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# Group 4 *ansa*-Cyclopentadienyl-Amido Catalysts for Olefin Polymerization

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## I. Introduction

### A. Background

The development of a new generation of well-defined coordination complexes has had an enormous impact on the development of new polymerization catalysts and reactions.[1−3] One of the central advantages of homogeneous polymerization catalysts over multisited heterogeneous catalysts is their well-defined active sites, which lead to polymers with specific microstructures and more narrow molecular weight distributions. Kaminsky and Sinn's initial discovery[4,5] that a hydrated form of trimethylaluminum, methylaluminoxane (MAO), afforded extremely active catalysts when combined with titanium and zirconium metallocenes led to an explosion of research into the use of metallocene catalysts. Since that finding, several advances have been made in which variation of the zirconocene symmetry was found to strongly influence the resulting polyolefin microstructure.[6−9] In Figure 1, examples are shown of propylene polymerization catalysts to illustrate this relationship between catalyst symmetry and polymer structure.[1]

Andrew McKnight was born in Columbia, SC, in 1970. He received his B.S. degree from Roanoke College (VA) and did undergraduate research for Professor Kenton H. Whitmire at Rice University. He recently received his Ph.D. in inorganic chemistry from Stanford University in the research group of Professor Robert M. Waymouth, and his dissertation research was concerned with exploring the selectivity of group 4 cyclopentadienyl-amido (CpA) catalysts in propylene homopolymerization and ethylene/olefin copolymerization. He is currently a senior chemist for DuPont Lycra in Waynesboro, VA.

Robert Waymouth was born in Warner Robins, GA, in 1960. He received bachelors degrees in mathematics and chemistry from Washington and Lee University and his Ph.D. from the California Institute of Technology in 1987 with Professor R. H. Grubbs. Following a year of postdoctoral research with the late Professor Pino at the ETH in Zurich, he joined the faculty at Stanford University in 1988, where he is now Professor of Chemistry. His research interests are in homogeneous catalysis, particularly the application of coordination compounds as catalysts in olefin polymerization.

The extraordinary potential of these zirconocenes notwithstanding, they are not without certain limitations including a limited temperature stability and the tendency to produce lower molecular weight materials under convenient commercial operating

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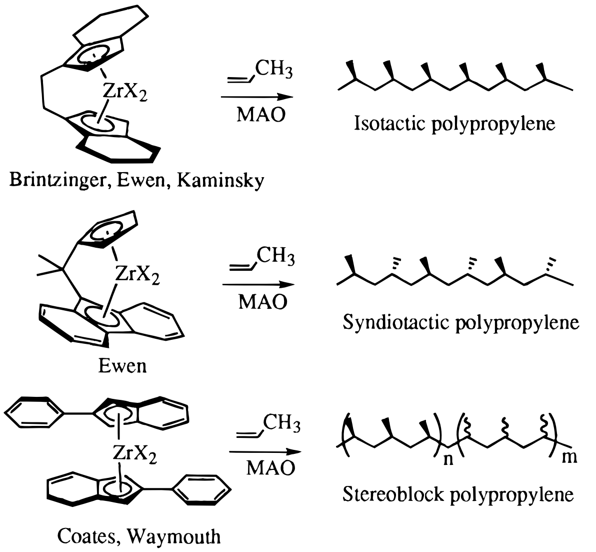


**Figure 1.** Key metallocene catalysts for stereospecific propylene polymerization.

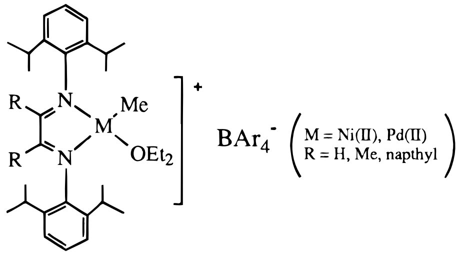


**Figure 2.** Brookhart late metal diimido olefin polymerization catalyst.

conditions. To that end, in commercial and academic labs efforts are underway to develop other coordination compounds, in which replacement of the cyclopentadienyl ligand fragment and/or the metal center is anticipated to yield increased selectivity and/or productivity.

Recent breakthroughs in the development of other classes of polymerization catalysts have generated intense interest because of each catalyst's own unique reactivity and our nascent understanding of ligand/metal effects on catalyst behavior. Catalysts developed by Brookhart[10] consisting of a late transition metal, such as nickel(II) or palladium(II), coupled with a bulky diimine ligand are a recent exciting example of a late transition metal catalyst that yields high molecular weight polyolefins of a unique microstructure[10] (Figure 2).

Largely because of the bulky aryl groups on the diimido ligand, the rates of associative displacement and chain transfer are greatly diminished and substantial long chain branches are produced in ethylene polymerizations. This catalyst system allows access to a range of materials from highly branched, amorphous polyolefins to linear, semicrystalline high-density polyolefins. These catalysts were also found to copolymerize functionalized vinyl monomers with α-olefins.[11]

Metallocene analogues that have received much commercial attention are the *ansa*-monocyclopentadienyl-amido (CpA) group IV catalysts developed concurrently by Dow and Exxon. These catalysts are based on a ligand design first introduced by Bercaw[12,13] for organoscandium olefin polymerization catalysts. Okuda's report in 1990 of the synthesis of a titanium CpA complex[14] and reports soon after in the patent literature[15−19] indicated that researchers at Dow and Exxon had begun what continues to be vigorous investigations into the olefin polymerization activity of these CpA catalysts. The generalized structure for the CpA catalyst is shown in Figure 3.

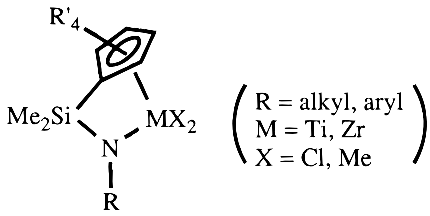


**Figure 3.** The CpA catalyst.

One of the key features of these catalysts is the open nature of the catalyst active site which allows them to incorporate other olefins into polyethylene. There are a number of reports in the patent literature which detail the copolymerization of ethylene with linear α-olefins such as hexene and octene[17,18,20−31] and with cyclic monomers such as norbornene.[21,25,27,30,32,33] These are also among the few classes of catalysts which efficiently incorporate styrene into polyethylene.[18,27,34−36] Additionally, when compared to bis-cyclopentadienyl metallocenes, CpA catalysts have increased stability toward MAO, are remarkably stable up to reaction temperatures of 160 °C, and give generally higher molecular weight polymers.[37]

## B. Catalyst Synthesis

CpA ligand synthesis can be accomplished in stepwise fashion, conventionally starting with the Cp fragment and adding the silyl bridge followed by the amine group. However, this route has two main disadvantages. First, there are problems with stoichiometric addition of the cyclopentadienyl fragment (Cp′) to $SiMe_2Cl_2$ such that, even in the presence of a large excess of the silyl chloride, a percentage of $Cp'_2SiMe_2$ is formed.[38,39] Purification of $Cp'SiMe_2Cl$ by distillation or sublimation is therefore necessary. Second, this addition is seldom quantitative, resulting in the loss of the valuable reagent ($Cp'SiMe_2Cl$). Nickias and co-workers reported[40] that it is more desirable to build the ligand from the amine first, giving high yields (>90%) of $R_2Si(NHR')Cl$ which can then be stoichiometrically reacted with the Cp′ fragment. The two routes are summarized in Figure 4.

A third method introduced by Royo[41] and used by Okuda[42] assembles the ligand framework on a metal template. In this procedure, reaction of $Cp(SiMe_2Cl)SiMe_3$ with $TiCl_4$ gives $Cp(SiMe_2Cl)TiCl_3$, which subsequently reacts with LiNHR to give the CpA titanium complex.

