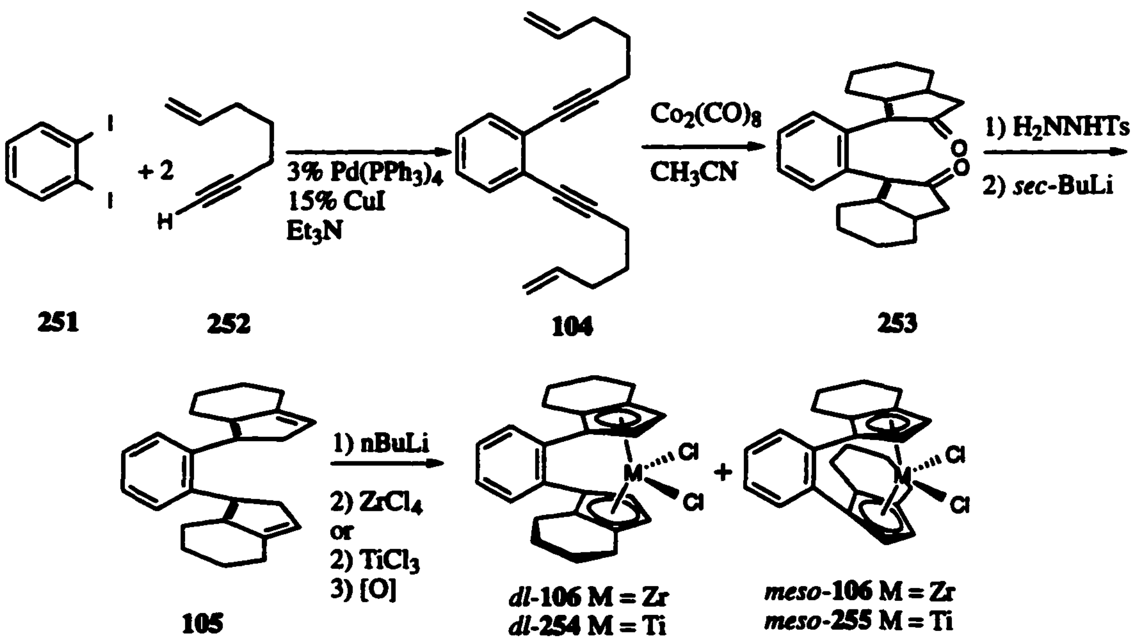
Figure 4-7. Gautheron and Urazowski's synthesis of annulated *ansa*-bis(Cp)metal dichlorides.



178 **246** **247** M = Zr **248** M = Ti **249** M = Zr **250** M = Ti

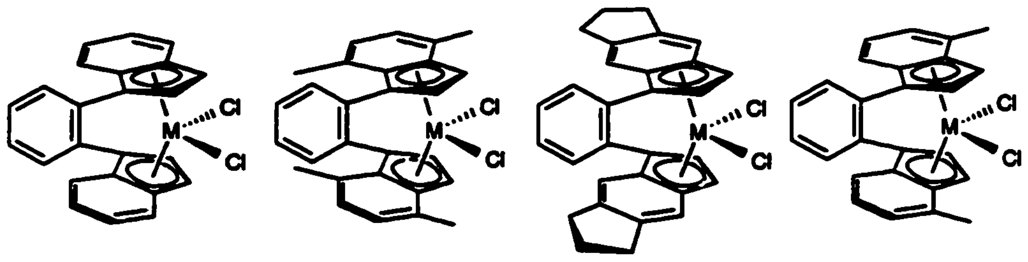
Bis(Cp) **246** was then metallated to afford the two possible diastereomers of the titanocene and zirconocene dichlorides.

Figure 4-8. The first synthesis of *ansa*-metallocene dichlorides with a phenyl bridge.



Two carbon bridged *ansa*-bis(indenyl)metal dichlorides have also addressed the problem of conformational flexibility seen in Brintzinger's complexes. This was accomplished by reverting to a phenyl bridging unit. The first to synthesize a phenyl bridged group 4 metallocene dichloride were Halterman and Ramsey (Figure 4-8).[58] This was carried out by first coupling enyne **252** with 1,2-diiodobenzene in the presence of Pd(PPh$_3$)$_4$ and copper(I)iodide to afford bis(enyne) **104**. The annulated rings were then formed via double Pauson-Khand cyclization to give bis(enone) **253**. Conversion of bis(enone) **253** to the bis(tosylhydrazone) afforded the necessary precursor for Shapiro reduction to phenyl bridged bis(tetrahydroindene) **105**. Subsequent metalation provided the corresponding titanocene dichloride **254** and zirconocene dichloride **106** in which the solid state structure of **254** contained a crystallographic C$_2$-axis equating the two tetrahydroindenyl rings. Halterman and Tretyakov have reported a shorter route to derivatives of these metallocenes (Figure 4-9).[57] The synthesis of these ligands and

Figure 4-9. Other derivatives of the phenyl bridged metallocene dichloride complex.



103 M = Zr
256 M = Ti

110 M = Zr
257 M = Ti

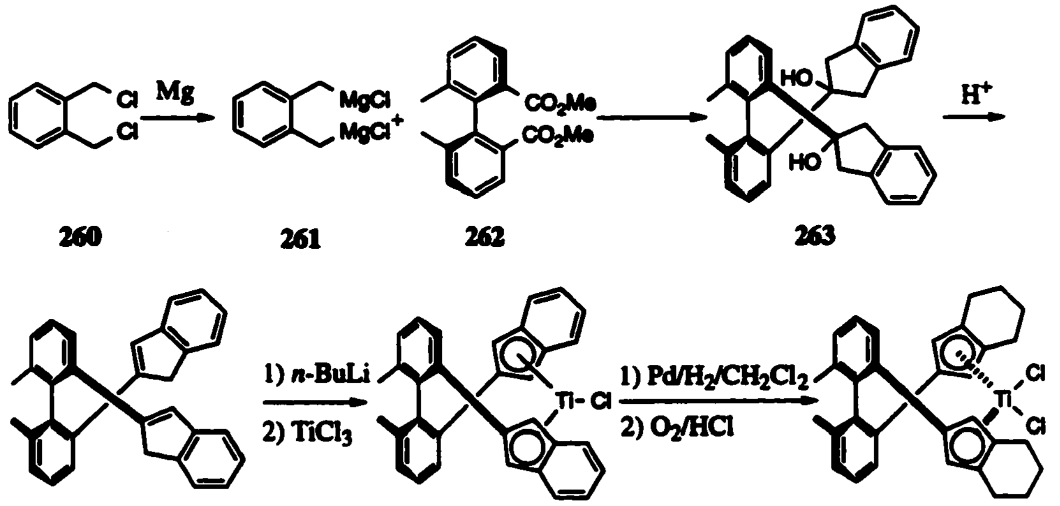
111 M = Zr
258 M = Ti

115 M = Zr
259 M = Ti

metallocene dichlorides were previously discussed in chapter 3. In no case with the phenyl bridged metal complexes was conformational mobility observed in the variable temperature ^{1}H NMR experiments.

Bosnich has prepared several biphenyl bridged metallocene dichlorides which are conformationally rigid despite the longer carbon bridging unit (Figure 4-10).[67] The biphenyl bridge was introduced by reacting Grignard **261** with diester **262**. The resulting diol afforded biphenyl bridged bis(indenyl) **264** after acid catalyzed dehydration. The bis(indene) was then deprotonated with *n*-butyllithium and metallated with titanium trichloride to afford the *ansa*-bis(indenyl)titanium(III) complex **265** which was

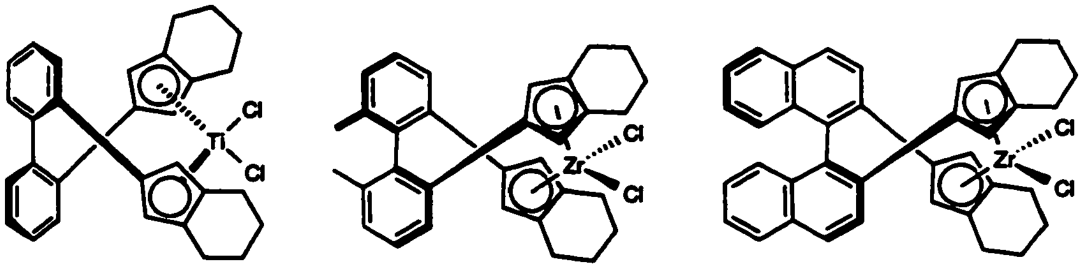
Figure 4-10. Bosnich's synthesis of the biphenyl bridged tetrahydroindenyls.



260 **261** **262** **263**

264 **265** **266**

Figure 4-11. Other biphenyl bridged metallocene dichlorides.

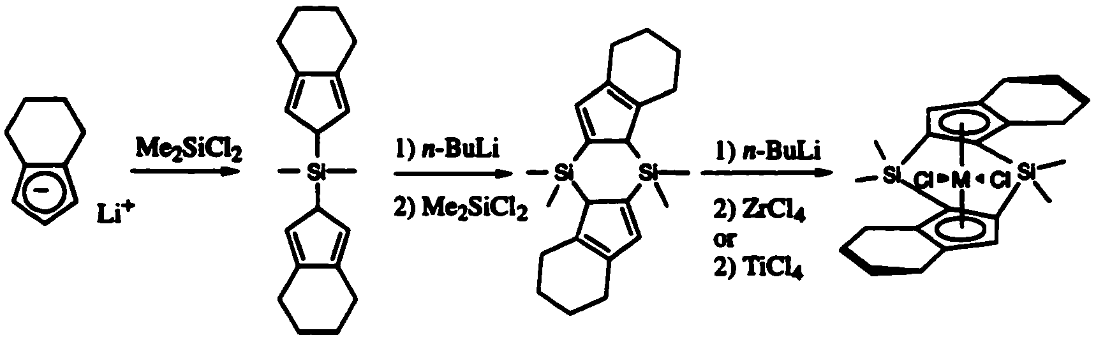


267[67] **121**[67] **268**[66]

hydrogenated and oxidized to give the *ansa*-bis(tetrahydroindenyl)titanium dichloride **266**. Other metallocenes with this type of bridging element are shown in Figure 4-11.[66,67]

Two bridging units have also been employed to create conformationally constrained complexes. Brintzinger accomplished the synthesis and metalation of the bis(dimethylsilanyl)-bridged ligand **271** to afford the first doubly bridged bis(tetrahydroindenyl)metal dichlorides (Figure 4-12).[104] The synthesis began with the treatment of anion **269** with dichlorodimethylsilane to afford dimethylsilane bridged bis(tetrahydroindenyl) ligand **270**. Formation of the dianion and its reaction with dichlorodimethylsilane yielded **271**. The corresponding metallocene dichlorides were prepared from the treatment of **271** with *n*-butyllithium and zirconium tetrachloride or titanium tetrachloride.

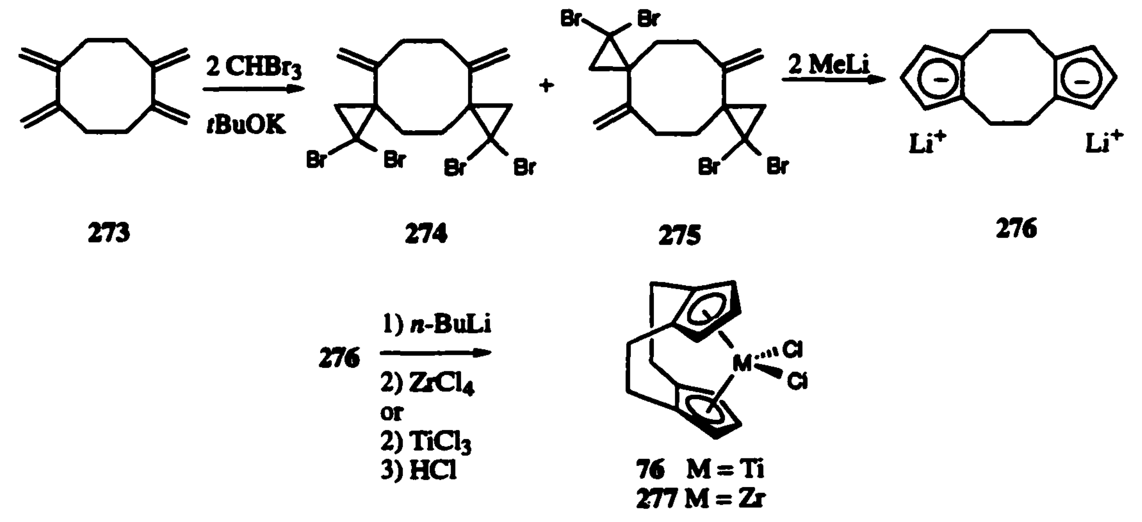
Figure 4-12. Synthesis of Brintzinger's doubly bridged bis(tetrahydroindenyl)metal dichlorides.



269 **270** **271** **272** M = Ti or Zr

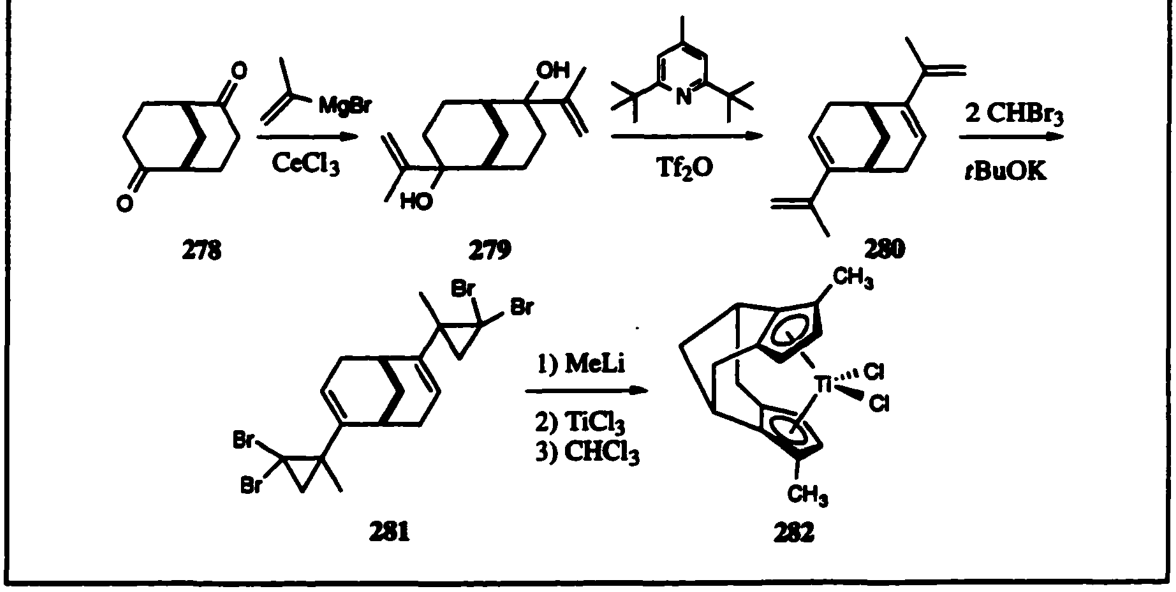
Doubly bridged bis(Cp) **276** had been known for some time.[105] However, group 4 metallocene dichlorides of ligand **276** were not reported until publications by Brintzinger[45] and Hafner[106] in 1995 (Figure 4-13). 1,2,5,6-Tetramethylenecyclooctane **273** was transformed into the tetrabromides **274** and **275** with bromoform and *tert*-butoxide. The tetrabromides **274** and **275** were treated with methyllithium to initiate Skattebøl rearrangement to give bis(Cp) **276**. Bis(Cp) **276** was then metallated with titanium and zirconium to give the corresponding metallocene dichlorides.

Figure 4-13. Synthesis and metalation of doubly bridged Cp **276**.



Chiral doubly bridged metallocene dichloride **282** has been formed through the same Skattebøl rearrangement (Figure 4-14).[105] Buchwald and coworkers began with the addition of a vinyl Grignard to diketone **278** to afford **279**. Treatment of diol **279** with base and triflic anhydride resulted in the formation of olefin **280**. Bis(cyclopropane) **281** was formed upon the reaction of **280** with *tert*-butoxide and bromoform. Bis(cyclopropane) **281** was treated with methyllithium to initiate Skattebøl rearrangement and afforded the desired bis(cyclopentadienyl) which was immediately metallated with titanium trichloride. Subsequent oxidation produced the titanocene dichloride in addition to the monochloro/monobromo- and dibromo titanocenes. Whereas **276** could only give one metallocene dichloride, **282** was formed in low yield which could be due to the diastereotopic faces or to the conformation of the ligand.

Figure 4-14. Buchwald's synthesis of chiral doubly bridged titanocene dichloride.



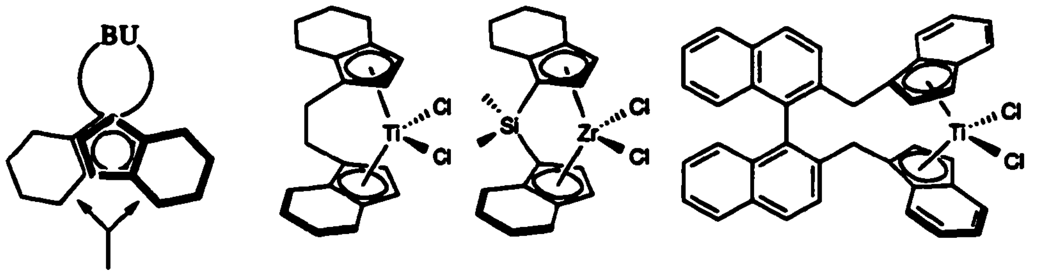
4.3 Conformational shape

The geometric shape of the molecule can have a direct affect on the stereoselectivity as well as the activity of the catalyst since the shape of the molecule will determine the spacial orientation of the directing groups around the metal center. As previously illustrated, the conformational rigidity is directly related to the type of bridging unit. In contrast, the shape of the metallocene dichloride is a function of the position and type of the bridging element, and position and types of substituents. The following sections will introduce methods for controlling the shape of metallocene dichlorides.

4.3.1 Conformationally *open* metallocene dichlorides

Conformational shape of metallocenes will be defined by the dihedral angle between the most forward substituents on the Cp ring. Conformationally "*open*" metallocenes will have a dihedral angle from 60-120° between carbons 3a-4 and 3a'-4' (Figure 4-15). Most

Figure 4-15. Conformationally *open* metallocene dichlorides.



60-120°
Open

94[5]

4[52]

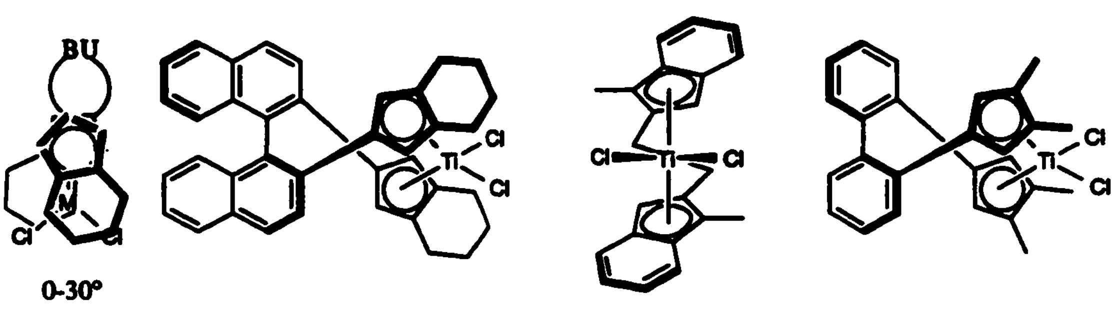
117[63]

ansa-bis(indenyl)titanium or zirconium complexes such as **4**, **94**, and **117** exist in a roughly "*open*" conformation, and are typically bridged through 1-indenyl positions.[5,52,63]

4.3.2 Conformationally *closed* metallocene dichlorides

The dihedral angle between the two most forward substituent on the Cp moiety will also define whether a metallocene dichloride is conformationally *closed*. Metallocenes with conformationally *closed* systems will have a dihedral angle of 0-30° between carbons 3a-4 and 3a'-4' (Figure 4-16). A handful of *ansa*-bis(indenyl)metallocene dichlorides have been synthesized with conformationally *closed* structures.[59,66,107] In contrast to the *open* metallocene dichlorides, conformationally *closed* metallocene dichlorides will have the bridging unit at the 2-indenyl position.

Figure 4-16. Conformationally *closed* metallocene dichlorides.



0-30°
Closed

120[66]

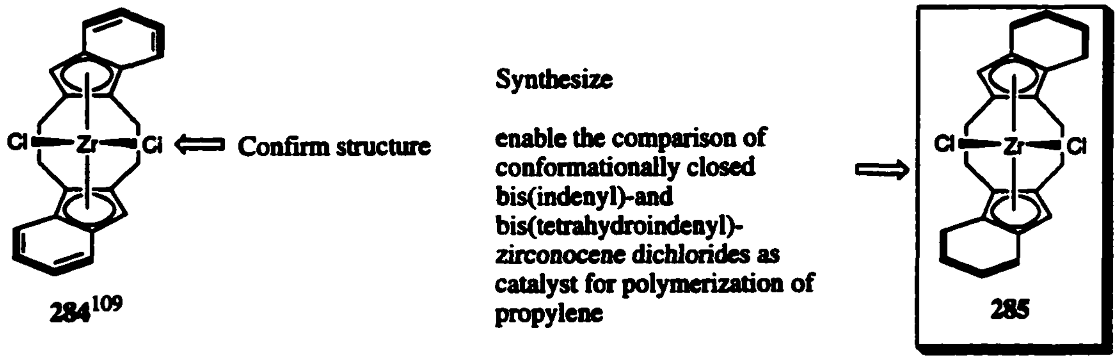
109[59]

283[107]

4.4 Objective

It was reported that closed *ansa*-metallocene dichlorides such as **283** are poor catalysts for the polymerization of propene because of the alkyl groups which are eclipsing one another at the 3-position on the Cp moiety (Figure 4-16).[108] An open question was whether one could increase the steric hinderance through incorporation of an indenyl ring as in **284**[109] while maintaining overall catalyst activity (Figure 4-17). The electronically different tetrahydroindenyl derivative **285** could then be synthesized and used to compare the reactivity difference between metallocene dichlorides **284** and **285**. Therefore, our first objective was to determine the structure of a bis(indenyl)zirconocene dichloride **284** which had been previously synthesized in our group. The second objective was to synthesize the desired bis(tetrahydroindenyl)zirconocene dichloride **285** which would give the needed metallocene dichloride for comparison.

