

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

MSU is An Affirmative Action/Equal Opportunity Institution

c:\circ\dtedue.pm3-p.1

**SYNTHESIS, CHARACTERIZATION AND USE OF
HETEROBIMETALLIC COMPOUNDS AS OLEFIN POLYMERIZATION
CATALYSTS**

By

Subramani N. Iyer

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1995

Dr. John R. Stille

exp
me
on
pro
Het
fun
olef
desc
poly

titani
The s
produ
ray st
analog
establi

ABSTRACT

SYNTHESIS, CHARACTERIZATION AND THE USE OF HETEROBIMETALLIC COMPOUNDS AS OLEFIN POLYMERIZATION CATALYSTS

by

Subramani N. Iyer

Research in the field of Ziegler-Natta catalysts for olefin polymerization has experienced exciting developments in the last decade. The extensive research on the mechanistic aspect of the Ziegler-Natta catalysts has allowed tailoring of the catalysts based on product requirements. The discovery of methyl aluminoxane has helped further the progress of the catalyst design by allowing stereoselective polymerization of olefins. Heterobimetallic compounds have been used in traditional organic chemistry to effect functional group transformations. However, the use of heterobimetallic compounds as olefin polymerization catalysts has not been studied in depth. The following work describes synthesis and the use of novel heterobimetallic compounds as olefin polymerization catalysts.

Syntheses of novel heterobimetallic compounds consisting of dicyclopentadienyl titanium moiety bridged to an aluminum atom *via* a methylene bridged were carried out. The synthetic routes were simplified to allow for a 'one-pot' reaction, to provide the final products in high yields. The chemical shifts of the heterobimetallic compounds and the x-ray structure reveal that the bonding of these compounds is vastly different from the analogous Tebbe reagent. A synthetic route using lithium tetramethyl aluminate, was established to replace the bridging chloride group of the Tebbe reagent .

Simplified routes towards heterobimetallic complexes consisting of dicyclopentadienyl zirconium bridged to aluminum atom *via* a carbon bridged were developed. Addition of zirconocene hydridechloride across alkynyl aluminum compounds were investigated to provide vinyl bridged compounds of zirconium and aluminum.

Polymerization studies of ethylene with the novel heterobimetallic compounds synthesized herein were carried out. It was found that the heterobimetallic compounds of titanium and aluminum polymerized ethylene efficiently with low amounts of methyl aluminoxane as the co-catalyst. The amounts of methyl aluminoxane as a co-catalyst, to observe polymerization activity, was much lower for the heterobimetallic catalysts when compared to conventional catalysts such as titanocene methyl chloride or dimethyl zirconocene. Mechanistic studies on the interaction of alkynes with the compounds of titanium and zirconium synthesized herein indicate that a heterobimetallic intermediate consisting of a metallocene and an aluminoxane chain is responsible for polymerization activity.

To my Parents, Lalitha & S. Natarajan

fr
Pl
la
ca

er
the
you
and
wo

can
coun
You
keep
the g
than

Dr. R
Dr. R
inter
Diane
and K
wond
tiansu

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to Dr. John R. Stille, for giving me the freedom to carry out reactions I dreamt about, yet keeping me in constant touch with the project at hand. Your mentoring skills have helped me develop my analytical thinking and laboratory techniques, for which I am eternally grateful. I wish you all the best in your career at Lilly. My best wishes to Aleta and the kids.

Thanks to all the wonderful Stille group members: past and present. I really enjoyed working with the finest bunch of chemists one can ever find. Paul, wish you all the best with your career in pharmaceuticals. Nancy, thanks for the company and wish you a fine academic career. Jake, whats going on?? good luck at Colorado. Art, get busy and come back to the mid-west. Carol, Jon, Adam, Brian, Lisa: here's wishing you all a wonderful career.

Greg and Lisa, what can I say, your company and friendship was the best anyone can ever wish for. Thanks a lot for the good times we have had and please, no more country music. Petr: Thanks for all your help during the last years of my stay at MSU. You sure know more than you are willing to admit. I wish you my very best in life. Mike, keep the humor coming; Thanks to Steve, Ali, Marty, Ed, Big 'Dave', Dean, Carl and all the graduate students who kept my life at MSU interesting. To the Baker group members, thanks and Mao, get to work.

Thanks to the following people for their help and support during my stay at MSU. Dr. Rathke for all the help with aluminum chemistry and also serving as my second reader. Dr. Kanatzidis, Allison, Maleczka for serving in my committee. Dr. Baker, for many interesting discussions and sparking my interest in polymer chemistry. Lisa, Beth and Diane, for their help with all the mailing, paper work and account numbers. Dr. Long Le and Kermit for being the best and helping me a lot with NMR's. Dr. Don Ward for doing a wonderful job solving the crystal structure. Dr. Mitch Smith for interesting discussions on titanium chemistry.

Cely: will never forget your help especially during the crunch time where you drove me to Denny's for late night coffee and waffles. It was wonderful knowing you and wish you all the best with the microbes. To my wonderful roommates Ram and Easwar, thanks for the wonderful company over the last five years. Wish you all the best in your future endeavors. My guru Dr. G. K. Trivedi at IIT Bombay, thanks for directing me towards chemistry and shaping my future.

Usha, Anil, Prabha, Balan, Chandri, Anand and all my relatives back in India, miss you all and will come home soon. To my Parents, I dedicate this thesis to you for I could not have done it without your love and support.

TABLE OF CONTENTS

LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF SCHEMES	xii
LIST OF ABBREVIATIONS	xiii
 CHAPTER I : THEORIES, MODEL COMPOUNDS, AND BACKGROUND ON 'SINGLE COMPONENT OLEFIN POLYMERIZATION CATALYSTS'	
BACKGROUND AND SIGNIFICANCE	1
CATIONIC CATALYSTS: THEORIES AND MODEL COMPOUNDS	4
GOALS	10
EVOLUTION OF CONCEPT	11
EVIDENCE	13
MODEL FOR SINGLE COMPONENT CATALYST	22
 CHAPTER II: SYNTHESIS AND CHARACTERIZATION OF HETEROBIMETALLIC OLEFIN POLYMERIZATION CATALYSTS	
OXYGEN BRIDGED SYSTEMS	24
METHYLENE BRIDGED COMPOUNDS OF TITANIUM WITH ALUMINUM	28
CARBON BRIDGED COMPOUNDS OF ZIRCONIUM WITH ALUMINUM	44
CONCLUSIONS	48

CHA
BRI

INT

POL

CHO

CHO

AMC

REPR

POLY

CAT

POLY

DISC

CONC

CHA
IN B

MECH

INSE

CONC

EXPE

REFE

APPE

A

A

A

CHAPTER III: POLYMERIZATION STUDIES OF ETHYLENE WITH BRIDGED HETEROBIMETALLIC CATALYSTS

INTRODUCTION	51
POLYMERIZATION SETUP	52
CHOICE OF CO-CATALYST	53
CHOICE OF SOLVENT	54
AMOUNT OF SOLVENT	55
REPRODUCIBILITY OF RESULTS	55
POLYMERIZATION PROCEDURE	56
CATALYTIC ACTIVITIES	56
POLYMERIZATION RESULTS UNDER INDUSTRIAL SETTING	61
DISCUSSION OF POLYMERIZATION RESULTS	61
CONCLUSIONS	62

CHAPTER IV: MECHANISTIC INVESTIGATION ON ACTIVE SITES IN BRIDGED HETEROBIMETALLIC POLYMERIZATION SYSTEMS

MECHANISM OF ACTION	63
INSERTION OF ALKYNES	68
CONCLUSIONS	72
EXPERIMENTAL	73
REFERENCES	83
APPENDICES	
Appendix I: Bond Lengths and Bond Angles for 69	90
Appendix II: Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 69	93
Appendix III: C-H Bond Lengths ($\text{\AA}$) and H-C-X Bond Angles ($^\circ$) of 69	94

Appendix IV:	¹H NMR of 67	97
Appendix V:	¹H NMR of 68	98
Appendix VI:	¹H NMR of 69	99
Appendix VII:	¹H NMR of 70	100
Appendix VIII	¹H NMR of reaction mixture of 27 and 10 eq. MAO	101
Appendix IX	¹H NMR of reaction mixture of 27 and 10 eq. MAO	102

CH
O

Table

Table

CH
HE

Table

Table

Table

Table

Table

CH
BRI

Table

Table

Table

Table

Table

Table

Table

Table

LIST OF TABLES

CHAPTER I : THEORIES, MODEL COMPOUNDS, AND BACKGROUND ON 'SINGLE COMPONENT OLEFIN POLYMERIZATION CATALYSTS'

Table I:	¹ H NMR Shifts (in ppm) of Compounds 27 and 28	15
Table II:	¹³ C NMR Shifts (in ppm) of Compounds in Equations 8-10	16

CHAPTER II: SYNTHESIS AND CHARACTERIZATION OF HETEROBIMETALLIC OLEFIN POLYMERIZATION CATALYSTS

Table III:	Comparison of NMR Shifts (in ppm) of Compounds 67-70	32
Table IV	Crystallographic Data and Structure Refinement for 69	36
Table V:	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 69	37
Table VI:	Selected Bond Lengths and Angles for 69	38
Table VII:	Comparison of NMR Shifts (in ppm) of Compounds 27 and 80	44

CHAPTER III: POLYMERIZATION STUDIES OF ETHYLENE WITH BRIDGED HETEROBIMETALLIC CATALYSTS

Table VIII:	Solvent Dependence on Polymer Yield	55
Table IX:	Polymerization of Ethylene with 69 and 100 eq. MAO	57
Table X:	Dependence of Polymer Yield on Ratio of 69 :MAO	58
Table XI	Polymerization of Ethylene with 69 and 1000 eq. MAO	58
Table XII:	Polymerization of Ethylene with 23 and 100 eq. MAO	59
Table XIII:	Dependence of Polymer Yield on Ratio of 95 :MAO	59
Table XIV:	Polymerization of Ethylene with Tebbe Reagent/MAO and Dimethyl Zirconocene/MAO	60
Table XV:	Summary of Yields of Polyethylene with various catalysts	60

CH
ON

Fig

Fig

Fig

CH.
HET

Figur

Figur

Figur

CHA
BRID

Figur

LIST OF FIGURES

CHAPTER I : THEORIES, MODEL COMPOUNDS, AND BACKGROUND ON 'SINGLE COMPONENT OLEFIN POLYMERIZATION CATALYSTS'

Figure 1.	Models Proposed for Methyl Aluminoxane	2
Figure 2.	Some Novel Metallocene Catalysts used in Olefin Polymerization	3
Figure 3.	Examples of Cationic Olefin Polymerization Catalysts	6

CHAPTER II: SYNTHESIS AND CHARACTERIZATION OF HETEROBIMETALLIC OLEFIN POLYMERIZATION CATALYSTS

Figure 4.	Various Methylene Bridged Titanium Species Synthesized	32
Figure 5.	Relevant Compounds for Comparison of Crystal Structures	33
Figure 6.	ORTEP of Compound 69	35

CHAPTER III: POLYMERIZATION STUDIES OF ETHYLENE WITH BRIDGED HETEROBIMETALLIC CATALYSTS

Figure 7.	Reactor Setup used for Polymerization Studies	52
-----------	---	----

CI
O2

Sch

Sch

Sch

Sch

Sche

Sche

CHA
HET

Schen

Schen

LIST OF SCHEMES

CHAPTER I : THEORIES, MODEL COMPOUNDS, AND BACKGROUND ON 'SINGLE COMPONENT OLEFIN POLYMERIZATION CATALYSTS'

Scheme I.	Oscillating Stereocontrolled Polymerization	3
Scheme II	Equilibria Resulting in 'Intermittent' Growth of Polymer	4
Scheme III.	Proposed Reactions of Dimethyl Zirconocene and MAO	5
Scheme IV.	Possible Intermediates in the Reaction of MAO with Cp_2MR_2	13
Scheme V.	Proposed Mechanism for Propylene Polymerization	18
Scheme VI	Reactions of Zirconocene Compounds with Methyl Aluminoxane	20

CHAPTER II: SYNTHESIS AND CHARACTERIZATION OF HETEROBIMETALLIC OLEFIN POLYMERIZATION CATALYSTS

Scheme VII.	Attempted Synthesis of Oxygen Bridged Systems	27
Scheme VIII.	Products of Reaction of 27 with Varying Amounts of 79	42

LIST OF ABBREVIATIONS

Cp	Cyclopentadienyl
Cp*	Pentamethyl cyclopentadienyl
M	Metal
MAO	Methyl aluminoxane
Et ₂ O	Diethyl ether
CH ₂ CH ₂	Ethylene
C ₆ D ₆	Benzene-d ₆
C ₇ D ₈	Toluene-d ₈
R	Alkyl
OAr	Aryloxy
Ar	Aryl
X	Substituent
psi	Pounds per square inch
THF	Tetrahydrofuran

ON

BAC

Guilic
facilit
acety
organ

cataly
(1000
allow
olefin
Most
hetero
 $TiCl_4$
 Hf), in
class
mainly
advanc
homop
weight
polyme

CHAPTER I

THEORIES, MODEL COMPOUNDS, AND BACKGROUND ON 'SINGLE COMPONENT OLEFIN POLYMERIZATION CATALYSIS'

BACKGROUND AND SIGNIFICANCE

The Nobel prize in chemistry in the year 1963 was awarded to Karl Ziegler and Giulio Natta in recognition for their development of a remarkable class of catalysts that facilitated olefin polymerization.¹ In general, the polymerizations of olefins, diolefins and acetylenes carried out by the co-catalytic action of transition metal salts and main group organometallics are referred to as 'Ziegler-Natta' systems.²

Industrial production of polyolefins, prior to the discovery of Ziegler-Natta catalysts, was mainly carried out by radical polymerization which required high pressures (1000-3000 atmospheres) and high temperatures (150-230 °C). The Ziegler-Natta catalysts allowed the syntheses of polyolefins at low pressures and temperatures. In addition, α -olefins could be polymerized into highly stereoselective isotactic or syndiotactic structures. Most Ziegler-Natta catalysts used in the industrial production of polymers are heterogeneous in nature. Some well known catalytic systems include $\text{TiCl}_3/\text{AlR}_3$ and $\text{TiCl}_4/\text{AlMe}_3$. Metallocene complexes such as Cp_2MCl_2 (Cp =cyclopentadienyl, M =Ti, Zr, Hf), in the presence of aluminum alkyl reagents (usually AlMe_3 , 1), constitute a separate class of homogeneous catalysts.³ These catalytic systems were discovered and used mainly to elucidate the mechanism of Ziegler-Natta polymerizations. However, recent advances in the area of soluble catalyst systems have helped in the synthesis of new homopolymers and block co-polymers with novel microstructures and narrow molecular weight distribution.⁴ Ring opening metathesis polymerization (ROMP) and living polymerization are also offshoots from the studies of these metallocene catalysts.⁵

co-
alun
stere
beer
has
some
MA
and
MA
meta
polym

Fig

polym
donati
cyclop
detail a
or isosp



A number of novel metallocene catalysts have been developed for stereospecific polymerization of α -olefins. These have maintained the characteristic of having a 6 π e⁻ donating ligands such as indenyl,⁸ substituted indenyl,⁹ and bridged *ansa*-cyclopentadienyls.¹⁰ Structure-activity relationships have been studied and reviewed in detail and the results used to fine tune the catalyst's ability to generate either syndiospecific or isospecific polymerization.¹¹ Some examples of these catalysts are shown in Figure 2.

©
©

Fig

is re-
that r
leadin
chiral
Wayn
than p
rate o
explai
highly
propert

So



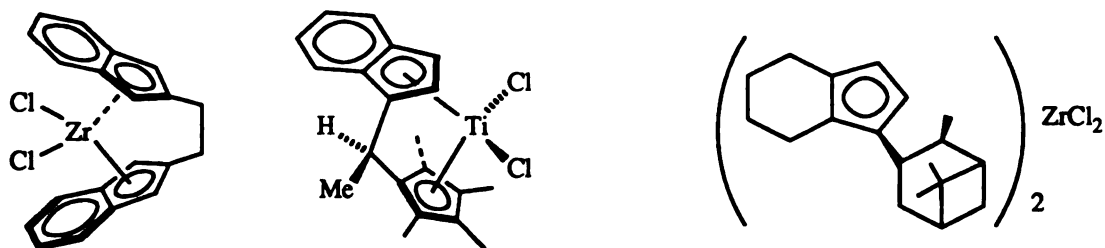
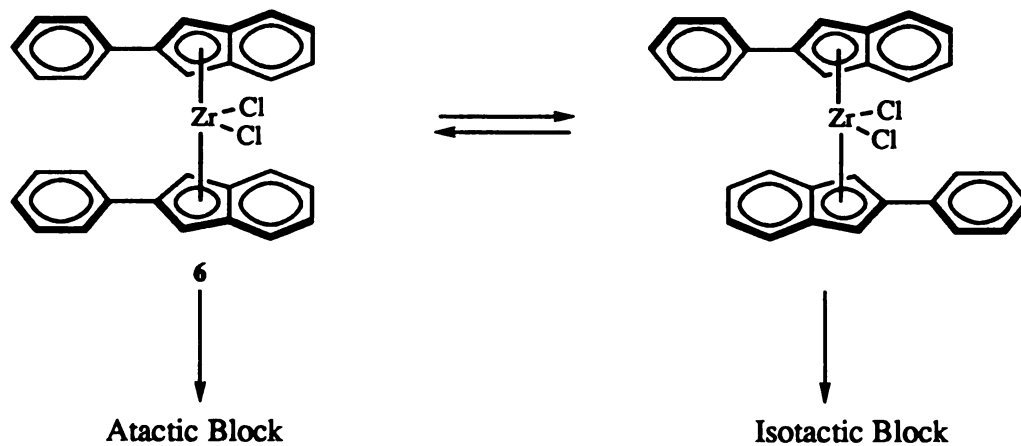


Figure 2: Some Novel Metallocene Catalysts used in Olefin Polymerization

An excellent example of design of a catalyst to tailor the needs of the final polymer is reflected in the work of Waymouth and co-workers (Scheme I).^{12a} It was suggested that the unbridged (2-phenylindenyl)₂ZrCl₂/MAO (6) isomerizes by restricted rotation leading to two different catalysts; a meso form providing atactic polypropylene while the chiral forms providing isotactic block polypropylene. However, recent results by the Waymouth group indicate that the mechanism of polymerization is much more complex than previously suggested. Specifically, the rate of isomerization is much faster than the rate of polymerization, and as such, the tacticity of the resulting polymer could not be explained by the isomerization of the active metallocene site.^{12b} The resulting polymer is a highly stretchable atactic-isotactic stereoblock polypropylene with good elastomeric properties.

Scheme I: Oscillating Stereocontrolled Polymerization



CATIONIC

Alth
responsible
research on
results have
responsible
bulky anion
been widely
the 'cationic

Reich
activated me
'intermittent
appears to al
This concept
and co-work
metallocene
aluminate an
NMR shifts a
pair was ter
considered ac

Sche

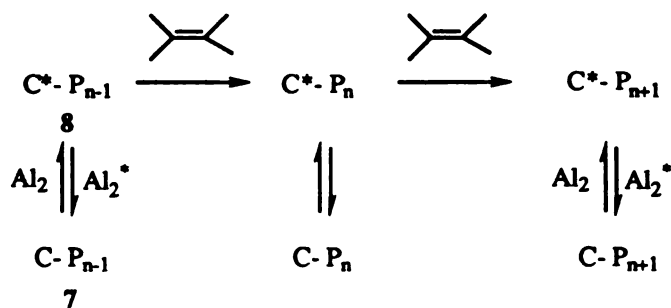
(C* = active

CATIONIC CATALYSTS: THEORIES AND MODEL COMPOUNDS

Although it was proposed almost 30 years ago that a cationic metal site is responsible for polymerization, only recently has this theory been put to test. The research on the olefin polymerization catalysts has been extensive and many conflicting results have been obtained based on the methods used for observing the active site responsible for polymerization. The hypothesis that a cationic metal atom, along with a bulky anion as the counterion is the key active species responsible for polymerization has been widely accepted in the research community. A detailed description of the evidence for the 'cationic active site' mechanism, along with various models is presented in this chapter.

Reichert and co-workers have carried out detailed kinetic studies on alkyl aluminum activated metallocene catalyst systems and proposed a concept for polymerization called the 'intermittent growth' model.¹³ According to the researchers, each metal-polymer species appears to alternate between a 'dormant' state (7) and a state in which it actively grows (8). This concept was further advanced by the work of Fink and co-workers¹⁴ and that of Eisch and co-workers.¹⁵ According to both studies, the alkyl aluminum compounds convert the metallocene halides into Lewis acid adducts thereby providing a cationic metal ion and an aluminate anion. Two species were detected in NMR studies and were characterized by NMR shifts as (1) a contact ion pair and (2) a solvent separated ion pair. The contact ion pair was termed as the 'dormant' species while the solvent separated ion pair was considered active in polymerization. This equilibria is shown in Scheme II.

Scheme II: Equilibria Resulting in 'Intermittent' Growth of Polymer



(C* = active species ; Al₂ = (AlEtCl₂)₂ ; Al₂* = unknown ; P_n = polymer with n chains

aluminum
aluminum
form the
and the
(5). The
made of

I
 Cp_2ZrN
 $[\text{Cp}_2\text{ZrN}]$
abstracti
the ring

N
mixtures
coordination
the coord
complexes
olefin pol

S

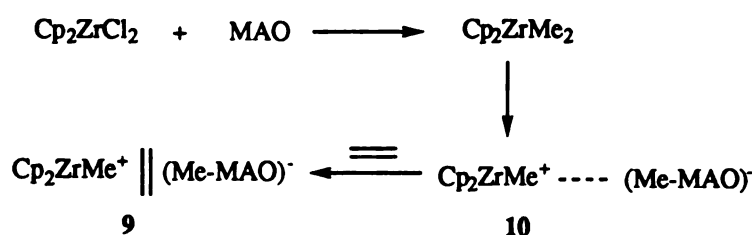
The
coordination
synthesize

Barron and co-workers have carried out detailed research on the structures of aluminoxanes.⁷ They have structurally characterized the *tert*-butyl analog compounds of aluminum (*i.e.* [RAlO]_n), where R=*tert*-butyl. According to the researchers, aluminoxanes form three dimensional cage-like clusters wherein the aluminum centers are tetracoordinate and the oxygen coordination environment involves the bridging of three aluminum atoms (5). This is in sharp contrast to the accepted notion that the methyl aluminoxane is just made of linear or cyclic oligomers of the type [MeAlO]_n.

During the study of the reaction of aluminoxane clusters like (μ-O)₆Al₆-*t*Bu₆ and Cp₂ZrMe₂ in d₈-toluene, Barron and co-workers found that complexes of the type [Cp₂ZrMe⁺... (μ-O)₆Al₆-*t*-Bu₆Me⁻] were formed which polymerized ethylene. The abstraction of the methyl anion by the aluminoxane clusters was attributed to the relief of the ring strain upon formation of the methyl complex.

Nuclear magnetic resonance studies (⁹¹Zr and ¹³C)¹⁶ and solid state XPS¹⁷ of mixtures of Cp₂ZrCl₂ and MAO indicate formation of a cation-like species, stabilized by coordinative contact with the counter ion, Me-MAO⁻ (10). However, it is presumed that the coordinative contacts for stabilization are lost in the presence of the olefin, giving rise to complexes of the type [Cp₂ZrR(olefin)]⁺A⁻ (9), which is considered as the active site for olefin polymerization. The sequence of reactions proposed are shown in Scheme III.

Scheme III: Proposed Reactions of Dimethyl Zirconocene and MAO



The idea that the active species is a cationic zirconium species along with a non coordinating anion in the zirconocene-based polymerization systems led researchers to synthesize and characterize various cationic complexes of zirconium. Homogeneous

cationic cat
 equimolar a
 $[(Cp)_2Zr(CH_3)_2]$
 activity was l



Simila
 many researc
 Many of the
 tetrahydrofura
 solvent. How
 the solvent dis
 cationic cataly
 coordinative co
 analogous to th



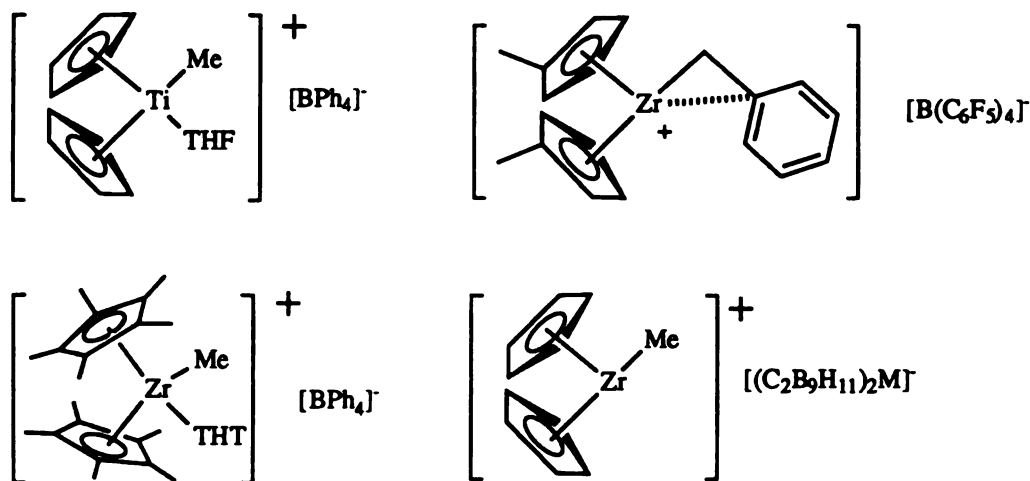
THF= Tetrahy
 M= Co, Fe, Ni

Figure 3:

cationic catalysts were synthesized by the reaction of dialkyl zirconocenes with an equimolar amount of $\text{Ag}[\text{BPh}_4]$ (eq. (1)).¹⁸ It was found that the cationic complex, $\{[\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})][\text{BPh}_4]\}$ polymerized ethylene in dichloromethane although the activity was low due to the presence of coordinating tetrahydrofuran.



Similar and modified syntheses of various cationic complexes were carried out by many researchers and the cationic compounds isolated and characterized (Figure 3).¹⁹ Many of the systems were synthesized/recrystallized in a coordinating solvent such as tetrahydrofuran, and as such, the cationic complexes were strongly coordinated to the solvent. However, it was assumed that the coordination of the solvent molecule is lost and the solvent displaced in the presence of olefin during polymerization. Crystal structures of cationic catalysts such as $[(\text{Me}_2\text{C}_5\text{H}_3)_2\text{ZrCH}_3^+ \cdots \text{H}_3\text{C}-\text{B}(\text{C}_6\text{H}_5)_3^-]$ revealed residual coordinative contacts between the cationic and the anionic site.²⁰ This was considered analogous to the interactions present in the metallocene systems *i.e.* 10.

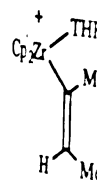


THF= Tetrahydrofuran; THT= Tetrahydrothiophene
M= Co, Fe, Ni

Figure 3: Examples of Cationic Olefin Polymerization Catalysts

It w
 prevent rap
 have been s
 coordinatin
 cationic cor
 metal atom
 and allows
 coordinates
 polymerizat
 systems due
 Polymerizat
 and/or prope

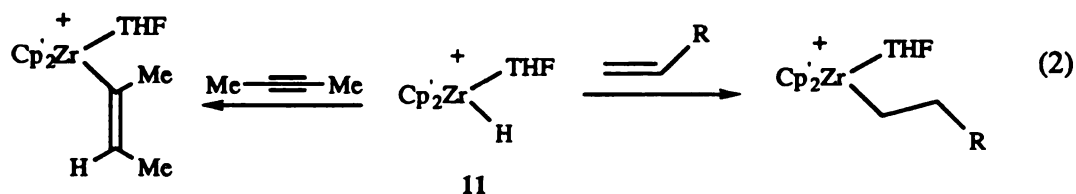
The n
 in dichlorom
 in a *cis* fashio
 dissociation o
 to be more rap
 to the increas
 solvate when
 was observed



The syn
 such as (EBI)
 ethylenebis(tetra
 and the olefin in
 the olefins betwe

It was found that the use of a bulky anion or bulky ligands on the metal helped prevent rapid degradation of the complexes. A large variety of these cationic complexes have been synthesized owing to the methodology developed for the synthesis of the 'non-coordinating' anions and their polymerization behavior were studied in detail.²¹ The cationic complexes synthesized (representative examples shown in Figure 3) consist of the metal atom which is a d^0 14 electron, coordinatively and electronically unsaturated system and allows for olefin coordination at the vacant site. It is presumed that the olefin coordinates at the vacant site and insertion occurs into the metal-alkyl bond. The cationic polymerization catalysts are considered to be surrogate systems for the aluminoxane based systems due to the indeterminate nature of the active sites in the aluminoxane systems. Polymerization studies on most of these catalysts have been carried out with ethylene and/or propene as the monomers.

The reactivity of cationic complex 11 was studied with various alkenes and alkynes in dichloromethane. It was found that the hydride adds across the double bond efficiently, in a *cis* fashion as shown in equation 2,²² and the insertion reactivity was related to the dissociation of the coordinated tetrahydrofuran ligand. The insertion of ethylene was found to be more rapid in dichloromethane than in tetrahydrofuran. This was presumed to be due to the increased steady state concentration of the naked cation or the dichloromethane solvate when the reaction was carried out in dichloromethane. Polymerization of ethylene was observed with alkenes but alkynes provided single insertion products.



The synthesis of cationic complexes was extended to *ansa* zirconocene complexes such as (EBI)ZrCl₂ and (EBTHI)ZrCl₂ [EBI= ethylenebis(indenyl) & EBTHI= ethylenebis(tetrahydroindenyl)]. The cations were stabilized with the help of 2-picoline, and the olefin insertion products were studied by Jordan and co-workers.²³ Insertion of the olefins between the metal-pyridyl bond provided azazirconacycles, as shown in eq. (3).

Thes
bond
equal

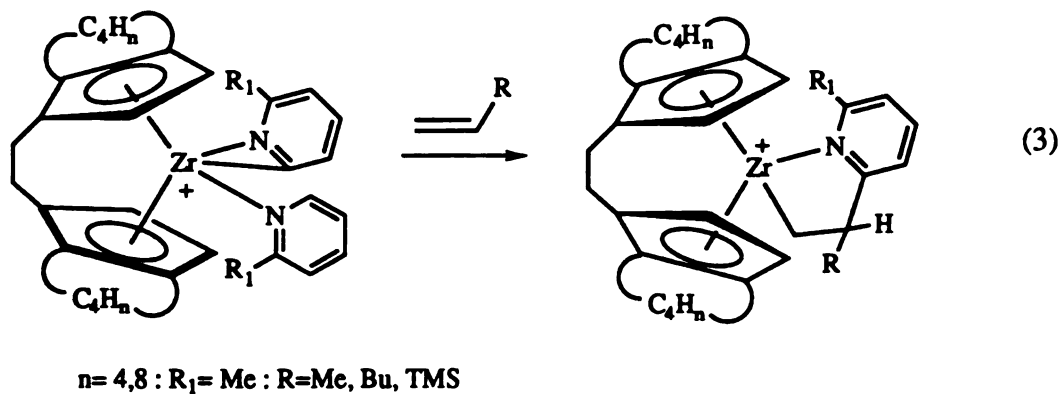
catalys
protona
zirconia
shown

Cp_2^+Z

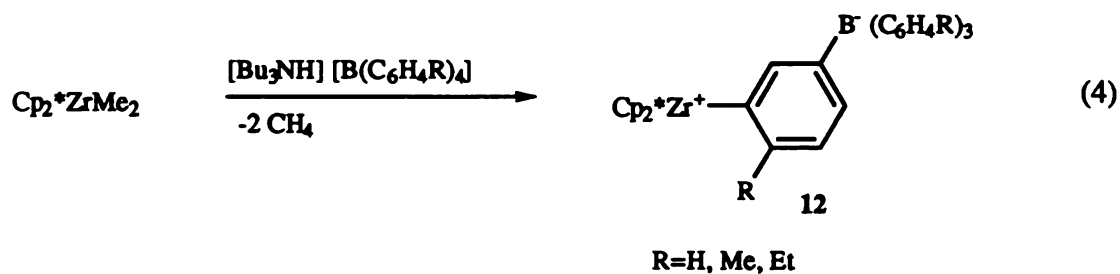
In
better th
determin
polymer.
is a distinc

Ho
oligomeriz

These results provided evidence that insertion of olefins is not limited to metal-methyl bonds, but are capable of inserting into other groups such as metal-aryl groups as shown in equation 3.



Hlatky and co-workers, while attempting to synthesize cationic zirconocene catalysts with bulky metallocene ligands such as Cp^* , discovered that the protonation of $\text{Cp}_2^*\text{ZrMe}_2$ with $[n\text{-Bu}_3\text{NH}][\text{BPh}_4]$ does not provide the expected cationic zirconium species ($\text{Cp}_2^*\text{Zr}(\text{Me})^+ [\text{BPh}_4]^-$), but afforded the zwitterionic species, 12, shown in eq. (4).²⁴



Interestingly, the species 12 rapidly polymerized ethylene and was found much better than the solvent coordinated cations discussed above. The authors could not determine if the tetraphenyl borate anion was incorporated as the head group of the polymer. This study also provided evidence that insertion of olefins into metal-aryl bonds is a distinct possibility and cannot be ruled out.

