

DESIGN AND SYNTHESIS OF NEW C_1 AND C_2 -SYMMETRIC ANSA-METALLOCENE CATALYSTS FOR ISOTACTIC POLYPROPYLENE FORMATION

A Thesis

by

KHALID A. AL-BAHILY

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2004

Major Subject: Chemistry

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ABSTRACT

Design and Synthesis of New C_1 and C_2 -Symmetric *Ansa*-Metallocene Catalysts for
Isotactic Polypropylene Formation. (December 2004)

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Several *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes based on zirconium have been prepared with different substituents at position 3 on the cyclopentadienyl ring. Isotactic polypropylene production from these systems depends highly on the size of these substituents. Therefore, large groups such as 1-methyl-4-*t*-butylcyclohexyl (metallocene **6**), 1-methyl-cyclohexyl (metallocene **7**), 1,3,3,5-tetramethylcyclohexyl (metallocene **8**), and 2,3,4-trimethyl-3-pentyl (metallocene **9**) have been investigated. In combination with methylaluminoxane (MAO), they showed good activity and produced high molecular weight of isotactic polypropylene. In terms of the tacticity of the polymers, metallocene **6** made the best isotactic polypropylene with ~88% *mmmm* pentad content. Also, it has been found that if the size of this substituent is large as in 2,3,4-trimethyl-3-pentyl (metallocene **9**), then it will block the polymerization active site which will deactivate the metallocene.

New synthetic pathways for the synthesis of cyclopentadienyl-fluorenyl metallocenes based on titanium have been achieved. Anchoring these types of ligands onto titanium by following the conventional method of using TiCl_4 in the metallation step has failed for the production of $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$

(metallocene **12**), $\text{Ph}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$ (metallocene **14**), and $\text{Ph}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{TiMe}_2$ (metallocene **15**); this is possibly due to the high reactivity of TiCl_4 . Therefore, $\text{TiCl}_4 \cdot 2\text{THF}$ has been prepared and used in that step to produce these new titanocenes with good yields.

A new *ansa*- C_2 -symmetric substituted bis-indenyl metallocene for isotactic polypropylene production has been successfully prepared. It is known that *ansa*- C_2 -symmetric metallocenes are good catalysts for isotactic polypropylene production, but in general, their synthesis suffers from the production of the *meso* C_s -stereoisomer of these catalysts, which generally produces only atactic polypropylene. Therefore, the *meso* stereoisomers must be removed and this is considered a loss of the material that increases the cost of the catalysts. Addition of bulky substituents on the indenyl groups as in $\text{Me}_2\text{Si}(5,5,8,8\text{-tetramethyl-5,6,7,8-tetrahydrobenz(f)indenyl})_2\text{ZrCl}_2$ (metallocene **5**) has prevented the *meso* stereoisomer production. **5**/MAO produces isotactic polypropylene with up to ~80% *mmmm* pentad content.

I would like to dedicate this thesis to my wife, Fowziah Al-Bahily, for her patience and encouragement and also to my father and mother for their constant support and help.

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TABLE OF CONTENTS

	Page
ABSTRACT	iii
DEDICATION	v
ACKNOWLEDGMENT	vi
TABLE OF CONTENTS	vii
LIST OF FIGURES	ix
LIST OF TABLES	xii
CHAPTER I INTRODUCTION	1
CHAPTER II PROPYLENE POLYMERIZATION USING C_1 -SYMMETRIC CYCLOPENTADIENYL-FLUORENYL METALLOCENES	3
2.1 Introduction	3
2.2 Polypropylene via Metallocene Catalysis	4
2.3 Production of Isotactic, Syndiotactic and Hemiisotactic Polypropylene Using C_1 -Symmetric Metallocenes	6
2.3.1 Syndiotactic Polypropylene from C_1 -Symmetric Cyclopentadienyl-Fluorenyl Metallocenes	8
2.3.2 Hemiisotactic Polypropylene from C_1 -Symmetric Cyclopentadienyl-Fluorenyl Metallocenes	12
2.3.3 Isotactic Polypropylene from C_1 -Symmetric Cyclopentadienyl- Fluorenyl Metallocenes	15
2.4 Conclusions	22
CHAPTER III NEW C_1 -SYMMETRIC ANSA- CYCLOPENTADIENYL- FLUORENYL METALLOCENES FOR ISOTACTIC POLYPROPYLENE PRODUCTION	23
3.1 Introduction	23
3.2 Mechanism of Isotactic Polypropylene Polymerization Using Ansa C_1 - Symmetric Cyclopentadienyl-Fluorenyl Metallocenes	25

	Page
3.3 Synthesis and Design of New <i>Ansa</i> C_1 -Symmetric Cyclopentadienyl-Fluorenyl Metallocenes.....	26
3.4 Synthesis of Isotactic Polypropylene	32
3.5 Conclusions	34
3.6 Experimental Section	34
 CHAPTER IV SYNTHESIS OF NEW ANSA- C_2 -SYMMETRIC SUBSTITUTED BIS-INDENYL METALLOCENES FOR ISOTACTIC POLYPROPYLENE PRODUCTION.....	
	55
4.1 Introduction	55
4.2 Synthesis of New <i>Ansa</i> C_2 -Symmetric Substituted Bis-Indenyl Metallocenes	56
4.3 Mechanism of Isotactic Polypropylene Polymerization Using <i>Ansa</i> C_2 -Symmetric Bis-Indenyl Metallocenes.....	58
4.4 Synthesis of Isotactic Polypropylene	60
4.5 Conclusions	61
4.6 Experimental Section	62
 CHAPTER V CONCLUSIONS.....	 69
 REFERENCES.....	 70
 APPENDIX A	 75
 APPENDIX B	 90
 APPENDIX C	 98
 APPENDIX D.....	 106
 VITA	 121

LIST OF FIGURES

FIGURE	Page
2.1 Tacticities of the polypropylene chains.....	3
2.2 The relationship between tacticity of the obtained polypropylene and the symmetry of the metallocene catalyst.....	5
2.3 Structure of the first cyclopentadienyl-fluorenyl C_s -symmetric metallocene..	6
2.4 Enantioselectivity of each site and their outcomes	7
2.5 Structures of metallocenes 2 and 3	9
2.6 C_1 -symmetric metallocenes for syndioselective polypropylene polymerization.....	9
2.7 Stereoerrors in syndiotactic polypropylene formation	10
2.8 Mechanism of syndiotactic polypropylene polymerization with cyclopentadienyl-fluorenyl metallocene. (Bridges omitted for clarity).....	11
2.9 Hemiisotactic polypropylene architecture.....	12
2.10 Cyclopentadienyl-fluorenyl metallocenes made for hemiisoselective polypropylene production	13
2.11 Mechanism of hemiisoselective polypropylene polymerization.....	14
2.12 Structure of metallocene $Me_2C(3-t-Bu-C_5H_3)(C_{13}H_8)ZrCl_2$ 14	15
2.13 Stereoselectivity in the two active sites for the production of isotactic polypropylene.....	16
2.14 Structures of metallocenes 15-76	17
3.1 Structure of metallocenes 1 and 2	23

FIGURE	Page
3.2 The relationship between group size on the cyclopentadienyl ring and polypropylene architecture	24
3.3 Proposed mechanism of isotactic polypropylene formation using C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes	25
3.4 Metallocenes 5-9 have different bulky groups in position 3 of the cyclopentadienyl ring	26
3.5 New targeted metallocenes having diphenylmethylidene bridges	27
3.6 Reaction of fluorenyllithium with 3-(substituted)-6,6-diphenylfulvene	28
3.7 Structures of new titanocenes 12, 14, 15 and vanadocene 13	29
3.8 Synthesis pathway of <i>ansa</i> C_1 -symmetric cyclopentadienyl-fluorenyl Metallocenes.....	30
3.9. Bond lengths and angles in metallocenes 5 and 12	31
3.10 Structure of titanocenes 16 and 17	34
4.1 Structure of metallocenes 1-4	55
4.2 Structure of the new targeted metallocene 5	57
4.3 Synthesis of a bridged <i>ansa</i> - C_2 -symmetric substituted bis-indenyl Zirconocene.....	58
4.4 Monomer insertion mechanism for <i>ansa</i> C_2 -symmetric bis-indenyl zirconocene system	59
4.5 Insertion mechanism using the <i>meso</i> stereoisomer of bis-indenyl metallocenes	59

FIGURE	Page
4.6 ^{13}C NMR spectrum of polypropylene from Entry 2 (Table 3.1).....	61

LIST OF TABLES

Table	Page
2.1 Behaviors of catalysts 1-9 in propylene polymerization.....	12
2.2 Propylene polymerization results of catalysts 10-13	14
2.3 Pentad analysis of hemiisotactic polypropylene produced by catalysts 10-13 .	15
2.4 Propylene polymerization results of catalysts 15-76	20
3.1 Propylene polymerization study of metallocenes 5-9	33
4.1 Propylene polymerization data for metallocenes 3 and 4 in liquid propylene using MAO cocatalyst.....	56
4.2 Propylene polymerization study of metallocene 5	60

CHAPTER I

INTRODUCTION

Nowadays, asymmetric and symmetric metallocenes of group IV became attractive to researchers because of their broad applications for the polypropylene production, from hemiisotactic to syndiotactic to isotactic. Tacticity of the polymer is highly dependent on the symmetry of the metallocene.

Chapter 2 discusses the history and the development of cyclopentadienyl or indenyl and fluorenyl based symmetric and asymmetric metallocenes. It shows the clear relationship between the symmetry and the tacticity of the product using these systems.

Chapter 3 focuses mainly on preparing highly isotactic polypropylene via *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl based metallocenes. Several *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes based on zirconium have been prepared, characterized, and tested for propylene polymerization. The results show the important relationship between the size of the substituent in position 3 of the cyclopentadienyl ring and the isotacticity of the polymer.

Chapter 4 discusses the synthesis of new *ansa*- C_2 -symmetric substituted bis-indenyl metallocenes for isotactic polypropylene production. It is known that C_2 -symmetric metallocenes are good catalysts for isotactic polypropylene production but they suffer from the formation of the *meso* C_s -stereoisomer of these catalysts, which generally produces only atactic polypropylene. Therefore, the *meso* stereoisomers must be removed and this is considered a loss of the material that increases the cost of the

This thesis follows the style of *Organometallics*.

catalysts. Addition of bulky substituents on the indenyl groups has prevented the *meso* stereoisomer production.

CHAPTER II
PROPYLENE POLYMERIZATION USING C_7 -SYMMETRIC
CYCLOPENTADIENYL-FLUORENYL METALLOCENES

2.1 Introduction

Industrially, propylene gas production has been increased in the last decade. The worldwide production of propylene has reached 57.6 million tons in 2003 and is expected to increase to 80 million tons by 2010.¹ The propylene can be produced as a by-product of ethylene production in steam-cracking plants, as a by-product of gasoline production in refineries, or by dehydrogenating propane to propylene. High availability and low cost make propylene attractive to the polymer chemist. Therefore, billions of tons of polypropylene are produced worldwide annually. The low cost and good physical and chemical properties of polypropylene resin make it one of the best polymers for a wide variety of applications, such as carpeting, film, automobile parts, and webbings.²

During the polymerization process, propylene monomers are joined together in a regular sequence determined by the shape or symmetry of the catalyst and the reaction conditions. Polypropylene chains have three different limiting tacticities: isotactic, syndiotactic and atactic (Figure 2.1).

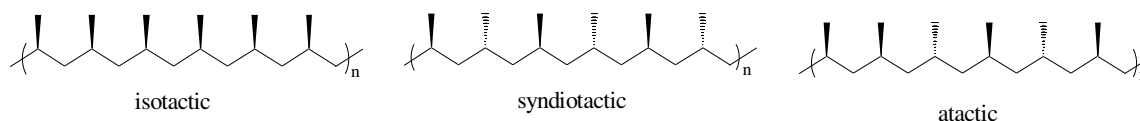


Figure 2.1. Tacticities of the polypropylene chains.

In isotactic chains, methine groups have the same stereochemical configuration whereas they have an alternating configuration in syndiotactic chains; atactic chains have no stereochemical configuration pattern. The chemical and physical properties of the polymer are determined by these stereoregularities. Isotactic and syndiotactic polypropylene have a high degree of crystallinity-in the range of 40% to 70%—whereas atactic polypropylene is amorphous. Isotactic polypropylene has the highest crystallinity between 60 and 70%³—which means it generally has better mechanical properties compared to the other polypropylene products.

2.2 Polypropylene via Metallocene Catalysis

Since the discovery of the combination of stereorigid metallocenes of group IV transition metals with MAO (MAO = methylaluminoxane) in the beginning of the 1980s,⁴⁻⁶ they became a subject of great interest academically and industrially for the production of polypropylene. The reasons are the good polymer properties and high stereoselectivity for propylene polymerization usually obtained from these metallocenes. The great advantage of metallocenes is controlling the tacticity of the polymer by changing metallocene symmetry. For example, C_2 -symmetric metallocenes produce highly isotactic polypropylene, C_{2v} -symmetric metallocenes produce, generally, atactic polypropylene and C_s -symmetric metallocenes make syndiotactic polypropylene. Moreover, C_1 -symmetric metallocenes produce polypropylene that varies from syndiotactic to hemiisotactic to isotactic, depending on the bulkiness of the substituents on the ligands. The difference in tacticity occurs because C_1 -symmetric metallocenes have two inequivalent coordination sites (Figure 2.2).⁷

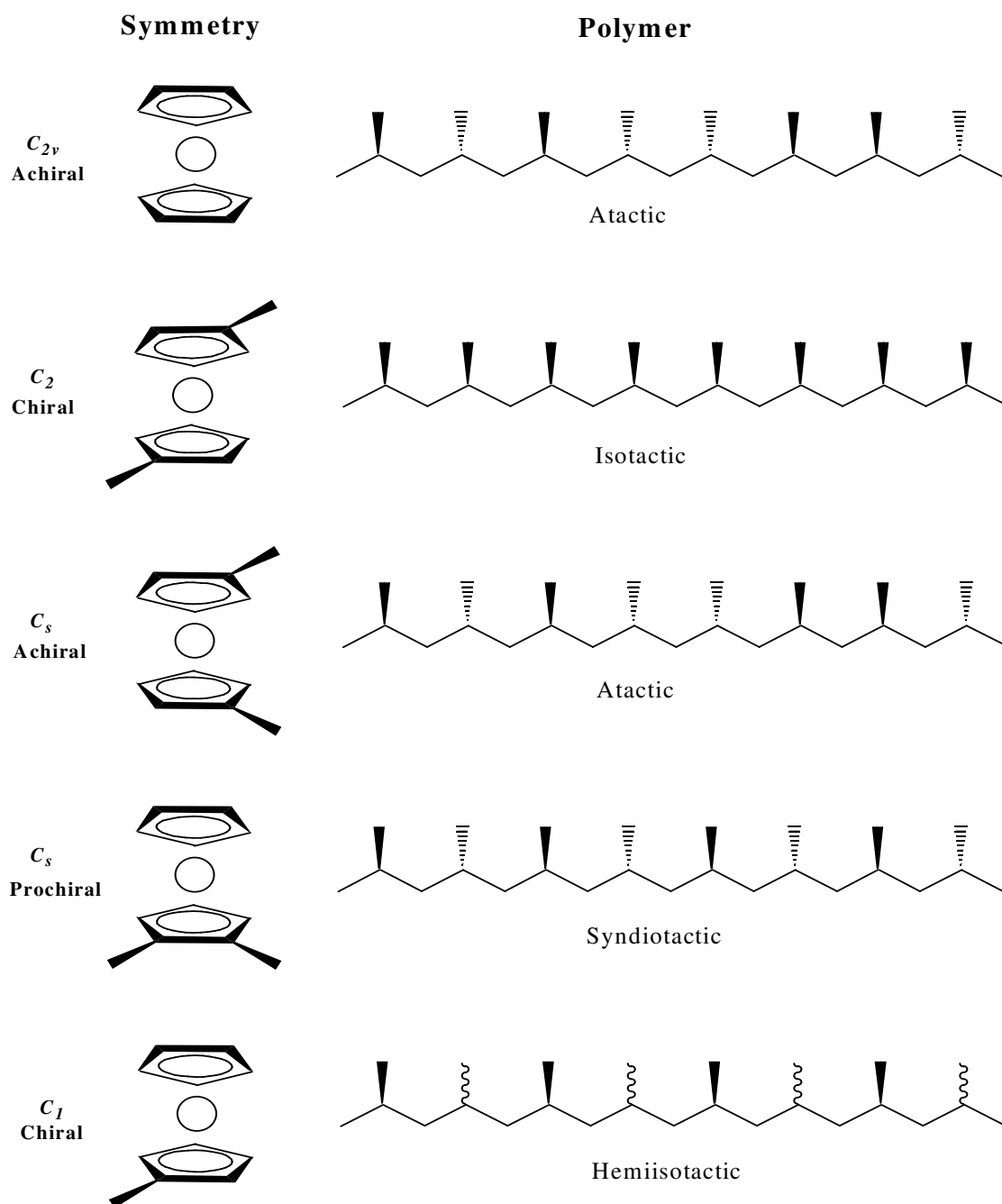


Figure 2.2. The relationship between tacticity of the obtained polypropylene and the symmetry of the metallocene catalyst.

2.3 Production of Isotactic, Syndiotactic, and Hemiisotactic Polypropylene Using C_1 -Symmetric Metallocenes

Nowadays, asymmetric metallocenes are competing with other types of symmetrical metallocenes. They became more attractive to the researchers because of their broad applications for the polypropylene production from hemiisotactic to syndiotactic to isotactic. After the discovery of the C_s -symmetric $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{-ZrCl}_2$ **1** (Figure 2.3) by Ewen and Razavi⁸ in 1988, it became a good precursor of the C_1 -symmetric metallocenes, because it is the backbone of these catalysts. Hundreds of C_1 -metallocenes have been made by reducing the symmetry of this metallocene by changing the substituents on the cyclopentadienyl or fluorenyl groups or both.

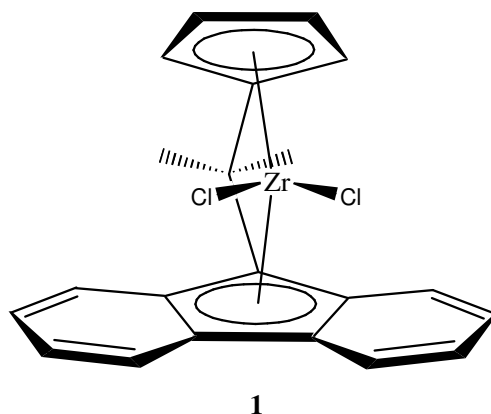


Figure 2.3. Structure of the first cyclopentadienyl-fluorenyl C_s -symmetric metallocene.

Cyclopentadienyl or indenyl and fluorenyl based asymmetric metallocenes could be stereorigid if these two groups are bridged. Many different bridges have been used. They have a low effect on the stereoselectivities of the catalyst because of their low influence

on the stereo insertion of the monomers. In contrast, they have a significant effect on the molecular weight as shown in the examples below.⁹

The *ansa*- C_1 -symmetric metallocenes have some advantages over *ansa* C_2 -symmetric metallocenes. For example, the synthesis of the C_2 -symmetric complexes is usually associated with the synthesis of the *meso* stereoisomer of that complex¹⁰ and is really hard to avoid because of the low energy of the *meso* complex. As result, about 50% of the metallocene product will be waste, because *meso* stereoisomer metallocenes generally produce low molecular weight atactic polypropylene. Therefore, the C_2 -complex must be separated from the C_s -complex before it can be used for isotactic polypropylene production.

Different tacticities of the polypropylene can be obtained from C_1 -symmetric metallocenes, whereas C_2 -symmetric metallocenes generally produce isotactic polypropylene. The reason is that, in contrast to C_2 -symmetric metallocenes, C_1 -symmetric metallocenes have two inequivalent, diastereotopic sites for the olefin insertion (A, B) (Figure 2.4).¹¹ These two sites have two enantiofacial selectivities, *re*-face and *si*-face of monomer insertion.

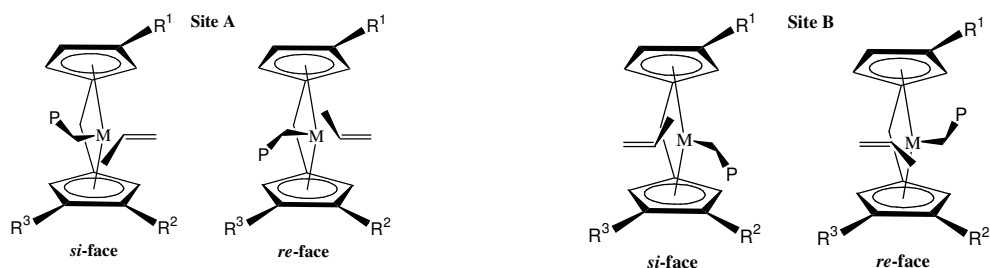


Figure 2.4. Enantioselectivity of each site and their outcomes.

<i>Pathway</i>	<i>Site A</i>	<i>Site B</i>	<i>Product</i>
1	<i>si</i>	<i>si</i>	Isotactic
2	<i>re</i>	<i>re</i>	Isotactic
3	<i>si</i>	<i>re</i>	Syndiotactic
4	<i>re</i>	<i>si</i>	Syndiotactic
5	<i>si</i>	both	Hemiisotactic
6	<i>re</i>	both	Hemiisotactic
7	both	both	Atactic

Figure 2.4. Continued.

2.3.1 Syndiotactic Polypropylene from C_1 -Symmetric Cyclopentadienyl-Fluorenyl Metallocenes

The first homogeneous catalyst made for syndioselective polypropylene polymerization was the C_s -symmetric metallocene $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **1** developed by Ewen and Razavi⁸ in 1988. It could produce up to 96% [*r*] with a 138°C melting point when activated with MAO (MAO = methylaluminoxane).⁹ This system has been improved by adding two bulky groups on both sides of the fluorenyl group as C_s -symmetric metallocenes. For example, Ewen prepared the cyclopentadienyl-fluorenyl metallocene with *tert*-butyl groups on the 2 and 7 positions of the fluorenyl group (**2**) which could produce up to 99.1% [*r*] or 98.7% [*rrrr*].^{12,13} Another good example of a C_s -symmetric metallocene is that prepared by Miller and Bercaw (**3**) (Figure 2.5) using an Oct group instead of fluorenyl, (Oct = octamethyloctahydrodibenzofluorenyl) which can produce more than 99% [*r*].¹⁴

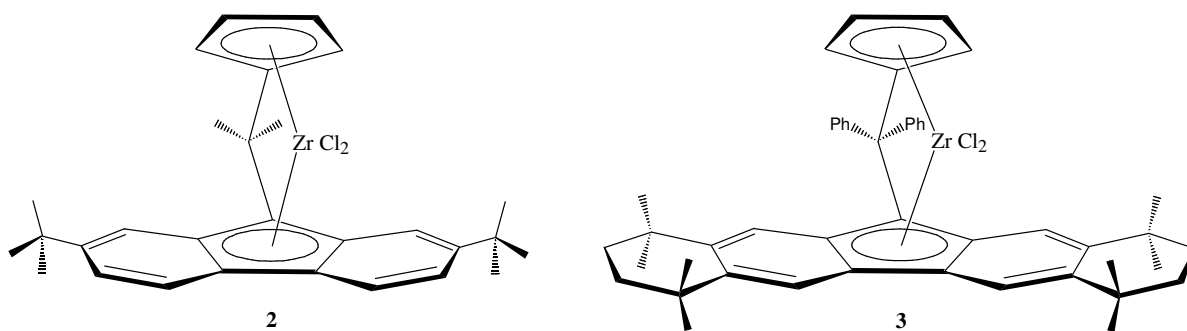


Figure 2.5. Structures of metallocenes **2** and **3**.

For the syndioselective polypropylene polymerization, C_s -symmetric metallocenes are the best choice and broadly used, but few a C_1 -symmetric metallocenes have been prepared (Figure 2.6). In order to get highly syndiotactic polypropylene from cyclopentadienyl-fluorenyl metallocenes, one active site should be highly selective for the *si*-face and the other should be highly selective for the *re*-face during monomer insertion. To make highly syndiotactic polypropylene precursors and reduce the stereoerrors, bulkier groups are used on the fluorenyl ring and small groups on the cyclopentadienyl ring. The reason is that the polymer chain should be strictly forced to go up on both sides in order to achieve the mechanism of insertion for the incoming monomers as explained below.

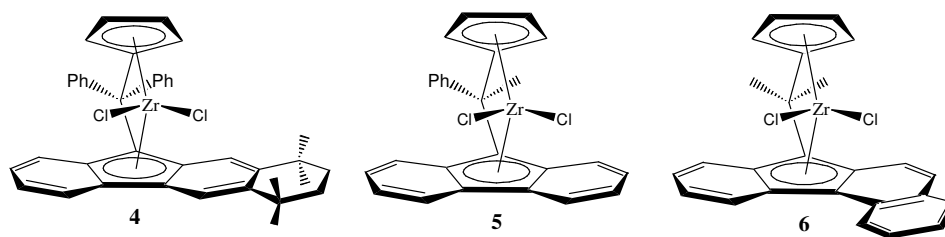


Figure 2.6. C_1 -symmetric metallocenes for syndioselective polypropylene polymerization.

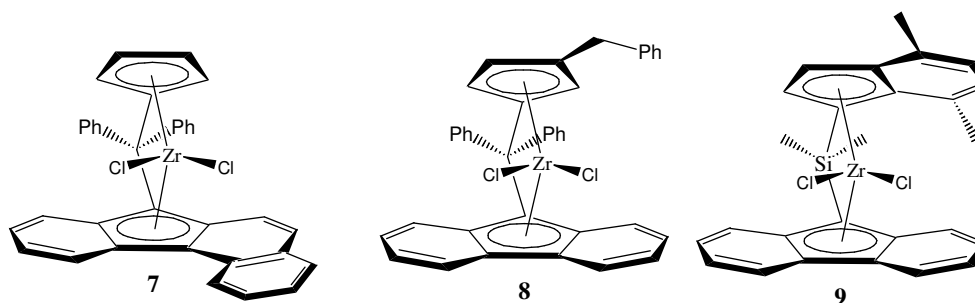


Figure 2.6. Continued.

The $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **1**/MAO system and other syndioselective C_1 -symmetric metallocenes systems suffer from two stereoerrors which reduce the syndiotacticity of the polymer. One is site epimerization,¹⁵ where the polymer chain migrates from one side to another at the stereogenic metal center without addition of a monomer; thus, an isolated *m* will occur in the polymer chain, resulting in [*..rrrmrrr..*] or [*...re-si-re-si-si-re-si-re...*] monomer type insertion. The other is enantiofacial misinsertion, making a double *m* in the polymer chain, resulting in [*...rrmmrrr..*] or [*...re-si-re-re-re-si-re-si...*] monomer type insertion, as shown in Figure 2.7.¹⁴

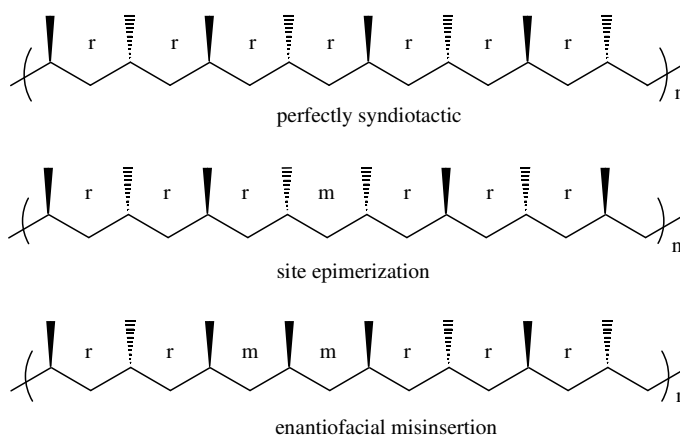


Figure 2.7. Stereoerrors in syndioselective polypropylene formation.

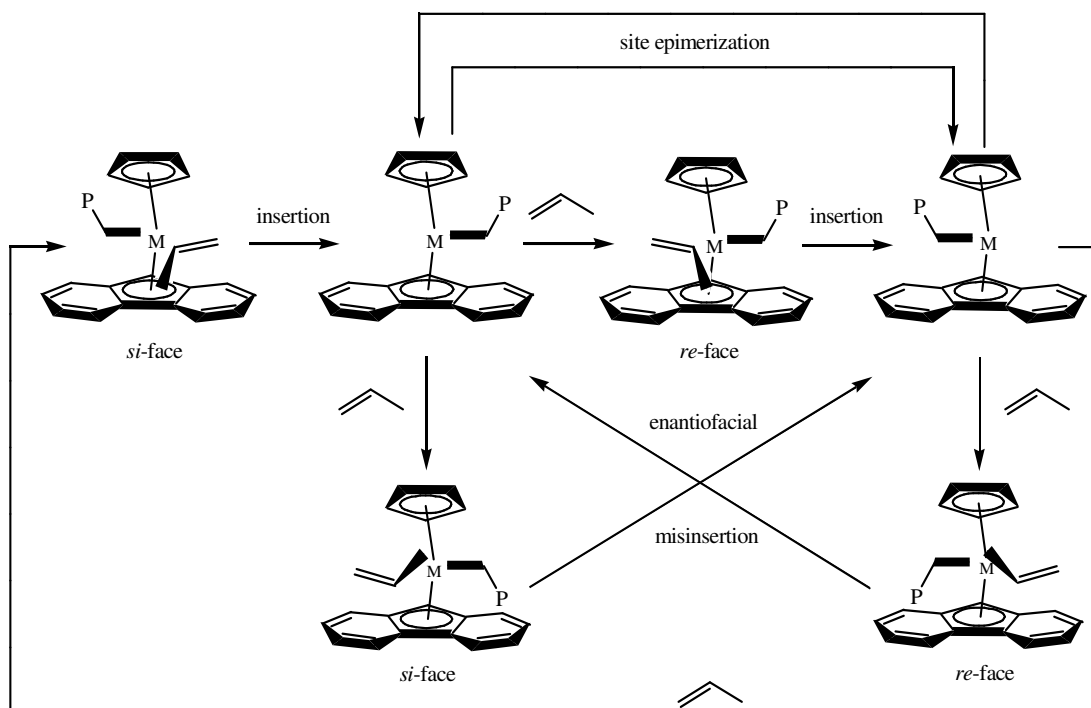


Figure 2.8. Mechanism of syndiospecific polypropylene polymerization with cyclopentadienyl-fluorenyl metallocene.¹⁶ (Bridges omitted for clarity).

The mechanism of the system in Figure 2.8 shows the best enantioselectivity of each site, *re*-face at one side and *si*-face on the other in order to get perfect syndiotactic polypropylene. To avoid enantiofacial misinsertions in that process, extra bulky groups are necessary to reduce those stereoerrors. The propylene polymerization behavior of C_1 -symmetric metallocene catalysts (**1-9**) is detailed in Table 2.1.

Table 2.1: Behaviors of catalysts **1-9** in propylene polymerization.

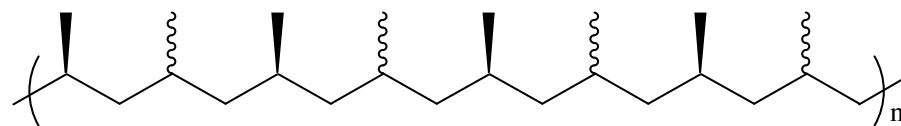
Catalyst	T_p [°C]	Cocatalyst	Activity	r [%]	$rrrr$ [%]	M_w	T_m [°C]	Ref
1 ^d	50	MAO	194,000 ^a	96		133,000	138	9
1 ^d	25	MAO			86	133,000		8
2 ^d	60	MAO		99.1			141	12
3 ^d	0	MAO	5,700 ^a	>99		961,000	153	14
3 ^d	20	MAO	14,000 ^a	>98		843,000	148	14
4 ^d	0	MAO	800 ^a	>98			140	14
5 ^d	60	MAO	39,200 ^b		99.0			17
6 ^d	61.8	MAO	34,900 ^b	93.7		37,500	121.1	18
7 ^d	59.2	MAO	42,900 ^b	96.3		520,000	128.4	18
8 ^c	40	TIBA [†] + Borane	3,300 ^b		78.1	>1,000,000	129	19
9 ^d	0	MAO	8,442 ^b		74.4			20
9 ^d	20	MAO	11,400 ^b		66.0			20

^a (PP g/g cat·h); ^b (g PP/mmol cat·h); ^c in toluene; ^d liquid propylene; ^e [Me₂PhNH][B(C₆F₅)₄][†], TIBAL = triisobutylaluminum chloride

2.3.2 Hemiisotactic Polypropylene from C_1 -Symmetric Cyclopentadienyl-Fluorenyl

Metallocenes

Hemisotactic polypropylene is another stereoregular polypropylene that can be produced by C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes. In this polypropylene, every other stereocenter has the same configuration and these are separated by stereocenters having random stereochemistry,^{21, 22, 15} as shown in Figure 2.9.



Hemiisotactic polypropylene

Figure 2.9. Hemiisotactic polypropylene architecture.

Ewen developed the first hemiisoselective metallocene catalyst, $\text{Me}_2\text{C}(3\text{-Me-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **10**/MAO (Figure 2.10).^{23, 24} This metallocene has two different coordination sites; one is highly isoselective and the other is aselective.

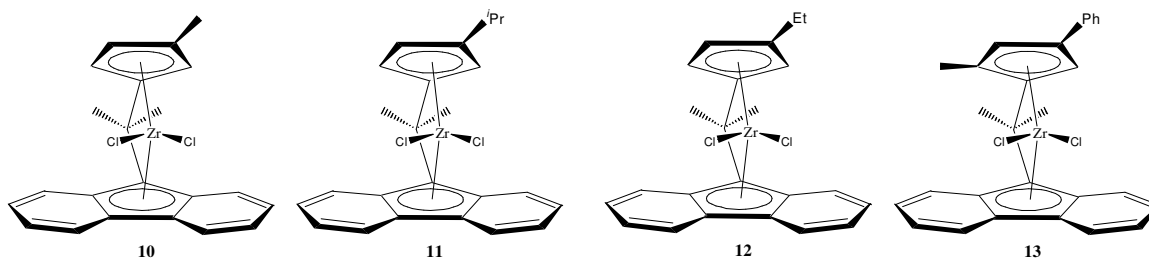


Figure 2.10. Cyclopentadienyl-fluorenyl metallocenes made for hemiisoselective polypropylene production.