Figure 4-17. Objectives for conformationally *closed* and rigid zirconocene dichlorides.

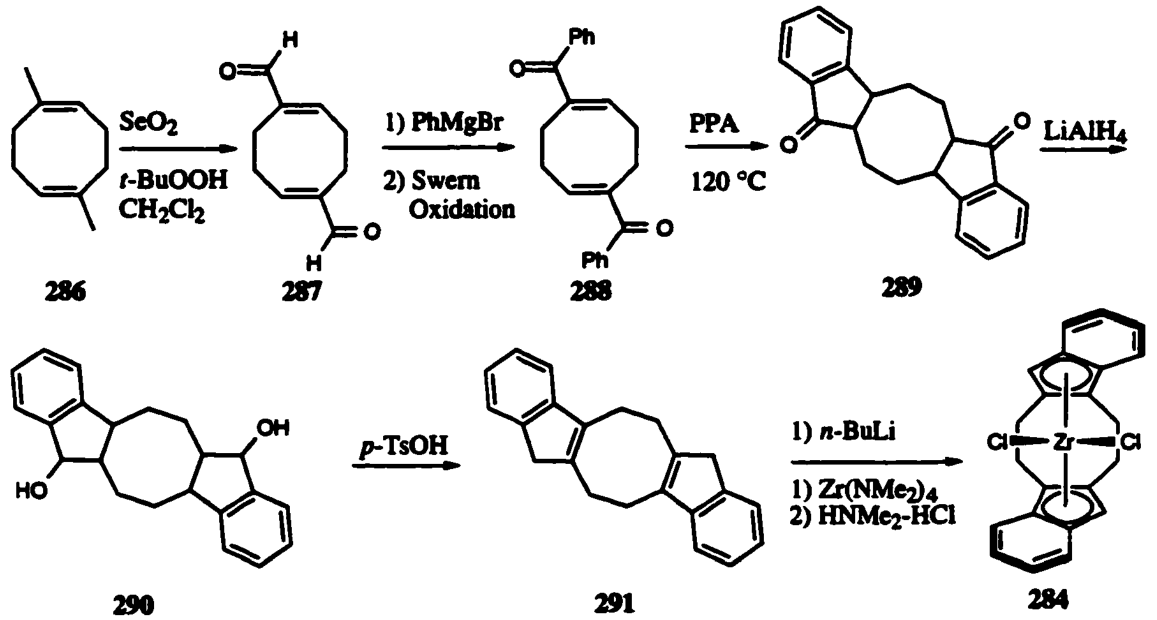


4.5 Structural conformation of doubly bridged bis(indenyl)zirconium dichloride 284, and the synthesis and structural conformation of bis(tetrahydroindenyl)zirconium dichlorides 285

The various routes to doubly bridged bis(indene) **284** have been extensively studied by our group.[57] The outcome of this work has provided an efficient synthesis of doubly bridged bis(indenyl) and doubly bridged bis(indenyl)zirconium dichlorides (Figure 4-17).[109] Treatment of **286** with selenium oxide afforded dialdehyde **287**. Dialdehyde

287 was converted to diketone **288** upon addition of phenylmagnesium chloride and oxidation. Diketone **288** was then cyclized to diketone **289** utilizing PPA to promote Nazarov cyclization.[110] The cyclic ketone was reduced with $LiAlH_4$ to provide diol **290**. The desired doubly bridged bis(indene) **291** was formed via acid catalyzed dehydration of diol **290** with *p*-toluene sulfonic acid. Metalation of bis(indene) **291** was done with tetrakis(dimethylamido)zirconium followed by treatment dimethylammonium chloride to yield zirconocene **284** as a bright yellow solid.

Figure 4-18. Synthesis of doubly bridged bis(indenyl)zirconium dichloride **284**.



Crystals of zirconocene dichloride **284** suitable for X-ray diffraction were grown at 0° C by diffusion of hexane into a methylene chloride solution of **284**. The solid state structure of **284** was solved as described in Table 4-1. ORTEP views of **284** are shown in Figure 4-18. The conformationally closed shape is clearly seen from top ORTEP view of zirconocene dichloride **284**. The Zr(1)-Cp_{cent}(1) and Zr(1)-Cp_{cent}(2) bond lengths are 2.219 Å and 2.218 Å, respectively. The Zr(1)-Cl(1) and Zr(2)-Cl(2) bond lengths are relatively uniform as they are 2.428 Å and 2.436 Å, respectively. The zirconium-carbon bonds of the Cp range from 2.42 Å to 2.60 Å. The Cp_{cent}-Zr-Cp_{cent} is 120.2° putting this angle at the lower end of the spectra for reported Cp_{cent}-Zr-Cp_{cent} bond angles. A summary of selected bond lengths and angles are given in Table 4-2.

Table 4-1. Crystal Data and Structure Refinement for 284.

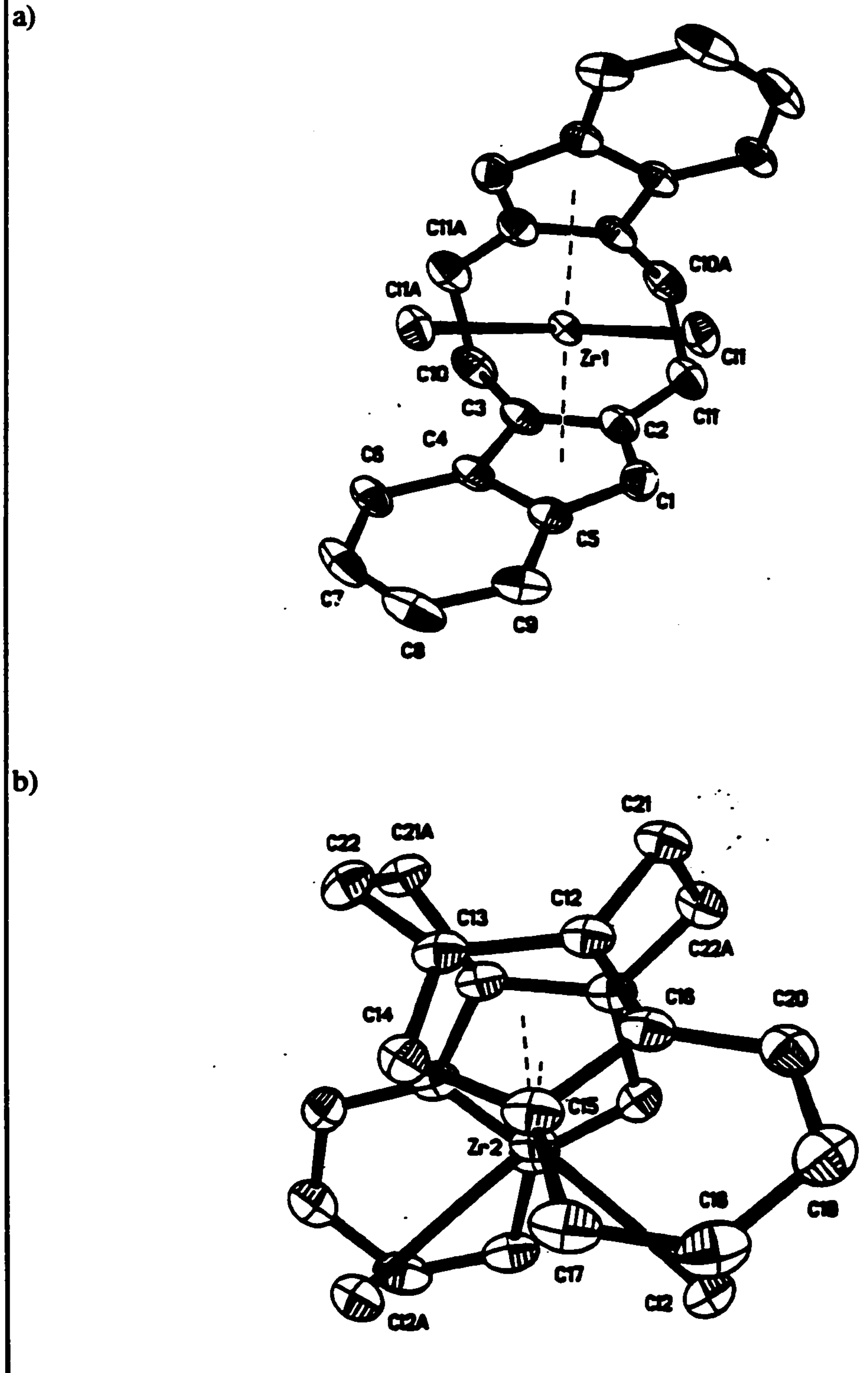
Identification code	rho3c
Empirical formula	$C_{22}H_{18}Cl_2Zr$
FW	444.48
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*P2/c*
Unit cell dimensions	a = 13.656(3) Å
	b = 11.374(2) Å
	c = 12.085(2) Å
	α = 90°
	β = 109.44(3)°
	γ = 90°
V, Z	1770.1(6) $Å^3$, 4
Density (calc)	1.668 Mg/m^3
Abs Coeff	0.924 mm^{-1}
F(000)	896
Crystal size	0.14 x 0.16 x 0.42 mm
θ range for data collection	1.58-25.00°
Limiting indices	$-16 \leq h \leq 15$, $-13 \leq k \leq 13$, $-1 \leq l \leq 14$
No. of reflections collected	3743
No. of independent reflections	3112 (R(int) = 0.0386)
Abs corr	semi-empirical from ψ scans
Max. and min. transmissions	0.3231 and 0.1933
Refinement method	full-matrix least squares of F^2
No. of data/restraints/parameters	3105/0/299
Goodness of fit on F^2	1.057
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0294, wR2 = 0.0667
R indices (all data)	R1 = 0.0446, wR2 = 0.0774
Largest difference peak and hole	+0.373 and -0.476 e/$Å^3$

Table 4-2. Selected bond lengths (Å) and angles (deg) for 284.

Zr(1)-Cl(1)	2.4283(8)	Zr(2)-Cl(2)	2.4355(9)
Zr(1)-Cp_{cent}(1)	2.219(3)	Zr(2)-Cp_{cent}(2)	2.218(3)
Zr(1)-C(1)	2.481(3)	Zr(2)-C(12)	2.493(3)
Zr(1)-C(2)	2.470(3)	Zr(2)-C(13)	2.472(3)
Zr(1)-C(3)	2.500(3)	Zr(2)-C(14)	2.493(3)
Zr(1)-C(4)	2.601(3)	Zr(2)-C(15)	2.586(3)
Zr(1)-C(5)	2.423(4)	Zr(2)-C(16)	2.593(3)

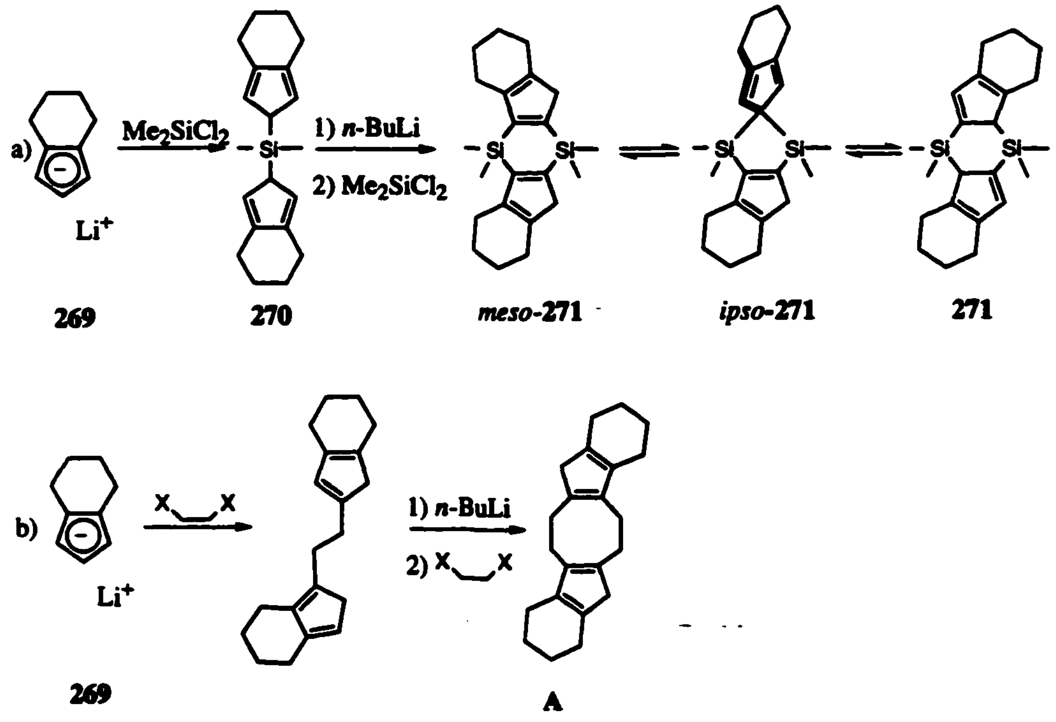
Cl(1)-Zr(1)-Cl(1')	93.88(4)
Cp_{cent}(1)-Zr(1)-Cp_{cent}(1')	120.2(1)
Cl(2)-Zr(2)-Cl(2')	96.43(4)
Cp_{cent}(2)-Zr(1)-Cp_{cent}(2')	120.4(1)

Figure 4-19. ORTEP plots of zirconocene dichloride **284** (a) Front view (b) Top view.



Since the stepwise alkylation of two equivalents of Cp **269** with two equivalents of Me_2SiCl_2 to obtain doubly bridged ligand **271** is known, one could imagine acquiring doubly bridged ligand **A** through a similar synthetic route (Figure 4-20).[104] However, the ability for silicon to undergo facile silatropic shifts allows for the formation of the desired ligand and removes the need for a selective alkylation. On the other hand, the corresponding rearrangement is not as facile with carbon changes which would require the desired ligand to be made through two selective alkylation of a disubstituted Cp with 1,2-dibromoethane or an equivalent ethylene unit which is unprecedented.

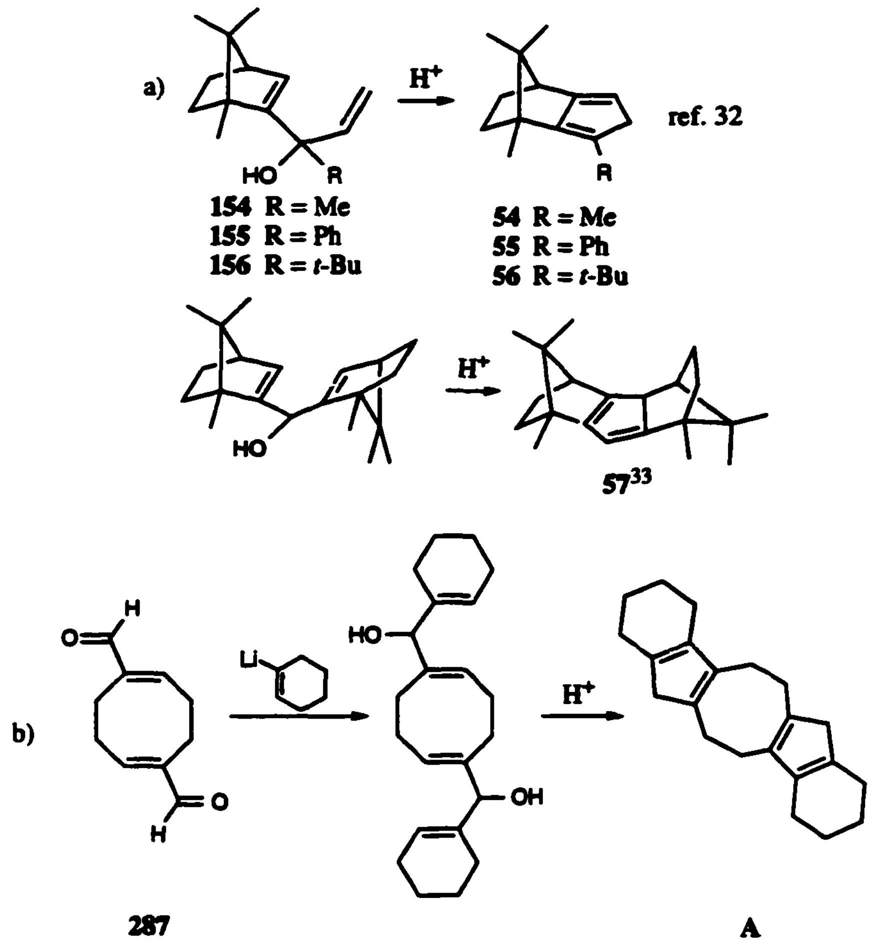
Figure 4-20. Direct bridging of the two cyclopentadienyl ligands.



It has been demonstrated that the Nazarov cyclization gives in excellent yield Cp ligands from the corresponding bis(allylic) alcohols (Figure 4-21).[32,33] Therefore, **A** could be obtained from the addition of vinyl anion to dialdehyde **269** to give the bis(allylic)alcohol. Treatment of bis(allylic)alcohol with acid could give the desired ligand. However, work done by J. Chang[111] and A. Tretyakov[57] have shown that a double

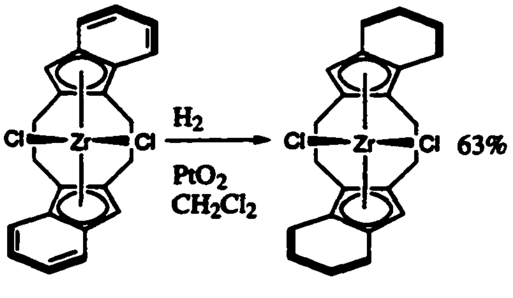
Nazarov cyclization which affords two Cp moieties leads to undesired intramolecular reactions and no sign of the desired product.

Figure 4-21. a) Known Nazarov cyclization b) Potential Nazarov cyclization.



A number of groups have hydrogenated the indenyl double bonds on the metallocene dichloride to acquire the *ansa*-bis(tetrahydroindenyl)metal dichlorides.[5,65,67] We have adopted this methodology toward the preparation of doubly bridged zirconocene **285** (Figure 4-22). Treatment of **284** for 12 h at 1100 psi hydrogen in the presence of catalytic PtO_2 at room temperature afforded bis(tetahydroindenyl)zirconium dichloride **285** as a white solid in 63% yield after trituration with hexanes.

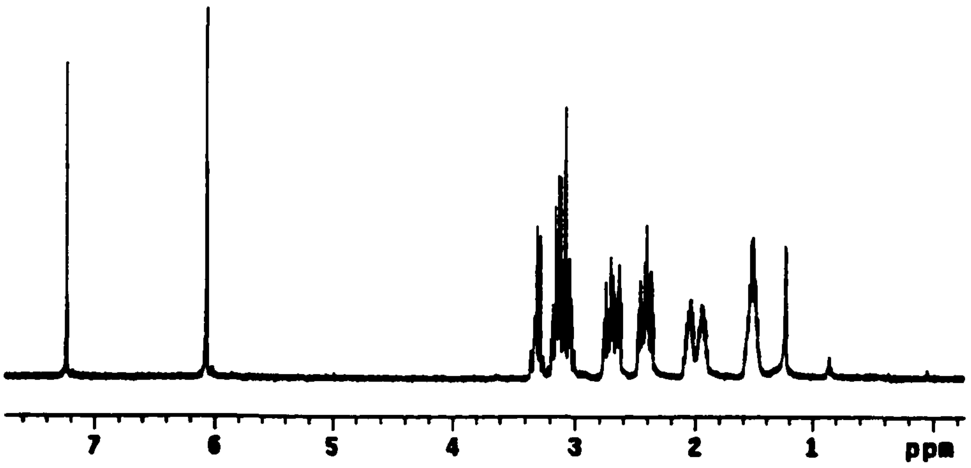
Figure 4-22. Hydrogenation of zirconocene dichloride 285.



284 **285**

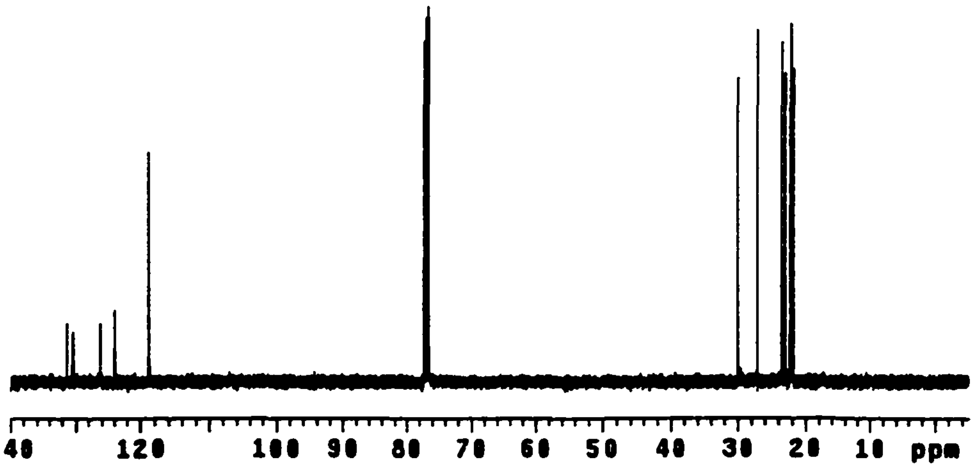
Evidence for the formation of **285** included the appearance of the methylene signals in the ^{1}H NMR spectrum at 3.00-3.40 and 1.40-2.10 ppm, and a shift in the cyclopentadienyl signals from 6.56 to 6.07 ppm (Figure 4-23 and 4-24). In addition, the phenyl proton signals in the ^{1}H NMR spectrum and the sp^{2} carbon signals in the ^{13}C NMR spectrum had disappeared.

Figure 4-23. ^{1}H NMR spectrum of zirconocene dichloride **285**.