Horton and co-workers found that peralkylated zirconocene cations rapidly oligomerized and dimerized alkynes, while such activity was diminished (>17%) when less

sterical
ligands
isolated
pathway
cation d

$[Zr(C_5Me_5)_2]$

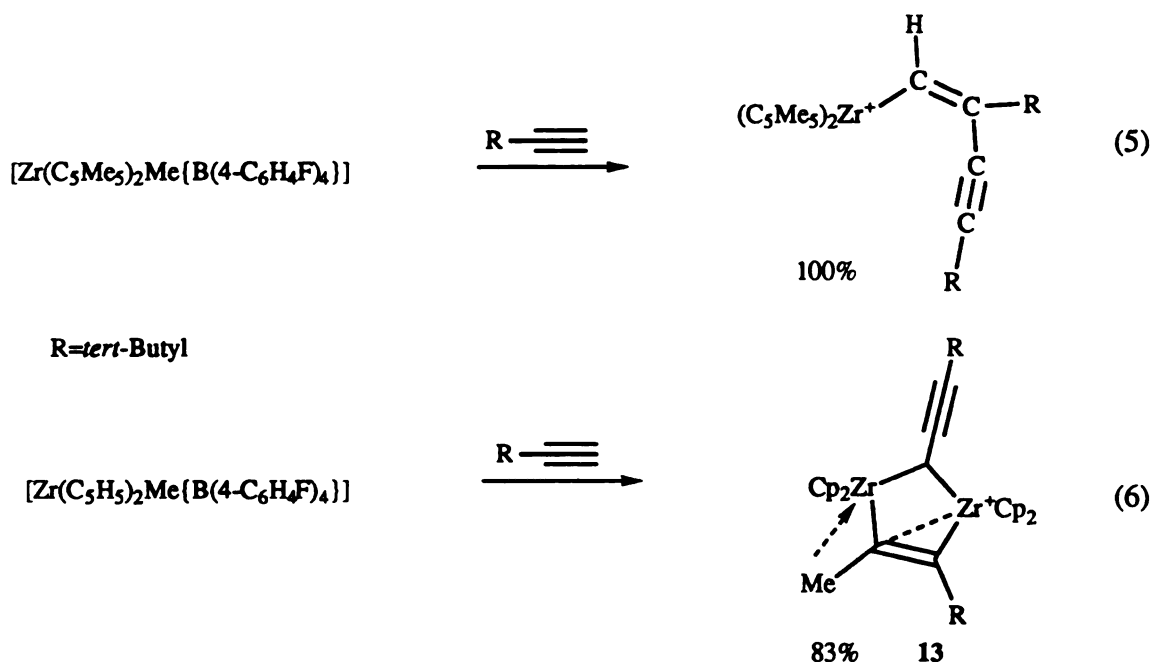
$R=tert$

$[Zr(C_5H_5)_2]$

Cy

such as the
studies in
rationale b
decomposi
surrogate to
dichloride/
sterically hi
indicate that
the activitie
activities of
traditional zi

sterically hindered metallocene catalysts were used (eq. 5).²⁵ Instead, when less hindered ligands (cyclopentadienyl) were used, a binuclear electron deficient cation, **13**, was isolated as the major product (eq. 6). The authors suggested that this forms a major pathway for deactivation of metallocene catalysts especially since the sterically congested cation did not yield such a binuclear cation.



Cyclopentadienyl ligands do not offer steric congestion when compared to ligands such as the indenyl or the pentamethyl cyclopentadienyl ligands. However, most of the studies in polymerization of cationic complexes have sterically hindered ligands. The rationale behind this is to prevent a strong coordination of the anion and to avoid any decomposition by binuclear reactions. As mentioned above, these systems are considered surrogate to bis(cyclopentadienyl) titanium dichloride or bis(cyclopentadienyl) zirconium dichloride/methyl aluminoxane systems. Correlation of results from the studies on sterically hindered cationic systems and the traditional titanocene or zirconocene systems indicate that at the most, the polymerization activity of the cationic complexes approached the activities of the $\text{Cp}_2\text{TiCl}_2/\text{MAO}$ or $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ systems. In most cases, the activities of the cationic complexes were far less or comparable to the activities of the traditional zirconocene/MAO systems.

differe
between
system
when
eviden
as to
regene
system
compo

GOAL

the hor
polyme
Polyme

1)

2)

3)

4)

5)

Pr

Studies with cyclopentadienyl metal systems sometimes have provided dramatically different results and rationalization of these results have proven difficult. As such, analogy between the cationic metal catalytic systems and the titanocene or zirconocene/MAO systems should be approached with an open mind since many different pathways may arise when MAO or aluminum based co-catalysts are used. Although there is overwhelming evidence that a cationic metal species is responsible for polymerization, the rationalization as to how the active center is generated, the different pathways for degradation or regeneration of the active species, etc., are still not known for the methyl aluminoxane systems. A systematic approach involves a careful study of evidence, synthesis of model compounds, and study of their behavior towards olefin polymerization.

GOALS

The aim of this work was to elucidate and mimic the actual intermediate involved in the homogeneous catalyst/MAO systems and to reduce the amounts of MAO required for polymerization of olefins. A primary goal was to synthesize a 'Single Component Polymerization Catalyst', with the following features :

- 1) The catalyst design should include the features of both a catalyst and a co-catalyst in a single molecule.
- 2) The catalyst should be able to polymerize olefins without the aid of a co-catalyst (MAO) or be able to polymerize olefins with significantly lower equivalents of MAO than currently required.
- 3) The synthesis should allow systematic variation of the electron density around the base metal atom and, as such, allow study of structure-polymerization activity relationship.
- 4) The synthetic route should allow for variation of electron density and sterics around the metal atom so as to include chirality on the metal center.
- 5) The catalyst should be able to generate a cationic and anionic species *in situ*, in the presence of olefin.

6)

EVOLU

remains
alkyls as
aluminum
structure

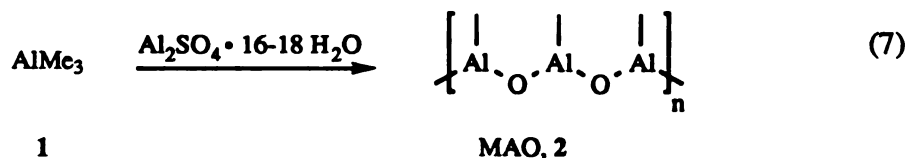
In
efficiency
stereoche
typically
compound

Th
catalyst i
enhance/e
active cata
for signific
of a single
catalyst/co-

- 6) The reactivity of these novel compounds towards olefin insertion and polymerization synthesized should help elucidate the mechanism of Ziegler-Natta polymerization.

EVOLUTION OF CONCEPT

As mentioned in the foregoing discussions, the role of MAO as a co-catalyst remains mystical. The discovery of MAO led to the replacement of traditional aluminum alkyls as the co-catalyst of choice. MAO is obtained by partial hydrolysis of trimethyl aluminum (AlMe_3 , 1) (eq. 7).²⁶ This results in oligomeric, cyclic or three dimensional structures of the type $[-\text{Al}(\text{Me})\text{O}-]_n$.



In concert with metallocene catalysts, this mixture produces a high degree of efficiency and selectivity in the polymerization of olefins and exceptionally high stereochemical control in polypropylene formation. However, these catalyst/MAO systems typically require 1,000 to 3,000 fold equivalents of MAO with respect to the metallocene compound to achieve such selectivities.

The rationale for the extreme excess equivalents include; (1) removal of poisons or catalyst inhibitors present as impurities in the monomer stock (2) the need to enhance/expedite the rate limiting activation of the catalyst and/or (3) stabilization of the active catalyst once it is formed. A greater understanding of these processes would allow for significant reduction of the amounts of MAO required and eventually allow the design of a single component Ziegler-Natta catalyst with features characteristic of the active catalyst/co-catalyst species.

Inter
polymeriza
for a dimeth
The initial
component
from the m
species (1
aluminoxan
discussion.

In a
Transmetall
which could
involve α -H
bridged spec
methyl grou
same M-X-X
the transfer o

Com
stabilizing t
consisting of
though imp
polymerizati

Interaction of MAO with a metallocene catalyst provides an active catalyst for polymerization. A number of possibilities exist for such activation. Some of the pathways for a dimethyl metallocene (14) and methyl aluminoxane (2) are illustrated in Scheme IV. The initial interaction is thought to be the coordination of MAO to the transition metal component to form a Lewis acid coordination complex 15. The transfer of a methyl group from the metal center to MAO could occur, generating a positively charged metallocene species (16), stabilized coordinatively by a complex, bulky, methylated methyl aluminoxane anion. This is the generally accepted pathway as stated in the foregoing discussion.

In addition to the above pathway, alternative pathways can also be envisaged. Transmetallation with the methyl aluminoxane could generate a oxygen bridged species 17, which could exist in equilibrium with a cationic active species 21. A related pathway could involve α -H activation of an alkyl group on the catalyst through 18 to generate methylene bridged species (19 and 20). This process could occur preferentially with either a terminal methyl group (19) or an internal methyl group (20) on the MAO co-catalyst mixture. This same M-X-Al type species could provide a route to the active anion/cation complex 22, by the transfer of a methyl group from the metal atom onto the aluminoxane chain.

Compound 22 would be similar to 21 except that instead of coordinative contacts stabilizing the cation in 21, the zwitterionic complex 22 would be a single molecule consisting of the active cationic species. A review of literature in this regard indicates that though implicated, heterobimetallic species have rarely been studied as olefin polymerization catalysts.

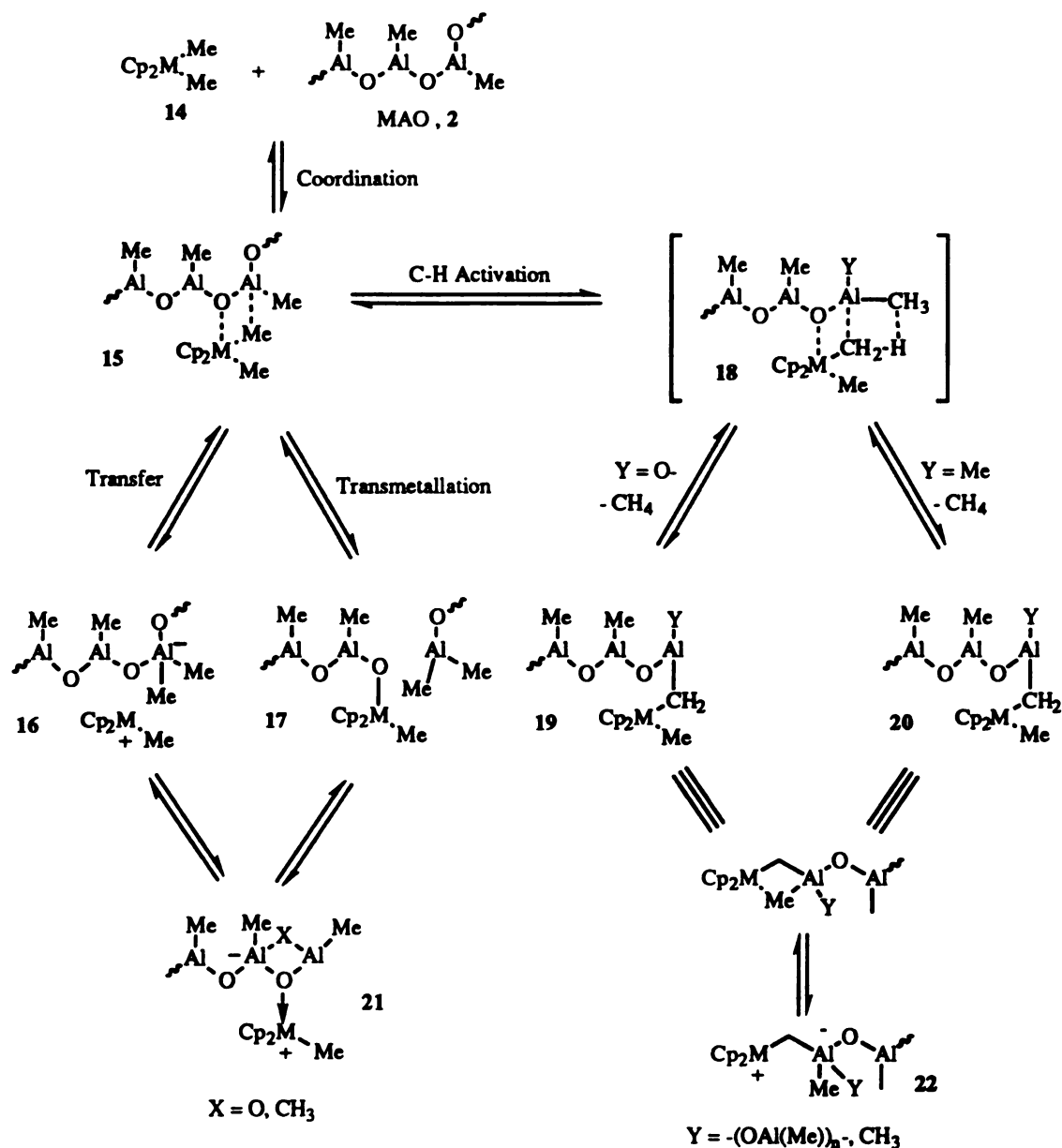
Schem



16 Cp

EVIDENC

In th
mechanistic
general inter
being hetero

Scheme IV : Possible Intermediates in the Reaction of MAO with Cp_2MR_2

EVIDENCE

In the preceding sections, a number of theories, model compounds, and mechanistic concepts were discussed wherein a cationic active site was postulated as a general intermediate for all metallocene-aluminoxane systems. The role of active sites being heterobimetallic in nature has been postulated in the heterogeneous Ziegler-Natta

system
compos
heterob

the met
methane
methane
soluble
monome
consequ
possibili
the poly
catalytic
tetrahydr
taken to
coordina
the prim
complex
tetrahydr

T
methyl c
adducts,
chloride
8-10). T
(24) and
8). The
identical
on this e
trimethyl

systems, however, the polymerization behavior of homogeneous heterobimetallic compounds have not been studied. Various evidence in the literature points to a heterobimetallic active site in olefin polymerization, some of which are listed herein.

It is known that methane gas is released when methyl aluminoxane is mixed with the metallocene catalyst.²⁷ Kaminsky and co-workers have observed a steady liberation of methane from MAO-activated zirconocene catalysts, which reached up to 50 equivalents of methane per zirconium center.²⁸ In general, the catalyst and the co-catalyst (MAO) in soluble polymerization systems needed to be premixed for at least fifteen minutes before the monomer was introduced to observe efficient polymerization. This requirement and the consequent delay in the catalytic activity of these systems remains unexplained. The possibility of a cationic mechanism wherein the aluminoxane acted as a bulky anion while the polymerization occurred on the cationic metal atom does not explain this delay in catalytic activity. The presence of minute amounts of coordinating solvents, such as tetrahydrofuran or diethyl ether, poisoned the catalyst and extreme precautions must be taken to avoid these impurities in the methyl aluminoxane systems. An irreversible coordination of a donor solvent molecule to a cationic species generated was considered as the primary reason for the donor solvents being a poison. However, various cationic complexes with coordinated solvent molecules such as tetrahydrofuran and tetrahydrothiophene have been synthesized and found to polymerize ethylene efficiently.

Tritto and co-workers undertook a systematic study of the interaction of titanocene methyl chloride (**23**) with MAO.²⁹ In order to study the formation and the nature of Ti/Al adducts, they monitored the ¹H and ¹³C NMR spectra of mixtures of titanocene methyl chloride (**23**) with trimethyl aluminum and MAO at different ratios and temperatures (eq. 8-10). The reaction of **23** with trimethyl aluminum at -70 °C provided dimethyl titanocene (**24**) and a new complex **25**, with ¹³C chemical shifts at 117.08 ppm and 60.22 ppm (eq. 8). The reaction of MAO with **23** at -70 °C provided **24** in 86% yield while under identical conditions trimethyl aluminum gave only a 2% yield of **24** (eq. 8 and 9). Based on this evidence, the authors concluded that MAO was a better alkylating agent than trimethyl aluminum.

Compound	$\mu\text{-CH}_2$	Cp's	Al-Me
(27)	8.28 (s, 2 H)	5.62 (s, 10 H)	-0.29 (s, 3 H)
(28)	7.66-7.63 (d, 1 H) 7.33-7.30 (d, 1 H)	5.49 (s, 5 H) 5.45 (s, 5 H)	-2.24 (s, 3 H)

The reaction of MAO with **23** at -70 °C resulted in a new complex **26**, with ¹³C chemical shifts at 117.96 and 64.6 ppm (eq. 9). The downfield shift of **26** when compared to **25** indicated that there was a further decrease in the electron density at the metal center when MAO is complexed with the metallocene catalyst. At 10 °C, additional resonances were seen. These were assigned to the so called 'Tebbe reagent', **27** and the methyldiene complex **28**, generated by an α-H abstraction by a methyl group (eq. 10).

Table II: ^{13}C NMR Shifts (in ppm) of Compounds in Equations 8-10

Compound	$\mu\text{-CH}_2$	Cp's	Ti-Me
$\text{Cp}_2\text{Ti} \begin{smallmatrix} \text{Me} \\ \diagup \\ \text{Cl} \end{smallmatrix} \text{ (23)}$		115.52	49.32
$\text{Cp}_2\text{Ti} \begin{smallmatrix} \text{Me} \\ \diagup \\ \text{Me} \end{smallmatrix} \text{ (24)}$		113.16	46.25
$\text{Cp}_2\text{Ti} \begin{smallmatrix} \text{Me} \\ \diagup \\ \text{Cl} \end{smallmatrix} \cdot \text{MAO} \text{ (26)}$		117.96	64.6
$\text{Cp}_2\text{Ti} \begin{smallmatrix} \text{Me} \\ \diagup \\ \text{Cl} \end{smallmatrix} \cdot \text{AlMe}_3 \text{ (25)}$		117.15	60.51
$\text{Cp}_2\text{Ti} \begin{smallmatrix} \diagup & \diagdown \\ & \text{Al} \\ \diagdown & \diagup \\ & \text{Cl} \end{smallmatrix} \text{ (27)}$	188.06	112.28	-4.11
$\text{Cp}_2\text{Ti} = \text{CH}_2$ $\swarrow$ $\text{MAO} \text{ (28)}$	178.98	112.98	-10.73

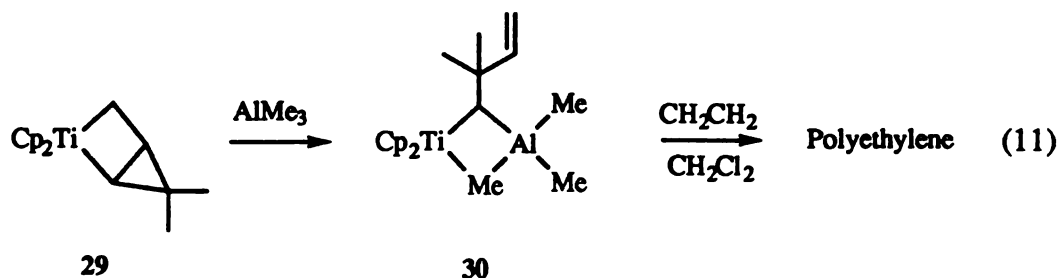
The authors also noted that at $\text{Al/Ti}=10$, the formation of Tebbe reagent, **27**, was faster with MAO than with AlMe_3 . With regard to the complex **28**, the authors observed that such a complex was not formed when trimethyl aluminum was reacted with **23**. Interestingly, at 10°C the predominant products were the alkylidene complex, **28**, and the Tebbe reagent, **27**, constituting 92% of the reaction products.

The experiments carried out by the authors led them to conclude that the active species in the MAO based catalytic system was the complex **26**, which had characteristics closer to a cation-like species. With regard to the other products (**27** and **28**), the authors did not consider them responsible for polymerization, but suggested that more study was needed to determine the role of the alkylidene complexes that are known active metathesis catalysts.

Resconi and co-workers also investigated the role of methyl aluminoxane in homogeneous olefin polymerization.³⁰ It is well known that methyl aluminoxane, despite repeated purifications, still retains some unreacted, strongly bound trimethyl aluminum (**2**).

Based on the yields of polymer obtained, the authors concluded that the bound trimethyl aluminum is the actual co-catalyst in MAO based systems and that the role of MAO is limited to a soluble carrier-activator of the ion pair formed upon reaction of the metallocene with trimethyl aluminum.

Grubbs and Tritto studied the reactions of titanacyclobutanes as ring opening polymerization catalysts.³¹ The reaction of trimethyl aluminum with metallacycle **29** provided the bimetallic alkylidene bridged complex **30** (eq. 11). The authors found that this bimetallic complex polymerized ethylene in the absence of any co-catalyst when dichloromethane was used as solvent. The authors concluded that the requirement of dichloromethane as a solvent for polymerization indicated that the active species in Ziegler-Natta polymerizations has an ion-pair like nature. Neither the details of polymerization nor the nature of active species generated in dichloromethane responsible for polymerization, were discussed by the authors.



Hoffmann and Lauher constructed molecular orbitals for various bis(cyclopentadienyl) metal complexes by extended Huckel calculations.³² They found that there were three valence molecular orbitals $1a_1$, b_2 and $2a_1$ lying in the yz plane and were available for bonding. This allowed three ligands ($2e^-$ donors) to be coordinated to the central metal atom. The presence of these orbitals have been confirmed by other experimental studies. Green and co-workers have carried out photoelectron studies and demonstrated clearly that there were two nonbonding orbitals for Cp_2MX , one nonbonding molecular orbital for Cp_2MX_2 and none for Cp_2MH_3 .^{32b-c}

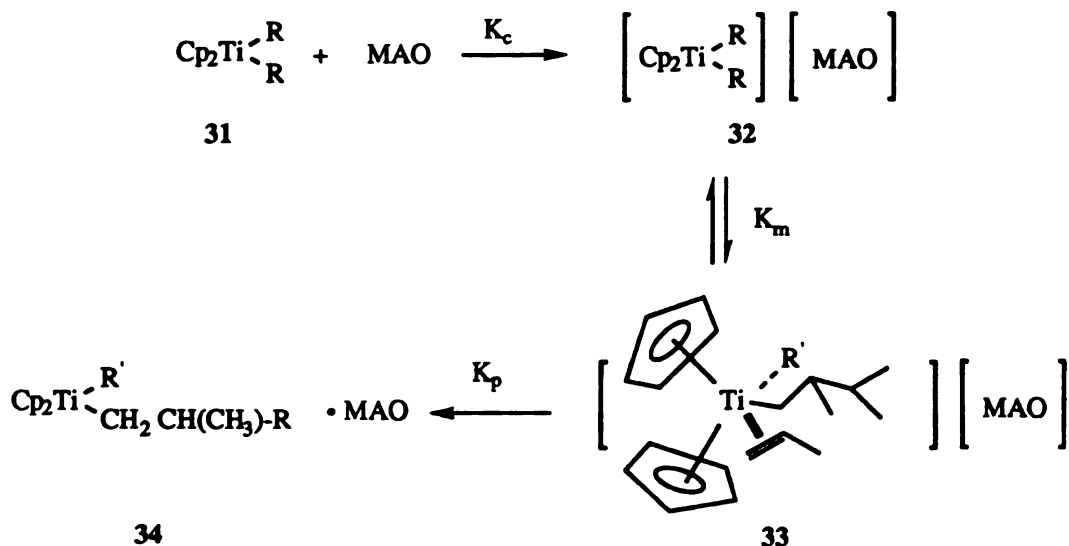
Ewen investigated the mechanism of stereochemical control in propylene polymerizations with soluble metallocene catalysts with methyl aluminoxane as the co-

catal
postu

formal
32. T
authors
ruled o
cyclope
between
33). T
alumin
site wou
in an eq
(IV) me
structure
carbama

catalyst.³³ The mechanism considered for this study was analogous to the mechanism postulated for titanocene derivatives with ethyl aluminum dichloride (EtAlCl₂) (Scheme V).

Scheme V: Proposed Mechanism for Propylene Polymerization

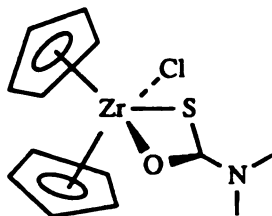


Compounds **31** and **34** are coordinatively unsaturated Ti(IV) complexes which are formally d^0 16 electron species. The co-catalyst MAO forms a complex with **31**, giving **32**. The exact nature of the species **32** has still not been identified and, as such, the authors denoted this ligand as R' and suggested that a bimetallic nature of **32** cannot be ruled out. Coordination of the monomer could occur at an a_1 orbital and the three non cyclopentadienyl ligands occupy a common equatorial plane with the growing chain held between the two lateral coordination sites (i.e. those occupied by R' and monomer, as in **33**). The studies on sterically hindered metallocene catalysts indicated that a bulky aluminoxane could be ruled out as a ligand since the coordination at the sterically hindered site would be difficult. The basic geometry of **33**, with three non-cyclopentadienyl ligands in an equatorial plane, is supported by isolation of pentacoordinate compounds of group (IV) metallocene compounds. Fay and co-workers have isolated and published crystal structures of pentacoordinate bis(η^5 -cyclopentadienyl) chloro-(*N,N*-dimethylmonothio-carbamato)zirconium(IV) (**35**).³⁴

dichlor
metallic
Follow
methan
that aft
place w
product
polyme
aluminu

NMR.
authors
Scheme
39. Zirc
(40), w
Loss of
to 41 by

reached
Further,
thorough
been sug

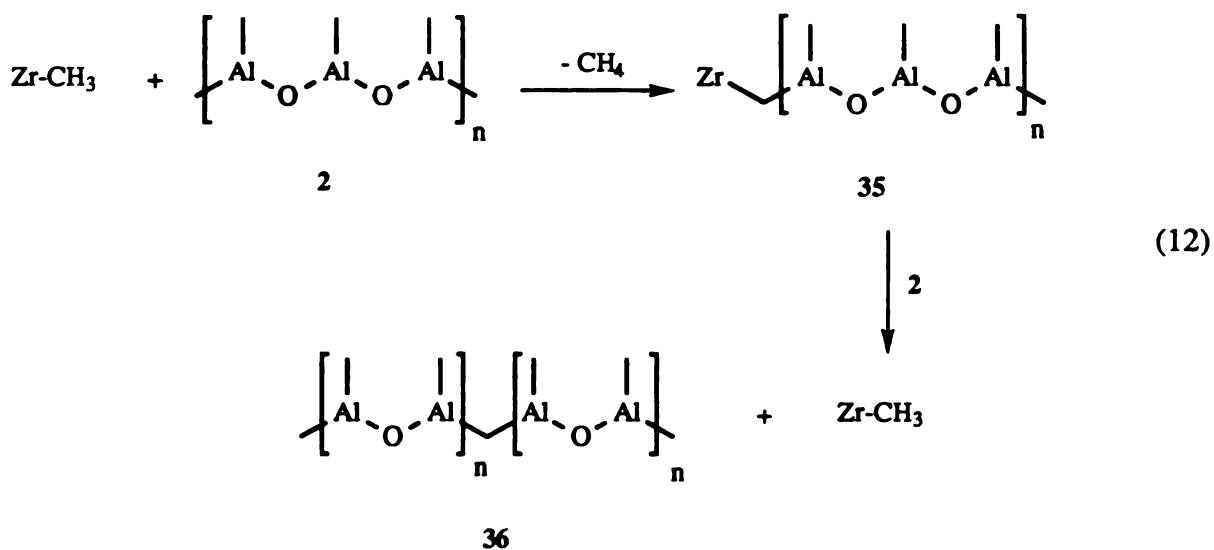


35

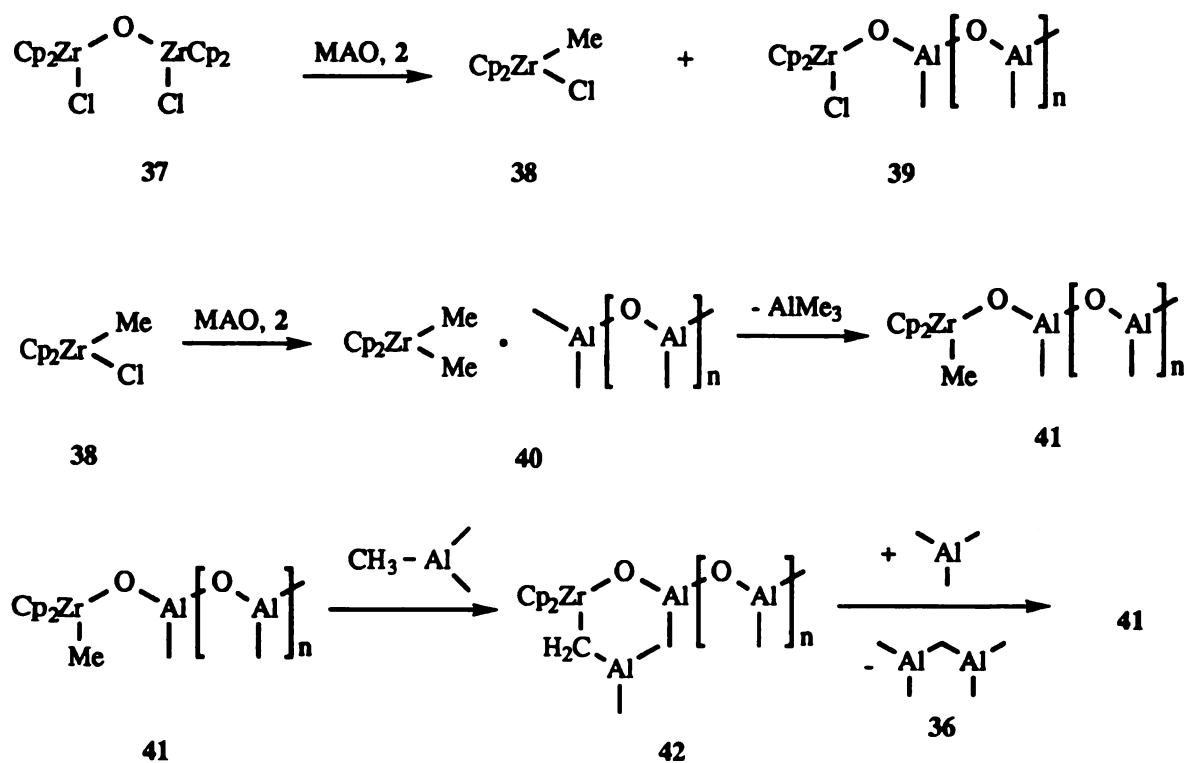
Kaminsky and co-workers studied the interaction of MAO (2) with zirconocene dichloride by infrared spectroscopy (eq. 12).³⁵ At temperatures as low as -60 °C, the metallocene and aluminoxane formed a complex, resulting in a new absorption at 400 nm. Following the complexation, rapid alkylations and loss of methane took place. The loss of methane occurred faster with MAO than with trimethyl aluminum. The authors suggested that after initial complexation, a condensation between the metallocene and MAO takes place with consequent loss of methane. An excess of MAO resulted in acceleration of the production of methane. The Zr-CH₂-Al (35) structures were deemed to be inactive for polymerization, and regeneration of the catalyst occurred by transmetallation onto aluminum resulting in Al-CH₂-Al structures (36).

The study also investigated the interaction of zirconocene compounds with MAO by NMR. The use of various zirconium compounds provided similar signals with MAO. The authors suggested a variety of reactions to explain the observed signals, as shown in Scheme VI. The reaction of 37 with MAO provided zirconocene methyl chloride (38) and 39. Zirconocene methyl chloride was converted to dimethyl zirconocene-MAO complex (40), which loses trimethyl aluminum and provides the oxygen bridged compound 41. Loss of methane with trimethyl aluminum provides compound 42, which is converted back to 41 by transmetallation.

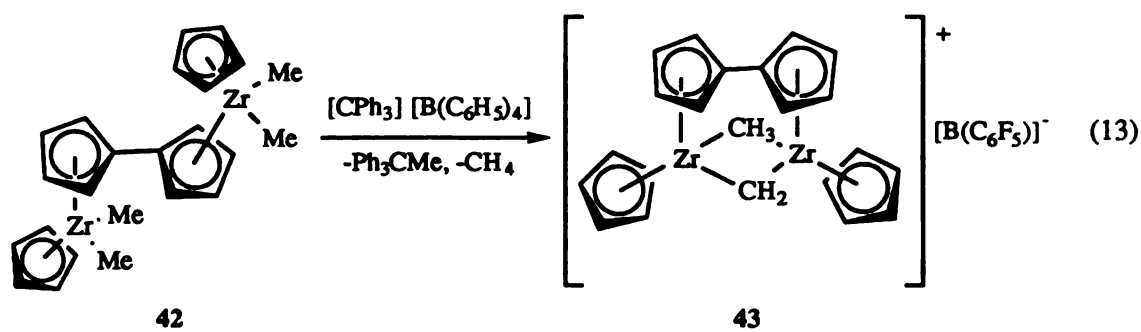
The authors, however, did not provide any experimental data for the conclusions reached above and commented that the reactions shown in Scheme VI were still too simple. Further, the authors suggested that the structure of MAO needs to be investigated more thoroughly for the picture to be more concrete. Similar heterobimetallic structures have been suggested by Nekhaeva and co-workers.^{35b}



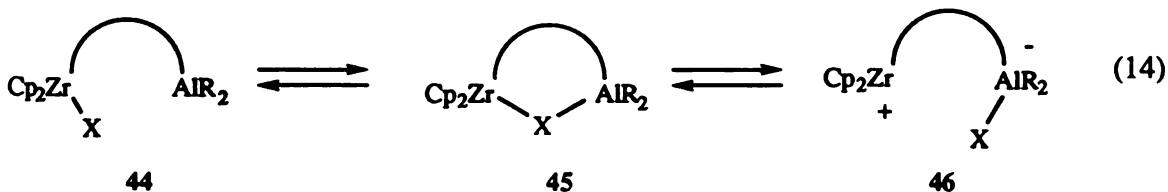
Scheme VI: Reactions of Zirconocene Compounds with Methyl Aluminoxane



Bochmann and co-workers reported formation of binuclear complexes such as **13** (eq. 6) while attempting to oligomerize alkynes with cyclopentadienyl cationic zirconium catalysts.³⁶ When the same authors attempted to prepare cationic catalysts with fulvalene ligands, a methylene bridged complex, **43**, was formed in 87% yield. (eq. 13). They suggested that the μ -methylene bridged complex is a possible deactivation pathway in the cationic zirconium based catalysts. However, when polymerization studies were carried out with **43**, it was found to be an efficient catalyst for ethylene polymerization, although it was an order of magnitude lower in the rate of polymerization than that of other zirconium cationic catalysts reported.

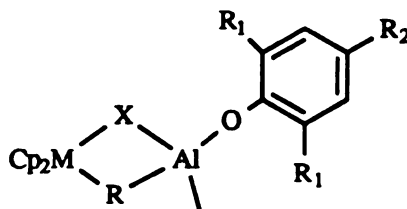


Erker and co-workers have implicated a betaine structure as the key species responsible for polymerization in zirconium/aluminum systems.³⁷ Although no conclusive proof was offered, the authors claimed that based on the evidence offered by the studies on various cationic complexes, it is possible that a bridged dimetallic species could be designed which though neutral, could be converted into a cation-anionic species through an intramolecular mechanism. The sequence of reactions suggested are shown in eq. 14.



MODEL FOR SINGLE COMPONENT POLYMERIZATION CATALYST

The evidence presented above strongly suggests that a bimetallic species could be envisaged as an active polymerization catalyst in the metallocene/aluminum based polymerization systems. Based on this assumption, a single component catalyst, **47**, was designed.