Reducing the symmetry of the $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **1**⁸ from C_s to C_1 -symmetry by the addition of a small group on the cyclopentadienyl ring is the main key for the production of hemiisotactic polypropylene in these systems. As a result, two different coordination sites will be formed; one is aselective and the other is highly isoselective. Therefore, during the polymerization process, the catalyst will alternate between these two sites, making an interesting architecture of polypropylene. The hemiisoselective mechanism is explained in Figure 2.11.^{25- 27}

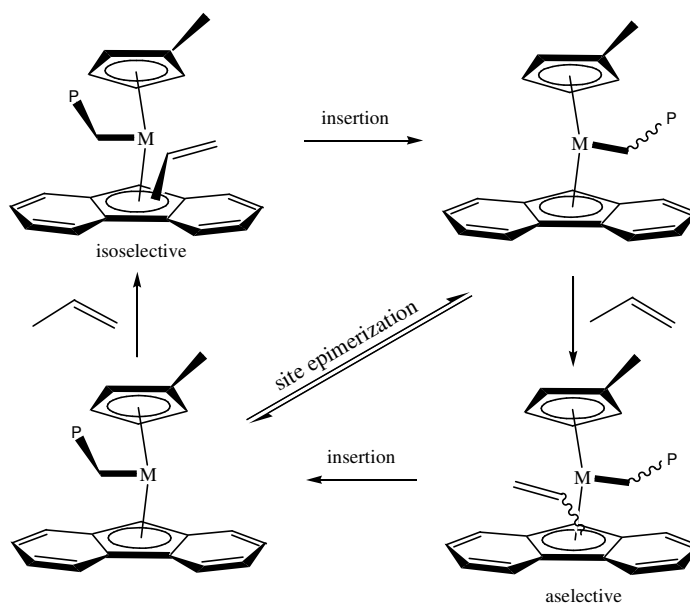


Figure 2.11. Mechanism of hemiisoselective polypropylene polymerization.

Polymerization studies of catalysts **10-13** are detailed in Table 2.2. The microstructure of the polymer should not have an isolated *r* or *m* like $[rrmr]$, $[mrmr]$, or $[mrmm]$ (Table 2.3).

Table 2.2. Propylene polymerization results of catalysts **10-13**.

Catalyst	T_p (°C)	Cocatalyst	Activity	M_w g/mol	ref
10 ^c	65	MAO	59,400 ^a		23
11 ^b	10	MAO			28
12 ^b	10	MAO			28
13 ^c	60	MAO	6,000 ^a	136,212	29

^a (g PP/g cat·h); ^b in toluene; ^c liquid propylene.

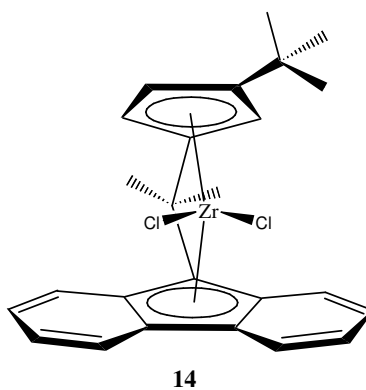
Table 2.3. Pentad analysis of hemiisotactic polypropylene produced by catalysts **10-13**.

Catalyst	[mmmm]	[mmm r]	[rmm r]	[mm rr]	[xm rx]	[m rmr]	[rrrr]	[rrrm]	[mrrm]
10	14	12	6	21	5	0	19	14	8
11	15.4	12.5	6.7	23.2	2.7	0.0	19.0	13.3	7.2
12	11.3	11.1	8.0	23.5	0.0	0.0	26.2	14.3	5.7
13	19.82	13.00	6.00	23.76	2.34	1.02	15.24	11.30	7.52

2.3.3 Isotactic Polypropylene from C_1 -Symmetric Cyclopentadienyl-Fluorenyl

Metallocenes

Isotactic polypropylene is more stereoregular than the other polypropylene types. Commercially, it is the dominant product in the polypropylene family, because of its excellent physical and chemical properties. Razavi and Atwood³⁰ developed the first C_1 -symmetric cyclopentadienyl-fluorenyl metallocene, $\text{Me}_2\text{C}(3\text{-}t\text{-Bu-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **14**, that is capable of producing highly isotactic polypropylene (Figure 2.12).

**Figure 2.12.** Structure of metallocene $\text{Me}_2\text{C}(3\text{-}t\text{-Bu-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **14**.

Addition of a bulky group such as *t*-butyl in position 3 on the cyclopentadienyl group gives both active sites the same enantioselectivity toward monomer insertion. Based on this strategy, hundreds of metallocenes have been made by adding big groups on either the cyclopentadienyl or indenyl groups in order to make highly isotactic polypropylene by following that mechanism (Figure 2.13).^{28, 31-34}

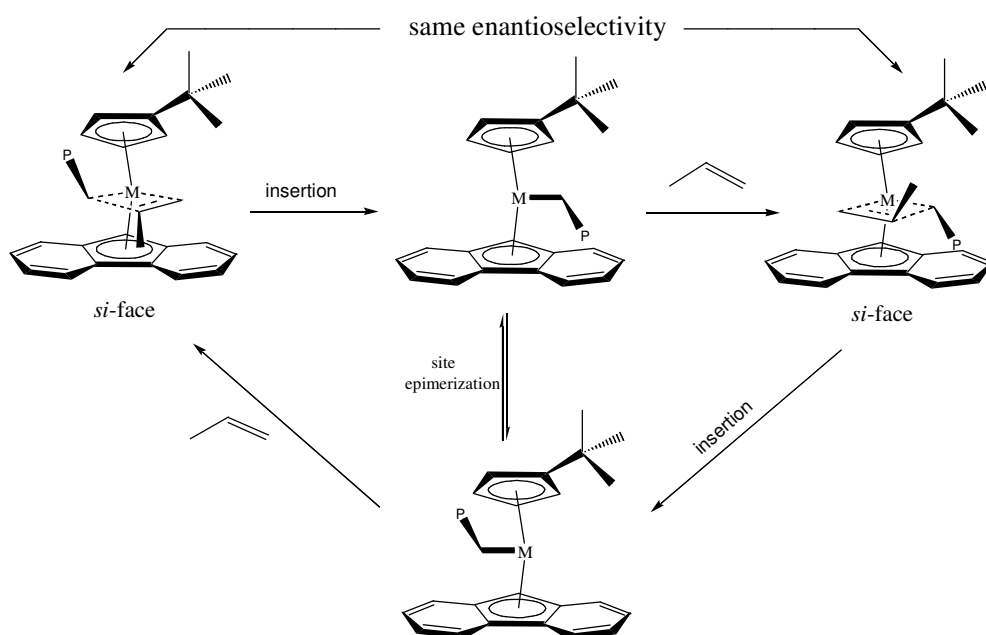


Figure 2.13. Stereoselectivity of the two active sites for the production of isotactic polypropylene.

In these metallocenes, enantioselectivity should be the same at both sites whether the *si* or *re* face is employed. In syndioselective C_s -symmetric metallocenes, the two coordination sites are enantiotopic and site epimerization introduces stereoerrors because the regular alternation of *si* and *re* enantiofaces is disrupted. In contrast, for C_1 -symmetric isotactic polypropylene metallocenes such as **14**, site epimerization has

almost no effect on the insertion mechanism due to the stereochemical similarity of both coordination sites.

Catalysts **15-76** (Figure 2.14) are examples of cyclopentadienyl-fluorenyl metallocenes that are designed for isotactic polypropylene production. Their polymerization behavior is detailed in Table 2.4.

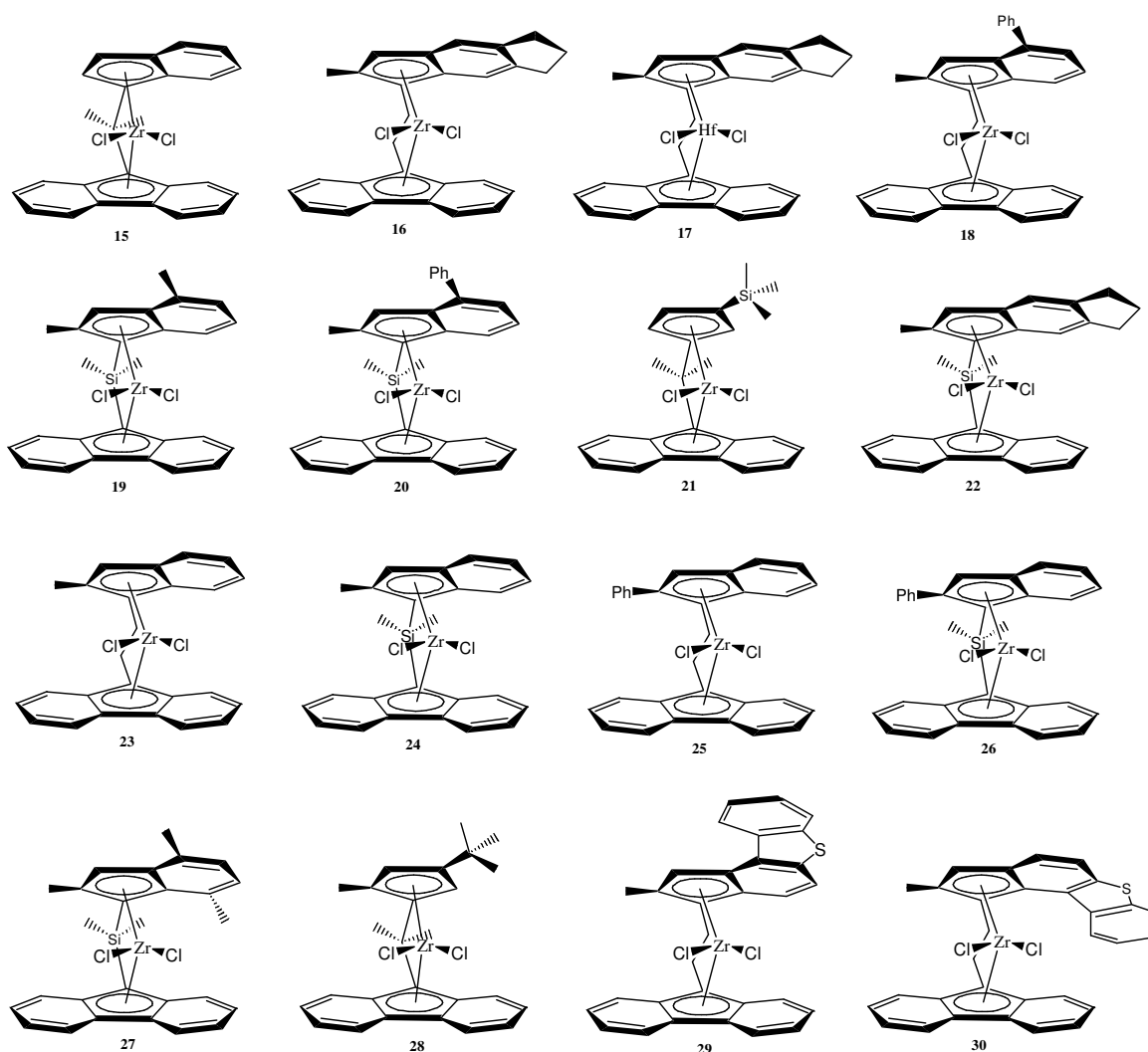


Figure 2.14. Structures of metallocenes **15-76**.

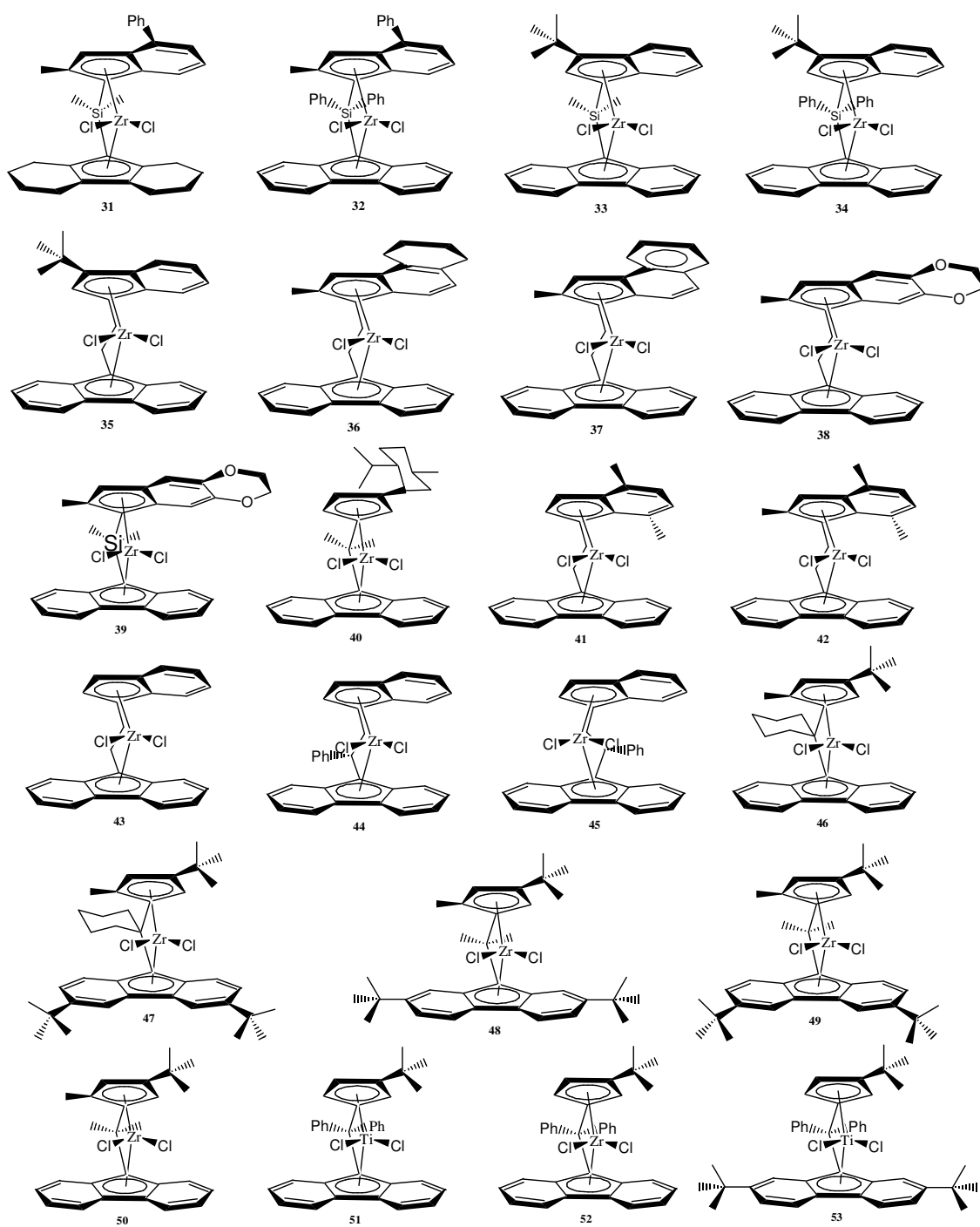


Figure 2.14. Continued.

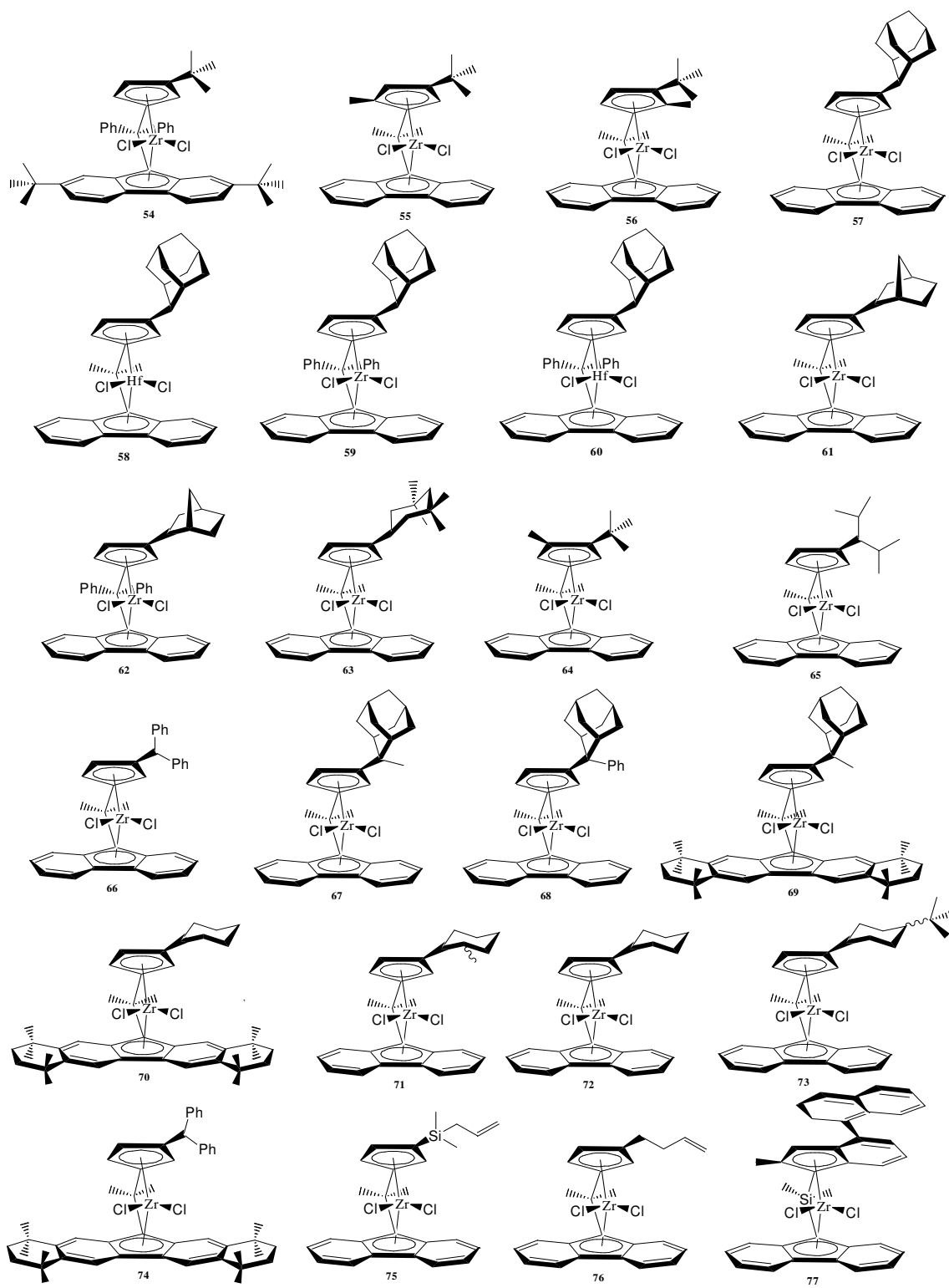


Figure 2.14. Continued.

Table 2.4. Propylene polymerization results of catalysts **15-76**.

Catalyst	T_p (°C)	Cocatalyst	Activity	M_w g/mol	T_m (°C)	[<i>mmmm</i>]%	[<i>mm</i>]%	ref
14 ^g	20	MAO		175,000	133	79.17		30
14 ^g	60	MAO		62,000	127	77.47		30
15 ^g	50	TIBA ^c /TPFPB ^d	22,000 ^a	5,200			27	35
16 ^g	50	TIBA/B(C ₆ F ₆) ₃	9,000 ^b	150,000		56.8		36
16 ^f	30	MAO	2,000 ^b	170,000		32		37
16 ^f	50	MAO	4,600 ^b	46,000		49.1		32
17 ^g	30	MAO	150 ^b	55,000		31		37
18 ^g	40	MAO	26,200 ^b	110,000	139		91	38
19 ^g	40	MAO	17,000 ^b	120,000	130		51	38
20 ^g	40	MAO	9,000 ^b	190,000	138		92	38
21 ^g	40	MAO		134,000	105.4	66.6		33
22 ^f	30	MAO		103,000		61.6		32
23 ^f	30	MAO	2,100 ^b	62,000		17.6		32
23 ^f	70	MAO	30,200 ^b		80	48		39
24 ^f	30	MAO		73,000		44.1		32
25 ^f	30	MAO	1,400 ^b	62,000		98.0		32
26 ^f	30	MAO		32,000		70.5		32
27 ^g	70	MAO	7,400 ^b	43,000	95.7	79		40
27 ^f	70	MAO	2,300 ^b		125	48.1		34
27 ^f	20	MAO	1,400 ^b		74	39.4		34
28 ^f	80	MAO		93,000		82		41
29 ^f	60	MAO		13,000		42.1		42
29 ^f	30	MAO		33,000		18.3		42
30 ^f	60	MAO		7,000		64.8		42
30 ^f	30	MAO		148,000		86.3		42
31 ^f	20	MAO	5,200 ^b		138	87		43
31 ^f	70	MAO	64,000 ^b		81	56		43
31 ^g	70	MAO	106,000 ^b	30,000	140		91	43
32 ^f	70	MAO	2,900 ^b	6,800		83		44
32 ^f	20	MAO	1,000 ^b	40,800		83		44
33 ^f	0	MAO	150 ^b	56,300		69		44
34 ^f	0	MAO	220 ^b	104,000		72		44
35 ^f	20	MAO	5,100 ^b	24,700		79		44
36 ^f	50	MAO	2,670 ^b	15,200	134.2	79.5		31
36 ^f	70	MAO	7,000 ^b	14,000		78.7		45
37 ^f	50	MAO	5,370 ^b	19,200	112.8	72.6		31
37 ^f	30	MAO	1,300 ^b	47,000		71.9		45
38 ^f	30	MAO	700 ^b	45,000		35.2		46
39 ^f	30	MAO	100 ^b	50,000		53.0		46

Table 2.4. Continued.

40 ^g	40	MAO	54,000 ^a	32,000			62.5	47
40 ^g	70	MAO	197,000 ^a	28,900			60.2	47
41 ^f	20	MAO	6300 ^b			5		39
42 ^f	20	MAO	14,000 ^b	9,000	132	86		39
43 ^f	50	MAO	2,660 ^b	27,800	110	63.9		48
44 ^f	50	MAO	990 ^b	26,600	121	70.5		48
45 ^f	50	MAO	900 ^b	27,900	wax	36.0		48
46 ^g	70	MAO		69,000	141	85.8		49
47 ^g	70	MAO		117,000	156	95.6		49
48 ^g	70	MAO		524,000	141	88.4		49
49 ^g	70	MAO		82,000	156	94.8		49
50 ^g	70	MAO		185,000	142	86.9		49
51 ^f	30	MAO + TIBA ^c	2,000 ^b	161,000	141	79.65		50
52 ^f	30	MAO + TIBA ^c	13,000 ^b		125	80		50
53 ^f	50	MAO + TIBA ^c	73,000 ^b	43,300	128	72.78		50
54 ^f	50	MAO + TIBA ^c	41,000 ^b	112,700	141	93.93		50
55 ^g	60	MAO	54,000 ^a	458,500	142.4	85.8		51
56 ^g	40	MAO	179,000 ^a	96,600	101.4	61.1		51
57 ^g	20	MAO	12,900 ^a	81,900	88	31.4		21
58 ^g	20	MAO	470 ^a		n. o. ^e	34.0		21
59 ^g	20	MAO	3,700 ^a	435,000	125	25.3		21
60 ^g	20	MAO	540 ^a	806,000	135	24.0		21
61 ^g	0	MAO	5,220 ^a	105,000	122	27.5		21
62 ^g	0	MAO	4,190 ^a	572,000	148	14.7		21
63 ^g	0	MAO	1,570 ^a	77,400	98	49.3		21
64 ^g	20	MAO	41,000 ^a	535,000	149	31.8		21
65 ^g	20	MAO	360 ^a	80,900	131	80.0		16
66 ^g	20	MAO	710 ^a		138	81.2		16
67 ^g	20	MAO	5,000 ^a	113,000	154	>98		16
68 ^g	20	MAO	3 ^a		n. o. ^e			16
69 ^g	0	MAO	440 ^a	370,000	167	>99		16
69 ^g	20	MAO	1,100 ^a	425,000	163	>99		16
70 ^g	0	MAO	530 ^a		103	5.1		16
71 ^g	0	MAO	3,700 ^a		n. o. ^e	13.1		16
72 ^g	0	MAO	4,300 ^a		n. o. ^e	13.2		16
73 ^g	0	MAO	2,000 ^a		n. o. ^e	24.2		16
74 ^g	0	MAO	60 ^a		125	74.4		16
75 ^g	60	MAO	10,600 ^b		80.71	80.1		17
76 ^g	60	MAO				17.1		17
77 ^g	20	TIBA ^c /TPFPB ^d	32,000 ^a	853,000		17		35

^a (g PP/g cat·h); ^b (g PP/mmol cat·h); ^c TIBA = tri-isobutylaluminum; ^d TPFPB = [Ph₃C][B(C₆F₅)₄]; ^e n.o.= not observed; ^f in toluene; ^g liquid propylene.

2.4 Conclusions

Many different polypropylene tacticities can be obtained from C_1 -symmetric *ansa* cyclopentadienyl-fluorenyl metallocenes of group IV. On the other hand, C_2 -symmetric *ansa*-metallocenes generally produce isotactic polypropylene. Moreover, preparation of C_2 -symmetric *ansa* metallocenes suffers from the by-product *meso* stereoisomer that has C_s symmetry, which is considered a waste and must be removed because it only produces atactic polypropylene. Therefore, the synthetic cost of C_2 -symmetric metallocenes often is much more than that of the C_1 -symmetric metallocenes. As a result, researchers are highly focused on C_1 -symmetric metallocenes and they keep trying to improve existing systems or make a whole new C_1 -symmetric ligands that can be anchored onto group IV metals, which are capable of producing a highly specific architecture of polypropylene polymers.

CHAPTER III

**NEW C_1 -SYMMETRIC ANSA- CYCLOPENTADIENYL-
FLUORENYL METALLOCENES FOR ISOTACTIC POLYPROPYLENE
PRODUCTION**

3.1 Introduction

The *ansa* cyclopentadienyl-fluorenyl metallocene, $\text{Me}_2\text{C}(3\text{-}t\text{-butyl-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **1**, was developed by Razavi and Atwood.³⁰ It demonstrates that a bulky group, such as *t*-butyl in position 3 on the cyclopentadienyl ring, is capable of producing highly isotactic polypropylene with $\sim 80\%$ [mmmm]. Recently, Bercaw and Miller prepared another catalyst **2** which has a bulky group in the 3-position that can make up to 99% [m] isotactic polypropylene (Figure 3.1).¹⁶

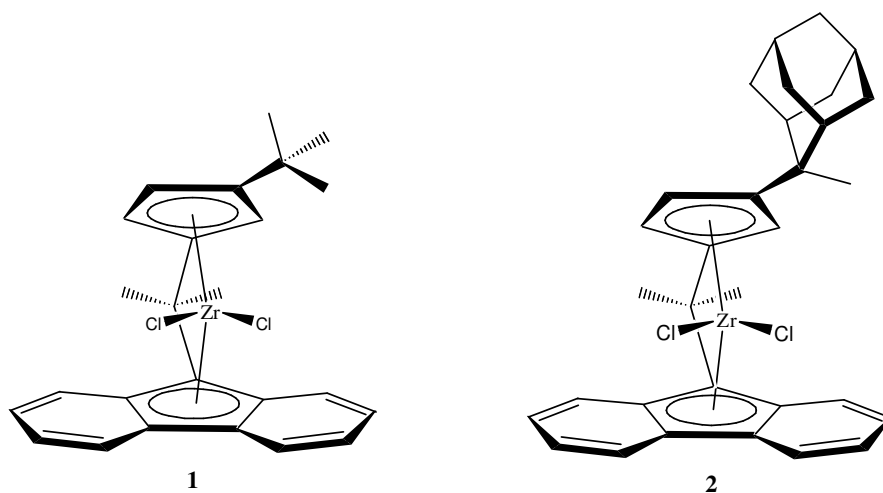


Figure 3.1. Structure of metallocenes **1** and **2**.

Using a small group like methyl as in $\text{Me}_2\text{C}(3\text{-Me-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **3** would make hemiisotactic polypropylene because one site is highly enantioselective and the other is aselective.^{9,21,52} On the other hand if all four substituents on the cyclopentadienyl group

are hydrogens as in $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **4**,^{23,22} catalyst symmetry will be C_s and it will make a highly syndioselective catalyst, because the enantioselectivities of the sites are opposite; one is *re*-selective and the other is *si*-selective. Therefore, in order to make highly isotactic polypropylene, both active sites should have the same enantioselectivity—for example [*si*-face/*si*-face] or [*re*-face/*re*-face]. Achieving that goal is quite simple and could be done by addition—of a large group on one side of the cyclopentadienyl ring at position 3, reducing the symmetry from C_s to C_1 . Therefore, polypropylene architecture highly depends on the size of this substituent on the cyclopentadienyl ring as shown in Figure 3.2.

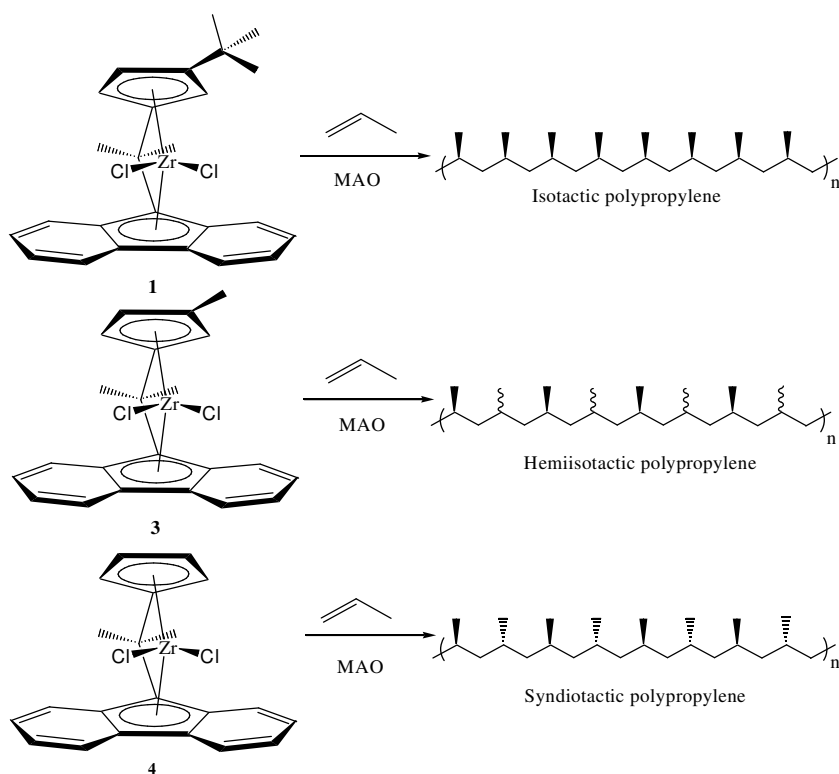


Figure 3.2. The relationship between group size on the cyclopentadienyl ring and polypropylene architecture.

3.2 Mechanism of Isoselective Polypropylene Polymerization Using *Ansa-C₁*-Symmetric Cyclopentadienyl-Fluorenyl Metallocenes

C₁-symmetric cyclopentadienyl-fluorenyl metallocenes have two inequivalent coordination sites. To make the metallocene a highly isoselective polymerization catalyst, both active sites must have the same enantioselectivity.⁷ *C₂*-symmetric metallocenes are highly isoselective polymerization catalysts, because both active sites have the same enantioselectivity for monomer insertion.^{53,54,55}

Therefore, in the $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ system, one site must be modified to have enantioselectivity very similar to the other; for example, it must have either a *si*-face/*si*-face or a *re*-face/*re*-face stereoselectivity for both sites. That scenario can be achieved by adding a bulky group at position 3 on the cyclopentadienyl ring. The main idea is to force the polymer chain to go down toward the benzo substituent of the fluorenyl, which will make this site (**B**) *si*-face enantioselective like the other site (**A**), as shown in Figure 3.3.^{28,31-34}

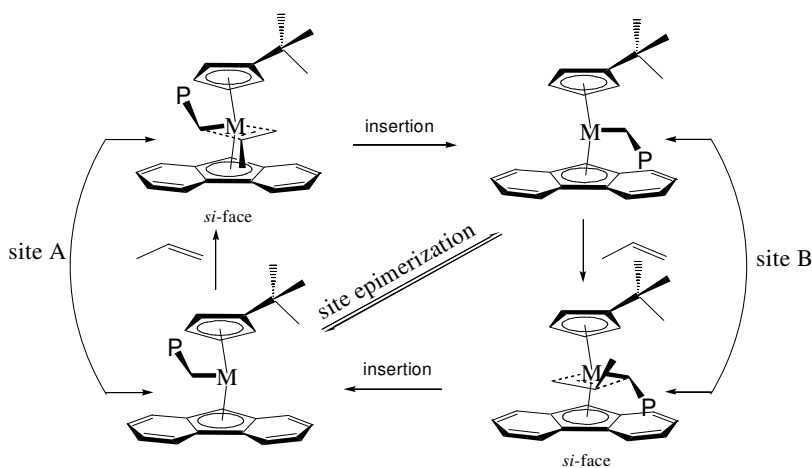


Figure 3.3. Proposed mechanism of isotactic polypropylene formation using *C₁*-symmetric cyclopentadienyl-fluorenyl metallocenes.

During the polymerization process, sometimes a polymer chain migrates from one site to the other before the addition of the next monomer. This is called site epimerization.¹⁵ In C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes systems with bulk substituents, this phenomenon has little effect on the tacticity of the polymer, because both active sites of the catalyst have similar enantioselectivities.

3.3 Synthesis and Design of New *Ansa*- C_1 -Symmetric Cyclopentadienyl-Fluorenyl Metallocenes

Based on the idea of catalyst $\text{Me}_2\text{C}(3\text{-}t\text{-butyl-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ **1**, several *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes with bulky groups at position three on the cyclopentadienyl ring have been prepared (Figure 3.4) in an attempt to make highly isotactic polypropylene with good catalytic activity and high molecular weight upon activation with MAO (MAO = methylaluminumoxane) in liquid propylene. X-ray crystal structures of metallocenes **5**, **6** and **7** have been obtained and are detailed in appendices A, B, and C, respectively.