Crystals suitable for X-ray analysis were obtained by the slow evaporation of methylene chloride from a solution of **285** and methylene chloride at room temperature. Details of the crystal data and refinement are given in Table 4-3. ORTEP plots of two views of **285** are illustrated in Figure 4-22. The presence of the tetrahydroindenyl moiety is evidenced by the longer bond lengths between C6-C7 (1.47 Å) C8-C9 (1.57Å), C19-

Figure 4-21. ^{13}C NMR spectrum of zirconocene dichloride **285**.



C20 (1.57 Å) and C21-C22 (1.48 Å) in addition to the puckering of these rings. As seen from the top view of the ORTEP plot zirconocene **285** is definitely closed. A summary of selected bond lengths and angles are given in Table 4-4.

Table 4-3. Crystal Data and Structure Refinement for 285.

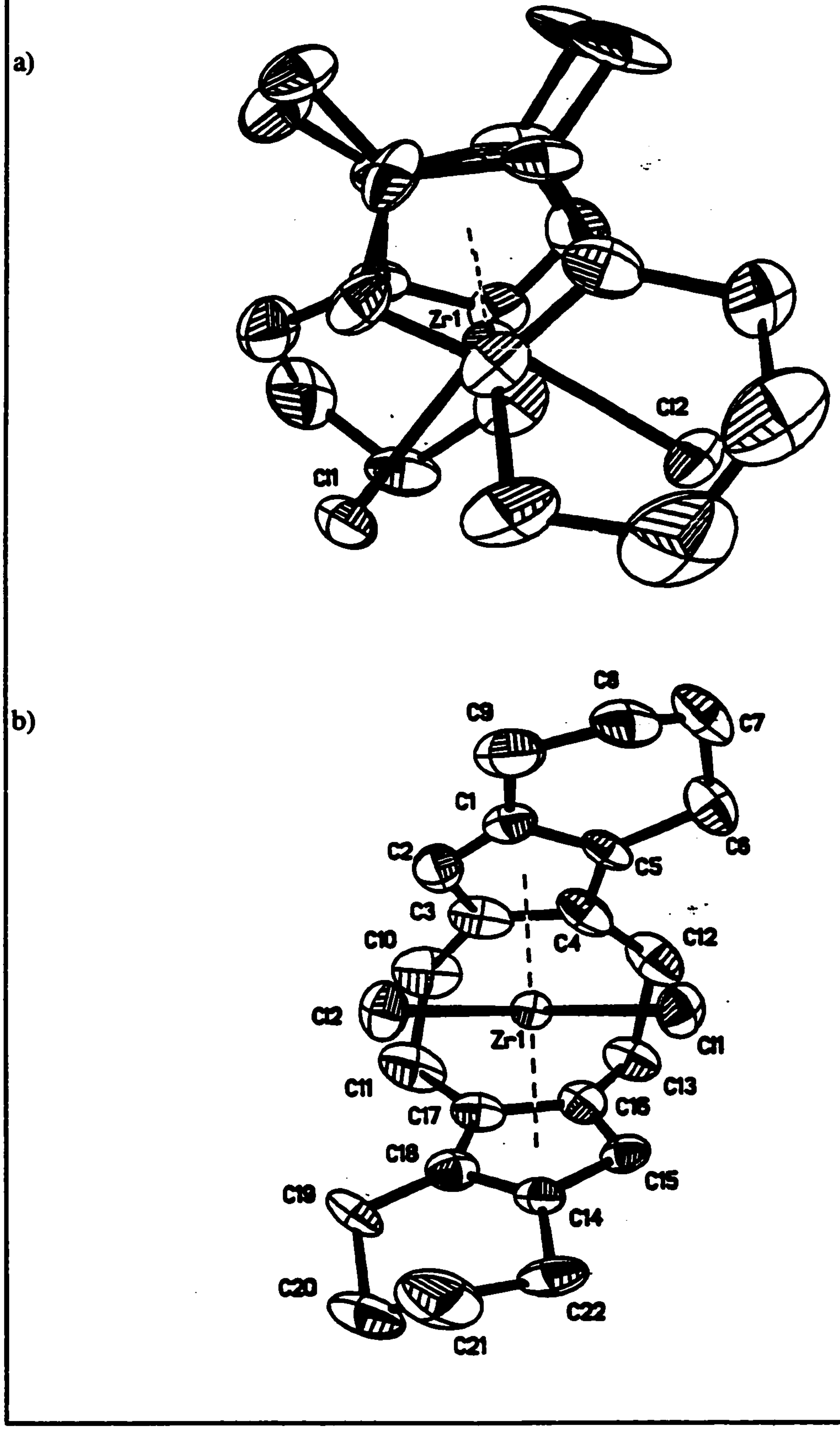
Identification code	rho9c
Empirical formula	$C_{22}H_{26}Cl_2Zr$
FW	452.55
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*Cc*
Unit cell dimensions	*a* = 17.8133(13) Å
	b = 8.2390(2) Å
	c = 13.9927(7) Å
	$\alpha = 90°$
	$\beta = 108.992(3)°$
	$\gamma = 90°$
V, Z	1941.8(2) $Å^3$, 4
Density (calc)	1.548 Mg/m^3
Abs Coeff	0.844 mm^{-1}
F(000)	928
Crystal size	0.46 x 0.38 x 0.40 mm
θ range for data collection	2.42-28.00°
Limiting indices	$-21 \leq h \leq 23$, $-1 \leq k \leq 10$, $-18 \leq l \leq 17$
No. of reflections collected	4517
No. of independent reflections	4241 (R(int) = 0.0383)
Abs corr	semi-empirical from ψ scans
Max. and min. transmissions	0.5464 and 0.4014
Refinement method	full-matrix least squares of F^2
No. of data/restraints/parameters	4229/2/228
Goodness of fit on F^2	1.033
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0301, wR2 = 0.0768
R indices (all data)	R1 = 0.0316, wR2 = 0.0816
Largest difference peak and hole	+0.630 and -0.553 e/ $Å^3$

Table 4-4. Selected bond lengths (Å) and angles (deg) for 285.

Zr(1)-Cl(1)	2.439(2)	Zr(1)-Cl(2)	2.442(2)
Zr(1)-Cp_{cent}(1)	2.189(3)	Zr(1)-Cp_{cent}(2)	2.2193(3)
C(6)-C(7)	1.471(14)	C(8)-C(9)	1.570(11)
C(19)-C(20)	1.566(13)	C(21)-C(22)	1.476(14)

Cl(1)-Zr(1)-Cl(2)	96.30(2)
Cp_{cent}(1)-Zr(1)-Cp_{cent}(2)	121.2(2)

Figure 4-25. ORTEP plots of zirconocene dichloride **285** (a) Top view (b) Front view.



4.6 Conclusion

The synthesis of *ansa*-bis(indenyl)zirconocium dichloride **285** was accomplished and the structures of *ansa*-bis(indenyl)zirconcium dichlorides **284** and **285** were determined by X-ray diffraction. Zirconocene dichlorides **284** and **285** allows for the direct comparison of chiral rigid conformationally closed bis(indenyl)- and bis(tetrahydroindenyl)metal complexes. Future studies on the reactivity of these complexes as polymerization catalysts as well as catalysts in applications, such as those discussed in chapter 2, should shed light on the reactivity differences between geometrally *closed* bis(indenyl)- and bis(tetrahydroindenyl)zirconium dichlorides.

Chapter 5

THE SYNTHESIS OF GEOMETRICALLY *VERY OPEN* METALLOCENE DICHLORIDES AND THEIR CP_{CENT}-METAL-CP_{CENT} BOND ANGLES

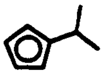
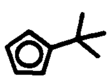
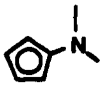
5.1 Introduction

Chapters 3 and 4 provided background on current methodologies for varying the steric hinderance around the metal center, conformational mobility, and geometric shape of Group 4 metallocene dichiorides. These modifications can have an impact on the metallocene dichloride structure other than the changes taking place on the environment around the metal center. Often subtle changes to the ligand can have profound effects on the metal center which in turn can alter the chemical reactivity of the catalyst. This chapter will provide information on the effects of various substituents and the bridging unit on the metal center, namely the Cp_{cent}-M-Cp_{cent} bond angle (Cp_{cent} = cyclopentadienyl centroid, M = metal) which vary from 115.9 to 138° for zirconocene dichlorides and 120.9 to 137.5° for titanocene dichlorides. In addition, the synthesis of novel Group 4 metallocene dichlorides with very open geometric shapes and their Cp_{cent}-M-Cp_{cent} bond angles will be discussed.

5.2 Titanocene and zirconocene dichlorides with two Cp or two monosubstituted Cp ligands

Nonbridged Cp ligands with no or one substituent provide a few interesting trends or lack of a trend (Table 5-1). The first pattern is seen upon the comparison of the corresponding titanocene and zirconocene with the same Cp ligands. In all cases the Cp_{cent}-Ti-Cp_{cent} bond angle is significantly greater than the Cp_{cent}-Zr-Cp_{cent} bond angle. This is likely due to the shorter Cp-Ti bond length which brings the two Cp units closer together,

Table 5-1. Cp_{cent}-M-Cp_{cent} bond angle of monosubstituted Cp's.

Cp	M	Cp_{cent}-M-Cp_{cent} (deg)		Ref. #
	**286** M = Ti	130.9		112
	125 M = Zr		128.3	113
	**287** M = Ti	130.2		114
	288 M = Zr		128.8	115
	**289** M = Ti	132.9		116
	290 M = Zr		129.7	117
	**291** M = Ti	131.5		118
	292 M = Zr		128.6	118
	**293** M = Ti	131.0		119[a]
	294 M = Zr		129.1	120[a]
	**295** M = Ti	133.6		121[a]

a = results from Cambridge data search, only partial references available

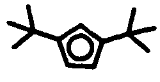
thus, causing an increase in the steric interactions between the Cp ligands. As a result the Cp ligands spread apart and lead to an increase in the Cp_{cent}-Ti-Cp_{cent} bond angle.

This would lead one to believe that the sterically larger groups would cause a further increase in these bond angles (Table 5-1). However, the Cp_{cent}-Ti-Cp_{cent} and Cp_{cent}-Zr-Cp_{cent} bond angles for the *tert*-butyl-substituted Cp's are 131.5° and 128.6°, respectively, while the corresponding unsubstituted Cp complexes are nearly identical (Ti: 132.2°, Zr: 128.3°). This is due to the ability of the Cp to rotate about the metal bond so that the substituents are orientated to minimize the steric interactions between the larger alkyl groups without the need for displacement of the ligands. Electronic effects could be a factor in the Cp_{cent}-M-Cp_{cent} bond angle. As the electron donating capability increases(R_2 > alkyl and R_3Si > alkyl) the Cp_{cent}-Ti-Cp_{cent} bond angle changes very little when comparing entry **291** (131.5°) with **293** (131.0°), and **289** (132.9°) with **295** (133.6°). The data suggests that the electron donating character has little effect on the Cp_{cent}-Ti-Cp_{cent} bond angle.

5.3 Titanocene and zirconocene dichlorides with two 1,3-disubstituted or two polysubstituted Cp ligands

The steric size of the alkyl groups have effects on the Cp_{cent}-M-Cp_{cent} bond angle since the Cp ligands could rotate to position the larger alkyl groups away from one another. This would be less likely to occur as the number of substituents on the Cp ligand increases. As seen in Table 5-2, metallocene dichlorides with 1,3-disubstituted Cp ligands have a Cp_{cent}-Ti-Cp_{cent} bond angle between 130-131° and a Cp_{cent}-Zr-Cp_{cent} bond angle between 129-131° which are again not significantly different from those of the unsubstituted or monosubstituted bis(Cp)metal complexes (Ti: 131-132°, Zr: 128-131°). This suggests the 1,3-substitutents are still being positioned so that the steric interactions between the alkyl groups is minimized.

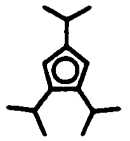
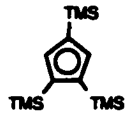
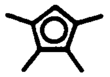
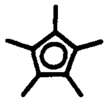
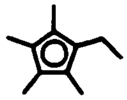
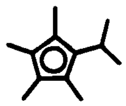
Table 5-2. 1,3-Disubstituted ligands and their effect on the Cp_{cent}-M-Cp_{cent} bond angles.

Cp	M	Cp_{cent}-M-Cp_{cent} (deg)	Ref. #
	**296** M = Ti	131.0	122[a]
	**297** M = Ti	132.2	123
	298 M = Zr	129.7[b]	124
	**299** M = Zr	130.8	125

a = results from Cambridge data search, only partial reference available
b = Cp_{cent}-M-Cp_{cent} bond angles provided by Cambridge data search

However, as the number of substituents increase to three and four the Cp_{cent}-Zr-Cp_{cent} bond angle begins to increase to 134.1°, 135.4°, and 133.1° for entries **300**, **301**, and **302**, respectively (Table 5-3). An even greater increase is seen with the pentasubstituted Cp's whose Cp_{cent}-M-Cp_{cent} bond angles approach 137-138° for both the titanocene and zirconocene dichlorides.

Table 5-3. Highly substituted Cp's and the effect on the Cp_{cent}-M-Cp_{cent} bond angles.

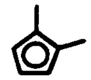
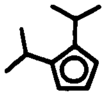
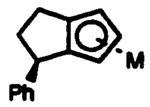
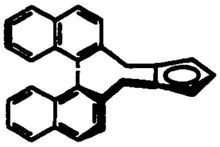
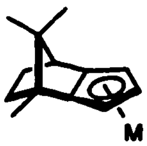
Cp	M	Cp_{cent}-M-Cp_{cent} (deg)	Ref. #
	**300** M = Zr	134.1[a]	126
	**301** M = Zr	135.4	127
	**302** M = Zr	133.1	128
	**303** M = Ti	137.5	129
	**304** M = Zr	136.8	130
	**305** M = Zr	137.4	131

a = Cp_{cent}-M-Cp_{cent} bond angles provided by Cambridge data search

5.4 Titanocene and zirconocene dichlorides with two 1,2-disubstituted or two fused Cp ligands

Cp ligands with 1,2-disubstituted alkyls include the fused Cp ligands which are of special interest since many fused Cp's are enantiomerically pure (Table 5-4). Although the substituents fused to the Cp moiety are often quite bulky such as the binaphthalene fused Cp **66**, the Cp_{cent}-M-Cp_{cent} bond angles are quite small as they range from 131-132° for

Table 5-4. 1,2-Alkyl-substituted Cp's and their effect on Cp_{cent}-M-Cp_{cent} bond angles.

Cp	M	Cp_{cent}-M-Cp_{cent} (deg)	Ref. #
	**306** M = Ti	132.7	132
	**307** M = Zr	128.4^a	133
	**23** M = Ti	131.0	17
	**61** M = Ti	132.2^a	35b
	**66** M = Ti	132.2^a	36b
	**308** M = Ti	131.0	31a
	309 M = Zr	129.0	31a
	**312** M = Zr	129.0	28

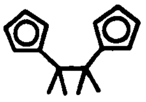
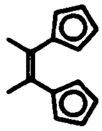
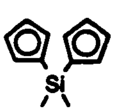
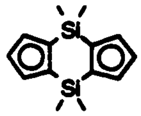
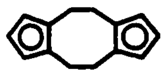
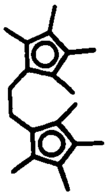
a = Cp_{cent}-M-Cp_{cent} bond angles provided by Cambridge data search

titanocene dichlorides and 128-129° for zirconocene dichlorides. The angles are quite similar to the angles found for the mono- and 1,3-disubstituted Cp metal complexes.

5.5 *ansa*-Bis(Cp)titanium and -zirconium dichlorides

Carbon and silicon bridging units were originally introduces to prevent the rotation of the Cp rings around the metal center. In addition to this, the bridging unit can have significant effects on the Cp_{cent}-M-Cp_{cent} bond angle. Incorporation of two carbon bridging unit leads to Cp_{cent}-M-Cp_{cent} bond angles between 128-129° even in the case where the sp^3 hybridized carbons were replaced with two sp^2 hybridized carbons, as seen in entries **71** and **312**. Single carbon bridging units have greatly reduced Cp_{cent}-M-Cp_{cent} bond angles for both the titanocene dichloride **74** (120.9°) and zirconocene dichloride **313** (115.9°), as would be expected from the smaller bridging unit. On the other hand, silicon bridged bis(Cp)complex **75** (128.9°) has a Cp_{cent}-Ti-Cp_{cent} bond angle closer to that of the two carbon bridged complex **71**. This is most likely due to the longer bond length between the silicon and carbon of the Cp ring, and its ability to accommodate the higher Cp_{cent}-M-Cp_{cent} bond angles when compared to the single carbon bridged complexes. Suprisingly, metallocene dichlorides with two ethylene or two dimethylsilane bridges have greatly reduced bond angles which range from 124-126° for the corresponding titnanocene dichlorides and 120-121° for the zirconocene dichlorides. Like the highly substituted nonbridged Cp's there appears to be an increase in the Cp_{cent}-M-Cp_{cent} bond angles when highly substituted Cp's are bridged as seen with entries **317** (131.0°) and **318** (127.0°).

Table 5-5. Bridging unit effect on the Cp_{cent}-M-Cp_{cent} bond angle.

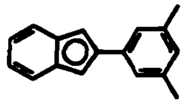
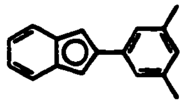
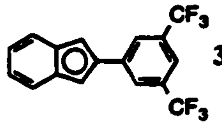
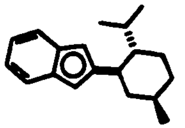
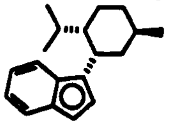
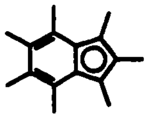
Cp	M	Cp_{cent}-M-Cp_{cent} (deg)	Ref. #
	**71** M = Ti	128.3	134
	**312** M = Ti	128.1	135
	**74** M = Ti	120.9	43b
	313 M = Zr	115.9	43b
	**75** M = Ti	128.9	136
	314 M = Zr	125.4	136
	**315** M = Ti	126.0	137
	316 M = Zr	120.6	137
	**76** M = Ti	124.5	45
	277 M = Zr	120.0	45
	**317** M = Ti	131.0	138
	318 M = Zr	127.0	138

5.5 Nonbridged bis(indenyl)titanium and -zirconium dichlorides

Since a monosubstituted indenyl ligand is essentially a trisubstituted Cp ligands, the Cp_{cent}-M-Cp_{cent} bond angles should be similar to that of the 1,2,4-trisubstituted Cp Ligand (Table 5-6). This is not the case with the bis(indenyl)zirconium complexes (entries **319-323**) which have slightly smaller Cp_{cent}-Zr-Cp_{cent} bond angles. This smaller Cp_{cent}-Zr-Cp_{cent} bond angle is likely due to the sterically less bulky sp^2 carbons at the 4- and 7-

indenyl positions which would not have the same steric interactions as sp^3 carbons. Like the Cp ligands, highly substituted indenyl ligands such as bis(pentamethylindenyl)zirconocene dichloride **324** have Cp$_{cent}$-Zr-Cp$_{cent}$ bond angles between 136-138°.

Table 5-6. Substitution effects on the Cp$_{cent}$-M-Cp$_{cent}$ bond angle in bis(indenyl)metal complexes.

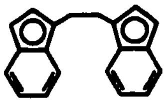
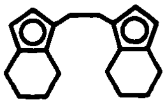
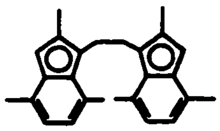
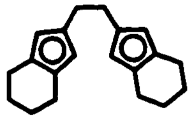
Indenyl	M	Cp$_{cent}$-M-Cp$_{cent}$ (deg)	Ref. #
	**319** M = Zr	131.2^a	139
	**320** M = Zr	130.1^a	140
	**321** M = Zr	130.9^a	140
	**322** M = Zr	135.4	141
	**323** M = Zr (C_2-symmetric)	128.8	25
	**324** M = Zr	138.3^a	142

a = Cp$_{cent}$-M-Cp$_{cent}$ bond angles provided by Cambridge data search

5.7 *ansa*-Bis(indenyl)- and bis(tetrahydroindenyl)titanium and -zirconium dichlorides

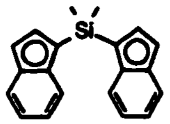
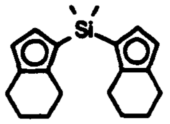
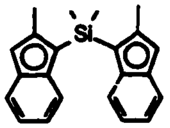
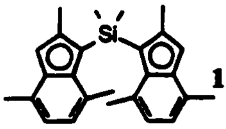
As previously seen with the *ansa*-bis(Cp)metal dichlorides, the bridging unit has a significant influence Cp$_{cent}$-M-Cp$_{cent}$ bond angle. The Cp$_{cent}$-M-Cp$_{cent}$ bond angles for ethylene bridged bis(indenyl) zirconocene dichlorides are typically around 125° when bridged in the 1-indenyl position (Table 5-7). From the limited data it appears there is little change in the Cp_{cent}-Zr-Cp_{cent} bond angle when comparing the bis(indenyl)zirconium **22** with the more sterically encumbered bis(tetrahydroindenyl)zirconium dichloride **8**. However, there is a slight increase in the Cp_{cent}-Zr-Cp_{cent} bond angle with ethylene bridged bis(2,4,7-trimethylindenyl)zirconium **325** (127.6° versus 125.3° for **22**). In addition, bridging at the 1- or 2-indenyl position on the bis(tetrahydroindenyl) has little or no effect on the Cp_{cent}-Ti-Cp_{cent} bond angle as seen with entries **94** and **326** which vary by a mere 1°. The silane bridged zirconocene complexes of the corresponding bis(indenyl) and bis(tetrahydroindenyl)metal complexes have on average a 1° increase in the Cp_{cent}-Zr-Cp_{cent} bond angle when compared to the ethylene bridged counter parts (Table 5-8).

Table 5-7. Cp_{cent}-M-Cp_{cent} bond angles for ethylene bridged bis(indenyl)- and bis(tetrahydroindenyl)metal dichlorides.