47 : M = Ti, Zr ; X = O, CH₂ ; R = Me ; R₁ = *tert*-butyl ; R₂ = Me, *tert*-butyl, H, Br

The bimetallic compound **47** consists of a dicyclopentadienyl titanium or zirconium connected to an aryloxy methyl aluminum *via* an oxygen or a methylene bridge. These compounds would mimic intermediates **21** and/or **20**, proposed in Scheme IV. The R₂ group could be varied at will with the proper choice of functional groups. This would help vary the electron density on the aluminum atom and sufficiently destabilize the M-R bond so as to produce a zwitterionic structure analogous to **22** proposed in Scheme IV. The R₁ group was chosen to be *tert*-butyl to sterically hinder any dimerization or ligand exchange. Upon optimization of the synthesis of these compounds, various other ligands could be used instead of cyclopentadienyls, thereby introducing stereochemistry on the metal center.

In addition to the above rationale, the synthesis of such compounds have not been reported in the literature. As such, the synthesis of such compounds would, in itself, pose a challenge and the structure of such compounds would add to the knowledge of the expanding research area of heterobimetallics.

Although implicated, the hypothesis that a bridged bimetallic species, i.e. Ti-X-Al, is an active species for polymerization of olefins in the methyl aluminoxane based systems

has not
synthesi

(a) 1
compare

(b) 7
made w
cationic
metallo

(c) 7
insertion
insertion

has not been proven. This hypothesis could be tested in many ways concurrent to the synthesis of these catalysts.

(a) Polymerization of olefins could be carried out and the polymerization ability compared to conventional catalysts.

(b) The interaction of MAO with the catalysts could be studied and a determination made whether the bridge between the metal and the aluminum atom is broken to generate a cationic and an anionic species as thought of and reflected in many of the cationic metallocene catalysts discussed above.

(c) The interaction of the catalysts with olefins could be studied to determine the insertion steps and the reaction products characterized so as to determine the mechanism of insertion into these bridged metallocene catalysts.

CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF HETEROBIMETALLIC OLEFIN POLYMERIZATION CATALYSTS

OXYGEN BRIDGED SYSTEMS

As mentioned in the introduction, the aim of this project was to synthesize a bridged heterobimetallic complex consisting of a main group IV metal atom bridged *via* an oxygen or a methylene group to a substituted aluminum moiety. The first attempts towards such a goal was directed towards the synthesis of an oxygen bridged systems.

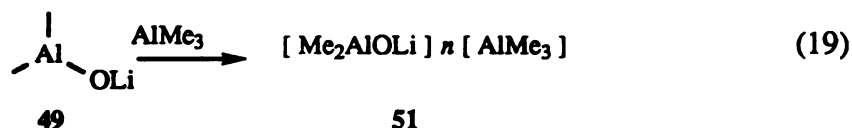
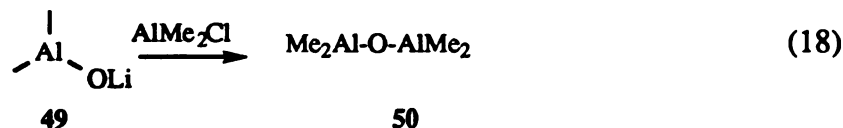
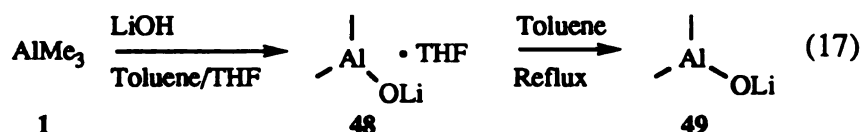
Oxygen bridged of titanium/zirconium systems with aluminum have not been reported in the literature. Although hydrolysis of titanocene methyl chloride with water provides a complex polymeric titanium oxide, the structure and properties of the compounds are not known. The synthesis of a Ti/Zr-O-AlR₃ systems would logically involve the synthesis of the transition metal-oxygen bond by simple displacement of a chloride or any other leaving group as shown in equation 15. Alternatively, the metal-oxygen bond could be kept intact, while the oxygen-alkyl bond could be cleaved by proper selection of reagents, and replaced with aluminum alkyls as shown in equation 16.



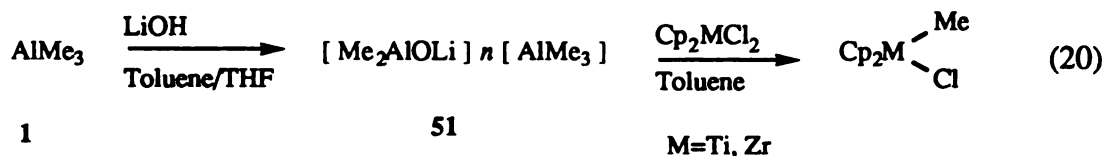
Although there could be many other pathways designed for the synthesis of the oxygen bridged systems, these two pathways were envisaged for their simplicity and ease

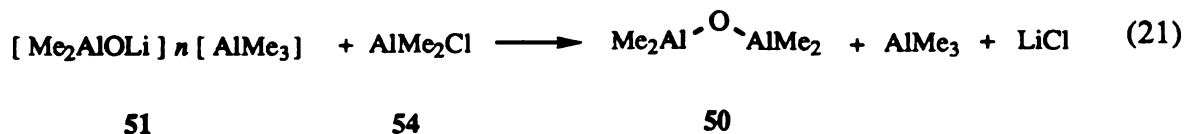
of execution. The attempts to synthesize the oxygen bridged systems and their transient nature are reported herein briefly.

Araki and co-workers carried out detailed studies on deprotonation of alkyl aluminum compounds with lithium hydroxide and sodium hydroxide.³⁸ The authors claimed to have isolated the compound **48**, a tetrahydrofuran complex. The salt **48** was stripped of the coordinated tetrahydrofuran by heating to reflux in toluene (eq. 17) to provide **49**. The authors carried out substitution reactions of **49** with dimethylaluminum chloride to provide dialuminoxane **50** (eq. 18).

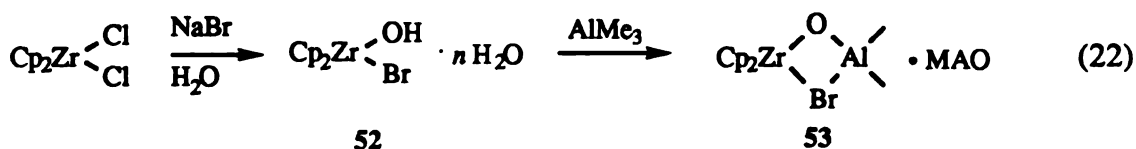


Following literature procedures, attempts were made to prepare **49**. However, the reaction of trimethyl aluminum with alkali hydroxide invariably provided the 'ate' salt, **51** (eq. 19). When **51** was treated with titanocene dichloride or zirconocene dichloride the products were characterized as titanocene methyl chloride and zirconocene methyl chloride (eq. 20). It is quite plausible that Araki and co-workers did manage to synthesize the compound **50**, *via* **51** since the reaction of **51** with AlMe_2Cl would provide **50**, albeit not in the way suggested by the authors, (eq. 21).

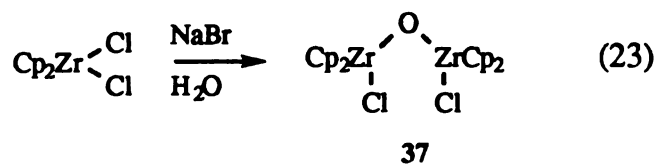




It has been reported that the reaction of sodium bromide or sodium iodide with zirconocene dichloride in water provides $\text{Cp}_2\text{Zr}(\text{OH})\text{X} \cdot n\text{H}_2\text{O}$ (eq. 22).³⁹ Compound 52, when treated with trimethyl aluminum could conveniently provide the desired oxygen bridged species 53 while the by-product, MAO, could easily be separated. The evidence for this product was the infra red spectrum which did not show a peak at 750 cm^{-1} , characteristic of Zr-O-Zr species.^{39b}

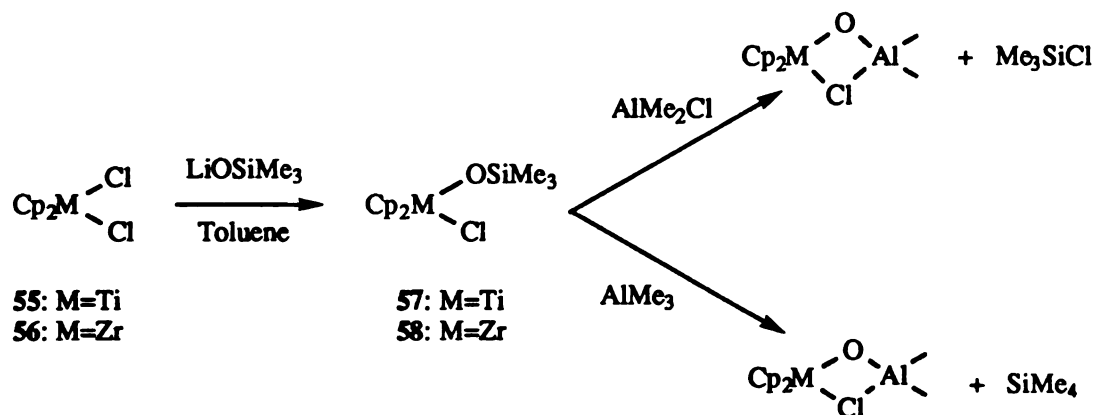


Synthesis of 52 was attempted by the reaction of zirconocene dichloride with sodium bromide in water (eq. 23). The product isolated and characterized was found to be 37, characterized by an infra red peak at 750 cm^{-1} and its mass spectrum. The formation of 52 was not detected.

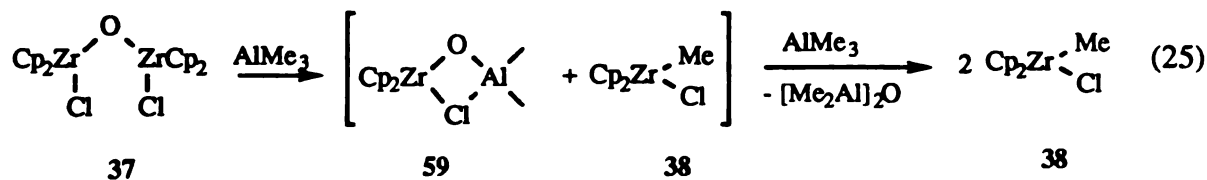
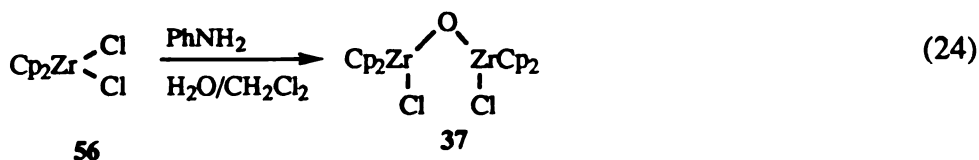


Attempts were made to synthesize the oxygen bridged systems by the metathesis of oxygen-silicon bond as shown in Scheme VII. The reaction of TMSOLi with titanocene dichloride and zirconocene dichloride provided 57 and 58, respectively. The products 57 and 58 were refluxed either with AlMe_2Cl or AlMe_3 in toluene but the reaction led to complex mixtures of products with no product predominant.

Scheme VII : Attempted Synthesis of Oxygen Bridged Systems



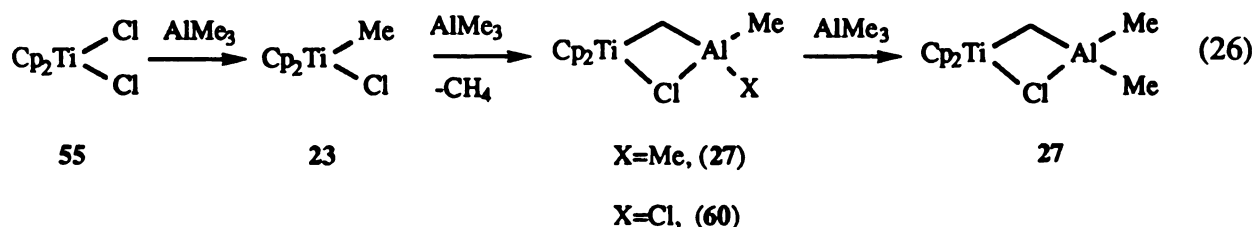
Surtees has reported that the reaction of 37 with two equivalents of trimethyl aluminum provided two equivalents of zirconocene methyl chloride (eq. 25).⁴⁰ The mechanism of this reaction was thought to proceed *via* the initial coordination of trimethyl aluminum onto the bridged oxygen and transfer of a methyl group onto the metal and consequent breaking of the bridged oxygen providing the intermediate 59. Attack of another molecule of trimethyl aluminum provides the dialuminoxane 50 and another equivalent of zirconocene methyl chloride, 38. The fact that the intermediate of this reaction was an oxygen bridged species led us to attempt this reaction and stop it at its intermediate stage. Compound 37 was prepared by the reaction of zirconocene dichloride with aniline/H₂O in excellent yields (eq. 24).³⁹ The product 37 was characterized by a peak at 750 cm⁻¹ peak in the infra red spectrum and also by its mass spectrum. Compound 37 was then treated with one equivalent of trimethyl aluminum and the only isolable products were zirconocene methyl chloride, 38 (eq. 25). Repeated attempts to isolate the intermediate by use of less polar solvents such as hexanes, toluene and low temperatures (-70 °C) failed to provide any products than other 38. Attempts to detect the intermediate by following the reaction in a NMR tube failed to provide any conclusive results. This can be explained by the fact that the dialuminoxane 50, a by-product, is as reactive as the trimethyl aluminum and probably reacts rapidly with any intermediate 59 formed in the reaction, or that the compound 59 is more reactive towards AlMe₃ than the compound 37. These results indicated that the zirconium-oxygen-aluminum bridge is fairly unstable and readily collapses to a more stable zirconocene methyl chloride.



Various attempts were made to synthesize, isolate and characterize the heterobimetallics of titanium/zirconium bridged *via* oxygen to aluminum alkyls. However, the desired heterobimetallic products were not obtained. Although thought of as an intermediate in some reactions, no precedent appears in the literature wherein such bridged heterobimetallic species of transition metals with group IV metals have been synthesized and/or characterized. Apparently, such a species is quite unstable and readily reacts with itself to provide the corresponding metallocene methyl chloride species.

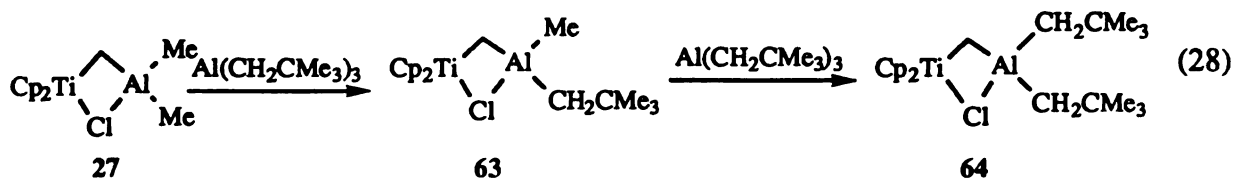
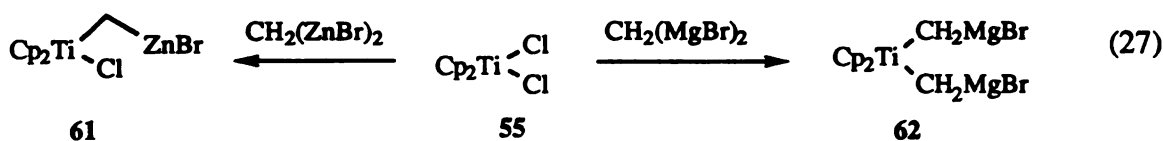
METHYLENE BRIDGED COMPOUNDS OF TITANIUM WITH ALUMINUM

Organometallic alkylidene complexes containing ligands with structural types M-CR₂-M and M=CR₂ have been extremely useful in organic synthesis. Stille has recently published a review of metal carbene complexes and their use in organic synthesis.⁴¹ The Tebbe reagent has been widely used as a methylenating agent for carbonyl groups.



Synthesis of the Tebbe reagent involves reaction of titanocene dichloride (**55**) with two equivalents of trimethyl aluminum providing an equilibrium mixture of **27** and **60** (eq. 26). The reaction is driven to completion by a second treatment of trimethyl aluminum providing **27** in high yields.^{42a} The reaction, carried out under inert atmosphere, requires about 60 hours for completion.

The mechanism of the formation of the Tebbe reagent is thought to involve an α -H abstraction of the titanocene methyl group, obtained by transmetallation from trimethyl aluminum.⁴³ In addition to the Tebbe reagent, various other methylene bridged heterobimetallics have been synthesized. These include **61** and **62** which have been prepared by the use of methylenedizinc⁴⁴ or methylenedimagnesium species respectively (eq. 27).⁴⁵ Tebbe and co-workers have reported the synthesis of **64** prepared by ligand exchange with tri-*neo*-pentyl aluminum (eq. 28).^{42b}



Although the Tebbe reagent is widely used in organic synthesis, no literature precedent exists for the synthesis of substituted Tebbe reagents with a heteroatom on the aluminum center. The synthesis of such compounds could add to the selectivity of the Tebbe reagent and could also provide differential reactivity between an ester carbonyl and aldehyde carbonyl groups. The aim of the synthesis of a substituted Tebbe reagent was two fold: a) to provide a general route towards all substituted Tebbe reagents, with substitution at the aluminum center and b) to study the activity of the resultant compounds and compare them to the Tebbe reagent. Since the formation of the Tebbe reagent involves an α -H abstraction, conceivably such an abstraction could be carried out with other alkyl aluminum compounds as shown in equation 29.

Cp₂Ti

2

Sy

either me

products

The synth

literature

toluene at

to mixture

mass spec

were not

presence o

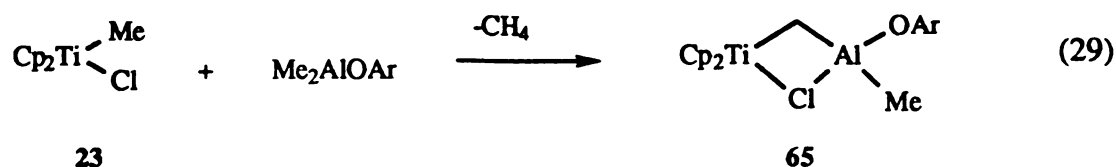
Tit

after 60 h

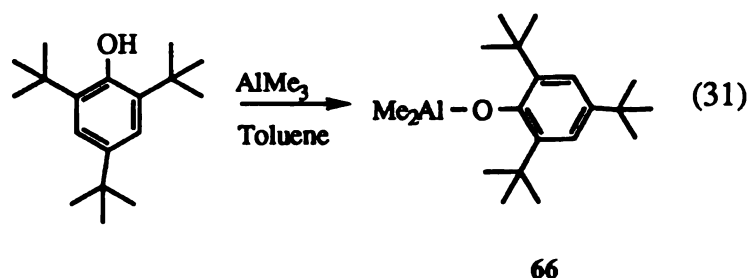
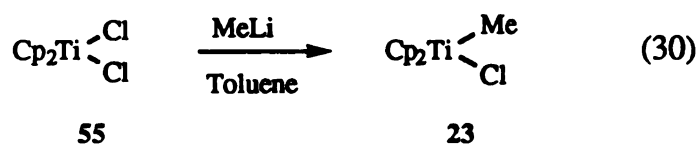
nuclear ma

not procee

mixture wa

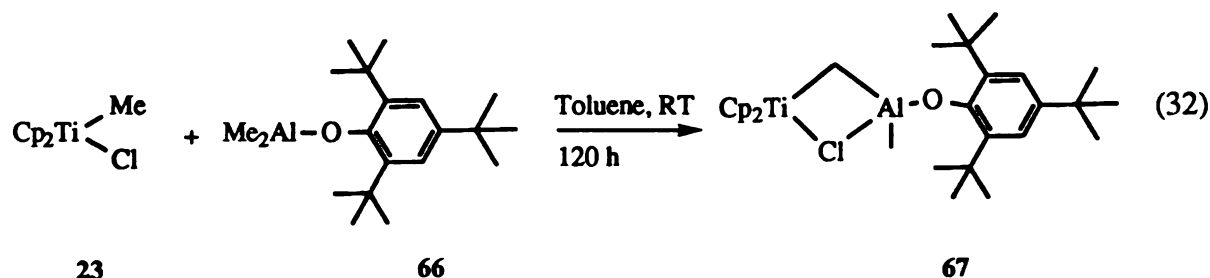


Synthesis of titanocene methyl chloride (23) was carried out by the reaction of either methyl lithium or methyl magnesium chloride with titanocene dichloride.⁴⁶ The products were isolated as per literature procedures and recrystallized with hexane/toluene. The synthesis of dimethyl-2,4,6-tri-*tert*-butylphenoxyaluminum (66) was carried out by literature procedures i.e. treatment of trimethyl aluminum with 2,4,6-tri-*tert*-butylphenol, in toluene at reflux.⁴⁷ Our attempts to isolate 66 through complete evaporation of solvent led to mixtures of 66 and bis(2,4,6-tri-*tert*-butylphenoxy) methyl aluminum as indicated in the mass spectra. To avoid the loss of trimethyl aluminum during evacuation, the solvents were not removed completely. The nuclear magnetic resonance spectra indicated the presence of one compound with integration ratios in agreement with the presence of 66.



Titanocene methyl chloride 23 and 66 were combined at room temperature and after 60 hours, a portion of the reaction mixture was taken to test for completion. The nuclear magnetic resonance spectra of the product mixture indicated that the reaction had not proceeded and only the starting compounds were seen in the spectra. The reaction mixture was allowed to stir for another 60 hours and a sample taken to test for completion.

indicated that the starting material had been consumed. In addition, two new doublets at 7.86 and 7.98 ppm were observed. The solvents of the reaction mixture were evaporated, washed with hexane, extracted with toluene and the toluene solution evaporated. This provided a deep red solid, **67**, which was recrystallized in toluene/hexane mixture in 78% yield.



The proton magnetic resonance spectra of the compound **67** isolated is included in Appendix IV and needs some description. The two protons on the bridged carbon are diastereotopic owing to a chiral aluminum center and appear as two doublets at 7.86 and 7.98 ppm with a coupling constant of 7.5 Hz. The chemical shifts of the two cyclopentadienyl groups appear at different positions at 5.61 and 5.95 ppm while the methyl group on aluminum resonates at -0.25 ppm. This is in stark contrast to the Tebbe reagent, **27**, where the methylene bridge resonates as a singlet at 8.28 ppm while the aluminum methyls resonate at -0.29 ppm. The cyclopentadienyl ligands of **27** appear as a singlet at 5.63 ppm. The ^{13}C spectrum of **67** shows a resonance at 170 ppm indicative of a bridged methylene unit between titanium and aluminum while the corresponding bridged carbon resonates at 180 ppm for **27**. A comparison of the spectrum of **67** with the Tebbe reagent (**27**) indicates that there is considerable change of electron density around the bridged carbon.

The synthesis of this compound was extended to other similar compounds (Figure 4). As can be seen, substitution at the para position could be changed at will without affecting the yield of the products. Synthesis of the bridged compounds with phenols such as 2,6-diphenyl phenol, 2-phenylphenol, catechol and phenol were attempted. All of these gave a complex mixtures of products. This implied that the 2,6-di-*tert*-butyl substitution pattern was required for synthesis of these novel bridged compounds.

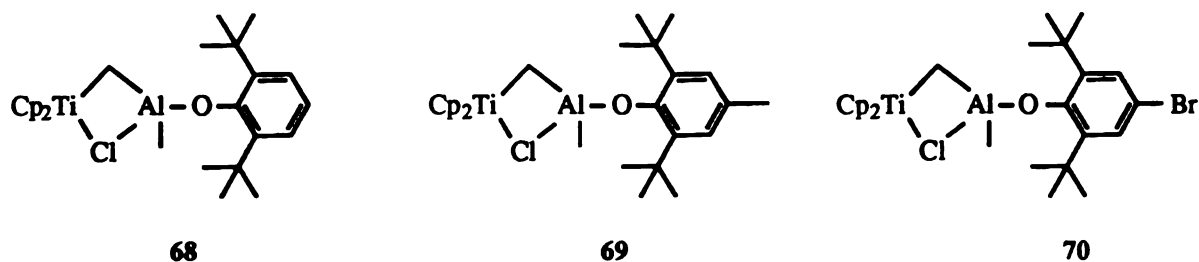


Figure 4 : Various Methylene Bridged Titanium Species Synthesized

A comparison of the proton magnetic resonance spectra of compounds **67-70** indicated that the methylene resonance appear as two doublets in the vicinity of 7.6-7.9 ppm. However, a 4-alkyl group (*i.e.* **67** and **69**) shifted the methylene doublets downfield. The substitution of bromine at the 4' position (**70**) shifts the methylene protons upfield by about 0.12 ppm. ^1H NMR spectra of compounds **67-70** are included in appendix IV-VIII respectively.

Table III: Comparison of NMR Shifts (in ppm) of Compounds 67-70

Compound	4-X'	$\delta_{\text{H}}(\mu\text{-CH}_2)$	$\delta_{\text{H}}(\text{Cp})$	$\delta_{\text{H}}(\text{Al-Me})$	$\delta_{\text{C}}(\mu\text{-CH}_2)$
67	- <i>tert</i> -butyl	7.86, 7.98	5.63, 5.97	-0.26	176.7
69	-Me	7.85, 7.97	5.63, 5.97	-0.23	176.4
68	-H	7.79, 7.89	5.63, 5.96	-0.29	175.7
70	-Br	7.68, 7.76	5.62, 5.92	-0.28	174.3

A crystal structure determination of the compound **69** was carried out. Only one crystal structure consisting of a titanium atom bridged to an aluminum atom *via* a methylene bridge has been reported.^{42b} A comparison of the crystal structure of **69** with **64** reveals that both compounds belong to the space group P2₁/c. In both cases, the structures are partially disordered with respect to the bridging chloride and the methylene groups. Both positions were refined as 0.5 Cl and 0.5 CH₂. In the case of **69**, the para methyl group of the phenoxy ring was also found to be disordered.

The crystal structure of **64** was solved by taking the bridging CH₂ and the Cl atoms as a composite atom and as such the values reported are average values. The solution of the crystal structure of **69** provided reasonably accurate distances and angles owing to the method used, and are discussed with comparison to various other titanocene and aluminum compounds herein (Figure 5). The average Ti-Cl distance in **69** was 2.492 (5) and 2.448 (6) Å which is considerably longer than in titanocene dichloride, **55**, (monomeric) where the average Ti-Cl is 2.364 (3) Å.⁴⁸ The Ti-CH₂ bond lengths were 2.01 (2) and 2.13 (3) Å in **69**, close to Ti-CH₂ distances in **71** (2.15 Å).⁴⁹ The Cl-Ti-CH₂ in **69** angles are 91.4 (3) ° and 86.9 (2) ° in comparison to the bond angle of 75 ° reported for **71**.

The Al-Me distance was 1.988 (5) Å, about 0.068 Å greater than that reported for a dimeric 2,6-Di-*tert*-butyl-4-methyl phenoxyethylaluminum chloride (**72**).⁵⁰ The Al-Cl distances in **69** are 2.238 (5) and 2.278 (6) compared to the dimeric compound **72** (2.277 (3) Å). The angle between Al-O-Ar in **69** was 143.8 (2), which is considerably acute than that reported for **72** (154.1 (3)). As a result, the Al-O distance in **69** is 1.724 (3), about 0.052 Å longer than in **72**. Hybridization changes owing to a decrease in angles explains the increase in bond lengths. The aluminum atom in **72** is more acidic than in **69**, leading to increase donation of the lone pair of electrons from the oxygen to the aluminum, consequently resulting in a decreased bond length.

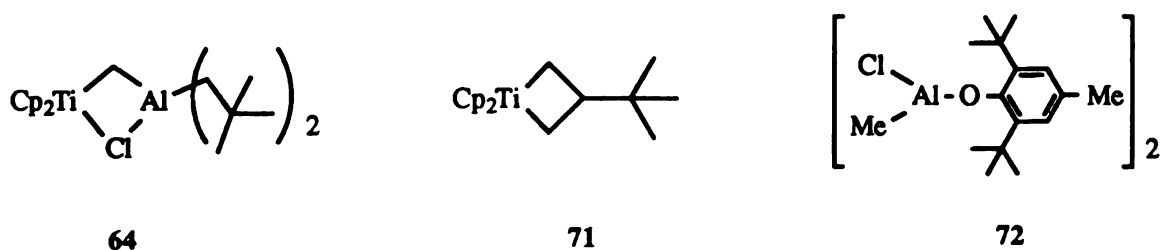


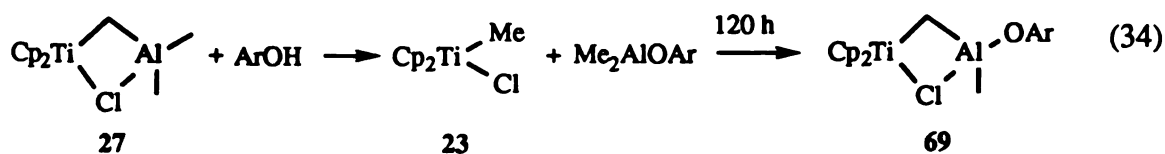
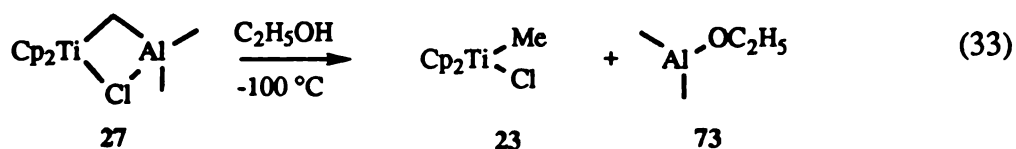
Figure 5: Relevant Compounds for Comparison of Crystal Structures

The Ti-CH₂-Al-Cl on both the disordered rings were found to be planar. The mean angle between Cl-Al-CH₂ was found to be 96.6° in **69** while a considerably higher value (104.66 (8)) was reported for **64**. The average values for the Ti-Cl-Al and Ti-CH₂-Al angles were determined to be 79.2 ° and 95 ° respectively and agreed well with that reported for **64**, wherein the values were reported to be 79.38(5)° and 93.09° respectively. Other

distances were found to be comparable to reported compounds and no appreciable changes in the distances of the cyclopentadienyl rings were observed.

Crystallographic data for **69** is reported in Table IV. Selected bond lengths and angles are reported in Table V. Atomic coordinates and equivalent isotropic displacement parameters are provided in Table VI. Additional data including the C-H bond lengths, complete bond angles, hydrogen coordinates and anisotropic factors are included in Appendix I. An ORTEP of **69** is shown in Figure 6.

Other routes to compound **69** were tried in an attempt to simplify the synthesis. Grubbs and Tritto treated ethanol with Tebbe reagent (**27**) in an attempt to carry out substitution at the aluminum methyls.³¹ However, despite using low temperatures (-100 °C), they found that protonolysis occurred at the bridging methylene group providing titanocene methyl chloride and dimethyl aluminum ethoxide (eq. 33). With a view that the sterics of 2,6-di-*tert*-butyl-4-methyl phenol would direct the reaction at the aluminum methyl, the reaction of the Tebbe reagent with 2,6-di-*tert*-butyl-4-methyl phenol was carried out. The products isolated, even at low reaction temperatures, were titanocene methyl chloride and dimethyl aluminum aryloxy (eq. 34), thereby implying that the reactivity of methylene-aluminum bond is far greater than the methyl groups on aluminum.