The synthesis of CpA catalysts has evolved from low-yielding metathesis routes to the use of post-metalation oxidation and protonolysis. Initial syntheses[15,16,18] of CpA complexes centered around reactions of the dilithio- or di(magnesiochloride) salts

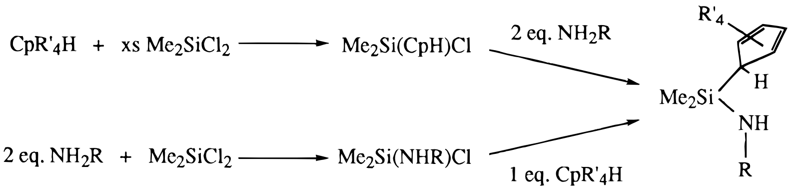


**Figure 4.** Synthetic routes to silyl-bridged CpA ligands.

of the ligand with $TiCl_4$, but yields for this route are generally low (20−40%). In their early report,[18] Dow researchers indicated that it is also possible to metalate the ligand with $TiCl_3(THF)_3$ and then oxidize to titanium(IV) with AgCl. They have subsequently reported[34] that less expensive alkyl chloride oxidants such as $CH_2Cl_2$ and $CCl_4$ work equally well; lead chloride is particularly effective.[43]

Several groups have recently reported more efficient metalation strategies which take advantage of the acidity of fully protonated CpA ligands. Teuben observed[44] that propyl-bridged CpA ligands react readily with $M(NMe_4)$ ($M = Zr$, Hf) with virtually quantitative conversion to the bis(dimethylamide) complex. Herrmann later found[45] this route could be extended to reactions of indenyl-based ligands with titanium tetrakis(dialkylamide)s. The amine elimination route is not completely general, as $Me_4Cp$-based ligands do not readily react with titanium tetrakisamides. This strategy has since been exploited by Peterson[46] and Waymouth[47] who found that treatment of the bis(dialkylamide)s with ammonium chlorides or excess $Me_3SiCl$ gave clean conversion to the dichlorides, although in the former case amine adducts were produced. In addition, protonation of $M(Bz)_4$ ($M = Zr$, Ti) by $Me_4Cp$-based ligands proceeds to yields of 60−90%,[48] giving in one step complexes which can be activated for polymerization by either MAO or borane reagents.

## *II. New Polymer Materials from CpA Catalysts*

### A. Ethylene/Olefin Copolymers

Until recently, three grades of polyethylene have been commercially available (Figure 5). Low-density polyethylene (LDPE) is produced in a high-pressure/high-temperature process, and its high processability has been shown to result from significant levels of side chain branching. High-density polyethylene (HDPE), on the other hand, is a linear polymer produced by heterogeneous and homogeneous Ziegler−Natta catalysts and is characterized by its high strength and poor processability. The same catalyst systems can be used to incorporate low levels of $\alpha$-olefins into the HDPE backbone to give linear low-density polyethylene (LLDPE).

One class of materials developed by Dow and Exxon using CpA catalysts was copolymers of ethylene and long $\alpha$-olefins such as hexene, octene, and decene.[17,18,21] The combination of decreased $\beta$-H elimination at high temperatures and high comonomer incorporation available with these open catalysts of this type led to the initial discovery of a new class of "substantially linear" polymers which have the strength and toughness of LLDPE while possessing the melt processability of LDPE.[28,49] The unique properties of this material are thought to stem from small amounts of long chain branches (LCBs) along the polymer chain (3 LCBs/1000 carbons). One possible mechanism[37] for the formation of LCBs is shown in Figure 6 and involves a critical level of $\beta$-H elimination of the polymer chain at elevated reaction temperatures to give a vinyl-terminated macromonomer, which can then reinsert into another growing polymer chain.

A critical feature of this reaction would appear to be the ability to conduct copolymerizations at temperatures (130−160 °C) above the polymer melting point and, by proper control of the polymerization process, to control the amount of long-chain branching formed while maintaining high catalyst efficiency and high comonomer reactivity.

Kinetic studies of these reaction systems are unavailable, and little is known about the mechanism

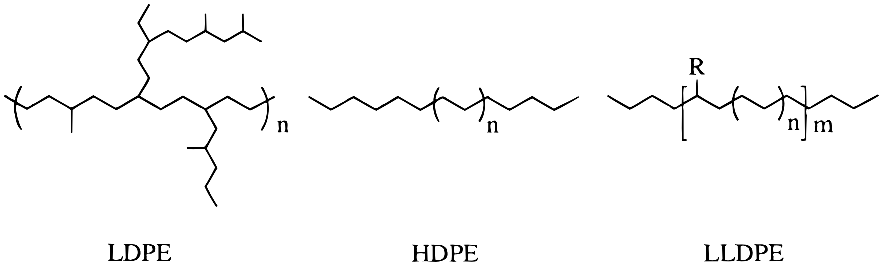


**Figure 5.** Commercial polyethylenes.

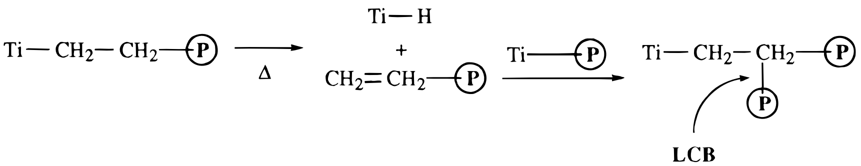


**Figure 6.** Mechanism for long chain branch formation (Ti = active catalyst, P = polymer chain, LCB = long chain branch).

**Table 1. Reactivity Parameters for CpA-Catalyzed Ethylene/Olefin Copolymerization**[a]

| comonomer | *T* (°C) | $r_1$ | $r_2$ | ref |
|---|---|---|---|---|
| butene | NA | 6.7 | NA | 25 |
| octene | NA | 4 | NA | 37 |
| octene | 85 | 2.6 | 0.5 | 50 |

[a] Catalyst system: **1**/MAO, NA = data not available.

of chain transfer. Table 1 shows the few reactivity ratios available from the literature for ethylene/butene and ethylene/octene copolymerizations with the prototypical catalyst [$Me_2Si(Me_4Cp)(N^tBu)$]$TiCl_2$ (**1**).

These data indicate that these catalysts incorporate α-olefins better than metallocenes such as $Cp_2ZrCl_2$ ($r_1 = 22.0$).[50] The product of the reactivity ratios ($r_1r_2 = 1.3$) indicates that, at least for octene, copolymerizations with ethylene are close to ideal, meaning there is a statistical distribution of the two monomers in the copolymer. $^{13}$C NMR spectroscopic analysis of the end groups of low molecular weight CpA-derived poly(ethylene-*co*-octene) by Soga[50] demonstrated that only vinyl unsaturated chain ends are observed.

## B. Copolymers with Higher α-Olefins and Norbornene

The Exxon group has since tested higher α-olefins in copolymerizations with ethylene and has found that these comonomers allow access to materials with novel properties. In the presence of the catalyst precursor [$Me_2Si(Me_4Cp)(NC_{12}H_{23})$]$TiCl_2$ catalyst (**2**), ethylene was efficiently copolymerized with olefins ranging in size from 1-decene ($C_{10}$) up to 1-octadecene ($C_{18}$), with incorporation levels and molecular weights as high as 11% and 80 000 Da, respectively.[22] At comonomer contents above 10%, these copolymers exhibit melting behavior suggestive of side chain crystallization. As a result, the strain to break for the hexadecene and octadecene copolymers is exceptionally high (800%). The storage and loss moduli, which indicate the ability to absorb and dissipate energy, are high for these copolymers; these copolymers have thus been targeted as shock-absorbing and vibration-dampening materials. Highly branched comonomers such as 3,5,5-trimethyl-1-hexene have also been copolymerized with ethylene by the Exxon group,[23] and the resulting materials have exceptionally high moduli of elasticity, strain to break, and strain hardening. Finally, these catalysts are able to incorporate up to 45 mol % isobutylene into copolymers with ethylene, which is remarkable since metallocene catalysts display poor activity in homo- or copolymerizations of 1,1-disubstituted olefins. The Exxon group recently reported[51] that the methyl cation of **2** has ethylene/isobutylene copolymerization activity comparable to the analogous ethylene/styrene copolymerizations. These copolymers are substantially alternating with vinylidene chain ends as judged by their $^{13}$C NMR spectra.