Cp	M	Cp_{cent}-M-Cp_{cent} (deg)	Ref. #
	22 M = Zr^{a}	125.3	99
	94 M = Ti^{a}	128.5	143
	8 M = Zr^{a}	125.2	143
	325 M = Zr^{a}	127.6	61
	326 M = Ti	129.5	59b

a) Angles given for the *dl*-isomers

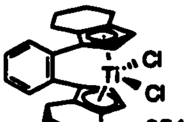
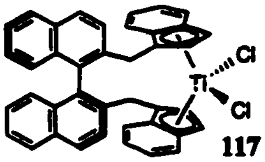
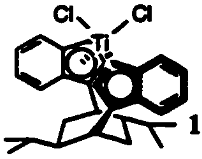
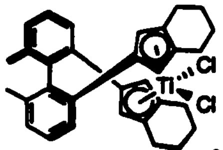
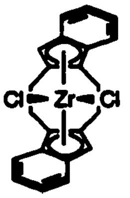
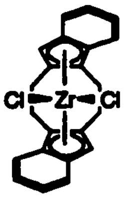
Table 5-8. Cp$_{cent}$-M-Cp$_{cent}$ bond angle of dimethylsilane bridged metallocene dichlorides.

Cp	M	Cp$_{cent}$-M-Cp$_{cent}$ (deg)	Ref. #
	**327** M = Zr^{a}	127.8	100
	**328** M = Zr^{a}	126.3	61
	**236** M = Zr^{a}	128.1	100
	**114** M = Zr^{a}	129.5	61

a) angles given for *dl*-isomers

Bridging units other than the ethano and silane moieties have been used (Table 5-9). In most instances the Cp$_{cent}$-Ti-Cp$_{cent}$ bond angle is increased from the ethylene bridged bis(indenyl)- and bis(tetrahydroindenyl)metal complexes as seen with entries **117**, **266**, and **118** with the exception of phenyl bridged titanocene **254** whose Cp$_{cent}$-Ti-Cp$_{cent}$ bond angle is slightly reduced. However, a significant reduction in the Cp$_{cent}$-Zr-Cp$_{cent}$ bond angle (~120-121°) is observed with the doubly bridged systems **284** and **285** which are similar to the bond angles found for the doubly bridged bis(Cp)metal complexes seen in an early section.

Table 5-9. Cp_{cent}-M-Cp_{cent} bond angles for *ansa*-metallocene dichlorides with other bridging units.

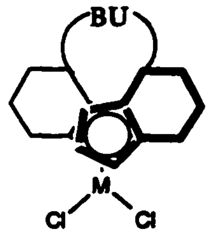
Cp	Cp_{cent}-M-Cp_{cent} (deg)	Ref. #
 **254**	129.4	58
 **117**	130.4[a]	63a
 **118**	131.2[a]	64
 **266**	133.7	67
 **284**	120.4	107
 **285**	121.2	Chapter 4

a = Cp_{cent}-M-Cp_{cent} bond angles provided by Cambridge data search

5.8 Project objectives

A number of metallocene dichlorides with geometrically closed shapes have been synthesized with conformationally constrained systems and variable Cp_{cent}-M-Cp_{cent} bond angles. Geometrically open systems exist with semi-rigid to rigid conformational constraints and Cp_{cent}-M-Cp_{cent} bond angles from the middle to upper range of Cp_{cent}-M-Cp_{cent} bond angles (Zr: 125-129.5° and Ti: 128.2-131.2°).

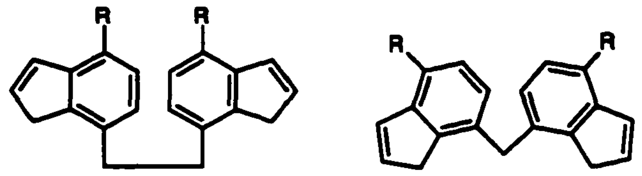
Figure 5-1. *Very open* system.



180°
VERY OPEN

Until now, there has been no convenient synthetic methodology for the facile preparation of "*very open*" systems (defined as *ansa*-metallocenes with a dihedral angle near 180° between the two most forward substituents on the Cp moiety) having structural or conformational variations (Figure 5-1). To accomplish this, bridging at the 1- and 2-indenyl positions needed to be abandoned, and the bridging position needed to be moved to the 6 membered ring on the indenyl moiety. This simple change would give access to the desired "*very open*" system. The generic targets for this new system are the ethano bridged ligand **A** and methano bridged ligand **B** shown in Figure 5-2.

Figure 5-2. Initial targets.

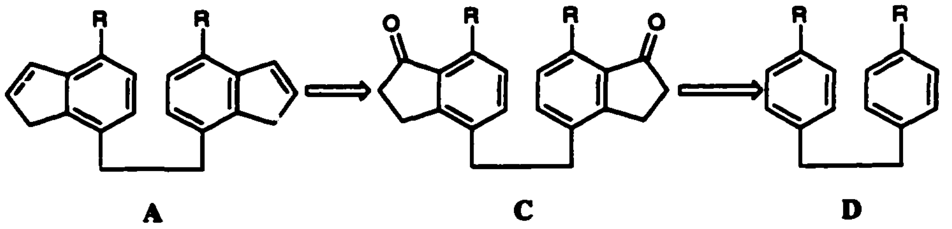


A **B**

5.9 Design, synthesis and properties of C7,C7' ethano bridge metallocene dichlorides

A retrosynthetic analysis of target compound **A** can be taken back to the corresponding bis(ketone) **C** (Figure 5-3). The removal of the three carbons which would make-up the Cp unit leaves an ethylene bridged bis(arene) **D**.

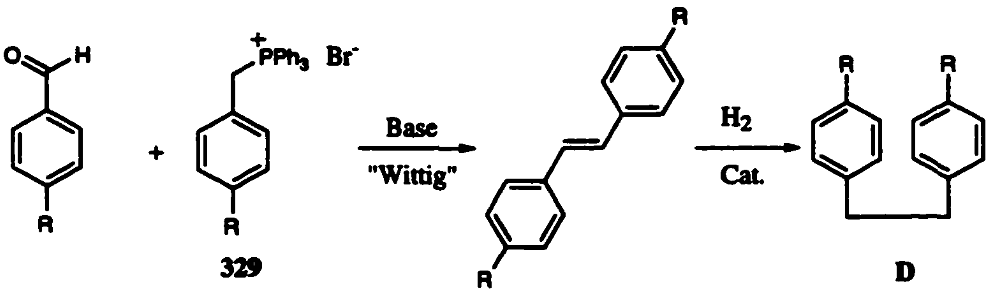
Figure 5-3. Retrosynthesis of the ethano bridged bis(indene) A.



R = alkyl group

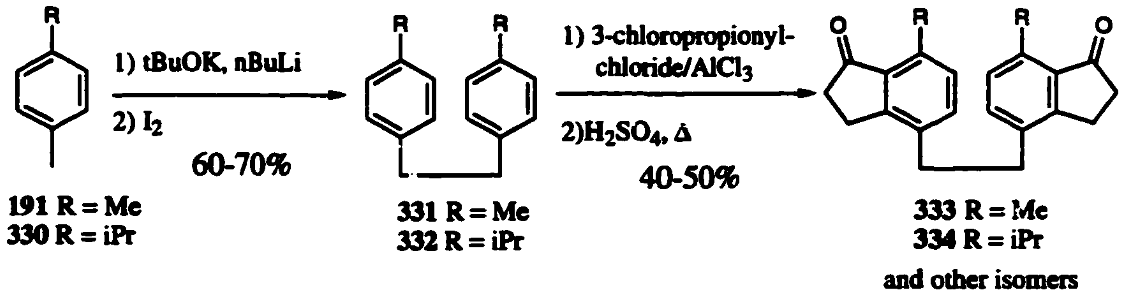
A number of potential routes exist for the synthesis of compounds such as bis(arene) **D**. One such route involves the addition of Wittig reagent **329** to an aldehyde to give a stilbene derivative (Figure 5-4). Subsequent hydrogenation of the double bond would have provided the necessary bis(arene) **D**. However, the desire to directly obtain derivatives of the bis(arene) **D** in order to reduce the cost and synthetic steps led to the use of an alternate route.

Figure 5-4. Wittig route to bis(arene) D.



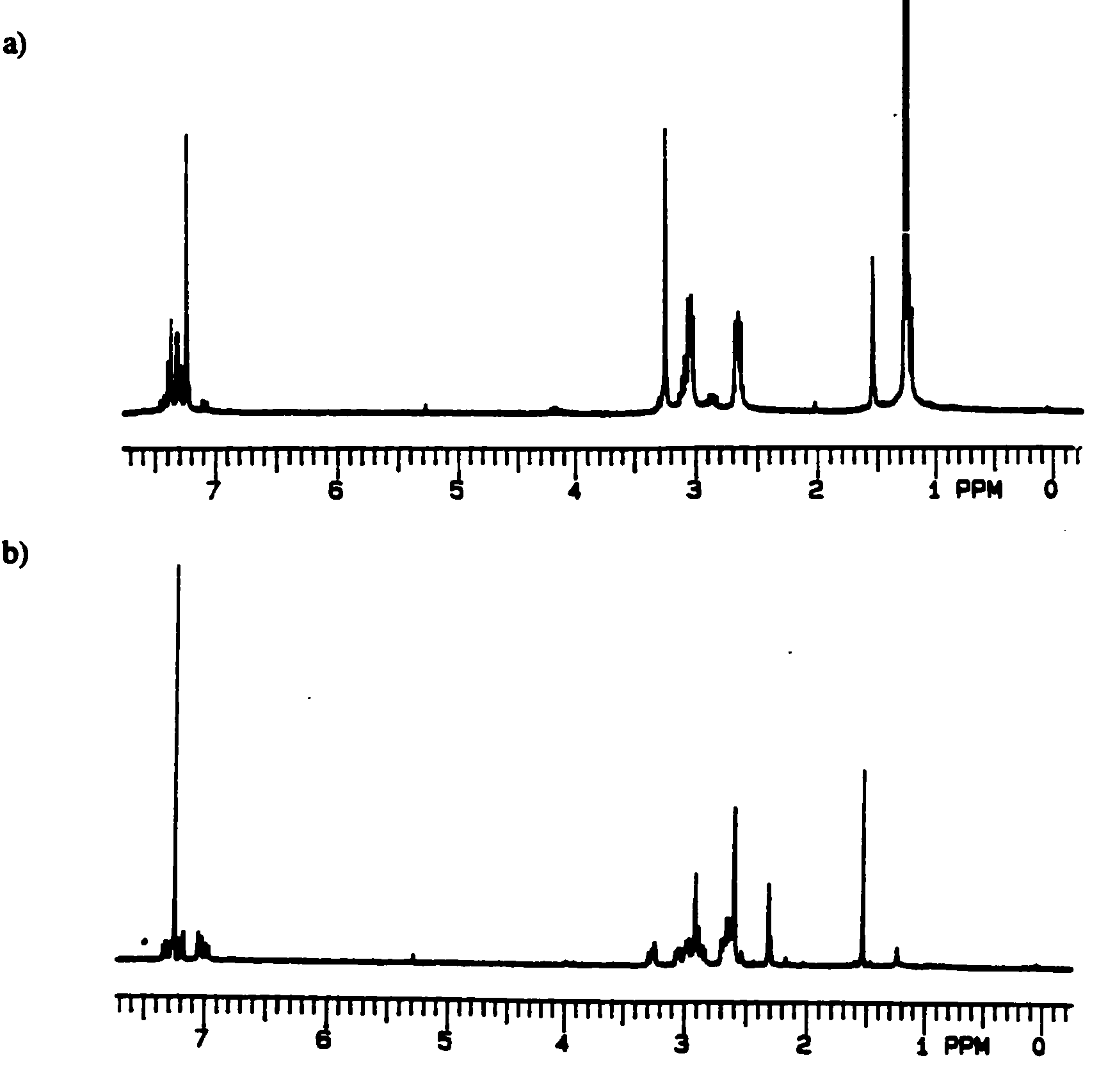
A convenient large scale synthesis of derivatives of bis(arene) **D** was found in literature. As shown in Figure 5-5, derivatives of this arene could be synthesized from inexpensive commercially available *p*-xylene **191** or *p*-cymene **330**. The selection of these starting materials was based upon the facile ability to introduce the ethano bridge using a coupling method described for *p*-xylene by Bates and Ogle[144], and the needed *para*-substituents to the ethano bridge which would later direct the introduction of the carbons for the Cp moiety during a Friedel-Crafts acylation in a future step. The selective coupling of these *para* -substituted arenes was carried out by deprotonation of the less substituted benzylic position with potassium *tert*-butoxide and *n*-butyllithium followed by the isolation of the potassium salt. The potassium salt was immediately oxidatively coupled using iodine in THF to give the 1,2-diaryl ethanes 331[144] and 332 in 65-70% yield.

Figure 5-5. Synthesis of the C7,C7'-ethano bridged bis(ketones) 333 and 334.



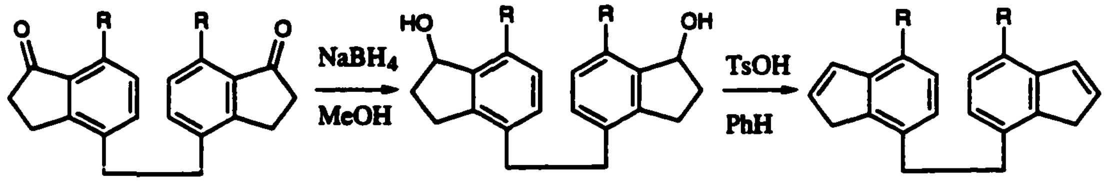
Of the possible routes[61] to add the three carbons, which would later become the Cp moiety, the route used by Picccolrovazzi[13] was chosen. The cyclopentanone moieties were introduced by Friedel-Crafts acylation followed by Nazarov cyclization in sulfuric acid to yield an isomeric mixture of the bis(indanones) 333 and 334 having the carbonyl group *ortho* to the alkyl group or *ortho* to the ethano bridge. Evidence for the formation of the desired ketone included the appearance two sets of proton signals at 3.00-3.20 and 2.50-2.70 ppm in the ^1H NMR spectrum of 334 (Figure 5-6a). A more complex picture was observed in the ^1H NMR spectrum of 333, but the expected pattern for the protons alpha and beta to the carbonyl group appeared between 2.50-3.4 ppm (Figure 5-6b).

Figure 5-6. ^1H NMR spectra of (a) **334** (b) **333**.



The carbonyls were reduced with sodium borohydride to yield the alcohols **335** and **336** in quantitative yields as complex mixtures of several isomers (Figure 5-7). Dehydration[13] with *p*-toluenesulfonic acid gave the corresponding bis(indenes) **337** and **338** as a simplified mixture of double bond isomers in approximately 50% yield based on bis(indanones) **333** and **334**. Evidence for the formation of **337** and **338** included the appearance of the H-1 indenyl signals at 6.45 and 6.60 ppm, respectively, and the H-2 indenyl signals appearing between 6.90-7.20 ppm which is typical for dialkyl substituted indenyls such as 4,7-dimethylindene[13,97] (Figure 5-8).

Figure 5-7. The synthesis of ethylene bridged bis(indenes) 337 and 338.



333 R = Me
334 R = iPr
and other isomers

335 R = Me
336 R = iPr
and other isomers

337 R = Me
338 R = iPr
and other isomers

Figure 5-8. ^{1}H NMR spectra of (a) 337 (b) 338.

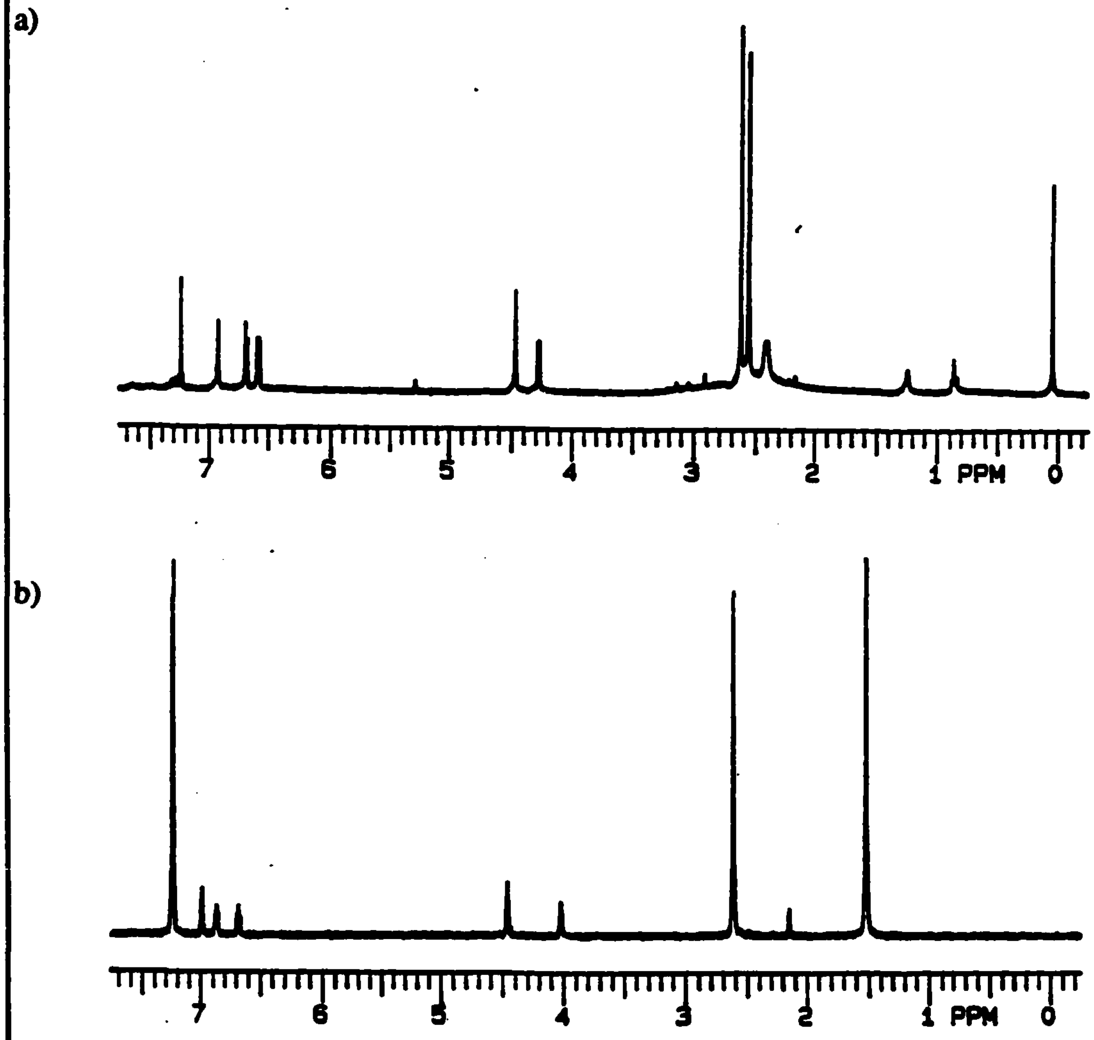
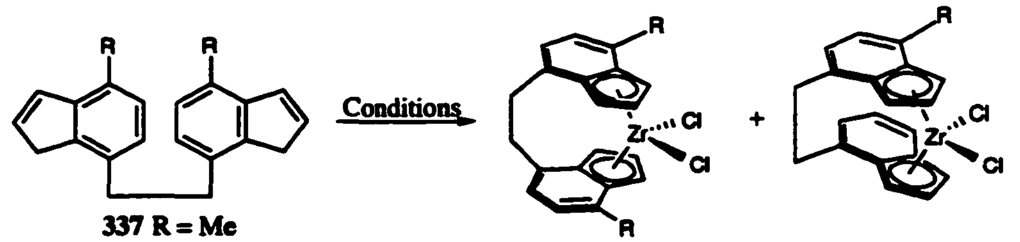


Figure 5-9. Metalation of ligands **337** and **338** with zirconium.



337 R = Me
338 R = iPr
and other isomers

dl

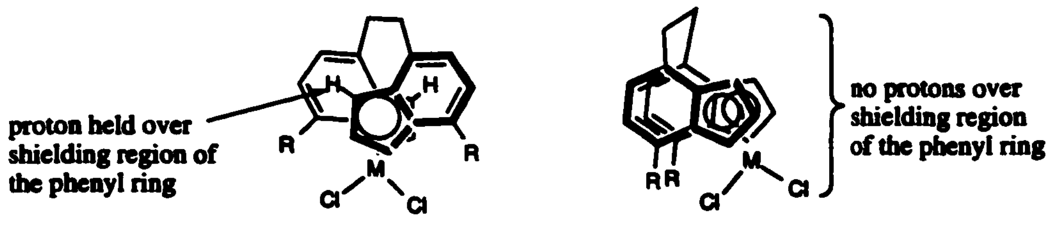
meso

Conditions		*dl/meso*	Yield
1) *n*-BuLi 2) $ZrCl_4$	**340** R = iPr	ca. 50:50	60%
1) $Zr(NMe_2)_4$	**339** R = Me	ca. 100:0	63%
2) Me_2NH_2Cl	**340** R = iPr	ca. 100:0	61%

Metalation of ligands **337** and **338** with zirconium was carried out under a variety of conditions (Figure 5-9). Following a procedure outlined by Jordan[145] using tetrakis(dimethylamido)zirconium in chlorobenzene or toluene followed by workup with dimethylammonium chloride, and purification gave the zirconium complexes *dl*-**339** and *dl*-**340**.

The metallocene complexes were assigned the structures of *dl*-**339** and *dl*-**340** based upon the unusually large chemical shift difference between indenyl H-1 (4.45 and 4.42 ppm) and H-3 (6.69 and 6.60 ppm) signals in the ^1H NMR spectrum, respectively (Figure 5-11). According to molecular models of the two complexes, the indenyls in the

Figure 5-10. Top view of the *dl*-metal complex and *meso*-metal complex.