OAr=2,6-Di-*tert*-butyl-4-methylphenoxy

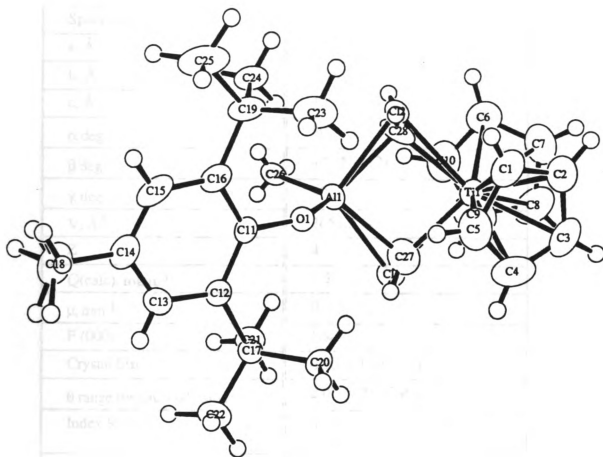
Figure 6: ORTEP of Compound 69

Table IV: Crystallographic Data and Structure Refinement for 69

Formula	C ₂₇ H ₃₈ AlClOTi
Formula Wt.	488.90
Crystal System	Monoclinic
Space Group	P21/c
a, Å	14.673 (2)
b, Å	9.183 (2)
c, Å	19.745 (3)
α deg	90
β deg	94.158 (12)
γ , deg	90
V, Å ³	2653.5 (7)
Z	4
Q(calc), mg/m ³	1.224
μ , mm ⁻¹	0.472
F (000)	1040
Crystal Size	0.20 x 0.60 x .85 mm
θ range for data collection	2.07 to 25.03 deg
Index Ranges	0 $\leq$ h $\leq$ 17, 0 $\leq$ k $\leq$ 10, -23 $\leq$ l $\leq$ 23
Reflections Collected	4910
Independent Reflections	4698 [R (int) = 0.0475]
Refinement Method	Full Matrix least squares on F ²
Data/Restraints/Parameters	4656/0/462
Goodness-of-fit on F ²	1.075
Final R Indices [I $>$ 2s(I)]	R ₁ =0.0518, wR ₂ =0.1188
R indices (all data)	R ₁ =0.1186, wR ₂ =0.2237
Largest diff. peak and hole	0.269 and -0.278 e Å ⁻³

Table V: Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 69

	x	y	z	U (eq)
Ti (1)	1722 (1)	2410 (1)	-2058 (1)	38 (1)
Cl (1)	2655 (4)	1112 (6)	-1142 (3)	38 (1)
Cl (2)	952 (5)	3982 (8)	-1277 (3)	37 (1)
Al (1)	1938 (1)	2758 (1)	-535 (1)	31 (1)
O (1)	2738 (2)	3969 (3)	-187 (1)	29 (1)
C (1)	2191 (4)	4797 (6)	-2360 (3)	57 (1)
C (2)	1988 (4)	4021 (6)	-2947 (3)	62 (2)
C (3)	2616 (4)	2888 (7)	-2971 (3)	68 (2)
C (4)	3198 (4)	2957 (7)	-2395 (3)	70 (2)
C (5)	2930 (4)	4136 (7)	-1996 (3)	61 (2)
C (6)	170 (3)	1719 (7)	-2293 (3)	61 (1)
C (7)	589 (4)	1593 (8)	-2885 (3)	70 (2)
C (9)	1216 (4)	-60 (7)	-2155 (4)	76 (2)
C (10)	564 (4)	698 (7)	-1831 (3)	64 (2)
C (11)	3114 (2)	4518 (4)	407 (2)	27 (1)
C (12)	3904 (2)	3859 (4)	732 (2)	29 (1)
C (13)	4235 (3)	4437 (5)	1355 (2)	37 (1)
C (14)	3863 (3)	5621 (5)	1652 (2)	45 (1)
C (15)	3131 (3)	6281 (5)	1304 (2)	45 (1)
C (16)	2744 (2)	5785 (4)	685 (2)	34 (1)
C (17)	4387 (2)	2555 (4)	436 (2)	32 (1)
C (18)	4235 (5)	6143 (10)	2350 (4)	73 (2)
C (19)	1945 (3)	6640 (4)	326 (2)	40 (1)
C (20)	4642 (3)	2876 (6)	-287 (2)	37 (1)
C (21)	3793 (3)	1183 (5)	459 (3)	41 (1)
C (22)	5287 (3)	2184 (7)	848 (3)	53 (1)
C (23)	2184 (7)	7117 (6)	-381 (3)	59 (2)
C (24)	1073 (3)	5737 (5)	282 (3)	41 (1)
C (25)	1708 (4)	8018 (6)	726 (4)	67 (2)
C (26)	1192 (4)	1739 (8)	120 (3)	29 (1)
*C (27)	2495 (18)	1512 (26)	-1287 (13)	68 (8)
*C (28)	1154 (19)	3625 (32)	-1272 (15)	53 (8)

U (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

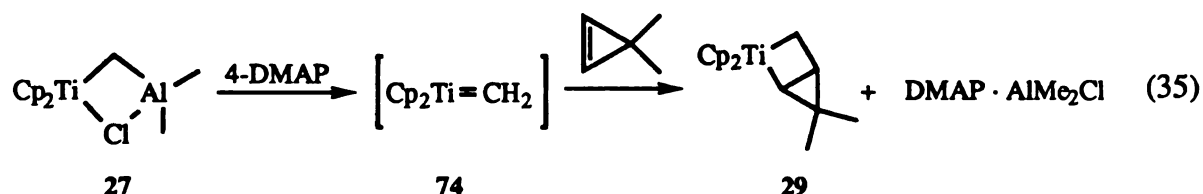
* : occupancy factor = 0.5

Table VI: Selected Bond Lengths and Angles for 69

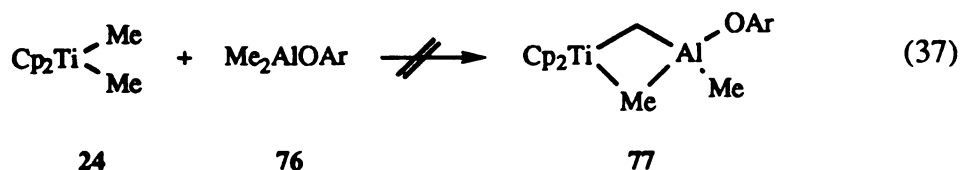
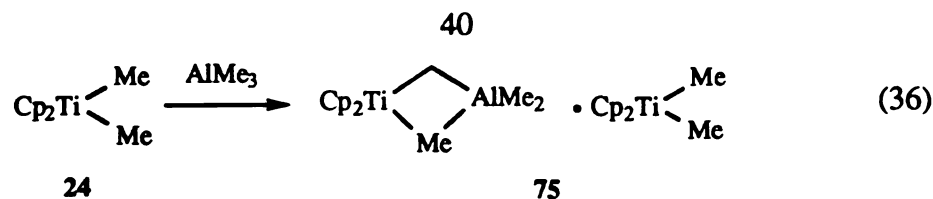
Bond Lengths (Å)		Bond Angles (°)	
Ti - Cl (1)	2.492 (5)	Ti - Cl (1) - Al	79.1 (2)
Ti - Cl (2)	2.448 (6)	Ti - Cl (2) - Al	79.3 (2)
Ti - C (27)	2.01 (2)	Ti - C (27) - Al	94.9
Ti - C (28)	2.13 (3)	Ti - C (28) - Al	95.1
Al - Cl (1)	2.238 (5)	Cl (1) - Ti - C (28)	86.9
Al - Cl (2)	2.278 (6)	Cl (2) - Ti - C (27)	91.4
Al - C (27)	2.09 (3)	Al - O - C (11)	143.8 (2)
Al - C (28)	1.96 (2)	C (26) - Al - O	115.8 (2)
Al - C (26)	1.988 (5)	C (27) - Al - O	110.2 (8)
Al - O	1.724 (3)	C (28) - Al - O	112.4 (10)
O - C (11)	1.357 (4)	Cl (1) - Al - O	108.4 (2)
Av. Ti - C(Cp) (1)	2.364 (5)	Cl (2) - Al - O	108.7 (2)
Av. Ti - C(Cp) (2)	2.375 (5)	C (27) - Al - Cl (2)	94.4 (5)
Av. C-C (Ar)	1.392 (5)	C (28) - Al - Cl (1)	98.7 (8)
C (27) - H (27A)	0.97 (8)	H (28A) - C (28) - H (28B)	104 (7)
C (27) - H (27B)	0.90 (7)	H (27A) - C (27) - H (27B)	92 (7)
C (28) - H (28B)	0.92 (8)		
C (28) - H (28B)	1.04 (7)		

Since the initial products of equation 34 were the same as the starting materials in the synthesis of **69**, the reaction of the Tebbe reagent with the phenol (eq. 34) was stirred for 120 hours to provide **69**. No appreciable changes in yield or reaction time required for completion were observed. However, this provided a easier route to these bridged compounds since it involved simply mixing two reagents, while the previous route involved synthesis of individual starting materials and reacting them together. The reaction scheme (eq. 34) was applied towards the synthesis of compounds **67**, **68**, and **70** by addition of the appropriate phenol to the Tebbe reagent (27). As with the previous synthesis, various phenols such as 2,6-diphenylphenol, 2-phenylphenol, catechol and phenol were attempted. All of these gave complex mixtures of products.

The methylene bridged compounds were stable for long periods of time under inert atmosphere. Compounds **67-70** have a chloride bridged between the titanocene and the aluminum species. Attempts were made to replace the chloride bridge with an methyl group. The reaction of methyl lithium and methyl magnesium chloride with **69** gave complex mixtures of products. This is probably due to the fact that these alkylating agents are available in coordinating solvents such as ether. The action of coordinating solvents on these bridged compounds (**67-70**) and the Tebbe reagent (**27**) results in unstable titanocene alkylidene complex **74**. Evidence for collapse of the methylene bridged Tebbe reagent into titanocene alkylidene complex (**74**) is found in the work of Grubbs and co-workers, wherein the Tebbe reagent is treated with *N,N*-dimethyl amino pyridine (DMAP) in the presence of olefins to provide titanacyclobutanes (**29**) (eq. 35).⁵¹

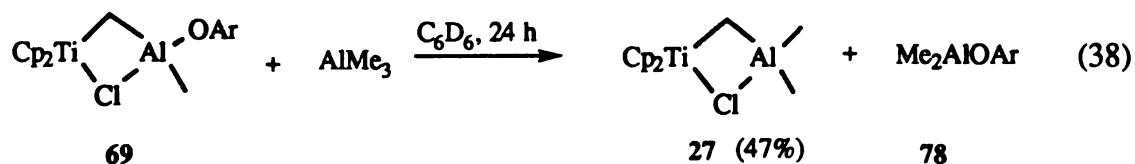


Attempts were made to use dimethyl zinc and dimethyl magnesium to replace the bridging chloride group so as to achieve a methyl bridged species. However, after 9 days, no change was observed in the reaction mixture. Tebbe has reported the synthesis of **75** by the reaction of dimethyl titanocene with trimethyl aluminum.^{42b} The product could not be purified and was always found coordinated to dimethyl titanocene. Our attempts to synthesize the aryloxy analog of **75**, i.e. **77**, through the use of **76** and dimethyl titanocene **24** did not succeed. No reaction products were seen after 9 days and prolonged stirring resulted in purple-green coloration indicative of some reduction/decomposition products of titanium.



OAr=2,4,6-tri-*tert*-butylphenoxy

The use of trimethyl aluminum to replace the bridging chloride group gave interesting results. A reaction of one equivalent of trimethyl aluminum with **69** at room temperature resulted in the cleavage of the aryloxy group providing the Tebbe reagent (**27**) and the dimethyl aryloxy aluminum, **78** (eq. 38). This transformation indicated that the aryloxy group on the aluminum was not stable to Lewis acids such as alkyl aluminums and was readily cleaved. No substitution of the bridging chloride with a methyl group was seen. This result is not surprising since even the Tebbe reagent (**27**) does not provide any substitution of the bridging chloride group upon reaction with trimethyl aluminum.

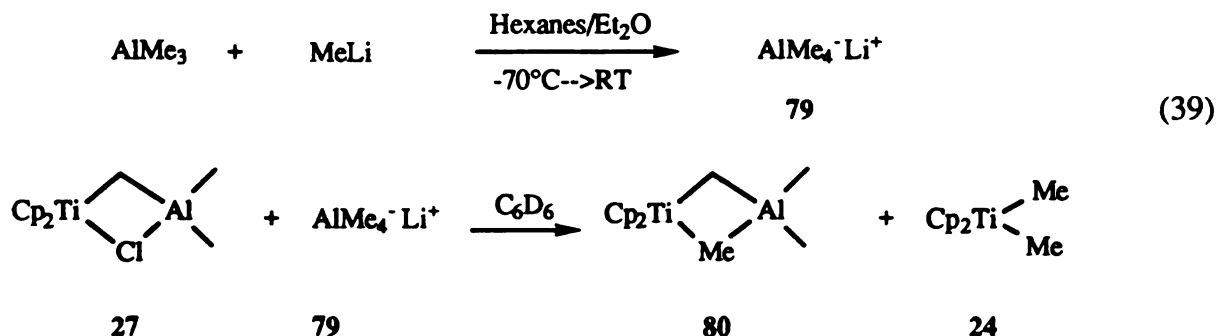


OAr=2,6-Di-*tert*-butylphenoxy

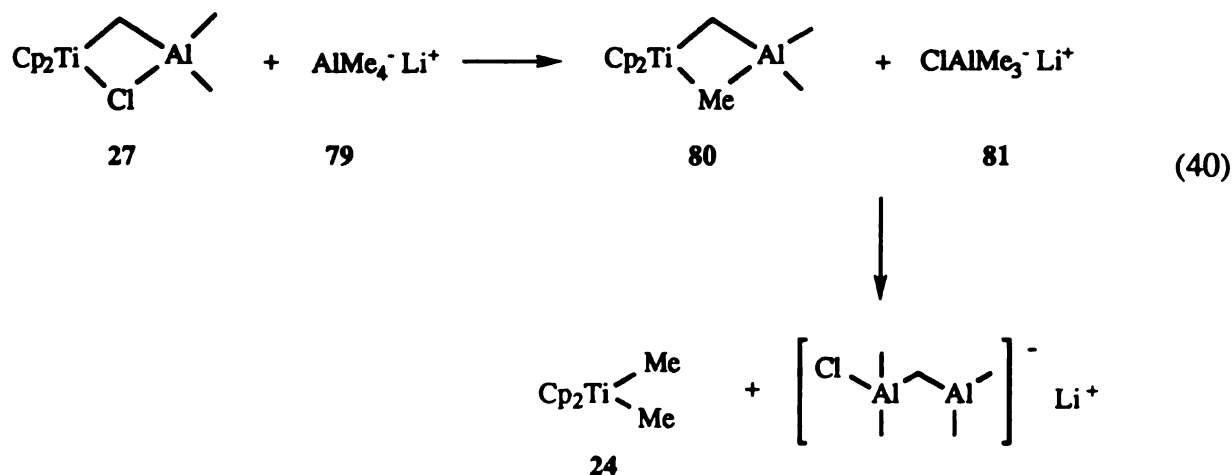
% values are based on integration of the PMR spectra of the reaction mixture

The use of conventional reagents to substitute the chloride group of **69** with a methyl group failed to provide the desired products. In order to obtain the required substitution, a novel reagent was designed based on the work described in the previous section. The reaction of methyl lithium with trimethyl aluminum provided the 'ate' salt, lithium tetramethylaluminate (**79**) (eq. 39). The product is obtained as a fine white powder, virtually free of the coordinating solvent, diethyl ether. It was found that the salt **79** was insoluble in non-polar solvents such as hexane, toluene and benzene.

The reaction of the Tebbe reagent (**26**) with an equivalent of the salt **79** resulted in rapid formation of the methyl bridged species **80** at $-20\text{ }^{\circ}\text{C}$ (eq. 39). However, monitoring the reaction by NMR at room temperature indicated formation of dimethyl titanocene (**24**) as a by-product.



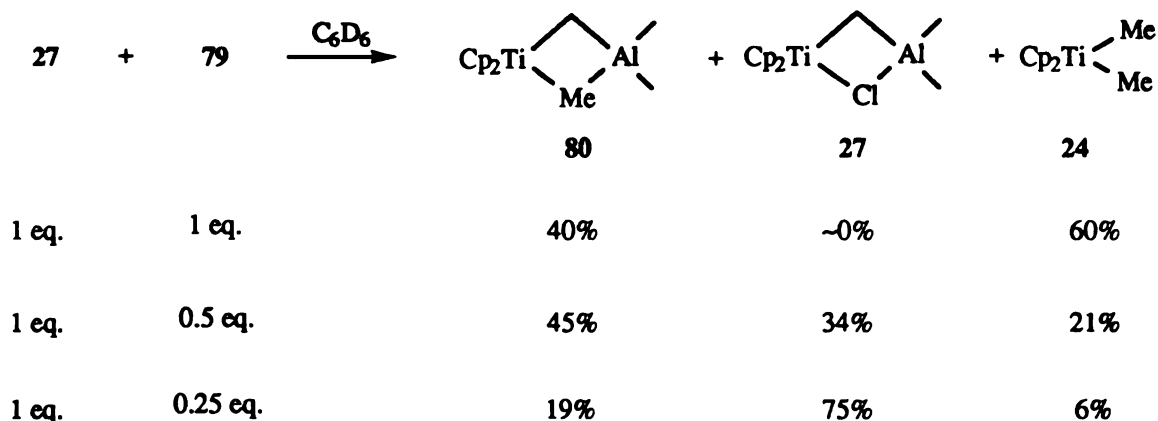
The substitution of the chloride bridging ligand in **27** with a methyl group also results in another active 'ate' salt lithium trimethylchloroaluminate (**81**). This could further alkylate another molecule of **27** and this process could go on until all the methyls groups of **79** are used up in substitution. The presence of unreacted **80** in the reaction mixture could replace the bridging alkyl moiety to provide dimethyl titanocene (eq. 40).



The use of less than one equivalent of **79** in equation 39 alleviated the problem of rapid formation of dimethyl titanocene at room temperatures. A comparison of the yields (based on integration of the proton magnetic resonance spectra) of the compounds in the reaction mixture when the amount of **79** was varied is provided in Scheme VIII. No

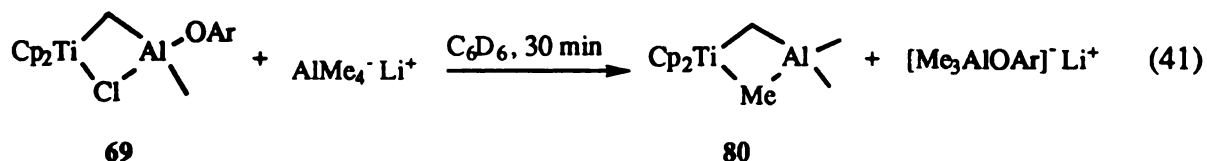
titanocene methyl chloride was observed in the reaction mixture. Despite varying the ratios of reactants in Scheme VIII, it was found that at all times the products were a mixture of **24** and **80** or a mixture of **27** and **80**. Tebbe and co-workers have reported that their attempts to prepare **80** in a pure form failed and that the synthesis of **80** was always achieved as a coordinated adduct of dimethyl titanocene (**24**).

Scheme VIII: Products of the Reaction of **27 with Varying Amounts of **79****

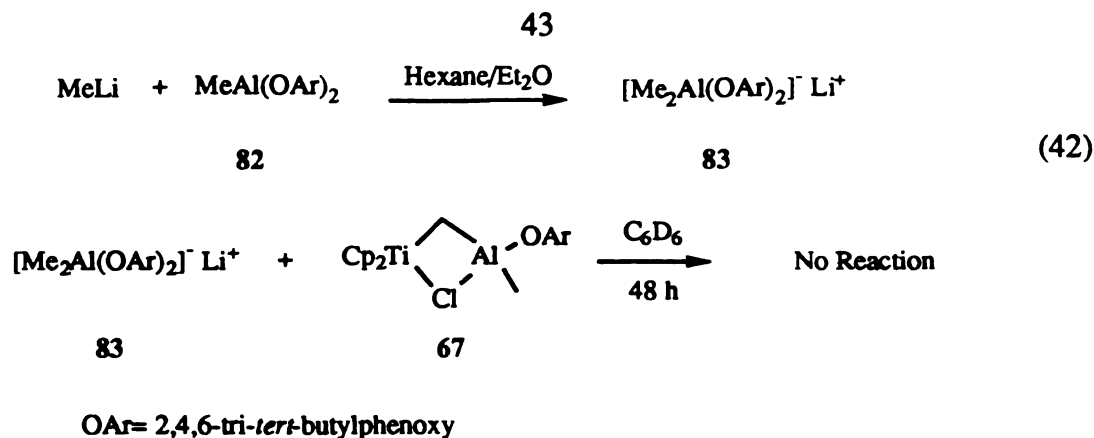


% yields are approximate values are based on integration of peaks in the proton magnetic resonance spectra

The reaction of **79** was tried with **69**, to obtain the substitution of the bridging chloride group (eq. 41). It was found that the reaction rapidly led to the formation of **80**, which was not unexpected since it was determined that the aryloxy group of **69** was labile and was easily cleaved by trimethyl aluminum.



OAr=2,6-di-*tert*-butyl-4-methylphenoxy



In order to reduce the oxophilicity of trimethyl aluminum, methyl lithium was treated with bis(2,4,6-tri-*tert*-butylphenoxy) methyl aluminum (82) which provided 83. The compound 67 was treated with an equivalent of 83 and the reaction monitored by NMR (eq. 42). It was found that the reaction mixture consisted of the starting materials and no substitution occurred, despite heating the reaction mixture up to 50 °C. This indicated that either the chloride bridge is strongly coordinated to the aluminum moiety in 67 or that the methyl groups on 83 are not nucleophilic enough to carry out the required substitution.

The substitution of the chloride bridging group of the Tebbe reagent 27, leading to the formation of 80, resulted in substantial changes in the proton and carbon nuclear magnetic resonance spectra. Proton and carbon NMR data of 27 and 80 are shown in Table VII . A comparison of the chemical shifts indicated that the substitution of the chloride ligand with the methyl group resulted in substantial downfield shift both in carbon and proton resonances of the bridging methylene unit. However, the cyclopentadienyl ligands show an upfield shift in the proton and the carbon NMR spectra.

Table VII: Comparison of NMR Shifts (in ppm) of Compounds 27 and 80

Compound	$\delta_{\text{H}} (\mu\text{-CH}_2)$	$\delta_{\text{H}} (\text{Cp})$	$\delta_{\text{H}} (\text{Al-Me})$	$\delta_{\text{C}} (\text{Cp})$	$\delta_{\text{C}} (\mu\text{-CH}_2)$
 (27)	8.28	5.606	-0.25	111.9	187.0
 (80)	8.89	5.37	-0.32	109.7	203.6

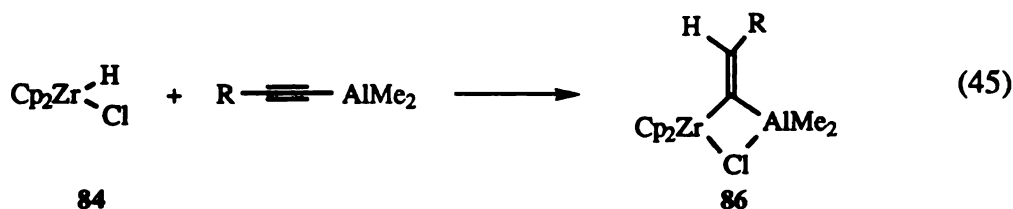
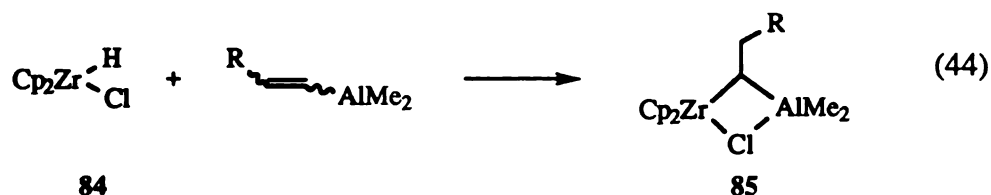
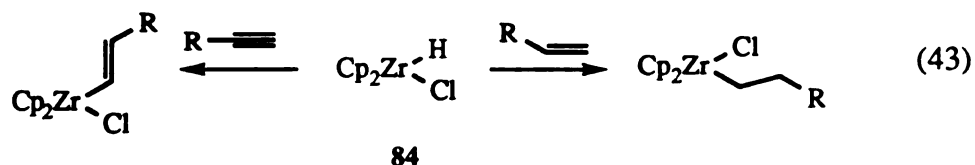
The synthesis of the heterobimetallic compounds of titanium bridged to an aluminum aryloxide *via* a methylene group was highly successful. The crystal structure of these bridged compounds provided accurate bond lengths, hitherto unavailable, due to the fact that the solution of the crystal structure was done, not as a composite unit consisting of a methylene and a chloride group, but rather as independent groups. This provided accurate angles and lengths thereby providing an insight to the coordinative distances between the bridging chloride and the aluminum. Such values are essential in the proper design of a catalyst since the bond length is indicative of the lability of the bonds and consequent dissociation into cationic and anionic sites, required if a cation is actually the active site in polymerization.

CARBON BRIDGED COMPOUNDS OF ZIRCONIUM WITH ALUMINUM

The reaction of zirconocene dichloride with two equivalents of trimethyl aluminum does not provide the methylene bridged Tebbe analog. Hence the reaction scheme used for the synthesis of titanium bridged species (eq. 26) could not be applied to the synthesis of zirconium analogs.

Literature reports indicate that zirconocene hydrido-chloride **84**, adds efficiently across alkenes and alkynes (eqs. 38). Also, the addition can be carried out regioselectively on alkenyl and alkynyl aluminum compounds, which then would provide the necessary bridged compounds (eq. 39-40).⁵² Our attempts to react trimethyl aluminum with zirconocene dichloride to provide the methylene bridged zirconium analogs failed despite

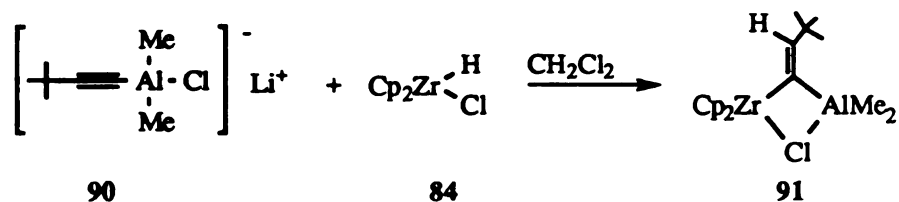
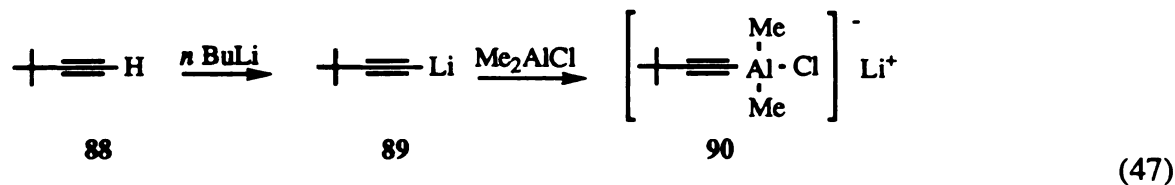
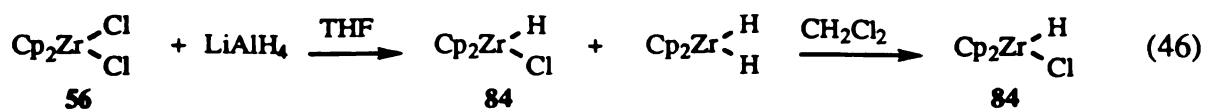
using harsh conditions such as high temperatures (110 °C) and concentrations (4 M). The reactions usually led to multiple products with no one product predominating.



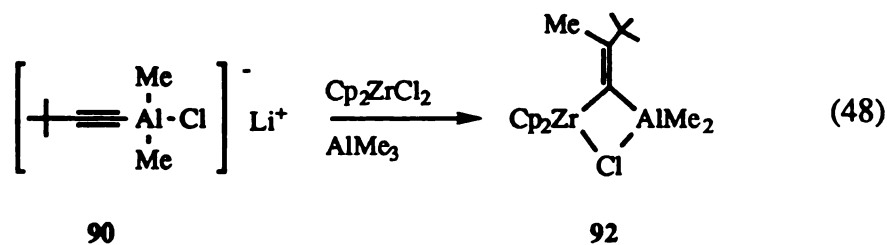
Zirconocene hydrido-chloride (**84**) was prepared in high yields by the reaction of lithium aluminum hydride with zirconocene dichloride (**56**) as reported in literature (eq. 46). The mixture of products, zirconocene hydrido-chloride and zirconocene dihydride was converted to zirconocene hydrido-chloride by washing with dichloromethane.⁵³

Deprotonation of *tert*-butyl acetylene (**88**) with *n*-butyl lithium provided the lithium *tert*-butylacetylde (**89**). This was then transmetalated onto aluminum by reaction with dimethyl aluminum chloride, to provide the ate salt **90**. Our attempts to 'salt out' **90**, to provide 3,3-dimethyl-1-butyne dimethyl aluminum, by heating to reflux and cooling in various solvents failed. However, when **90** was treated with zirconocene hydrido-chloride in dichloromethane, compound **91** was isolated, as an impure product. Sublimation of the reaction mixture at 100 °C (0.013 mm Hg) provided **91** in 34% yield.⁵⁴

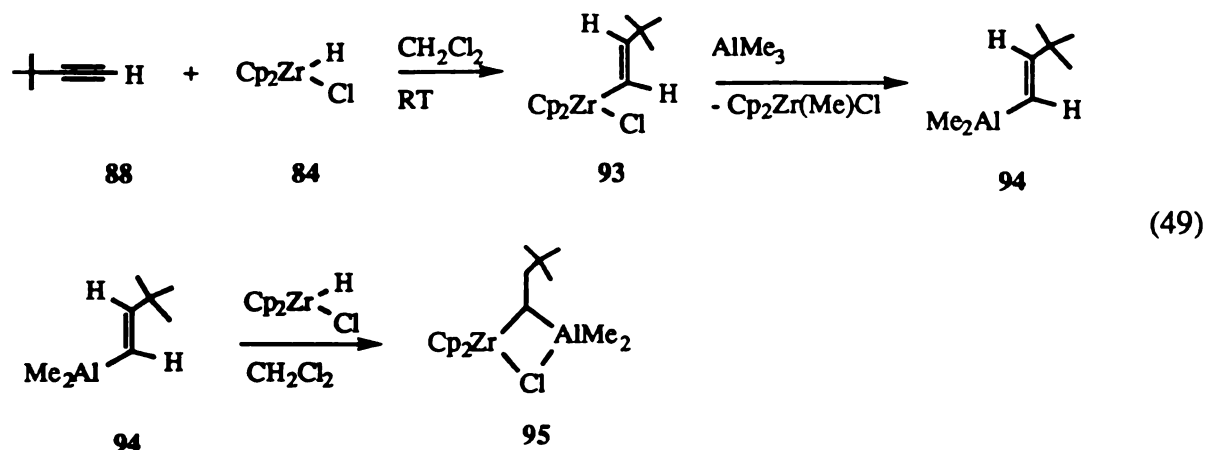
46



Carbometallation of alkynes is an area of intense research in organometallic chemistry.⁵⁵ Reports indicate that a mixture of trimethyl aluminum with zirconocene dichloride carbometallates alkynes. Following literature reports, a mixture of trimethyl aluminum and zirconocene dichloride was treated with **90** to provide **92** in 68% yield (eq. 43).⁵⁶



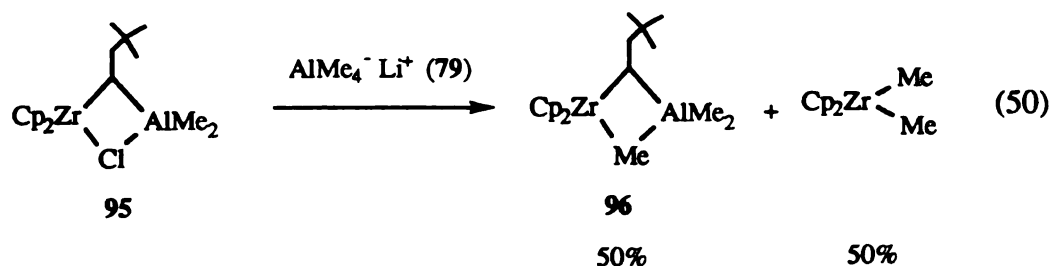
The addition of zirconocene hydrido-chloride to alkynes provides vinyl zirconocene. The reaction of zirconocene hydrido-chloride with *tert*-butylacetylene provided 2-*tert*-butylvinyl zirconocene chloride (**93**). Addition of trimethyl aluminum to **93** provided 2-*tert*-butylvinyl dimethyl aluminum (**94**), which upon addition of another equivalent of zirconocene hydrido-chloride (**84**), provided the expected bridged heterobimetallic **95** (eq. 49). The by-product, zirconocene methyl chloride, was separated from the final product **95**, by dissolution of **95** in hexane, a solvent in which zirconocene methyl chloride was found to be insoluble.



The spectral data of **95** agreed with the literature report of the identical compound. Schwartz and co-workers have reported the synthesis of **95** by the reaction of **94** with zirconocene hydridochloride (**84**).⁵⁷ The transformation carried out in equation 49 provided an easier route with simple available reagents. The transformation from **88** to **95** was also achieved as a 'one-pot' reaction with two equivalents of zirconocene hydridochloride, one equivalent of trimethyl aluminum and an equivalent of the acetylene.

Our efforts to use dimethyl-2,6-di-*tert*-butyl phenoxy aluminum instead of trimethyl aluminum in the scheme of reactions (eq. 49) to provide a substituted analog failed. The reaction usually led to an inseparable mixture of products. The use of trimethyl silyl acetylene instead of *tert*-butyl acetylene for reaction with zirconocene hydridochloride led to a mixture of regioisomers, as has been reported in literature. Attempts to substitute the methyl groups of the aluminum moiety in the final heterobimetallic product **95** with bulky phenols failed to give desired products. Despite many setbacks, the work in this area led to a facile synthesis of compounds such as **95**.

Attempts were made to replace the chloride bridge with a methyl group of **95**. The use of methyl lithium or methyl magnesium chloride (both available in coordinating solvents) failed. The reaction of trimethyl aluminum with **95** was monitored by NMR. No substitution or cleavage of the methine bridge was seen even at high temperatures (60 °C).



The reaction of lithium tetramethyl aluminate (79) with **95** was followed by NMR (eq. 50). It was found that the salt **79** rapidly alkylates **95** to provide **96** at room temperature within 15 minutes. As a result, the reaction was carried out in large scale in an attempt to obtain pure **96**. Addition of **79** to **95** in hexane provided **96**, as an adduct of dimethyl zirconocene and trimethyl aluminum. Attempts to remove the coordinated dimethyl zirconocene or trimethyl aluminum from **96** failed. It is interesting to note the similarity between **96** and **80**. Both compounds were always formed and isolated as adducts rather than pure compounds. A comparison of the nuclear magnetic resonance spectra of compounds **95** and **96** revealed interesting changes. The proton of the bridged methine carbon of **96** is shifted downfield by 0.6 ppm with respect to **95** while the methylene group of **96** is shifted downfield by 0.04 ppm. The protons of the cyclopentadienyl groups, however, are shifted upfield by 0.17 ppm. The bridged carbon of **96** was found to be shifted downfield by 10 ppm (from 158 ppm in **95** to 168 ppm in **96**).

CONCLUSIONS

The synthesis of methylene bridged titanium species in accordance with our aims were carried out successfully. Synthetic sequences developed were not only simplified, 'one-pot' reactions but were also high yielding with straightforward purification steps. Each reaction could be monitored by proton magnetic resonance spectroscopy. Substitution on the aluminum center was readily carried out in order to affect the electronics at the bridged center. Methylene bridged heterobimetallic compounds of titanium and aluminum that were synthesized were unique and have not appeared in the chemical literature, despite attempts by other research groups.

The 2,6-di-*tert*-butyl substitution was found necessary for the synthesis of these methylene bridged systems. This is probably due to the tendency for aluminum compounds to form highly stable dimers, if such a substitution were not present. Resonances of the methylene protons showed a slight dependency on the substitution of the para position of the aryl group on aluminum. The methylene bridged compounds were found to be stable under inert atmosphere and decomposed rapidly in coordinating solvents such as tetrahydrofuran or diethyl ether.

Crystal structure of the compound **69** provided an insight into the angles adopted by the compound in the solid state. It was solved for disordered methylene and chloride groups independently. This solution provided accurate bond lengths and angles, unlike the literature reports where ambiguous bond lengths were obtained due to the method by which the crystal structure was solved.

Synthesis of the oxygen bridged systems were difficult to carry out. The synthesis of such heterobimetallics with titanium and zirconium have not appeared in chemical literature. Isolation of such compounds would be difficult owing to its instability and tendency to undergo elimination to provide the highly stable titanium oxo polymers.