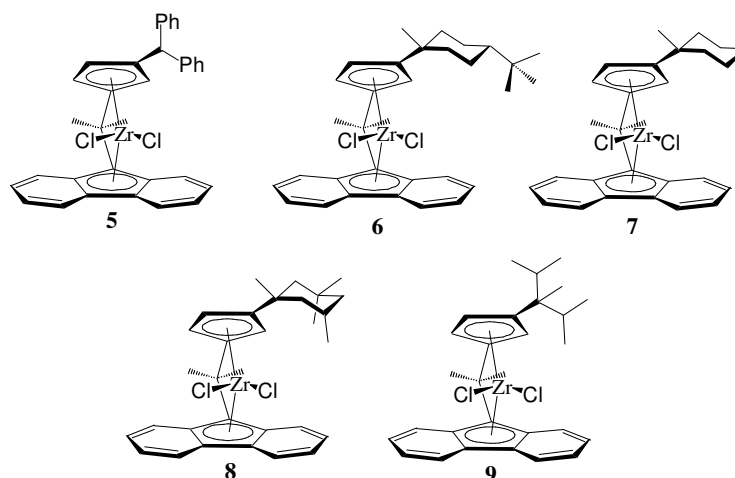


Figure 3.4. Metallocenes **5-9** have different bulky groups in position 3 of the cyclopentadienyl ring.

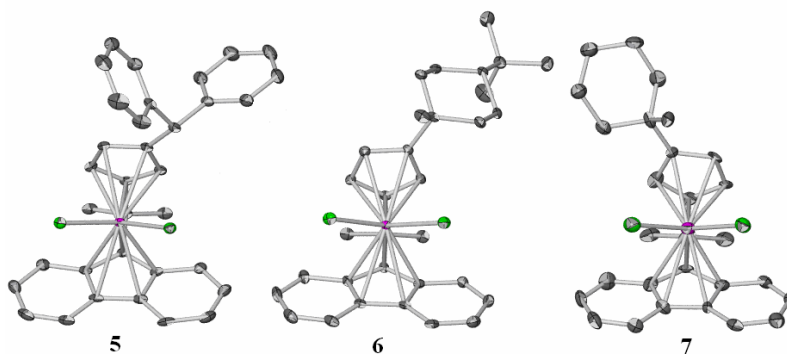


Figure 3.4. Continued.

Catalyst **5** was developed by Miller¹⁶ and re-prepared to use as a standard catalyst to compare with other new metallocenes. Bridges other than isopropylidene, such as diphenylmethylidene, were investigated to measure the influence of huge groups as bridges on the tacticity of the polypropylene polymer. Therefore, two catalysts with a diphenylmethylidene bridge were targeted (Figure 3.5).

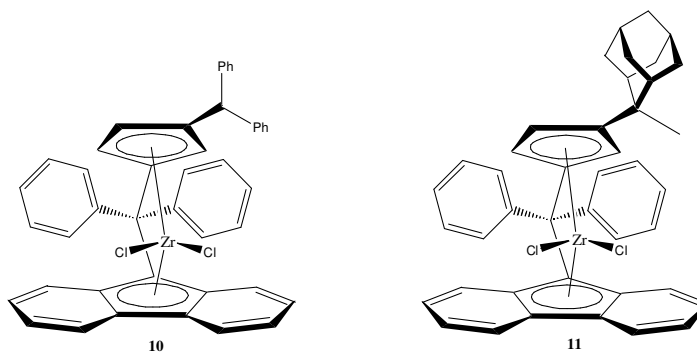


Figure 3.5. New targeted metallocenes having diphenylmethylidene bridges.

Unfortunately, the syntheses of metallocenes **10** and **11** have failed. It is believed that having a bulky group on the fulvene *and* a large bridge makes the attack of fluorenyllithium harder on the 3-(substituted)-6,6-diphenylfulvene as shown in Figure 3.6.

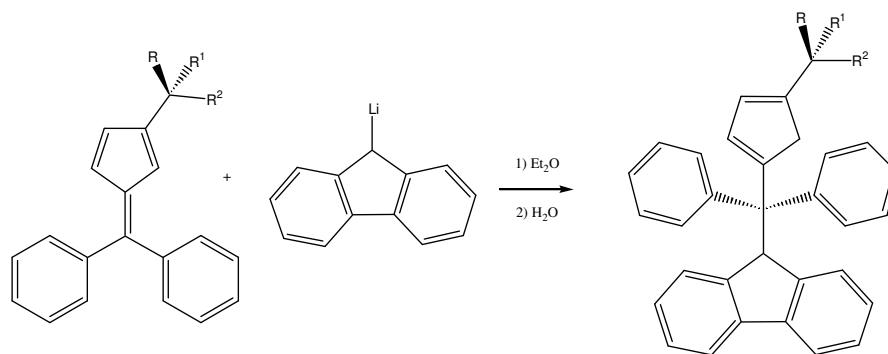


Figure 3.6. Reaction of fluorenyllithium with 3-(substituted)-6,6-diphenylfulvene.

Most of the cyclopentadienyl-fluorenyl metallocenes have been anchored on either zirconium or hafnium, but a few have been metallated with titanium or vanadium. As a part of the project, finding a new way of making these interesting titanocenes and vanadocenes became a primary goal. Therefore, two new *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes (titanocene) **12** and (vanadocene) **13** have been developed. In addition, two new *ansa*- C_s -symmetric titanocenes **14** and **15** (Figure 3.7) have been made to have a complete study of these new systems with different symmetry. All new titanocenes have been characterized by ^1H NMR, but unfortunately the paramagnetic vanadocene was hard to characterize by NMR, mass spectroscopy or X-ray crystallography.

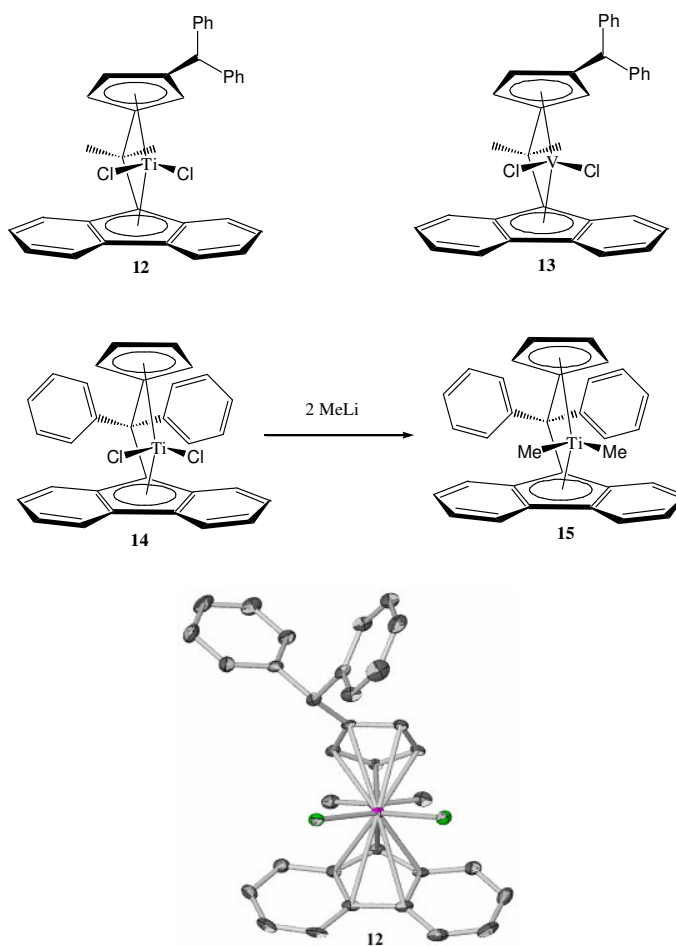


Figure 3.7. Structures of new titanocenes **12**, **14**, **15** and vanadocene **13**.

The synthetic pathway to *ansa*- C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes is detailed in Figure 3.8.¹⁶ Anchoring these new ligands onto zirconium is easily done by using $ZrCl_4$ in diethyl ether or hexanes as solvent in the metallation step with the dilithium salt of the ligand. In contrast, this reaction failed for the preparation of the titanocenes and the vanadocene, because $TiCl_4$ and VCl_4 are highly reactive in comparison to $ZrCl_4$. Therefore, $TiCl_4 \cdot 2THF$ and $VCl_4 \cdot 2THF$ have been used instead of

TiCl₄ or VCl₄ and diethyl ether as solvent. The X-ray crystal structure of metallocene **12** has been obtained and is detailed in Appendix D.

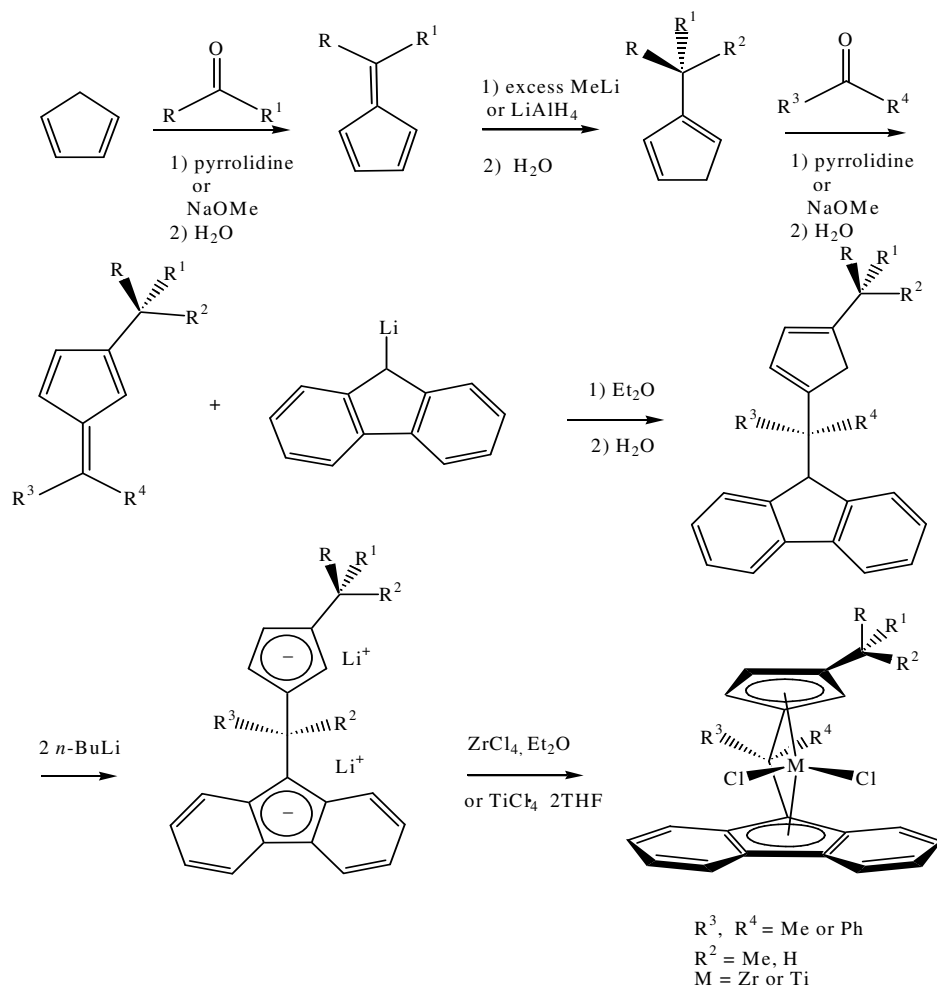
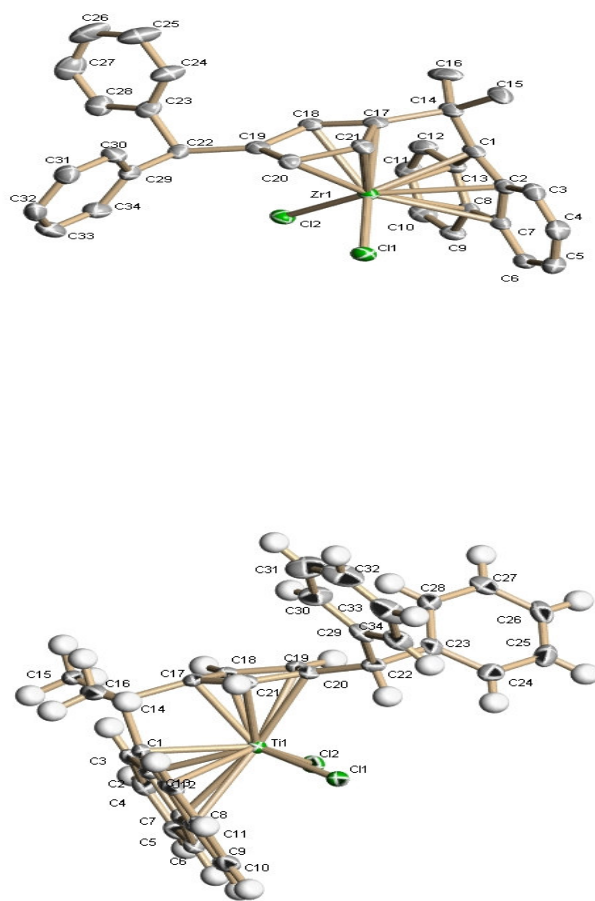


Figure 3.8. Synthetic pathway toward *ansa*-C₁-symmetric cyclopentadienyl-fluorenyl metallocenes.

The crystal structures of zirconocene **5** and titanocene **12** differ slightly. They have the same packing system in their respective unit cells, but the angle of the cyclopentadienyl-fluorenyl-metal sandwich, shifts from 99.2° in the zirconocene to 96.0°

in the titanocene. The small difference is expected, because titanium has a smaller covalent radius while the metal-carbon bond lengths are similar as shown in Figure 3.9.



Bond Lengths	Metalocene 5		Bond Lengths	Metalocene 12	
	Å	Angle [°]		Å	Angle [°]
Zr(1)-Cl(1)	2.4134(9)	C(17)-C(14)-C(1) 99.2(3)	Ti(1)-Cl(1)	2.320(10)	C(17)-C(14)-C(1) 96.0(2)
Zr(1)-C(20)	2.552(3)		Ti(1)-C(20)	2.495(3)	
Zr(1)-C(17)	2.422(3)		Ti(1)-C(17)	2.305(3)	
Zr(1)-C(1)	2.411(3)		Ti(1)-C(1)	2.304(3)	
Zr(1)-C(8)	2.633(3)		Ti(1)-C(8)	2.619(3)	

Figure 3.9. Bond lengths and angles in metallocenes **5** and **12**.

3.4 Synthesis of Isotactic Polypropylene

All metallocenes that have been made were tested for the production of isotactic polypropylene upon activation with MAO (MAO = methylaluminoxane) in liquid propylene and a temperature range of 0-20°C. Starting with metallocene **5** that has a diphenyl methyl group at position 3 of the cyclopentadienyl group, the maximum tacticity that could be obtained is 84-85 % [*mmmm*], with a low molecular weight about 50,000 as shown in Entries 1 and 2 of Table 3.1. Catalysts **7** and **8** provide polymers with low isotacticity and that suggests these metallocenes have smaller groups than the diphenyl methyl group as in catalyst **5** at position 3 of the cyclopentadienyl group. In contrast to all these catalysts, metallocene **6** provides better isotactic polypropylene with about 87-88% [*mmmm*] and that is because of the size of the substituent on the cyclopentadienyl group is bigger than the others. There is a limit to the size of the substituent that is beneficial at the 3-position on the cyclopentadienyl group because having a huge group at that position will block the polymerization sites, halting the catalysis; this explains the poor activity of metallocene **9**. In general, metallocenes **6-8**, showed excellent activity at both 0 and 20 °C and great molecular weight as well as narrow molecular weight distributions except for metallocene **8**, possibly because of the existence of four diastereomers of that metallocene which were not separated.

Table 3.1. Propylene polymerization study of metallocenes **5-9**.^a

Entry	Catalyst (mg)	T_p (°C)	C ₃ H ₆ (mL)	Toluene (mL)	Time (min)	Yield g	Activity g P/gcat-h	M _w g/mol	MWD ^b	T_m (°C)	% [mmmm]
1	5 (10)	0	150	5	20	1.45	430	54,350	2.18	140	84
2	5 (10)	20	150	5	20	1.30	390	42,000	2.15	140	85
3	6 (5.0)	0	100	4	20	7.9	4,740	273,500	2.34	146	85.5
4	6 (2.0)	0	100	4	20	4.13	6,200	391,500	2.37	146	87.7
5	6 (2.0)	20	100	4	6	5.6	28,000	205,500	2.18	149	86.7
6	7 (2.0)	0	100	4	20	3.14	7,300	429,500	3.67	128	66
7	7 (2.0)	20	100	4	6	3.89	19,700	259,000	2.94	126	71
8	8 (2.0)	0	100	4	23	5.6	4,700	159,500	1.93	103	60
9	8 (2.0)	20	100	4	4	2.63	19,400	10,700	2.54	119	60.5
10	9 (2.0)	0	100	5	20	n.a.	na	-	-	-	-
11	9 (5.0)	20	100	10	20	0.07	40	-	-	-	-

^a MAO, Al/Zr ratio = 1000:1, ^b MWD = molecular weight distribution (M_w/M_n)

Vanadocene **13** and titanocenes **12**, **14** and **15** were tested for polymerization and showed no activity in the temperature range 0-25 °C with activators such as MAO (MAO = methylaluminumoxane), TIBAL (TIBAL = triisobutylaluminumchloride), DEAC (DEAC= diethylaluminumchloride), and MAO combined with TIBAL. From the literature, it is believed that these titanocenes can be active for propylene polymerization, because similar titanocenes **16** and **17** (Figure 3.10) were made and showed good activity and isoselectivity: 79.7% and 72.8% of *mmmm*, respectively.⁵⁰ One reason for that may be the high sensitivity of these systems to impurities in the propylene gas that was used in the polymerizations test (Matheson, 99.5%, OXYSORBTM scavenging column).

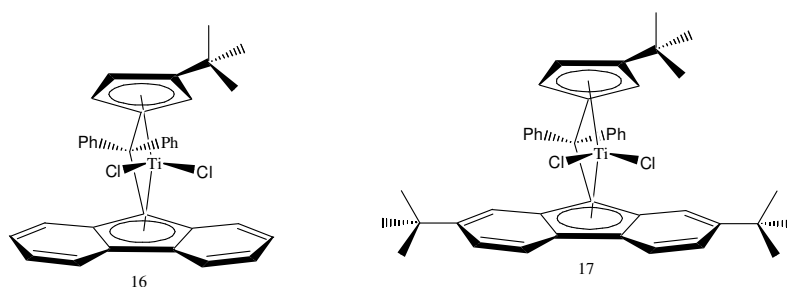


Figure 3.10. Structure of titanocenes **16** and **17**.

3.5 Conclusions

The *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes have been significantly improved recently and modified for the production of isotactic polypropylene. It is expected that these systems may overtake *ansa*- C_2 -symmetric metallocenes for this application. The reasons are: they are easy to synthesize and the *meso* isomer is not produced as in the synthesis of most C_2 -symmetric metallocenes. Therefore, several *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes have been made and tested for isotactic polypropylene production. Several showed good stereoselectivities, high activity, and made polymer with high molecular weight.

3.6 Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere using standard glove box and Schlenk line techniques. Diethyl ether, toluene and tetrahydrofuran were dried and distilled from sodium. Methylene chloride and hexanes were dried and distilled from CaH_2 and subsequently degassed. The following reagents were purchased and used without further purification: (Acros) cyclohexanone 99.8%, 3,3,5-trimethylcyclohexanone (97%), fluorene (98%), vanadium tetrachloride (99+%),

indane (95%), lithium aluminum hydride (95%), and sodium methoxide, (Avocado) benzophenone 98%, 2-adamantanone (98%), and pyrrolidine (99%), (Alfa Aesar) *n*-BuLi (2.87M in hexanes) and zirconium tetrachloride (99.5+%), (Strem) AlCl₃ 99%, (Aldrich) MeLi (1.5 M in diethyl ether), (TCI) 2,4-dimethyl-3-pentanone.

Fluorenyllithium. In the glove box, 30 g of fluorene (180 mmol) and 120 mL of toluene were added in 250 mL flask. The flask was attached to a swivel frit and connected to the Schlenk line. At 0°C, 79 mL of *n*-BuLi (226 mmol, 2.87 M in hexane) were syringed in, stirred at 55°C for 24 h, filtered and dried on the vacuum line to give 30 g (96%) of the product as orange powder.

Preparation of metallocene 5

6,6-diphenylfulvene. In a 500 mL round bottom flask, 111.7 g of benzophenone (613.0 mmol) and 35.6 g of sodium methoxide (659 mmol) were dissolved in 500 mL of ethanol. After the mixture became homogeneous, 87.0 mL of cyclopentadiene (1055 mmol) were added, giving a red colored solution. After 68 hour of stirring, the orange precipitate was collected by filtration and rinsed with 50 mL of ethanol and then refluxed with 200 mL of methanol and filtered again to give 115 g of product as orange powder (81.4%). MS (GC-MS) *m/z* 230.18(M⁺). ¹H NMR (CDCl₃, 300 MHz) δ 6.24, 6.54 (d, ³*J*_{HH} = 5.09, 4.49, 4H, Cp-*H*), 7.23-7.38 (m, 10H, phenyl-*H*).

(Diphenylmethyl)cyclopentadiene. 20.0 g of 6,6-diphenylfulvene (86.8 mmol) was dissolved in 70 mL of THF. Then at 0°C the solution was syringed into a 500 mL flask containing 7 g of LiAlH₄ (186 mmol) and 50 mL of THF. The reaction was stirred for 48 hours at room temperature. At 0°C, the reaction was stopped by addition of 60 mL of

aqueous NH_4Cl solution followed by 300 mL of water and 20 mL of concentrated aqueous HCl together. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50mL). The collected organic layers were dried over MgSO_4 , filtered, rotovapped and dried on the vacuum line to give 21.1 g (95.6%) of product as a light brown oil.

3-(diphenylmethyl)-6,6-dimethylfulvene. A 500 mL flask was charged with 10 g of (diphenylmethyl)cyclopentadiene (43 mmol), 15.0 mL of Acetone (204 mmol) and 50 mL of methanol. After obtaining a homogeneous solution, 5 mL of pyrrolidine (60 mmol) were syringed in. The product begins to precipitate out after 10 min. The reaction was stirred for 66 h. The yellow precipitate was filtered, washed with 40 mL of methanol and dried on the vacuum line to give 5.71 g (48.8%). MS (GC-MS) (EI) m/z 272 (M^+). ^1H NMR (CDCl_3 , 300 MHz) δ 2.14, 2.07 (s, 6H, $(\text{CH}_3)_2\text{C-Cp}$), 5.18 (s, 1H, CHPh_2), 5.92, 6.27, 6.53 (m, 3H, Cp-H), 7.17 -7.30 (m, 10H, phenyl-H).

$\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$. In the glove box, a 500 mL flask was charged with 5.67 g of 3-(diphenylmethyl)-6,6-dimethylfulvene (20.8 mmol), 100 mL of THF and then 3.576 g of flourenyllithium (20.80 mmol). The flask was equipped with a 180° needle valve and connected to the Schlenk line. After 26 hours of stirring, 60 mL of aqueous NH_4Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The collected organic layers were dried over MgSO_4 and rotovapped to give 8.85 g of product as yellow oil (97.1%).

$\text{Me}_2\text{C}(\text{diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{Li}_2$. In the glove box, a 250 mL round bottom flask was charged with 8.85 g of $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$ (20.2

mmol) and 80 mL of diethyl ether. The flask was attached to a swivel frit and connected to the Schlenk line. At 0°C, 14.2 mL of *n*-BuLi (40.4 mmol, 2.87M in hexane) were syringed in. After stirring for 18 h at room temperature, a red solid was isolated by filtration and dried to give 7.86 g (86.4%) of product.

Me₂C(3-(diphenylmethyl)-C₅H₃)(C₁₃H₈)ZrCl₂. In the glove box, a 100 mL round bottom flask was charged with 1.93 g of Me₂C(diphenylmethyl)-C₅H₃(C₁₃H₈)Li₂ (4.29 mmol) and ZrCl₄ (1.0 g, 4.3 mmol). The flask was attached to a swivel frit and connected to the Schlenk line. 50 mL of diethyl ether were syringed in. The reaction was stirred for 48 hours. Then solvent was removed and 60 mL of methylene chloride were condensed and stirred for 30 minutes and filtered. The methylene chloride was removed and 60 mL of diethyl ether were syringed in and stirred for 20 min, filtered and dried on the vacuum line to give 1.155 g of product as a pink precipitate (44.9 %). ¹H NMR (C₆D₆, 300 MHz) δ 1.67, 1.85 (s, 6H, (CH₃)₂C-Flu-Cp), 5.34, 5.47, 5.84 (m, 3H, Cp-H), 6.0 (s, 1H, CHPh₂), 6.95-7.20 (m, 10H, phenyl-H), 6.9-7.34 (m, 4H, Flu-H) 7.40, 7.49, 7.90, 7.95 (d, ³J_{HH} = 8.5, 8.4, 8.0, 8.1 Hz, 4H, Flu-H).

Preparation of metallocene 6

1-tert-butyl-4-cyclopenta-2,4-dienylidene-cyclohexane. A 500 mL round bottom flask was charged with 50 mL (605 mmol) of cyclopentadiene, 46.5 g (302 mmol) of 4-*t*-butylcyclohexanone and 250 mL of methanol. Then 5.0 mL (60 mmol) of pyrrolidine were syringed in. After stirring for 21 hours, the yellow precipitate was filtered and refluxed in 200 mL of methanol for one hour. After cooling, product was filtered and dried in vacuum line to give 37.51g (61.51%) of product. MS (EI) *m/z* 202 (M⁺).

(4-*t*-butylcyclohexyl-1-methyl)cyclopentadiene. A 500 mL round bottom flask was charged with 9.1 g (45 mmol) of 1-tert-butyl-4-cyclopenta-2,4-dienylidene-cyclohexane. The flask then was equipped with a 180° needle valve and evacuated. Then 60 mL of diethyl ether were syringed in and at 0°C, 60 mL (135 mmol) of methyllithium (1.5 M in diethyl ether) were syringed in followed by 6 mL of dimethoxyethane. After stirring for 48 hours, 60 mL of NH₄Cl solution were added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic layers were dried over MgSO₄ and filtered. The solution was rotovapped to give 9.30 g (99.8%) of product as a yellow oil. MS (EI) *m/z* 218 (M⁺).

3-(4-*t*-butylcyclohexyl-1-methyl)-6,6-dimethylfulvene. In a 500 mL flask, (4-*t*-butylcyclohexyl-1-methyl)cyclopentadiene (10.05 g, 46.06 mmol), 18.0 mL (245 mmol) of acetone and 80 mL of methanol were mixed together. After obtaining a homogeneous solution, 6.0 mL (72 mmol) of pyrrolidine were added slowly. After stirring for 72 hours, 7 mL acetic acid and 300 mL of water were added followed by 100 mL of diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (4 x 50 mL). The combined organic layers were extracted with H₂O (3 x 50 mL) and then 10% sodium hydroxide solution (3 x 30 mL). The combined organic layers were dried over MgSO₄, filtered and rotovapped to give 11.21 g (94.28%) of product as an orange oil. MS (EI) *m/z* 258 (M⁺).

Me₂C(3-(4-*t*-butylcyclohexyl-1-methyl)-C₅H₃)(C₁₃H₈)H₂. In the glove box, a 500 mL round bottom flask was charged with 7.74 g (30.0 mmol) of 3-(4-*t*-butylcyclohexyl-1-methyl)-6,6-dimethylfulvene and 80 mL of diethyl ether. Then 5.16 g (30.0 mmol) of

fluorenyllithium were added to the solution. After stirring for 96 hours under a nitrogen atmosphere, 60 mL of NH₄Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered and rotovapped to give 11.64g (91.50%) of product as an orange oil. MS (MALDI) *m/z* 425 (M + H)⁺.

Me₂C(3-(4-*t*-butylcyclohexyl-1-methyl)-C₅H₃)(C₁₃H₈)ZrCl₂. In the glove box, a 100 mL round bottom flask was charged with 11.26 g (26.53 mmol) of Me₂C(3-(4-*t*-butylcyclohexyl-1-methyl)-C₅H₃)(C₁₃H₈)H₂ and 60 mL of diethyl ether. The flask then was attached to a swivel frit. At 0°C, 23.1 mL of *n*-BuLi (53.06 mmol, 2.3 M in hexanes) were syringed in and stirred for 48 hours at room temperature. The solid was removed by filtration (0.81 g of impurity). Then solvent was removed by vacuum and 5.77 g (24.7 mmol) of ZrCl₄ were added; then 80 mL of diethyl ether were condensed in. The reaction was stirred for 48 hours, and then solvent was removed by vacuum. Then 70 mL of methylene chloride were condensed in, stirred and filtered by flipping the swivel frit; then the solvent was removed by vacuum. After that 60 mL of diethyl ether were condensed in and stirred. The product was isolated by filtration and dried by high vacuum to give 4.65g (30%) of product as a pink powder. ¹H NMR (CDCl₃, 300 MHz) δ 0.84 (s, 9H, *t*-butyl-*H*), 1.25 (s, 3H, Me-*H*), 0.80-2.19 (m, 9H, cyclohexyl-*H*), 2.36, 2.39 (s, 6H, (CH₃)₂C-Flu-Cp), 5.72, 5.84, 6.19 (t, ³J_{HH} = 2.7, 3.3, 2.3, 3H, Cp-*H*), 7.23, 7.29, 8.12, 8.15 (d, ³J_{HH} = 6.0, 5.9, 6.9, 6.1 Hz, 4H, Flu-*H*), 7.54, 7.54, 7.82, 7.82 (t, ³J_{HH} = 8.1, 8.1, 8.7, 8.7 Hz, 4H, Flu-*H*).

Preparation of metallocene 7

Cyclopenta-2,4-dienylidene-cyclohexane. A 500 mL round bottom flask was charged with 60.0 mL of cyclopentadiene (727 mmol), 65.0 mL of cyclohexanone (627 mmol) and 100 mL of methanol. Then 20.0 mL of pyrrolidine (239mmol) were syringed in. After stirring for 96 hours, 30 mL of glacial acetic acid, 300 mL water and 200 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The collected organic layers were extracted with water (3 x 30 mL) and then 10% NaOH solution (3 x 30 mL). Then it was dried over MgSO₄ and rotovapped to give 74.8 g of product as a brown oil (70.3%).

(1-methylcyclohexyl)cyclopentadiene. In the glove box, a 500 mL round bottom flask was charged with 8.0 g of cyclopenta-2,4-dienylidene-cyclohexane (54.7 mmol) and 60 mL of diethyl ether. The flask was equipped with a 180° needle valve and then connected to the Schlenk line. At 0°C, 60.0 mL of MeLi (172 mmol, 1.5 M in diethyl ether, Aldrich) were syringed in slowly followed by 4.0 mL of dimethoxyethane. After stirring for 9 days at room temperature, 60 mL of aqueous NH₄Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL) then dried over MgSO₄ and rotovapped to give 7.84 g of product as a brown oil (88.4%). MS (GC-MS) (EI) *m/z* 162 (M⁺).

3-(1-methylcyclohexyl)-6,6-dimethylfulvene. In a 500 mL flask, 7.84 g of (1-methylcyclohexyl)cyclopentadiene (48.3 mmol), 15.0 mL of acetone (204 mmol), 50 mL of ethanol, and 50 mL of methanol were mixed. Then 2.0 mL of pyrrolidine (24

mmol) were syringed in. After 6 days of reaction time, 10 mL of glacial acetic acid, 300 mL of water, and 100 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (4 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL) and 10% NaOH aqueous solution (3 x 30 mL). Then the organic layer was dried over MgSO_4 , filtered and rotovapped to give 10.0 g of product as a brown oil (93.1%). MS (GC-MS) m/z 202 M^+ .

$\text{Me}_2\text{C}(3-(1\text{-methylcyclohexyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$. In the glove box, a 500 mL round bottom flask was charged with 6.0 g of 3-(1-methylcyclohexyl)-6,6-dimethylfulvene (30 mmol). Then 100 mL of diethyl ether and 5.1 g of fluorenyllithium (30 mmol) were added. Then the flask was equipped with a 180° needle valve and connected to the Schlenk line. After stirring for 72 hours, 60 mL of aqueous NH_4Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic layers were extracted with water (3 x 50 mL) then dried over MgSO_4 , filtered and rotovapped to give 9.24 g of product as an orange waxy solid (84.5%).

$\text{Me}_2\text{C}(3-(1\text{-methylcyclohexyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_4$. In a 250 mL round bottom flask, 8.95 g of $\text{Me}_2\text{C}(3-(1\text{-methylcyclohexyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$ (24.3 mmol) and 70 mL of diethyl ether were added. The flask was attached to a swivel frit and connected to the Schlenk line. At 0°C , 17.0 mL of *n*-BuLi (48.8 mmol, 2.87 M in hexanes) were syringed in. After stirring for 24 hours, solvent was removed. In the glove box, 5.69 g of ZrCl_4 (24.3 mmol) were added. Then 80 mL of diethyl ether were syringed in. After 2 days of stirring, the solvent was removed and 60 mL of methylene chloride were condensed in,

stirred and filtered. Methylene chloride was removed and 60 mL of diethyl ether were condensed in, stirred for 30 minutes, filtered and dried using the vacuum line to give 3.4 g of orange powder (27%). ^1H NMR (CDCl_3 , 300 MHz) δ 1.16 (s, 3H, Me-*H*), 1.20-1.61 (m, 10H, cyclohexyl-*H*), 2.20, 2.23 (s, 6H, $(\text{CH}_3)_2\text{C}$ -Flu-Cp), 5.62, 5.77, 6.17 (t, $^3J_{\text{HH}} = 2.7, 3.0, 3.0$, 3H, Cp-*H*), 7.22, 7.26, 7.80, 8.15 (d, $^3J_{\text{HH}} = 8.7, 8.7, 8.4, 8.4$ Hz, 4H, Flu-*H*), 7.40, 7.43, 7.58, 7.58 (t, $^3J_{\text{HH}} = 6.9, 6.7, 7.2, 7.2$ Hz, 4H, Flu-*H*).

Preparation of metallocene 8

3-cyclopenta-2,4-dienylidene-1,1,5-trimethyl-cyclohexane. A 250 mL round bottom flask was charged with 50.0 mL of cyclopentadiene (606 mmol), 48.0 mL of 3,3,5-trimethylcyclohexanone (303 mmol) and 100 mL of methanol. Then 15.0 mL of pyrrolidine (179 mmol) were syringed in. After 108 hours of stirring, 30 mL glacial acetic acid, 300 mL water, and 200 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The collected organic layers were extracted with water (3 x 30 mL) and then 10% NaOH solution (3 x 30 mL). Then the solution was dried over MgSO_4 and rotovapped to give 55.83 g of product as a brown oil (48.9%).