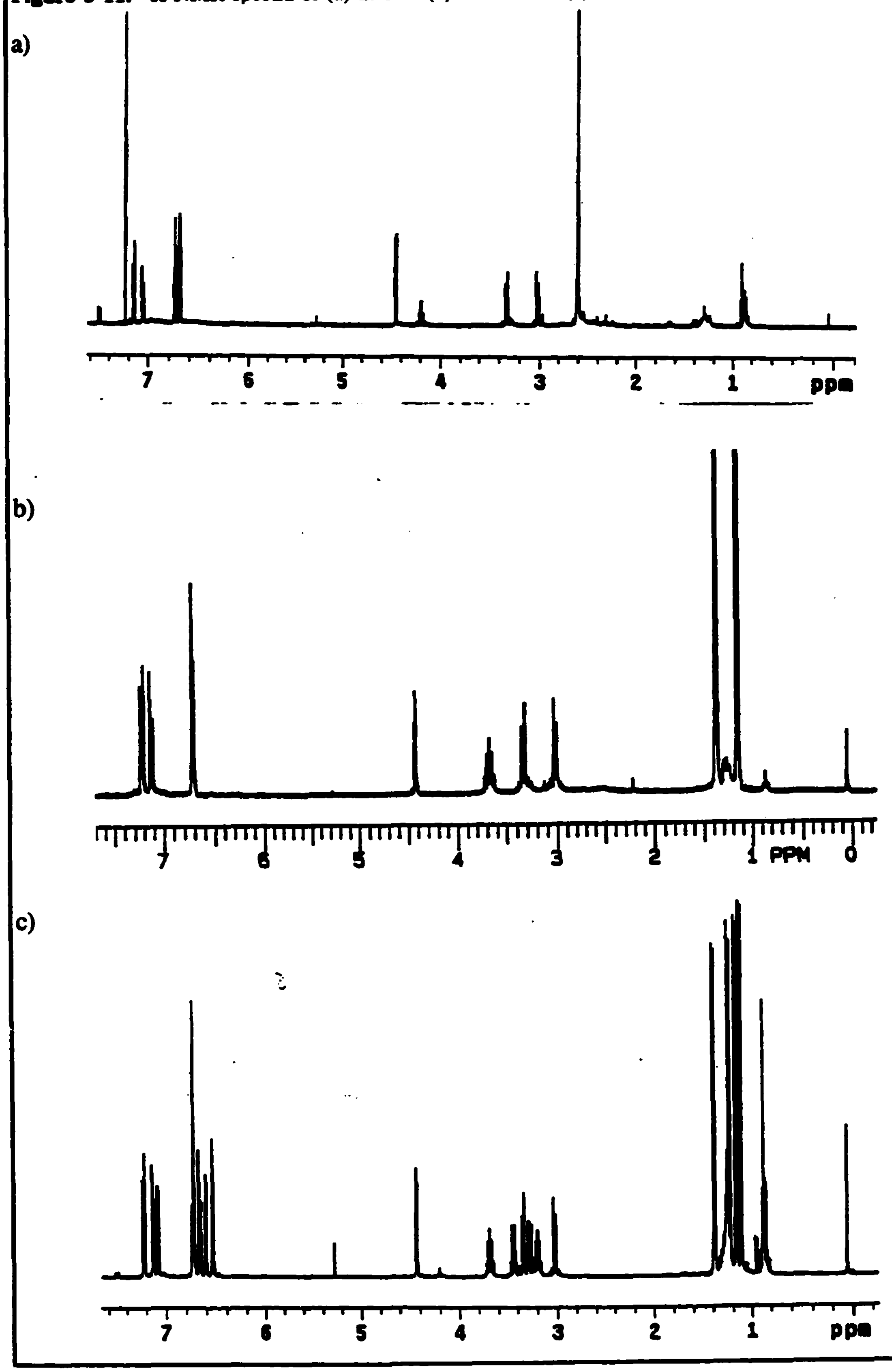


dl-complex

meso-complex

dl-complexes are positioned so that protons at C1 and C1' are held over the phenyl ring of the opposite indene (Figure 5-10). With the position of the protons over the shielding region of the phenyl rings, the high-field shift of 4.42 and 4.45 ppm could be readily explained. On the other hand, molecular models of the *meso*-metal complexes led us to expect typical indenyl shifts for all three protons. This was later found upon metalation of compound **338** using *n*-butyllithium and zirconium tetrachloride which gave a 1:1 mixture of *meso*-**340** and *dl*-**340**. As was expected the *meso*-**340** could be identified by an extra set of indenyl signals appearing at 6.65, 6.60 and 6.53 ppm in the ^{1}H NMR spectrum of the zirconocene dichlorides (Figure 5-11c).

Figure 5-11. ^{1}H NMR spectra of (a) *dl*-339 (b) *dl*-340 and (c) *meso*-340.



Fortunately, crystals of zirconium dichloride complex *dl*-**339** suitable for X-ray diffraction could be grown by diffusion of hexanes into a solution of *dl*-**339** in toluene at 0 °C. The solid state structure of *dl*-**339** could be solved as described in table 5-10. The front and top ORTEP view of *dl*-**339** are shown in Figure 5-12. The angle found between Cp_{cent}-Zr- Cp_{cent} is 130.4°. The Cp_{cent}-Zr distances are 2.221 Å and 2.217 Å. The dihedral angle between the C5-C6 bond and C15-C16 bond is 191° and confirms our design notion of creating a "very open" complex as well as confirming the C_2-symmetric complex.

Crystals of zirconium dichloride complex *dl*-**340** suitable for X-ray diffraction could be grown by diffusion of hexanes into a solution of *dl*-**340** and dichloromethane at 0° C, and the solid state structure of *dl*-**340** could be solved as described in Table 5-10. The lateral and top ORTEP view of *dl*-**340** is shown in Figure 5-13. The angle found between Cp_{cent}-Zr-Cp_{cent} is 130.3°. The Cp_{cent}-Zr distances are 2.208 Å and 2.231 Å. The dihedral angle between the C5-C6 bond and C15-C16 bond is 192° and confirms the assignment of the C_2-symmetric complex.

Table 5-10. Crystallographic data for *dl*-339 and *dl*-340.

	***dl*-339**	***dl*-340**
empirical formula	$C_{22}H_{20}Cl_2Zr$	$C_{26}H_{28}Cl_2Zr$
molecular weight	446.50	502.60
temperature	188 (2) K	153 (2) K
wavelength (Å)	0.71073	0.71073
crystal system	Monoclinic	Monoclinic
space group	P2 (1) / n	C2 / c
a (Å)	6.7670 (10)	21.671 (9)
b (Å)	16.921 (3)	17.383 (9)
c (Å)	16.123 (3)	12.063 (6)
alpha	90°	90°
beta	95.770 (10)°	98.46°
gamma	90°	90°
volume ($Å^3$), Z	1836.8 (5), 4	4495 (4), 8
D_{calc} (Mg / m^3)	1.615	1.485
absorption coefficient (mm^{-1})	0.881	0.737
F(000)	904	2064
crystal size (mm)	0.14 x 0.60 x 0.20	0.06 x 0.14 x 0.52
theta range	2.41 to 24.99 °	1.51 to 23.00 °
reflections collected	3511	3213
independent reflections	3220 R_{int} = 0.0331	3089 R_{int} = 0.0820
max. and min. transmission	0.2765, 0.2489	
data/restraints/parameters	3214 / 265 /227	3080 / 305/ 262
goodness of fit on F^2	1.011	1.058
final R_1 [I > 2 sigma (I)]	0.0384	0.0754
final wR_2 [I > 2 sigma (I)]	0.0909	0.1730
min. and max.	0.547, -0.628	1.699, -1.914
Refinement Method	Full-matrix least-squares on F^2	

Figure 5-12. **ORTEP plots of *dl*-339** (a) Front view (b) Top view.

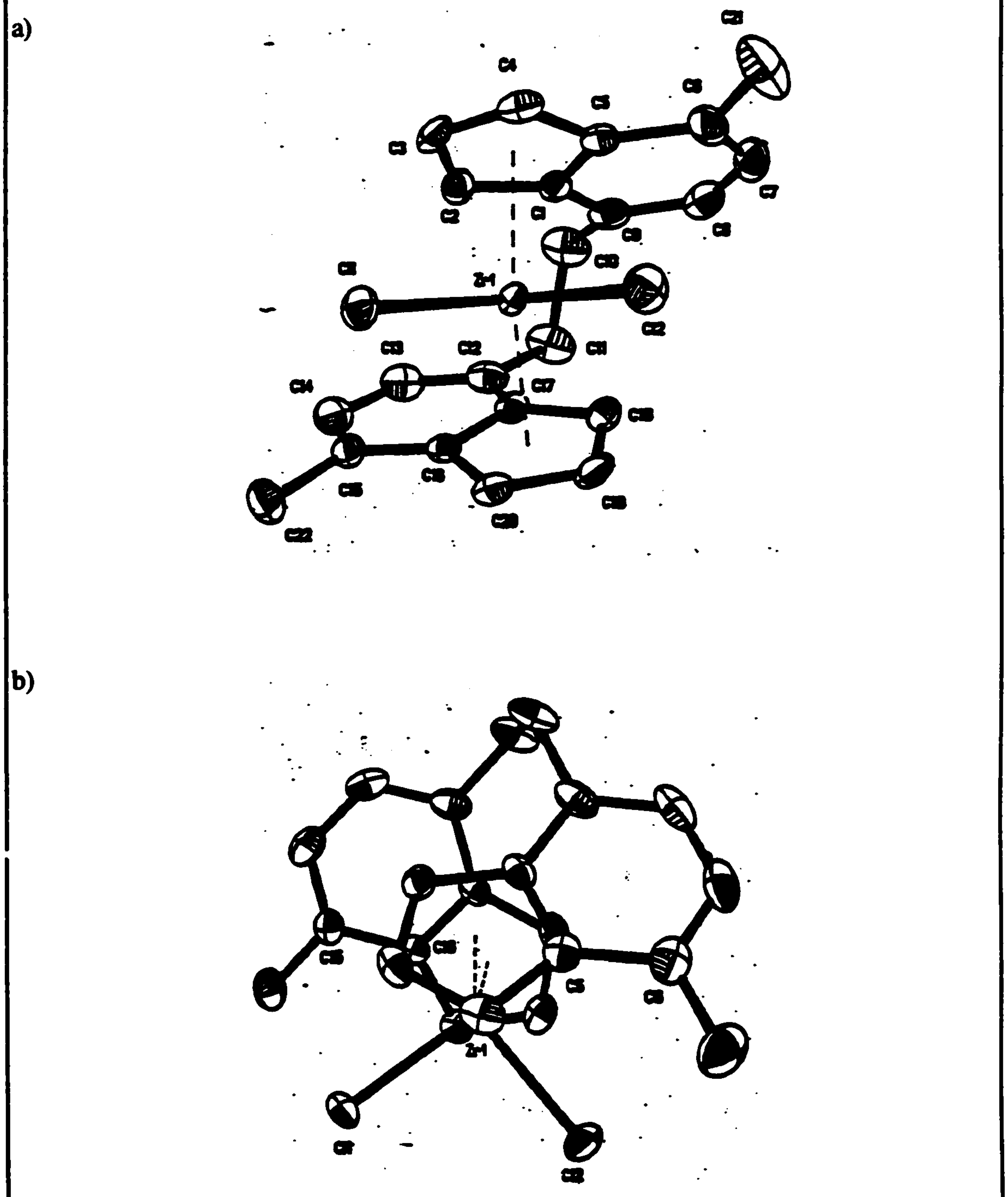


Figure 5-13. ORTEP plots of *dl*-**340** (a) Lateral view (b) Front view.

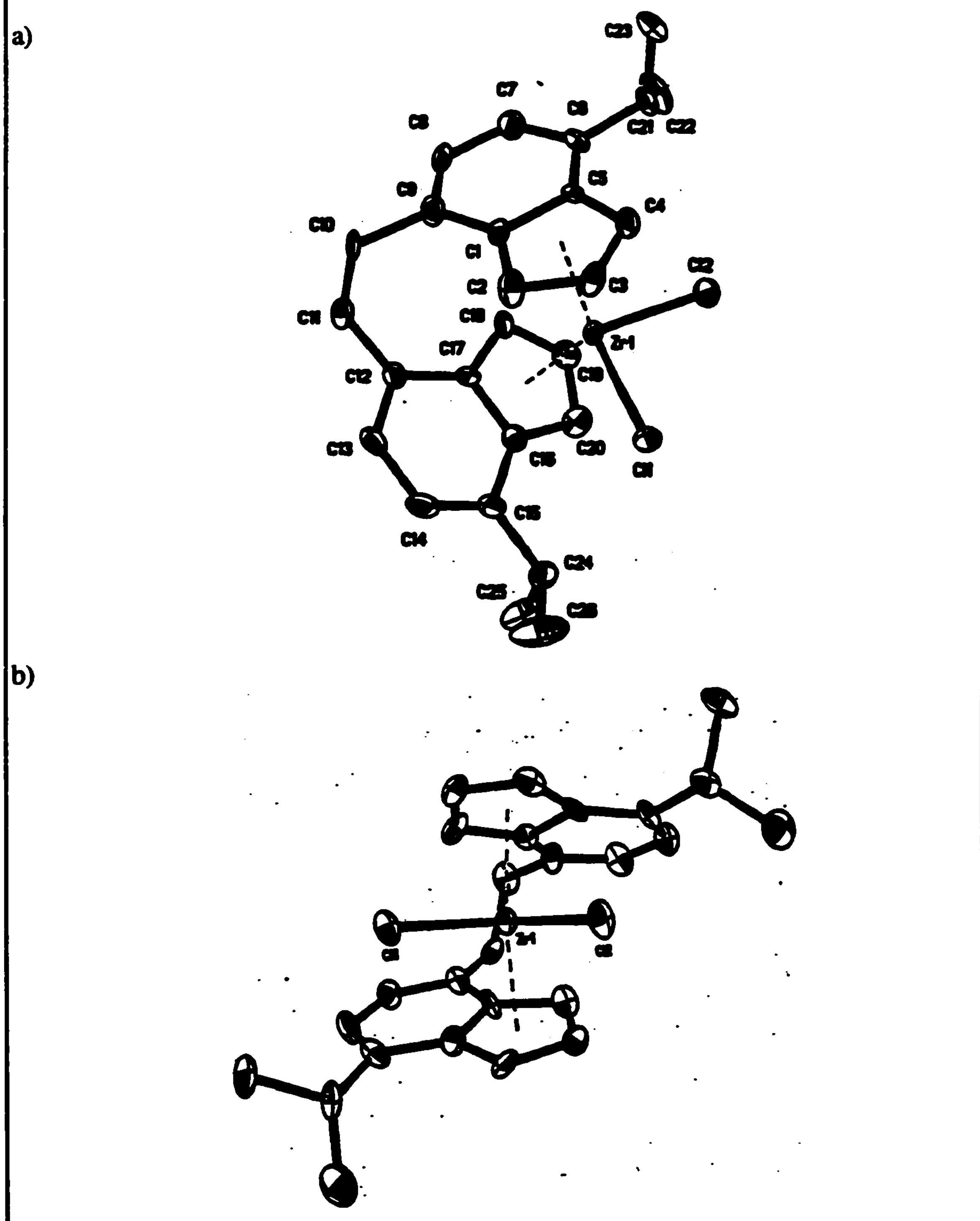
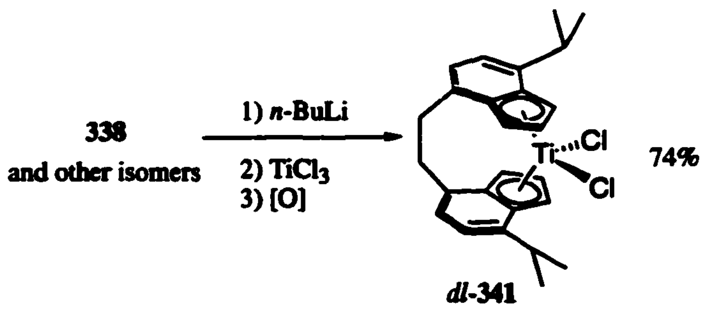


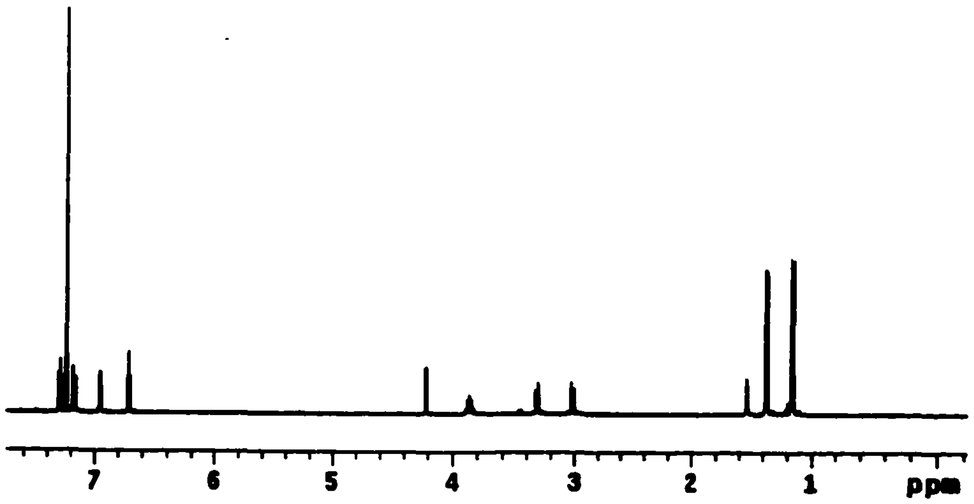
Figure 5-14. Metalation of bis(indene) **338** with titanium.



dl-**341**
no meso detected

Metalation of the *iso*propyl-substituted ligand **339** with titanium trichloride followed by oxidation resulted in the isolation of only the C_2-symmetric complex of the titanocene *dl*-**341** in 74% yield (Figure 5-14). Assignment of the metallocene structure was based upon the chemical shift found for indenyl H-1 at 4.21 ppm in the ^{1}H NMR for *dl*-**341** (Figure 5-15). A similar upfield shift was found for an indenyl signal in the ^{1}H NMR spectra of zirconocene *dl*-**339** and *dl*-**340**. Crystals of titanocene *dl*-**341** suitable for X-ray diffraction were grown from the slow evaporation of solvent from a chloroform solution of *dl*-**341** at room temperature, and the solid state structure was solved as described in Table 5-11. The lateral and front ORTEP view is shown in Figure 5-16 and confirms the C_2-symmetric assignment. The angle between Cp_{cent}-Ti-Cp_{cent} is 131.6°. The

Figure 5-15. ^{1}NMR spectrum of *dl*-**341**.



bond distance between Cp_{cent}-Ti are 2.097 Å and 2.083 Å. The dihedral angle defined by the C5-C6 bond and the C15-C16 bond is approximately 192°, again showing a "*very open*" structure. In all cases the Cp_{cent}-M-Cp_{cent} angle is fairly wide for all *ansa*-metallocene dichlorides, but fall within the range found for *ansa*-metallocene dichlorides with larger than two carbon bridging units. A summary of selected bond lengths and angles for the ethano bridged metallocene dichlorides is given in Table 5-12.

Table 5-11. Crystallographic data for *dl*-341.

empirical formula	$C_{26}H_{28}Cl_2Ti$
molecular weight	698.02
temperature	188 (2)
wavelength	0.71073 Å
crystal system	Monoclinic
space group	P2 (1) / c
a	15.822 (3) Å
b	17.255 (3) Å
c	11.681 (2) Å
alpha	90°
beta	107.180 (10)°
gamma	90°
volume (Å^3), Z	3046.7 (9), 4
D_{calc} (Mg / m^3)	1.522
absorption coefficient (mm^{-1})	1.001
F(000)	1424
crystal size (mm)	0.02 x 0.34 x 0.26
theta range	1.79 to 24.99 °
reflections collected	3479
independent reflections	3244 R_{int} = 0.0631
max. and min. transmission	0.6847, 0.4776
data/restraints/parameters	3239 / 0 / 334
goodness of fit on F^2	1.039
final R_1 [I > 2 sigma (I)]	0.0658
final wR_2 [I > 2 sigma (I)]	0.1447
min. and max.	0.909, -0.735
Refinement Method	Full-matrix least-squares on F^2

Figure 5-16. ORTEP plots of *dl*-**341** (a) Lateral view (b) Top view.

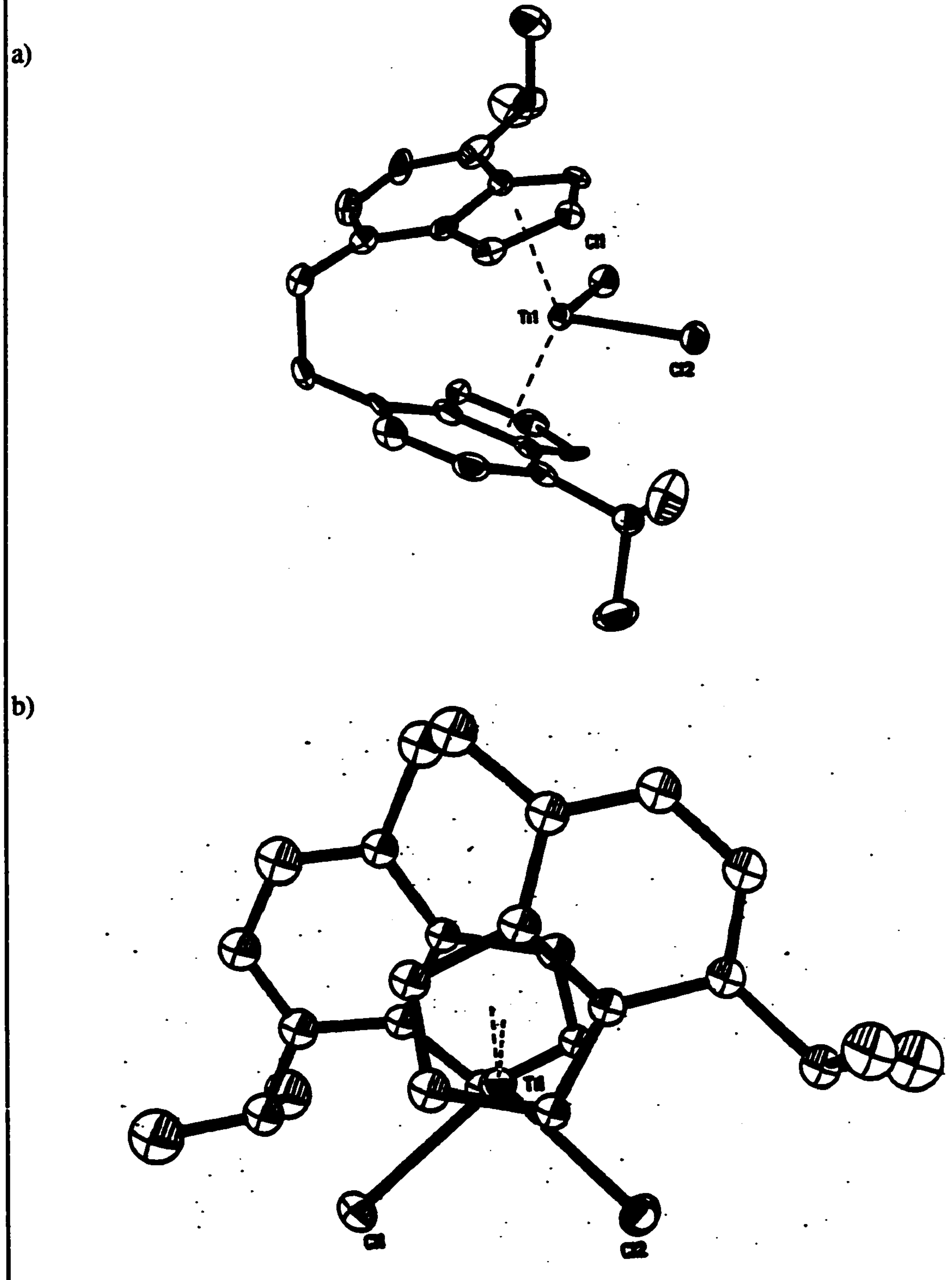


Table 5-12. Summary of bond length and angles for *dl*-339, *dl*-340, and *dl*-341.