The syntheses of bridged zirconium catalysts were based on modified literature syntheses. The synthetic scheme developed here provides for a simple one step, 'one pot' process and the products were isolated in high yields. The scheme could be applied to all sterically hindered alkynes thereby providing a handle for substitution on the bridge between zirconium and aluminum. Attempts to substitute the methyl groups of the aluminum metal with a bulky aryloxy group were unsuccessful.

Substitution of the bridging chloride group of the Tebbe reagent using lithium tetramethyl aluminate was successfully carried out though it was found to be sensitive to the reaction conditions. Attempts to carry out similar substitution of the bridging chloride ligand of compounds **67-70** failed as the aryloxy moiety of these compounds were found to be labile. Substitution of the bridging chloride ligand of the zirconocene compound **95**

to provide **96** was carried out successfully by the use of lithium tetramethyl aluminate and it was found to be coordinated to dimethyl zirconocene.

CHAPTER III

POLYMERIZATION STUDIES OF ETHYLENE WITH BRIDGED HETEROBIMETALLIC CATALYSTS

INTRODUCTION

Polyolefins have occupied an important position in consumer industry. Some the uses of polyolefins include packaging, coatings, plastics, novel engineering material composites, membranes etc. Considerable research and development efforts by the polymer industry are aimed at the discovery and implementation of new processes which provide improved yields of polymer and polymers with better mechanical and thermal properties. As such, research efforts are directed towards improvement of catalyst properties and the productivity of the catalysts.

The turnover of a catalyst in polymer chemistry is defined as the number of monomer units inserted before the catalyst is no longer active.⁵⁸ Some possible modes of catalyst deactivation include a) poisoning of the catalyst by impurities in the monomer, b) poisoning by oxygen or trace amounts of coordinating solvents and c) β -hydride elimination and subsequent reductive coupling. Increases in the yield of a polymer (in units of grams of polymer per mole of catalyst per hour) could be achieved by reducing the possible modes of catalyst deactivation. Also, an increase in the number of active sites for polymerization would result in increase in the polymer yield. In conventional homogeneous Ziegler-Natta catalyst systems, the catalyst and the co-catalyst are premixed for about 15 minutes before introduction into the reactor. The choice of the time of mixing, the solvent in which the polymerization is carried out, the temperature of mixing and polymerization, and pressure are all factors to be considered and studied in order to maximize the yield of a catalyst.

Although extremely pure ethylene monomer gas can be obtained after repeated purification, such measures were not taken in this study. Commercial grade ethylene (97% pure) was purchased and used without purification. As a result, the polymer yields obtained are lower than would be expected in an industrial setting. In order to test the catalyst turnover activity and compare the results obtained to the conventional catalyst systems, polymerization of some of the commercial catalysts were also carried out under identical reaction conditions.

POLYMERIZATION SETUP

A manifold of four reactors was constructed so that each reactor could be switched between gas pressure and vacuum independently (Figure 7). The reactors could be used independently or as a set of parallel reactors. Each reactor was connected to a pressure gauge, to allow monitoring of the pressure of monomer. In addition, each reactor had an independent septum inlet for introduction of dry solvents and reactants.

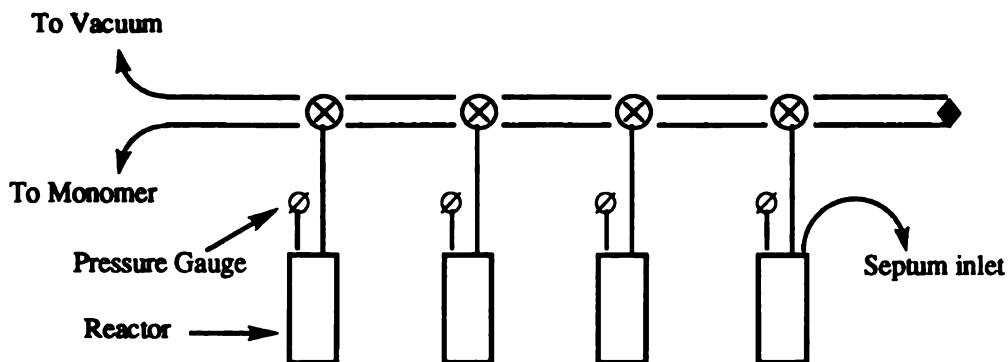
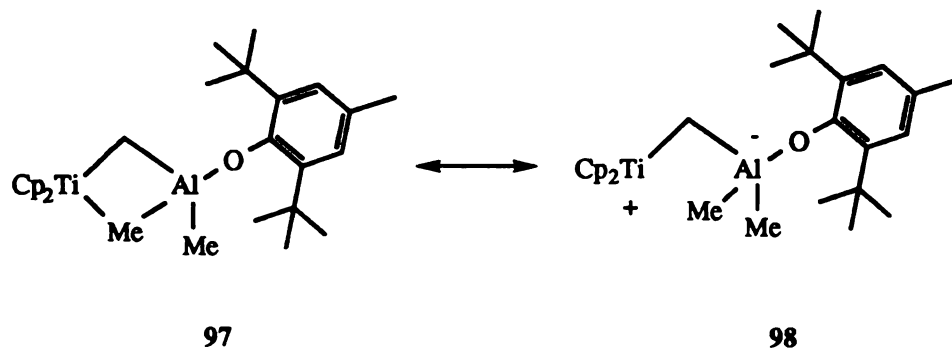


Figure 7: Reactor Setup used for Polymerization Studies

Typically, the polymerization reactors were washed sequentially with concentrated acid, water, base and acetone. The reactors were dried in an oven and connected to the pressure manifold. The reactors were evacuated and purged with ethylene repeatedly. The two reactants i.e. the catalyst and the co-catalyst were diluted to the required concentrations

and mixed in a separate Schlenk flask for fifteen minutes and introduced into the reactors using a canula. The reactors were pressurized with ethylene to the required level and the reactions were stirred for one hour. The reactors were vented and the polymerization reaction mixture quenched with 5% HCl in methanol. The polymers were dried under vacuum over phosphorus pentoxide and weighed.

According to the hypothesis presented in Chapter I, the actual single component catalyst would be the methylated version of **69**, i.e. **97**, which in its zwitterionic form (**98**) would carry out olefin polymerization. Compound **97** could be obtained by the replacement of the bridging chloride with a bridging methyl group. However, repeated attempts to replace the chloride ligand with an alkyl group failed as mentioned in Chapter II. As such, catalyst **69** was not expected to polymerize ethylene. To test this hypothesis, the compound **69** was dissolved in dichloromethane and subjected to ethylene at 45 psi. No polymer formation was observed. This implied that a small amount of co-catalyst MAO would be required as it is well known that MAO alkylates titanocene compounds rapidly at room temperature.



CHOICE OF CO-CATALYST

The co-catalyst chosen for this study was methyl aluminoxane (MAO). As mentioned in chapter I, methyl aluminoxane is considered to be a mixture of linear and cyclic oligomers of $-\text{[OAl(Me)]}_n$, with $M_n \approx 2700$. Depending on the synthesis and/or the source of methyl aluminoxane, the activity of methyl aluminoxane varies. Also, as mentioned in Chapter I, a considerable amount of trimethyl aluminum remains coordinated to the methyl aluminoxane chains. The amount of coordinated trimethyl aluminum varies

based on the synthesis of methyl aluminoxane. Synthesis of methyl aluminoxane was carried out by the published procedure. Since the activity or the structure of the methyl aluminoxane of the product was not known, methyl aluminoxane was obtained by commercial sources and the activity of the methyl aluminoxane synthesized compared with the commercial methyl aluminoxane. The yields of polymer obtained in either cases were comparable.

CHOICE OF SOLVENT

Electron donating solvents such as diethyl ether or tetrahydrofuran are known to poison the catalyst in the metallocene/MAO systems. This is probably because the lone pair of electrons on the oxygen of the solvents compete with the olefin monomer for the coordination sites. This strong coordination by solvents thus results in deactivation of catalyst active sites.

The yield of polymer is strongly dependent on the polarity of the solvents used. An increase of polarity results in increased yield of the polymer. The dependence of polarity on polymer yield is considered important evidence in explaining the cationic mechanism as discussed in Chapter I. Some of the solvents used in homogeneous polymerizations include hexane, toluene, dichloromethane and 1,2-dichloroethane. The dependence polymer yield on solvent polarity was studied to determine the optimum solvent for ethylene polymerization by the bridged heterobimetallic catalysts synthesized during this project.

The catalyst chosen for the solvent dependence study was **69**, along with 100 eq. MAO. Hexane, toluene, dichloromethane and 1,2-dichloroethane were chosen as solvents because of their polarities and the solubility of ethylene. The results of polymerization are provided in Table VIII. As seen from Table VIII, the polymer yield increases with increase in polarity. 1,2-Dichloroethane was found to be the best solvent to carry out the polymerization studies. Interestingly, the polymer yield in hexane was higher than in toluene. This could be explained by the solubility of ethylene in hexane being higher than in toluene. This increases the local concentration of ethylene around the catalyst sites,

thereby increasing the yield. Since 1,2-dichloroethane was found to be the best solvent, all further polymerization studies were carried out with 1,2-dichloroethane.

Table VIII: Solvent Dependence on Polymer Yield^a

Solvent	gm of Polyethylene	gm P.E [mmol (cat)] ⁻¹ h ⁻¹
Cl-CH ₂ -CH ₂ -Cl	2.16	43
CH ₂ Cl ₂	1.77	35
Toluene	0.50	10
Hexane	0.88	18

^a[MAO]/[69]= 100 ; Pressure = 45 psi, t_p= 1h

AMOUNT OF SOLVENT

In a polymerization reactions in concentrated media (2.5×10^{-3} M), the polymers engulf the solvent and essentially after 15 minutes, the solvent is entirely absorbed by the growing polymer chain. This results in a 'dry' reaction with only two phases existing i.e. gas and the solids. As the reactors were designed in such a way that the polymerization be carried out in a solvent, the catalysts had to be diluted to about 50 mL of solvent (at least 1.0×10^{-3} M). This resulted in the polymerization being carried out as a suspension of the polymer chains in the solvent. However, when the polymer yield was high as in the case, when higher equivalents of MAO (=1000) with respect to the metallocene catalyst were used, the solvent would be absorbed by the polymer and despite increase in the amount of solvent, usually resulted in a biphasic system.

REPRODUCIBILITY OF RESULTS

To ascertain whether the polymerization studies provided consistent results i.e. repeatable polymer yields, three parallel reactors were loaded with catalyst 69 and 100 equivalents of MAO with respect to 69 and subjected to an ethylene pressure of 45 psi. Within experimental error, the polymer yield obtained was consistent with the values

obtained in parallel experiments using the same MAO to **69** ratios. The results are provided in Table IX.

Occasionally erratic values with very high polymer yields were obtained during the course of the studies. In one run with 100 equivalents of MAO per equivalent of **69**, a polymer yield corresponding to 694 gms PE mmol⁻¹ hr⁻¹ was obtained, as compared to the average of 50 gms PE mmol⁻¹ hr⁻¹ in Table IX. The cause of such high catalyst activity could not be ascertained. As such, repetitive experiments were needed to confirm the results and provide internally consistent values.

POLYMERIZATION PROCEDURE

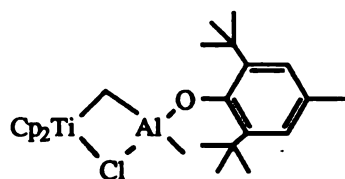
The required amounts of catalyst and MAO were weighed out in separate flasks in the dry box and 10 mL of 1,2-dichloromethane added to each of the flasks. The MAO solution was transferred to the catalyst solution *via* a canula and the reaction mixture stirred for 15 minutes. 45 mL of 1,2-dichloromethane was added to the four reactors, with each equipped with a magnetic stirbar, and the reactors purged with ethylene. The catalyst-MAO solution (5 mL) was injected into each of the four reactors and the reaction mixture stirred vigorously with a magnetic stirrer. Ethylene gas was introduced and the pressure maintained at 45 psi throughout the entire manifold. In all cases where polymerization was observed, the solution became turbid instantaneously. The polymerization was terminated after one hour by addition of methanol/HCl after releasing the excess ethylene gas. The polymers were filtered, dried in *vacuo* over P₂O₅ and weighed.

CATALYTIC ACTIVITIES

The aim of this project was to lower the amount of methyl aluminoxane required to obtain catalytic activity similar to commercial catalysts. Some catalysts used commercially are titanocene dichloride, titanocene methyl chloride and dimethyl zirconocene, in conjunction with methyl aluminoxane. In all of these cases, the amount of methyl aluminoxane required to obtain good turnover numbers is about a 3000 equivalent excess with respect to the metal catalyst. Dimethyl zirconocene/MAO and titanocene methyl

chloride/MAO catalyst system were used as the standard and its catalytic activity compared to the synthetic bridged catalysts.

Polymerization of ethylene with **69** and 100 equivalents of MAO was carried out as described above. The results are provided in Table IX. Fairly constant values were observed for three different runs with the same catalyst-MAO solution. Dependence of polymerization activity on amounts of MAO on was studied by varying the equivalents of MAO per equivalent of **69**. The results are provided in Table X. Polymerization of ethylene was also carried with 1000 equivalents of MAO with respect to **69**. The polymer yields are provided in Table XI.



69

Table IX : Polymerization of Ethylene with **69 and 100 eq. MAO**

mmol of 69	mmol of MAO	[MAO]/ [69]	Polyethylene (gm)	Polymer Yield (gm PE [mmol 69 , hr] ⁻¹)
0.05	5	100	2.68	53
0.05	5	100	2.51	50
0.05	5	100	2.37	47

Table X : Dependence of Polymer Yield on Ratio of 69:MAO

mmol of 69	mmol of MAO	[MAO]/ [69]	Polyethylene (gm)	Polymer Yield (gm PE [mmol. 69, hr] ⁻¹)
0.05	0.05	1	0	0
0.05	0.1	2	~0*	0
0.05	0.5	10	1.5	30
0.05	5	100	2.5	50

*Polymer yield was too low to be isolated

Table XI : Polymerization of Ethylene with 69 and 1000 eq. MAO

mmol of 74	mmol of MAO	[MAO]/ [69]	Polyethylene (gm)	Polymer Yield (gm PE [mmol. 69, hr] ⁻¹)
0.0025	2.5	1000	3.4	1364
0.0025	2.5	1000	4.7	1880
0.0025	2.5	1000	4.2	1684

In order to compare the polymer yields obtained with 69 with a known catalyst system, titanocene methyl chloride (23) was chosen as the metallocene catalyst with MAO as the co-catalyst. No polymerization of ethylene was seen with ten equivalents of MAO per equivalent of titanocene methyl chloride (23). Polymerization results of ethylene with 100 equivalents MAO with respect to titanocene methyl chloride (23) are provided in Table XII.

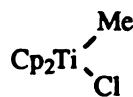
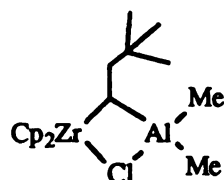


Table XII: Polymerization of Ethylene with 23 and 100 eq. MAO

mmol of 23	mmol of MAO	[MAO]/ [23]	Polyethylene (gm)	Polymer Yield (gm PE [mmol 23, hr] ⁻¹)
0.025	2.5	100	1.43	57
0.025	2.5	100	1.13	45
0.025	2.5	100	1.63	65

Polymerization of ethylene with **95** and MAO was studied at varying catalyst/MAO ratios. It was found that increase in the catalyst/MAO ratio equivalents of MAO resulted in increase in polymer yield. The results are provided in Table XIII.

**95****Table XIII : Dependence on Polymer Yield on Ratio of 95:MAO**

mmol of 95	mmol of MAO	[MAO]/ [95]	Polyethylene (gm)	Polymer Yield (gm PE [mmol. 95, hr] ⁻¹)
0.05	0.05	1	0	0
0.05	0.5	10	~0*	0
0.05	5	100	4.63	93
0.001	1	1000	1.94	1940

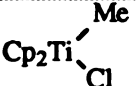
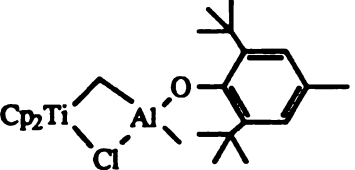
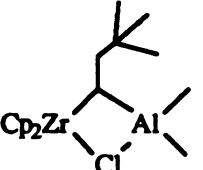
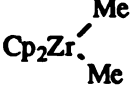
*Polymer yield too low to be isolated

The Tebbe reagent (**27**) and dimethyl zirconocene were also tested for polymerization activity. The results of polymerization of ethylene with the Tebbe reagent/MAO and dimethyl zirconocene/MAO are provided in Table XIV.

Table XIV : Polymerization of Ethylene with Tebbe Reagent/MAO and Dimethyl Zirconocene/MAO

Catalyst	mmol of catalyst	mmol of MAO	[MAO]/[cat]	PE (gm)	Polymer Yield (gm PE [mmol cat., hr] ⁻¹)
Cp ₂ ZrMe ₂	0.01	1.0	100	2.90	290
27	0.05	0.5	10	1.34	27
27	0.05	0.5	10	1.30	26
27	0.05	0.5	10	1.18	23

Table XV: Summary of Yields of Polyethylene with Various Catalysts

Compounds	10 equiv. MAO*	100 equiv. MAO	1000 equiv. MAO
 23	0	55**	
 69	30	50	1642
 27	25		
 95	~0	93	1940
		290	

* equivalents of MAO per equivalent of Catalyst; t_p=1 hour, P=45 psi;

**values are in units of (gm PE [mmol cat., hr]⁻¹)

POLYMERIZATION RESULTS UNDER INDUSTRIAL SETTING

The project was sponsored by B.P. Chemicals (subsidiary of British Petroleum Inc.). As such, the catalysts were sent to the parent company for further testing of polymerization of ethylene under industrial scale. The procedure used by the researchers at B.P. Chemicals, involved polymerization in *iso*-butane at 75 °C, with trimethyl aluminum as scavenger and aliquots of MAO and catalyst added periodically, under a ethylene pressure of 10 bar. The results obtained indicate that the yield of polyethylene by catalyst **95** was higher than that of zirconocene dichloride when the polymerization was carried out with 40 equivalents of MAO with respect to the metallocene component.⁵⁹

DISCUSSION OF POLYMERIZATION RESULTS

From the polymerization results, it was seen that the catalysts **69** and **95** polymerize ethylene in an efficient manner. Catalyst **69** was found to exhibit polymerization behavior with as low as 2 equivalents of MAO though the polymer yield was too low to be isolated. Titanocene methyl chloride (**23**) exhibited polymerization behavior only with 100 equivalents of MAO while no polymerization of ethylene was seen with titanocene methyl chloride (**23**) and 10 equivalents of MAO. This was in sharp contrast to the polymerization activity of **69**. The polymer yield was substantial when 10 equivalents of MAO was used with **69** thereby indicating that a lower amount of MAO was needed for catalyst **69** as compared to titanocene methyl chloride (**23**). The use of 100 equivalents of MAO with **23** or **69** resulted in similar yields of polymer. Also, the yield of polymer increased with increased amounts of MAO. The Tebbe reagent, **27** was also found to polymerize ethylene with 10 equivalents of MAO. The yield of the polymer was lower than that obtained by **69**.

The zirconocene catalyst **95** was compared to dimethyl zirconocene. Polymerization behavior was seen when catalyst **95** was used with 10 equivalents of MAO, while no such behavior was seen when dimethyl zirconocene was used with 10 equivalents of MAO. It was seen that dimethyl zirconocene polymerized ethylene more efficiently with 100 equivalents of MAO comparison to **95**. In general, the polymer yields

using the zirconium based catalysts were higher than that of the titanium based catalysts. The activities of zirconium based catalysts have been reported to be higher than that of titanium based catalysts in all studies reported in the literature. The polymerization studies carried out at B. P. Chemicals Laboratories compared the catalyst **95** with zirconocene dichloride. The yields of polymer using catalyst **95** were higher than yields obtained by the use of zirconocene dichloride.

The reaction of **69** with methyl aluminoxane provides the active catalyst. The reaction of titanocene methyl chloride with methyl aluminoxane also provides the active species responsible for polymerization. Based on the polymerization results, it can be reasoned that the catalysts **69** and **27** form active species with lower amounts of MAO when compared to **23** and a leveling off is seen when 100 equivalents of MAO are used. Polymer yields with 100 equivalents of MAO and catalyst **69** or **23** were similar, indicating that approximately the same number of active species were generated when 100 equivalents of MAO was used. It is expected that such a leveling off would continue and similar polymer yields would be obtained when higher equivalents (>100) are used with **69** or **23**.

CONCLUSIONS

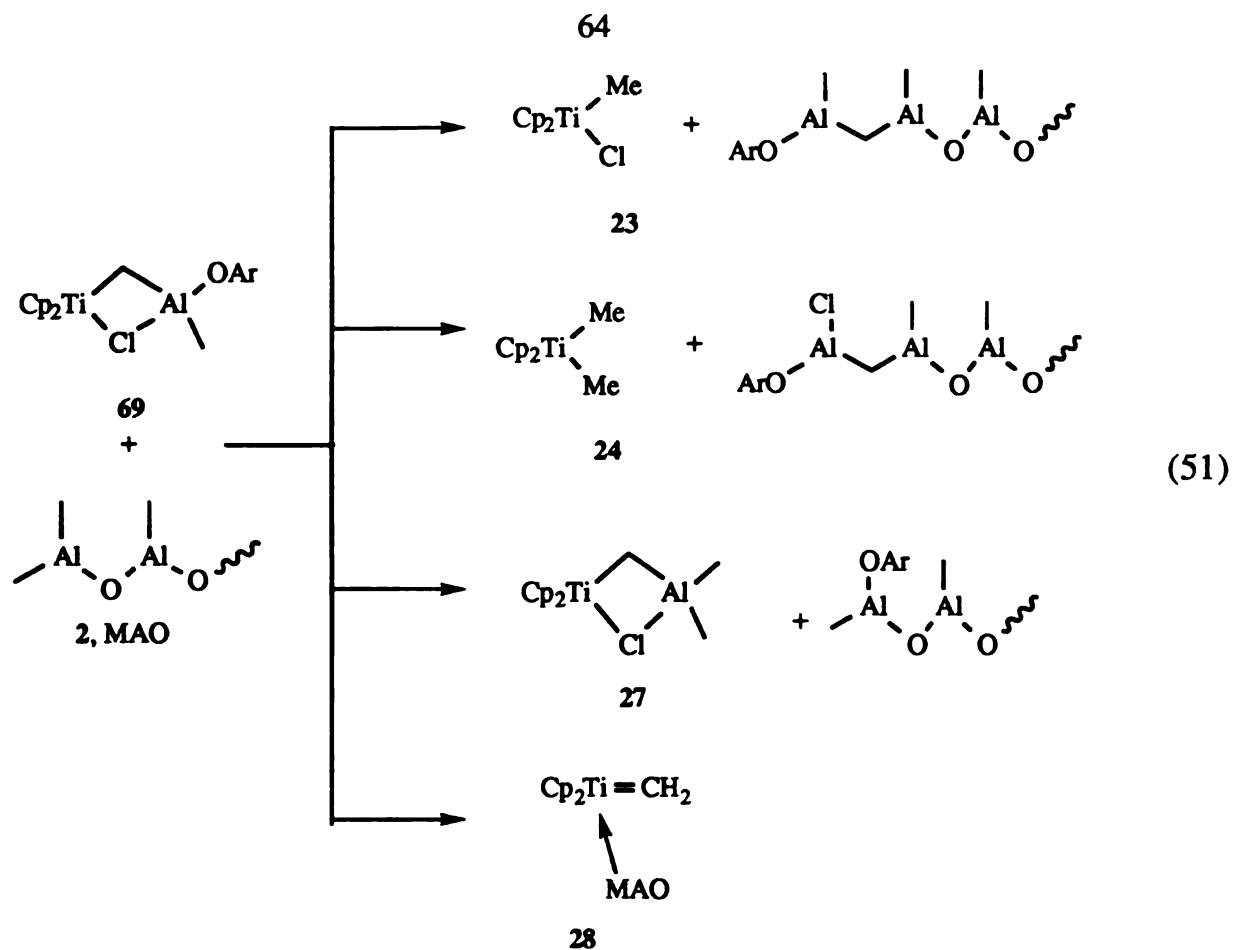
It was found that the catalysts **69** and **95** were efficient polymerization catalysts and comparable to the commercial catalysts. The amount of MAO to observe polymerization was substantially reduced when the bridged catalysts **69**, **27**, and **95** were used as the metallocene component of the catalyst system. The catalysts were tested at an industrial setting to translate the efficiency in the laboratory scale to an industrial setting. The industrial tests revealed that there is a modest increase in polymer yield when **95** was used as the catalyst and compared to the polymer yield when zirconocene dichloride was used. A PCT (Patent Cooperation Treaty) application is being filed at the United States Patent Office for patent protection of this and ongoing research.

CHAPTER IV

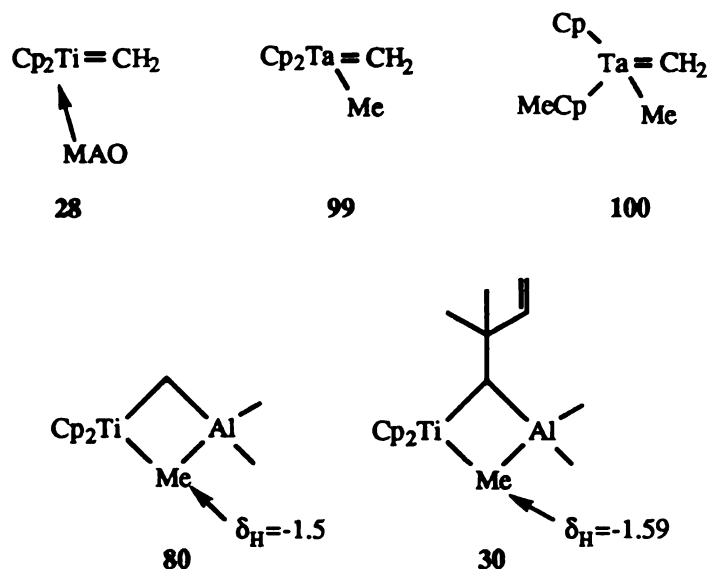
MECHANISTIC INVESTIGATION ON ACTIVE SPECIES IN BRIDGED HETEROBIMETALLIC POLYMERIZATION SYSTEMS

MECHANISM OF ACTION

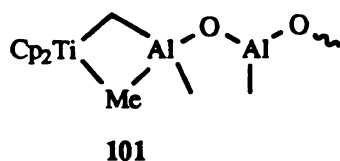
Catalyst **69** does not polymerize ethylene except in the presence of MAO. In obvious terms, the reaction of methyl aluminoxane with **69** provides an active species responsible for olefin polymerization. The reaction of **69** with 100 equivalents of MAO was monitored by NMR to determine the intermediates formed in the reaction. It was found that at low temperatures (-60 °C), only peaks corresponding to **69** and MAO were observed. However, as the temperature was raised, peaks corresponding to a number of products were observed. These were assigned to the Tebbe reagent (**27**), dimethyl titanocene (**24**), and titanocene methyl chloride (**23**). In addition to the resonances of these three compounds, additional resonances were seen. A compound exhibiting peaks at -2.42 ppm along with two doublets at 7.66-7.63 and 7.33-7.30 ppm ($J \approx 8$ Hz) could be seen in the spectra along with corresponding cyclopentadienyl peaks at 5.49 ppm and 5.45 ppm. The spectra of this compound was identical to that observed by Tritto and co-workers in the reaction of titanocene methyl chloride and MAO wherein the authors had tentatively characterized it as **28** (eq. 10).²⁹ The products formed in the reaction of **69** and MAO are shown in equation 51.



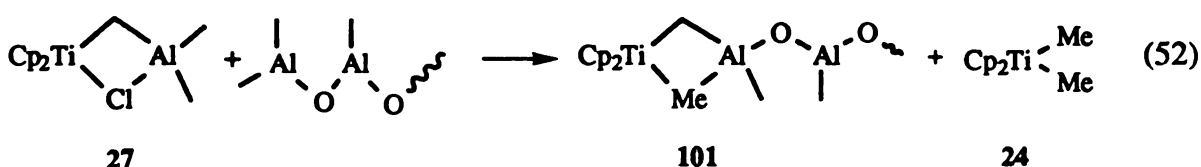
The complex **28** was characterized based on its proton and ^{13}C NMR. A reference was made to a tantalum based compound **99** and the splitting pattern of the methylene protons of **28** compared to **99**.⁶⁰ The existence of coupling between the hydrogens of the methylene carbon was considered to be due to an asymmetry in the adduct **28**. Compound **99** exhibits a singlet for the methylene peaks, along with singlets for methyl and cyclopentadienyl peaks. The $J_{\text{H-H}} = \text{ca } 9 \text{ Hz}$ was actually compared to the coupling constant of **100** (though mistakenly referred to as compound **99**) wherein the coupling constant was 7.6 Hz .⁶⁰ Compound **100** is asymmetric owing to the presence of different cyclopentadienyl groups.



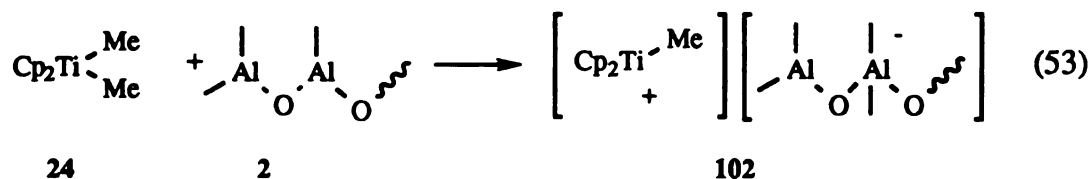
The methylene group of **28** appears as two doublets with a coupling constant of approximately 9 Hz. The cyclopentadienyl groups of **28** appear as two singlets at 5.49 ppm and 5.45 ppm. A singlet at -2.24 ppm for a methyl group remained unassigned, with a corresponding peak at -10.73 ppm for the ^{13}C NMR. The bridged carbon resonated at 178 ppm by ^{13}C NMR. A comparison of various methylene bridged compounds reported in literature is essential to suggest the actual structure of compound **28**. The protons of the bridging methyl group of **80** were found to resonate at -1.5 ppm while the bridging methyl group of **30** has been reported to resonate at -1.59 ppm. The methylene group of **28** has been reported to resonate at 178.9 ppm on the ^{13}C NMR. When the Tebbe reagent was converted to **69**, the methylene protons shifted upfield as AB doublets with a coupling constant of 7.5 Hz. In addition the chemical shifts of the cyclopentadienyl rings and the methylene bridge of **28** parallels the shifts of resonances observed for compounds **67-70** (Table III). As mentioned in chapter II, presence of an aryloxy group shifted the proton resonances of the cyclopentadienyl rings upfield. The coupling constant of the methylene protons in **70** was found to be 7.8 Hz indicating that presence of electron withdrawing group on the aluminum atom increases the coupling constant. Based on the foregoing discussion, it is reasonable to assume that the species **28** is actually the methyl bridged compound **101**. The chemical shifts of the bridging methyl group of **101** (-2.42 ppm) and **80** (-1.56 ppm) indicate that the methyl group of **101** has more anionic character than the bridging methyl group in **80**.



The product mixture was found identical to that in the study by Tritto and co-workers, wherein the authors studied the interaction of titanocene methyl chloride with MAO (eq. 8-10). Owing to the multiple products formed by the reaction of MAO with **69**, determination of the key species responsible for polymerization, was difficult. In order to avoid the complexity of the spectra overwhelmed by the intensities of the *tert*-butyl groups on the phenoxy ring, a reaction of Tebbe reagent with MAO was monitored by NMR. As with **69**, the reaction of **27** with MAO led to the formation of **101** and dimethyl titanocene (eq. 52).

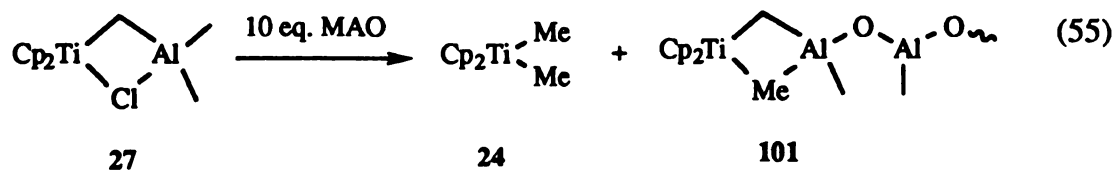
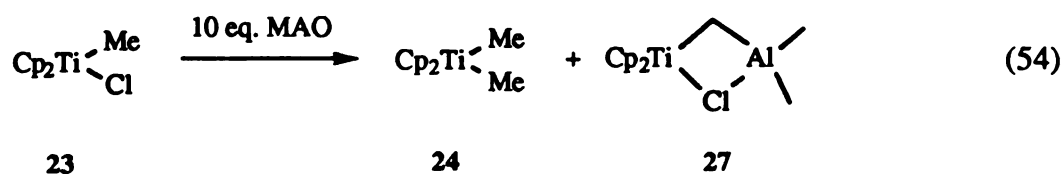


The formation of identical products from the reactions of Tebbe reagent, **27**, titanocene methyl chloride, **23** and catalyst **69** with MAO can be rationalized by simple transmetallation reactions and α -activation reactions. The species active for polymerization is generally considered to be a cationic species (**102**) generated by abstraction of a methyl group by MAO (eq. 53).



Results from Chapter III indicate that titanocene methyl chloride did not polymerize ethylene with 10 equivalents of MAO, while the Tebbe reagent (**27**), polymerized ethylene efficiently. As such, the reaction of titanocene methyl chloride with 10 equivalents of MAO was monitored by NMR. The reaction mixture of 10 equivalents of MAO with titanocene

methyl chloride (**23**) contained dimethyl titanocene (**24**), Tebbe reagent (**27**) and unreacted titanocene methyl chloride (eq. 54). No formation of **101** was detected. The resonance of the bridging methyl peak at -2.42 ppm and the doublet at 7.66 ppm is diagnostic for the presence of **101**. A reaction of Tebbe reagent with 10 equivalents of MAO led to a reaction mixture consisting of **101**, dimethyl titanocene and unreacted Tebbe reagent (eq. 55). The reactions were carried out and monitored at similar concentration, amount of reactants and temperature. Proton NMR of reaction mixtures of equations 54 and 55 are included as appendix VIII and IX respectively. The product ratios did not change over long periods (6 hours) and running the reaction overnight led to partial decomposition of the products. Since the delay times of the titanium based compounds were long (>120 secs) and the resonances of the methyl peaks of dimethyl titanocene overlap with the peaks of MAO, proper integration could not be obtained for product ratios.