(1,3,3,5-tetramethylcyclohexyl)cyclopentadiene. In the glove box, a 500 mL round bottom flask was charged with 10.0 g of 3-cyclopenta-2,4-dienylidene-1,1,5-trimethyl-cyclohexane (53.2 mmol) and 60 mL of diethyl ether. The flask was equipped with a 180° needle valve and then connected to the Schlenk line. At 0°C , 55.6 mL of MeLi (159.5 mmol, 1.5 M in diethyl ether, Aldrich) were syringed in slowly and then 3.73 mL of dimethoxyethane were added. After stirring for 10 days at room temperature,

60 mL of aqueous NH_4Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL) then dried over MgSO_4 and rotovapped to give 9.55 g (88.9%) of product as a brown oil. MS (GC-MS) m/z 204.15 (M^+).

3-(1,3,3,5-tetramethylcyclohexyl)-6,6-dimethylfulvene. In a 500 mL round bottom flask, a 9.55 g of (1,3,3,5-tetramethylcyclohexyl)cyclopentadiene (47.2 mmol), 20.0 mL of acetone (272 mmol), and 50 mL of methanol were mixed. Then 2.0 mL of pyrrolidine (24 mmol) were syringed in. After stirring for 72 hours, 10 mL of concentrated acetic acid, 300 mL of water, and 100 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (4 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL) and 10 % NaOH aqueous solution (3 x 30 mL). Then the organic layer was dried over MgSO_4 , filtered and rotovapped to give 13.20 g (95.6%) of the product as brown oil. MS (GC-MS) (EI) m/z 244 (M^+)

$\text{Me}_2\text{C}(\text{3-(1,3,3,5-tetramethylcyclohexyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$. In the glove box, a 250 mL round bottom flask was charged with 7.0 g of 3-(1,3,3,5-tetramethylcyclohexyl)-6,6-dimethylfulvene (29 mmol). Then 100 mL of diethyl ether and 4.93 g of fluorenyllithium (29.0 mmol) were added. Then the flask was equipped with a 180° needle valve and connected to the Schlenk line. After stirring for 72 hours, 60 mL of aqueous NH_4Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic layers were extracted with water

(3 x 50 mL) then dried over MgSO_4 , filtered and rotovapped to give 9.32 g of the product as an orange oil (79.2%). MS (GC-MS) (EI) m/z 410 (M^+).

$\text{Me}_2\text{C}(1,3,3,5\text{-tetramethylcyclohexyl})\text{-C}_5\text{H}_3(\text{C}_{13}\text{H}_8)\text{ZrCl}_4$. In a 250 mL round bottom flask, 9.09 g of $\text{Me}_2\text{C}(3\text{-}(1,3,3,5\text{-trimethylcyclohexyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$ (22.2 mmol) and 70 mL of diethyl ether were added. The flask was attached to a swivel frit and connected to the Schlenk line. At 0°C , 15.7 mL of *n*-BuLi (45.0 mmol, 2.87 M in hexanes) were syringed in. After stirring for 20 h, solvent was removed. In the glove box, 5.183 g of ZrCl_4 (22.15 mmol) were added. Then 60 mL of diethyl ether were syringed in. After stirring for 24 hours, the solvent was removed and 60 mL of methylene chloride were syringed in, stirred. Methylene chloride was removed and 60 mL of diethyl ether were syringed in. Catalyst was isolated by filtration and dried using high vacuum to give 3.60 g (28.5%) of pink powder. From ^1H NMR, more than two isomers were observed. ^1H NMR (C_6D_6 , 300 MHz) δ 0.48 (s), 0.50-0.81 (m), 0.85 (d), 1.02-1.39 (m), 1.40 (s), 1.53 (s), 1.84, 1.88 (s), 5.49, 5.65, 5.69, 6.10, 6.29 (m), 6.94-7.03 (m), 7.20-7.39 (m), 7.42-7.54 (m), 7.75-7.86 (m).

Preparation of metallocene 9

5-(1-isopropyl-2-methyl-propylidene)-cyclopenta-1,3-diene. 150 mL (778 mmol) of 2,4-dimethyl-3-pentanone were mixed with 60.0 mL (1.06 mol) of cyclopentadiene and 44.0 g (815 mmol) of sodium methoxide. The mixture was shaken using a mechanical shaker for 25 days. After that 300 mL of NH_4Cl solution were added, followed by 200 mL of diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were

extracted with H₂O (4 x 100 mL). Then it was dried over MgSO₄ and rotovapped to give 66.15 g of product as an oil (52.4%). MS (EI) *m/z* 162 (M⁺)

(2,3,4-trimethyl-3-pentyl)cyclopentadiene. A 500 mL round bottom flask was charged with 7.29 g (45.0 mmol) of 5-(1-isopropyl-2-methyl-propylidene)-cyclopenta-1,3-diene. The flask then was equipped with a 180° needle valve and evacuated. 80 mL of diethyl ether were syringed in and then at 0 °C, 90.0 mL (135 mmol) of methyllithium (1.5 M in diethyl ether) were syringed in, followed by 6 mL of dimethoxyethane. After stirring for 7 days, 60 mL of NH₄Cl solution were added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H₂O (3 x 50 mL), then dried over MgSO₄ and filtered. The solution was rotovapped to give 7.52 g (93.8%) of product as an orange oil.

3-(2,3,4-trimethyl-3-pentyl)-6,6-dimethylfulvene. In a 500 mL flask, 9.10 g (51 mmol) of (2,3,4-trimethyl-3-pentyl)cyclopentadiene, 30.0 mL (409 mmol) of acetone and 60 mL of methanol were mixed together. After obtaining a homogeneous mixture, 10.0 mL (120 mmol) of pyrrolidine were added slowly. After stirring for 7 days, 15 mL of acetic acid and 300 ml of water were added followed by 100 mL of diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H₂O (3 x 30 mL) and then 10% sodium hydroxide solution (3 x 30 mL). The combined organic layers were dried over MgSO₄, filtered, and rotovapped to give 9.84 g (88.3%) of product as an oil. MS (EI) *m/z* 218 (M⁺). MS (ESI) *m/z* 219 (M + H)⁺.

Me₂C(3-(2,3,4-trimethyl-3-pentyl)-C₅H₃)(C₁₃H₈)H₂. In the glove box, a 500 mL round bottom flask was charged with 7.54 g (34.7 mmol) of 3-(2,3,4-trimethyl-3-pentyl)-6,6-dimethylfulvene and 100 mL of diethyl ether. Then 5.94 g (34.6 mmol) of fluorenyllithium were added. After stirring for 10 days, 60 mL of NH₄Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 40 mL). The combined organic layers were dried over MgSO₄, filtered and rotovapped to give 11.21 g (84.41%) of product as an oil. MS (ESI) *m/z* 384 (M + H)⁺.

Me₂C(3-(2,3,4-trimethyl-3-pentyl)-C₅H₃)(C₁₃H₈)Li₂. In the glove box, a 100 mL round bottom flask was charged with 11.0 g (28.6 mmol) of Me₂C(3-(2,3,4-trimethyl-3-pentyl)-C₅H₃)(C₁₃H₈)H₂ and 60 mL of diethyl ether. The flask then was attached to a swivel frit. At 0°C, 25.0 mL (57.2 mmol) of *n*-BuLi (2.3 M) were syringed in and stirred for 48 hours at room temperature. The solvent was removed by vacuum and 70 mL of hexane were condensed in and stirred for 1 hour at room temperature. The product was filtered and dried to give 9.44 g (83.3%) of product as an orange solid.

Me₂C (3-(2,3,4-trimethyl-3-pentyl)-C₅H₃)(C₁₃H₈)ZrCl₂. In the glove box, a 100 mL round bottom flask was charged with 3.00 g (7.572 mmol) of Me₂C (3-(2,3,4-trimethyl-3-pentyl)-C₅H₃)(C₁₃H₈)Li₂ and 1.771 g (7.572 mmol) of ZrCl₄. The flask then was attached to a swivel frit. Then 70 mL of diethyl ether were condensed in and this was stirred for 48 hours at room temperature. The solvent was removed by vacuum, and then 60 mL of methylene chloride were condensed in, stirred and filtered by flipping the swivel frits then the solvent was removed by vacuum. After that, 70 mL of diethyl ether were condensed in and stirred for 30 minutes at room temperature. The product was

isolated by filtration and dried under high vacuum to give 1.51g (36.6%) of orange powder. $^1\text{H NMR}$ (C_6D_6 , 300 MHz) δ 0.37, 0.70, 0.72, 1.21 (d, $^3J_{\text{HH}} = 6.59, 6.60, 6.59, 5.39$ Hz, 12H, $\text{C}(\text{Me})(\text{CH}(\text{CH}_3)_2)_2$), 1.20 (s, 3H, $\text{C}(\text{CH}_3)(\text{CH}(\text{CH}_3)_2)_2$), 1.61, 2.11 (sep, $^3J_{\text{HH}} = 6.59, 6.89$ Hz, 2H, $\text{C}(\text{CH}_3)(\text{CH}(\text{CH}_3)_2)_2$), 1.83, 1.87 (s, 6H, $(\text{CH}_3)_2\text{C}(-\text{Flu})(-\text{Cp})$), 5.44, 5.55, 6.06 (t, $^3J_{\text{HH}} = 2.7, 3.0, 2.4$ Hz, 3H, Cp-*H*), 7.15, 7.32, 7.78, 7.81 (d, $^3J_{\text{HH}} = 8.4, 8.6, 8.7, 8.1$ Hz, 4H, Flu-*H*), 6.97, 7.01, 7.44, 7.47 (t, 6.9, 6.6, 7.0, 6.9 Hz, 4H, Flu-*H*).

Preparation of metallocene 10

6,6-diphenylfulvene. In a 500 mL round bottom flask, 111.7g of benzophenone (613.0 mmol) and 35.6 g of sodium methoxide (660 mmol) were dissolved in 500 mL of ethanol. After obtaining a homogeneous mixture, 87.0 mL of cyclopentadiene (1055 mmol) were added, giving a red colored solution. After 68 h of stirring, the orange precipitate was collected by filtration, rinsed with 50 mL of ethanol, refluxed with 200 mL of methanol and collected by filtration again to give 115 g of product as orange powder (81.4%). MS (GC-MS) m/z 230.18(M^+). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 6.24, 6.54 (d, $^3J_{\text{HH}} = 5.1, 4.5$, 4H, C_5H_4), 7.23-7.38 (m, 10H, phenyl-*H*).

(diphenylmethyl)cyclopentadiene. First, 12.0 g of 6,6-diphenylfulvene (52.1 mmol) were dissolved in 50 mL of THF. Then at 0°C , the solution was added to a 500 mL flask containing 6.50 g of LiAlH_4 (133 mmol) and 50 mL of THF. The reaction was stirred for 48 hours at room temperature. At 0°C , the reaction was stopped by addition of 60 mL of aqueous NH_4Cl solution followed by 300 mL of water and 20 mL of concentrated aqueous HCl . The organic layer was isolated and the aqueous layer was

extracted with diethyl ether (3 x 50 mL). The collected organic layers were dried over MgSO_4 , filtered, rotovapped and dried under vacuum line to give 12.88 g of product as a light brown oil (99.8%).

3-(diphenylmethyl)-6,6-diphenylfulvene. A 500 mL flask was charged with 5.00 g of (diphenylmethyl)cyclopentadiene (21.5 mmol), 50.0 mL of ethanol, and 3.922 g of benzophenone (21.55 mmol). After obtaining a homogeneous mixture, 3.30 mL of pyrrolidine (39.7 mmol) were syringed in. The color changed to orange. The reaction was stirred for 9 days. 10 mL of glacial acetic acid, 200 mL of water and 100 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL) and 10 % NaOH aqueous solution (3 x 30 mL). The organic layer was dried over MgSO_4 , filtered and rotovapped to give 7.88 g of product as an oil (92.3%). MS (GC-MS) (EI) m/z 397 ($\text{M}^+\text{+H}$).

Attempted of synthesis of $\text{Ph}_2\text{C}(\text{3-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{H}_2$. In the glove box, a 500 mL flask was charged with 7.88 g of 3-(diphenylmethyl)-6,6 diphenylfulvene (19.88 mmol), 100 mL of diethyl ether and then 3.421 g of fluorenyllithium (19.88 mmol). The flask was equipped with a 180° needle valve then connected to the Schlenk line. After stirring for 10 days, 60 mL of aqueous NH_4Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The collected organic layers were dried over MgSO_4 and rotovapped to give 10.64 g of a brown waxy solid that was tested by ^1H NMR and MS, indicating starting material.

Preparation of metallocene 11

2-adamantylfulvene. First, 25.0 g of 2-admantanone (166 mmol), 30.0 mL cyclopentadiene (0.364 mol) and 250 mL methanol were mixed in a 500 mL round bottom flask. Then 10 mL of pyrrolidine were syringed in and the mixture was stirred for 92 h. Yellow precipitate (24.1 g, 73.8%) was collected by suction filtration, washed with 60 mL of methanol, and then dried under high vacuum. ^1H NMR (CDCl_3 , 300 MHz) δ 1.90, 2.11 (m, 14H, adamantyl-*H*), 6.53, 6.60 (d, $^3J_{\text{HH}} = 6.6, 6.6$ Hz, 4H, C_5H_4).

(2-methyladamantyl)cyclopentadiene. In the glove box, a 500 mL round bottom flask was charged with 5.00 g of adamantylfulvene and 50 mL of diethyl ether. The flask was equipped with a 180° needle valve. At 0 °C, 50.5 mL (75.70 mmol) of methyllithium (1.5 M in diethyl ether) were added slowly followed by 3.4 mL of dimethoxyethane. The reaction was left stirring at room temperature for 10 days. Then 60 mL of NH_4Cl solution were added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 50 mL), then dried over MgSO_4 and filtered. The solution was rotovapped to give 5.29 g (97.9%) of product as an oil.

3-(2-methyladamantyl)-6,6-diphenylfulvene. In a 500 mL flask, (2-methyladamantyl)cyclopentadiene (5.29 g, 24.7 mmol) was dissolved in 100 mL of ethanol and then 4.49 g (24.7 mmol) of benzophenone were added. After obtaining a homogeneous solution, 2.66 g (49.4 mmol) of sodium methoxide were added. After stirring for 7 days, 60 mL of aqueous NH_4Cl solution were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The

combined organic layers were extracted with H₂O (4 x 50 mL) and then 10% aqueous sodium hydroxide solution (3 x 30 mL). The combined organic layers were dried over MgSO₄, filtered and rotovapped to give 8.67 g (92.8%) of product as an oil. MS (EI) m/z 378 (M⁺).

Attempted of synthesis of Ph₂C(3-(2-methyladamantyl)-C₅H₃)(C₁₃H₈)H₂. A 500 mL round bottom flask was charged with 8.67 g (22.9 mmol) of 3-(2-methyladamantyl)-6,6-diphenylfulvene and 100 mL of diethyl ether. Then 3.94 g (22.9 mmol) of fluorenyllithium were added. After stirring for 7 days, 60 mL of aqueous NH₄Cl solution were added, followed by 50 mL of diethyl ether. The solution then was stirred for two hours. The solid was isolated by filtration and dissolved in 250 mL of THF, and then dried over MgSO₄. Then it was filtered and rotovapped to give 3.75 g (30%). The organic filtrate was extracted with H₂O (3 x 50 mL), dried over MgSO₄ and rotovapped to give 7.75g (62.1%) that has been tested by ¹H NMR and MS showed no product, only starting material.

Preparation of metallocene 12

TiCl₄·2THF. In the glove box, a 100 mL round bottom flask was charged with 5.261g (27.74 mmol) of TiCl₄. The flask then was attached to a swivel frit. On the vacuum line, 60 mL of methylene chloride were condensed in. Then at 0°C, 7 mL of THF were syringed in slowly and then stirred at room temperature for 24 hours. The yellow solid was filtered and dried under high vacuum to give 6.2g (66%) of yellow solid.

Me₂C(3-(diphenylmethyl)-C₅H₃)(C₁₃H₈)TiCl₂. In the glove box, a 100 mL round bottom flask was charged with 1.00 g of Me₂C (diphenylmethyl)-C₅H₃(C₁₃H₈)Li₂ (2.22 mmol) and TiCl₄·2THF (0.74 g, 2.22mmol). The flask was attached to a swivel frit and connected to the Schlenk line. 60 mL of diethyl ether were condensed in. After stirring the mixture for 2 days, the solvent was removed and 60 mL of methylene chloride were condensed in and stirred for 24 hours at room temperature and then filtered. Methylene chloride was removed and 60 mL of diethyl ether were condensed in and stirred for 2 hours. The solid was collected by filtration and dried under vacuum line to give 0.622 g of a brown powder (50.5 %). ¹H NMR (C₆D₆, 300 MHz) δ 1.79, 1.96 (s, 6H, (CH₃)₂C-Flu-Cp), 5.30, 5.45, 6.15 (m, 3H, Cp-H), 6.29 (s, 1H, CHPh₂), 7.09-7.30 (m, 10H, phenyl-H), 7.09-7.30 (m, 4H, Flu-H) 7.39, 7.85, 8.02, 8.04 (d, ³J_{HH} = 8.7, 8.6, 8.1, 8.1 Hz 4H, Flu-H).

Preparation of metallocene 14

Ph₂C(C₅H₄)(C₁₃H₈)H₂. In the glove box, a 500 mL round bottom flask was charged with 4.67 g of 6,6-diphenylfulvene (20.3 mmol) and 3.50 g of fluorenyllithium (20.3 mmol). The flask then was equipped with a 180° needle valve. Then 100 mL of diethyl ether were syringed in at 0°C. The reaction was stirred for 8 days at room temperature. At 0°C, 50 mL of distilled water and 50 mL of NH₄Cl solution were added slowly. The slurry was filtered and washed with 100 mL of distilled water. The solid then was boiled in 80 mL ethanol for 2 hours then filtered hot and dried to give 6.20 g (77.1%) of light yellow powder, MS (GC-MS) m/z 395(M⁺- H).

Ph₂C(C₅H₄)(C₁₃H₈)Li₂. A 100 mL round bottom flask was charged with 5.00 g (12.6 mmol) of Ph₂C(C₅H₄)(C₁₃H₈)H₂. The flask then was attached to a swivel frit and 60 mL of diethyl ether was condensed in. At 0 °C, 10.17 mL (25.22 mmol) of *n*-BuLi (2.48 M in hexane) was syringed in. The reaction was stirred for 18 h at room temperature and 5 h at 40°C. The orange solid was isolated by filtration, extracted with diethyl ether, and dried under high vacuum to give 6.0 g (116% as ether adduct) of orange powder.

Ph₂C(C₅H₄)(C₁₃H₈)TiCl₂. In the glove box, a 100 mL round bottom flask was charged with 3.00 g (7.35 mmol) of Ph₂C(C₅H₄)(C₁₃H₈)Li₂ and 2.46 g (7.35 mmol) of TiCl₄·2THF and then the flask was attached to a swivel frit and connected to a Schlenk line. 60 mL of diethyl ether were condensed in then the reaction was allowed to warm to room temperature and stirred for 48 hours. The solvent was removed by vacuum and 70 mL of methylene chloride were condensed in and stirred for 30 minutes and filtered by flipping the swivel frit. Methylene chloride was removed and 50 mL of diethyl ether were condensed in, and stirred for 30 minutes at room temperature. The product then was filtered and dried under vacuum to give 0.58 g (15.4%) of brown powder. ¹H NMR (CDCl₃, 300 MHz) δ 5.48, 6.14 (t, ³J_{HH} = 3.0 Hz, d, ³J_{HH} = 8.7 Hz, 4H, C₅H₄), 7.20-7.39 (m, 10H, phenyl-*H*), 7.44, 7.70 (t, ³J_{HH} = 6.0, 6.9 Hz, 4H, Flu-*H*), 7.81 8.10 (d, 8.8 ,8.1 Hz , 4H, Flu-*H*).

Preparation of metallocene 15

Ph₂C(C₅H₄)(C₁₃H₈)TiMe₂. In the glove box, a 100 mL round bottom flask was charged with 0.450 g (0.877 mmol) of Ph₂C(C₅H₄)(C₁₃H₈)TiCl₂ and 50 mL of toluene

and then attached to a swivel frit. Under a nitrogen atmosphere, 1.31 mL (3.50 mmol) of MeMgCl (25% wt in THF) were syringed in at 0 °C. The reaction was stirred for 42 hours before solvent was removed by vacuum and 50 mL of methylene chloride were condensed in, stirred for 1. The solution was filtered and then the solvent was removed under high vacuum. 40 mL of diethyl ether were condensed in and stirred for 30 minutes. The product was isolated by filtration and dried under high vacuum. The reaction was monitored by ^1H NMR and showed that the reaction was not complete. Therefore, using the same flask, 1.0 mL (2.7 mmol) of MeMgCl (25% wt) and 50 mL of toluene were added. The reaction was stirred for 7 days. Then solvent was removed by high vacuum and 50 mL of methylene chloride were condensed in, stirred for 1 hour. The solution was filtered and then the solvent was removed under high vacuum. 40 mL of diethyl ether were condensed in and stirred for 30 minutes. The product was filtered and dried under high vacuum to give 0.10 (24%) g of a light pink powder. ^1H NMR (CDCl_3 , 300 MHz) δ -1.39 (s, 6H, $\text{Ti}(\text{CH}_3)_2$) 5.11, 6.10 (t, $^3J_{\text{HH}} = 5.1$ Hz, d, $^3J_{\text{HH}} = 8.7$ Hz, 4H, Cp-*H*), 7.20-7.39 (m, 10H, phenyl-*H*), 7.44, 7.81 (t, $^3J_{\text{HH}} = 6.4$, 6.1 Hz, 4H, Flu-*H*), 7.83 8.30 (d, $^3J_{\text{HH}} = 8.0$, 8.1 Hz, 4H, Flu-*H*).

Propylene polymerization procedure

All polymerization reactions were performed under a nitrogen atmosphere. The polymerizations were performed using a 600 mL Parr polymerization reactor. Methylaluminoxane (MAO) was purchased from Albemarle Corporation as a solution in toluene and used as the dry powder after removing all volatiles under high vacuum. Propylene gas was purchased from Matheson (polymerization grade, >99.5%) and

purified with a Matheson 6110 drying system equipped with an OXYSORBTM column. Polymerizations were initiated by adding methylaluminoxane (MAO) (dissolved in toluene) in the reactor vessel and then condensing the desired amount of propylene gas into the reactor at 0°C. After setting the reaction temperature and obtaining constant temperature readings, metallocene that is dissolved in toluene is injected into the reactor using Hamilton type syringes. During the polymerization reaction, the stirring speed is set in the range of 40 to 50 RPM. When the reaction is done, a small volume of diluted methanol/ aqueous HCl solution (10:1) is added to quench the catalyst and the polymerization stops. The collected polymer is then isolated by filtration, washed with methanol and dried under high vacuum.

Polymer characterization

The polymer pentad distribution was determined by ¹³C NMR spectrum by comparing the integration of the nine resolved peaks in the methyl region (19-22) of the spectra.^{56,57} The test was done at 130°C with tetrachloroethane-*d*₂ and 1,2,4-trichlorobenzene (1:1) as solvents and applying a 90 degree pulse with broadband decoupling and a delay time of 3 seconds; at least 1000 scans were used. Polymer melting temperature was determined by differential scanning calorimetry (Perkin-Elmer DCS 7 (25-200 °C)) using the second scan from 25-200 °C at 10 °C / minute. Molecular weights were determined by gel permeation chromatography (Waters Alliance GPC 2000 Gel Permeation Chromatograph with Refractive Index Detector and/or Polymer Labs HT GPC with Refractive Index detector).

CHAPTER IV
SYNTHESIS OF NEW ANSA-C₂-SYMMETRIC
SUBSTITUTED BIS-INDENYL METALLOCENES FOR
ISOTACTIC POLYPROPYLENE PRODUCTION

4.1 Introduction

The first bridged bis-indenyl metallocene **1** was prepared by Brintzinger¹⁰ in 1982 and tested by Ewen⁵ in 1984 for propylene polymerization. It was a breakthrough in isotactic polypropylene production. Ewen has demonstrated the relationship between the symmetry of the metallocene and tacticity of the obtained polymer.⁵ He found that the chiral *C*₂-symmetric metallocenes generally are highly isoselective, whereas the achiral *meso* analogue **2** (Figure 4.1) of that metallocene can only produce low molecular weight atactic polypropylene.

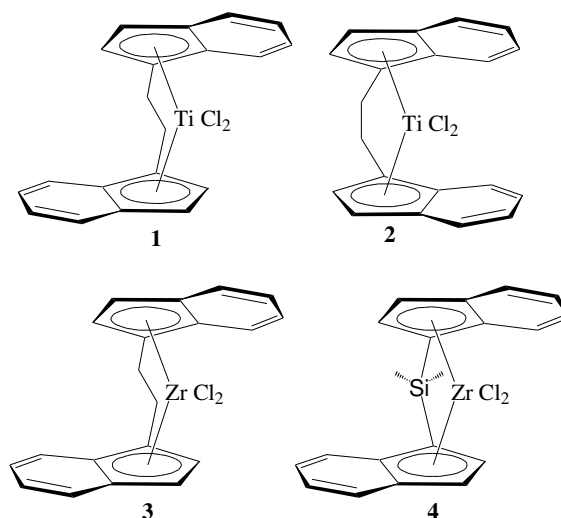


Figure 4.1. Structure of metallocenes 1-4.

However, these systems have some disadvantages. First, both *racemo* and *meso* stereoisomers are usually obtained; so when making catalyst ethylene-bis(indenyl)zirconocene, only 45% of racemic metallocene **3** will be obtained⁵⁸ and when making dimethylsilylene-bis(indenyl)zirconocenes, only 42% of the racemic metallocene **4** will be obtained⁵⁹; thus, a separation step is necessary to remove the *meso* stereoisomer in order to make highly isotactic polypropylene. Second, the production of *meso* metallocene reduces the yield of the racemic metallocene to about 50% less of the material.

In the propylene polymerization process, ethylene-bis(indenyl)zirconocene **3**/ MAO (MAO = methylaluminoxane) and dimethylsilylene-bis(indenyl)zirconocenes **4**/ MAO could make isotactic polypropylene with up to 78.5% and 81.7% [*mmmm*], respectively, as detailed in Table 4.1.⁶⁰

Table 4.1. Propylene polymerization data for metallocenes **3** and **4** in liquid propylene using MAO cocatalyst.

Metalocene	T_p (°C)	Activity ^a	M_w g/mol	T_m (°C)	[<i>mmmm</i>]%	Ref
3	70	188	24000	132	78.5	60
3	50		33600	134	87.4	61
4	70	190	36000	137	81.7	60

^a kg of PP/(mmol of M·h).

4.2 Synthesis of New *Ansa-C₂*-Symmetric Substituted Bis-Indenyl Metallocenes

In this project, to address all these problems and increase the selectivity of the catalyst, a shorter bridge such as SiMe₂ and indenyl groups having two bulky

substituents (tetramethyltetrahydrobenzo groups) such as in metallocene **5** (Figure 4.2) were employed. This is predicted to avoid the *meso* metallocene formation because of the steric interaction between these two substituents and increase the selectivity of the catalyst. Synthesis of the *racemo* stereoisomer of catalyst **5** is described in Figure 4.3.

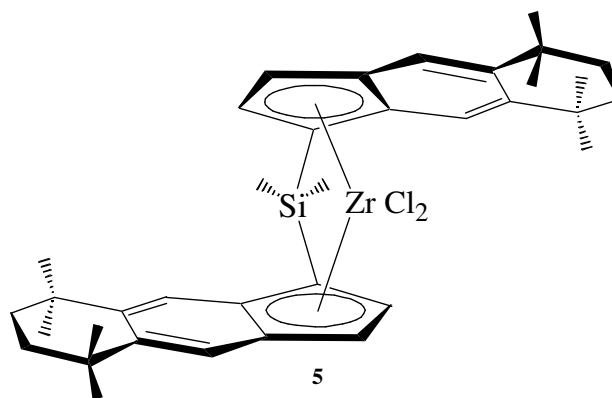


Figure 4.2. Structure of the new targeted metallocene **5**.

Catalyst **5** has been made with 40% yield in the metallation step and has a yellow orange color. Unfortunately, this metallocene is highly soluble in many different kinds of solvents such as diethyl ether, methylene chloride, hexanes, heptane, and toluene, but not in hexamethyl disiloxane. Therefore, purification of that catalyst is hard because the low polarity of this solvent does not help to remove unreacted ligands or other impurities.

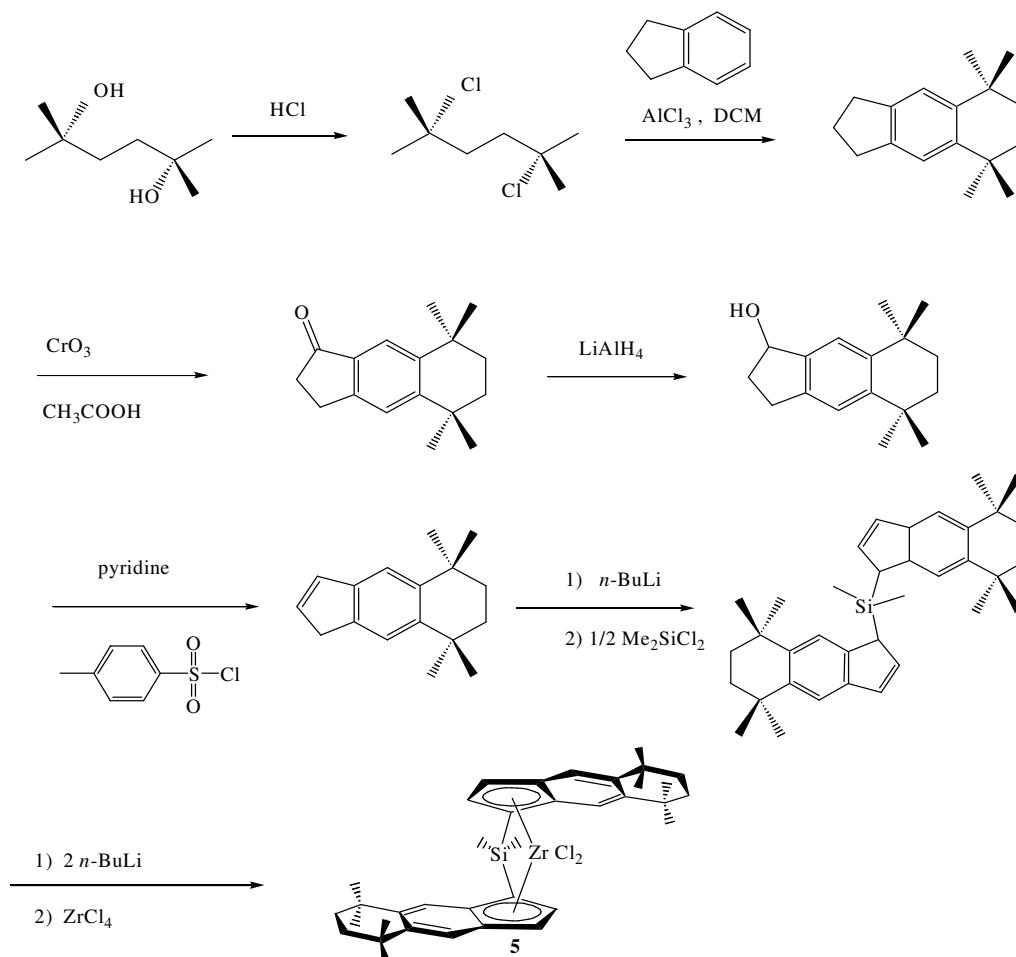


Figure 4.3. Synthesis of the *ansa*- C_2 -symmetric substituted bis-indenyl zirconocene.

4.3 Mechanism of Isotactic Polypropylene Polymerization Using *Ansa*- C_2 -Symmetric Bis-Indenyl Metallocenes

In C_2 -symmetric metallocenes, the two proposed coordination sites are homotopic. Therefore, we would expect both sites to have the same insertion mechanism, which employs the *si*-face of the incoming monomer for the enantiomer shown in Figure 4.4.⁵⁴ Addition of a bulky group on the indenyl groups should reduce the stereoerrors of

monomer insertion, leading to be an interesting system for isotactic polypropylene production.^{62,55,53}

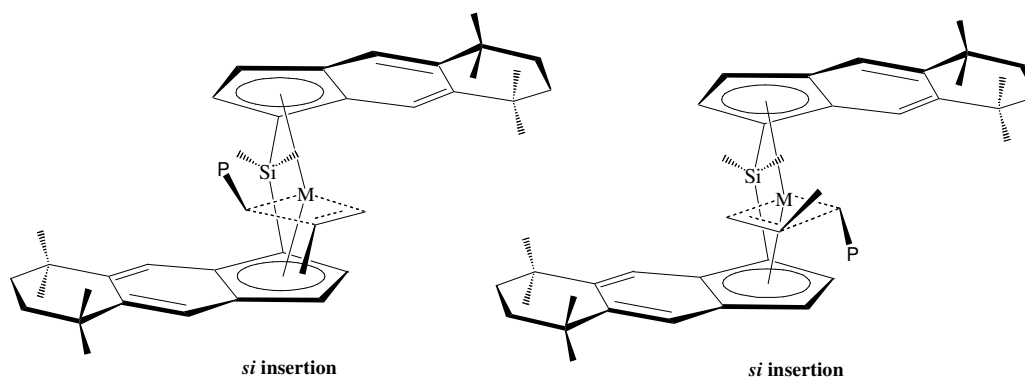


Figure 4.4. Monomer insertion mechanism for *ansa* C_2 -symmetric bis-indenyl zirconocene system.

In contrast, the *meso* C_s -symmetric *ansa* metallocene has no enantioselectivity at either coordination site, which makes it only an atactic polypropylene producer. The reason is that both coordination sites allow *si* and *re*-face type insertion with about 50% probability of each (Figure 4.5).⁶³

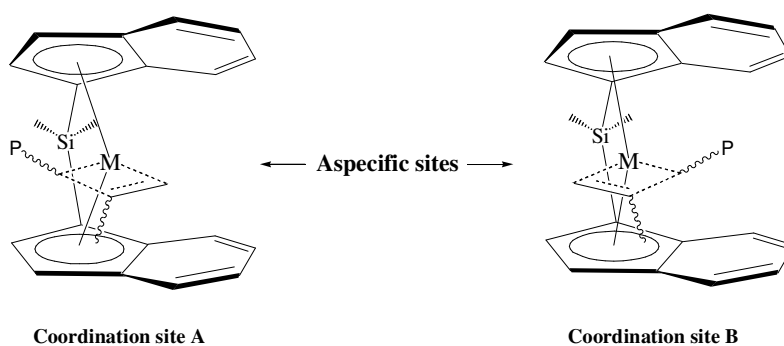


Figure 4.5. Insertion mechanism using the *meso* stereoisomer of bis-indenyl metallocenes.