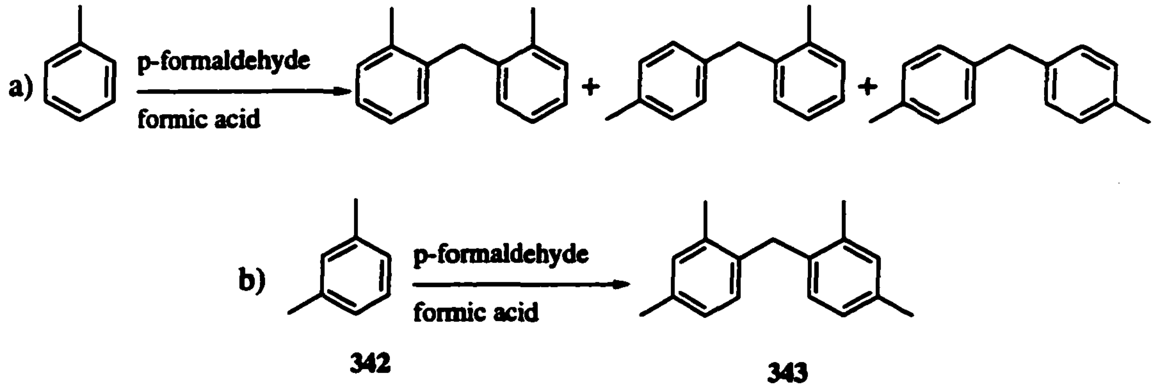
Bond lengths and Angles	*dl*-339 M = Zr	*dl*-340 M = Zr	*dl*-340 M = Ti
Cp_{cent}-M-Cp_{cent}	130.4°	130.3°	131.7°
Cp_{cent}-M	2.221 Å 2.217 Å	2.208 Å 2.231 Å	2.097 Å 2.083 Å
C5-C6/C15-C16 dihedral angle	191°	192°	192°

Low temperature ^{1}H NMR experiments were performed using metallocene *dl*-**340** to see if the molecule could be constrained into the constitutional conformations indicated by molecular models. However, there was little or no change in the ^{1}H NMR spectrum at -60 °C suggesting the molecule continues to fluctuate between any accessible conformations.

5.10 Synthesis and properties of C7,C7' methano bridged metallocene dichlorides

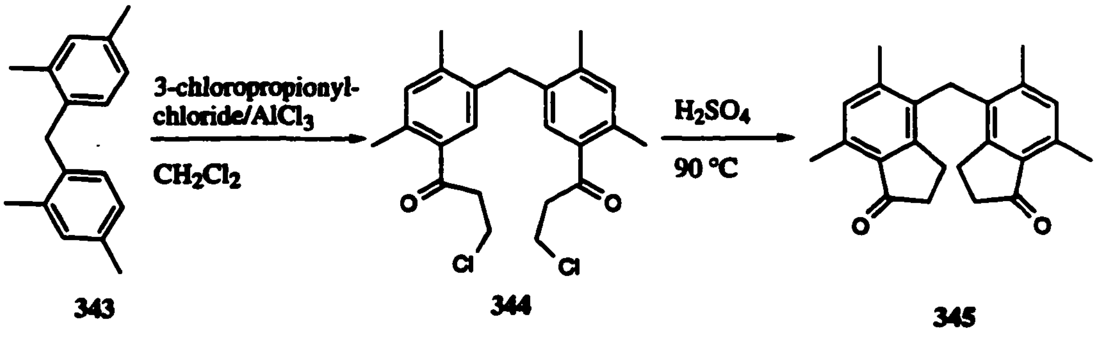
In order to increase the rigidity of the metal complexes containing bridges between the C7-C7' positions, a one carbon bridged ligand became the desired target. Much like the preparation for the ethano bridged metallocenes, the synthesis was begun by first introducing the methylene bridge (Figure 5-17). Our initial attempt in forming the methylene bridge from toluene and *para*-formaldehyde using a procedure outlined by Cornell and Gollis[146] led to the formation of an inseparable mixture of products due to competing sites for the acylation and alkylation to occur. To combat potential selectivity problems in forming the methylene bridge, *m*-xylene **342** was selected as the starting material since the two methyl groups would provide the necessary steric bulk to slow the reaction at the positions *ortho* to both methyl groups while activating the positions *para* to the methyl groups which are now equivalent. Using the procedure described by Cornell and Gollis[146] in the reaction with *p*-toluene, **343** could be isolated in excellent yield after purification.

Figure 5-17. a) Initial attempt with toluene b) Synthesis of the methano bridged arene **343**.



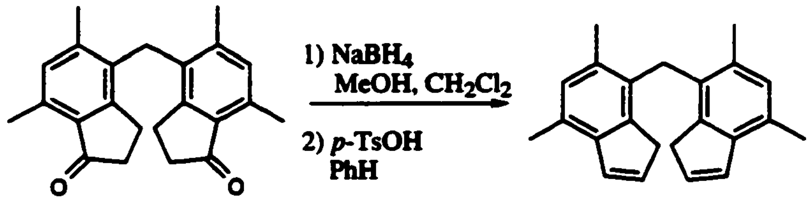
Care was taken with the Friedel-Crafts acylation using aluminum trichloride and 3-propionylchloride (Figure 5-18). It was found that the desired product from the Friedel-Crafts reaction could not be isolated, and the starting material had decomposed if the reaction mixture was warmed to room temperature or if the reaction was run for more than 30 min at 0 °C. When proper care was taken diketone **344** was isolated in 43% yield and treated with sulfuric acid to promote cyclization to give bis(indanone) **345** as a single regioisomer in 49% yield.

Figure 5-18. Friedel-Crafts acylation and acid promoted cyclization.



Reduction of **345** with sodium borohydride (structure of diol **346** is not shown) followed by dehydration promoted by *p*-toluenesulfonic acid yielded the bis(indene) **347**

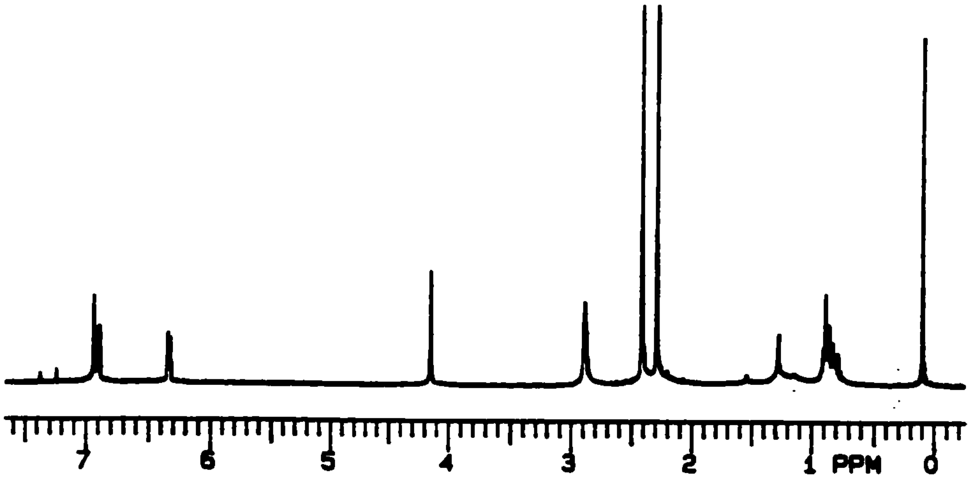
Figure 5-19. Conversion of bis(ketone) **345** to bis(indene) **347**.



345 **347**

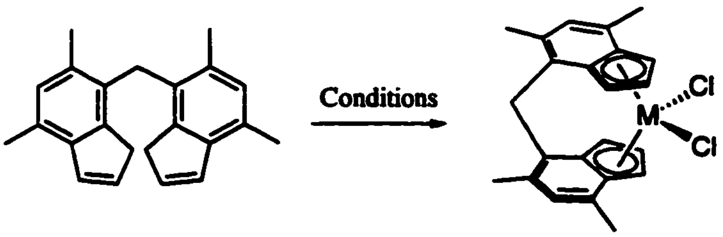
(Figure 5-19). Bis(indene) **347** was isolated by column chromatography in 80% yield as a white solid. In contrast to ethylene bridged bis(indenes) **337** and **338**, the methylene bridged bis(indene) **347** was isolated as a single double bond isomer which could be identified by a single set of proton signals for the methyl groups at 2.41 and 2.29 ppm, and indenyl signals at 6.89 and 6.32 ppm in the ^{1}H NMR spectrum of **347** (Figure 5-20).

Figure 5-20. ^{1}H NMR spectrum of methano bridged bis(indene) **347**.



Metalation of methylene bridged bis(indene) **347** with *n*-butyllithium and zirconium tetrachloride in ether or tetrakis(dimethylamido)zirconium in chlorobenzene followed by workup with dimethylammonium chloride gave the C_2-symmetric zirconocene dichloride *dl*-**348** (Figure 5-21).[145] The formation of titanocene dichloride *dl*-**349** was also found to form cleanly upon treatment with *n*-butyllithium, titanium trichloride, and oxidation.[94]

Figure 5-21. Metalation of the methano bridged bis(indene) **347**.



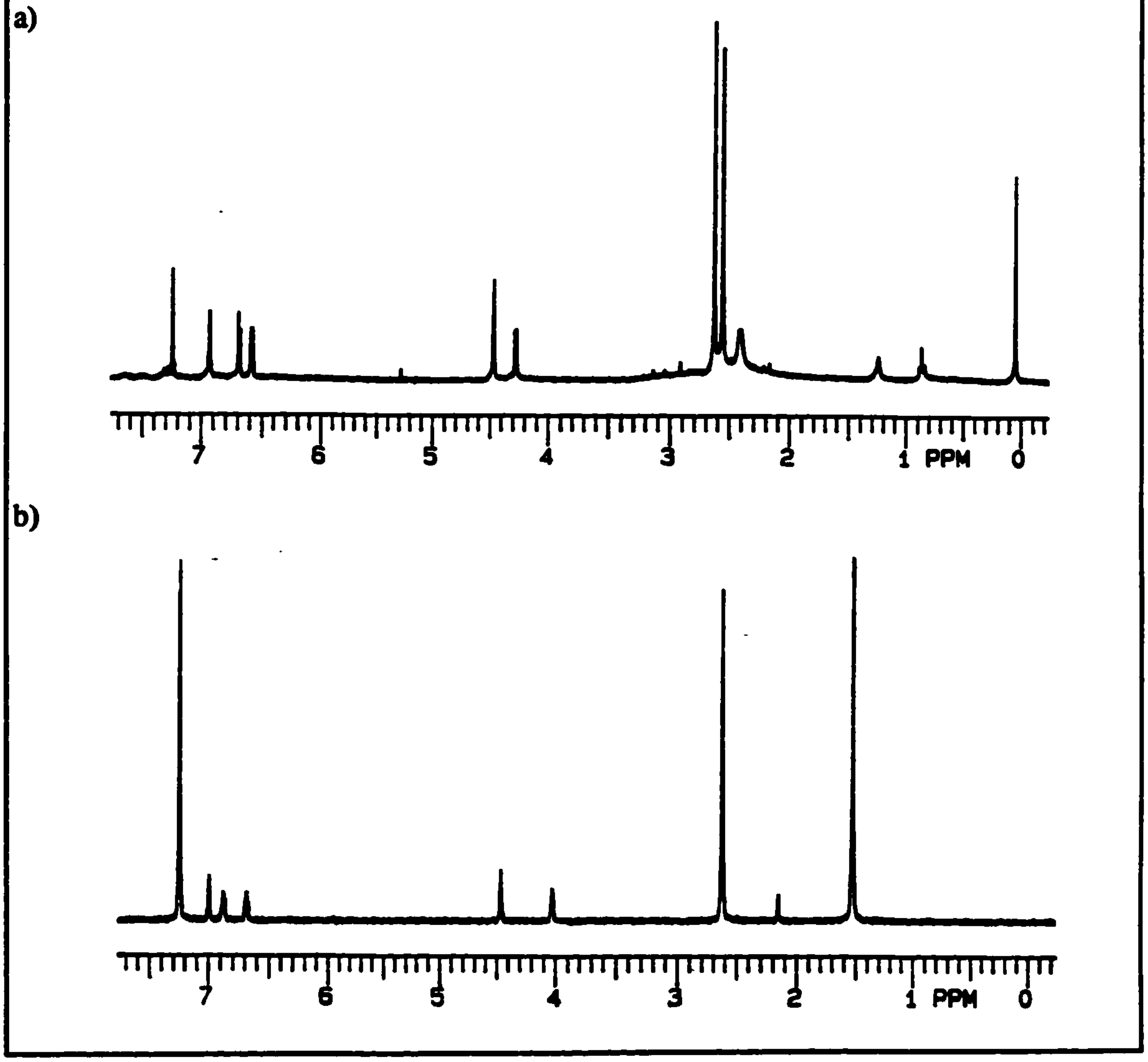
347

dl-**348** M = Zr
dl-**349** M = Ti

Conditions	M	Yield
1) *n*-BuLi 2) $ZrCl_4$	Zr	N.A.
1) $Zr(NMe_2)_4$ 2) Me_2NH_2Cl	Zr	43%
1) *n*-BuLi 2) $TiCl_3$ 3) [O]	Ti	38%

The assignment of the zirconocene dichloride *dl*-**348** and titanocene dichloride *dl*-**349** as the C_2-symmetric complexes was based upon the chemical shifts of the H-1 indenyl signals in the ^1H NMR spectrum found at 4.27 and 4.02 ppm, respectively (Figure 5-22). The C_2-symmetric complexes *dl*-**348** and *dl*-**349** would have a proton positioned directly over the phenyl ring on the indenyl moiety causing the unusual upfield shift. Unfortunately, due to insolubility and instability of these complexes in solution a ^{13}C NMR spectrum could not be obtained.

Figure 5-22. ^{1}H NMR spectra of (a) zirconocene dichloride **348** (b) titanocene dichloride **349**.



5.11 Conclusion

We have shown C7,C7' ethano bridged bis(indenyl) ligands could be prepared in a short and efficient synthesis with very open geometric shape. We have also demonstrated that the exclusive formation of the *dl*-zirconium complexes could be done using a metalation procedure described by Jordan[145] while the *meso*-zirconium complex formed in a 1:1 mixture with the *dl*-zirconium complex using conventional metalation procedures. On the other hand, the *dl*-titanium complex of **341** was the only product seen in the crude ^{1}H NMR using conventional metalation procedures. The reason for the exclusive formation of

341 is still unclear. In addition, the structural determination of the three ethano bridged metallocene dichlorides confirms the very open geometric shape which gives a new class of ligand with steric modifications while the methano bridged bis(indenyl)metal complexes provide very open sterically rigid complex.

Summary

Our efforts to contribute to an already competitive field has lead to the development of several of group 4 *ansa*-metallocene dichlorides with varying steric modifications, conformational mobility and geometric shapes. With the information gained from their synthesis and their solid state structures we may find answers to very important questions in a effort to develop highly reactive yet selective catalysts for enantioselective transformations.

We have applied methodologies previously used for introducing steric modifications in metallocene dichlorides with achiral bridges toward the chiral 2,2'-dimethyl-1,1'-binaphthalene bridge to give sterically modified bis(indenyl)titanium and zirconium dichlorides **232** and **233**. These additional metal complexes gives a nice series of systematically modified bis(indenyl)metal dichlorides which can be compared to one another in asymmetric syntheses.

We have determined the X-ray structure of doubly bridged zirconocene dichloride **284**, and have confirmed the closed conformation. In addition, the doubly bridged bis(tetrahydroindenyl)zirconium dichloride was prepared and the structure was confirmed by X-ray analysis. With these two metal complexes we now have two closed systems to compare as catalysts for propylene polymerization to determine if the closed shape or the tetrahydroindenyl units are detrimental to the catalyst activity.

We have prepared a series of very open ethano C7,C7' and two methano C7,C7' bridged metallocene dichloride complexes via a short and convenient synthetic route. We believe the C7,C7'-ethano bridged zirconium complex *dl*-**340** is conformationally mobile as the ^{1}H NMR spectrum of the *dl*-**340** changed very little at low temperatures. These new metal complexes will compliment the closed and open metallocene dichlorides known in literature and could potentially answer whether or not the opening of the metal center increases the catalyst activity.

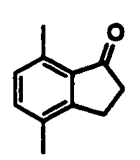
Experimental

General: Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Ether, THF, hexanes, toluene, and benzene were distilled under N_2 from sodium and benzophenone. Dichloromethane and chloroform were distilled under nitrogen from $LiAlH_4$ and $CaCl_2$, respectively. All reactions involving air or moisture sensitive compounds were performed under argon or nitrogen atmospheres utilizing standard Schlenk line techniques and/or in a Vacuum Atmospheres Dri-Box (under nitrogen). All metalations were conducted on Schlenk line, and run under purified Argon. All glassware was oven dried prior to use. Routine solvent removal was performed on a Buchi RE-111 rotary evaporator using water aspiration. Solvent removal *in vacuo* was accomplished on a vacuum line at < 0.01 mm Hg or on a Schlenk line at < 0.001 mm Hg (oil diffusion).

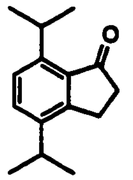
All ^1H NMR and ^{13}C NMR spectra were obtained using a Varian XL-300 or Varian XL-400 instrument. Data are reported as follows: chemical shifts (X scale) in parts per million (ppm) relative to residual solvent peaks (multiplicity, coupling constants in hertz (rounded to 0.5 Hz), number of hydrogens). For ^1H NMR spectra, the peaks due to residual $CHCl_3$, $C_6D_5H_1$, or DMSO-H_6 are listed at 7.24 ppm, 7.15 ppm or 2.49 ppm, respectively, and for ^{13}C spectra, the central peak of the $CDCl_3$, C_6D_6, and DMSO-d_6 multiplets are assigned chemical shifts of 77.0 ppm, 128.0 ppm, or 39.5 ppm, respectively. Unless otherwise noted, multiplicities and compound ratios are deduced from electronic integration. Infrared spectra were recorded on a Bio-Rad FTS-7 FT-IR with a Bio-Rad 3240-SPC computer. Only characteristic and/or strong signals are reported. Low-resolution mass spectra (reported as m/z (relative intensity at 70 eV or 12 eV)) were recorded on a Hewlett Packard 5985 instrument.

Preparative column chromatography was performed on flash silica gel (E. Merck Reagents silica gel 60 Å, 230-400 mesh ASTM). Melting Points were determined in Pyrex capillary tubes on a Mel-Temp apparatus and are uncorrected. Analytical thin layer chromatography was performed on 0.2 mm Kieselgel silica gel 60F-254. Compounds were sent to commercial laboratories for elemental analysis (Midwest Micro Labs or Desert Analytics).

***dl*-2,2'-Bis(dibromomethyl)-1,1'-binaphthalene and S-(-)-2,2'-bis(dibromomethyl)-1,1'-binaphthalene (221).**[96] Racemic and resolved 2,2'-bis(dibromomethyl)-1,1'-binaphthalene were prepared from 1-methylnaphthalene.