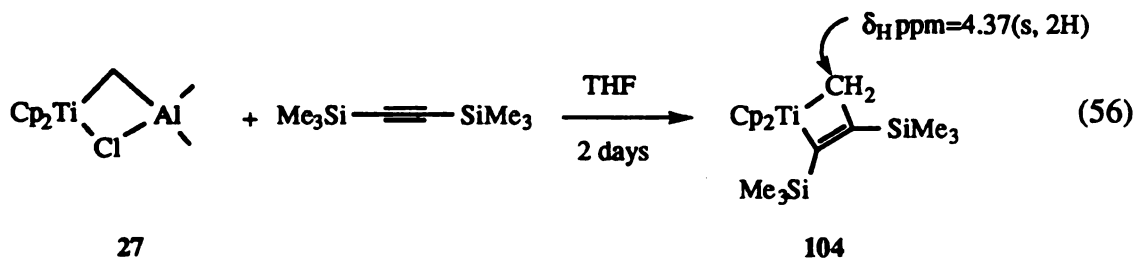


The presence of dimethyl titanocene (**24**) and MAO in both reactions (eq. 54) and (eq. 55) does not explain the relative difference in the polymerization abilities of the reaction mixture. The presence of **101** in the reaction of Tebbe with 10 equivalents of MAO and the absence of **101** in the reaction of titanocene methyl chloride with 10 equivalents of MAO could provide an explanation to the reactivity. Alternatively, it is quite possible that the suggested active species **102** is formed faster with the Tebbe reagent than with **23**, although such a species was not detected in either case.

INSERTION OF ALKYNES

Eisch and co-workers have suggested that a bulky alkyne such as phenyl trimethylsilyl acetylene could be considered as a surrogate to alkenes and that the repeated insertion does not occur owing to steric considerations.⁶¹ In order to test the progress of insertion of an alkyne to any one of the above products, mixture of Tebbe reagent and MAO (25 equiv.) was taken up in an NMR tube with an equimolar amount of alkyne, phenyl trimethylsilyl acetylene (**103**) at -30 °C. This sample was loaded in the NMR probe and the reaction monitored with time. As soon as the tube was inserted and the first initial spectra was taken, the peak at -2.42 ppm and doublets at 7.66-7.60 ppm and 7.33-7.30 ppm corresponding to **101** disappeared. The cyclopentadienyl peaks at 5.49 and 5.45 corresponding to **101** had also disappeared. Substantial changes were seen in the intensities of MAO peaks. A sharp singlet at 3.63 was observed, with an intensity much greater than that of the bridging methyl group or the bridging methylene groups of **101**. Two peaks corresponding to the Tebbe reagent and dimethyl titanocene were observed along with small peaks around that region.

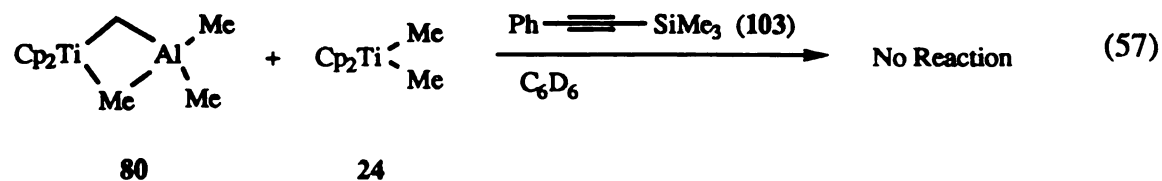
Tebbe and co-workers have carried out insertions onto various alkynes, shown in equation 56. The reaction of Tebbe reagent with bis-trimethylsilyl acetylene provides intermediate titanocene methylene complexes which add across triple bonded compounds to provide titanacyclobutenes. The reaction takes two days to go to completion in tetrahydrofuran while it is sluggish in toluene (eq. 56).⁶²



A reaction of alkyne **103** with **101** analogous to equation 56 could not be rationalized owing to the high intensity of the peak at 3.63 ppm, which would be expected to match the intensities of the AB doublets of the methylene protons of **101**. Negishi and

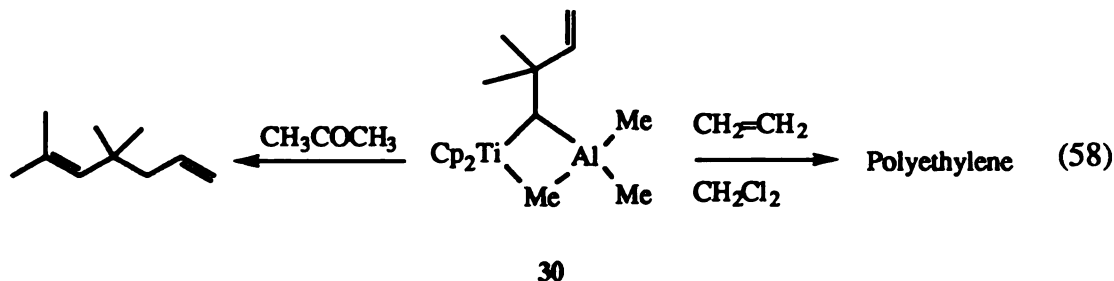
co-workers have reported carbometallation of disubstituted alkynes in the presence of titanocene dichloride and trimethyl aluminum⁶³ and Wipf and co-workers have reported increases in rates of carbometallation of alkynes with zirconocene dichloride/MAO mixtures.⁶⁴ Based on the available literature and the fact that changes were seen in the intensities of MAO during the reaction of alkyne **103** with a mixture of **101** and MAO, it is plausible that carbometallation of alkyne **103** occurred in the reaction mixture. Results of similar reaction with 3,3-dimethyl-1-butene were not conclusive in determining the nature of the active species.

In order to further simplify the model, tests were carried out with **80**. The compound **80** is similar to **101** in many respects *i.e.* having the methyl bridge and the methylene bridge. As mentioned in Chapter II, **80** could only be synthesized as an adduct with dimethyl titanocene. Compounds **80** and dimethyl titanocene, **24** were taken in an NMR tube and the alkyne **103** was introduced into the tube. No reaction was seen even at elevated temperatures (50 °C). Attempts to treat alkenes such as norbornylene, 3,3-dimethyl-1-butene with a mixture of **80** and **24** failed to provide any reaction products.

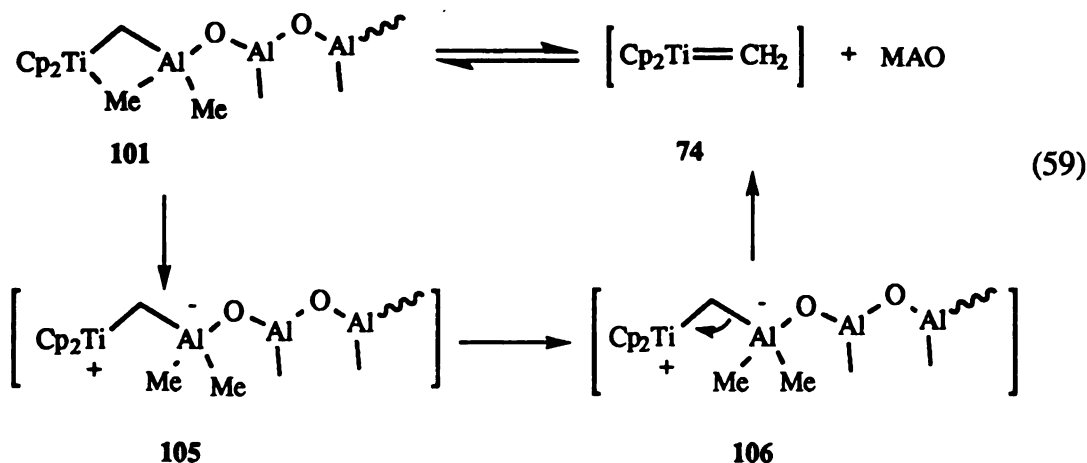


Attempts were made to study the reactivity of complex **95** with MAO. No reaction was observed with MAO at room temperatures. At elevated temperatures (50 °C), a distinct color change was observed (greenish-yellow to pale orange). However, no changes in the NMR peaks were observed. Prolonged heating resulted in some formation of dimethyl zirconocene as a side product. These results indicated that the zirconocene based catalyst **95** did not undergo cleavage by MAO. Studies were also carried out to observe insertion of alkynes (phenyl trimethylsilyl acetylene) and alkenes (norbornylene, 3,3-dimethyl-1-butene) with **96** (obtained as a mixture with dimethyl zirconocene). No reaction was observed with any of the olefins studied.

Tritto and Grubbs have reported that heterobimetallic compounds of titanium and aluminum such as **30** behave as borderline catalytic complex between metathesis and Ziegler-Natta catalysts depending on the reaction conditions. Specifically compound **30** was shown to exhibit Wittig type reactivity towards ketones, while exhibiting polymerization activity with ethylene in dichloromethane.³¹

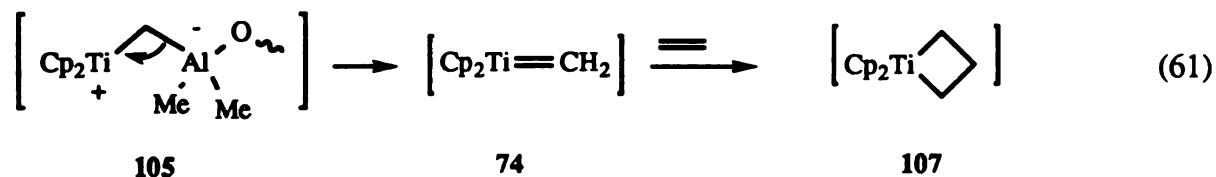
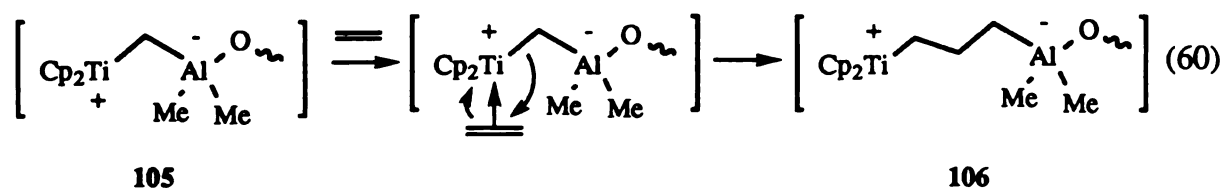


Although attempts were made to determine the nature of active species in the study carried out herein, the results were inconclusive. However, it was observed that compound **101** was formed in the reaction of **27** and 10 equivalents of MAO and hence the reactivity pattern of **101** can be speculated and rationalized based on available literature precedent. Based on the work of Tritto and Grubbs, a reaction scheme can be shown to indicate the possible modes (metathesis or ion-pair) of the reactivity of **101** (eq. 53).

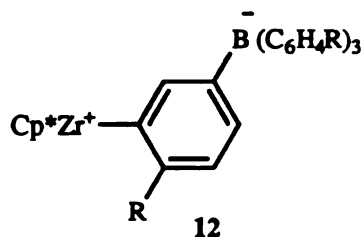


The compound **105**, if trapped by an olefin could undergo insertion onto the titanium-methylene bond to provide **106**. Repeated insertions of the olefin would result in a growing polymer chain (eq. 60). Alternatively, if the carbon-aluminum bond is facile, a

titanacyclobutane could be expected providing **107**, which would represent deactivation of an active catalyst site (eq. 61).

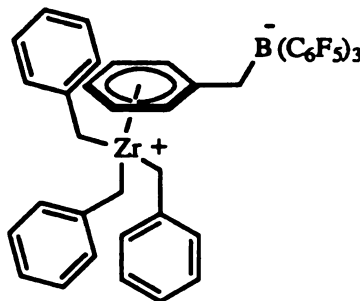


As mentioned in Chapter I, Hlatky and co-workers²⁴ and Petersen and co-workers⁶⁵ have carried out synthesis of zwitterionic complexes such as **12** through different routes, which were found to polymerize ethylene in the absence of an aluminum co-catalyst. Zambelli and co-workers have isolated and characterized zwitterionic complexes of the non-metallocene complex **108** and observed that **108** polymerized ethylene under mild conditions.⁶⁶



R=H, Me, Et

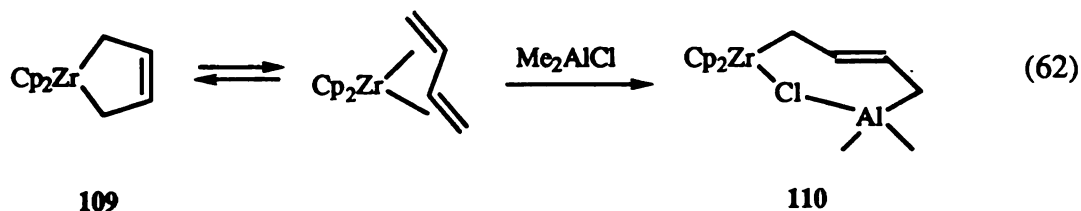
12



108

Compounds **105** as well as **12** and **107** are different in the sense that the anion and the cation are farther apart in **12** and **107**. The existence of **105** and the bond strengths of titanium-carbon *versus* carbon-aluminum would play an important role in determining whether **101** would exhibit polymerization behavior or deactivate to titanacyclobutanes.

Erker and co-workers have carried out syntheses of hydrocarbyl bridged zirconium- and aluminum containing mixed metal complexes such as **110** and are studying the opening of these complexes into betaine like structures (eq. 62).³⁷



A few reports in the literature indicate the steps of alkene insertion and these include catalytically inactive complexes such as $\text{Cp}_2\text{Zr}(\text{benzynes})^{67}$, $[\text{Cp}_2\text{Zr}(\eta^2\text{-N,C-pyridyl})]^+$,⁶⁸ and lanthanide complexes such as $(\text{C}_5\text{Me}_5)\text{MMe}$ ($\text{M}=\text{Lu}, \text{Y}, \text{Sc}$)⁶⁹ which are active towards ethylene polymerization.

A simple observation that compound **101** is formed with 10 equivalents of MAO while a similar compound is not formed with titanocene methyl chloride and MAO is not a conclusive proof that compound **101** is an active species responsible for polymerization. It should be noted that Tritto and co-workers observed the formation of **101** with 10 equivalents of MAO in 43% yield at +10 °C. At temperatures less than +10 °C, the formation of **101** was not observed. Further, all the product mixtures were found to polymerize ethylene, although no relative yields or experimental details were provided.

CONCLUSIONS

The mechanistic studies to observe insertion products provided some insight into the reactivity of the intermediates produced by the metallocene-MAO mixtures, though the results were not conclusive. Models for the catalysts **101** and **95**, i.e. **80** and **96** did not exhibit any insertion with alkynes and strained olefins. Alkyne **103** was found to react rapidly with **101**. However, the products of the reaction could not be characterized. Models for insertion or termination modes for the reaction of **101** with olefin were proposed based on the available results.

EXPERIMENTAL

GENERAL

All reactions were conducted under argon atmospheres using standard Schlenk techniques. THF, diethyl ether, toluene, and benzene were distilled from sodium/benzophenone prior to use. CH_2Cl_2 was distilled from calcium hydride. Hexane was stirred over sulfuric acid, and after 5 days, the hexane was washed sequentially with H_2O , saturated aqueous NaHCO_3 , dried (CaCl_2), and distilled from calcium hydride. All phenols were purchased from Aldrich Chemical Co., 2,6-di-*tert*-butyl phenol was purified by distillation prior to use, and the other phenols were used without further purification. Zirconocene dichloride and titanocene dichloride were purchased from Boulder Scientific. Butyllithium, methyllithium, trimethyl aluminum, dimethyl aluminum chloride, and methylaluminum dichloride were purchased from Aldrich Chemical Co. Ethylene (CP grade, 98% pure) was purchased from Air Products Inc.

NMR spectra were obtained on a Varian Gemini 300, VXR-300 or VXR-500 instrument with C_6D_6 or C_7D_8 as solvent. Signals are reported in units of ppm relative residual protons ($\delta = 7.15$ ppm for C_6D_6 or $\delta = 2.09$ ppm for C_7D_8) and ^{13}C of the deuterated solvents ($\delta = 128$ ppm for C_6D_6 or $\delta = 137$ ppm for C_7D_8). Mass spectral data were obtained at the Michigan State University Mass Spectrometry facility which is supported, in part, by a grant (BBR-00480) from the biotechnology research technology program, National Center for Research Resources, National Institutes of Health.

Synthesis of Methyl aluminoxane (1):

$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (9.27 g, 14 mmol) was placed in a well dried Schlenk flask and the flask evacuated and purged with argon. Toluene (125 mL) was added to the salt and the suspension cooled to $-70\text{ }^\circ\text{C}$. Trimethyl aluminum (12.5 mL, 140 mmol) was added dropwise *via* a canula and the reaction mixture was allowed to warm up to room temperature. The reaction mixture was stirred for 24 h and filtered with a Schlenk frit funnel to separate the aluminum sulfate salt. The filtrate was concentrated to dryness, redissolved in toluene (25 mL) and the toluene evacuated to provide 3.7 g MAO.

Preparation of Titanocene methyl chloride (23):

Titanocene dichloride (2.49 g, 10 mmol) was placed in a dry Schlenk flask, which was evacuated and purged with argon. Dichloromethane (20 mL) was added and the solution was cooled to 0°C . Methyl magnesium chloride (3.33 mL, 10 mmol, 3 M solution in THF) was added dropwise, and the mixture was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was filtered through a frit and the solvents were evacuated and the solids were redissolved in toluene, cooled to 0°C and filtered. The mixture was concentrated in *vacuo*, to provide 23 (2.03 g, 89% yield) as a orange-red solid. ^1H NMR (300 MHz, C_6D_6) δ 0.85 (s, 3 H), 5.74 (s, 10 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 49.20, 115.57 ppm.

Preparation of Dimethyl titanocene (24):

The reaction was carried out in dark : To a solution of titanocene dichloride (2.49 g, 10 mmol) in 50 mL diethylether at $-5\text{ }^\circ\text{C}$, was added methyl lithium (22.8 mL, 32 mmol, 1.4 M in diethyl ether) and the reaction stirred for 15 minutes at room temperature. The reaction mixture was cooled to $0\text{ }^\circ\text{C}$ and 1.5 mL water was introduced into the reaction mixture. The organic layer was dried with sodium sulfate and the ether evaporated to almost dryness. The dimethyl titanocene•etherate (80% yield) was used without any attempts to remove the coordinated solvent. Note: Complete evacuation of the reaction

mixture resulted in explosive autocatalytic decomposition. ^1H NMR (300 MHz, C_6D_6) δ 0.05 (s, 6 H), 5.67 (s, 10 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 113.1, 46.2 ppm.

Synthesis of Dimethyl zirconocene:

To a solution of zirconocene dichloride (2.92 g, 10 mmol) in toluene (20 mL) was added dropwise methyl lithium (14.3 mL, 20 mmol, 1.4 M in THF) at 0 °C and the reaction mixture allowed to warm to room temperature and stirred for 4 hours. The reaction mixture was cooled to 0 °C and solids filtered with a Schlenk frit funnel. The toluene solution was evacuated to provide a yellow-white solid which was sublimed (100 °C, 0.1 mm Hg) to obtain pure dimethyl zirconocene (2.1 g, 86% yield). ^1H NMR (300 MHz, C_6D_6) δ 0.31 (s, 6 H), 5.748 (s, 10 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 32.08, 112.50 ppm.

Synthesis of Tebbe Reagent (27):

To a solution of titanocene dichloride (2.49 g, 10 mmol) in 40 mL toluene was added trimethyl aluminum (10 mL, 20 mmol, 2.0 M in toluene) at room temperature and the reaction mixture stirred for 2 days. The volatile components (toluene and dimethyl aluminum chloride) were evacuated and additional toluene (20 mL) added to the solids. Trimethyl aluminum (10 mL, 20 mmol, 2.0 M in toluene) was added to the solution and the reaction mixture stirred for an additional day. The reaction mixture was then evacuated to dryness, dissolved in 15 mL toluene, cooled to 0 °C, and filtered through a Schlenk frit funnel. The toluene was evacuated to provide a deep red solid (2.21 g, 78% yield). Note: Trimethyl aluminum and dimethyl aluminum chloride are pyrophoric and extreme precaution should be taken in disposal of the volatile liquids condensed in the traps. This is achieved by venting the vacuum part of the Schlenk line along with the traps while cold, to argon and diluting the contents of the traps with hexanes. ^1H NMR (300 MHz, C_6D_6) δ -0.29 (s, 6 H), 5.62 (s, 10 H), 8.28 (s, 2 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 187.58, 112.30, -6.0--8.0 (br) ppm.

General Synthesis of Dimethyl 2,6-*tert*-butyl-4-X-aryloxy aluminum:

To a solution of phenol (6 mmol) in 15 ml toluene was added AlMe₃ (6 mmol, 2.0 M in toluene), dropwise. The reaction mixture was heated to reflux for 4 hours after the evolution of gases stopped. Attempts to isolate the compound, by evaporation of toluene frequently led to additional products such as methyl aluminum diaryloxy. Hence the aryloxy dimethylaluminum was used as a solution *in situ* for further reactions.

Dimethyl-2,6-di-*tert*-butylphenoxy aluminum (89 % yield): ¹H NMR (300 MHz, C₆D₆) δ -0.3 (s, 6 H), 1.55 (s, 18 H), 6.91 (t, *J*=7.5 Hz, 1 H), 7.29 (d, *J*=7.5 Hz, 2 H).

Synthesis of 69 with Titanocene methyl chloride (23):

A solution solution of dimethyl 2,6-di-*tert*-butyl-4-methylphenoxy aluminum (1.2 eq.) was transferred *via* a canula into a flask containing titanocene methyl chloride (1.0 eq.) and the reaction mixture was stirred for 6 days. The reaction mixture was monitored for completion of the reaction by ¹H NMR (disappearance of titanocene methyl chloride). After completion of the reaction, the mixture was evacuated to remove all volatiles and the solids washed with hexane (2 x 20 mL) to remove excess aluminum compounds. The solids were then taken in up toluene (20 mL), filtered through a frit and the solution evacuated to provide 69 as a deep red solid.

General Synthesis of Compounds 67-70 with Tebbe Reagent (27):

To a solution of Tebbe reagent (1.42 g, 5 mmol) in 15 mL toluene, was added a solution of 2,6-di-*tert*-butyl-4-X-phenol (6 mmol) and stirred for 6 days at room temperature. A sample of the reaction mixture was periodically transferred into another Schlenk flask, evacuated and tested for completion by ¹H NMR (disappearance of titanocene methyl chloride). After completion of the reaction, the solvents was evaporated and the solids washed with hexane (2 x 20 mL), taken up in toluene and filtered. The solution was then evacuated off the volatiles, to provide a deep red product.

67 (1.91 g, 72% yield): ^1H NMR (300 MHz, C_6D_6) δ -0.26 (s, 3 H), 1.43 (s, 9 H), 1.71 (s, 18 H), 5.63 (s, 5 H), 5.97 (s, 5 H), 7.55 (s, 2 H), 7.86 (d, $J=7.5$ Hz, 1 H), 7.98 (d, $J=7.5$ Hz, 1 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 176.7, 154.5, 139.2, 138.3, 122.3, 113.5, 113.0, 35.6, 34.6, 32.1, 31.7, -6.6 ppm. HRMS calcd for $\text{C}_{30}\text{H}_{44}\text{AlClOTi}$ 530.2375, obsd 530.2382.

68 (1.25 g, 53% yield): ^1H NMR (300 MHz, C_6D_6) δ -0.29 (s, 3 H), 1.62 (s, 18 H), 5.63 (s, 5 H), 5.96 (s, 5 H), 6.89 (t, $J=7.8$ Hz, 1 H), 7.37 (d, $J=7.8$ Hz, 2 H), 7.79 (d, $J=7.5$ Hz, 1 H), 7.89 (d, $J=7.5$ Hz, 1 H). ^{13}C NMR (75.5 MHz, C_6D_6) 175.7, 157.0, 139.3, 125.6, 119.1, 113.6, 113.1, 35.3, 31.6 ppm.

69 (1.85 g, 76% yield): ^1H NMR (300 MHz, C_6D_6) δ -0.23 (s, 3 H), 1.676 (s, 18 H), 2.354 (s, 3 H), 5.63 (s, 5 H), 5.97 (s, 5 H), 7.26 (s, 2 H), 7.855 (d, $J=7.5$ Hz, 1 H), 7.97 (d, $J=7.5$ Hz, 1 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 176.3, 154.7, 138.9, 126.2, 113.5, 113.0, 35.2, 31.6, 21.4, -6.8 (br) ppm. HRMS calcd for $\text{C}_{27}\text{H}_{38}\text{AlClOTi}$ 488.1906, obsd 488.1908.

70 (1.70 g, 62% yield): ^1H NMR (300 MHz, C_6D_6) δ -0.28 (s, 3 H), 1.49 (s, 18 H), 5.62 (s, 5 H), 5.92 (s, 5 H), 7.60 (s, 2 H), 7.68 (d, $J=7.8$ Hz, 1 H), 7.76 (d, $J=7.8$ Hz, 1 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 174.3, 156.2, 141.8, 128.8, 113.7, 113.1, 111.2, 35.3, 31.3, 31.1 ppm. HRMS calcd for $\text{C}_{26}\text{H}_{35}\text{AlBrClOTi}$ 552.0854, obsd 552.0873.

Crystal Structure Determination of **69**:

To a concentrated solution of **69** in toluene was added hexane as a top layer and allowed to stand without any agitation for two days. Deep red crystals were seen to deposit along the sides of the test-tube. The mother liquor was separated from the crystals and the crystals coated with Paratone-N oil and brought out of the dry box. A deep red crystal of dimensions 0.20 mm x 0.60 mm x 0.85 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Nicolet P3F diffractometer equipped with a graphite crystal incident beam monochromator.

so
T
A
de
fr

co
co
sc
co
cr
49
ob

co
sc
wi

hy
we
po
inc
R₁
1.0
est

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $20.5 < 2\theta < 25.0^\circ$. The orthorhombic cell parameters and calculated volume are $a=14.673(2) \text{ \AA}$, $b=9.183(2) \text{ \AA}$, $c=19.745(3) \text{ \AA}$ and $V=2653.5(7) \text{ \AA}^3$. For $Z=4$ and $M_r=488.90$, the calculated density is 1.224 Mg/m^3 . From systematic absences of $h0l$, $l=2n+1$, $0k0$, $k=2n+1$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$.

The data were collected at a temperature of $175(5) \text{ K}$ by θ - 2θ technique, at a constant scan rate of $2^\circ/\text{min}$. The scan range (in deg) was determined as a function of 2θ to correct for the separation of the $K\alpha$ doublet, the scan width was calculated as follows: $2\theta \text{ scan width} = 1.5 + (2\theta(K\alpha_2) - (2\theta(K\alpha_1)))$. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.5 mm and the crystal to detector distance was 19 cm. A total of 4910 reflections were collected, of which 4968 reflections were unique and not systematically absent. No decay of the crystal was observed and as such no correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 0.472 mm^{-1} for Mo $K\alpha$ radiation. An empirical absorption correction, based scans, was applied to the data. Relative transmission coefficients ranged from 0.93 to 1.00 with an average value of 0.97. No secondary extinction correction was applied.

The structure was solved using SIR92 which revealed the positions of all non-hydrogen atoms. The chloride and the methylene units along with the 4'-methyl group were found to be disordered and refined with an occupancy factor of 0.5. Hydrogen atom positions and isotropic thermal parameters were refined. The final cycle of refinement included 462 variable parameters and converged with agreement factors of $R_1=0.052$ and $wR_2=0.1188$. The standard deviation of an observation of unit weight was 1.074. The highest peak in the final difference Fourier had a height of $0.27 \text{ e/\AA}^3$ with an estimated error based on σ_F of 0.06.

Synthesis of Zirconocene hydridochloride (**84**):

Zirconocene dichloride (8.76 g, 30 mmol) was dissolved by heating in THF (60 mL), and the solution cooled to room temperature. To this solution, was added dropwise a solution of lithium aluminum hydride (8.32 g, 22 mmol) in 20 mL THF at room temperature and the reaction mixture stirred for 30 minutes. The reaction mixture was filtered under argon using a Schlenk frit funnel, and the white solid collected, washed successively with THF (2 x 20 mL), dichloromethane (2 x 20 mL), and dried *in vacuo* to provide 5.6 g of **84** in 72% yield.

Synthesis of **91**:

To a solution of *tert*-butyl acetylene (0.205 g, 2.5 mmol) in toluene (10 mL), at 0°C, was added *n*-butyl lithium dropwise (1 mL, 2.5 M in hexane). The reaction mixture was stirred for 3 hours at room temperature and cooled to 0°C. Dimethylaluminum chloride (1.25 mL, 2.5 mmol, 2.0 M in toluene) was added to the lithium *tert*-butylacetylide, dropwise and the reaction mixture was stirred overnight. This suspension was then transferred to a flask containing a suspension of Cp₂Zr(H)Cl (0.76 g, 2.9 mmol) in CH₂Cl₂ (20 mL), cooled at 0°C. The reaction mixture was stirred for 6 hours at room temperature. The reaction mixture was filtered using a Schlenk frit funnel and the solvents evacuated to provide 0.71 g of crude **91**. The crude product was sublimed at 100 °C (0.013 mm Hg) to provide 0.31 g of fairly pure **91** in 31% yield. ¹H NMR (300 MHz, C₆D₆) δ -0.21 (s, 6 H), 0.95 (s, 9 H), 5.70 (s, 10 H), 7.0 (s, 1 H).

Synthesis of **92**:

To a solution of *tert*-butyl acetylene (0.205 g, 2.5 mmol) in toluene (15 mL), at 0°C, was added *n*-butyl lithium dropwise (1 mL, 2.5 M in hexane). The reaction mixture was stirred for 3 hours at room temperature and cooled to 0°C. Dimethylaluminum chloride (1.25 mL, 2.5 mmol, 2.0 M in toluene) was added to the lithium *tert*-butylacetylide, dropwise and the reaction mixture was stirred overnight to provide **90**. In a separate flask, Cp₂ZrCl₂ (0.73 g, 2.5 mmol) was dissolved in CH₂Cl₂ (15 mL) and trimethyl aluminum

(1.25 mL, 2.5 mmol, 2 M in toluene) added dropwise and the reaction stirred at room temperature for 10 minutes. The suspension of **90** was transferred to the flask containing zirconocene dichloride and trimethyl aluminum using a canula and the reaction mixture stirred for 3 hours. The reaction mixture filtered using a Schlenk frit funnel and the volatile solvents evacuated to provide 0.46 g of fairly pure **92** in 45% yield. (Note: The procedure followed paralleled to that in reference 56). ^1H NMR (300 MHz, C_6D_6) δ -0.14 (s, 6 H), 0.94 (s, 9 H), 1.97 (s, 3 H), 5.71 (s, 10 H).

Synthesis of **95**:

To a suspension of $\text{Cp}_2\text{Zr(H)Cl}$ (0.51 g, 2 mmol) in 15 mL of dichloromethane was added tert-butylacetylene (0.14 g, 2 mmol), dropwise. The reaction mixture was stirred for 3 hours at room temperature. The reaction mixture was cooled to $-40\text{ }^\circ\text{C}$ and a solution of AlMe_3 (1 mL, 2 mmol, 2M in toluene) was added to the reaction mixture and stirred for additional 3 hours. The reaction mixture was evacuated and the product, the alkenyl dimethylaluminum was taken up in hexane (20 mL).

The hexane solution of alkenyl dimethylaluminum was then transferred dropwise to a flask containing $\text{Cp}_2\text{Zr(H)Cl}$ (0.51 g, 2 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 3 hours at room temperature. After evacuation of volatiles, the product was taken up in hexane (20 mL), filtered and evacuated to provide 0.55 g of **95** as a yellow colored product in 70% overall yield. ^1H NMR (300 MHz, C_6D_6) δ -0.25 (s, 6 H), 0.85 (s, 9 H), 2.9 (dd, $J=15.11\text{ Hz}$, 4.67 Hz, 1 H), 3.15 (dd, $J=9.89\text{ Hz}$, 15.11 Hz, 1 H), 5.70 (s, 5 H), 5.74 (s, 5 H), 6.9 (dd, $J=4.67\text{ Hz}$, 9.89 Hz, 1 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 151.6, 111.0, 58.8, 33.3, 29.4 ppm.

Synthesis of $\text{Me}_4\text{Al}^- \text{Li}^+$:

A solution of trimethyl aluminum (0.721 g, 1 mmol) in 5 mL hexane was cooled to $-70\text{ }^\circ\text{C}$, and methyl lithium (0.71 mL, 1 mmol, 1.4 M in diethyl ether) was added dropwise with vigorous stirring. After the addition was complete, the reaction mixture was allowed

to warm to room temperature and the hexane evacuated to provide a white amorphous powder insoluble in toluene or benzene in 98% yield.

Synthesis of **96**:

To a solution of **95** (0.078 g, 0.198 mmol) in 5 mL hexane, cooled to -70 °C, was added a cold solution of **95** (0.047 g, 0.5 mmol) dropwise and the reaction mixture stirred for 15 min. at 0 °C. The reaction mixture was cooled to -10 °C, filtered with a Schlenk frit funnel and the hexane evaporated to provide an oily compound as a mixture of dimethyl zirconocene and **96** (0.065 g, 41% yield). ¹H NMR (300 MHz, C₆D₆) δ -1.01 (s, 3 H), -0.38 (s, 3 H), -0.35 (s, 3 H), 0.91 (s, 9 H), 2.92 (dd, *J*=4.6 Hz, 15.0 Hz, 1 H), 3.09 (dd, *J*=9.9 Hz, 15.0 Hz, 1 H), 5.51 (s, 5 H), 5.56 (s, 5 H), 7.58 (dd, *J*=4.7 Hz, 9.8 Hz, 1 H); ¹³C NMR (75.5 MHz, C₆D₆) δ 168.0, 109.2, 108.9, 59.3, 33.1, 29.5, -7.2 ppm.