4.4 Synthesis of Isotactic Polypropylene

The metallocene **5** that has been made was tested for the production of isotactic polypropylene upon activation with MAO in liquid propylene and a temperature range of 0-20 °C. From the polymerization reactions (Table 4.2) there was big difference in the catalyst activity from 0 to 20 °C; it is about 10 times more active at the higher temperature. This metallocene shows good isoselectivity at low temperatures in the range of 80 to 83 % [mmmm] pentad as shown in Figure 4.6. From the isotacticity ranges of metallocene **5** (80-83%) and dimethylsilylene-bis(indenyl)zirconocenes (81%), it seems that tetramethyltetrahydrobenzo substituent helped in preventing the *meso* formation but has little influence on the stereoselectivity.

Table 4.2. Propylene polymerization study of metallocene **5**.^a

Entry	Catalyst (mg)	T_p (°C)	C ₃ H ₆ (mL)	Toluene (mL)	Time (min)	Yield (g)	Activity (gP/gcat·h)	M _w	MWD ^b	T_m (°C)	[mmmm] %
1	5 (5.0)	0	100	3.0	20	0.21	126	78,850	3.31	142	82.7
2	5 (5.0)	20	100	3.0	20	1.6	960	39,550	2.70	141	80.5

^a Al:Zr ratio = 1000:1 ^b MWD= molecular weight distribution (M_w/M_n)

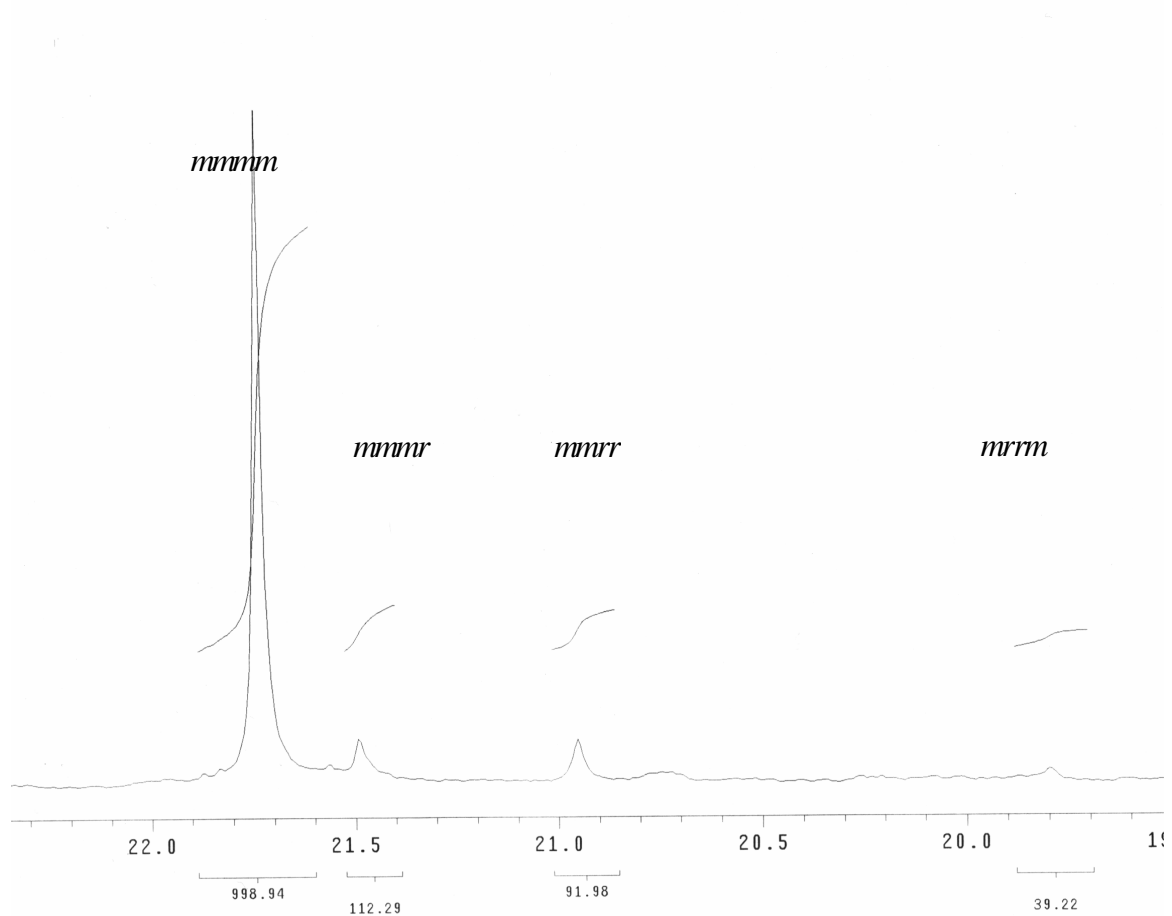


Figure 4.6. ^{13}C NMR spectrum of polypropylene from Entry 2 (Table 3.2).

4.5 Conclusions

Making a C_2 -symmetric metallocene without *meso* stereoisomeric contaminants is a significant step. It may reduce the cost and increase the yield of these isotactic polypropylene precursors. In this project, a new *ansa* C_2 -symmetric substituted bis-indenyl metallocene has been made successfully in a good yield without any detection of the *meso* analogue of that metallocene.

4.6 Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere using standard glove box and Schlenk line techniques. Solvents were dried and distilled from sodium (diethyl ether, toluene, and tetrahydrofuran) or from CaH_2 (methylene chloride, and hexanes). The following reagents were purchased and used without further purification: (Acros) dichlorodimethylsilane (99%), and lithium aluminum hydride (95%), (Avocado) indane (95%), (Alfa Aesar) *n*-BuLi (2.87 M in hexanes) and zirconium tetrachloride (99.5+%), (Strem) AlCl_3 (99%), and (TCI) 2,5-dimethyl-2,5-hexanediol (99%).

Preparation of metallocene 5

2,5-dichloro-2,5-dimethylhexane. (Synthesis modified from reference 16) In a 2 liter vessel, 200.0 g (1.368 mol) of 2,5-dimethyl-2,5-hexanediol and 1.50 L (18.3 mol) of concentrated aqueous hydrochloric acid were mixed and shaken for 48 hours. The white solid was filtered and washed with 1L of water and then dissolved in 1L of diethyl ether. The aqueous layer was removed and the organic layers were dried over MgSO_4 and filtered. The organic layer was flashed through an alumina column. The solution then was rotovapped to give a white solid that was dried briefly using high vacuum to give 191 g (71.0%) of product. ^1H NMR (CDCl_3 , 300 MHz) δ 1.61 (s, 12H, CH_3), 1.98 (s, 4H, CH_2).

5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indane. (Synthesis modified from reference 64) A 1 liter round bottom flask was charged with 46.47g (0.2540 mol) of 2,5-dichloro-2,5-dimethylhexane and 30.0 mL (0.254 mol) of indane. The flask was then

equipped with a condenser and purged with nitrogen for 10 min. Then 500 mL of methylene chloride were added and the solution was heated to 40°C. A slurry of 3.6 g of AlCl₃ and 100 mL of methylene chloride was added dropwise over 30 minutes. After stirring for 48 hours at 40°C, 500 mL of 5% HCl/ice were added. The organic layer was separated and washed with water until neutral according to pH paper. Then the solution was dried over MgSO₄ and rotovapped to give crude brown oil. The product was distilled under high vacuum (140 to 160°C, 0.4-0.45 mmHg) to give 16.2 g (28.0%) of a white waxy solid. GC-MS (EI) *m/z* 228 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ 1.27 (s, 12H, CH₃), 1.66 (s, 4H, CH₂-CH₂), 2.06 (quintet, ³J_{HH} = 7.2 Hz, 2H, CH₂-CH₂-CH₂), 2.86 (t, ³J_{HH} = 7.5 Hz, 4H, CH₂-CH₂-CH₂), 7.18 (s, 2H, aromatic-*H*).

5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indane-2-one. (Synthesis modified from reference 64) A 3 neck 500 mL round bottom flask was charged with 21.77 g (95.49 mmol) of 5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indane and 100 mL of glacial acetic acid. The mixture was heated to 105°C then 28.64 g (286.5 mmol) of CrO₃ were added slowly over 20 minutes. After stirring for 26 hour at 110°C, the reaction was cooled to room temperature and quenched with 400 mL of 5 % HCl/ ice. The product was extracted with diethyl ether. The combined organic layers were washed with H₂O (4 x 100 mL) and 60 mL of 5% NaOH. Then it was dried over MgSO₄, filtered and rotovapped to give 14.5 g (62.6%) of product as a light yellow solid. GC-MS (EI) *m/z* 242 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ 1.33 (s, 12H, CH₃), 1.71 (s, 4H, CH₂-CH₂), 2.68 (t, ³J_{HH} = 5.4 Hz, 2H, COCH₂CH₂), 3.10 (t, ³J_{HH} = 4.5 Hz, 2H, COCH₂CH₂), 7.44, 7.76 (s, 2H, aromatic-*H*).

5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indane-2-ol. (Synthesis modified from reference 64) A 500 mL round bottom flask was charged with 13.0 g (53.7 mmol) of 5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indane-2-one. The flask was then equipped with a 180° needle valve. On the Schlenk line, air was removed by vacuum and replaced with nitrogen and 100 mL of diethyl ether were syringed in. In another 250 mL flask, 10.17 g (268.1 mmol) of LiAlH₄ were suspended in 100 mL of diethyl ether. At 0°C, the LiAlH₄ slurry was added to the ketone slowly over 10 minutes. The reaction was allowed to warm to room temperature and stirred for 3.5 days. At 0°C, 100 mL of NH₄Cl solution were added dropwise over 15 minutes followed by 200 mL of 10% aqueous HCl solution and 200 mL of diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with water (3 x 60 mL), dried over MgSO₄, filtered, and rotovapped to give 11.85 g (90.50%) of an oil. GC-MS (EI) *m/z* 244 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ 1.28 (s, 12H, CH₃), 1.65 (s, 4H, CH₂-CH₂), 1.91 (m, 1H), 2.46 (m, 1H), 2.77 (m, 1H), 3.00(m, 1H), 4.68 (s, OH), 5.19 (t, 1H), 7.21, 7.38 (s, 1H, aromatic-H).

5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indene. (Synthesis modified from reference 64) A 500 mL round bottom flask was charged with 11.44 g (46.85 mmol) of 5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indane-2-ol, 8 mL of anhydrous toluene, 11.70 mL (143.4 mmol) of pyridine and 11.16 g (58.56 mmol) of *p*-toluenesulfonyl chloride. The flask was fitted with a condenser, bubbler, and nitrogen inlet. The mixture was heated to 126°C and stirred for 18 hours. Then 200 mL of 5% HCl/ice and 200 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer was

extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with 5% of HCl solution (2 x 100 mL), 100 mL of 5% aqueous NaOH solution and water (3 x 100 mL). Then the organic layer was dried over MgSO₄, filtered, rotovapped, and dried on the vacuum line to give 7.13 g (67.2%) of waxy solid product. GC-MS (EI) *m/z* 226 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ 1.29 (s, 12H, CH₃), 1.69 (s, 4H, CH₂-CH₂), 3.33 (s, 2H, CH₂-CH-CH), 6.45, 6.81 (d, ³J_{HH} = 5.1, 4.8 Hz, 2H, CH₂-CH-CH), 7.35, 7.43 (s, 2H, aromatic-H).

Me₂Si-bis-1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indenyl). 7.130 g (31.52 mmol) of 5,5,8,8-Tetramethyl-5,6,7,8-tetrahydrobenz(f)indene was added to a 500 mL round bottom flask. The flask then was equipped with a 180° needle valve. Air was removed by vacuum and replaced with nitrogen. Then 80 mL of toluene and 30 mL of tetrahydrofuran were syringed in. At 0°C, 12.6 mL of *n*-BuLi (31.52 mmol, 2.5 M in hexanes) were syringed in slowly over 5 minutes. After 27 hours of stirring at room temperature, the flask was cooled to 0°C to syringe in 1.92 mL (15.80) of dichlorodimethylsilane (distilled from CaH₂) and heated to 50°C with stirring for 24 hours. The reaction was quenched with 130 mL of distilled water and then 200 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered, rotovapped and dried on the vacuum line to give 7.83 g of brown oil that was purified by chromatography on silica gel (50 g silica gel/hexane eluent) to give 3.61 g (22.5%) of light yellow oil. GC-MS (MALDI, EI) *m/z* 508 (M⁺). ¹H NMR

(CDCl₃, 300 MHz) δ -0.07 (s, 6H, Si(CH₃)₂), 1.25 (s, 24H, CH₃), 1.68 (s, 8H, CH₂-CH₂), 3.38, 6.28, 6.52 (m, 8H, Cp-H), 7.19 (s, 8H, aromatic-H).

Me₂Si-bis-1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indenyl)ZrCl₂. In a 100 mL round bottom flask, 3.61 g (7.10 mmol) of Me₂Si-bis-1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenz(f)indene) and 60 mL of diethyl ether were combined. The flask was then attached to a swivel frit. At 0°C, 5.68 mL (14.2 mmol) of *n*-BuLi (2.5 M in hexanes) was syringed in slowly over 5 minutes. The reaction was allowed to warm to room temperature and stirred for 24 hours. The solvent was removed by vacuum and then 1.65 g (7.10 mmol) of ZrCl₄ were added and 30 mL of diethyl ether and 40 mL of *n*-heptane were condensed in. After stirring for 72 hours at room temperature, the solution was filtered by flipping the frit to remove the salt and the solvents were removed by vacuum. 50 mL of methylene chloride were condensed in and stirred for 20 hours and then removed by vacuum. Then 60 mL of hexamethyl disiloxane were condensed in. After stirring for 24 hours, the product precipitated as yellow solid. The frit then was flipped to filter the product and extracted with the same solvent and then dried to give 1.9 g (40%) of yellow powder. ¹H NMR (CDCl₃, 300 MHz) δ -0.06 (s, 6H, Si(CH₃)₂), 1.26 (s, 24H, CH₃), 1.65 (s, 8H, CH₂-CH₂), 5.89, 6.21 (d, 4H, ³J_{HH} = 4.0, 4.0 Hz, Cp-H), 7.19 (s, 4H, aromatic-H).

Propylene polymerization procedure

All polymerization reactions were performed under a nitrogen atmosphere. The polymerizations were performed using a 600 mL Parr polymerization reactor. Methylaluminoxane (MAO) was purchased from Albemarle Corporation as a solution in

toluene and used as a dry powder after removing all volatiles under high vacuum. Propylene gas was purchased from Matheson (polymerization grade, >99.5%) and purified with a Matheson 6110 drying system equipped with an OXYSORB™ column. Polymerizations were initiated by adding methylaluminoxane (MAO) (dissolved in toluene) in the reactor vessel and then condensing the desired amount of propylene gas into the reactor at 0°C. After setting the reaction temperature and obtaining constant temperature readings, metallocene that is dissolved in toluene is injected into the reactor using Hamilton type syringes. During the polymerization reaction, the stirring speed is set at in the range of 40 to 50 RPM. When the reaction is done, a small volume of diluted methanol/aqueous HCl solution (10:1) is added to quench the catalyst and the polymerization stops. The collected polymer is then isolated by filtration, washed with methanol and dried under high vacuum.

Polymer characterization

The polymer pentad distribution was determined by ¹³C NMR spectrum by comparing the integration of the nine resolved peaks in the methyl region (19-22) of the spectra.^{56,57} The test was done at 130°C with tetrachloroethane-*d*₂ and 1,2,4-trichlorobenzene (1:1) as solvents and applying a 90 degree pulse with broadband decoupling and a delay time of 3 seconds; at least 1000 scans were used. Polymer melting temperature was determined by differential scanning calorimetry (Perkin-Elmer DCS 7 (25-200 °C)) using the second scan from 25-200 °C at 10 °C / minute. Molecular weights were determined by gel permeation chromatography (Waters Alliance GPC

2000 Gel Permeation Chromatograph with Refractive Index Detector and/or Polymer Labs HT GPC with Refractive Index detector).

CHAPTER V

CONCLUSIONS

Many different polypropylene tacticities can be obtained from C_1 -symmetric *ansa* cyclopentadienyl-fluorenyl metallocenes of group IV. On the other hand, C_2 -symmetric *ansa*-metallocenes generally produce isotactic polypropylene. The *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes have been significantly improved recently and modified for the production of isotactic polypropylene. It is expected that these systems may overtake *ansa*- C_2 -symmetric metallocenes for this application. The reasons are: they are easy to synthesize and the *meso* isomer is not produced as in the synthesis of most C_2 -symmetric metallocenes. Therefore, several *ansa* C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes have been made and tested for isotactic polypropylene production. Several showed good stereoselectivities, high activity, and made polymer with high molecular weight.

Making a C_2 -symmetric metallocene without *meso* stereoisomeric contaminants is a significant step. It may reduce the cost and increase the yield of these isotactic polypropylene precursors. In this project, a new *ansa* C_2 -symmetric substituted bis-indenyl metallocene has been made successfully in a good yield without any detection of the *meso* analogue of that metallocene.

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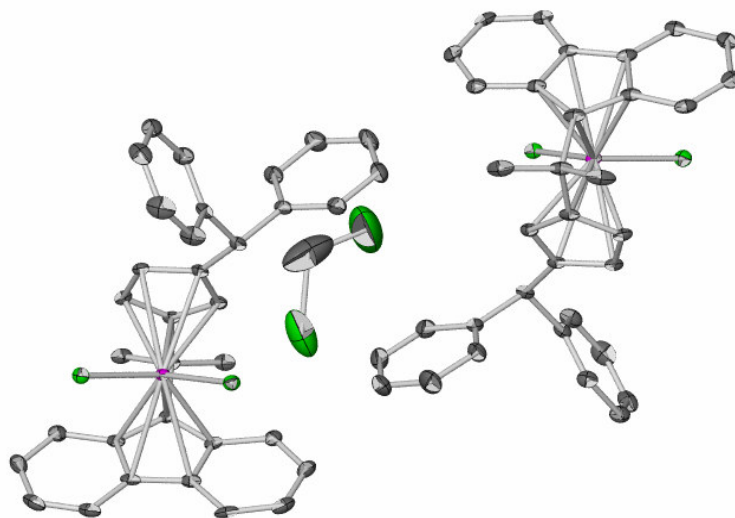
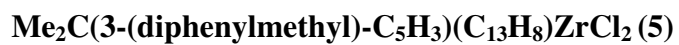
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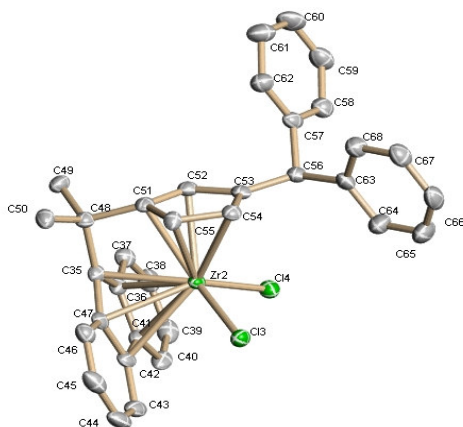
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APPENDIX A

X-RAY CRYSTAL STRUCTURE OF METALLOCENE



Labeled view with 50% probability ellipsoids



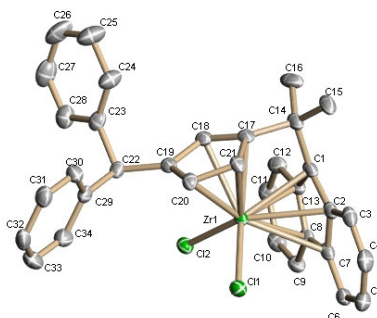


Table A.1. Crystal data and structure refinement for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-5H}_3\text{)(C}_{13}\text{H}_8\text{)ZrCl}_2$.

Identification code	$\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-5H}_3\text{)(C}_{13}\text{H}_8\text{)ZrCl}_2$, sm44a	
Empirical formula	$\text{C}_{34.50} \text{H}_{29} \text{Cl}_3 \text{Zr}$	
Formula weight	641.15	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 30.708(5) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 9.1280(15) \text{ \AA}$	$\beta = 97.470(3)^\circ$.
	$c = 20.298(3) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$5641.3(16) \text{ \AA}^3$	
Z	8	
Density (calculated)	1.510 Mg/m^3	
Absorption coefficient	0.698 mm^{-1}	
F(000)	2616	
Crystal size	$0.40 \times 0.40 \times 0.10 \text{ mm}^3$	
Theta range for data collection	1.34 to 28.04° .	
Index ranges	$-38 \leq h \leq 39$, $-12 \leq k \leq 11$, $-26 \leq l \leq 26$	
Reflections collected	62245	
Independent reflections	13185 [R(int) = 0.0385]	
Completeness to $\theta = 28.04^\circ$	96.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9335 and 0.7678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13185 / 0 / 698	
Goodness-of-fit on F^2	1.083	
Final R indices [I > 2 σ (I)]	R1 = 0.0524, wR2 = 0.1248	
R indices (all data)	R1 = 0.0667, wR2 = 0.1388	
Largest diff. peak and hole	2.057 and $-1.504 \text{ e.\AA}^{-3}$	

Table A.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
 For $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$. $U(\text{eq})$ is defined as one third of the trace of the
 orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Zr(1)	643(1)	2256(1)	3922(1)	13(1)
Zr(2)	4322(1)	2738(1)	6023(1)	13(1)
Cl(1)	185(1)	528(1)	3250(1)	19(1)
Cl(2)	1060(1)	495(1)	4642(1)	18(1)
Cl(3)	4721(1)	4743(1)	6599(1)	18(1)
Cl(4)	3863(1)	4241(1)	5236(1)	19(1)
Cl(5)	3001(1)	7944(2)	4741(1)	101(1)
Cl(6)	2126(1)	7299(5)	5030(2)	172(2)
C(1)	426(1)	4647(4)	4262(2)	19(1)
C(2)	12(1)	4002(4)	3972(2)	19(1)
C(3)	-275(1)	4259(4)	3376(2)	22(1)
C(4)	-646(1)	3436(4)	3238(2)	25(1)
C(5)	-756(1)	2310(4)	3660(2)	25(1)
C(6)	-487(1)	2012(4)	4237(2)	21(1)
C(7)	-101(1)	2844(4)	4395(2)	18(1)
C(8)	232(1)	2772(4)	4958(2)	18(1)
C(9)	271(1)	1836(4)	5514(2)	20(1)
C(10)	622(1)	1996(4)	5999(2)	23(1)
C(11)	936(1)	3099(4)	5938(2)	24(1)
C(12)	908(1)	4020(4)	5410(2)	22(1)
C(13)	549(1)	3901(4)	4886(2)	18(1)
C(14)	721(1)	5651(4)	3895(2)	22(1)
C(15)	471(1)	6711(4)	3396(2)	30(1)
C(16)	1042(1)	6553(4)	4368(2)	31(1)
C(17)	958(1)	4483(4)	3540(2)	18(1)
C(18)	1320(1)	3643(4)	3834(2)	17(1)
C(19)	1378(1)	2421(4)	3421(2)	17(1)
C(20)	1037(1)	2451(4)	2893(2)	17(1)
C(21)	774(1)	3708(3)	2963(2)	17(1)
C(22)	1769(1)	1393(4)	3539(2)	18(1)
C(23)	2195(1)	2273(4)	3665(2)	21(1)
C(24)	2251(1)	3575(5)	3343(2)	29(1)
C(25)	2643(1)	4345(6)	3469(2)	43(1)
C(26)	2986(1)	3799(6)	3913(2)	43(1)
C(27)	2932(1)	2512(5)	4234(2)	38(1)
C(28)	2540(1)	1748(5)	4110(2)	29(1)
C(29)	1789(1)	295(4)	2984(2)	20(1)
C(30)	1859(1)	722(4)	2348(2)	23(1)
C(31)	1889(1)	-315(4)	1856(2)	27(1)
C(32)	1850(1)	-1781(4)	1990(2)	30(1)
C(33)	1781(1)	-2216(4)	2613(2)	35(1)
C(34)	1752(1)	-1190(4)	3108(2)	27(1)
C(35)	4626(1)	376(3)	5824(2)	16(1)

C(36)	4452(1)	870(4)	5163(2)	17(1)
C(37)	4083(1)	450(4)	4699(2)	21(1)
C(38)	3997(1)	1180(4)	4107(2)	25(1)
C(39)	4259(1)	2356(4)	3943(2)	27(1)
C(40)	4615(1)	2792(4)	4366(2)	24(1)
C(41)	4713(1)	2075(4)	4980(2)	19(1)
C(42)	5063(1)	2305(4)	5513(2)	20(1)
C(43)	5415(1)	3301(4)	5566(2)	25(1)
C(44)	5715(1)	3264(4)	6121(2)	31(1)
C(45)	5673(1)	2262(4)	6635(2)	29(1)
C(46)	5333(1)	1284(4)	6600(2)	22(1)
C(47)	5018(1)	1251(4)	6023(2)	18(1)
C(48)	4388(1)	-622(4)	6273(2)	17(1)
C(49)	4121(1)	-1838(4)	5893(2)	22(1)
C(50)	4695(1)	-1355(4)	6828(2)	22(1)
C(51)	4098(1)	524(4)	6551(2)	17(1)
C(52)	3705(1)	1122(4)	6206(2)	17(1)
C(53)	3595(1)	2423(4)	6530(2)	17(1)
C(54)	3931(1)	2680(4)	7053(2)	16(1)
C(55)	4241(1)	1525(4)	7067(2)	17(1)
C(56)	3180(1)	3308(4)	6343(2)	18(1)
C(57)	2772(1)	2349(4)	6290(2)	20(1)
C(58)	2422(1)	2666(4)	5804(2)	24(1)
C(59)	2039(1)	1851(4)	5749(2)	30(1)
C(60)	1998(1)	705(5)	6180(2)	35(1)
C(61)	2345(1)	372(5)	6664(2)	33(1)
C(62)	2730(1)	1192(4)	6715(2)	25(1)
C(63)	3153(1)	4601(4)	6807(2)	20(1)
C(64)	3279(1)	5973(4)	6613(2)	31(1)
C(65)	3269(2)	7175(4)	7030(2)	39(1)
C(66)	3134(1)	7016(4)	7645(2)	33(1)
C(67)	3006(1)	5660(4)	7846(2)	29(1)
C(68)	3015(1)	4458(4)	7431(2)	26(1)
C(69)	2557(3)	8059(11)	5303(4)	122(4)

Table A.3. Bond lengths [\AA] and angles [$^\circ$] for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$.

Zr(1)-C(1)	2.411(3)
Zr(1)-Cl(1)	2.4134(9)
Zr(1)-C(17)	2.422(3)
Zr(1)-Cl(2)	2.4224(8)
Zr(1)-C(21)	2.432(3)
Zr(1)-C(18)	2.461(3)
Zr(1)-C(13)	2.514(3)
Zr(1)-C(2)	2.522(3)
Zr(1)-C(20)	2.552(3)
Zr(1)-C(19)	2.597(3)
Zr(1)-C(8)	2.633(3)
Zr(1)-C(7)	2.648(3)
Zr(2)-C(35)	2.405(3)
Zr(2)-Cl(4)	2.4164(9)
Zr(2)-Cl(3)	2.4165(9)

Zr(2)-C(51)	2.429(3)
Zr(2)-C(55)	2.431(3)
Zr(2)-C(52)	2.467(3)
Zr(2)-C(36)	2.509(3)
Zr(2)-C(47)	2.530(3)
Zr(2)-C(54)	2.543(3)
Zr(2)-C(53)	2.594(3)
Zr(2)-C(41)	2.637(3)
Zr(2)-C(42)	2.651(3)
Cl(5)-C(69)	1.890(8)
Cl(6)-C(69)	1.533(11)
C(1)-C(13)	1.445(5)
C(1)-C(2)	1.454(5)
C(1)-C(14)	1.546(5)
C(2)-C(3)	1.422(5)
C(2)-C(7)	1.433(4)
C(3)-C(4)	1.362(5)
C(4)-C(5)	1.409(5)
C(5)-C(6)	1.370(5)
C(6)-C(7)	1.407(5)
C(7)-C(8)	1.432(5)
C(8)-C(9)	1.407(5)
C(8)-C(13)	1.438(5)
C(9)-C(10)	1.371(5)
C(10)-C(11)	1.409(5)
C(11)-C(12)	1.356(5)
C(12)-C(13)	1.433(5)
C(14)-C(16)	1.526(5)
C(14)-C(17)	1.526(4)
C(14)-C(15)	1.533(5)
C(17)-C(18)	1.416(5)
C(17)-C(21)	1.421(5)
C(18)-C(19)	1.419(4)
C(19)-C(20)	1.398(5)
C(19)-C(22)	1.518(4)
C(20)-C(21)	1.421(4)
C(22)-C(29)	1.515(5)
C(22)-C(23)	1.526(5)
C(23)-C(24)	1.378(5)
C(23)-C(28)	1.387(5)
C(24)-C(25)	1.390(5)
C(25)-C(26)	1.386(7)
C(26)-C(27)	1.363(7)
C(27)-C(28)	1.385(6)
C(29)-C(34)	1.386(5)
C(29)-C(30)	1.391(5)
C(30)-C(31)	1.387(5)
C(31)-C(32)	1.374(6)
C(32)-C(33)	1.369(6)
C(33)-C(34)	1.384(6)
C(35)-C(36)	1.449(4)
C(35)-C(47)	1.456(4)
C(35)-C(48)	1.540(4)

C(36)-C(37)	1.429(5)
C(36)-C(41)	1.438(5)
C(37)-C(38)	1.369(5)
C(38)-C(39)	1.406(5)
C(39)-C(40)	1.360(6)
C(40)-C(41)	1.406(5)
C(41)-C(42)	1.437(5)
C(42)-C(43)	1.404(5)
C(42)-C(47)	1.433(5)
C(43)-C(44)	1.360(6)
C(44)-C(45)	1.407(6)
C(45)-C(46)	1.368(5)
C(46)-C(47)	1.421(5)
C(48)-C(50)	1.526(5)
C(48)-C(49)	1.528(5)
C(48)-C(51)	1.529(4)
C(51)-C(55)	1.416(4)
C(51)-C(52)	1.421(5)
C(52)-C(53)	1.420(5)
C(53)-C(54)	1.401(5)
C(53)-C(56)	1.515(4)
C(54)-C(55)	1.419(4)
C(56)-C(63)	1.518(5)
C(56)-C(57)	1.521(4)
C(57)-C(62)	1.380(5)
C(57)-C(58)	1.390(5)
C(58)-C(59)	1.386(5)
C(59)-C(60)	1.380(6)
C(60)-C(61)	1.384(6)
C(61)-C(62)	1.393(5)
C(63)-C(64)	1.383(5)
C(63)-C(68)	1.393(5)
C(64)-C(65)	1.388(6)
C(65)-C(66)	1.374(6)
C(66)-C(67)	1.377(6)
C(67)-C(68)	1.386(5)
C(1)-Zr(1)-Cl(1)	126.23(9)
C(1)-Zr(1)-C(17)	57.91(11)
Cl(1)-Zr(1)-C(17)	126.50(8)
C(1)-Zr(1)-Cl(2)	124.90(9)
Cl(1)-Zr(1)-Cl(2)	97.51(3)
C(17)-Zr(1)-Cl(2)	123.26(8)
C(1)-Zr(1)-C(21)	79.43(11)
Cl(1)-Zr(1)-C(21)	92.77(8)
C(17)-Zr(1)-C(21)	34.05(11)
Cl(2)-Zr(1)-C(21)	135.69(8)
C(1)-Zr(1)-C(18)	79.79(11)
Cl(1)-Zr(1)-C(18)	136.94(8)
C(17)-Zr(1)-C(18)	33.70(11)
Cl(2)-Zr(1)-C(18)	90.05(8)
C(21)-Zr(1)-C(18)	55.38(11)
C(1)-Zr(1)-C(13)	34.03(11)
Cl(1)-Zr(1)-C(13)	135.46(8)

C(17)-Zr(1)-C(13)	80.75(11)
Cl(2)-Zr(1)-C(13)	91.82(8)
C(21)-Zr(1)-C(13)	110.21(11)
C(18)-Zr(1)-C(13)	86.17(11)
C(1)-Zr(1)-C(2)	34.20(11)
Cl(1)-Zr(1)-C(2)	92.37(8)
C(17)-Zr(1)-C(2)	79.85(11)
Cl(2)-Zr(1)-C(2)	137.99(8)
C(21)-Zr(1)-C(2)	84.02(11)
C(18)-Zr(1)-C(2)	109.80(11)
C(13)-Zr(1)-C(2)	54.81(11)
C(1)-Zr(1)-C(20)	110.47(11)
Cl(1)-Zr(1)-C(20)	83.49(8)
C(17)-Zr(1)-C(20)	55.08(11)
Cl(2)-Zr(1)-C(20)	105.70(7)
C(21)-Zr(1)-C(20)	33.02(10)
C(18)-Zr(1)-C(20)	53.79(11)
C(13)-Zr(1)-C(20)	135.25(11)
C(2)-Zr(1)-C(20)	115.97(10)
C(1)-Zr(1)-C(19)	110.27(11)
Cl(1)-Zr(1)-C(19)	106.80(8)
C(17)-Zr(1)-C(19)	54.69(10)
Cl(2)-Zr(1)-C(19)	81.79(8)
C(21)-Zr(1)-C(19)	54.02(11)
C(18)-Zr(1)-C(19)	32.45(10)
C(13)-Zr(1)-C(19)	117.63(11)
C(2)-Zr(1)-C(19)	133.68(10)
C(20)-Zr(1)-C(19)	31.48(10)
C(1)-Zr(1)-C(8)	55.20(10)
Cl(1)-Zr(1)-C(8)	105.28(8)
C(17)-Zr(1)-C(8)	111.03(11)
Cl(2)-Zr(1)-C(8)	84.69(8)
C(21)-Zr(1)-C(8)	133.50(10)
C(18)-Zr(1)-C(8)	117.63(11)
C(13)-Zr(1)-C(8)	32.35(10)
C(2)-Zr(1)-C(8)	53.36(10)
C(20)-Zr(1)-C(8)	165.66(10)
C(19)-Zr(1)-C(8)	146.48(11)
C(1)-Zr(1)-C(7)	55.09(11)
Cl(1)-Zr(1)-C(7)	82.56(8)
C(17)-Zr(1)-C(7)	110.23(11)
Cl(2)-Zr(1)-C(7)	109.18(7)
C(21)-Zr(1)-C(7)	114.86(10)
C(18)-Zr(1)-C(7)	134.39(10)
C(13)-Zr(1)-C(7)	53.40(11)
C(2)-Zr(1)-C(7)	32.06(10)
C(20)-Zr(1)-C(7)	143.76(10)
C(19)-Zr(1)-C(7)	164.90(10)
C(8)-Zr(1)-C(7)	31.47(10)
C(35)-Zr(2)-Cl(4)	127.10(8)
C(35)-Zr(2)-Cl(3)	125.21(8)
Cl(4)-Zr(2)-Cl(3)	96.05(3)
C(35)-Zr(2)-C(51)	57.79(11)