The ability of CpA catalysts to copolymerize cyclic olefins such as norbornene has only recently been investigated.[21,25,27,32,33,52,53] As with *ansa*-metallocenes,[54,55] the reactivity ratios for CpA catalysts for ethylene/norbornene copolymerization are remarkably low ($r_1 = 1.9-5.1$), allowing for facile incorporation of norbornene into ethylene copolymers.[52,53] These copolymers derived from CpA catalysts show virtually no norbornene block sequences in their $^{13}$C NMR spectra, and accordingly no more than 50 mol % norbornene can be incorporated into the copolymer. Harrington recently reported that chiral hafnium and zirconium CpA catalysts derived from [$Me_2Si$-(3-$^t$BuCp)(1-adamantyl amido)]$MX_2$ are able to produce semicrystalline P(E-*co*-N)s with remarkably high melting points (approximately 250 °C).[32] It was suggested that the crystallinity was due to a stereospecific and alternating comonomer distribution in the polymer chain. The tacticity (isotactic or syndiotactic) for the alternating polymer was not specified.

## C. Copolymers with Vinyl Macromonomers

In 1994 scientists at Exxon detailed[20,24] a new strategy for developing long chain-branched polyolefins by copolymerizing ethylene with vinyl-terminated macromonomers. Their process is conceptually related to the mechanism proposed by Dow scientists for formation of long chain branches in the high-temperature (130−160 °C) ethylene/olefin copolymerization process (vide infra). Nonbranched macromonomers with a low degree of polymerization (150−1500 to maintain solubility for the subsequent solution phase polymerization process) were produced at high temperatures by unbridged metallocenes such as $Cp_2ZrCl_2$ or $Cp^*{}_2ZrCl_2$. These macromonomers were copolymerized either with ethylene alone or with ethylene and a small amount of termonomer using CpA catalysts to give a material with approximately 1 mol % incorporated macromonomer (i.e. 5.0 branches per 1000 carbon atoms in the main chain). Processability and mechanical properties of these materials are claimed to be identical to those of branched LLDPEs.

Soga and co-workers[50] have examined ethylene/macromonomer copolymers in more detail. Ethylene polymerization catalyzed by **1** and MAO in decahydronaphthalene yielded an oligomer ($M_w = 1700$) with exclusively vinyl and *n*-propyl end groups and no detectable long chain branches as judged by $^{13}$C NMR spectroscopy. In toluene, however, ethylene polymerizes to give a polymer with high intrinsic viscosity. Copolymerization of ethylene with oligoethylene containing vinyl, vinylidene, and internal vinyl unsaturation resulted in a polymer with practically quantitative incorporation of the vinyl-terminated comonomers as determined by IR and NMR spectroscopy. These results contrast with identical experiments performed with $Cp_2ZrCl_2$, which gave appreciable amounts of unreacted vinyl macromonomer. The results of both the oligomerization and copolymerization experiments (Figure 7) demonstrate the effect that solvent can have on the relative rates of $\beta$-hydrogen elimination versus propagation. This further underscores the level of architectural control possible with CpA catalysts.

A further extension of this methodology was detailed by Soto and co-workers at Dow,[56] who exploited

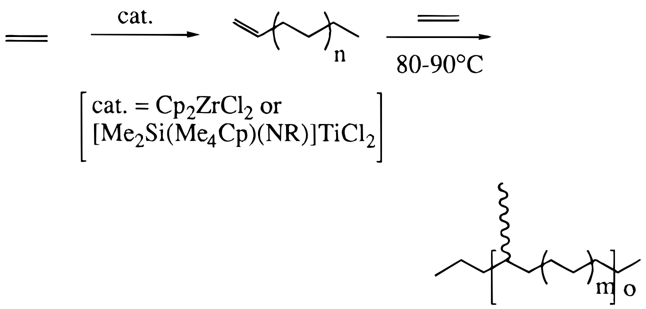


**Figure 7.** Copolymerization of ethylene and oligoethylene.

the unique reactivity of the CpA catalyst to prepare "segmented multicomponent interpolymers". Styrene was polymerized anionically and then capped with allyl chloride to give a low molecular weight ($M_w$ = 5500−6000) vinyl-terminated polystyrene macromonomer. This macromonomer was then terpolymerized with a mixture of ethylene and octene using [$Me_2Si(Me_4Cp)(N^tBu)]TiMe_2$ (**3**)/$B(C_6F_5)_3$ to afford materials which were judged by transmission electron microscopy (TEM) to be phase-separated into polystyrene and poly(ethylene-*co*-octene) domains. Temperature scans of the terpolymers showed similar phase separation as two distinct glass transition temperatures for the polyolefin (−50 °C) and polystyrene (75 °C) domains, confirming the TEM results.

## D. Ethylene/Styrene Copolymers

### 1. Copolymerization Dynamics

Another interesting class of polymers that can be prepared with CpA catalysts are copolymers of ethylene and vinyl aromatic monomers, such as styrene. Heterogeneous Ziegler−Natta catalysts have traditionally been plagued by low styrene incorporation (<1% styrene)[57,58] or low molecular weights.[59,60] Biscyclopentadienyl metallocenes show very low activities and poor regiospecificity in such copolymerizations.[61] In contrast, Dow reported examples of 37% styrene incorporation for ethylene/styrene copolymers produced by CpA catalysts,[18,27,34] and Xu has reported the synthesis of alternating ethylene/styrene copolymers containing 50% styrene.[36] The elastomeric properties of poly(ethylene-*co*-styrene) were briefly mentioned by the Dow group as it was noted that the elastic modulus at high melt indices was higher than that for conventional polymers. Target applications for these copolymers are as films or foams, compatibilizers, and as modifiers for bitumens and asphalts.

The $^{13}C$ NMR spectra show that no more than two consecutive styrene units are found along the copolymer chains, and of the three possible dyad structures (Figure 8), only tail-to-tail coupling is observed.