Reaction of Me₄Al⁻ Li⁺ (**79**) with Tebbe Reagent (**27**):

To a suspension of **79** in benzene-d₆ was added a solution of Tebbe reagent (**27**) and the NMR taken periodically to check for completion. It was found that the product ratio depended on the amount of **79** added and the ratios of compounds formed are provided in Scheme VIII.

NMR Studies of **23** + 10 eq. MAO:

To a solution of **23** (0.025 mmol, 0.1 mL, 0.25 M in d₆-benzene) was added 0.7 mL d₆-benzene and the solution cooled to 5 °C. To this NMR tube was injected, MAO (0.25 mmol, 0.1 mL, 2.5 M in d₆-benzene) and the NMR tube shaken for 15 minutes. The NMR tube was then loaded and the proton spectra taken. The resultant spectrum consisted peaks for **23** and MAO. No formation of **101** was detected.

NMR Studies of 27 + 10 eq. MAO:

To a solution of **27** (0.025 mmol, 0.1 mL, 0.25 M in d_6 -benzene) cooled to 5 °C, was added 0.7 mL d_6 -benzene and the solution cooled to 5 °C. To this NMR tube was injected, MAO (0.25 mmol, 0.1 mL, 2.5 M in d_6 -benzene) and the NMR tube shaken for 15 minutes. The NMR tube was then loaded and the proton spectra taken. The NMR tube was then loaded and the proton spectra taken. The resultant spectrum consisted peaks for **27**, **24**, **101** and MAO. **101**: ^1H NMR (300 MHz, C_6D_6) δ -2.24 (s, 3 H), 5.45 (s, 5 H), 5.49 (s, 5 H), 7.66-7.63 (d, 1 H), 7.33-7.30 (d, 1 H).

General Procedure for Polymerization:

Four parallel reactors were constructed as described in Chapter III. Each reactor was washed with concentrated HCl and base (KOH/ethanol) and dried under vacuum overnight. The reactors were purged with ethylene and evacuated again to ensure complete removal of oxygen. The reactors were filled with ethylene to 1 atmosphere, and the appropriate solvent (50 mL) injected *via* the septum inlet. Solutions of the appropriate catalyst in toluene and MAO in toluene were mixed and the total catalyst+co-catalyst mixture was brought to 20 mL with appropriate solvent, and the reaction mixture was stirred for 15 minutes. Except for solvent studies in Table VIII, the solvent used in all the polymerization studies was 1,2-dichloroethane. The polymerization catalyst mixture was then transferred into the reactors using a canula. The septa inlet were sealed and the reactors pressurized with ethylene simultaneously to 30 psi. The polymerization mixture was stirred vigorously, while maintaining the ethylene pressure at 30 psi. After 1 hour of polymerization time, the ethylene gas was stopped, the reactors were vented and the polymerization reactors were quenched with 5% HCl/MeOH. The polymers were filtered, dried on phosphorous pentoxide, under vacuum until a constant weight was obtained. The polymer yields are provided in Chapter III. No polymerization of ethylene was seen with the use of 0.05 equivalents of **23** with 0.5 equivalents of MAO.

REFERENCES

1. (a) Ziegler, K. *Angew. Chem.* **1964**, *76*, 545. (b) Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979; p 670.
2. Organometallic Compounds of Group III. 52. Part 51: Eisch, J. J.; Pombrik, S.; Zheng, G. -X. *Macromol. Chem. Macromol. Symp.* **1993**, *66*, 109. For recent reviews in Ziegler-Natta polymerization, see: (a) Kissin, Y. V. *Isospecific Polymerization of Olefins with Heterogeneous Ziegler-Natta Catalysts*; Springer-Verlag, New York, 1985. (b) Minsker, K. S.; Karpasas, M. M.; Zaikov, G. E. *Russ. Chem. Rev.* **1986**, *55*, 17. (c) Tait, P. J. T.; Allen, G.; Bevington, J. C. (Eds) *Comprehensive Polymer Science*; Pergamon Press, Oxford, 1989, Chap. 1. (d) Tait, P. J. T.; Watkins, N. D.; Allen, G. (Eds) *Comprehensive Polymer Science*; Pergamon Press, Oxford, 1989, Chap. 2. (e) Krentsel, B. A.; Nekhaeva, L. A. *Russ. Chem. Rev.* **1990**, *59*, 1193. (f) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613. (g) Odian, G. *Principles of Polymerization*; Wiley, New York, 1991.
3. (a) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.*, **1980**, *18*, 99. (b) Kaminsky, W. *Angew. Makromol. Chemie*, **1986**, 145. (c) Ewen, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2728.
4. a) Okuda, J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 47. (b) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Amer. Chem. Soc.* **1990**, *112*, 2030. c) Coates, G. W.; Waymouth, R. M. *J. Amer. Chem. Soc.* **1993**, *115*, 91.
5. (a) Irvin, K. J. *Olefin Metathesis*, Academic Press: London 1983. (b) Grubbs, R. H. in *Comprehensive Organometallic Chemistry*, Wilkinson, G., Ed., Pergamon Press, Oxford, 1982, Vol. II, p. 499.

6. (a) Pasynkiewicz, S. *Tetrahedron* **1990**, *9*, 429. (b) Sugano, T.; Matsubara, K.; Fujita, T.; Takahashi, T. *J. Mol. Catal.* **1993**, *82*, 93.
7. (a) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Amer. Chem. Soc.* **1993**, *115*, 4971. (b) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957.
8. (a) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1511. (b) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 279. (c) Mengele, W., Diebold, J., Troll, C., Roll, W.; Brintzinger, H. H. *Organometallics* **1993**, *12*, 1931. (d) Ready, T. E.; Day, R. O.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1993**, *26*, 5822.
9. (a) Erker, G.; Aulbach, M.; Kruger, C.; Werner, S. *J. Organomet. Chem.*, **1993**, *450*, 1. (b) Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1992**, *13*, 954. (c) Mallin, D. T.; Rausch, M. D.; Lin, Y.; Dong, S.; Chien, J. C. W. *J. Amer. Chem. Soc.* **1990**, *112*, 2030. (d) Llinas, G. H.; Day, R. O.; Rausch, M. D.; Chien, J. C. W. *Organometallics* **1993**, *12*, 1283.
10. (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organometal. Chem.* **1982**, *232*, 233. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507. (c) Hortmann, K.; Brintzinger, H. H. *New J. Chem.* **1992**, *16*, 51.
11. Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth R. M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143.
12. (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217. (b) Waymouth, R. M. at the Arthur C. Cope Award Symposium, 210th American Chemical Society Meeting, Chicago, USA, August 20-24, 1995 .
13. (a) Reichert, K. H.; Schubert, E. *Makromol. Chem.* **1969**, *123*, 58. (b) Reichert, K. H. *Angew. Makromol. Chem.* **1970**, *12*, 125.

14. (a) Schnell, D.; Fink, G *Angew. Makromol. Chem.* **1974**, *39*, 131. (b) Mynott, R.; Fink, G.; Fenzl, W. *Angew. Makromol. Chem.* **1987**, *154*, 1.
15. (a) Eisch, J. J.; Pombrik, S. I.; Zheng, G, -X. *Organometallics*, **1993**, *12*, 3856. (b) Eisch, J. J.; Caldwell, K. R.; Werner, S.; Kruger, C. *Organometallics*, **1991**, *10*, 3417.
16. Siedle, A. R.; Newmark, R. A.; Lamanna, W. M., Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.
17. Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112.
18. (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Amer. Chem. Soc.* **1986**, *108*, 1718. (b) Jordan, R. F.; Bajgur, C. S.; Willet, R.; Scott, B. *J. Amer. Chem. Soc.* **1986**, *108*, 7410. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. *J. Amer. Chem. Soc.* **1987**, *109*, 4111.
19. (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Amer. Chem. Soc.* **1991**, *113*, 3623. (b) Taube, R.; Krukowka, L. *J. Organometal. Chem.* **1988**, *347*, C9. (c) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H. *Organometallics* **1992**, *11*, 362. (d) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633.
20. Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1375.
21. (a) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413. (b) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (c) Bochmann, M.; Lancaster, S. J. *J. Organometal. Chem.* **1992**, *434*, C1. (d) Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem. Intl. Ed. Engl.* **1990**, *29*, 780.
22. Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics*, **1989**, *8*, 2892.
23. Rodewald, S.; Jordan, R. F. *J. Amer. Chem. Soc.* **1994**, *116*, 4491.

24.

25.

26.

27.

28.

29.

30.

31.

32.

33.

34.

35.

36.

24. Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Amer. Chem. Soc.* **1989**, *111*, 2728.
25. (a) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185. (b) Horton, A. D.; Orpen, A. G. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 876.
26. Kaminsky, W.; Hahnsen, H. U. S. Patent 4, 544, 762, Oct. 1. 1985.
27. (a) Kaminsky, W.; Moller, L. N. *Bull. Chim. Belg.* **1990**, *99*, 103. (b) Kaminsky, W.; Steigler, R. *Polyhedron* **1988**, *7*, 2375.
28. Kaminsky, W.; Bark, A.; Steiger, R. *J. Mol. Catal.* **1992**, *74*, 109.
29. Tritto, I.; Li, S.; Sacchi, M. C.; Zannoni, G. *Macromolecules* **1993**, *26*, 7111.
30. Resconi, L.; Bossi, S. *Macromolecules* **1990**, *23*, 4489.
31. Tritto, I.; Grubbs, R. H. in *Catalytic Olefin Polymerization*, Keii, T.; Soga, K.; Eds., 1990, 301.
32. (a) Lauher, J. W.; Hoffmann, R. *J. Amer. Chem. Soc.* **1976**, *98*, 1729. (b) Green, J. C.; Green, M. L. H.; Prout, C. K. *Chem. Commun.* **1972**, 421. (c) Green, M. L. H. *Pure Appl. Chem.* **1972**, *30*, 373.
33. Ewen, J. A. *J. Amer. Chem. Soc.* **1984**, *106*, 6355.
34. Silver, M. E.; Fay, R. C. *Organometallics* **1983**, *2*, 44.
35. (a) Kaminsky, W.; Bark, A.; Steiger, R. *J. Mol. Catal.* **1992**, *74*, 109. (b) Nekhaeva, L. A.; Bondarenko, G. N.; Rykov, S. V.; Nekhaev, A. I.; Krenstel, B. A.; Mar'in, V. P.; Vyshinskaya, L. I.; Khrapova, I. M.; Polonskii, A. V.; Korneev, N. N. *J. Organomet. Chem.* **1991**, *406*, 139.
36. Bochmann, M.; Cuenca, T.; Hardy, D. T. *J. Organometal. Chem.* **1994**, *484*, C10.

37. (a) Temme, B.; Erker, G.; Frohlich, R.; Grehl, M. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1480. (b) Erker, G.; Noe, R.; Wingbermuhle, D. *Chem. Ber.* **1994**, *127*, 805.
38. (a) Aoyagi, T.; Araki, T.; Oguni, N.; Tani, H. *Inorg. Chem.* **1973**, *12*, 817. (b) Aoyagi, T.; Araki, T.; Oguni, N.; Mikumo, M.; Tani, H. *Inorg. Chem.* **1973**, *12*, 2702.
39. (a) Samuel, E. *Bull. Soc. Chim. Fr.* **1966**, 3548. (b) Reid, A. F.; Shannon, J. S.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem.* **1965**, *18*, 173.
40. Surtees, J. R. *Chem. Commun.* **1965**, 567.
41. Stille J. R. "Metal Carbene Complexes in Organic Synthesis" in *Comprehensive Organometallic Chemistry*, Wilkinson, G., Ed., Pergamon Press, Oxford, in press.
42. (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37.42.
43. Ott, K. C.; deBoer, J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.
44. Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, *24*, 2043.
45. (a) Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 5191. (b) Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *308*, 1.
46. Claus, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, 654, 8.
47. Starowieyski, K. B.; Pasynkiewicz, S.; Skowronska, P. M. *J. Organometal. Chem.* **1975**, *90*, C43.
48. Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R. *Can. J. Chem.* **1975**, *53*, 1622.

49. Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358.
50. Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992**, *11*, 3041.
51. (a) Gilliom, L. R.; Grubbs, R. H. *Organometallics*, **1986**, *5*, 721. (b) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.
52. Schwartz, J.; Labinger, J. A. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 333.
53. Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B.T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.
54. Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.
55. (a) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (b) Negishi, E. I.; Takahashi, T. *Aldrichchim. Acta* **1985**, *18*, 31.
56. Van Horn, D. E.; Negishi, E. I. *J. Am. Chem. Soc.* **1978**, *100*, 2253.
57. Hartner, F. W.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979.
58. Odian, G. *Principles of Polymerization*; Wiley, New York, 1991.
59. Pratt, D. personal communication
60. Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
61. (a) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *109*, 4111. (b) Eisch, J. J.; Caldwell, K. R.; in *Homogeneous Transition Metal Catalyzed Reactions*, Advances in Chemistry Series, 230, p575.
62. Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

63. Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E. *J. Organomet. Chem.* **1978**, *158*, C20.
64. Wipf, P.; Lim, S. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1068.
65. Amorose, D. M.; Lee, R. A.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191.
66. (a) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. (b) Pellecchia, C.; Grassi, A.; Zambelli, A. *J. Mol. Catal.* **1993**, *82*, 57. (c) Pellecchia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (d) Pellecchia, C.; Immirzi, A.; Zambelli, A. *J. Organometal. Chem.* **1994**, *479*, C9.
67. Buchwald, S. L.; Watson, B. T.; Lum, B. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137.
68. Jordan, R. F.; Taylor, D. F.; *J. Am. Chem. Soc.* **1989**, *111*, 778.
69. Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

APPENDICES

**APPENDIX I : BOND LENGTHS (Å) AND BOND ANGLES (°)
FOR COMPOUND 69**

Bond Lengths (Å)

Ti(1)–C(1)	2.386(5)	C(1)–C(5)	1.395(7)
Ti(1)–C(2)	2.350(5)	C(2)–C(3)	1.392(7)
Ti(1)–C(3)	2.346(5)	C(3)–C(4)	1.373(8)
Ti(1)–C(4)	2.365(5)	C(4)–C(5)	1.412(8)
Ti(1)–C(5)	2.375(5)	C(6)–C(7)	1.365(7)
Ti(1)–C(6)	2.377(5)	C(6)–C(10)	1.403(8)
Ti(1)–C(7)	2.366(5)	C(7)–C(8)	1.401(8)
Ti(1)–C(8)	2.362(5)	C(8)–C(9)	1.379(9)
Ti(1)–C(9)	2.390(6)	C(9)–C(10)	1.376(8)
Ti(1)–C(10)	2.381(5)	C(11)–C(16)	1.411(5)
Ti(1)–Cl(1)	2.492(5)	C(11)–C(12)	1.419(5)
Ti(1)–Cl(2)	2.448(6)	C(12)–C(13)	1.396(5)
Ti(1)–C(27)	2.01(2)	C(12)–C(17)	1.529(5)
Ti(1)–C(28)	2.13(3)	C(13)–C(14)	1.368(6)
Al(1)–Cl(1)	2.238(5)	C(14)–C(15)	1.372(6)
Al(1)–Cl(2)	2.278(6)	C(14)–C(18)	1.522(7)
Al(1)–O(1)	1.724(3)	C(15)–C(16)	1.388(6)
Al(1)–C(26)	1.988(5)	C(16)–C(19)	1.540(5)
Al(1)–C(27)	2.09(3)	C(17)–C(20)	1.529(5)
Al(1)–C(28)	1.96(2)	C(17)–C(21)	1.535(6)
Cl(1)–C(27)	0.51(2) *	C(17)–C(22)	1.538(5)
Cl(2)–C(28)	0.44 *	C(19)–C(24)	1.523(6)
O(1)–C(11)	1.357(4)	C(19)–C(23)	1.528(7)
C(1)–C(2)	1.376(7)	C(19)–C(25)	1.545(6)

Bond Angles (°)

C(1)---Ti(1)–C(2)	33.8(2)	C(2)---Ti(1)–C(4)	56.7(2)
C(1)---Ti(1)–C(3)	56.6(2)	C(2)---Ti(1)–C(5)	56.9(2)
C(1)---Ti(1)–C(4)	56.5(2)	C(2)---Ti(1)–C(6)	103.4(2)
C(1)---Ti(1)–C(5)	34.1(2)	C(2)---Ti(1)–C(7)	80.3(2)
C(1)---Ti(1)–C(6)	119.1(2)	C(2)---Ti(1)–C(8)	93.6(2)
C(1)---Ti(1)–C(7)	108.7(2)	C(2)---Ti(1)–C(9)	127.3(2)
C(1)---Ti(1)–C(8)	127.3(2)	C(2)---Ti(1)–C(10)	135.7(2)
C(1)---Ti(1)–C(9)	161.0(2)	C(2)---Ti(1)–C(27)	135.2(9)
C(1)---Ti(1)–C(10)	151.2(2)	C(2)---Ti(1)–C(28)	108.1(8)
C(1)---Ti(1)–C(27)	114.1(8)	C(3)---Ti(1)–C(4)	33.9(2)
C(1)---Ti(1)–C(28)	80.6(9)	C(3)---Ti(1)–C(5)	57.2(2)
C(2)---Ti(1)–C(3)	34.5(2)	C(3)---Ti(1)–C(6)	118.8(2)

Bond Angles (°) continued..

C(3)---Ti(1)--C(7)	86.2(2)	C(9)---Ti(1)--C(28)	114.8(9)
C(3)---Ti(1)--C(8)	79.5(2)	C(10)--Ti(1)--C(27)	87.6(8)
C(3)---Ti(1)--C(9)	107.7(2)	C(10)--Ti(1)--C(28)	83.5(10)
C(3)---Ti(1)--C(10)	135.6(2)	C(27)--Ti(1)--C(28)	83.8(10)
C(3)---Ti(1)--C(27)	110.0(9)	Ti(1)--Cl(1)--Al(1)	79.1(2)
C(3)---Ti(1)--C(28)	137.1(9)	Ti(1)--Cl(1)--C(27)	17(4) *
C(4)---Ti(1)--C(5)	34.7(2)	Al(1)--Cl(1)--C(27)	67(4) *
C(4)---Ti(1)--C(6)	152.3(2)	Ti(1)--Cl(2)--Al(1)	79.3(2)
C(4)---Ti(1)--C(7)	119.0(2)	Ti(1)--Cl(2)--C(28)	39.3 *
C(4)---Ti(1)--C(8)	102.5(2)	Al(1)--Cl(2)--C(28)	40.1 *
C(4)---Ti(1)--C(9)	117.7(2)	Ti(1)--Al(1)--Cl(1)	54.17(13)
C(4)---Ti(1)--C(10)	150.8(2)	Ti(1)--Al(1)--Cl(2)	52.8(2)
C(4)---Ti(1)--C(27)	79.7(9)	Ti(1)--Al(1)--O(1)	118.99(9)
C(4)---Ti(1)--C(28)	120.5(9)	Ti(1)--Al(1)--C(26)	125.2(2)
C(5)---Ti(1)--C(6)	152.8(2)	Ti(1)--Al(1)--C(27)	41.6(5)
C(5)---Ti(1)--C(7)	137.0(2)	Ti(1)--Al(1)--C(28)	44.7(8)
C(5)---Ti(1)--C(8)	135.5(2)	Cl(1)--Al(1)--Cl(2)	106.9(2)
C(5)---Ti(1)--C(9)	149.7(2)	Cl(1)--Al(1)--O(1)	108.4(2)
C(5)---Ti(1)--C(10)	166.2(2)	Cl(1)--Al(1)--C(26)	109.4(3)
C(5)---Ti(1)--C(27)	81.7(8)	Cl(1)--Al(1)--C(27)	13.0(5) *
C(5)---Ti(1)--C(28)	86.7(10)	Cl(1)--Al(1)--C(28)	98.7(8)
C(6)---Ti(1)--C(7)	33.5(2)	Cl(2)--Al(1)--O(1)	108.7(2)
C(6)---Ti(1)--C(8)	56.4(2)	Cl(2)--Al(1)--C(26)	107.3(3)
C(6)---Ti(1)--C(9)	56.2(2)	Cl(2)--Al(1)--C(27)	94.4(5)
C(6)---Ti(1)--C(10)	34.3(2)	Cl(2)--Al(1)--C(28)	8.2(9) *
C(6)---Ti(1)--C(27)	121.2(8)	O(1)---Al(1)--C(26)	115.8(2)
C(6)---Ti(1)--C(28)	82.1(9)	O(1)---Al(1)--C(27)	110.2(8)
C(7)---Ti(1)--C(8)	34.5(2)	O(1)---Al(1)--C(28)	112.4(10)
C(7)---Ti(1)--C(9)	56.3(2)	C(26)--Al(1)--C(27)	117.9(7)
C(7)---Ti(1)--C(10)	56.3(2)	C(26)--Al(1)--C(28)	110.7(10)
C(7)---Ti(1)--C(27)	136.3(8)	C(27)--Al(1)--C(28)	86.2(9) *
C(7)---Ti(1)--C(28)	112.1(8)	Al(1)--O(1)---C(11)	143.8(2)
C(8)---Ti(1)--C(9)	33.7(2)	Ti(1)--C(1)---C(2)	71.7(3)
C(8)---Ti(1)--C(10)	56.2(2)	Ti(1)--C(1)---C(5)	72.5(3)
C(8)---Ti(1)--C(27)	106.8(8)	C(2)---C(1)---C(5)	108.7(5)
C(8)---Ti(1)--C(28)	136.9(9)	C(1)---C(2)---C(3)	108.2(5)
C(9)---Ti(1)--C(10)	33.5(2)	Ti(1)--C(2)---C(1)	74.6(3)
C(9)---Ti(1)--C(27)	80.0(8)	Ti(1)--C(2)---C(3)	72.6(3)

Bond Angles (°) continued..

C(2)---C(3)---C(4)	108.1(6)	C(11)--C(12)--C(17)	123.2(3)
Ti(1)--C(3)---C(2)	72.9(3)	C(13)--C(12)--C(17)	119.6(3)
Ti(1)--C(3)---C(4)	73.8(3)	C(12)--C(13)--C(14)	123.8(4)
C(3)---C(4)---C(5)	108.4(5)	C(13)--C(14)--C(15)	117.3(4)
Ti(1)--C(4)---C(3)	72.3(3)	C(13)--C(14)--C(18)	120.7(5)
Ti(1)--C(4)---C(5)	73.1(3)	C(15)--C(14)--C(18)	122.0(5)
C(1)---C(5)---C(4)	106.5(5)	C(14)--C(15)--C(16)	123.5(4)
Ti(1)--C(5)---C(1)	73.4(3)	C(11)--C(16)--C(15)	117.9(4)
C(7)---C(6)---C(10)	108.0(6)	C(11)--C(16)--C(19)	122.9(3)
Ti(1)--C(6)---C(7)	72.8(3)	C(15)--C(16)--C(19)	119.2(4)
Ti(1)--C(6)---C(10)	73.0(3)	C(12)--C(17)--C(20)	111.0(3)
C(6)---C(7)---C(8)	108.1(6)	C(12)--C(17)--C(21)	110.5(3)
Ti(1)--C(7)---C(6)	73.7(3)	C(12)--C(17)--C(22)	112.0(3)
Ti(1)--C(7)---C(8)	72.6(3)	C(20)--C(17)--C(21)	111.3(4)
C(7)---C(8)---C(9)	107.7(6)	C(20)--C(17)--C(22)	106.2(3)
Ti(1)--C(8)---C(7)	72.9(3)	C(21)--C(17)--C(22)	105.6(4)
Ti(1)--C(8)---C(9)	74.3(3)	C(16)--C(19)--C(23)	110.4(3)
C(8)---C(9)---C(10)	108.4(6)	C(16)--C(19)--C(24)	110.9(3)
Ti(1)--C(9)---C(8)	72.0(4)	C(16)--C(19)--C(25)	112.0(4)
Ti(1)--C(9)---C(10)	72.9(3)	C(23)--C(19)--C(24)	110.6(4)
C(6)---C(10)--C(9)	107.8(6)	C(23)--C(19)--C(25)	107.9(4)
Ti(1)--C(10)--C(6)	72.7(3)	C(24)--C(19)--C(25)	104.8(4)
Ti(1)--C(10)--C(9)	73.6(3)	Ti(1)--C(27)--Cl(1)	158(5) *
O(1)---C(11)--C(16)	119.9(3)	Ti(1)--C(27)--Al(1)	94.9(9)
O(1)---C(11)--C(12)	119.9(3)	Cl(1)--C(27)--Al(1)	101(4) *
C(12)--C(11)--C(16)	120.1(3)	Ti(1)--C(28)--Cl(2)	133.2 *
C(11)--C(12)--C(13)	117.2(4)	Ti(1)--C(28)--Al(1)	95.1(8)
		Cl(2)--C(28)--Al(1)	131.6 *

**APPENDIX II : HYDROGEN COORDINATES ($\times 10^4$) and ISOTROPIC
DISPLACEMENT PARAMETERS ($\text{\AA}^2 \times 10^3$) for 69**

	x	y	z	U(eq)
H(1)	1929(26)	5462(43)	-2196(20)	32(13)
H(2)	1513(31)	4214(51)	-3284(23)	67(16)
H(3)	2631(30)	2152(50)	-3329(23)	68(15)
H(4)	3624(36)	2401(58)	-2207(26)	88(20)
H(5)	3105(27)	4409(45)	-1585(21)	44(13)
H(6)	-271(28)	2466(46)	-2172(20)	53(13)
H(7)	537(34)	2227(55)	-3256(25)	79(18)
H(8)	1612(30)	175(49)	-3099(23)	59(15)
H(9)	1594(31)	-769(52)	-1937(22)	62(16)
H(10)	463(30)	636(51)	-1385(24)	65(16)
H(13)	4695(21)	4010(33)	1562(15)	9(8)
H(15)	2911(23)	7069(40)	1494(17)	28(10)
* H(18A)	3793(57)	5477(96)	2808(41)	53(12)
* H(18B)	4110(79)	7225(115)	2415(54)	53(12)
* H(18C)	5005(64)	6178(114)	2386(44)	53(12)
* H(18D)	3822(65)	6465(144)	2553(50)	53(12)
* H(18E)	4504(76)	6957(140)	2231(51)	53(12)
* H(18F)	4743(71)	5436(95)	2579(43)	53(12)
H(20A)	4888(27)	2053(46)	-505(20)	49(13)
H(20B)	4103(26)	3084(39)	-599(18)	36(11)
H(20C)	5131(27)	3548(43)	-314(18)	43(12)
H(21A)	3220(26)	1288(41)	198(18)	37(11)
H(21B)	4105(26)	305(46)	281(19)	46(12)
H(21C)	3757(26)	904(44)	868(21)	41(13)
H(22A)	5182(27)	1781(45)	1356(22)	60(13)
H(22B)	5565(28)	1345(49)	627(21)	54(13)
H(22C)	5630(31)	2979(51)	860(23)	62(17)
H(23A)	2657(32)	7748(50)	-295(22)	62(16)
H(23B)	2350(28)	6393(47)	-724(21)	51(14)
H(23C)	1655(31)	7583(51)	-620(22)	66(14)
H(24A)	628(28)	6197(47)	43(20)	50(14)
H(24B)	1136(24)	4796(42)	35(18)	34(11)
H(24C)	868(28)	5552(46)	763(22)	60(14)
H(25A)	2270(30)	8681(49)	725(21)	61(14)
H(25B)	1231(33)	8543(52)	412(23)	72(16)
H(25C)	1498(42)	7765(68)	1252(32)	132(26)
H(26A)	1431(30)	1418(50)	324(23)	35(19)
H(26B)	915(35)	1339(56)	-30(25)	52(24)
H(26C)	987(39)	2196(61)	277(28)	69(27)
* H(27A)	2375(50)	564(77)	-1100(37)	5(13)
* H(27B)	3082(47)	1503(87)	-1113(35)	5(13)
* H(28A)	1254(49)	4615(73)	-1255(34)	5(13)
* H(28B)	458(43)	3516(67)	-1214(29)	5(13)

* occupancy factor = 0.5

**APPENDIX III: C-H BOND LENGTHS (Å) AND
H-C-X BOND ANGLES (°) OF 69**

Bond Lengths (Å)

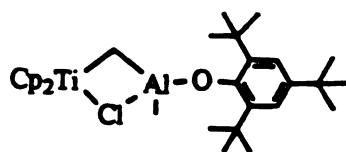
Cl(1)-H(27A)	0.66(7) *	C(20)-H(20C)	0.95(4)
Cl(1)-H(27B)	0.72(7) *	C(21)-H(21A)	0.96(4)
Cl(2)-H(28A)	0.73(6) *	C(21)-H(21B)	1.00(4)
Cl(2)-H(28B)	0.86(7) *	C(21)-H(21C)	0.85(4)
C(1)-H(1)	0.80(4)	C(22)-H(22A)	1.09(4)
C(2)-H(2)	0.95(4)	C(22)-H(22B)	0.99(4)
C(3)-H(3)	0.98(4)	C(22)-H(22C)	0.89(4)
C(4)-H(4)	0.87(5)	C(23)-H(23A)	0.91(5)
C(5)-H(5)	0.87(4)	C(23)-H(23B)	0.99(4)
C(6)-H(6)	0.98(4)	C(23)-H(23C)	0.98(5)
C(7)-H(7)	0.93(5)	C(24)-H(24A)	0.88(4)
C(8)-H(8)	0.87(4)	C(24)-H(24B)	1.00(4)
C(9)-H(9)	0.94(5)	C(24)-H(24C)	1.03(4)
C(10)-H(10)	0.91(5)	C(25)-H(25A)	1.03(5)
C(13)-H(13)	0.86(3)	C(25)-H(25B)	1.02(5)
C(15)-H(15)	0.89(4)	C(25)-H(25C)	1.13(6)
C(18)-H(18A)	1.30(9)	C(26)-H(26A)	0.59(4)
C(18)-H(18B)	1.02(10)	C(26)-H(26B)	0.61(5)
C(18)-H(18C)	1.13(9)	C(26)-H(26C)	0.61(5)
C(18)-H(18D)	0.81(10)	C(27)-H(27A)	0.97(8)
C(18)-H(18E)	0.88(11)	C(27)-H(27B)	0.90(7)
C(18)-H(18F)	1.06(9)	C(28)-H(28A)	0.92(8)
C(20)-H(20A)	0.95(4)	C(28)-H(28B)	1.04(7)
C(20)-H(20B)	0.98(4)		

H-C-X Bond Angles (Å)

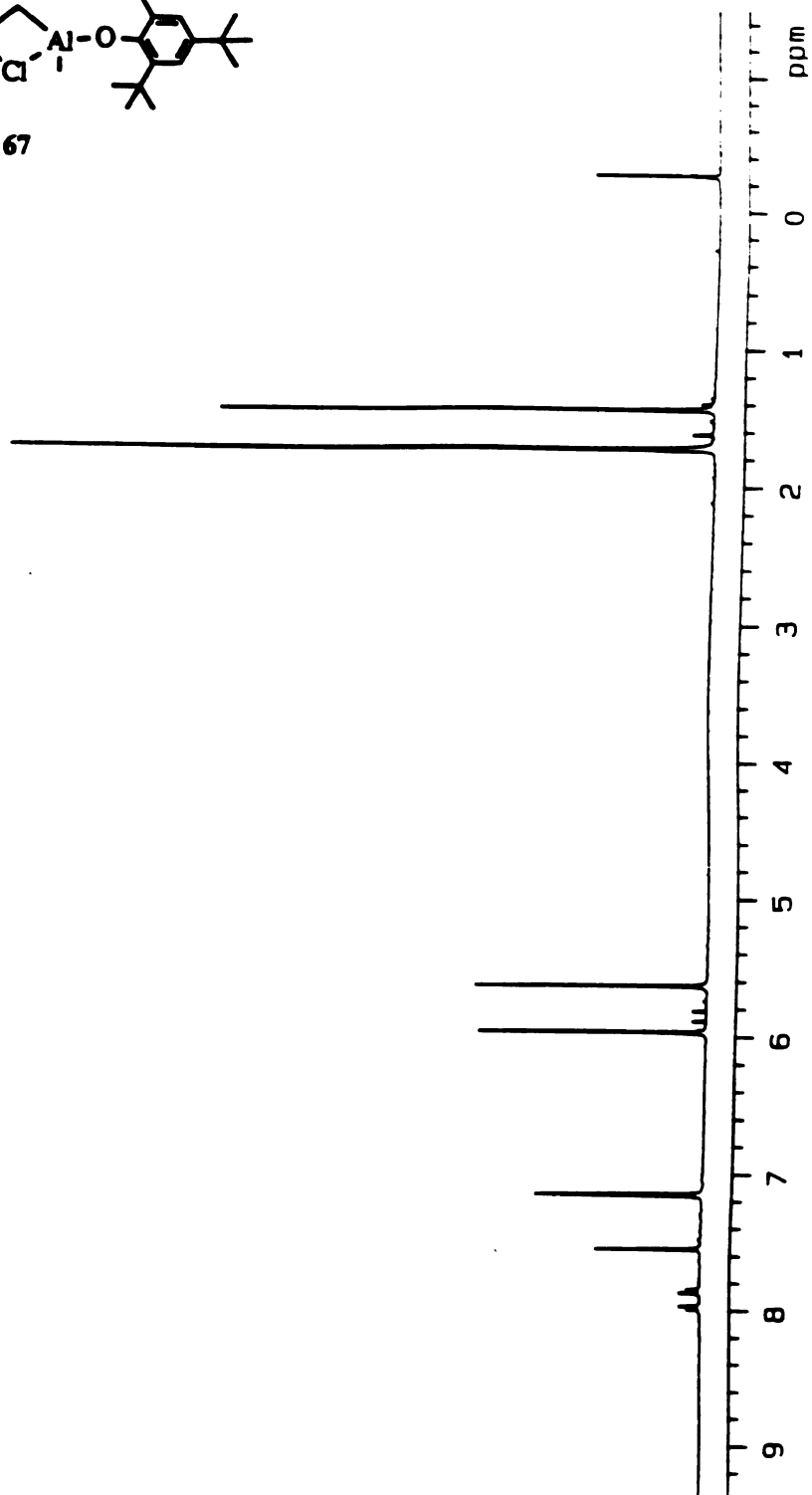
Ti(1)--Cl(1)--H(27A)	98(7) *	C(7)---C(8)---H(8)	128(3)
Ti(1)--Cl(1)--H(27B)	104(6) *	C(9)---C(8)---H(8)	124(3)
Al(1)--Cl(1)--H(27A)	97(6) *	Ti(1)--C(9)---H(9)	117(3)
Al(1)--Cl(1)--H(27B)	94(6) *	C(8)---C(9)---H(9)	128(3)
C(27)--Cl(1)--H(27A)	111(7) *	C(10)--C(9)---H(9)	123(3)
C(27)--Cl(1)--H(27B)	93(6) *	Ti(1)--C(10)--H(10)	113(3)
H(27A)-Cl(1)--H(27B)	157(9) *	C(6)---C(10)--H(10)	126(3)
Ti(1)--Cl(2)--H(28A)	102(6) *	C(9)---C(10)--H(10)	126(3)
Ti(1)--Cl(2)--H(28B)	103(4)*	C(12)--C(13)--H(13)	117(2)
Al(1)--Cl(2)--H(28A)	90(6)*	C(14)--C(13)--H(13)	119(2)
Al(1)--Cl(2)--H(28B)	99(4)*	C(14)--C(15)--H(15)	116(2)
C(28)--Cl(2)--H(28A)	99.8 *	C(16)--C(15)--H(15)	120(2)
C(28)--Cl(2)--H(28B)	103.9 *	C(14)--C(18)--H(18A)	109(4)
H(28A)-Cl(2)--H(28B)	155(7)*	C(14)--C(18)--H(18B)	111(5)
Ti(1)--C(1)---H(1)	116(3)	C(14)--C(18)--H(18C)	111(4)
C(2)---C(1)---H(1)	131(3)	C(14)--C(18)--H(18D)	109(7)
C(5)---C(1)---H(1)	120(3)	C(14)--C(18)--H(18E)	99(7)
Ti(1)--C(2)---H(2)	119(3)	C(14)--C(18)--H(18F)	113(5)
C(1)---C(2)---H(2)	127(3)	H(18A)-C(18)--H(18B)	106(8)
C(3)---C(2)---H(2)	125(3)	H(18A)-C(18)--H(18C)	121(6)
Ti(1)--C(3)---H(3)	118(3)	H(18A)-C(18)--H(18D)	53(8)*
C(2)---C(3)---H(3)	126(3)	H(18A)-C(18)--H(18E)	147(8)*
C(4)---C(3)---H(3)	126(3)	H(18A)-C(18)--H(18F)	78(6)*
Ti(1)--C(4)---H(4)	114(4)	H(18B)-C(18)--H(18C)	99(8)
C(3)---C(4)---H(4)	135(4)	H(18B)-C(18)--H(18D)	55(8) *
C(5)---C(4)---H(4)	116(4)	H(18B)-C(18)--H(18E)	45(8)*
Ti(1)--C(5)---H(5)	114(3)	H(18B)-C(18)--H(18F)	132(8)*
C(1)---C(5)---H(5)	121(3)	H(18C)-C(18)--H(18D)	138(9) *
C(4)---C(5)---H(5)	132(3)	H(18C)-C(18)--H(18E)	62(7)*
Ti(1)--C(6)---H(6)	114(2)	H(18C)-C(18)--H(18F)	47(5)*
C(7)---C(6)---H(6)	128(3)	H(18D)-C(18)--H(18E)	101(10)
C(10)--C(6)---H(6)	124(3)	H(18D)-C(18)--H(18F)	123(9)
Ti(1)--C(7)---H(7)	111(3)	H(18E)-C(18)--H(18F)	108(8)
C(6)---C(7)---H(7)	127(3)	C(17)--C(20)--H(20A)	113(2)
C(8)---C(7)---H(7)	124(3)	C(17)--C(20)--H(20B)	112(2)
Ti(1)--C(8)---H(8)	120(3)	C(17)--C(20)--H(20C)	114(2)
H(20A)-C(20)--H(20B)	101(3)	C(19)--C(25)--H(25A)	106(2)