Cl(4)-Zr(2)-C(51)	126.13(8)
Cl(3)-Zr(2)-C(51)	124.91(8)
C(35)-Zr(2)-C(55)	79.90(11)
Cl(4)-Zr(2)-C(55)	135.89(8)
Cl(3)-Zr(2)-C(55)	91.54(8)
C(51)-Zr(2)-C(55)	33.89(11)
C(35)-Zr(2)-C(52)	79.14(11)
Cl(4)-Zr(2)-C(52)	92.63(8)
Cl(3)-Zr(2)-C(52)	137.00(8)
C(51)-Zr(2)-C(52)	33.74(11)
C(55)-Zr(2)-C(52)	55.18(11)
C(35)-Zr(2)-C(36)	34.22(10)
Cl(4)-Zr(2)-C(36)	93.27(8)
Cl(3)-Zr(2)-C(36)	137.24(8)
C(51)-Zr(2)-C(36)	79.69(11)
C(55)-Zr(2)-C(36)	109.89(11)
C(52)-Zr(2)-C(36)	83.84(11)
C(35)-Zr(2)-C(47)	34.18(10)
Cl(4)-Zr(2)-C(47)	136.36(8)
Cl(3)-Zr(2)-C(47)	91.81(8)
C(51)-Zr(2)-C(47)	80.90(11)
C(55)-Zr(2)-C(47)	86.47(11)
C(52)-Zr(2)-C(47)	110.11(11)
C(36)-Zr(2)-C(47)	54.86(11)
C(35)-Zr(2)-C(54)	110.80(11)
Cl(4)-Zr(2)-C(54)	104.97(8)
Cl(3)-Zr(2)-C(54)	83.28(8)
C(51)-Zr(2)-C(54)	55.16(10)
C(55)-Zr(2)-C(54)	33.04(10)
C(52)-Zr(2)-C(54)	53.83(10)
C(36)-Zr(2)-C(54)	133.82(11)
C(47)-Zr(2)-C(54)	118.58(11)
C(35)-Zr(2)-C(53)	109.91(11)
Cl(4)-Zr(2)-C(53)	82.36(8)
Cl(3)-Zr(2)-C(53)	107.54(8)
C(51)-Zr(2)-C(53)	54.86(10)
C(55)-Zr(2)-C(53)	54.06(11)
C(52)-Zr(2)-C(53)	32.46(10)
C(36)-Zr(2)-C(53)	115.04(11)
C(47)-Zr(2)-C(53)	135.32(11)
C(54)-Zr(2)-C(53)	31.63(10)
C(35)-Zr(2)-C(41)	55.35(10)
Cl(4)-Zr(2)-C(41)	83.47(8)
Cl(3)-Zr(2)-C(41)	107.85(8)
C(51)-Zr(2)-C(41)	110.36(11)
C(55)-Zr(2)-C(41)	134.74(11)
C(52)-Zr(2)-C(41)	114.97(11)
C(36)-Zr(2)-C(41)	32.34(10)
C(47)-Zr(2)-C(41)	53.40(11)
C(54)-Zr(2)-C(41)	165.52(10)
C(53)-Zr(2)-C(41)	142.98(11)
C(35)-Zr(2)-C(42)	55.12(10)
Cl(4)-Zr(2)-C(42)	106.41(8)

Cl(3)-Zr(2)-C(42)	83.96(8)
C(51)-Zr(2)-C(42)	110.83(11)
C(55)-Zr(2)-C(42)	117.60(11)
C(52)-Zr(2)-C(42)	133.21(11)
C(36)-Zr(2)-C(42)	53.42(11)
C(47)-Zr(2)-C(42)	32.01(10)
C(54)-Zr(2)-C(42)	147.13(11)
C(53)-Zr(2)-C(42)	165.03(11)
C(41)-Zr(2)-C(42)	31.54(11)
C(13)-C(1)-C(2)	106.2(3)
C(13)-C(1)-C(14)	126.8(3)
C(2)-C(1)-C(14)	125.5(3)
C(13)-C(1)-Zr(1)	76.92(18)
C(2)-C(1)-Zr(1)	77.11(18)
C(14)-C(1)-Zr(1)	101.38(19)
C(3)-C(2)-C(7)	117.4(3)
C(3)-C(2)-C(1)	133.7(3)
C(7)-C(2)-C(1)	108.9(3)
C(3)-C(2)-Zr(1)	117.7(2)
C(7)-C(2)-Zr(1)	78.80(19)
C(1)-C(2)-Zr(1)	68.69(18)
C(4)-C(3)-C(2)	119.5(3)
C(3)-C(4)-C(5)	122.6(3)
C(6)-C(5)-C(4)	119.9(3)
C(5)-C(6)-C(7)	119.1(3)
C(6)-C(7)-C(8)	130.5(3)
C(6)-C(7)-C(2)	121.5(3)
C(8)-C(7)-C(2)	107.9(3)
C(6)-C(7)-Zr(1)	123.2(2)
C(8)-C(7)-Zr(1)	73.71(18)
C(2)-C(7)-Zr(1)	69.14(18)
C(9)-C(8)-C(7)	130.1(3)
C(9)-C(8)-C(13)	121.9(3)
C(7)-C(8)-C(13)	108.0(3)
C(9)-C(8)-Zr(1)	122.1(2)
C(7)-C(8)-Zr(1)	74.82(18)
C(13)-C(8)-Zr(1)	69.27(17)
C(10)-C(9)-C(8)	119.2(3)
C(9)-C(10)-C(11)	119.8(3)
C(12)-C(11)-C(10)	122.5(3)
C(11)-C(12)-C(13)	120.2(3)
C(12)-C(13)-C(8)	116.4(3)
C(12)-C(13)-C(1)	134.7(3)
C(8)-C(13)-C(1)	108.9(3)
C(12)-C(13)-Zr(1)	117.9(2)
C(8)-C(13)-Zr(1)	78.38(18)
C(1)-C(13)-Zr(1)	69.05(17)
C(16)-C(14)-C(17)	111.4(3)
C(16)-C(14)-C(15)	107.6(3)
C(17)-C(14)-C(15)	110.9(3)
C(16)-C(14)-C(1)	112.9(3)
C(17)-C(14)-C(1)	99.2(3)
C(15)-C(14)-C(1)	114.7(3)

C(18)-C(17)-C(21)	106.5(3)
C(18)-C(17)-C(14)	125.2(3)
C(21)-C(17)-C(14)	125.0(3)
C(18)-C(17)-Zr(1)	74.66(18)
C(21)-C(17)-Zr(1)	73.34(18)
C(14)-C(17)-Zr(1)	101.50(19)
C(17)-C(18)-C(19)	109.2(3)
C(17)-C(18)-Zr(1)	71.64(18)
C(19)-C(18)-Zr(1)	79.07(19)
C(20)-C(19)-C(18)	107.3(3)
C(20)-C(19)-C(22)	129.1(3)
C(18)-C(19)-C(22)	123.4(3)
C(20)-C(19)-Zr(1)	72.49(18)
C(18)-C(19)-Zr(1)	68.49(17)
C(22)-C(19)-Zr(1)	127.8(2)
C(19)-C(20)-C(21)	108.6(3)
C(19)-C(20)-Zr(1)	76.03(18)
C(21)-C(20)-Zr(1)	68.81(17)
C(20)-C(21)-C(17)	108.2(3)
C(20)-C(21)-Zr(1)	78.16(18)
C(17)-C(21)-Zr(1)	72.61(17)
C(29)-C(22)-C(19)	113.5(3)
C(29)-C(22)-C(23)	110.9(3)
C(19)-C(22)-C(23)	110.1(3)
C(24)-C(23)-C(28)	118.3(3)
C(24)-C(23)-C(22)	122.1(3)
C(28)-C(23)-C(22)	119.5(3)
C(23)-C(24)-C(25)	120.5(4)
C(26)-C(25)-C(24)	120.3(4)
C(27)-C(26)-C(25)	119.5(4)
C(26)-C(27)-C(28)	120.3(4)
C(27)-C(28)-C(23)	121.1(4)
C(34)-C(29)-C(30)	117.9(3)
C(34)-C(29)-C(22)	120.0(3)
C(30)-C(29)-C(22)	122.1(3)
C(31)-C(30)-C(29)	120.7(3)
C(32)-C(31)-C(30)	120.4(4)
C(33)-C(32)-C(31)	119.6(4)
C(32)-C(33)-C(34)	120.4(4)
C(33)-C(34)-C(29)	121.0(4)
C(36)-C(35)-C(47)	106.1(3)
C(36)-C(35)-C(48)	125.8(3)
C(47)-C(35)-C(48)	126.8(3)
C(36)-C(35)-Zr(2)	76.83(18)
C(47)-C(35)-Zr(2)	77.62(18)
C(48)-C(35)-Zr(2)	101.84(19)
C(37)-C(36)-C(41)	117.1(3)
C(37)-C(36)-C(35)	133.8(3)
C(41)-C(36)-C(35)	109.0(3)
C(37)-C(36)-Zr(2)	117.2(2)
C(41)-C(36)-Zr(2)	78.71(19)
C(35)-C(36)-Zr(2)	68.96(17)
C(38)-C(37)-C(36)	119.6(3)

C(37)-C(38)-C(39)	121.9(3)
C(40)-C(39)-C(38)	120.8(3)
C(39)-C(40)-C(41)	119.1(3)
C(40)-C(41)-C(42)	130.7(3)
C(40)-C(41)-C(36)	121.5(3)
C(42)-C(41)-C(36)	107.8(3)
C(40)-C(41)-Zr(2)	122.5(2)
C(42)-C(41)-Zr(2)	74.76(18)
C(36)-C(41)-Zr(2)	68.96(17)
C(43)-C(42)-C(47)	121.7(3)
C(43)-C(42)-C(41)	130.1(3)
C(47)-C(42)-C(41)	108.1(3)
C(43)-C(42)-Zr(2)	124.3(2)
C(47)-C(42)-Zr(2)	69.38(17)
C(41)-C(42)-Zr(2)	73.70(18)
C(44)-C(43)-C(42)	118.6(4)
C(43)-C(44)-C(45)	120.8(3)
C(46)-C(45)-C(44)	122.0(4)
C(45)-C(46)-C(47)	119.4(3)
C(46)-C(47)-C(42)	117.5(3)
C(46)-C(47)-C(35)	133.7(3)
C(42)-C(47)-C(35)	108.8(3)
C(46)-C(47)-Zr(2)	118.3(2)
C(42)-C(47)-Zr(2)	78.62(19)
C(35)-C(47)-Zr(2)	68.20(17)
C(50)-C(48)-C(49)	107.0(3)
C(50)-C(48)-C(51)	111.2(3)
C(49)-C(48)-C(51)	112.5(3)
C(50)-C(48)-C(35)	113.6(3)
C(49)-C(48)-C(35)	113.4(3)
C(51)-C(48)-C(35)	99.2(3)
C(55)-C(51)-C(52)	106.2(3)
C(55)-C(51)-C(48)	125.1(3)
C(52)-C(51)-C(48)	125.3(3)
C(55)-C(51)-Zr(2)	73.14(18)
C(52)-C(51)-Zr(2)	74.59(18)
C(48)-C(51)-Zr(2)	101.19(19)
C(53)-C(52)-C(51)	109.4(3)
C(53)-C(52)-Zr(2)	78.68(19)
C(51)-C(52)-Zr(2)	71.67(18)
C(54)-C(53)-C(52)	107.1(3)
C(54)-C(53)-C(56)	127.8(3)
C(52)-C(53)-C(56)	125.1(3)
C(54)-C(53)-Zr(2)	72.21(18)
C(52)-C(53)-Zr(2)	68.85(17)
C(56)-C(53)-Zr(2)	125.5(2)
C(53)-C(54)-C(55)	108.5(3)
C(53)-C(54)-Zr(2)	76.16(18)
C(55)-C(54)-Zr(2)	69.14(17)
C(51)-C(55)-C(54)	108.8(3)
C(51)-C(55)-Zr(2)	72.97(18)
C(54)-C(55)-Zr(2)	77.83(18)
C(53)-C(56)-C(63)	111.8(3)

C(53)-C(56)-C(57)	111.7(3)
C(63)-C(56)-C(57)	112.3(3)
C(62)-C(57)-C(58)	118.5(3)
C(62)-C(57)-C(56)	122.6(3)
C(58)-C(57)-C(56)	118.9(3)
C(59)-C(58)-C(57)	121.0(4)
C(60)-C(59)-C(58)	120.1(4)
C(59)-C(60)-C(61)	119.5(4)
C(60)-C(61)-C(62)	120.1(4)
C(57)-C(62)-C(61)	120.8(4)
C(64)-C(63)-C(68)	118.2(3)
C(64)-C(63)-C(56)	119.2(3)
C(68)-C(63)-C(56)	122.6(3)
C(63)-C(64)-C(65)	120.9(4)
C(66)-C(65)-C(64)	120.2(4)
C(65)-C(66)-C(67)	119.8(4)
C(66)-C(67)-C(68)	120.1(4)
C(67)-C(68)-C(63)	120.8(4)
Cl(6)-C(69)-Cl(5)	114.5(5)

Table A.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_5)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2 \text{a}^* \text{U}^{11} + \dots + 2 \text{h k a}^* \text{b}^* \text{U}^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	16(1)	10(1)	14(1)	0(1)	6(1)	1(1)
Zr(2)	14(1)	13(1)	13(1)	-1(1)	5(1)	-1(1)
Cl(1)	21(1)	17(1)	21(1)	-3(1)	5(1)	-1(1)
Cl(2)	22(1)	14(1)	18(1)	2(1)	6(1)	2(1)
Cl(3)	20(1)	16(1)	21(1)	-2(1)	4(1)	-2(1)
Cl(4)	20(1)	21(1)	17(1)	3(1)	4(1)	1(1)
Cl(5)	61(1)	91(1)	141(2)	37(1)	-26(1)	-18(1)
Cl(6)	98(2)	291(5)	119(2)	50(2)	-20(2)	-87(2)
C(1)	26(2)	11(2)	24(2)	-2(1)	13(1)	2(1)
C(2)	23(2)	13(2)	22(2)	0(1)	13(1)	4(1)
C(3)	28(2)	18(2)	22(2)	3(1)	13(1)	8(1)
C(4)	26(2)	28(2)	23(2)	2(2)	5(1)	10(2)
C(5)	19(2)	26(2)	30(2)	-2(2)	8(1)	4(1)
C(6)	22(2)	16(2)	27(2)	0(1)	10(1)	2(1)
C(7)	25(2)	14(2)	19(2)	0(1)	11(1)	5(1)
C(8)	23(2)	14(2)	20(2)	-4(1)	13(1)	1(1)
C(9)	26(2)	15(2)	20(2)	-1(1)	11(1)	0(1)
C(10)	34(2)	23(2)	14(2)	-1(1)	11(1)	3(2)
C(11)	26(2)	28(2)	18(2)	-7(1)	6(1)	1(2)
C(12)	27(2)	19(2)	23(2)	-7(1)	11(1)	-5(1)
C(13)	23(2)	14(2)	20(2)	-4(1)	12(1)	0(1)
C(14)	29(2)	13(2)	28(2)	0(1)	18(2)	1(1)
C(15)	38(2)	15(2)	44(2)	10(2)	27(2)	8(2)
C(16)	44(2)	18(2)	37(2)	-7(2)	24(2)	-12(2)
C(17)	22(2)	13(2)	22(2)	3(1)	13(1)	-3(1)

C(18)	19(2)	15(2)	19(2)	0(1)	8(1)	-4(1)
C(19)	19(2)	15(2)	19(2)	2(1)	10(1)	-2(1)
C(20)	19(2)	17(2)	16(2)	3(1)	8(1)	3(1)
C(21)	24(2)	13(2)	15(2)	3(1)	9(1)	3(1)
C(22)	15(2)	18(2)	21(2)	3(1)	7(1)	2(1)
C(23)	18(2)	30(2)	17(2)	-4(1)	6(1)	-1(1)
C(24)	22(2)	37(2)	29(2)	4(2)	3(2)	-8(2)
C(25)	34(2)	50(3)	45(3)	2(2)	6(2)	-20(2)
C(26)	24(2)	66(3)	40(2)	-14(2)	7(2)	-18(2)
C(27)	23(2)	61(3)	30(2)	-11(2)	-1(2)	5(2)
C(28)	26(2)	35(2)	25(2)	-3(2)	5(2)	5(2)
C(29)	14(2)	20(2)	26(2)	2(1)	5(1)	2(1)
C(30)	25(2)	17(2)	28(2)	-1(1)	9(1)	1(1)
C(31)	23(2)	30(2)	28(2)	-6(2)	9(2)	3(2)
C(32)	19(2)	26(2)	44(2)	-13(2)	4(2)	5(2)
C(33)	34(2)	16(2)	55(3)	-1(2)	7(2)	0(2)
C(34)	25(2)	22(2)	36(2)	6(2)	9(2)	0(2)
C(35)	19(2)	14(2)	16(2)	-3(1)	6(1)	1(1)
C(36)	21(2)	16(2)	15(2)	-2(1)	8(1)	2(1)
C(37)	22(2)	21(2)	19(2)	-5(1)	6(1)	0(1)
C(38)	29(2)	30(2)	17(2)	-4(1)	5(1)	4(2)
C(39)	37(2)	29(2)	17(2)	2(1)	10(2)	9(2)
C(40)	35(2)	20(2)	21(2)	2(1)	19(2)	3(2)
C(41)	22(2)	15(2)	23(2)	-3(1)	12(1)	1(1)
C(42)	20(2)	18(2)	24(2)	-3(1)	14(1)	1(1)
C(43)	25(2)	21(2)	33(2)	-6(2)	18(2)	-5(1)
C(44)	19(2)	30(2)	45(2)	-15(2)	16(2)	-8(2)
C(45)	17(2)	37(2)	33(2)	-14(2)	3(2)	1(2)
C(46)	20(2)	24(2)	24(2)	-4(1)	6(1)	3(1)
C(47)	17(2)	17(2)	21(2)	-5(1)	10(1)	2(1)
C(48)	20(2)	17(2)	17(2)	1(1)	7(1)	-2(1)
C(49)	27(2)	14(2)	28(2)	-2(1)	11(2)	-3(1)
C(50)	26(2)	20(2)	21(2)	3(1)	9(1)	5(1)
C(51)	20(2)	15(2)	16(2)	2(1)	9(1)	-2(1)
C(52)	17(2)	17(2)	19(2)	0(1)	7(1)	-4(1)
C(53)	15(2)	17(2)	21(2)	1(1)	8(1)	-3(1)
C(54)	19(2)	17(2)	14(1)	0(1)	7(1)	-1(1)
C(55)	22(2)	16(2)	14(1)	0(1)	5(1)	3(1)
C(56)	16(2)	17(2)	21(2)	0(1)	6(1)	-2(1)
C(57)	18(2)	20(2)	23(2)	-6(1)	9(1)	-3(1)
C(58)	22(2)	24(2)	27(2)	-3(2)	6(1)	-1(1)
C(59)	19(2)	35(2)	35(2)	-11(2)	2(2)	-2(2)
C(60)	22(2)	38(2)	46(2)	-10(2)	6(2)	-13(2)
C(61)	31(2)	32(2)	38(2)	1(2)	10(2)	-11(2)
C(62)	23(2)	23(2)	29(2)	-1(2)	5(2)	-4(1)
C(63)	12(2)	21(2)	27(2)	0(1)	5(1)	1(1)
C(64)	34(2)	20(2)	41(2)	3(2)	15(2)	-1(2)
C(65)	45(3)	17(2)	57(3)	-1(2)	20(2)	-2(2)
C(66)	26(2)	24(2)	49(2)	-13(2)	10(2)	3(2)
C(67)	25(2)	32(2)	31(2)	-10(2)	8(2)	2(2)
C(68)	26(2)	24(2)	29(2)	-3(2)	9(2)	0(2)
C(69)	186(10)	121(7)	66(5)	20(5)	45(6)	60(7)

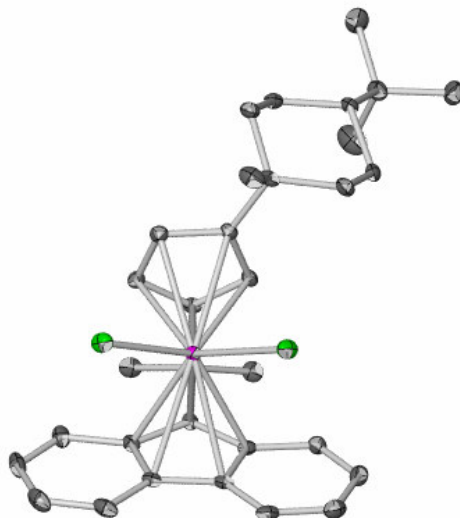
Table A.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$.

	x	y	z	U(eq)
H(3)	-209	5000	3075	26
H(4)	-837	3629	2841	30
H(5)	-1017	1757	3546	30
H(6)	-558	1255	4525	25
H(9)	56	1103	5552	24
H(10)	654	1366	6374	28
H(11)	1176	3200	6281	29
H(12)	1127	4746	5387	27
H(15A)	677	7420	3246	46
H(15B)	247	7232	3609	46
H(15C)	328	6159	3013	46
H(16A)	1258	5900	4615	47
H(16B)	881	7083	4680	47
H(16C)	1193	7257	4113	47
H(18)	1535	3966	4219	21
H(20)	1002	1760	2508	20
H(21)	541	4092	2616	20
H(22)	1741	826	3953	21
H(24)	2020	3949	3032	35
H(25)	2677	5251	3250	52
H(26)	3256	4317	3993	52
H(27)	3164	2139	4543	46
H(28)	2508	849	4335	34
H(30)	1887	1732	2250	27
H(31)	1936	-9	1424	32
H(32)	1870	-2488	1652	36
H(33)	1753	-3228	2707	42
H(34)	1705	-1509	3539	33
H(37)	3898	-330	4801	25
H(38)	3754	884	3799	30
H(39)	4185	2850	3532	33
H(40)	4795	3571	4248	29
H(43)	5442	3986	5221	30
H(44)	5957	3923	6161	37
H(45)	5887	2265	7018	35
H(46)	5309	632	6958	27
H(49A)	4033	-2560	6209	34
H(49B)	4300	-2318	5590	34
H(49C)	3858	-1417	5637	34
H(50A)	4529	-2072	7056	32
H(50B)	4819	-611	7146	32
H(50C)	4932	-1853	6638	32
H(52)	3509	609	5847	21
H(54)	3934	3481	7390	20
H(55)	4485	1343	7435	21
H(56)	3196	3720	5890	21
H(58)	2447	3453	5505	29

H(59)	1803	2082	5414	36
H(60)	1735	149	6145	42
H(61)	2319	-417	6962	40
H(62)	2967	951	7045	30
H(64)	3374	6095	6189	37
H(65)	3356	8111	6889	46
H(66)	3129	7839	7931	39
H(67)	2911	5548	8271	35
H(68)	2927	3525	7574	31
H(69A)	2669	7615	5737	146
H(69B)	2495	9104	5381	146

APPENDIX B

X-RAY CRYSTAL STRUCTURE OF METALLOCENE

 $\text{Me}_2\text{C}(\text{3-(4-}t\text{-butylcyclohexyl-1-methyl)-C}_5\text{H}_3\text{)}(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ (6)

Labeled view with 50% probability ellipsoids

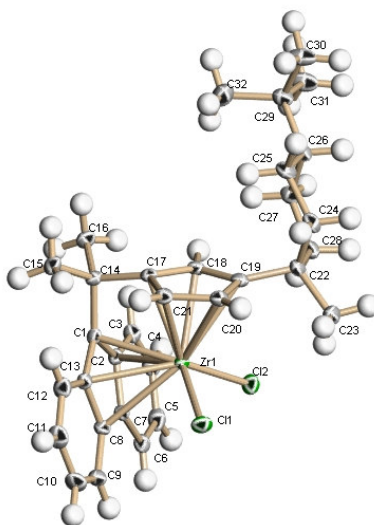


Table B.1. Crystal data and structure refinement for Me₂C(3-(4-*t*-butylcyclohexyl-1-methyl)-C₅H₃)(C₁₃H₈)ZrCl₂.

Identification code	Me ₂ C(3-(4- <i>t</i> -butylcyclohexyl-1-methyl)-C ₅ H ₃)(C ₁₃ H ₈)ZrCl ₂ . sm50.	
Empirical formula	C ₃₂ H ₃₈ Cl ₂ Zr	
Formula weight	584.74	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.146(2) Å	α = 103.623(3)°.
	b = 9.965(2) Å	β = 91.975(3)°.
	c = 17.876(4) Å	γ = 116.457(3)°.
Volume	1399.1(5) Å ³	
Z	2	
Density (calculated)	1.388 Mg/m ³	
Absorption coefficient	0.603 mm ⁻¹	
F(000)	608	
Crystal size	0.40 x 0.30 x 0.20 mm ³	
Theta range for data collection	1.19 to 28.43°.	
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23	
Reflections collected	19592	
Independent reflections	6632 [R(int) = 0.0440]	
Completeness to theta = 28.43°	94.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8889 and 0.7945	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6632 / 0 / 323	
Goodness-of-fit on F ²	1.083	
Final R indices [I > 2σ(I)]	R1 = 0.0411, wR2 = 0.0935	
R indices (all data)	R1 = 0.0577, wR2 = 0.1053	
Extinction coefficient	0.0087(10)	
Largest diff. peak and hole	0.829 and -0.539 e.Å ⁻³	

Table B.2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for Me₂C(3-(4-*t*-butylcyclohexyl-1-methyl)-C₅H₃)(C₁₃H₈)ZrCl₂ (SM50). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	2044(1)	4882(1)	3222(1)	11(1)
Cl(1)	-876(1)	3020(1)	3011(1)	20(1)
Cl(2)	1891(1)	7308(1)	3693(1)	20(1)
C(1)	4274(3)	4438(3)	3682(2)	13(1)
C(2)	4518(3)	5855(3)	4257(2)	14(1)
C(3)	5733(3)	7461(3)	4434(2)	18(1)
C(4)	5608(4)	8545(3)	5027(2)	22(1)
C(5)	4291(4)	8136(3)	5466(2)	23(1)
C(6)	3097(4)	6616(3)	5314(2)	19(1)
C(7)	3188(3)	5468(3)	4711(2)	14(1)

C(8)	2138(3)	3803(3)	4445(2)	15(1)
C(9)	720(3)	2842(4)	4722(2)	22(1)
C(10)	-36(4)	1270(4)	4384(2)	26(1)
C(11)	598(4)	608(3)	3774(2)	26(1)
C(12)	1961(3)	1506(3)	3489(2)	21(1)
C(13)	2814(3)	3165(3)	3826(2)	14(1)
C(14)	5126(3)	4345(3)	2949(2)	14(1)
C(15)	5127(4)	2773(3)	2622(2)	20(1)
C(16)	6927(3)	5620(3)	3075(2)	19(1)
C(17)	3980(3)	4549(3)	2393(2)	14(1)
C(18)	4057(3)	6004(3)	2369(2)	14(1)
C(19)	2569(3)	5716(3)	1923(2)	14(1)
C(20)	1522(3)	4094(3)	1728(2)	16(1)
C(21)	2367(3)	3372(3)	2017(2)	15(1)
C(22)	2188(3)	6816(3)	1580(2)	17(1)
C(23)	463(3)	6639(4)	1713(2)	25(1)
C(24)	2173(3)	6321(3)	689(2)	20(1)
C(25)	3881(3)	6650(3)	467(2)	19(1)
C(26)	5105(3)	8405(3)	759(2)	16(1)
C(27)	5210(3)	8986(3)	1647(2)	17(1)
C(28)	3496(3)	8543(3)	1903(2)	18(1)
C(29)	6829(4)	8849(3)	494(2)	21(1)
C(30)	6609(4)	8360(4)	-397(2)	31(1)
C(31)	7927(4)	10627(3)	778(2)	28(1)
C(32)	7732(4)	8060(4)	808(2)	37(1)

Table B.3. Bond lengths [Å] and angles [°] for Me₂C(3-(4-*t*-butylcyclohexyl-1-methyl)-C₃H₃)(C₁₃H₈)ZrCl₂.

Zr(1)-C(1)	2.428(2)
Zr(1)-Cl(1)	2.4296(8)
Zr(1)-C(21)	2.430(3)
Zr(1)-C(17)	2.431(2)
Zr(1)-Cl(2)	2.4336(8)
Zr(1)-C(18)	2.475(3)
Zr(1)-C(2)	2.529(3)
Zr(1)-C(13)	2.547(3)
Zr(1)-C(20)	2.563(3)
Zr(1)-C(19)	2.634(3)
Zr(1)-C(7)	2.656(3)
Zr(1)-C(8)	2.669(3)
C(1)-C(2)	1.457(4)
C(1)-C(13)	1.458(4)
C(1)-C(14)	1.552(4)
C(2)-C(3)	1.431(4)
C(2)-C(7)	1.443(4)
C(3)-C(4)	1.372(4)
C(4)-C(5)	1.418(4)
C(5)-C(6)	1.368(4)
C(6)-C(7)	1.411(4)
C(7)-C(8)	1.441(4)
C(8)-C(9)	1.415(4)

C(8)-C(13)	1.443(4)
C(9)-C(10)	1.363(4)
C(10)-C(11)	1.417(5)
C(11)-C(12)	1.370(4)
C(12)-C(13)	1.432(4)
C(14)-C(17)	1.530(3)
C(14)-C(16)	1.534(4)
C(14)-C(15)	1.538(4)
C(17)-C(21)	1.422(4)
C(17)-C(18)	1.431(4)
C(18)-C(19)	1.428(4)
C(19)-C(20)	1.408(4)
C(19)-C(22)	1.529(3)
C(20)-C(21)	1.424(4)
C(22)-C(23)	1.541(4)
C(22)-C(28)	1.541(4)
C(22)-C(24)	1.550(4)
C(24)-C(25)	1.534(4)
C(25)-C(26)	1.539(4)
C(26)-C(27)	1.540(4)
C(26)-C(29)	1.560(4)
C(27)-C(28)	1.546(4)
C(29)-C(30)	1.531(4)
C(29)-C(31)	1.536(4)
C(29)-C(32)	1.540(4)
C(1)-Zr(1)-Cl(1)	124.63(7)
C(1)-Zr(1)-C(21)	78.91(9)
Cl(1)-Zr(1)-C(21)	90.02(7)
C(1)-Zr(1)-C(17)	57.68(9)
Cl(1)-Zr(1)-C(17)	123.68(7)
C(21)-Zr(1)-C(17)	34.02(9)
C(1)-Zr(1)-Cl(2)	124.23(6)
Cl(1)-Zr(1)-Cl(2)	99.85(3)
C(21)-Zr(1)-Cl(2)	138.07(6)
C(17)-Zr(1)-Cl(2)	124.77(6)
C(1)-Zr(1)-C(18)	80.08(9)
Cl(1)-Zr(1)-C(18)	134.97(7)
C(21)-Zr(1)-C(18)	55.44(9)
C(17)-Zr(1)-C(18)	33.89(8)
Cl(2)-Zr(1)-C(18)	91.59(6)
C(1)-Zr(1)-C(2)	34.10(8)
Cl(1)-Zr(1)-C(2)	135.98(6)
C(21)-Zr(1)-C(2)	109.87(9)
C(17)-Zr(1)-C(2)	80.65(9)
Cl(2)-Zr(1)-C(2)	90.88(6)
C(18)-Zr(1)-C(2)	86.62(9)
C(1)-Zr(1)-C(13)	33.98(8)
Cl(1)-Zr(1)-C(13)	91.26(6)
C(21)-Zr(1)-C(13)	83.37(9)
C(17)-Zr(1)-C(13)	79.48(8)
Cl(2)-Zr(1)-C(13)	136.34(7)
C(18)-Zr(1)-C(13)	109.82(8)
C(2)-Zr(1)-C(13)	54.66(8)

C(1)-Zr(1)-C(20)	109.99(8)
Cl(1)-Zr(1)-C(20)	81.53(6)
C(21)-Zr(1)-C(20)	33.00(8)
C(17)-Zr(1)-C(20)	54.98(8)
Cl(2)-Zr(1)-C(20)	108.10(6)
C(18)-Zr(1)-C(20)	53.62(9)
C(2)-Zr(1)-C(20)	135.15(8)
C(13)-Zr(1)-C(20)	115.28(9)
C(1)-Zr(1)-C(19)	110.22(8)
Cl(1)-Zr(1)-C(19)	105.55(6)
C(21)-Zr(1)-C(19)	54.01(8)
C(17)-Zr(1)-C(19)	54.68(8)
Cl(2)-Zr(1)-C(19)	84.15(6)
C(18)-Zr(1)-C(19)	32.27(8)
C(2)-Zr(1)-C(19)	118.02(8)
C(13)-Zr(1)-C(19)	133.20(8)
C(20)-Zr(1)-C(19)	31.40(8)
C(1)-Zr(1)-C(7)	55.08(8)
Cl(1)-Zr(1)-C(7)	106.62(6)
C(21)-Zr(1)-C(7)	132.80(8)
C(17)-Zr(1)-C(7)	110.71(8)
Cl(2)-Zr(1)-C(7)	83.21(6)
C(18)-Zr(1)-C(7)	117.97(9)
C(2)-Zr(1)-C(7)	32.20(8)
C(13)-Zr(1)-C(7)	53.22(8)
C(20)-Zr(1)-C(7)	165.07(8)
C(19)-Zr(1)-C(7)	146.97(8)
C(1)-Zr(1)-C(8)	54.91(8)
Cl(1)-Zr(1)-C(8)	82.92(6)
C(21)-Zr(1)-C(8)	114.14(9)
C(17)-Zr(1)-C(8)	109.83(8)
Cl(2)-Zr(1)-C(8)	107.51(6)
C(18)-Zr(1)-C(8)	134.54(8)
C(2)-Zr(1)-C(8)	53.24(8)
C(13)-Zr(1)-C(8)	32.00(8)
C(20)-Zr(1)-C(8)	143.02(8)
C(19)-Zr(1)-C(8)	164.51(8)
C(7)-Zr(1)-C(8)	31.40(8)
C(2)-C(1)-C(13)	106.2(2)
C(2)-C(1)-C(14)	126.5(2)
C(13)-C(1)-C(14)	125.9(2)
C(2)-C(1)-Zr(1)	76.76(14)
C(13)-C(1)-Zr(1)	77.46(14)
C(14)-C(1)-Zr(1)	101.35(15)
C(3)-C(2)-C(7)	117.4(2)
C(3)-C(2)-C(1)	133.7(2)
C(7)-C(2)-C(1)	108.9(2)
C(3)-C(2)-Zr(1)	117.91(17)
C(7)-C(2)-Zr(1)	78.72(15)
C(1)-C(2)-Zr(1)	69.14(14)
C(4)-C(3)-C(2)	119.4(3)
C(3)-C(4)-C(5)	122.2(3)
C(6)-C(5)-C(4)	120.4(3)