It was postulated by Stevens[18] that steric effects dictate the ordering of insertion of consecutive styrenes. Also, the inability of the CpA catalyst to homopolymerize styrene was thought to be a result of catalyst deactivation by the phenyl ring of a 2,1-inserted monomer. The catalyst system [$Me_2Si(Me_4Cp)(N^tBu)]TiMe_2$ (**3**)/$B(C_6F_5)_3$ appears to be as active as the MAO-activated analogue, albeit with lower styrene incorporation (<2%).[27]

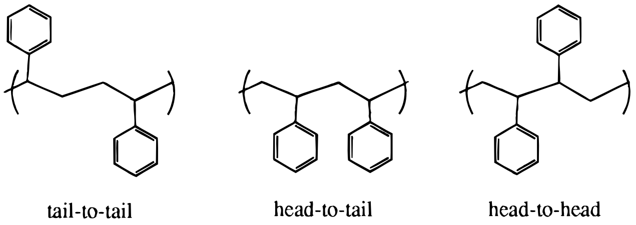


**Figure 8.** Possible styrene dyad structures.

Sernetz and workers systematically studied[35] ethylene/styrene copolymerizations using [$Me_2Si(Me_4Cp)(N^tBu)]TiCl_2$ (**1**)/MAO and drew several conclusions regarding the effect of comonomer incorporation on productivity, microstructure, molecular weights, and thermal behavior. The reactivity ratios $r_E$ (= 23.4) and $r_S$ (= 0.015) calculated from a Fineman−Ross plot revealed a clear preference for ethylene insertions. This is borne out on the microstructural level as only tail-to-tail coupling of styrene dyads was observed in the $^{13}C$ NMR spectra. The observed decrease in productivity with increasing styrene feed concentration is postulated to result from increased catalyst deactivation by the phenyl ring of the last 2,1-inserted styrene unit. Similar decreases in copolymer molecular weights with increasing styrene in the feed were observed. While lower molecular weights might be postulated to be the result of an increased rate of chain transfer following styrene insertion, styrene end groups could not be detected. Investigation of the copolymers' thermal behavior showed that with increasing styrene content, the melting temperature ($T_m$) quickly decreases from 133 °C for polyethylene to 68 °C for a copolymer with 17 mol % styrene. Also, the glass transition temperature ($T_g$) increases from −17 °C (6 mol % styrene) to 6 °C (29 mol % styrene) with styrene incorporation.

Temperature rising elution fractionation (TREF) of a copolymer containing 13.8 mol % styrene gave several fractions which were analyzed by $^{13}C$ NMR spectroscopy, size exclusion chromatography (SEC), wide-angle X-ray scattering (WAXS), and differential scanning calorimetry (DSC) to determine differences in composition.[62] The comonomer distribution was found to be very narrow, decreasing from 14.5% to 11.3% styrene with increasing dissolution temperature. The molar masses of the fractions, whose polydispersities were narrow ($M_w/M_n$ = 2.0), decreased with increasing styrene content, reinforcing Sernetz's earlier observation that higher styrene concentration lowers molecular weight and productivity. Crystallinity also decreased with increasing styrene content. Altogether, the results clearly reflect the single-site nature of the CpA catalyst and its ability to produce copolymers with a uniform comonomer distribution.

In collaboration with Okuda,[63] Sernetz and Mülhaupt probed ligand effects on the ethylene/styrene copolymerization behavior. They found that sterically hindered **1** is the most active, presumably due to higher electron density vis a vis indene, fluorene, or benzylamine derivatives. The more open indenyl analogue [$Me_2Si(Ind)(N^tBu)]TiCl_2$ (**4**) and the benzylamino analogue [$Me_2Si(Me_4Cp)(NCH_2Ph)]TiCl_2$ (**5**)

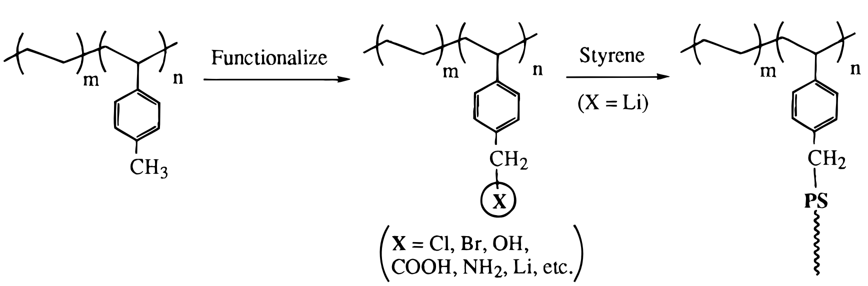


**Figure 9.** Functionalization of poly(ethylene-*co*-methylstyrene).

**Table 2. Reactivity Ratios for Copolymerizations of Ethylene with Styrene and *p*-Methylstyrene**[a,67]

| $M_1$ | $M_2$ | $T$ (°C) | $r_1$ | $r_2$ | $r_1r_2$ |
|---|---|---|---|---|---|
| E | S | 40 | 32.7 | 0.017 | 0.54 |
| E | S | 60 | 66 | 0.36 | 24 |
| E | MS | 40 | 19.6 | 0.04 | 0.78 |
| E | MS | 60 | 21 | 0.08 | 1.7 |

[a] E = ethylene, S = styrene, MS = *p*-methylstyrene. Catalyst: **1**/MAO.

promote the highest styrene incorporation, and the latter catalyst actually gives a small percentage of head-to-tail styrene coupling as determined by $^{13}$C NMR spectroscopy. The fluorenyl analogue [$Me_2Si(Flu)(N^tBu)]ZrCl_2$ (**6**) gives molecular weights at least twice as high as those of any other catalyst studied.

In a recent extension of Sernetz and Mühaupt's catalyst studies, Xu[36] detailed the copolymerization of ethylene and styrene by the cationic [$Me_2Si(Flu)(N^tBu)TiMe^+][B(C_6F_5)_4^-]$ system. This catalyst system yielded exclusively polyethylene at 0 °C, but at 50 °C only 20% polyethylene was produced as determined by fractionation in boiling THF. The remaining THF soluble fractions were analyzed by $^{13}$C NMR and were found to be enriched in $S_{\beta\beta}$ (SES), $S_{\alpha\beta}$ (SES), and $T_{\delta\delta}$ (ESE) signals in a 1:2:1 ratio, indicating a perfectly alternating structure. Xu also found that the microstructure and composition was independent of feed composition. Furthurmore, comparison of the main chain and phenyl ipso carbons in the $^{13}$C NMR spectra with the assignments of Suzuki et al. for hydrogenated 1,4-poly(1-phenylbutadiene)[64] suggests only isotactic dyads (m) and triads (mm) are present along the backbone.

### 2. Functionalized Poly(Ethylene-co-Methylstyrene)

The ability of CpA catalysts to efficiently copolymerize ethylene with styrenic monomers and the vast number of known benzylic chemical transformations prompted Chung and Lu to study the preparation of poly(ethylene-*co*-methylstyrene)s[65] for functionalization reactions (Figure 9).[66]

Chung found that *p*-methylstyrene is incorporated into ethylene copolymers more readily than styrene. Both *o*- and *m*-methylstyrene are incorporated to a lesser degree than the para isomer. Chung also reported[67] reactivity ratios for ethylene/*p*-methylstyrene versus ethylene/styrene (Table 2) and found that the reactivity ratios for ethylene/methylstyrene (E/MS) did not change significantly with increasing polymerization temperature in contrast to those for ethylene/styrene (E/S).

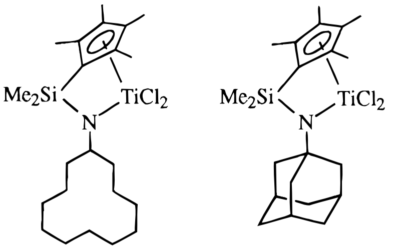
It was reported that copolymers containing 10% MS show no MS−MS units in the $^{13}$C NMR spectrum whereas for a styrene copolymer one can observe S−S units for the same level of incorporation. Last, addition of a small amount of octene to the E/MS copolymer gave a material with a lower $T_g$ (−50 °C) and elastomeric properties. On the other hand, the related E−*p*-MS terpolymers only show low $T_g$ values (<−45 °C) when *p*-MS incorporation is below 2 mol %.[68] Chung noted that α-olefin incorporation in such terpolymerizations is much slower than in the analogous ethylene/olefin copolymerizations, suggesting steric crowding of the propagating site by the last inserted *p*-MS unit.