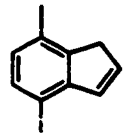


227

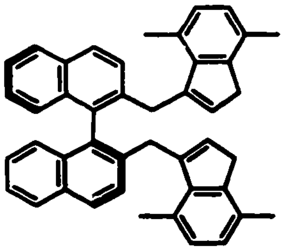


228

4,7-Dialkylindanones (227) and (228).[13] (Note: If older reagents (3-chloropropionyl chloride and $AlCl_3$ are used the yields ranged from 0-50%). To a solution of $AlCl_3$ (125 mmol) and dichloromethane (200 mL) was added 3-chloropropionyl chloride (125 mmol) in dichloromethane (50 mL) at 0 °C. The reaction mixture was allowed to stir for 30 min at 0 °C. To this solution was added dropwise at 0 °C 1,4-dimethylbenzene or 1,4-diisopropylbenzene (100 mmol) in dichloromethane (50 mL). After the addition the reaction solution was warmed to room temperature and stirred 2 h. The dark red solution was poured over ice and the organic phase was separated. The aqueous layer was extracted with dichloromethane (3 x 100 mL), and the combined organic portions was washed with water (50 mL) and dried with magnesium sulfate. The solvents were removed *in vacuo* to afford a thick green liquid. The crude product was added to the same concentrated sulfuric acid (200 mL) at 0 °C (Note: if the crude material was left to the next day yields dropped significantly). The sulfuric acid solution was slowly warmed to 80 °C and stirred for 1 h. The reaction solution was cooled to room temperature and poured over ice. The aqueous portion was extracted with ether (3 x 100 mL). The organic phase was washed with water (50 mL) and saturated aqueous sodium bicarbonate (100) mL). The solvents were removed *in vacuo* and the crude product was purified by column chromatography (SiO$_2$/10% ethyl acetate/pet. ether) to give the products in approximately 65-75% yield based on starting material. The ^{1}H NMR spectra matched those found in the literature.[13]

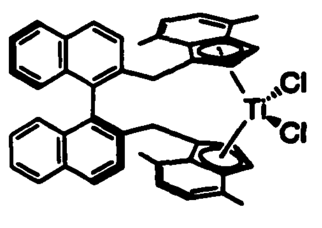

229

4,7-Dimethylindene (229).[97] To sodium (19.6 g, 855 mmol) was added slowly via addition funnel methanol at 0 °C. Freshly cracked cylcopentadiene (33.9 g, 513 mmol) was then added at once followed by a dropwise addition of 2,5-hexadione (39.0 g, 342 mmol). The reaction solution was stirred for 2 h at room temperature after the addition was complete. Water (100 mL) and ether (500 mL) were add, and the organic phase was separated. The aqueous layer was extracted with ether (3 x 100 mL) and the combined organic portions were washed with brine (100 mL) and dried over magnesium sulfate. The solvents were removed *in vacuo* and **229** was purified by distillation (bp 63 °C, at 0.01 mm Hg) as a slightly yellow liquid in 79% yield (38.9 g, 270 mmol). The ^{1}H NMR spectra matched the ^{1}H NMR found in literature.[97]


(S)-(-)-212

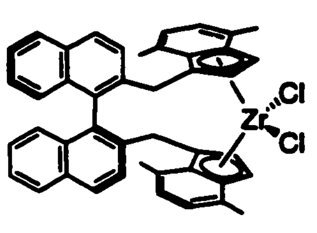
S-(-)-2,2'-Bis[1-(4,7-dimethylindenylmethyl)]-1,1'-binaphthalene (S)-(-)-(212). To a solution of 4,7-dimethylindene **229** (1.77 g, 12.3 mmol) in THF (5 mL) was added *n*-butyllithium (2.70 M in hexanes, 4.55 mL, 12.3 mmol) dropwise at -78 °C resulting in a heterogeneous reaction mixture. Upon warming the reaction mixture to room temperature the solid white precipitate dissolved, and the reaction became a clear red solution which was allowed to stir for an additional 30 min. The reaction solution was then cooled to 0 °C, and a solution of S-(-)-2,2'-bis(dibromomethyl)-1,1'-binaphthalene **(S)-(-)-221**[96] (1.35 g, 3.1

mmol) in THF (5 mL) was added dropwise. The resulting solution was then allowed to warm to room temperature, and stir for an additional 3 h. The reaction mixture was then quenched with a saturated solution of NH_4Br, and separated. The aqueous layer was extracted with ethyl acetate, and the organic layers were combined. The organic layer was then washed with brine followed by water, dried with $MgSO_4$, filtered, and concentrated. The crude yellow solid was then purified by column chromatography (SiO_2, PE) yielding (S)-(-)-**212** (1.21 g, 69%) as a white solid. mp. 129-130 °C; $[\alpha]_{589}^{23}$ -22.2 (c=0.814, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.46 (m, 2H), 7.26 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.90 (s, 4H), 5.89 (bs, 2H), 3.89 (bs, 4H), 2.98 (dd, J = 25.0 Hz, 2H), 2.68 (dd, J = 25.0 Hz, 2H), 2.25 (s, 6H), 2.24 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.84, 143.98, 142.55, 136.98, 134.80, 133.17, 132.48, 130.76, 130.33, 129.11, 128.29, 128.05, 127.91, 127.61, 126.28, 125.96, 125.66, 125.28, 36.08, 35.08, 19.78, 18.11; IR (thin film) 3046, 2967, 2934, 2865, 1498, 1454, 1379, 1117; (EI 70 eV, *m/z* , rel intensity) 566 (77 %), 421 (37), 408 (10), 279 (27), 265 (21), 145 (72), 40 (100).



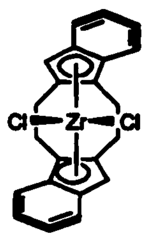
(S)-(+)-232

S-(+)-2,2'-Bis[1-(4,7-dimethylindenylmethyl)]-1,1'-binaphthyldichlorotitanium (S)-(+)-(232). *n*-Butyllithium (2.70 M in hexanes, 0.16 mL, 0.43 mmol) was added dropwise to a solution of S-(-)-2,2'-bis[1-(4,7-dimethylindenylmethyl)]-1,1'-binaphthalene (S)-(-)-**212** (117 mg, 0.21 mmol) in THF (2 mL) at -78 °C. After the addition the reaction mixture was allowed to warm, and upon reaching room temperature the reaction mixture became a dark blood red solution. The solution was then cooled to 0 °C, and added slowly via syringe to a slurry of $TiCl_3$ (48 mg, 0.31 mmol) in THF (1 mL) at -78 °C. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature, and was heated to reflux for 6 h which resulted in a dark solution. The solution was then cooled to room temperature and concentrated *in vacuo*. The solid green residue was then dissolved in chloroform (5 mL) at 0 °C, and air was slowly bubbled into the green solution for 2 h. 2 N HCl was then added, and the aqueous layer was separated. The aqueous layer was extracted twice with dichloromethane, and the combined organic layers were washed with 2 N HCl, water, dried with $MgSO_4$. filtered, and concentrated. The solid green powder was then dissolved in dichloromethane followed by slow addition of pentane until a precipitate was seen. The solution was allowed to sit for 30 min at room temperature, and filtered. The green solid was washed twice with pentane yielding (S)-(+)-**232** (34 mg, 24%) as a dark green powder. Mp 216-230 °C dec.;$[\alpha]_{589}^{23}$ +2490 (c = 0.026, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.47 (m, 2H), 7.27 (m, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 7.0 Hz, 2H), 6.89 (d, J = 7.0 Hz, 2H), 6.37 (bs, 2H), 5.28 (bs, 2H), 4.53 (d, J = 16.5 Hz, 2H), 4.38 (d, J = 16.5 Hz, 2H), 2.35 (s, 6H), 2.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 135.67, 135.25, 135.14, 135.10, 133.29, 132.56 (2C), 129.60, 129.54 (2C), 128.68, 128.30, 128.16, 127.96, 126.59, 125.91, 125.70, 121.30, 113.99, 35.09, 21.54, 18.33; IR (neat) 3054, 2961, 1506, 1457, 1426, 1332, 1263, 1026; (EI 12 eV, *m/z* , rel intensity) 682 (24%), 647 (56), 564 (93), 421 (100), 408 (25), 395 (30), 279 (11), 143 (65).



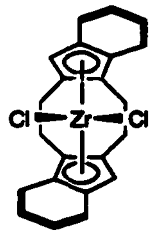
233

dl-2,2'-Bis[1-(4,7-dimethylindenylmethyl)]-1,1'-binaphthyldichlorozirconium (233). To a solution of *dl*-2,2'-bis[1-(4,7-dimethylindenylmethyl)]-1,1'-binaphthalene **212** (685 mg, 1.21 mmol) in ether (5 mL) was added dropwise n-butyllithium (1.05 mL, 2.54 mmol, 2.69 M in hexanes) at -78 °C. After the addition the reaction mixture was allowed to slowly warm to room temperature, and stir for 6 h at which time a fine white precipitate could be seen. $ZrCl_4$ (423 mg, 1.82 mmol) was added via side arm to the heterogeneous mixture causing an instantaneous color change from white to a bright yellow. The yellow heterogeneous mixture was allowed to stir for an additional 12 h at room temperature, and then concentrated *in vacuo* to give a bright yellow solid. To the crude solid was added dichloromethane (5 mL) resulting in an orange heterogeneous mixture which was then Schlenk filtered. The resulting orange solution was concentrated to 0.5 mL *in vacuo* followed by the slow addition of hexanes causing a light yellow precipitate to form. The heterogeneous mixture was back filtered, and the yellow powder was rinsed with hexanes (2x2 mL) then concentrated *in vacuo* to give **233** (0.181g, 21%). mp >290 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.47 (m, 2H), 7.28(m, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.81 (s, 4H), 6.49 (d, J = 3.5 Hz, 2H), 5.23 (d, J = 3.5 Hz, 2H), 4.47 (d, J = 16.0 Hz, 2H), 4.34 (d, J = 16.0 Hz, 2H), 2.23 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 136.03, 135.10, 133.68, 133.40, 132.71, 132.64, 129.53, 128.97, 128.44, 128.24, 127.52, 126.69, 126.60, 125.90, 125.77, 125.28, 121.01, 119.26, 103.66, 33.97, 21.58, 18.40; IR (thin film) 3049, 2963, 2923, 1634, 1495, 1449, 1328, 1258, 1075, 1026; (EI 12 eV, *m/z* , rel intensity) 724 (M^+, 4 %), 725 (M^++1, 6), 726 (M^++2, 4), 728 (M^++4, 7), 564 (63), 421 (46), 408 (23), 279 (29), 171 (37), 145 (100).



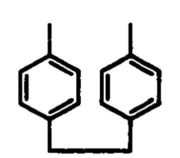
284

Crystals of [1,2'-(Ethane-1,2-diyl)-2,1'-(ethane-1,2-diyl)bis(indenyl)]dichlorozirconium (284). Bis(indene) **284** was purified further before crystallization by dissolving the crude compound in dichloromethane and Schlenk filtering. The dichloromethane was concentrated *in situ* until 1-2 mL total volume remained and a sufficient volume of hexanes (5 mL) was added to cause a precipitate to drop from the solution. The slurry was stirred and Schlenk filtered to give a solid bright yellow powder. Crystals suitable for X-ray diffraction were grown at 0 °C by diffusion of hexane into a solution of methylene chloride and **284**. Crystallographic data is given in Table 4-1. Anal. calculated for $C_{22}H_{18}Cl_2Zr$: 59.45% C, 4.08% H. Found: 59.69% C, 4.08% H.



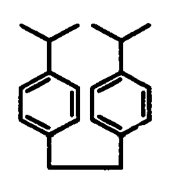
285

[1,2'-(Ethane-1,2-diyl)-2,1'-(ethane-1,2-diyl)bis(4,5,6,7-tetrahydroindenylmethyl)dichlorozirconium (285). An autoclave was charged with bis(indenyl)zirconium dichloride **284** (203 mg, 0.457 mmol), PtO_2 (18 mg, 0.079 mmol), and dichloromethane (100 mL), and was brought to 1100 psi of hydrogen gas with stirring. After 12 h the reaction was complete as seen from the ^1H NMR spectrum of the aliquot. The reaction solution was diluted with dichloromethane (100 mL) and filtered in a dry box. The filter was washed with dichloromethane (25 mL). The solvent was removed *in vacuo*. The crude off white solid was purified by precipitation of **285** from toluene (1 mL) with hexanes (5 mL). The resulting precipitate was washed with hexanes (2 x 5 mL) and gave 151 mg (63% yield) of **285** as a white solid. mp/dec = 195-205 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 2 H), 3.40-3.00 (m, 8H), 2.60-2.80 (m, 4H), 2.45-2.25 (m, 4H), 2.1-1.80 (m, 4H), 1.40-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.39, 130.55, 126.36, 124.06, 118.87, 30.04, 27.11, 23.54, 23.08, 22.23, 21.91; (EI 12 eV, *m/z* , rel intensity) 452 (4%), 451 (7), 450 (36), 449 (25), 448 (76), 447 (60), 446 (99), 445 (66), 444 (100), 414 (4), 412 (15), 411 (9), 410 (21), 409 (15), 407 (30). Anal. calculated for $C_{22}H_{26}Cl_2Zr$: 58.39% C, 5.79% H. Found: 58.29% C, 5.99% H.



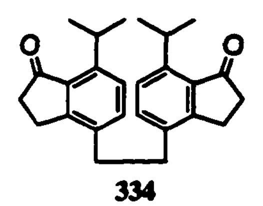
331

1,2-Di(4-methylphenyl)ethane (331).[144] 331 was synthesized in one step from *p*-xylene according to the literature procedure. Note: the potassium salt needed to be used immediately after isolation. If this was used the next day the desired product was isolated in low yield. The ^{1}H NMR spectra matched the ^{1}H NMR spectrum found in literature.[144]



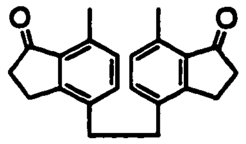
332

1,2-Di(4-isopropylphenyl)ethane (332): To *p*-cymene (8.99 g, 67 mmol), potassium *tert*-butoxide (5.6 g, 50 mmol) in hexanes (50 mL) was added dropwise at room temperature *n*-butyllithium (18.6 mL, 2.69 M in hexanes, 50 mmol) resulting in an orange slurry. The slurry was stirred an additional 1 h at room temperature to yield a brick red precipitate. The precipitate was filtered, rinsed with hexanes (2x10 mL) and dried *in vacuo*. The solid was then transferred to an addition funnel and dissolved in THF (100 mL). The THF solution was then added dropwise to a solution of iodine (6.38 g, 25 mmol) in THF (100 mL) at room temperature. Upon completion of the addition the reaction mixture was stirred an additional 30 min to yield a white slurry. This mixture was quenched with saturated aqueous NH_4Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with ether (3x50 mL), and the combined organic portion washed with $NaHSO_3$, water, brine, dried over $MgSO_4$, filtered and concentrated to give a brown solid. The crude solid was purified by column chromatography (SiO_2/pet. ether) to give **332** (4.61 g, 17 mmol) in 69% yield as a white solid. Mp 52-54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (bs, 8H), 2.88 (sept, J = 7.0 Hz, 2H), 2.87 (s, 4H), 1.23 (d, J = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.41, 139.40, 128.28, 126.39, 37.61, 33.73, 24.10; IR (thin film) 3048, 2957, 2923, 2872, 1458, 828 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 266 (10%), 133 (100), 105 (21), 91 (12).



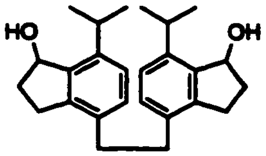
334

1,2-Di(4-isopropylindanon-7-yl)ethane (334): To aluminum trichloride (2.55 g, 19.1 mmol) in dichloromethane (50 mL) at 0 °C was added 3-chloropropionyl chloride (2.43 g, 19.1 mmol). The mixture was stirred for 30 min at 0 °C then **332** (2.29 g, 8.5 mmol) in dichloromethane (50 mL) was added dropwise. The resulting red solution was slowly warmed to room temperature and stirred for 2 h. The reaction was poured over ice, separated and extracted with dichloromethane (3x30 mL). The combined organic layers were washed with water, sodium bicarbonate (sat.), dried over $MgSO_4$, filtered and concentrated. The crude material was then added to concentrated sulfuric acid at 0 °C. The reaction solution was then brought to 80 °C for 2 h and cooled to room temperature, poured over ice and extracted with ether (3x50 mL). The combined ether layer was washed with water, sodium bicarbonate (sat.), brine, dried over $MgSO_4$, filtered, and concentrated. The crude white solid was purified by column chromatography (SiO_2/ 10% ethyl acetate/pet. ether) to yield ketone **334** as a mixture of isomers (1.32 g, 3.5 mmol) in 41% yield. Mp 121-125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.05 (m, 4H), 3.30-2.60 (m, 10H), 3.25 (bs, 4H), 1.30-1.20 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.32, 209.02, 208.95, 155.74, 154.65, 154.27, 148.77, 145.20, 144.62, 141.18, 140.44, 137.59, 135.27, 134.63, 134.51, 133.71, 131.13, 130.03, 129.90, 124.87, 54.32, 37.91, 37.61, 37.56, 34.19, 33.47, 33.37, 30.59, 29.95, 27.64, 24.74, 24.67, 24.60, 24.07, 23.89; IR (thin film) 2953, 2922, 2864, 1699, 1574, 1492, 1254 1058, 846 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 374 (18%), 200 (12), 187 (100), 172 (10), 159 (14), 145 (33), 141 (10), 129 (14), 128 (29), 115 (24), 91 (13).



333

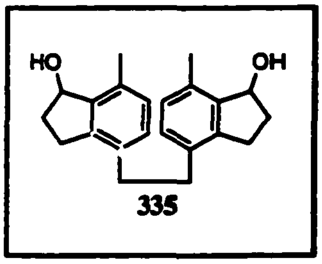
1,2-Di(4-methylindanon-7-yl)ethane (333). Diketone **333** was prepared according to the procedure outlined for the synthesis of **334** but using **331** (0.500 g, 2.4 mmol) to give white solid **333** as a mixture of isomers (0.390g, 1.2 mmol) in 51% yield. Mp. 184-187 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35-6.95 (m, 4H), 3.40-2.30 (m, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 208.39, 208.32, 207.83, 205.88, 155.14, 154.49, 154.00, 140.18, 139.41, 136.75, 136.28, 136.01, 134.55, 134.48, 134.42, 134.25, 133.93, 133.86, 133.55, 129.50, 129.29, 128.75, 128.58, 36.76, 36.70, 36.66, 36.57, 33.18, 32.31, 32.11, 29.65, 24.33, 24.26, 23.85, 17.97, 17.87, 17.40; IR (thin film) 2955, 2924, 2857, 1703, 1580, 1492, 1446, 1248 cm^{-1}; (EI 12eV, *m/z*, rel. intensity) 318 (11%), 159 (100), 106 (14), 91 (18).



336

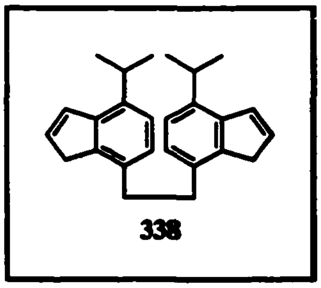
1,2-Di(4-isopropylindanol-7-yl)ethane (336). To **334** (1.32 g, 3.5 mmol) in methanol (100 mL) was added at 0 °C NaBH$_4$ (0.335 g, 8.8 mmol) in four portions. The solution was then stirred for 12 h at room temperature. The solvent was removed leaving a solid residue. The residue was partitioned between water (100 mL), and extracted with methylene chloride (3x50 mL). The combined organic layers were washed with water (25 mL), dried over MgSO$_4$, filtered and concentrated to give crude **336** (0.997 g, 2.6 mmol) as an off white solid. Crude **336** (mixture of isomers) was used for characterization and carried on without further purification. Mp 154-158 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.25-7.00 (m, 4H), 5.70-5.40 (m, 2H), 3.30-2.20 (m, 16H), 1.40-1.10 (m, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.63, 14258, 142.55, 142.39, 141.55, 141.51, 136.44, 136.21, 128.10, 127.95, 125.03, 124.87, 75.40, 75.04, 35.58, 34.87, 34.51, 34.47, 30.43, 30.38, 28.42, 28.16, 23.03, 22.30, 22.94; IR (thin film) 3327, 2958, 2925, 2869, 1701, 1492, 1456 cm^{-1}; (EI

70eV, *m/z*, rel. intensity) 360 (18%), 342 (57), 327 (16), 317 (26), 299 (31) 200, (28), 173 (100), 171 (29), 159 (9).



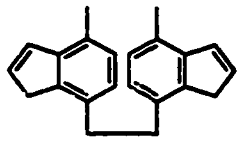
335

1,2-Di(4-methylindanol-7-yl)]ethane (335): Diol **335** was prepared following the procedure outlined for the preparation of **336** but using **333** (2.301 g, 7.2 mmol) to give crude **335** as a mixture of isomers (1.69 g, 5.2 mmol). The crude white solid was used for characterization and carried on to the next step. Mp 91-94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-6.90 (m, 4H), 5.40-5.00 (m, 2H), 3.10-2.00 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.11, 143.08, 142.97, 142.92, 142.83, 142.75, 142.55, 142.48, 142.45, 142.42, 142.39, 142.25, 136.47, 136.24, 136.19, 136.09, 135.53, 135.41, 135.35, 135.31, 132.71, 131.84, 129.72, 129.70, 129.61, 129.50, 129.01, 128.87, 128.83, 128.63, 128.44, 128.37, 128.35, 127.76, 127.61, 127.39, 127.33, 35.08, 34.91, 24.83, 34.70, 34.59, 33.93, 33.15, 32.81, 29.67, 29.36, 28.88, 28.80, 28.69, 28.48, 28.45, 28.31, 18.65, 17.99; (EI 70eV, *m/z*, rel. intensity) 304 (12%), 289 (9), 386 (31), 271 (11), 160 (46), 145 (25) 143 (100), 131 (20), 128 (53), 117 (6), 115 (23) 91 (15), 77 (6).

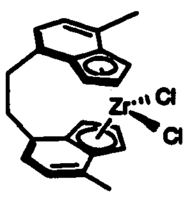


338

1,2-Di(4-isopropylinden-7-yl)ethane (338): To crude **336** (0.997 g, 2.6 mmol) in benzene (75 mL) was added a few crystals of *p*-toluenesulfonic acid hydrate. The reaction vessel was then fitted with a Dean Stark apparatus, and the solution was refluxed 3 h. The reaction was cooled to room temperature and washed with a saturated solution of sodium bicarbonate (50 mL) followed by water (25 mL). The organic layers were dried over $MgSO_4$, filtered and concentrated to give an off white solid. The solid was purified by column chromatography (SiO_2/pet. ether) to give **338** as a mixture of double bond isomers (0.631 g, 1.8 mmol) as a white solid in 52% yield based on starting ketone. Mp 54-56 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.25-7.00 (m, 6H), 6.70-6.50 (m, 2H), 3.45-3.00 (m, 10H), 1.40-1.25 (m, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.94, 142.33, 143.31, 141.94 (2C), 141.61, 141.57, 141.04, 139.16, 134.55, 133.32, 133.27, 133.10, 132.16, 130.32, 130.22, 126.95, 126.93, 123.14, 121.38, 37.90, 37.84, 35.04, 34.98, 33.65, 30.86, 30.58, 29.70, 23.55, 23.06; IR (thin film) 3066, 2998, 2924, 2871, 1488, 1456, 1388 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 342 (10%), 299 (14), 171 (100), 156 (15), 143 (11), 141 (20), 128 (25), 115 (10).