C(5)-C(6)-C(7)	119.0(3)
C(6)-C(7)-C(8)	130.4(3)
C(6)-C(7)-C(2)	121.6(2)
C(8)-C(7)-C(2)	108.0(2)
C(6)-C(7)-Zr(1)	123.04(17)
C(8)-C(7)-Zr(1)	74.82(14)
C(2)-C(7)-Zr(1)	69.08(14)
C(9)-C(8)-C(7)	130.1(3)
C(9)-C(8)-C(13)	121.9(3)
C(7)-C(8)-C(13)	107.9(2)
C(9)-C(8)-Zr(1)	124.32(18)
C(7)-C(8)-Zr(1)	73.77(14)
C(13)-C(8)-Zr(1)	69.31(14)
C(10)-C(9)-C(8)	118.8(3)
C(9)-C(10)-C(11)	120.6(3)
C(12)-C(11)-C(10)	122.1(3)
C(11)-C(12)-C(13)	119.8(3)
C(12)-C(13)-C(8)	116.8(2)
C(12)-C(13)-C(1)	134.3(2)
C(8)-C(13)-C(1)	108.9(2)
C(12)-C(13)-Zr(1)	119.11(18)
C(8)-C(13)-Zr(1)	78.69(14)
C(1)-C(13)-Zr(1)	68.55(13)
C(17)-C(14)-C(16)	112.4(2)
C(17)-C(14)-C(15)	110.6(2)
C(16)-C(14)-C(15)	106.7(2)
C(17)-C(14)-C(1)	99.05(19)
C(16)-C(14)-C(1)	113.9(2)
C(15)-C(14)-C(1)	114.1(2)
C(21)-C(17)-C(18)	106.2(2)
C(21)-C(17)-C(14)	124.9(2)
C(18)-C(17)-C(14)	125.7(2)
C(21)-C(17)-Zr(1)	72.94(14)
C(18)-C(17)-Zr(1)	74.73(14)
C(14)-C(17)-Zr(1)	101.89(16)
C(19)-C(18)-C(17)	109.4(2)
C(19)-C(18)-Zr(1)	80.01(15)
C(17)-C(18)-Zr(1)	71.37(14)
C(20)-C(19)-C(18)	106.6(2)
C(20)-C(19)-C(22)	123.0(2)
C(18)-C(19)-C(22)	129.7(2)
C(20)-C(19)-Zr(1)	71.49(15)
C(18)-C(19)-Zr(1)	67.73(14)
C(22)-C(19)-Zr(1)	133.26(17)
C(19)-C(20)-C(21)	109.1(2)
C(19)-C(20)-Zr(1)	77.11(15)
C(21)-C(20)-Zr(1)	68.38(15)
C(17)-C(21)-C(20)	108.4(2)
C(17)-C(21)-Zr(1)	73.05(15)
C(20)-C(21)-Zr(1)	78.62(15)
C(19)-C(22)-C(23)	110.8(2)
C(19)-C(22)-C(28)	113.2(2)
C(23)-C(22)-C(28)	109.7(2)

C(19)-C(22)-C(24)	107.0(2)
C(23)-C(22)-C(24)	108.1(2)
C(28)-C(22)-C(24)	107.9(2)
C(25)-C(24)-C(22)	113.7(2)
C(24)-C(25)-C(26)	111.0(2)
C(25)-C(26)-C(27)	109.6(2)
C(25)-C(26)-C(29)	114.0(2)
C(27)-C(26)-C(29)	113.4(2)
C(26)-C(27)-C(28)	113.1(2)
C(22)-C(28)-C(27)	116.0(2)
C(30)-C(29)-C(31)	107.7(2)
C(30)-C(29)-C(32)	108.5(3)
C(31)-C(29)-C(32)	108.6(3)
C(30)-C(29)-C(26)	109.5(2)
C(31)-C(29)-C(26)	110.0(2)
C(32)-C(29)-C(26)	112.4(2)

Table B.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{C}(3-(4-t\text{-butylcyclohexyl-1-methyl})\text{-C}_3\text{H}_5)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	10(1)	13(1)	12(1)	5(1)	4(1)	6(1)
Cl(1)	12(1)	26(1)	20(1)	8(1)	4(1)	6(1)
Cl(2)	26(1)	20(1)	18(1)	5(1)	4(1)	15(1)
C(1)	12(1)	13(1)	16(1)	5(1)	2(1)	7(1)
C(2)	14(1)	17(1)	12(1)	5(1)	2(1)	9(1)
C(3)	18(1)	17(1)	18(1)	6(1)	1(1)	8(1)
C(4)	25(2)	16(1)	22(2)	3(1)	-2(1)	9(1)
C(5)	34(2)	23(2)	17(2)	2(1)	1(1)	20(1)
C(6)	27(2)	28(2)	12(1)	7(1)	4(1)	19(1)
C(7)	15(1)	20(1)	12(1)	7(1)	4(1)	11(1)
C(8)	16(1)	20(1)	13(1)	8(1)	5(1)	10(1)
C(9)	18(1)	31(2)	24(2)	17(1)	9(1)	14(1)
C(10)	14(1)	29(2)	36(2)	22(2)	8(1)	4(1)
C(11)	21(2)	16(2)	38(2)	12(1)	3(1)	4(1)
C(12)	21(1)	16(1)	26(2)	6(1)	3(1)	9(1)
C(13)	12(1)	16(1)	18(1)	7(1)	3(1)	7(1)
C(14)	13(1)	16(1)	15(1)	5(1)	5(1)	8(1)
C(15)	24(2)	25(2)	20(2)	6(1)	7(1)	18(1)
C(16)	12(1)	24(2)	23(2)	9(1)	5(1)	8(1)
C(17)	13(1)	18(1)	13(1)	6(1)	6(1)	8(1)
C(18)	13(1)	14(1)	16(1)	7(1)	6(1)	5(1)
C(19)	14(1)	16(1)	14(1)	7(1)	6(1)	7(1)
C(20)	15(1)	18(1)	14(1)	5(1)	4(1)	7(1)
C(21)	17(1)	15(1)	13(1)	2(1)	4(1)	8(1)
C(22)	17(1)	20(1)	18(1)	11(1)	5(1)	10(1)
C(23)	19(1)	33(2)	30(2)	17(1)	8(1)	16(1)
C(24)	20(1)	20(2)	18(1)	10(1)	0(1)	7(1)
C(25)	22(1)	20(1)	12(1)	6(1)	3(1)	7(1)
C(26)	19(1)	16(1)	15(1)	8(1)	4(1)	8(1)

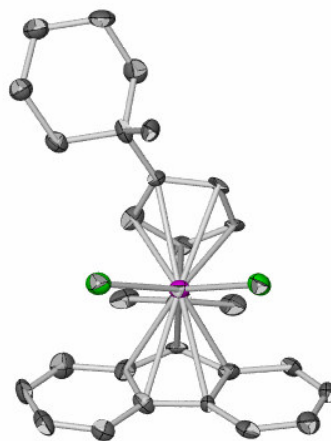
C(27)	21(1)	12(1)	16(1)	5(1)	4(1)	5(1)
C(28)	24(1)	16(1)	19(1)	8(1)	7(1)	12(1)
C(29)	21(1)	21(2)	21(2)	9(1)	7(1)	8(1)
C(30)	31(2)	29(2)	23(2)	5(1)	15(1)	7(1)
C(31)	25(2)	23(2)	24(2)	5(1)	8(1)	2(1)
C(32)	28(2)	45(2)	52(2)	24(2)	16(2)	23(2)

Table B.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $\text{Me}_2\text{C}(3-(4-t\text{-butylcyclohexyl-1-methyl})-\text{C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$.

	x	y	z	U(eq)
H(3)	6619	7773	4144	21
H(4)	6430	9606	5147	26
H(5)	4238	8922	5868	27
H(6)	2219	6338	5611	23
H(9)	303	3285	5135	26
H(10)	-996	612	4560	32
H(11)	61	-493	3554	31
H(12)	2339	1030	3070	25
H(15A)	3996	1959	2397	30
H(15B)	5553	2502	3043	30
H(15C)	5833	2857	2217	30
H(16A)	7429	5412	2614	29
H(16B)	7547	5622	3534	29
H(16C)	6957	6639	3156	29
H(18)	5078	7036	2541	17
H(20)	409	3530	1393	19
H(21)	1990	2222	1874	18
H(23A)	-366	5540	1504	37
H(23B)	199	7276	1446	37
H(23C)	458	6987	2273	37
H(24A)	1410	5190	480	24
H(24B)	1735	6884	438	24
H(25A)	3778	6289	-107	23
H(25B)	4310	6060	699	23
H(26)	4610	8949	518	19
H(27A)	5885	10136	1818	20
H(27B)	5778	8538	1910	20
H(28A)	3650	8815	2480	22
H(28B)	3053	9193	1742	22
H(30A)	7697	8776	-564	46
H(30B)	5945	8773	-607	46
H(30C)	6047	7218	-592	46
H(31A)	8185	10959	1349	42
H(31B)	7341	11148	608	42
H(31C)	8956	10908	559	42
H(32A)	8799	8362	622	56
H(32B)	7055	6923	622	56
H(32C)	7917	8392	1379	56

APPENDIX C

X-RAY CRYSTAL STRUCTURE OF METALLOCENE

 $\text{Me}_2\text{C}(\text{3-(1-methylcyclohexyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ (7)

Labeled view with 50% probability ellipsoids

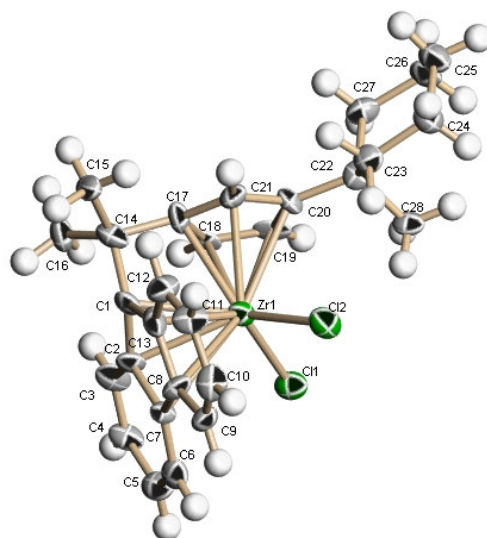


Table C.1. Crystal data and structure refinement for $\text{Me}_2\text{C}(3\text{-(1-methylcyclohexyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$.

Identification code	$\text{Me}_2\text{C}(3\text{-(1-methylcyclohexyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$, sm45.	
Empirical formula	$\text{C}_{28} \text{H}_{30} \text{Cl}_2 \text{Zr}$	
Formula weight	528.64	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 11.764(4) \text{ Å}$	$\alpha = 90^\circ$.
	$b = 20.563(7) \text{ Å}$	$\beta = 97.113(7)^\circ$.
	$c = 9.396(3) \text{ Å}$	$\gamma = 90^\circ$.
Volume	$2255.5(12) \text{ Å}^3$	
Z	4	
Density (calculated)	1.557 Mg/m^3	
Absorption coefficient	0.739 mm^{-1}	
F(000)	1088	
Crystal size	$0.20 \times 0.10 \times 0.05 \text{ mm}^3$	
Theta range for data collection	$2.40 \text{ to } 24.99^\circ$.	
Index ranges	$-13 \leq h \leq 13, -24 \leq k \leq 24, -10 \leq l \leq 11$	
Reflections collected	14623	
Independent reflections	3859 [R(int) = 0.1583]	
Completeness to theta = 24.99°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9640 and 0.8663	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3859 / 0 / 283	
Goodness-of-fit on F^2	1.033	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0684, wR2 = 0.1142	
R indices (all data)	R1 = 0.1572, wR2 = 0.1342	
Largest diff. peak and hole	0.901 and -1.132 e.Å^{-3}	

Table C.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $\text{Me}_2\text{C}(3\text{-(1-methylcyclohexyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	2499(1)	752(1)	2883(1)	26(1)
Cl(1)	2569(2)	16(1)	4887(2)	33(1)
Cl(2)	2138(2)	1725(1)	4189(2)	38(1)
C(1)	1700(7)	543(4)	444(8)	25(2)
C(2)	1291(6)	-8(4)	1239(8)	25(2)
C(3)	1579(7)	-677(4)	1355(9)	32(2)
C(4)	1070(7)	-1047(4)	2262(9)	32(2)
C(5)	278(7)	-827(4)	3144(8)	34(2)
C(6)	-42(7)	-184(4)	3055(8)	30(2)
C(7)	457(7)	235(3)	2135(8)	18(2)

C(8)	293(7)	913(4)	1865(8)	25(2)
C(9)	-459(7)	1353(4)	2423(8)	26(2)
C(10)	-443(7)	1978(4)	1963(9)	37(2)
C(11)	249(7)	2176(4)	941(9)	34(2)
C(12)	966(8)	1763(4)	394(9)	37(2)
C(13)	1030(7)	1098(4)	832(8)	29(2)
C(14)	2744(7)	545(4)	-343(9)	36(2)
C(15)	2767(7)	1066(4)	-1484(7)	35(2)
C(16)	2955(7)	-102(4)	-1075(8)	36(2)
C(17)	3644(7)	674(4)	920(8)	29(2)
C(18)	4077(6)	185(4)	1955(9)	24(2)
C(19)	4627(7)	490(4)	3147(10)	29(2)
C(20)	4583(7)	1165(3)	2942(8)	23(2)
C(21)	3923(7)	1284(4)	1596(8)	30(2)
C(22)	5243(7)	1650(4)	3960(8)	28(2)
C(23)	4849(7)	2348(4)	3669(8)	31(2)
C(24)	5645(7)	2861(4)	4411(9)	34(2)
C(25)	6914(7)	2768(4)	4195(9)	38(2)
C(26)	7298(7)	2086(4)	4515(8)	35(2)
C(27)	6504(7)	1594(4)	3682(8)	34(2)
C(28)	5123(7)	1461(3)	5510(7)	28(2)

Table C.3. Bond lengths [\AA] and angles [$^\circ$] for $\text{Me}_2\text{C}(3\text{-(cyclohexylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$.

Zr(1)-C(1)	2.406(8)
Zr(1)-Cl(1)	2.410(2)
Zr(1)-Cl(2)	2.413(2)
Zr(1)-C(17)	2.419(8)
Zr(1)-C(18)	2.442(7)
Zr(1)-C(21)	2.443(7)
Zr(1)-C(2)	2.511(8)
Zr(1)-C(13)	2.526(8)
Zr(1)-C(19)	2.543(8)
Zr(1)-C(20)	2.588(8)
Zr(1)-C(7)	2.641(8)
Zr(1)-C(8)	2.673(8)
C(1)-C(13)	1.459(10)
C(1)-C(2)	1.470(10)
C(1)-C(14)	1.510(10)
C(2)-C(3)	1.417(10)
C(2)-C(7)	1.458(9)
C(3)-C(4)	1.338(9)
C(4)-C(5)	1.397(10)
C(5)-C(6)	1.374(10)
C(6)-C(7)	1.400(10)
C(7)-C(8)	1.426(10)
C(8)-C(9)	1.410(10)
C(8)-C(13)	1.431(10)
C(9)-C(10)	1.356(10)
C(10)-C(11)	1.395(10)
C(11)-C(12)	1.344(10)

C(12)-C(13)	1.427(10)
C(14)-C(17)	1.512(11)
C(14)-C(15)	1.518(10)
C(14)-C(16)	1.533(10)
C(17)-C(21)	1.426(10)
C(17)-C(18)	1.447(10)
C(18)-C(19)	1.374(10)
C(19)-C(20)	1.401(9)
C(20)-C(21)	1.421(10)
C(20)-C(22)	1.526(10)
C(22)-C(28)	1.531(9)
C(22)-C(23)	1.522(9)
C(22)-C(27)	1.543(10)
C(23)-C(24)	1.521(10)
C(24)-C(25)	1.543(10)
C(25)-C(26)	1.492(10)
C(26)-C(27)	1.525(10)
C(1)-Zr(1)-Cl(1)	127.14(18)
C(1)-Zr(1)-Cl(2)	124.10(19)
Cl(1)-Zr(1)-Cl(2)	96.55(8)
C(1)-Zr(1)-C(17)	56.7(3)
Cl(1)-Zr(1)-C(17)	125.8(2)
Cl(2)-Zr(1)-C(17)	126.4(2)
C(1)-Zr(1)-C(18)	78.4(3)
Cl(1)-Zr(1)-C(18)	91.43(19)
Cl(2)-Zr(1)-C(18)	140.1(2)
C(17)-Zr(1)-C(18)	34.6(2)
C(1)-Zr(1)-C(21)	79.6(3)
Cl(1)-Zr(1)-C(21)	135.1(2)
Cl(2)-Zr(1)-C(21)	93.16(19)
C(17)-Zr(1)-C(21)	34.1(2)
C(18)-Zr(1)-C(21)	55.9(3)
C(1)-Zr(1)-C(2)	34.7(2)
Cl(1)-Zr(1)-C(2)	92.99(18)
Cl(2)-Zr(1)-C(2)	135.04(18)
C(17)-Zr(1)-C(2)	79.4(2)
C(18)-Zr(1)-C(2)	83.1(3)
C(21)-Zr(1)-C(2)	110.2(3)
C(1)-Zr(1)-C(13)	34.3(2)
Cl(1)-Zr(1)-C(13)	136.6(2)
Cl(2)-Zr(1)-C(13)	90.46(19)
C(17)-Zr(1)-C(13)	80.2(3)
C(18)-Zr(1)-C(13)	109.9(3)
C(21)-Zr(1)-C(13)	86.7(3)
C(2)-Zr(1)-C(13)	54.8(3)
C(1)-Zr(1)-C(19)	108.6(3)
Cl(1)-Zr(1)-C(19)	81.53(19)
Cl(2)-Zr(1)-C(19)	111.0(2)
C(17)-Zr(1)-C(19)	55.0(3)
C(18)-Zr(1)-C(19)	31.9(2)
C(21)-Zr(1)-C(19)	54.3(3)
C(2)-Zr(1)-C(19)	113.8(3)
C(13)-Zr(1)-C(19)	135.0(3)

C(1)-Zr(1)-C(20)	109.7(3)
Cl(1)-Zr(1)-C(20)	104.37(18)
Cl(2)-Zr(1)-C(20)	86.72(17)
C(17)-Zr(1)-C(20)	54.8(3)
C(18)-Zr(1)-C(20)	53.5(2)
C(21)-Zr(1)-C(20)	32.7(2)
C(2)-Zr(1)-C(20)	132.8(2)
C(13)-Zr(1)-C(20)	118.8(3)
C(19)-Zr(1)-C(20)	31.7(2)
C(1)-Zr(1)-C(7)	55.9(2)
Cl(1)-Zr(1)-C(7)	84.10(17)
Cl(2)-Zr(1)-C(7)	104.93(16)
C(17)-Zr(1)-C(7)	110.1(2)
C(18)-Zr(1)-C(7)	114.8(2)
C(21)-Zr(1)-C(7)	134.9(2)
C(2)-Zr(1)-C(7)	32.8(2)
C(13)-Zr(1)-C(7)	52.9(2)
C(19)-Zr(1)-C(7)	142.5(2)
C(20)-Zr(1)-C(7)	164.9(2)
C(1)-Zr(1)-C(8)	55.5(2)
Cl(1)-Zr(1)-C(8)	107.17(17)
Cl(2)-Zr(1)-C(8)	81.67(17)
C(17)-Zr(1)-C(8)	110.1(3)
C(18)-Zr(1)-C(8)	132.7(2)
C(21)-Zr(1)-C(8)	117.5(3)
C(2)-Zr(1)-C(8)	53.6(2)
C(13)-Zr(1)-C(8)	31.8(2)
C(19)-Zr(1)-C(8)	164.1(3)
C(20)-Zr(1)-C(8)	147.4(2)
C(7)-Zr(1)-C(8)	31.1(2)
C(13)-C(1)-C(2)	104.8(6)
C(13)-C(1)-C(14)	128.1(7)
C(2)-C(1)-C(14)	126.1(7)
C(13)-C(1)-Zr(1)	77.4(4)
C(2)-C(1)-Zr(1)	76.6(4)
C(14)-C(1)-Zr(1)	102.7(5)
C(3)-C(2)-C(7)	117.3(7)
C(3)-C(2)-C(1)	134.2(7)
C(7)-C(2)-C(1)	108.4(6)
C(3)-C(2)-Zr(1)	116.4(5)
C(7)-C(2)-Zr(1)	78.5(4)
C(1)-C(2)-Zr(1)	68.7(4)
C(4)-C(3)-C(2)	118.7(7)
C(3)-C(4)-C(5)	125.2(8)
C(6)-C(5)-C(4)	118.3(8)
C(5)-C(6)-C(7)	119.8(8)
C(6)-C(7)-C(8)	130.8(7)
C(6)-C(7)-C(2)	120.6(7)
C(8)-C(7)-C(2)	108.6(7)
C(6)-C(7)-Zr(1)	121.4(5)
C(8)-C(7)-Zr(1)	75.7(4)
C(2)-C(7)-Zr(1)	68.7(4)
C(9)-C(8)-C(13)	122.8(7)

C(9)-C(8)-C(7)	129.7(7)
C(13)-C(8)-C(7)	107.5(7)
C(9)-C(8)-Zr(1)	124.9(5)
C(13)-C(8)-Zr(1)	68.4(5)
C(7)-C(8)-Zr(1)	73.2(4)
C(10)-C(9)-C(8)	117.1(7)
C(9)-C(10)-C(11)	121.9(8)
C(12)-C(11)-C(10)	121.7(8)
C(11)-C(12)-C(13)	120.6(8)
C(12)-C(13)-C(8)	115.8(8)
C(12)-C(13)-C(1)	133.5(8)
C(8)-C(13)-C(1)	110.7(7)
C(12)-C(13)-Zr(1)	119.7(6)
C(8)-C(13)-Zr(1)	79.8(5)
C(1)-C(13)-Zr(1)	68.3(4)
C(17)-C(14)-C(15)	111.1(7)
C(17)-C(14)-C(1)	98.6(7)
C(15)-C(14)-C(1)	115.8(7)
C(17)-C(14)-C(16)	111.6(7)
C(15)-C(14)-C(16)	106.1(6)
C(1)-C(14)-C(16)	113.8(7)
C(21)-C(17)-C(18)	105.6(7)
C(21)-C(17)-C(14)	127.1(8)
C(18)-C(17)-C(14)	124.1(7)
C(21)-C(17)-Zr(1)	73.8(4)
C(18)-C(17)-Zr(1)	73.6(4)
C(14)-C(17)-Zr(1)	102.0(5)
C(19)-C(18)-C(17)	108.7(7)
C(19)-C(18)-Zr(1)	78.1(5)
C(17)-C(18)-Zr(1)	71.8(4)
C(18)-C(19)-C(20)	109.6(8)
C(18)-C(19)-Zr(1)	70.0(5)
C(20)-C(19)-Zr(1)	76.0(5)
C(19)-C(20)-C(21)	107.4(7)
C(19)-C(20)-C(22)	123.7(8)
C(21)-C(20)-C(22)	128.6(7)
C(19)-C(20)-Zr(1)	72.4(5)
C(21)-C(20)-Zr(1)	68.0(4)
C(22)-C(20)-Zr(1)	129.4(5)
C(20)-C(21)-C(17)	108.4(7)
C(20)-C(21)-Zr(1)	79.3(4)
C(17)-C(21)-Zr(1)	72.1(4)
C(28)-C(22)-C(23)	110.5(6)
C(28)-C(22)-C(20)	109.3(6)
C(23)-C(22)-C(20)	112.5(7)
C(28)-C(22)-C(27)	110.3(6)
C(23)-C(22)-C(27)	108.5(7)
C(20)-C(22)-C(27)	105.7(6)
C(24)-C(23)-C(22)	114.5(7)
C(23)-C(24)-C(25)	113.9(7)
C(26)-C(25)-C(24)	111.3(7)
C(25)-C(26)-C(27)	111.7(7)
C(26)-C(27)-C(22)	113.8(7)

Table C.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{C}(3\text{-}(1\text{-methylcyclohexyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Zr(1)	20(1)	26(1)	30(1)	-1(1)	4(1)	-1(1)
Cl(1)	28(1)	35(1)	37(1)	5(1)	5(1)	2(1)
Cl(2)	28(2)	36(1)	50(2)	-11(1)	7(1)	2(1)
C(1)	10(5)	32(5)	30(5)	0(4)	-4(4)	-4(4)
C(2)	14(5)	29(5)	35(5)	-2(4)	11(4)	-1(4)
C(3)	17(5)	27(5)	54(6)	-2(5)	9(4)	7(4)
C(4)	25(6)	20(5)	50(6)	9(4)	3(5)	1(4)
C(5)	32(6)	37(6)	33(6)	11(5)	1(4)	0(5)
C(6)	21(6)	39(6)	28(5)	0(4)	-6(4)	4(4)
C(7)	17(5)	14(4)	24(5)	2(4)	3(4)	0(4)
C(8)	23(5)	34(5)	20(5)	6(4)	9(4)	9(4)
C(9)	26(6)	34(5)	20(5)	0(4)	8(4)	2(4)
C(10)	38(6)	31(5)	39(6)	0(5)	-3(5)	15(5)
C(11)	35(6)	24(5)	43(6)	12(5)	7(5)	10(4)
C(12)	41(7)	39(6)	32(6)	5(5)	12(5)	-2(5)
C(13)	35(6)	28(5)	23(5)	1(4)	-7(4)	-7(4)
C(14)	26(6)	34(5)	46(6)	1(5)	4(5)	-11(4)
C(15)	31(6)	54(6)	18(5)	8(4)	-3(4)	-14(5)
C(16)	32(6)	41(6)	33(5)	-17(5)	-5(4)	-1(4)
C(17)	27(6)	30(5)	30(5)	-14(5)	-3(4)	-2(4)
C(18)	6(5)	24(5)	43(6)	-7(5)	9(4)	1(4)
C(19)	8(5)	32(5)	49(6)	13(5)	13(4)	10(4)
C(20)	18(5)	18(5)	31(5)	-2(4)	-3(4)	-3(4)
C(21)	38(6)	32(5)	21(5)	1(4)	11(4)	-9(4)
C(22)	31(6)	24(5)	29(5)	5(4)	2(4)	10(4)
C(23)	26(6)	36(5)	29(5)	5(4)	1(4)	4(4)
C(24)	30(6)	32(5)	39(6)	-4(4)	5(5)	-2(4)
C(25)	30(6)	42(6)	41(6)	5(5)	-1(5)	-7(5)
C(26)	19(6)	46(6)	40(6)	3(5)	0(4)	-5(4)
C(27)	32(6)	37(5)	36(6)	3(4)	14(5)	4(4)
C(28)	31(6)	24(5)	32(5)	10(4)	8(4)	-3(4)

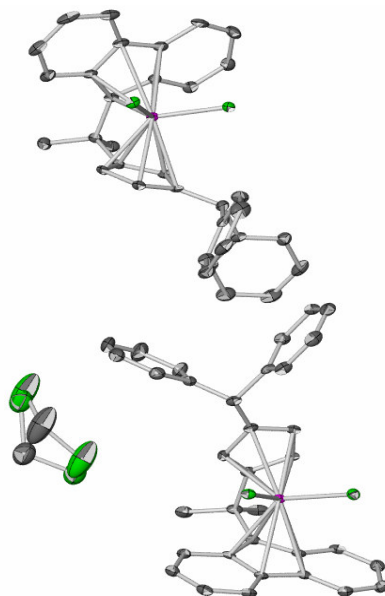
Table C.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) For $\text{Me}_2\text{C}(3\text{-}(1\text{-methylcyclohexyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$.

	x	y	z	U(eq)
H(3)	2123	-858	801	39
H(4)	1262	-1496	2309	38
H(5)	-31	-1114	3789	41
H(6)	-601	-24	3615	36
H(9)	-955	1217	3091	32
H(10)	-917	2289	2349	44

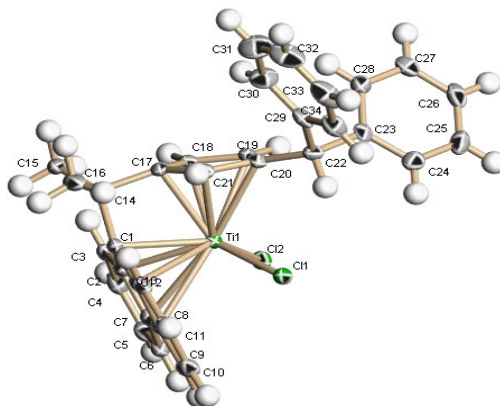
H(11)	213	2615	623	40
H(12)	1435	1914	-291	44
H(15A)	2942	1488	-1023	52
H(15B)	2017	1087	-2067	52
H(15C)	3356	960	-2098	52
H(16A)	2238	-255	-1612	54
H(16B)	3233	-425	-346	54
H(16C)	3529	-40	-1734	54
H(18)	4103	-293	1761	28
H(19)	5060	265	3988	35
H(21)	3826	1718	1114	36
H(23A)	4771	2426	2621	37
H(23B)	4081	2401	3982	37
H(24A)	5580	2852	5451	41
H(24B)	5390	3295	4043	41
H(25A)	7016	2875	3192	46
H(25B)	7394	3070	4833	46
H(26A)	7318	2003	5555	42
H(26B)	8084	2030	4262	42
H(27A)	6783	1151	3943	41
H(27B)	6545	1654	2644	41
H(28A)	5558	1766	6167	43
H(28B)	5420	1020	5697	43
H(28C)	4313	1475	5658	43

APPENDIX D

X-RAY CRYSTAL STRUCTURE OF METALLOCENE

 $\text{Me}_2\text{C}(\text{3-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$ (12)

Labeled view with 50% probability ellipsoids



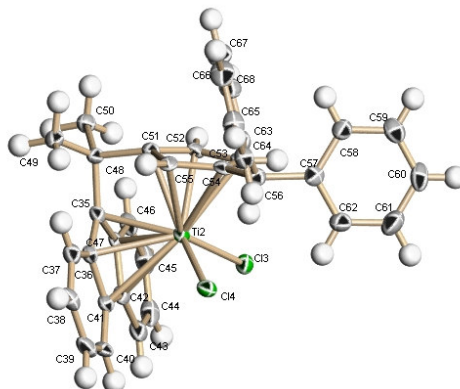


Table D.1. Crystal data and structure refinement for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$.

Identification code	$\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$, sm53	
Empirical formula	$\text{C}_{34.50}\text{H}_{29}\text{Cl}_3\text{Ti}$	
Formula weight	597.83	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 30.504(9)$ Å	$\alpha = 90^\circ$.
	$b = 9.074(3)$ Å	$\beta = 97.080(6)^\circ$.
	$c = 20.229(6)$ Å	$\gamma = 90^\circ$.
Volume	$5557(3)$ Å ³	
Z	8	
Density (calculated)	1.429 Mg/m ³	
Absorption coefficient	0.620 mm ⁻¹	
F(000)	2472	
Crystal size	0.60 x 0.20 x 0.10 mm ³	
Theta range for data collection	2.34 to 25.00°.	
Index ranges	-36 ≤ h ≤ 34, -10 ≤ k ≤ 10, -23 ≤ l ≤ 24	
Reflections collected	43228	
Independent reflections	9739 [R(int) = 0.0636]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9406 and 0.7072	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9739 / 3 / 698	
Goodness-of-fit on F ²	1.114	
Final R indices [I > 2σ(I)]	R1 = 0.0544, wR2 = 0.1182	
R indices (all data)	R1 = 0.0739, wR2 = 0.1274	
Largest diff. peak and hole	0.808 and -0.722 e.Å ⁻³	

Table D.2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{C}(3\text{-}(\text{diphenylmethyl})\text{-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ti(1)	4358(1)	2331(1)	1098(1)	14(1)
Ti(2)	684(1)	2333(1)	3959(1)	14(1)
Cl(1)	3968(1)	644(1)	391(1)	18(1)
Cl(2)	4793(1)	599(1)	1712(1)	19(1)
Cl(3)	299(1)	356(1)	3440(1)	20(1)
Cl(4)	1118(1)	896(1)	4727(1)	20(1)
C(1)	4592(1)	4610(3)	781(2)	18(1)
C(2)	5005(1)	3933(3)	1059(2)	17(1)
C(3)	5299(1)	4190(3)	1655(2)	20(1)
C(4)	5672(1)	3351(4)	1782(2)	23(1)
C(5)	5773(1)	2227(4)	1347(2)	24(1)
C(6)	5502(1)	1948(3)	770(2)	20(1)
C(7)	5118(1)	2797(3)	627(2)	17(1)
C(8)	4782(1)	2753(3)	64(2)	16(1)
C(9)	4741(1)	1831(3)	-500(2)	20(1)
C(10)	4389(1)	2025(4)	-982(2)	22(1)
C(11)	4078(1)	3151(4)	-921(2)	25(1)
C(12)	4108(1)	4057(3)	-376(2)	21(1)
C(13)	4464(1)	3884(3)	142(2)	16(1)
C(14)	4307(1)	5663(3)	1139(2)	20(1)
C(15)	4564(1)	6692(3)	1647(2)	27(1)
C(16)	3991(1)	6613(4)	671(2)	28(1)
C(17)	4067(1)	4462(3)	1485(2)	17(1)
C(18)	4254(1)	3630(3)	2045(2)	15(1)
C(19)	3989(1)	2366(3)	2097(2)	17(1)
C(20)	3642(1)	2380(3)	1577(2)	18(1)
C(21)	3704(1)	3634(3)	1181(2)	18(1)
C(22)	3250(1)	1357(3)	1453(2)	19(1)
C(23)	3218(1)	255(3)	2014(2)	19(1)
C(24)	3236(1)	-1248(4)	1892(2)	26(1)
C(25)	3196(1)	-2268(4)	2392(2)	31(1)
C(26)	3136(1)	-1796(4)	3018(2)	29(1)
C(27)	3112(1)	-312(4)	3151(2)	26(1)
C(28)	3153(1)	709(4)	2653(2)	24(1)
C(29)	2821(1)	2224(4)	1313(2)	21(1)
C(30)	2758(1)	3569(4)	1617(2)	31(1)
C(31)	2364(1)	4327(5)	1479(2)	45(1)
C(32)	2026(1)	3763(5)	1040(2)	43(1)
C(33)	2080(1)	2436(5)	741(2)	39(1)
C(34)	2475(1)	1677(4)	870(2)	29(1)
C(35)	372(1)	4572(3)	4158(2)	18(1)
C(36)	553(1)	4108(3)	4824(2)	17(1)
C(37)	919(1)	4556(4)	5283(2)	22(1)
C(38)	1008(1)	3858(4)	5879(2)	25(1)
C(39)	748(1)	2670(4)	6058(2)	29(1)
C(40)	391(1)	2207(4)	5638(2)	25(1)
C(41)	290(1)	2906(3)	5016(2)	20(1)

C(42)	-61(1)	2646(3)	4492(2)	21(1)
C(43)	-414(1)	1645(4)	4454(2)	28(1)
C(44)	-716(1)	1651(4)	3897(2)	33(1)
C(45)	-680(1)	2646(4)	3376(2)	31(1)
C(46)	-341(1)	3639(4)	3400(2)	24(1)
C(47)	-19(1)	3672(3)	3968(2)	18(1)
C(48)	598(1)	5619(3)	3711(2)	18(1)
C(49)	864(1)	6858(3)	4089(2)	23(1)
C(50)	284(1)	6337(4)	3154(2)	23(1)
C(51)	889(1)	4449(3)	3440(2)	17(1)
C(52)	738(1)	3404(3)	2940(2)	17(1)
C(53)	1051(1)	2243(3)	2963(2)	18(1)
C(54)	1393(1)	2532(3)	3472(2)	17(1)
C(55)	1284(1)	3859(3)	3785(2)	17(1)
C(56)	1812(1)	1647(3)	3656(2)	19(1)
C(57)	1841(1)	343(3)	3192(2)	20(1)
C(58)	1982(1)	476(4)	2565(2)	24(1)
C(59)	1993(1)	-745(4)	2156(2)	30(1)
C(60)	1863(1)	-2104(4)	2358(2)	32(1)
C(61)	1725(1)	-2254(4)	2974(2)	37(1)
C(62)	1710(1)	-1042(4)	3386(2)	28(1)
C(63)	2224(1)	2615(3)	3707(2)	20(1)
C(64)	2574(1)	2316(4)	4200(2)	24(1)
C(65)	2960(1)	3137(4)	4243(2)	31(1)
C(66)	3002(1)	4253(4)	3800(2)	35(1)
C(67)	2655(1)	4586(4)	3313(2)	33(1)
C(68)	2268(1)	3763(4)	3269(2)	26(1)
C(1S)	2424(2)	8131(10)	-345(4)	68(1)
Cl(1S)	2923(1)	7568(4)	-50(1)	68(1)
Cl(2S)	2013(1)	7916(6)	179(2)	68(1)
C(1T)	2275(5)	6840(20)	-75(12)	111(3)
Cl(1T)	1975(4)	7860(15)	329(6)	111(3)
Cl(2T)	2826(2)	6702(12)	12(5)	111(3)

Table D.3. Bond lengths [\AA] and angles [$^\circ$] for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$.