In an earlier patent, Chung reported[66] that E/MS copolymers made using ethylene(bis-indenyl)zirconium dichloride ($EBIZrCl_2$) with low levels of MS can be selectively brominated to high levels (60%) with *N*-bromosuccinamide (NBS) and benzoyl peroxide. Oxidation with $Co^{III}(OAc)\cdot(H_2O)_4/O_2$ and carboxylation with $^nBuLi/CO_2$ was also demonstrated for these copolymers.

While similar functionalizations of CpA-derived E/MS copolymers have not been reported to date, Chung recently detailed[67,69] the use of the lithiated poly(ethylene-*co*-methylstyrene)s for preparation of polyethylene-*graft*-polystyrene (PE-*g*-PS). A copolymer with 0.9% *p*-methylstyrene was metalated with $^n$BuLi/TMEDA to form a macromolecular anionic initiator, which was then treated with varying amounts styrene to afford polystyrene side chains with well-defined structure. The thermal properties of the graft copolymer were surprising, as the $T_m$ decreased only slightly from that of polyethylene (128 °C) regardless of graft length or density. Also, with increasing graft composition, the $T_g$ saturates at about 104 °C. The unique composition of this material could lead to applications as a compatibilizer, and indeed Chung observed that 45:45:10 blends of HDPE, PS, and PE-*g*-PS lacked large phase separations seen for 50:50 blends of crystalline HDPE and amorphous PS.

## E. High Molecular Weight Atactic Polypropylene

Because of their amorphous nature, atactic polymers lack the strength characteristics of crystalline isotactic and syndiotactic polymers and most often find application as adhesives, compatibilizers, and additives. As many aspecific homogeneous catalysts produce low molecular weight polymers, one goal in polyolefin research has been to find catalysts which give higher molecular weight atactic polymers.[70] While a few reports suggest that certain catalyst



**2** **6**

**Figure 10.** Bulky amide CpA catalysts.

structures are iso-[15] and syndiospecific,[71−73] the vast majority of CpA catalysts produce slightly syndiotactic-enriched atactic polypropylene (aPP).[18,20,27,74]

In the last two years, the Exxon group has filed patents detailing the incorporation of bulky amido groups into the CpA framework to produce high molecular weight aPPs. Large aliphatic amines such as cyclododecylamine or 1-adamantylamine[25] (see Figure 10) afforded catalysts which yielded polymers of low polydispersity (<2.0).[74]

The cyclododecyl analogue yielded polymers with molecular weights between 1 300 000 and 1 800 000 Da (at 40−50 °C). By comparison, a zirconocene catalyst for aPP, $[Me_2Si(Flu)_2]ZrCl_2$, gives molecular weights up to 400 000 at the same reaction temperatures.[70] The molecular weights for polymers produced by the adamantyl analogue were also higher (500−700 000 Da) than those for typical CpA catalysts. DSC analysis of the polymers were indicative of some degree of crystallinity, as melting temperatures of 123−129 °C were reported. Typically, atactic polypropylene shows no melting point. Further details on these polymers' mechanical properties are unavailable at present.

In Resconi's study of the silyl-bridged fluorenyl zirconcocenes, high molecular weights were attributed to nonbonded interactions between the fluorenyl ligand's $\beta$-substituents and the growing chain, which destablized chain conformations leading to $\beta$-H transfer.[70] The predominant chain termination mechanism for this system was unimolecular $\beta$-Me transfer. A similar mechanism is difficult to envision for the CpA catalysts in light of the open nature of the coordination site; electronic effects provided by the amido ligation is the likely origin of higher molecular weight, as suggested by McConville's observation of "living" catalysts containing bis-amido ligation.[75,76]

There are conflicting reports in the literature on stereospecificity of CpA catalysts for propylene polymerization and the influence of the counterion on the stereoselectivity. Canich reported[15] that certain MAO-activated chiral and achiral CpA metal dichlorides gave crystalline polypropylenes with high isotacticities ([*mmmm*] > 75%). One complex in particular, $[Me_2Si(Flu)(N^tBu)]ZrCl_2$ (**12**), was reported to yield a polymer with [*mmmm*] = 93%. McKnight and Waymouth subsequently reported that they were unable to obtain tactic polymers under similar conditions.[47] Turner reported[71] that conversion of this same zirconium dichloride complex to the dimethyl complex $[Me_2Si(Flu)(N^tBu)]ZrMe_2$ (**13**) and activation with $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ gave a syndiotactic microstructure with a racemic dyad content of greater than 90%. Shiomura investigated the counterion effect and in one report indicated that activation of **12** with MAO and $Al^iBu_3$ yielded a small amount of syndiotactic PP ([*rrrr*] = 77%) while activation with $[Ph_3C^+][B(C_6F_5)_4^-]$ and $Al^iBu_3$ gave isotactic PP ([*mmmm*] = 95%).[72] A subsequent report corrected these findings, reporting that MAO-activated catalysts yielded atactic polypropylene, while activation with $[Ph_3C^+][B(C_6F_5)_4^-]$ and $Al^iBu_3$ yielded a polymer that could be fractionated to give 30% of a syndiotactically enriched ([*rrrr*] = 80%) fraction.[73] Further research is warranted to resolve the issue of stereospecificity and the potential role of the counterion.

Exxon has used the bulky amide CpA technology to produce[77,78] thermoplastic elastomeric blends of high molecular weight aPPs with lower molecular weight (50 000 Da) isotactic polypropylene (iPP) produced by $C_2$-symmetric metallocene catalysts. While blends of aPP and iPP often display interesting flexibility, they generally lack the elastic recovery properties of traditional elastomers. In the Exxon blends, however, the higher molecular weight of the atactic fractions presumably imparts increased strength to the blend. A typical material, consisting of 60−90% aPP produced by $[Me_2Si(Me_4Cp)(NC_{12}H_{23})]TiCl_2$ (**2**)/MAO and 40−10% iPP produced by *rac*-$[Me_2Si(Ind)_2]MCl_2$/MAO (M = Zr, Hf), was reported to have good recovery properties (82−94%) and high tensile strength (1000−2300 psi) while retaining high crystallinities ($T_m$ = 143−146 °C). In addition, performance of reactor blends was reported to be better than that of comparable physical blends, allowing one-pot preparation of a range of thermoplastic elastomers by simple variation of catalyst ratios in the reactor.

## *III. Catalyst Studies*

### A. Ligand and Metal Effects on Catalyst Behavior

One of the advantages of the CpA geometry is that there are a number of components which can be systematically varied to achieve a desired catalytic behavior. Poly(ethylene-*co*-octene)s are among the most extensively developed materials produced by these catalysts. Since properties such as density and melt index ($I_2$) relate to their processability and strength, they offer a good measure of a CpA catalyst's range. Table 3 provides a summary of the effects of changing ligand and metal fragments on the polymer properties.