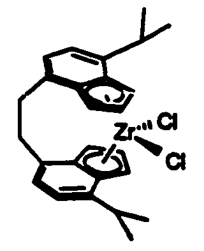

337

1,2-Di(4-methylinden-7-yl)]ethane (337): Bis(indene) **337** was prepared following the procedure outlined for **338** but using **335** (1.34 g, 4.2 mmol) to afford **337** as a mixture of isomers (0.671 g, 2.4 mmol) in 56% yield. Mp 132-136 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10-6.95 (m, 6H), 6.60-6.50 (m, 2H), 3.40-2.90 (m, 8H), 2.45-2.35 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.55, 142.74, 142.46, 141.74, 134.48, 133.64, 133.61, 133.17, 132.80, 132.18, 130.68, 130.52, 130.45, 130.21, 130.12, 129.51, 128.12, 128.09, 127.81, 126.69, 126.66, 125.97, 125.15, 124.70, 38.72, 38.28, 37.96, 37.92, 36.34, 35.17, 35.11, 33.86, 33.76, 29.70, 18.52, 18.35; IR (thin film) 3086, 3060, 2998, 2874, 1473, 1420 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 287 (6%), 286 (57), 271 (45), 256 (8), 239 (13) 143 (100), 128 (24).



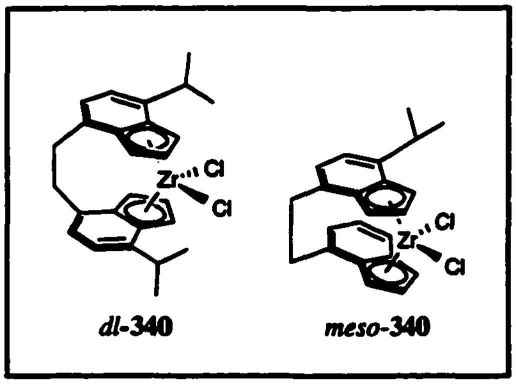
***dl*-339**

***dl*-1,2-Di(4-methylinden-7-yl)]ethylidenezirconium dichloride (*dl*-339):** Toluene (3 mL) was added to **337** (0.292 g, 1.02 mmol) and zirconium tetrakis(dimethylamido) (0.273 g, 1.02 mmol) at 0 °C. The clear yellow solution was then brought to 125 °C for 24 h taking care the vessel is left open to the Schlenk line to ensure the escape of dimethylamine. The resulting light orange solution was concentrated *in vacuo*, and dimethylammonium chloride (0.162 g, 1.99 mmol) in dichloromethane (50 mL) was added at 0 °C. This solution was warmed to room temperature, and stirred an addition 3 h. The resulting yellow solution was concentrated to 1-2 mL total volume, and hexanes (5 mL) were added dropwise until a yellow precipitate began to form. This slurry was stirred for 30 min, filtered, and rinsed with hexanes (2x5 mL) to give pure *dl*-**339** (0.196 g, 0.44 mmol) as a yellow powder in 63% yield. Mp/dec. 210-220 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (d, J = 7.0 Hz, 2H), 7.05 (dq, J = 7.0, 1.0 Hz, 2H), 6.74 (dd, J = 3.5, 3.5 Hz, 2H), 6.69 (dd, J = 3.5, 2.0 Hz, 2H), 4.45 (dd, J = 3.5, 2.0 Hz, 2H), 3.34 (d, J = 9.0 Hz, 2H), 3.02 (d, J = 9.0 Hz, 2H), 2.60 (d, J = 1.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.49, 134.84, 130.25, 126.55, 126.12, 126.00, 124.62, 108.16, 101.67, 36.28, 19.81; (EI 12eV, *m/z*, rel. intensity) 452.1 (4%), 451.1 (7), 450 (36), 449 (25), 447 (76), 447 (60), 446 (99), 445 (66), 444 (100), 413 (4), 412 (15), 411 (9), 410 (21), 409 (15), 408 (30) 286 (5), 92 (11). Combustion calculated 59.18% C, 4.51% H; actual 56.57% C, 4.74% H.



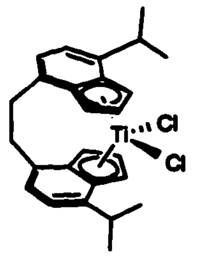
dl-**340**

***dl*-1,2-Di(4-isopropylinden-7-yl)]ethylidenezirconium dichloride (*dl*-340)**: To **338** (0.292 g, 0.90 mmol) and zirconium tetrakis(dimethylamido) (0.235 g, 0.35 mmol) was added chlorobenzene (5 mL) at 0 °C. The clear yellow solution was then brought to 125 °C for 24 h taking care the vessel is left open to the Schlenk line to ensure the escape of dimethylamine. The resulting light orange solution was concentrated *in vacuo*, and dimethylammonium chloride (0.134 g, 1.64 mmol) in dichloromethane (50 mL) was added at 0 °C. This solution was warmed to room temperature, and stirred an additional 3 h. The resulting yellow solution was concentrated to 1-2 mL total volume *in vacuo*, and hexanes were then added dropwise until a yellow precipitate began to form. This slurry was stirred for 30 min then filtered and rinsed with hexanes (2x5 mL) to give pure *dl*-**340** (0.259 g, 0.52 mmol) as a yellow powder in 61% yield. Crystals suitable for X-ray analysis were grown by diffusion of hexanes into a solution of dichloromethane and *dl*-**340** at 0 °C. Mp/dec. 205-215 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 6.71 (m, 4H), 4.42 (dd, J = 3.5, 2.0 Hz, 2H), 3.68 (qq, J = 7.0, 7.0 Hz, 2H), 3.34 (d, J = 9.0 Hz, 2H), 3.02 (d, J = 9.0 Hz, 2H), 1.37 (d, J = 7.0 Hz, 6H), 1.15 (d, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.46, 136.30, 129.67, 125.76, 125.70, 124.87, 121.46, 107.51, 101.96, 36.28, 30.25, 24.19, 20.59; IR (thin film) 3111, 2962, 2844, 1461, 1448, 1257, 1076, 846, 822, 778 cm^{-1}; (EI 12eV, *m/z*, rel. intensity) 506 (31%), 505 (18), 504 (65), 503 (41), 502 (100), 501 (55), 500 (92), 468 (38), 467 (32), 466 (68), 465 (45), 464 (85), 342 (23), 299 (18), 171 (71). Anal. calculated for C26H28Cl2Zr: 62.13% C, 5.61% H. Found 60.60% C, 5.60% H.



dl-**340** *meso*-**340**

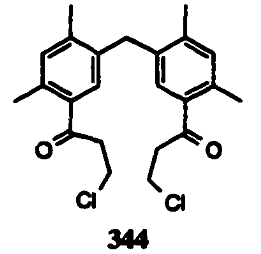
***dl*- and *meso*-1,2-Di(4-isopropylinden-7-yl)ethylidenezirconium dichloride (340):** To **338** (1.04 g, 3.0 mmol) in diethyl ether (20 mL) at -78 °C was added *n*-butyllithium (3.2 mL, 2.40M in hexanes, 7.7 mmol). The resulting slurry was warmed to room temperature and stirred an additional 5 h. The dilithio salt was Schlenk filtered and washed twice with hexanes (2x5 mL). The salt was vacuum dried and used immediately. The dilithio salt (0.309 g, 0.87 mmol) and zirconium tetrachloride (0.224 g, 0.96 mmol) were placed in a Schlenk flask. To the solid mixture was added ether (3 mL) at 0 °C resulting in a yellow slurry. The yellow slurry was stirred for 10 h at room temperature followed by the removal of the solvent *in vacuo* and replaced with dichloromethane (5 mL). The dichloromethane was then Schlenk filtered and concentrated to 1 mL total volume followed by the addition of hexanes (5 mL) until a fine yellow precipitate formed. The precipitate was back filtered and washed with hexanes (2x2 mL) to give a 1:1 mixture of ***meso*-340** and ***dl*-340** (0.263 g, 0.52 mmol) as a yellow powder in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 7.07 (dd, J = 3.0, 2.0 Hz, 2H), 6.74-6.70 (m, 6H), 6.65 (d, J = 7.0, 2H), 6.60 (dd, J = 3.5, 2.0 Hz, 2H), 6.53 (dd, J = 3.5, 3.5 Hz, 2H), 4.42 (dd, J = 3.5, 2.0 Hz, 2H), 3.68 (qq, J = 7.0, 7.0 Hz, 2H), 3.50-3.10 (m, 8H), 3.02 (d, J = 9.0 Hz, 2H), 1.38 (d, J = 7.0 Hz, 6H), 1.23 (d, J = 7.0 Hz, 6H), 1.16 (d, J = 7.0 Hz, 6H), 1.11 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.43, 142.91, 136.28, 133.66, 129.64, 129.60, 125.74, 125.67, 125.63, 124.84, 121.44, 120.91, 120.85, 107.48, 105.71, 101.95, 101.92, 98.34, 36.26, 30.51, 30.22, 24.17, 23.62, 20.57, 20.30.



***dl*-341**

***dl*-1,2-Di(4-isopropylinden-7-yl)ethylidenetitanium dichloride (*dl*-341)**: To the dilithio salt isolated from the above procedure for compound **338** (0.229 g, 4.1 mmol) was added titanium trichloride (0.070 g, 4.5 mmol). To the solid mixture at -78°C was added THF dropwise (5 mL), and after the addition the reaction slurry was brought to room temperature and refluxed for 5 h. The reaction mixture was cooled to room temperature, and the solvents were removed *in vacuo* leaving a solid green residue. The residue was dissolved in chloroform (5 mL) and 2 N hydrochloric acid (1 mL) was added at 0 °C. The mixture was then stirred while open to air for 2 h at room temperature then the layers were separated. The aqueous layer was extracted with dichloromethane (3x5 mL), and the combined organic layers were washed with water, brine, dried over $MgSO_4$, filtered and concentrated. The solid green residue was recrystallized from dichloromethane and hexanes to give pure ***dl*-341** (0.153 g, 3.3 mmol) as a fine green precipitate in 74% yield. Crystals suitable for X-ray analysis were obtained from the slow evaporation of chloroform at room temperature. Mp/dec. 200-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.0

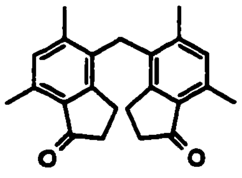
Hz, 2H), 7.17 (d, J = 7.0 Hz, 2H), 6.95 (dd, J = 3.5, 2.0 Hz, 2H), 6.72 (dd, J = 3.5, 3.5 Hz, 2H), 4.21 (dd, J = 3.5, 2.0 Hz, 2H), 3.86 (qq, J = 7.0, 7.0 Hz, 2H), 3.31 (d, J = 9.0 Hz, 2H), 3.01 (d, J = 9.0 Hz, 2H), 1.36 (d, J = 7.0 Hz, 6H), 1.15 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.15, 137.25, 133.92, 127.35, 127.11, 126.48, 123.06, 116.00, 110.22, 36.59, 30.36, 24.49, 20.74; IR (thin film) 2964, 2960, 2938, 1493, 1446, 1395, 1258 cm^{-1}; (EI 12eV, *m/z*, rel. intensity) 462 (2%), 460 (13), 458 (18), 424 (15), 423 (16), 422 (50), 420 (7), 387 (14), 386 (100) 384 (14); Anal. Calculated for $C_{26}H_{28}Cl_2Ti$: 67.99% C, 6.14% H. Found 66.97% C, 6.13% H.



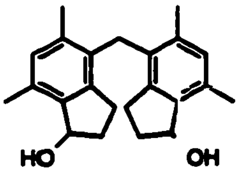
344

Bis[1-(3-chloropropanon-1-yl)-2,4-dimethylphen-5-yl]methane (344): To an aluminum trichloride (11.8 g, 88.5 mmol) suspension in dichloromethane (100 mL) was added slowly at 0 °C 3-chloropropionyl chloride (10.6 mL, 111 mmol). The suspension was stirred for 30 min. resulting in a clear green solution. To this solution was added dropwise **343** (10.0 g, 44.6 mmol) in dichloromethane (50 mL) at 0°C. Upon completion of the addition the mixture was stirred an additional 30 min. to give a red solution which was poured over ice, separated and extracted with dichloromethane (3x100 mL). The combined organic layers were washed with sodium bicarbonate, water, dried over $MgSO_4$, filtered and concentrated. The crude solid was purified by Soxhlet extraction (pet. ether) to give **344** (7.39g, 18.2 mmol) as a white solid in 41% yield. Pure **344** was obtained by chromatography (SiO_2/10% ethyl acetate/pet. ether). Mp 112-113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.10(s, 2H), 3.91 (s, 2H), 3.80 (t, J = 6.5 Hz, 4H), 3.17 (t, J = 6.5 Hz, 4H), 2.48 (s, 6H), 2.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.69, 141.08, 137.16, 135.17, 134.75, 134.30, 129.53, 43.44, 39.11, 35.83, 21.03, 19.53; IR (thin film) 3014, 2966, 1674, 1549, 1443, 1343, 1206, 1090, 1032 cm^{-1}; (EI 70eV, *m/z*, rel.

intensity) 407 (1%), 406 (6), 405 (3), 404 (9), 343 (33), 342 (24), 341 (100), 313 (9), 305 (11), 303 (4), 272 (19), 207 (16), 191 (9), 139 (20).

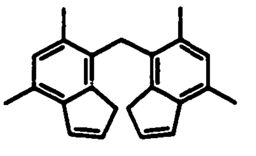

345

Bis(4,6-dimethylindanon-7-yl)]methane (345): To concentrated sulfuric acid (40 mL) at 0 ^{0}C was added **344** (3.71 g, 9.1 mmol). After the addition the red solution was warmed to 80 ^{0}C for 1 h. The reaction mixture was then cooled to room temperature, poured over ice, and extracted with ether (3x100 mL). The combined organic layers were washed with saturated $NaHCO_3$, water, brine, and dried over $MgSO_4$, filtered and concentrated. The crude solid was purified by column chromatography (SiO_2/10% ethylacetate/pet. ether) to give **345** (1.33 g, 4.0 mmol) in 49% yield. Mp 186-188 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2H), 4.07 (s, 2H), 2.57 (s, 6H), 2.64 (dt, J = 2.0, 6.0 Hz, 4H), 2.54 (dt, J = 2.0, 6.0 Hz, 4H), 2.24 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.72, 155.01, 143.20, 136.56, 133.02, 132.69, 132.35, 36.86, 29.45, 24.67, 20.61, 17.96; IR (thin film) 3007, 2949, 2920, 1701, 1574, 1479, 1439, 1253 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 332 (46%), 317 (12), 172 (100), 144 (36), 129 (24), 128 (17), 115 (10).


346

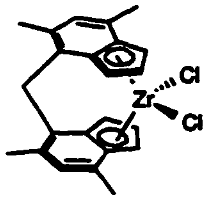
Bis(4,6-dimethylindanol-7-yl)]methane (346): To **345** (0.899 g, 2.7 mmol) in methanol (50 mL), and dichloromethane (25 mL) was slowly added at 0 ^{0}C $NaBH_4$ (0.257 g, 6.8 mmol). After the addition the reaction mixture was continued at room temperature for 12 h. The solvents were removed, and the crude material was partitioned between water and dichloromethane (3x50 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated. The crude white solid was characterized and used in the next step without purification. Mp 144-147 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 2H), 5.23

(m, 2H), 3.92 (s, 2H), 2.75-2.60 (m, 2H), 2.50-2.25 (m, 2H), 2.36 (s, 6H), 2.14 (s, 6H), 2.30-1.50 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.34, 143.30, 141.05, 141.02, 137.23, 137.16, 132.31, 132.21, 132.19, 130.78, 130.71, 75.16, 75.06, 35.04, 35.02, 31.72, 31.63, 29.20, 29.16, 20.05 (2C), 17.90; IR (thin film) 3300, 3002, 2954, 2921, 2851, 1455, 1039 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 336 (42%), 318 (20), 303 (18), 300 (24), 285 (10), 174 (100), 159 (18), 156 (19), 145 (18).



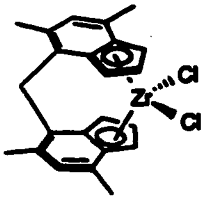
347

Bis(4,6-dimethylinden-7-yl)]methane (347): Crude **346** was placed in benzene (100 mL) with a few crystals of *p*-toluenesulfonic acid hydrate. The reaction flask was fitted with a Dean Stark apparatus and refluxed 3 h. The reaction was cooled to room temperature and aqueous $NaHCO_3$ (50 mL) was added. The organic layers were dried with $MgSO_4$, filtered and concentrated. The crude solid was purified by column chromatography (SiO_2/pet. ether) to give **347** (0.583 g, 1.94 mmol) as a white solid in 72% yield based on starting ketone **345**. Mp 132-133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.89 (dt, J = 5.5, 2.0 Hz, 2H), 6.32 (dt, J = 5.5, 2.0 Hz, 2H), 4.15 (s, 2H), 2.88 (bs, 4H), 2.41 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.80, 141.81, 133.31, 132.68, 131.24, 129.87, 129.82, 127.82, 38.54, 31.94, 20.02, 18.23; IR (thin film) 3055, 3000, 2957, 2914, 2855, 1474, 1437, 1386 cm^{-1}; (EI 70eV, *m/z*, rel. intensity) 301 (6%), 300 (60), 285 (17), 157 (12), 156 (100), 142 (8), 141 (12), 128 (8), 115 (6).



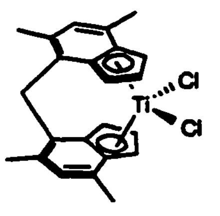
dl-**348**

Bis(4,6-dimethylinden-7-yl)]methylidenezirconium dichloride (*dl*-348): To **347** (0.396 g, 1.32 mmol) and zirconium tetrakis(dimethylamido) (0.347 g, 1.30 mmol) was added chlorobenzene (8 mL) at 0 °C. The clear yellow solution was then brought to 125 °C for 24 h with the vessel open to the Schlenk line to ensure the escape of dimethylamine. The resulting light orange solution was concentrated *in vacuo*, and dimethylammonium chloride (0.100 g, 1.23 mmol) in dichloromethane (50 mL) was added at 0 °C. This solution was warmed to room temperature, and stirred an additional 3 h (Note: Precipitate forms over the 3 h period). The resulting yellow solution was concentrated to 2 mL total volume, and hexanes (5 mL) were added dropwise. This slurry was stirred for 30 min then filtered and rinsed with hexanes (2x5 mL) to give *dl*-**348** (0.259 g, 0.56 mmol) as a yellow powder in 43% yield (Note: the metallocene is thermally unstable in solution and as a solid. In addition, the compound is only slightly soluble in solvents such as methylene chloride and chloroform). Mp/dec. 235-245 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.68 (dd, J = 3.5, 3.5 Hz, 2H), 6.57 (dd, J = 3.5, 2.0 Hz, 2H) 4.46 (s, 2H), 4.27 (dd, J = 3.5, 2.0 Hz, 2H), 2.63 (s, 6H), 2.55 (s, 6H); (EI 12eV, *m/z*, rel. intensity) 466 (2), 465 (5) 464 (28), 463 (20), 462 (70), 461 (42), 460 (42), 459 (60), 458 (100), 426 (21) 425 (12), 424 (35), 423 (21), 422 (52), 300 933), 156 (45).



dl-**348**

Bis[4-(5,7-dimethylindenyl)]methylidenezirconium dichloride (*dl*-348): To **347** (0.198 g, 0.66 mmol) in ether (5 mL) at -78°C was added *n*-butyllithium (0.51 mL, 2.69 M in hexanes, 1.4 mmol). The resulting slurry was warmed to room temperature and stirred an additional 5 h. To the dilithio salt was added zirconium tetrachloride (0.231 g, 0.99 mmol) via sidearm. The yellow slurry was stirred for 12 h at room temperature followed by the removal of the solvent *in vacuo*. Dichloromethane (5 mL) was added to the solid and stirred 30 min. The dichloromethane was Schlenk filtered, and the solid residue was further rinsed with dichloromethane (2x10 mL). The residue was dried *in vacuo* and an ^{1}H NMR spectrum revealed the desired product remained with the lithium chloride salt, and was identical with that found with the procedure described above. The yield was not be calculated.



dl-349

Bis(4,6-dimethylinden-7-yl)]methylidenetitanium dichloride (*dl*-349): To 347 (0.660 g, 2.19 mmol) in tetrahydrofuran (2 mL) was added at -78°C *n*-butyllithium (1.70 mL, 2.69 M in hexanes, 4.6 mmol). After the addition the reaction was warmed to room temperature and stirred for 30 min. The dilithio salt solution was then added dropwise via syringe to titanium trichloride (0.41 g, 2.64 mmol) in tetrahydrofuran (1 mL) at -78 °C. Upon warming to room temperature the solution went from a purple to a dark green solution. After reaching room temperature the mixture was brought to reflux for 5 h then cooled to room temperature. The solvents were removed *in vacuo*, and replaced with chloroform (10 mL) and 1N hydrochloric acid (2 mL). The dark green liquid was stirred for 2 h in air during which time a precipitate formed. The layers were separated and the aqueous layer extracted with dichloromethane (3x50 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated (Note: a substantial portion of the titanocene remained with the $MgSO_4$ due to product insolubility. Like the zirconocene dichloride the product was thermally unstable as a solid and would decompose over 48 h and faster in solution). The solid residue was rinsed with hexanes to give *dl*-**349** (0.352 g, 0.84 mmol) as a green precipitate in 38% yield. Mp dec. 200-220°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.87 (m, 2H), 6.68 (m, 2H), 4.46 (s, 2H), 4.02 (m, 2H), 2.62 (bs, 12H); (EI 12eV, *m/z*, rel. intensity) 420 (4%), 418 (78), 417 (36), 414

(13), 383 (5), 382 (45), 381 (24), 380 (100), 378 (18), 344 (11), 300 (7), 298 (6), 297 (10), 283(6) 156 (8).

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