Ti(1)-C(1)	2.304(3)
Ti(1)-C(18)	2.304(3)
Ti(1)-C(17)	2.305(3)
Ti(1)-Cl(2)	2.3171(10)
Ti(1)-Cl(1)	2.3208(10)
Ti(1)-C(21)	2.342(3)
Ti(1)-C(19)	2.432(3)
Ti(1)-C(13)	2.447(3)
Ti(1)-C(2)	2.459(3)
Ti(1)-C(20)	2.495(3)
Ti(1)-C(8)	2.619(3)
Ti(1)-C(7)	2.647(3)
Ti(2)-C(35)	2.300(3)
Ti(2)-C(52)	2.303(3)
Ti(2)-C(51)	2.312(3)
Ti(2)-Cl(4)	2.3148(10)

Ti(2)-Cl(3)	2.3227(10)
Ti(2)-C(55)	2.355(3)
Ti(2)-C(53)	2.424(3)
Ti(2)-C(36)	2.447(3)
Ti(2)-C(47)	2.466(3)
Ti(2)-C(54)	2.492(3)
Ti(2)-C(41)	2.631(3)
Ti(2)-C(42)	2.649(3)
C(1)-C(2)	1.451(4)
C(1)-C(13)	1.460(4)
C(1)-C(14)	1.532(4)
C(2)-C(7)	1.421(4)
C(2)-C(3)	1.431(4)
C(3)-C(4)	1.368(5)
C(4)-C(5)	1.406(5)
C(5)-C(6)	1.369(4)
C(6)-C(7)	1.401(4)
C(7)-C(8)	1.434(4)
C(8)-C(9)	1.408(4)
C(8)-C(13)	1.434(4)
C(9)-C(10)	1.371(4)
C(10)-C(11)	1.409(5)
C(11)-C(12)	1.369(5)
C(12)-C(13)	1.421(4)
C(14)-C(17)	1.530(4)
C(14)-C(16)	1.531(4)
C(14)-C(15)	1.531(4)
C(17)-C(21)	1.413(4)
C(17)-C(18)	1.422(4)
C(18)-C(19)	1.414(4)
C(19)-C(20)	1.397(4)
C(20)-C(21)	1.417(4)
C(20)-C(22)	1.512(4)
C(22)-C(29)	1.524(4)
C(22)-C(23)	1.525(4)
C(23)-C(24)	1.389(4)
C(23)-C(28)	1.393(5)
C(24)-C(25)	1.388(5)
C(25)-C(26)	1.370(5)
C(26)-C(27)	1.377(5)
C(27)-C(28)	1.386(5)
C(29)-C(34)	1.389(5)
C(29)-C(30)	1.390(5)
C(30)-C(31)	1.384(5)
C(31)-C(32)	1.374(6)
C(32)-C(33)	1.367(6)
C(33)-C(34)	1.383(5)
C(35)-C(36)	1.454(4)
C(35)-C(47)	1.456(4)
C(35)-C(48)	1.532(4)
C(36)-C(37)	1.421(4)
C(36)-C(41)	1.435(4)
C(37)-C(38)	1.359(4)

C(38)-C(39)	1.412(5)
C(39)-C(40)	1.362(5)
C(40)-C(41)	1.409(4)
C(41)-C(42)	1.430(5)
C(42)-C(43)	1.401(5)
C(42)-C(47)	1.429(4)
C(43)-C(44)	1.367(5)
C(44)-C(45)	1.403(5)
C(45)-C(46)	1.366(5)
C(46)-C(47)	1.419(4)
C(48)-C(51)	1.529(4)
C(48)-C(50)	1.530(4)
C(48)-C(49)	1.536(4)
C(51)-C(55)	1.420(4)
C(51)-C(52)	1.421(4)
C(52)-C(53)	1.419(4)
C(53)-C(54)	1.396(4)
C(54)-C(55)	1.420(4)
C(54)-C(56)	1.516(4)
C(56)-C(57)	1.520(4)
C(56)-C(63)	1.528(4)
C(57)-C(62)	1.389(5)
C(57)-C(58)	1.392(5)
C(58)-C(59)	1.386(5)
C(59)-C(60)	1.373(5)
C(60)-C(61)	1.371(5)
C(61)-C(62)	1.384(5)
C(63)-C(68)	1.385(5)
C(63)-C(64)	1.395(4)
C(64)-C(65)	1.387(5)
C(65)-C(66)	1.369(5)
C(66)-C(67)	1.389(5)
C(67)-C(68)	1.389(5)
C(1S)-Cl(1S)	1.645(7)
C(1S)-Cl(2S)	1.750(8)
C(1T)-Cl(1T)	1.597(16)
C(1T)-Cl(2T)	1.674(15)
C(1)-Ti(1)-C(18)	81.48(11)
C(1)-Ti(1)-C(17)	59.15(11)
C(18)-Ti(1)-C(17)	35.94(11)
C(1)-Ti(1)-Cl(2)	125.55(9)
C(18)-Ti(1)-Cl(2)	91.72(8)
C(17)-Ti(1)-Cl(2)	127.36(8)
C(1)-Ti(1)-Cl(1)	124.96(8)
C(18)-Ti(1)-Cl(1)	137.51(8)
C(17)-Ti(1)-Cl(1)	124.96(9)
Cl(2)-Ti(1)-Cl(1)	95.68(4)
C(1)-Ti(1)-C(21)	82.08(11)
C(18)-Ti(1)-C(21)	58.45(11)
C(17)-Ti(1)-C(21)	35.39(11)
Cl(2)-Ti(1)-C(21)	137.83(8)
Cl(1)-Ti(1)-C(21)	90.06(8)

C(1)-Ti(1)-C(19)	114.25(11)
C(18)-Ti(1)-C(19)	34.61(10)
C(17)-Ti(1)-C(19)	57.96(11)
Cl(2)-Ti(1)-C(19)	81.79(8)
Cl(1)-Ti(1)-C(19)	105.45(8)
C(21)-Ti(1)-C(19)	56.53(11)
C(1)-Ti(1)-C(13)	35.65(10)
C(18)-Ti(1)-C(13)	114.09(11)
C(17)-Ti(1)-C(13)	83.07(11)
Cl(2)-Ti(1)-C(13)	133.74(8)
Cl(1)-Ti(1)-C(13)	90.00(8)
C(21)-Ti(1)-C(13)	87.84(11)
C(19)-Ti(1)-C(13)	140.30(11)
C(1)-Ti(1)-C(2)	35.27(11)
C(18)-Ti(1)-C(2)	85.30(11)
C(17)-Ti(1)-C(2)	81.94(11)
Cl(2)-Ti(1)-C(2)	90.53(8)
Cl(1)-Ti(1)-C(2)	136.21(8)
C(21)-Ti(1)-C(2)	113.41(11)
C(19)-Ti(1)-C(2)	118.34(10)
C(13)-Ti(1)-C(2)	56.59(10)
C(1)-Ti(1)-C(20)	114.05(11)
C(18)-Ti(1)-C(20)	56.74(10)
C(17)-Ti(1)-C(20)	57.37(10)
Cl(2)-Ti(1)-C(20)	105.99(8)
Cl(1)-Ti(1)-C(20)	81.06(8)
C(21)-Ti(1)-C(20)	33.89(10)
C(19)-Ti(1)-C(20)	32.92(10)
C(13)-Ti(1)-C(20)	120.24(10)
C(2)-Ti(1)-C(20)	138.21(10)
C(1)-Ti(1)-C(8)	56.37(10)
C(18)-Ti(1)-C(8)	136.16(10)
C(17)-Ti(1)-C(8)	113.43(10)
Cl(2)-Ti(1)-C(8)	102.69(7)
Cl(1)-Ti(1)-C(8)	82.55(7)
C(21)-Ti(1)-C(8)	119.48(10)
C(19)-Ti(1)-C(8)	170.55(10)
C(13)-Ti(1)-C(8)	32.67(10)
C(2)-Ti(1)-C(8)	53.87(10)
C(20)-Ti(1)-C(8)	148.11(10)
C(1)-Ti(1)-C(7)	56.05(10)
C(18)-Ti(1)-C(7)	115.74(10)
C(17)-Ti(1)-C(7)	112.33(10)
Cl(2)-Ti(1)-C(7)	80.30(7)
Cl(1)-Ti(1)-C(7)	106.75(7)
C(21)-Ti(1)-C(7)	137.42(10)
C(19)-Ti(1)-C(7)	144.39(10)
C(13)-Ti(1)-C(7)	54.30(10)
C(2)-Ti(1)-C(7)	32.05(9)
C(20)-Ti(1)-C(7)	169.69(10)
C(8)-Ti(1)-C(7)	31.60(9)
C(35)-Ti(2)-C(52)	81.94(11)
C(35)-Ti(2)-C(51)	59.09(11)

C(52)-Ti(2)-C(51)	35.87(10)
C(35)-Ti(2)-Cl(4)	126.52(8)
C(52)-Ti(2)-Cl(4)	137.77(9)
C(51)-Ti(2)-Cl(4)	127.45(8)
C(35)-Ti(2)-Cl(3)	124.31(8)
C(52)-Ti(2)-Cl(3)	90.54(8)
C(51)-Ti(2)-Cl(3)	125.90(8)
Cl(4)-Ti(2)-Cl(3)	94.83(4)
C(35)-Ti(2)-C(55)	81.49(11)
C(52)-Ti(2)-C(55)	58.39(11)
C(51)-Ti(2)-C(55)	35.40(10)
Cl(4)-Ti(2)-C(55)	92.34(8)
Cl(3)-Ti(2)-C(55)	138.23(8)
C(35)-Ti(2)-C(53)	114.71(11)
C(52)-Ti(2)-C(53)	34.83(11)
C(51)-Ti(2)-C(53)	58.10(11)
Cl(4)-Ti(2)-C(53)	104.73(8)
Cl(3)-Ti(2)-C(53)	81.88(8)
C(55)-Ti(2)-C(53)	56.54(11)
C(35)-Ti(2)-C(36)	35.51(10)
C(52)-Ti(2)-C(36)	113.45(11)
C(51)-Ti(2)-C(36)	81.68(11)
Cl(4)-Ti(2)-C(36)	91.23(8)
Cl(3)-Ti(2)-C(36)	135.46(8)
C(55)-Ti(2)-C(36)	85.31(11)
C(53)-Ti(2)-C(36)	138.53(11)
C(35)-Ti(2)-C(47)	35.36(11)
C(52)-Ti(2)-C(47)	87.50(11)
C(51)-Ti(2)-C(47)	83.00(11)
Cl(4)-Ti(2)-C(47)	134.29(8)
Cl(3)-Ti(2)-C(47)	89.55(8)
C(55)-Ti(2)-C(47)	113.76(11)
C(53)-Ti(2)-C(47)	120.92(10)
C(36)-Ti(2)-C(47)	56.70(10)
C(35)-Ti(2)-C(54)	113.75(11)
C(52)-Ti(2)-C(54)	56.92(11)
C(51)-Ti(2)-C(54)	57.52(10)
Cl(4)-Ti(2)-C(54)	81.60(8)
Cl(3)-Ti(2)-C(54)	107.04(8)
C(55)-Ti(2)-C(54)	33.92(10)
C(53)-Ti(2)-C(54)	32.96(10)
C(36)-Ti(2)-C(54)	117.50(10)
C(47)-Ti(2)-C(54)	139.88(10)
C(35)-Ti(2)-C(41)	56.15(10)
C(52)-Ti(2)-C(41)	137.20(11)
C(51)-Ti(2)-C(41)	112.41(10)
Cl(4)-Ti(2)-C(41)	81.21(8)
Cl(3)-Ti(2)-C(41)	105.26(8)
C(55)-Ti(2)-C(41)	116.50(11)
C(53)-Ti(2)-C(41)	170.50(10)
C(36)-Ti(2)-C(41)	32.57(10)
C(47)-Ti(2)-C(41)	53.95(10)
C(54)-Ti(2)-C(41)	144.42(10)

C(35)-Ti(2)-C(42)	55.93(10)
C(52)-Ti(2)-C(42)	118.57(11)
C(51)-Ti(2)-C(42)	112.94(11)
C1(4)-Ti(2)-C(42)	103.65(8)
C1(3)-Ti(2)-C(42)	81.64(7)
C(55)-Ti(2)-C(42)	135.97(10)
C(53)-Ti(2)-C(42)	148.16(11)
C(36)-Ti(2)-C(42)	54.13(10)
C(47)-Ti(2)-C(42)	32.18(10)
C(54)-Ti(2)-C(42)	169.64(10)
C(41)-Ti(2)-C(42)	31.44(10)
C(2)-C(1)-C(13)	106.0(3)
C(2)-C(1)-C(14)	126.6(3)
C(13)-C(1)-C(14)	126.5(3)
C(2)-C(1)-Ti(1)	78.21(17)
C(13)-C(1)-Ti(1)	77.52(17)
C(14)-C(1)-Ti(1)	102.42(19)
C(7)-C(2)-C(3)	117.4(3)
C(7)-C(2)-C(1)	109.6(3)
C(3)-C(2)-C(1)	133.0(3)
C(7)-C(2)-Ti(1)	81.29(18)
C(3)-C(2)-Ti(1)	119.4(2)
C(1)-C(2)-Ti(1)	66.51(16)
C(4)-C(3)-C(2)	119.3(3)
C(3)-C(4)-C(5)	121.8(3)
C(6)-C(5)-C(4)	120.8(3)
C(5)-C(6)-C(7)	118.5(3)
C(6)-C(7)-C(2)	122.2(3)
C(6)-C(7)-C(8)	130.2(3)
C(2)-C(7)-C(8)	107.7(3)
C(6)-C(7)-Ti(1)	125.7(2)
C(2)-C(7)-Ti(1)	66.66(17)
C(8)-C(7)-Ti(1)	73.12(17)
C(9)-C(8)-C(7)	130.0(3)
C(9)-C(8)-C(13)	121.3(3)
C(7)-C(8)-C(13)	108.7(3)
C(9)-C(8)-Ti(1)	123.8(2)
C(7)-C(8)-Ti(1)	75.27(17)
C(13)-C(8)-Ti(1)	67.03(16)
C(10)-C(9)-C(8)	119.0(3)
C(9)-C(10)-C(11)	120.5(3)
C(12)-C(11)-C(10)	121.8(3)
C(11)-C(12)-C(13)	119.8(3)
C(12)-C(13)-C(8)	117.6(3)
C(12)-C(13)-C(1)	134.4(3)
C(8)-C(13)-C(1)	108.0(3)
C(12)-C(13)-Ti(1)	118.9(2)
C(8)-C(13)-Ti(1)	80.30(17)
C(1)-C(13)-Ti(1)	66.84(16)
C(17)-C(14)-C(16)	112.5(3)
C(17)-C(14)-C(15)	111.3(3)
C(16)-C(14)-C(15)	107.6(3)
C(17)-C(14)-C(1)	96.0(2)

C(16)-C(14)-C(1)	114.2(3)
C(15)-C(14)-C(1)	115.1(3)
C(21)-C(17)-C(18)	106.3(3)
C(21)-C(17)-C(14)	125.0(3)
C(18)-C(17)-C(14)	125.0(3)
C(21)-C(17)-Ti(1)	73.76(17)
C(18)-C(17)-Ti(1)	72.02(17)
C(14)-C(17)-Ti(1)	102.44(19)
C(19)-C(18)-C(17)	108.2(3)
C(19)-C(18)-Ti(1)	77.63(17)
C(17)-C(18)-Ti(1)	72.04(17)
C(20)-C(19)-C(18)	108.9(3)
C(20)-C(19)-Ti(1)	76.04(18)
C(18)-C(19)-Ti(1)	67.75(17)
C(19)-C(20)-C(21)	107.0(3)
C(19)-C(20)-C(22)	129.0(3)
C(21)-C(20)-C(22)	123.9(3)
C(19)-C(20)-Ti(1)	71.04(18)
C(21)-C(20)-Ti(1)	67.13(17)
C(22)-C(20)-Ti(1)	129.6(2)
C(17)-C(21)-C(20)	109.4(3)
C(17)-C(21)-Ti(1)	70.85(17)
C(20)-C(21)-Ti(1)	78.99(18)
C(20)-C(22)-C(29)	111.0(3)
C(20)-C(22)-C(23)	113.7(3)
C(29)-C(22)-C(23)	110.2(3)
C(24)-C(23)-C(28)	118.0(3)
C(24)-C(23)-C(22)	120.2(3)
C(28)-C(23)-C(22)	121.7(3)
C(25)-C(24)-C(23)	121.1(3)
C(26)-C(25)-C(24)	119.9(3)
C(25)-C(26)-C(27)	120.2(3)
C(26)-C(27)-C(28)	120.0(3)
C(27)-C(28)-C(23)	120.8(3)
C(34)-C(29)-C(30)	117.7(3)
C(34)-C(29)-C(22)	120.1(3)
C(30)-C(29)-C(22)	122.2(3)
C(31)-C(30)-C(29)	120.7(3)
C(32)-C(31)-C(30)	120.6(4)
C(33)-C(32)-C(31)	119.6(4)
C(32)-C(33)-C(34)	120.3(4)
C(33)-C(34)-C(29)	121.2(4)
C(36)-C(35)-C(47)	106.6(3)
C(36)-C(35)-C(48)	125.5(3)
C(47)-C(35)-C(48)	127.2(3)
C(36)-C(35)-Ti(2)	77.79(18)
C(47)-C(35)-Ti(2)	78.57(18)
C(48)-C(35)-Ti(2)	102.68(19)
C(37)-C(36)-C(41)	117.5(3)
C(37)-C(36)-C(35)	134.4(3)
C(41)-C(36)-C(35)	108.1(3)
C(37)-C(36)-Ti(2)	118.1(2)
C(41)-C(36)-Ti(2)	80.75(18)

C(35)-C(36)-Ti(2)	66.70(16)
C(38)-C(37)-C(36)	120.1(3)
C(37)-C(38)-C(39)	121.8(3)
C(40)-C(39)-C(38)	120.4(3)
C(39)-C(40)-C(41)	119.3(3)
C(40)-C(41)-C(42)	130.5(3)
C(40)-C(41)-C(36)	121.0(3)
C(42)-C(41)-C(36)	108.5(3)
C(40)-C(41)-Ti(2)	124.4(2)
C(42)-C(41)-Ti(2)	74.99(18)
C(36)-C(41)-Ti(2)	66.67(17)
C(43)-C(42)-C(47)	121.4(3)
C(43)-C(42)-C(41)	130.3(3)
C(47)-C(42)-C(41)	108.2(3)
C(43)-C(42)-Ti(2)	126.8(2)
C(47)-C(42)-Ti(2)	66.85(17)
C(41)-C(42)-Ti(2)	73.58(18)
C(44)-C(43)-C(42)	118.5(3)
C(43)-C(44)-C(45)	120.9(3)
C(46)-C(45)-C(44)	121.8(3)
C(45)-C(46)-C(47)	119.2(3)
C(46)-C(47)-C(42)	118.0(3)
C(46)-C(47)-C(35)	133.5(3)
C(42)-C(47)-C(35)	108.5(3)
C(46)-C(47)-Ti(2)	120.0(2)
C(42)-C(47)-Ti(2)	80.97(19)
C(35)-C(47)-Ti(2)	66.07(17)
C(51)-C(48)-C(50)	111.7(3)
C(51)-C(48)-C(35)	96.0(2)
C(50)-C(48)-C(35)	114.4(3)
C(51)-C(48)-C(49)	113.0(3)
C(50)-C(48)-C(49)	107.4(3)
C(35)-C(48)-C(49)	114.1(3)
C(55)-C(51)-C(52)	106.2(3)
C(55)-C(51)-C(48)	125.5(3)
C(52)-C(51)-C(48)	124.4(3)
C(55)-C(51)-Ti(2)	73.95(17)
C(52)-C(51)-Ti(2)	71.69(17)
C(48)-C(51)-Ti(2)	102.23(19)
C(53)-C(52)-C(51)	108.3(3)
C(53)-C(52)-Ti(2)	77.27(18)
C(51)-C(52)-Ti(2)	72.44(17)
C(54)-C(53)-C(52)	108.9(3)
C(54)-C(53)-Ti(2)	76.19(18)
C(52)-C(53)-Ti(2)	67.89(17)
C(53)-C(54)-C(55)	107.0(3)
C(53)-C(54)-C(56)	127.7(3)
C(55)-C(54)-C(56)	125.2(3)
C(53)-C(54)-Ti(2)	70.85(18)
C(55)-C(54)-Ti(2)	67.75(17)
C(56)-C(54)-Ti(2)	127.5(2)
C(51)-C(55)-C(54)	109.4(3)
C(51)-C(55)-Ti(2)	70.65(17)

C(54)-C(55)-Ti(2)	78.33(17)
C(54)-C(56)-C(57)	111.8(3)
C(54)-C(56)-C(63)	111.9(3)
C(57)-C(56)-C(63)	112.2(3)
C(62)-C(57)-C(58)	117.8(3)
C(62)-C(57)-C(56)	119.3(3)
C(58)-C(57)-C(56)	122.9(3)
C(59)-C(58)-C(57)	120.5(3)
C(60)-C(59)-C(58)	120.7(3)
C(61)-C(60)-C(59)	119.5(3)
C(60)-C(61)-C(62)	120.3(3)
C(61)-C(62)-C(57)	121.2(3)
C(68)-C(63)-C(64)	118.5(3)
C(68)-C(63)-C(56)	122.3(3)
C(64)-C(63)-C(56)	119.2(3)
C(65)-C(64)-C(63)	120.7(3)
C(66)-C(65)-C(64)	120.2(3)
C(65)-C(66)-C(67)	120.0(3)
C(66)-C(67)-C(68)	119.8(3)
C(63)-C(68)-C(67)	120.8(3)
Cl(1S)-C(1S)-Cl(2S)	116.5(5)
Cl(1T)-C(1T)-Cl(2T)	128.3(12)

Table D.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ti(1)	16(1)	12(1)	14(1)	0(1)	5(1)	0(1)
Ti(2)	13(1)	16(1)	15(1)	0(1)	4(1)	0(1)
Cl(1)	20(1)	17(1)	18(1)	-3(1)	7(1)	-2(1)
Cl(2)	21(1)	18(1)	20(1)	4(1)	5(1)	1(1)
Cl(3)	18(1)	18(1)	24(1)	-3(1)	5(1)	-1(1)
Cl(4)	18(1)	23(1)	18(1)	4(1)	5(1)	2(1)
C(1)	24(2)	12(2)	19(2)	0(1)	10(1)	-3(1)
C(2)	20(2)	15(2)	18(2)	2(1)	11(1)	-2(1)
C(3)	26(2)	20(2)	16(2)	-3(1)	10(1)	-8(1)
C(4)	22(2)	28(2)	21(2)	2(1)	2(2)	-8(2)
C(5)	18(2)	26(2)	30(2)	4(2)	6(2)	0(2)
C(6)	19(2)	17(2)	24(2)	-1(1)	9(1)	-2(1)
C(7)	20(2)	13(2)	18(2)	2(1)	8(1)	-4(1)
C(8)	19(2)	14(2)	17(2)	4(1)	10(1)	-3(1)
C(9)	23(2)	17(2)	21(2)	0(1)	13(2)	-2(1)
C(10)	28(2)	25(2)	15(2)	-3(1)	7(2)	-6(2)
C(11)	22(2)	32(2)	21(2)	6(2)	5(2)	-3(2)
C(12)	20(2)	21(2)	22(2)	6(1)	9(1)	1(1)
C(13)	21(2)	14(2)	16(2)	5(1)	9(1)	-3(1)
C(14)	25(2)	13(2)	25(2)	1(1)	13(2)	-1(1)
C(15)	34(2)	17(2)	34(2)	-9(2)	21(2)	-8(2)
C(16)	34(2)	17(2)	36(2)	7(2)	20(2)	10(2)

C(17)	19(2)	12(2)	22(2)	-3(1)	10(1)	2(1)
C(18)	18(2)	16(2)	14(2)	-5(1)	8(1)	-1(1)
C(19)	19(2)	19(2)	15(2)	-2(1)	8(1)	-2(1)
C(20)	16(2)	17(2)	22(2)	-2(1)	9(1)	0(1)
C(21)	18(2)	18(2)	18(2)	2(1)	5(1)	7(1)
C(22)	18(2)	20(2)	21(2)	-5(1)	8(1)	-2(1)
C(23)	8(2)	21(2)	28(2)	1(1)	4(1)	-4(1)
C(24)	21(2)	24(2)	36(2)	-5(2)	8(2)	-1(2)
C(25)	25(2)	17(2)	51(2)	2(2)	8(2)	0(2)
C(26)	19(2)	25(2)	43(2)	11(2)	7(2)	-4(2)
C(27)	19(2)	32(2)	27(2)	3(2)	8(2)	-2(2)
C(28)	24(2)	20(2)	29(2)	-1(1)	9(2)	-1(1)
C(29)	16(2)	28(2)	21(2)	6(1)	5(1)	-4(1)
C(30)	20(2)	39(2)	32(2)	-5(2)	1(2)	4(2)
C(31)	36(3)	48(3)	50(3)	-2(2)	5(2)	19(2)
C(32)	22(2)	67(3)	39(2)	13(2)	4(2)	15(2)
C(33)	23(2)	66(3)	28(2)	11(2)	-1(2)	-9(2)
C(34)	22(2)	39(2)	24(2)	1(2)	3(2)	-7(2)
C(35)	18(2)	19(2)	18(2)	-3(1)	9(1)	0(1)
C(36)	18(2)	17(2)	18(2)	-1(1)	7(1)	3(1)
C(37)	21(2)	22(2)	24(2)	-4(1)	7(2)	0(1)
C(38)	26(2)	34(2)	16(2)	-5(2)	4(2)	6(2)
C(39)	39(2)	36(2)	15(2)	3(2)	10(2)	12(2)
C(40)	34(2)	22(2)	23(2)	4(1)	20(2)	3(2)
C(41)	22(2)	19(2)	21(2)	-1(1)	12(1)	4(1)
C(42)	19(2)	19(2)	27(2)	-3(1)	12(2)	0(1)
C(43)	29(2)	24(2)	35(2)	-7(2)	20(2)	-3(2)
C(44)	19(2)	31(2)	53(3)	-19(2)	18(2)	-9(2)
C(45)	16(2)	38(2)	38(2)	-17(2)	3(2)	1(2)
C(46)	19(2)	27(2)	26(2)	-5(2)	8(2)	4(2)
C(47)	17(2)	20(2)	20(2)	-3(1)	11(1)	3(1)
C(48)	21(2)	17(2)	19(2)	3(1)	8(1)	2(1)
C(49)	25(2)	18(2)	27(2)	0(1)	10(2)	-3(1)
C(50)	27(2)	21(2)	24(2)	4(1)	8(2)	7(2)
C(51)	18(2)	18(2)	15(2)	2(1)	6(1)	0(1)
C(52)	20(2)	21(2)	12(2)	2(1)	6(1)	3(1)
C(53)	19(2)	22(2)	15(2)	1(1)	7(1)	0(1)
C(54)	13(2)	21(2)	18(2)	3(1)	8(1)	-3(1)
C(55)	16(2)	16(2)	20(2)	2(1)	7(1)	-7(1)
C(56)	16(2)	19(2)	21(2)	2(1)	5(1)	1(1)
C(57)	12(2)	21(2)	28(2)	2(1)	4(1)	4(1)
C(58)	22(2)	21(2)	32(2)	0(2)	9(2)	0(1)
C(59)	23(2)	38(2)	31(2)	-5(2)	9(2)	4(2)
C(60)	21(2)	28(2)	46(2)	-14(2)	6(2)	5(2)
C(61)	39(2)	20(2)	54(3)	-1(2)	10(2)	-2(2)
C(62)	29(2)	25(2)	31(2)	4(2)	13(2)	-1(2)
C(63)	17(2)	20(2)	23(2)	-6(1)	10(1)	1(1)
C(64)	21(2)	26(2)	24(2)	-4(1)	3(2)	2(2)
C(65)	17(2)	38(2)	39(2)	-13(2)	1(2)	0(2)
C(66)	22(2)	33(2)	52(2)	-10(2)	11(2)	-13(2)
C(67)	29(2)	28(2)	44(2)	0(2)	10(2)	-8(2)
C(68)	22(2)	28(2)	29(2)	-1(2)	8(2)	-5(2)
C(1S)	54(1)	86(2)	63(1)	-4(1)	1(1)	5(1)

Cl(1S)	54(1)	86(2)	63(1)	-4(1)	1(1)	5(1)
Cl(2S)	54(1)	86(2)	63(1)	-4(1)	1(1)	5(1)
C(1T)	65(3)	79(5)	179(6)	-54(4)	-26(3)	18(3)
Cl(1T)	65(3)	79(5)	179(6)	-54(4)	-26(3)	18(3)
Cl(2T)	65(3)	79(5)	179(6)	-54(4)	-26(3)	18(3)

Table D.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$)
For $\text{Me}_2\text{C}(3\text{-(diphenylmethyl)-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{TiCl}_2$.

	x	y	z	U(eq)
H(3A)	5235	4935	1958	24
H(4A)	5869	3533	2176	28
H(5A)	6032	1653	1455	29
H(6A)	5572	1197	473	23
H(9A)	4954	1085	-545	24
H(10A)	4355	1397	-1361	27
H(11A)	3842	3284	-1267	29
H(12A)	3892	4798	-345	25
H(15A)	4357	7325	1849	41
H(15B)	4765	7306	1422	41
H(15C)	4736	6105	1995	41
H(16A)	3820	7250	935	42
H(16B)	3790	5975	385	42
H(16C)	4161	7223	395	42
H(18A)	4494	3976	2392	18
H(19A)	4030	1624	2465	21
H(21A)	3493	3974	793	21
H(22A)	3285	777	1043	23
H(24A)	3276	-1583	1458	32
H(25A)	3211	-3293	2301	37
H(26A)	3110	-2494	3361	35
H(27A)	3068	12	3584	31
H(28A)	3137	1731	2748	29
H(30A)	2989	3973	1922	37
H(31A)	2327	5246	1691	54
H(32A)	1757	4291	945	51
H(33A)	1846	2034	442	47
H(34A)	2510	765	652	34
H(37A)	1102	5344	5173	26
H(38A)	1251	4178	6183	30
H(39A)	822	2190	6474	35
H(40A)	213	1421	5763	30
H(43A)	-441	978	4809	34
H(44A)	-955	971	3862	40
H(45A)	-896	2630	2996	37
H(46A)	-322	4299	3040	29
H(49A)	1068	6433	4451	34
H(49B)	662	7539	4275	34
H(49C)	1032	7393	3783	34
H(50A)	108	5573	2903	35

H(50B)	457	6873	2854	35
H(50C)	88	7023	3348	35
H(52A)	487	3557	2580	21
H(53A)	1041	1398	2644	22
H(55A)	1479	4379	4145	20
H(56A)	1795	1233	4111	22
H(58A)	2071	1410	2418	29
H(59A)	2091	-639	1731	36
H(60A)	1868	-2934	2073	38
H(61A)	1639	-3195	3119	45
H(62A)	1609	-1158	3808	33
H(64A)	2548	1542	4508	28
H(65A)	3196	2924	4582	38
H(66A)	3270	4800	3826	42
H(67A)	2681	5374	3011	39
H(68A)	2031	3991	2934	31
H(1SA)	2331	7591	-764	82
H(1SB)	2441	9188	-459	82
H(1TA)	2189	7092	-550	133
H(1TB)	2167	5823	-20	133

VITA

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