With $[Me_2Si(Me_4Cp)(N^tBu)]TiCl_2$ **1** as a standard, it is evident that changing the cyclopentadienyl group from $Me_4Cp$ to Cp (**7**) or to Ind (**4**) results in a steady drop in productivity and melt index, as well as a rise in copolymer density (i.e. less octene incorporation). The same could be said for changing the *tert*-butylamido group to phenylamido (**8**) and phenylphosphido (**9**) groups, which leads to lower productivity and higher polymer density. As expected, increasing the size of the bridging group increases the ligand "bite angle" ($\theta$) (substitution of $Me_2Si$ ($\theta$ = 107.7°) for $(CH_2)_2$ (**10**, $\theta$ = 107.9°) and $(Me_2Si)_2$ (**11**, $\theta$ = 120.5°)) which in turn leads to decreased productivity and decreased octene incorporation, presumably because

**Table 3. Ligand and Metal Effects on CpA-Produced Poly(ethylene-*co*-octene)[a]**

| catalyst[b] | prod.[c] | $M_w$ | density | $I_2$[d] | ref |
|---|---|---|---|---|---|
| $[\mathrm{Me_2Si(Me_4Cp)(N^tBu)]TiCl_2}$ (**1**) | 43 100 | | 0.8850 | 10.73 | 79 |
| $[\mathrm{Me_2Si}(\mathbf{Cp})(\mathrm{N^tBu})]\mathrm{TiCl_2}$ (**7**) | 16 900 | 108 000 | 0.9073 | 2.92 | 18 |
| $[\mathrm{Me_2Si}(\mathbf{Ind})(\mathrm{N^tBu})]\mathrm{TiCl_2}$ (**4**) | 8900 | | 0.9179 | 0.92 | 18, 79 |
| $[\mathrm{Me_2Si(Me_4Cp)}(\mathbf{NPh})]\mathrm{TiCl_2}$ (**8**) | 7680 | 103 000 | 0.9387 | 6.37 | 18 |
| $[\mathrm{Me_2Si(Me_4Cp)}(\mathbf{PPh})]\mathrm{TiCl_2}$ (**9**) | 8600 | 27 700 | 0.9690 | 251 | 18 |
| $[\mathbf{(CH_2)_2}\mathrm{(Me_4Cp)(N^tBu)]TiCl_2}$ (**10**) | 19 400 | | 0.9262 | 3.21 | 18 |
| $[\mathbf{(Me_2Si)_2}\mathrm{(Me_4Cp)(N^tBu)]TiCl_2}$ (**11**) | 7300 | 62 400 | 0.9441 | 6.14 | 18 |
| $[\mathrm{Me_2Si(Me_4Cp)(N^tBu)]}\mathbf{Zr}\mathrm{Cl_2}$ (**12**) | 60 200 | | 0.9571 | 250 | 79 |

[a] Conditions: 10 μmol of catalyst, 1000 mL of solvent, 200 mL of octene, 450 psig of ethylene, 50 Δpsig of hydrogen, 130 °C, $t$ = 10 min. [b] Bold font indicates the ligand and metal fragments that were varied from catalyst **1**. [c] Productivity in g polymer/mmol metal h. [d] Melt index.

of steric effects.[79] Finally, changing the metal from titanium to zirconium gives a modest increase in productivity, but this gives a copolymer with a much higher density, close to that of HDPE, and a very high melt flow index. The efficiency of the titanium catalyst, measured on a gram of polymer per gram of metal basis, is 50% higher than that of the zirconium analogue **12**, meaning less metal residue remains in the polymer. Overall, it is apparent that catalyst **1** is the most productive and has the highest affinity for octene of the catalysts in Table 3.

## B. CpA Cationic Catalysts

The indeterminate nature of methylaluminoxane and the typical requirement for high ratios of Al/Ti limit the attractiveness of this cocatalyst system for olefin polymerization. In a search for alternative means of activation, workers at Dow[19,27,80] and Exxon[71,81−84] found that CpA alkyl complexes combined with fluorinated aryl borane and borate noncoordinating anions (NCAs) are up to 100 times more productive than catalysts activated by MAO. As a result, they are able to produce polymers without aluminum residues.

Chen and Marks have applied sterically encumbered NCAs (Figure 11) to CpA alkyl catalysts to probe the effect of counterion on ion pairing, activity, chain transfer, and comonomer reactivity. One such NCA, tris(perfluorobiphenyl)borane (PBB),[85] improved the activity of titanium CpA catalysts by a factor of 50 over $B(C_6F_5)_3$-activated ethylene and ethylene/hexene polymerizations. Similarly, zirconium analogues, which were virtually inactive at 25 °C in $B(C_6F_5)_3$-activated polymerizations, showed good activities when PBB was used. While the level of hexene incorporation was similar for the two borane systems, polymer molecular weights and polydispersities were lower for PBB than for $B(C_6F_5)_3$. NMR spectra of the CpA/PBB complexes suggested weaker ion pairing than for the perfluorophenyl analogues. Another large NCA, tris(perfluorobiphenyl)fluoroaluminate (PBA⁻),[86] shut down CpA ethylene polymerization at room temperature but afforded good yields of ultrahigh molecular weight polyethylene ($M_w = 2.05 \times 10^6$) at a reaction temperature of 110 °C. Crystal structure and $^{19}$F−Al NMR examination of the zirconium CpA cation revealed a strong $Zr^+{-}F{-}Al^-$ interaction, which would be expected to lower productivity while stabilizing the metal center against chain transfer pathways. It is clear from these two studies that the open CpA cations are very sensitive to appropriate choice of counterion, which affects ion pairing and thus the polymerization behavior.

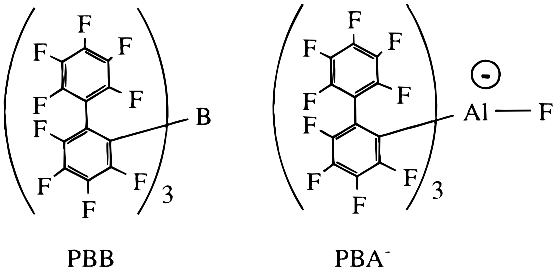


**Figure 11.** "Very large" counterions for CpA-catalyzed cationic olefin polymerization.

## C. Reduced CpA Catalyst Precursors

The nature of the CpA active species and the role of CpA ancillary ligation has been the subject of several studies by the group at Dow, who have been examining the use of stabilized reduced titanium and zirconium CpA catalysts. In early work, LaPointe and co-workers[26] reported the preparation of Ti(III) CpA complexes of the type shown in Figure 12 and their use in ethylene/octene copolymerizations using a ferrocenium oxidant as the cocatalyst.

The productivity of these catalysts (>300 000 g/mmol Ti h) was on the order of the typical nonstabilized CpA cationic catalysts. It was later reported[29] that in the absence of an oxidizing species, high productivities are still possible with a variety of activators, such as $B(C_6F_5)_3$, MAO, $PhB(C_6F_5)_2$, and $BPh_3$. The highest productivities (500 000 g/mmol Ti h) were observed for systems where [Ti] was kept low (<1 μmol/L) and an excess of borane was used.

Another disclosure by the Dow group[87] suggests that active catalysts can alternatively be prepared by electrochemical oxidation of titanium(III) and -(IV) precatalyst species, obviating the need for chemical oxidizing agents such as ferrocenium. Summarized

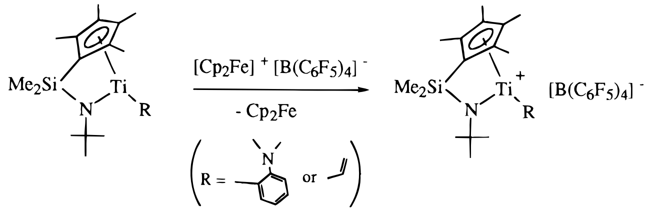
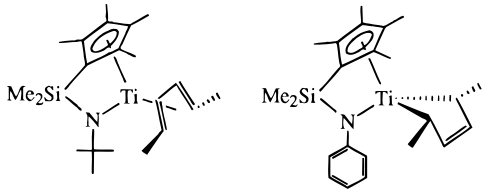


**Figure 12.** "Stabilized" titanium CpA catalysts.

**Table 4. Ethylene/Octene Polymerization by Electrochemically Prepared CpA Catalysts[a,87]**

| catalyst[b] | co-catalyst | potential (V) | productivity (g/mmol h) |
|---|---|---|---|
| $L_2Ti(\mathbf{\textit{o}-CH_2C_6H_4NMe_2})$ (**14**) | $(^nBu)_4NB(C_6F_5)_4$ | −1.0 | 120 000 |
| $L_2Ti\mathbf{Me_2}$ (**3**) | $(^nBu)_4NB(C_6F_5)_4$ | +1.4 | 188 000 |
| $L_2Ti\mathbf{Cl_2}$ (**1**) | $Al(^iBu)_3$ | +2.2 | 11 400 |
| $L_2Ti\mathbf{Bz_2}$ (**15**) | $(^nBu)_4NB(C_6F_5)_4$ | +1.0 | 92 000 |

[a] General conditions: 500 psig of ethylene, 100−120 g of octene, 140 °C, 10−15 min, 750 mL of Isopar solvent. [b] $L_2 = Me_2Si(Me_4Cp)(N^tBu)$. Bold font indicates ligands that were varied from catalyst **14**.