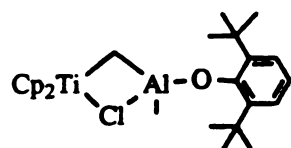
H(20A)-C(20)--H(20C)	100(3)	C(19)--C(25)--H(25B)	104(3)
H(20B)-C(20)--H(20C)	114(3)	C(19)--C(25)--H(25C)	113(3)
C(17)--C(21)--H(21A)	112(2)	H(25A)-C(25)--H(25B)	104(4)
C(17)--C(21)--H(21B)	112(2)	H(25A)-C(25)--H(25C)	113(4)
C(17)--C(21)--H(21C)	110(3)	H(25B)-C(25)--H(25C)	116(4)
H(21A)-C(21)--H(21B)	107(3)	Al(1)--C(26)--H(26A)	111(5)
H(21A)-C(21)--H(21C)	115(4)	Al(1)--C(26)--H(26B)	110(5)
H(21B)-C(21)--H(21C)	99(3)	Al(1)--C(26)--H(26C)	109(6)
C(17)--C(22)--H(22A)	113(2)	H(26A)-C(26)--H(26B)	112(7)
C(17)--C(22)--H(22B)	108(2)	H(26A)-C(26)--H(26C)	107(7)
C(17)--C(22)--H(22C)	107(3)	H(26B)-C(26)--H(26C)	109(7)
H(22A)-C(22)--H(22B)	104(3)	Ti(1)--C(27)--H(27A)	123(6)
H(22A)-C(22)--H(22C)	112(4)	Ti(1)--C(27)--H(27B)	140(6)
H(22B)-C(22)--H(22C)	114(4)	Cl(1)--C(27)--H(27A)	40(5)*
C(19)--C(23)--H(23A)	104(3)	Cl(1)--C(27)--H(27B)	53(5)*
C(19)--C(23)--H(23B)	121(2)	Al(1)--C(27)--H(27A)	98(5)
C(19)--C(23)--H(23C)	110(3)	Al(1)--C(27)--H(27B)	98(6)
H(23A)-C(23)--H(23B)	109(4)	H(27A)-C(27)--H(27B)	92(7)
H(23A)-C(23)--H(23C)	112(4)	Ti(1)--C(28)--H(28A)	118(5)
H(23B)-C(23)--H(23C)	101(4)	Ti(1)--C(28)--H(28B)	118(4)
C(19)--C(24)--H(24A)	111(3)	Cl(2)--C(28)--H(28A)	? *
C(19)--C(24)--H(24B)	113(2)	Cl(2)--C(28)--H(28B)	? *
C(19)--C(24)--H(24C)	110(2)	Al(1)--C(28)--H(28A)	107(5)
H(24A)-C(24)--H(24B)	104(3)	Al(1)--C(28)--H(28B)	114(4)
H(24A)-C(24)--H(24C)	108(3)	H(28A)-C(28)--H(28B)	104(7)
H(24B)-C(24)--H(24C)	111(3)		

* indicates distance or angle involving atoms in disordered sites that would not be simultaneously present.

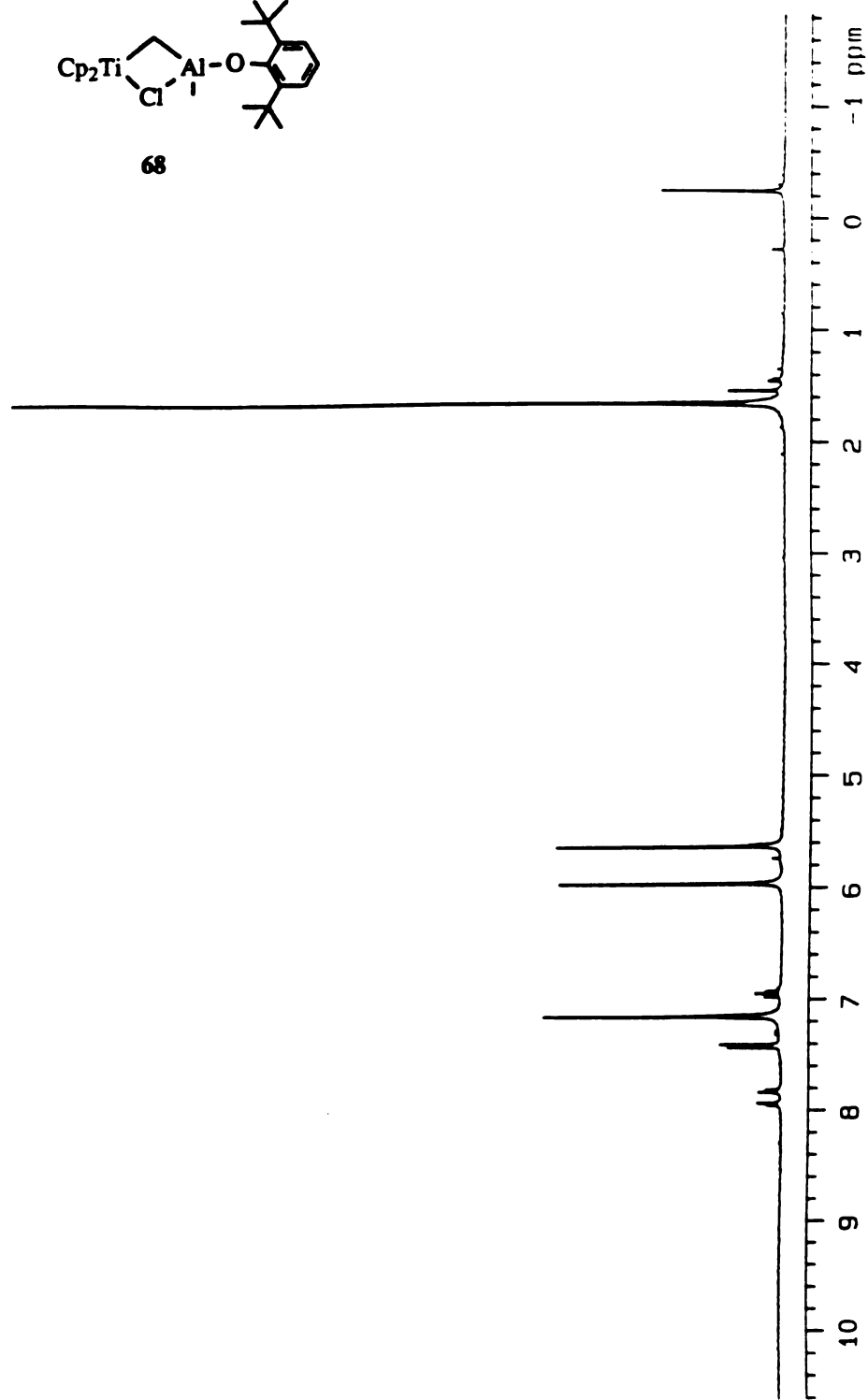
APPENDIX IV: ^1H NMR OF 67

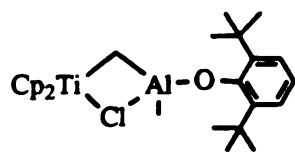
67



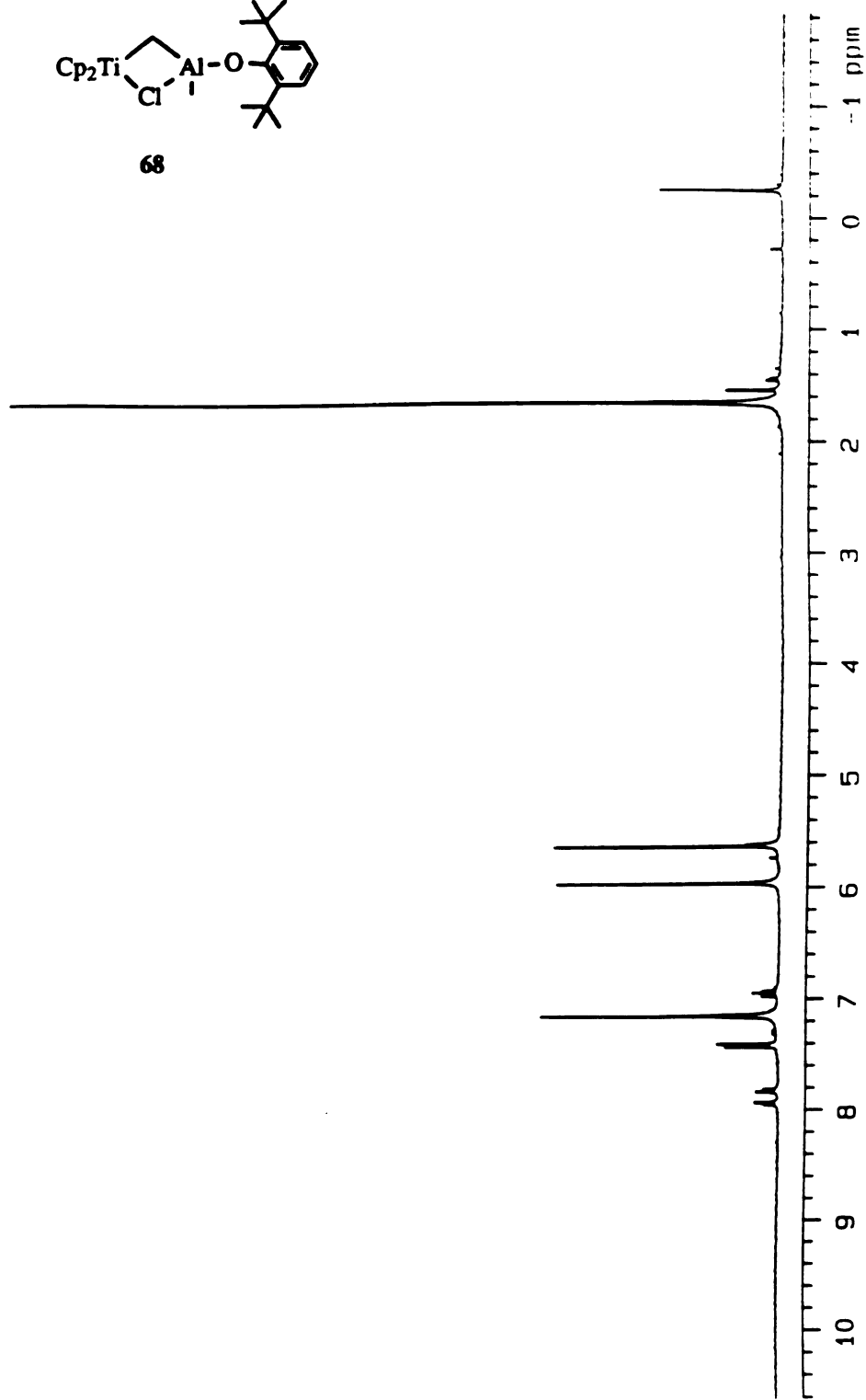
APPENDIX V: ^1H NMR OF 68

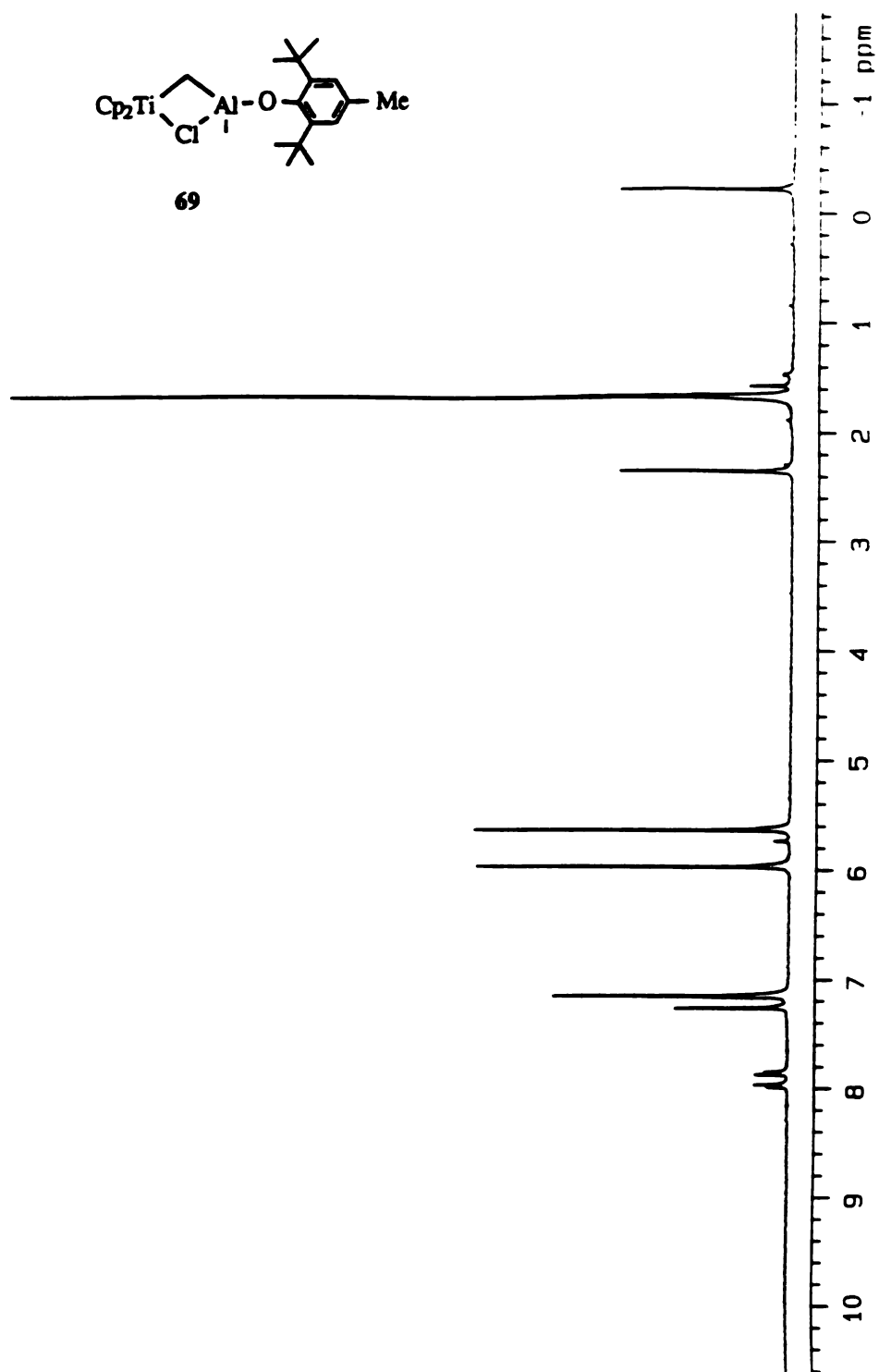
68

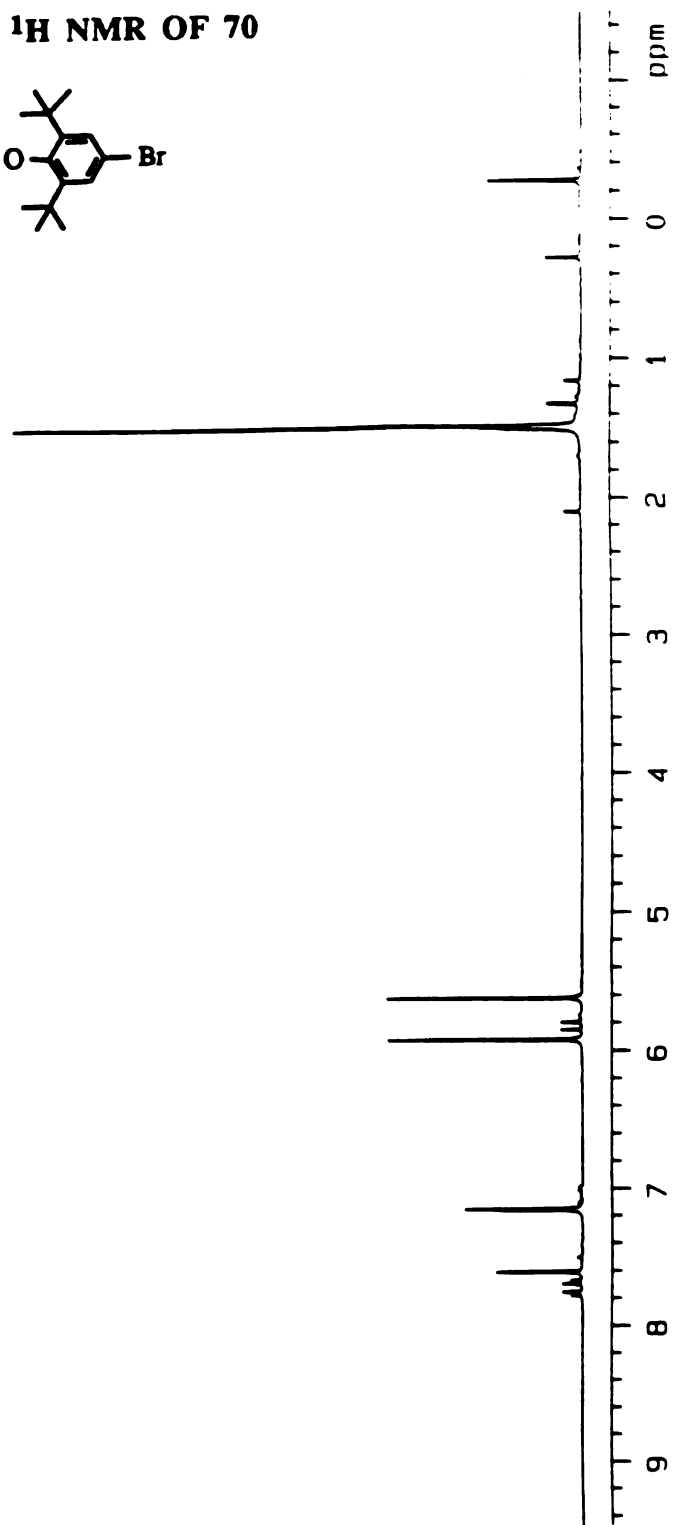
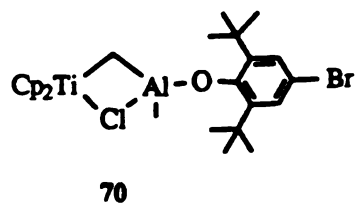


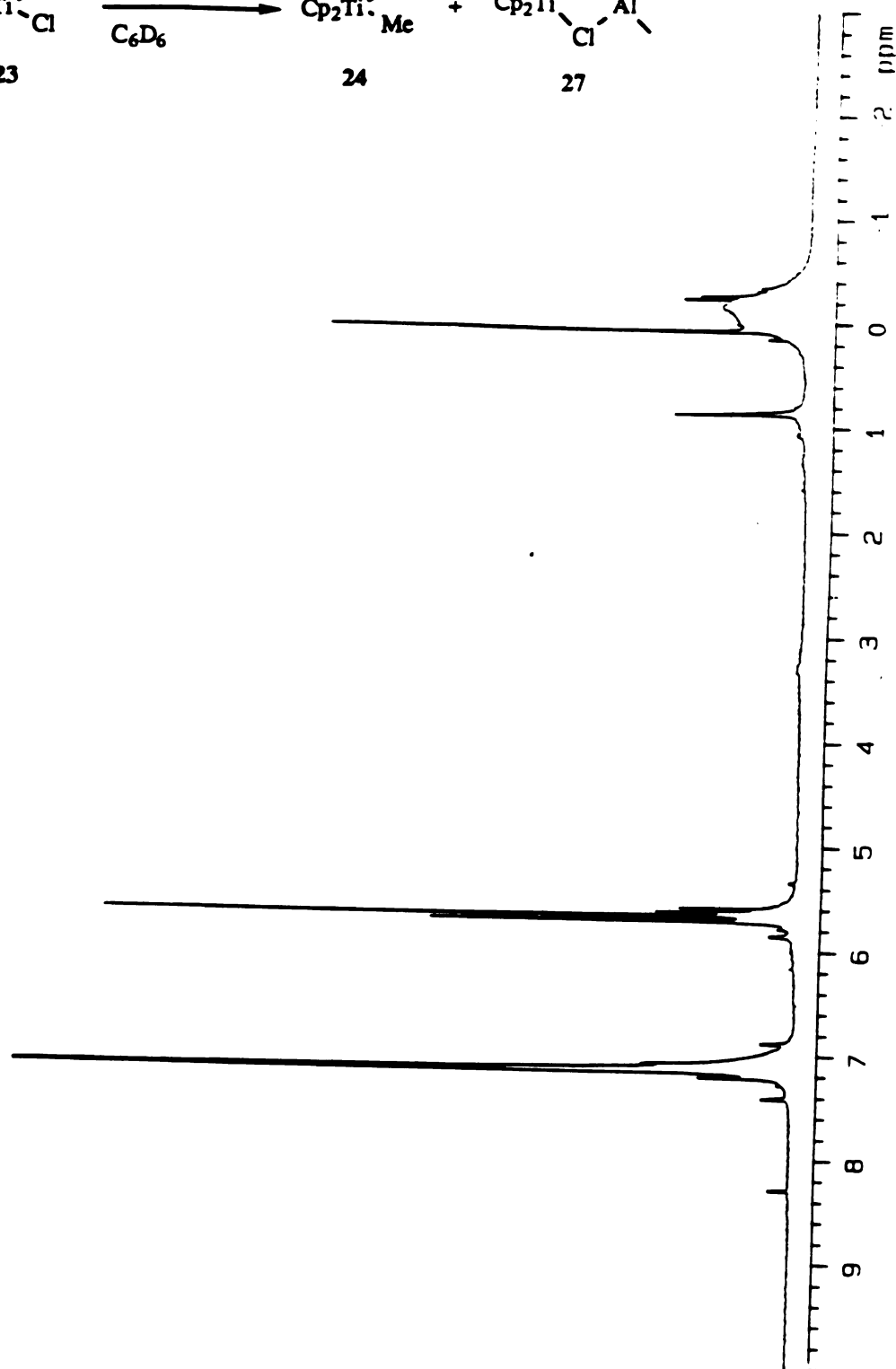
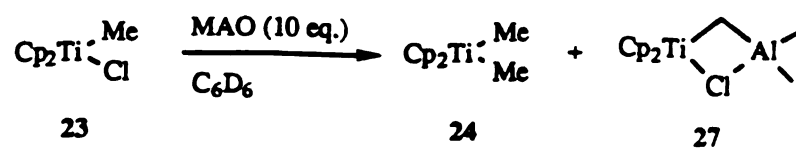
APPENDIX V: ^1H NMR OF 68

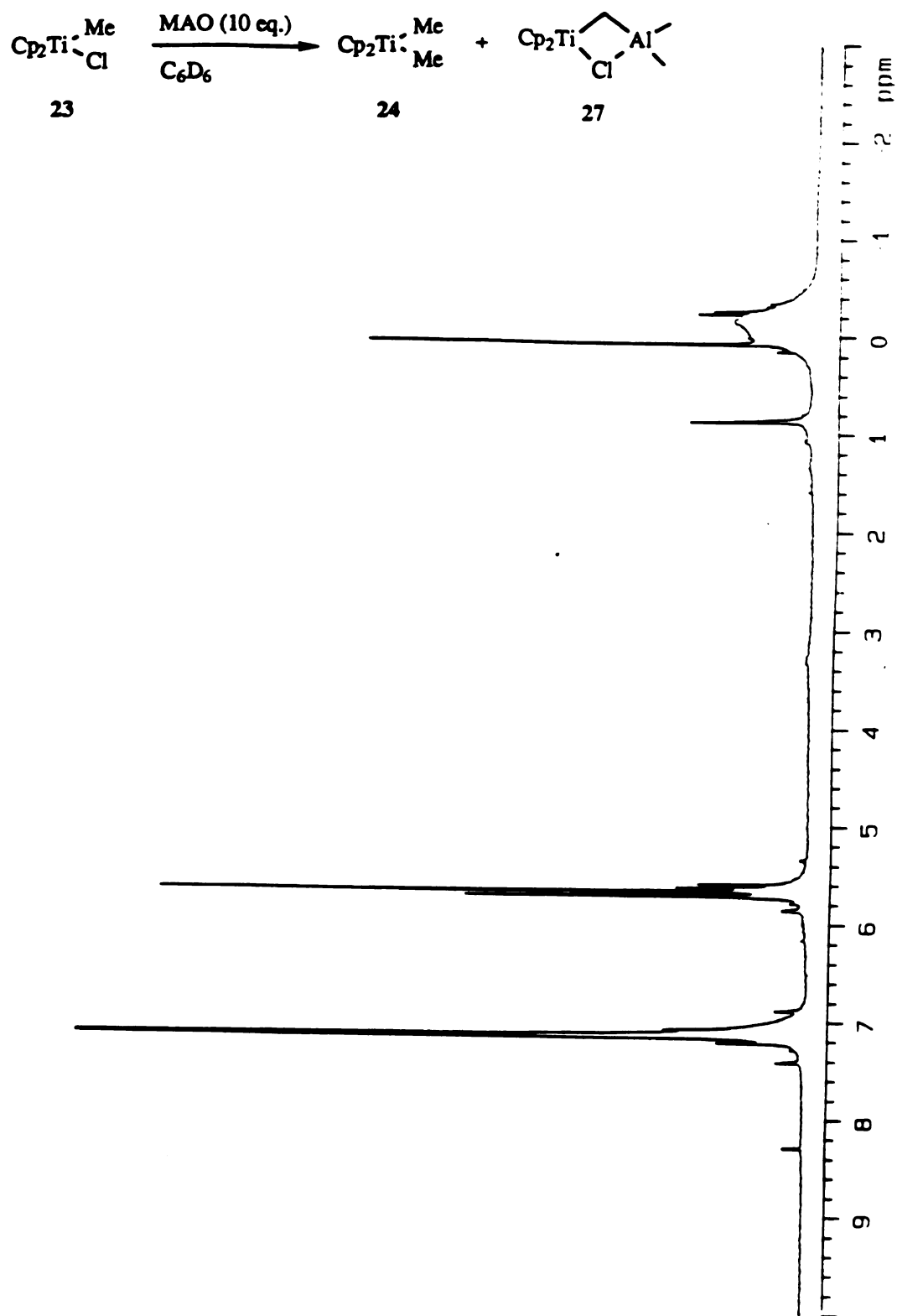
68



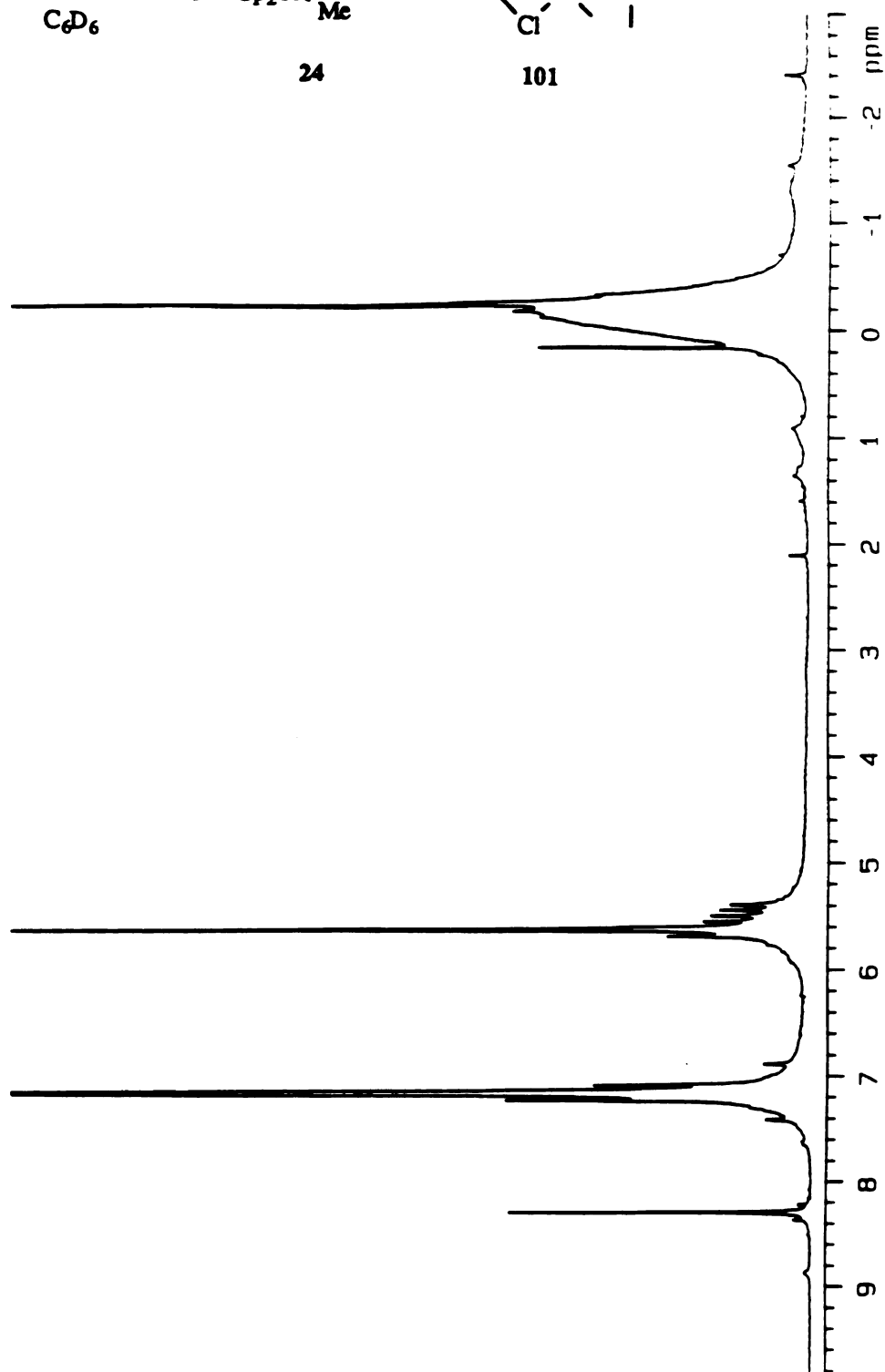
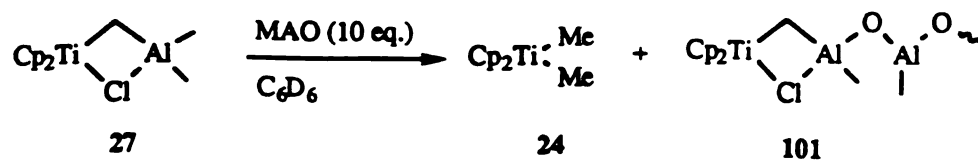
APPENDIX VI: ^1H NMR OF 69

APPENDIX VII: ^1H NMR OF 70

APPENDIX VIII: ^1H NMR of Reaction Mixture of 23 and 10 eq. MAO

APPENDIX VIII: ^1H NMR of Reaction Mixture of 23 and 10 eq. MAO

APPENDIX IX: ^1H NMR of Reaction Mixture of 27 and 10 eq. MAO



MICHIGAN STATE UNIV. LIBRARIES



31293013902972