**16** **17**

**Figure 13.** CpA titanium diene complexes.

in Table 4 are the electrochemical conditions and the resulting copolymerization productivities for several catalyst species.

The productivity of the Ti(III)-derived catalyst is roughly 3 times lower than its chemically oxidized analogue. The variation in productivities for the Ti(IV)-derived catalysts could reflect differences in the efficiency of activation and/or counteranion binding affinity.

The Dow group recently reported[30,88−90] the preparation of Ti and Zr CpA diene complexes (Figure 13). Complexes of this type can be synthesized from either the M(III) or M(IV) halides and reducing agents such as Grignard reagents, organolithiums, magnesium, or lithium in the presence of a conjugated diene. When activated by $[PhNMe_2H^+][B(C_6F_5)_4{}^-]$, these diene complexes exhibit productivity in ethylene/α-olefin copolymerizations similar to that of the dialkyl M(IV) catalysts.

In a more detailed study of the structure and ligand effects of the CpA titanium diene complexes, the Dow group in collaboration with Marks reported[91] NMR and X-ray structural evidence for the reduced metal oxidation state and for the $\eta^4$-binding mode of the diene fragment as shown in Figure 13. The crystal structure of one derivative, $Me_2Si(Me_4Cp)(N^tBu)Ti$-(2,4-hexadiene) (**16**), revealed a “prone” binding of hexadiene and an increased Ti−N distance of 2.007 Å (vs 1.90−1.98 Å for CpA Ti(IV)).

It was discovered that changing the amine from *tert*-butylamine to aniline resulted in a 70:30 mixture of “prone” diene to “supine” metallacyclopentene which is constant even at higher temperatures. Moreover, the ethylene polymerization activity with $B(C_6F_5)_3$ as cocatalyst was influenced by the nature of the amine group and thus the mode of diene binding, with **16** being 25 times more productive than **17**.

Another effort at finding improved synthetic routes to CpA complexes was described by Wilson, who found that substitution reactions of the CpA Grignard reagent with various mono-, bi-, and tricyclopentadienylmetal complexes gave CpA cyclopentadienyl products in yields up to 99% (Figure 14).[92]

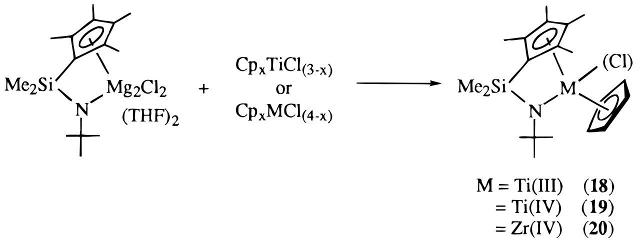


**Figure 14.** Synthesis of CpA cyclopentadienyl complexes.

The ethylene/octene polymerization activity was high for the Zr(IV) (**20**) analogue but low for both Ti(III) (**18**) and Ti(IV) (**19**), potentially indicating differences in catalyst activation.

## D. Theoretical Studies

Ziegler and co-workers performed static and density functional studies of the titanium CpA resting state cation and its subsequent olefin insertion processes.[93,94] Simulations using the model complex $[H_2Si(Cp)(NH)]Ti{-}R^+$ revealed several differences from bis-cyclopentadienyl metallocenes. First, it was observed that the CpA cation is stabilized by several agostic interactions with the polymer chain and the $\gamma$-H structure is only slightly preferred over the $\beta$-H agostic structure. This contrasts with metallocenes, which show a strong preference for the $\beta$-agostic structure. Also, CpA catalysts appear to form much stronger olefin $\pi$-complexes than metallocenes, most likely due to stronger back-donation to the olefin by the electron-donating amido group. The strength of this complex results in an increased barrier to olefin insertion ($\Delta\Delta G^\ddagger = 5$ kcal/mol) into the metal−alkyl bond, and it is this step which becomes the overall propagation barrier. Finally, Figure 15 illustrates two possible insertion processes which lead to inversion (frontside insertion) and retention (backside insertion) of the configuration about the metal center. For CpA catalysts, these two pathways are energetically very similar, indicating that there is a high probability for the occurrence of stereoerrors in α-olefin polymerization according to the Cossee−Arlman mechanism.[95]

## E. New CpA Ligand Designs

Following Bercaw’s initial discovery of the CpA ligand system,[13] research began into variations on the CpA ligand design with the expectation that they may lead to enhanced reactivity and/or selectivity. One effort has been to mimic the steric and electronic characteristics of the highly active $Me_4Cp$ fragment by replacing it with “wing-span modified” Cp ligands,[96] such as $FluH_8$,1,3-$Me_2$-$IndH_4$,[27] and others listed in Table 5.

Very high ethylene/octene copolymerization activity was observed for $[Me_2Si(1,3\text{-}Me_2\text{-}IndH_4)(N^tBu)]TiX_2$ **25** even at lower temperatures (50 °C). The dimethyl derivatives of the substituted indenyl complexes, though having 20% lower ethylene/octene efficiency than the parent $Me_4Cp$ complex, gave copolymers

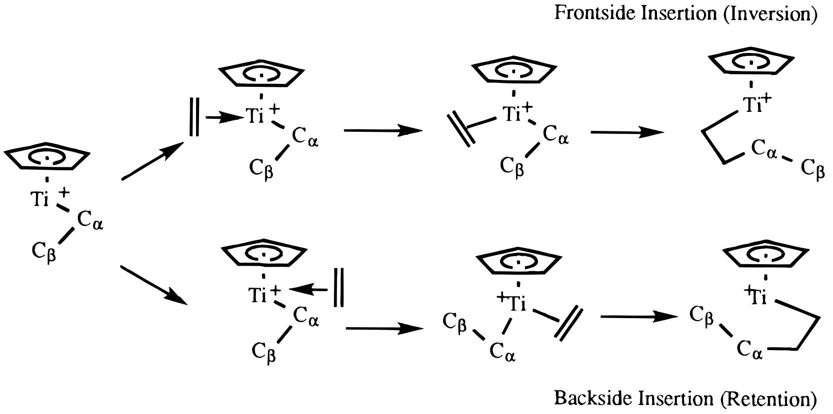
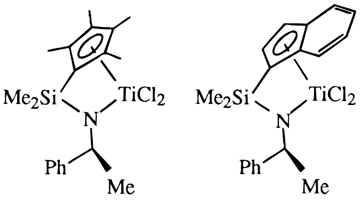


**Figure 15.** Possible propagation pathways for CpA ethylene polymerization.

**Table 5. “Wingspan-Modified” CpA Catalysts**

| complex[a] | | ref |
|---|---|---|
| [Me$_2$Si(**2-R−Ind**)(N$^t$Bu)]TiX$_2$ | R = Me (**21**) | 31 |
| | Et (**22**) | |
| | Pr (**23**) | |
| [Me$_2$Si(**3-Me-Ind**)(N$^t$Bu)]TiX$_2$ | (**24**) | 31, 40 |
| [Me$_2$Si(**1,3-Me$_2$-IndH$_4$**)(N$^t$Bu)]TiX$_2$ | (**25**) | 27 |
| [Me$_2$Si(**2,3-Me$_2$-Ind**)(N$^t$Bu)]TiX$_2$ | (**26**) | 31 |
| [Me$_2$Si(**2-Me-4-Ph-Ind**)(N$^t$Bu)]TiX$_2$ | (**27**) | 31 |
| [Me$_2$Si(**2,3,4,6-Me$_4$-Ind**)(N$^t$Bu)]TiX$_2$ | (**28**) | 31 |
| [Me$_2$Si(**2,3,4,6,7-Me$_5$-Ind**)(N$^t$Bu)]TiX$_2$ | (**29**) | 31 |
| [Me$_2$Si(**FluH$_4$**)(N$^t$Bu)]TiX$_2$ | (**30**) | 40 |
| [Me$_2$Si(**FluH$_8$**)(N$^t$Bu)]TiX$_2$ | (**31**) | 40 |

[a] Bold font indicates ligand that was varied.



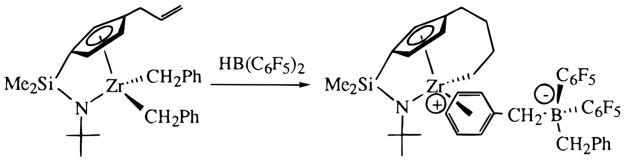
32 33

**Figure 16.** Chiral CpA complexes.

with significantly higher molecular weights, higher comonomer content, and lower melt indices.[31] While it remains to be seen what effect the Flu-H$_8$ group has, Dow researchers in collaboration with the Marks group recently reported[96] the application of the Flu-H$_8$ ligand to isospecific metallocenes. Additionally, Dow researchers have applied the Flu-H$_8$ ligand to syndiospecific styrene polymerization catalysts.[97,98] In the former case, they observe higher isospecificity, higher molecular weight, and higher productivity than the Me$_4$Cp and Flu anologues.

The presence of the amido group in the CpA ligand framework has made it possible to incorporate readily available chiral amines and thereby synthesize optically active polymerization catalysts without difficult resolution procedures. Figure 16 shows examples based on Cp*[42] and Ind.[47]

Okuda found that **32** was catalytically active for the hydrogenation of acetophenone *N*-benzylimine, although with very poor enantioselectivity (12% ee). The catalyst derived from **33** containing a chiral amine exhibited lower stereospecificity in propylene polymerization than the analogous catalyst containing the $^t$Bu amine.[47]



34 35

**Figure 17.** Hydroboration of an allyl-CpA zirconium dibenzyl complex.

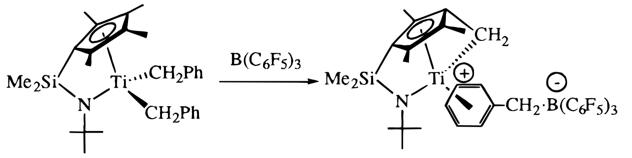
While it has been shown[79] that increasing the size of the bridging group decreases catalyst efficiency in ethylene/olefin copolymerizations, Dias and co-workers[99,100] have explored the increased protection of the metal center offered by CH$_2$SiMe$_2$-bridged amido-fluorenyl ligands. A measure of the ligand's steric influence is the observation that [Me$_2$Si(Flu)(N$^t$Bu)]ZrCl$_2$ (**12**)[39] and [(Flu)CH$_2$CH$_2$(O)]ZrCl$_2$[101] form adducts with THF and Et$_2$O while the analogous [(Flu)CH$_2$SiMe$_2$(NtBu)]ZrCl$_2$ complex does not. Also, in [(Flu)CH$_2$SiMe$_2$(N$^t$Bu)]Zr(CH$_2$SiMe$_3$)$_2$, the amine substituent is oriented more toward the metal center (Zr−N−CMe$_3$ = 118.2 °) whereas [Me$_2$Si(Flu)(N$^t$Bu)]Zr(CH$_2$SiMe$_3$)$_2$ is more open (Zr−N−CMe$_3$ = 130.1°),[39] indicating increased crowding at the metal center.

Spence and Piers have attempted to exploit the CpA ligand environment for the preparation of single-component catalysts.[102] Synthesis of [Me$_2$Si(Cp-allyl)(N$^t$Bu)]ZrX$_2$ followed by hydroboration with HB(C$_6$F$_5$)$_2$ gave [Me$_2$Si(Cp-propyl-BAr$_2$)(N$^t$Bu)]ZrX$_2$ (X = Cl, Me, CH$_2$SiMe$_3$, CH$_2$Ph). Alkyl abstraction by the borane fragment occurs to form an “internally activated catalyst system”. Interesting is the case of **34** which forms the “tuck-in” complex **35** of the general structure shown in Figure 17.

Similar tucked-in CpA cations have been observed by Marks, who found that addition of B(C$_6$F$_5$)$_3$ or [Ph$_3$C$^+$][B(C$_6$F$_5$)$_4$$^-$] to **36** gave the ring metalated complex **37** shown in Figure 18.[48]

The productivity of **37** in ethylene/hexene copolymerizations is very low, but addition of MAO gives a catalyst with productivity similar to that of [Me$_2$Si(Me$_4$Cp)(N$^t$Bu)]TiCl$_2$ (**1**).

An intriguing discovery by the Marks group challenges the electronic requirements necessary for CpA-like polymerization activity. They found that treatment of TiBz$_4$ with an *o*-Cp-phenol ligand gives a complex with ethylene and propylene activity similar to that of silyl-bridged Cp amido catalysts.[103] The



**36** **37**

**Figure 18.** C−H activation of a ring methyl in a CpA titanium dibenzyl complex.

"bite angle" (Cp−Ti−O=107.7°) of this ligand is exactly equal to that of **1**. Similarly, Rieger found that ethylene-bridged fluorenyl alkoxide zirconium complexes were active for ethylene polymerization.[101]

## IV. Conclusions

The monocyclopentadienyl-amido catalyst continues to generate interest in academic and industrial laboratories because of its high productivity and ability to produce unique polymer architectures with increased processablity due to the incorporation of low levels of long chain branches. These catalysts can access materials ranging from high-density polyethylene to linear low-density polyethylene to poly(ethylene-*graft*-stryrene)s to high molecular weight elastomers. Changes in the nature of the cyclopentadienyl, bridge, and amido groups of the ligand give profound effects on molecular weights and densities of poly(ethylene-*co*-octene)s. Additionally, the borane- and borate-activated CpA complexes are extremely active catalysts, and as a result they are among the first homogeneous Ziegler−Natta catalysts to be used in commercial polymerizations.[37]

Several challenges still exist for further elaboration of the catalyst's potential. A deeper understanding of the ethylene/styrene propagation mechanism may lead to new catalyst structures that allow higher incorporation levels, efficiencies, and molecular weights. Moreover, while the open nature of the catalyst clearly limits site control in α-olefin polymerization, a number of reports indicate that chain end control is possible under certain conditions; it is not yet clear whether appropriate choice of counterion or use of "wingspan-modified" Cp ligands will lead to higher stereoselectivities. The nature of the catalyst oxidation state is still being debated, as the Dow group has reported several reduced titanium precatalysts which show reactivity similar to that of Ti(IV) parent complexes. Recent efforts have been directed at incorporating bulky cyclopentadienyl groups and chiral amines to increase the regio- and stereoselectivity of the CpA but have so far met with little success. Finally, at this point the tolerance of the CpA catalysts toward functional monomers has received no attention, although preliminary results from our laboratory would suggest that these catalysts are far less tolerant than zirconium *ansa*-metallocenes.[104]

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