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Development of Group IV Molecular Catalysts for High Temperature Ethylene-α-Olefin Copolymerization Reactions

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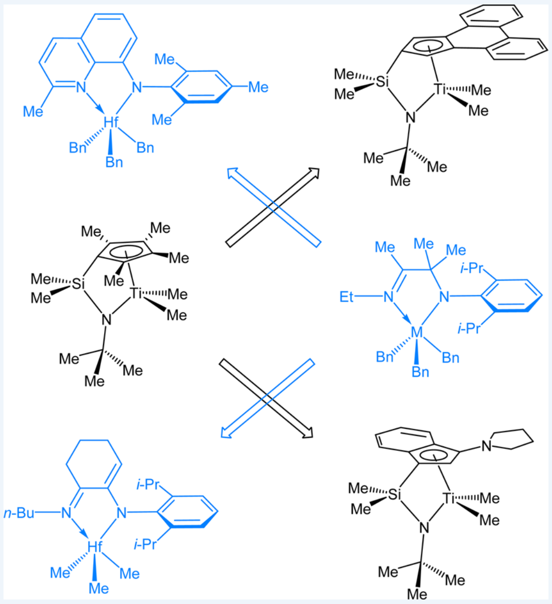

CONSPECTUS: This Account describes our research related to the development of molecular catalysts for solution phase olefin polymerization. Specifically, a series of constrained geometry and non-metallocene (imino-amido-type) complexes were developed for high temperature olefin polymerization reactions. We have discovered many highly active catalysts that are capable of operating at temperatures above 120 °C and producing copolymers with a useful range of molecular weights (from medium to ultrahigh depending on precatalyst identity and polymerization conditions) and α-olefin incorporation capability. Constrained geometry catalysts (CGCs) exhibit very high activities and are capable of producing a variety of copolymers including ethylene-propylene and ethylene-1-octene copolymers at high reactor temperatures. Importantly, CGCs have much higher reactivity toward α-olefins than classical Ziegler–Natta catalysts, thus allowing for the production of copolymers with any desired level of comonomer. In search of catalysts with improved performance, we discovered 3-amino-substituted indenyl-based CGCs that exhibit the highest activity and produce copolymers with the highest molecular weight within this family of catalysts. Phenanthrenyl-based CGCs were found to be outstanding catalysts for the effective production of high styrene content ethylene-styrene copolymers under industrially relevant conditions.

In contrast to CGC ligands, imino-amido-type ligands are bidentate and monoionic, leading to the use of trialkyl group IV precatalysts. The thermal instability of imino-amido complexes was addressed by the development of imino-enamido and amidoquinoline complexes, which are not only thermally very robust, but also produce copolymers with higher molecular weights, and exhibit improved α-olefin incorporation. Imido-amido and imino-enamido catalysts undergo facile chain transfer reactions with metal alkyls, as evidenced by a sharp decrease in polymer molecular weight when the polymerization reactions were conducted in the presence of diethylzinc, an essential requirement for use in the production of olefin block copolymers via chain shuttling polymerization. Overall, the excellent characteristics of imino-amido-type catalysts, including high catalytic activities and ultrahigh molecular weight capabilities, make them good candidates for high temperature syntheses of block and random ethylene-α-olefin copolymers. Additionally, trialkyl imino-enamido complexes react quickly with various protic and unsaturated organic fragments, leading to a library of dialkyl precatalysts that, in several instances, resulted in superior catalysts.

In conjunction with the development of transition metal catalysts, we also synthesized and evaluated activators for olefin polymerization. We found, for example, that, when conducted in coordinating solvents, the reaction between aluminum alkyls and tris(pentafluorophenyl)borane leads to the exclusive formation of alumenium borates, which are excellent activators for CGC complexes. Additionally, we developed a series of highly effective new activators featuring a very weakly coordinating anion composed of two Lewis acids coordinated to an imidazole fragment.

1. INTRODUCTION

Olefin polymerization catalyzed by transition metal complexes is one of the most important processes in the chemical industry today, and this prominence represents a great achievement of organometallic chemistry and catalysis. Polyethylene production (84 881 KTA in 2014)[1] accounts for about 38% of all the plastic made in the world, with about 77% of it being produced via transition metal catalyzed reactions. The hundreds of different grades of ethylene-based polymers produced today are used in

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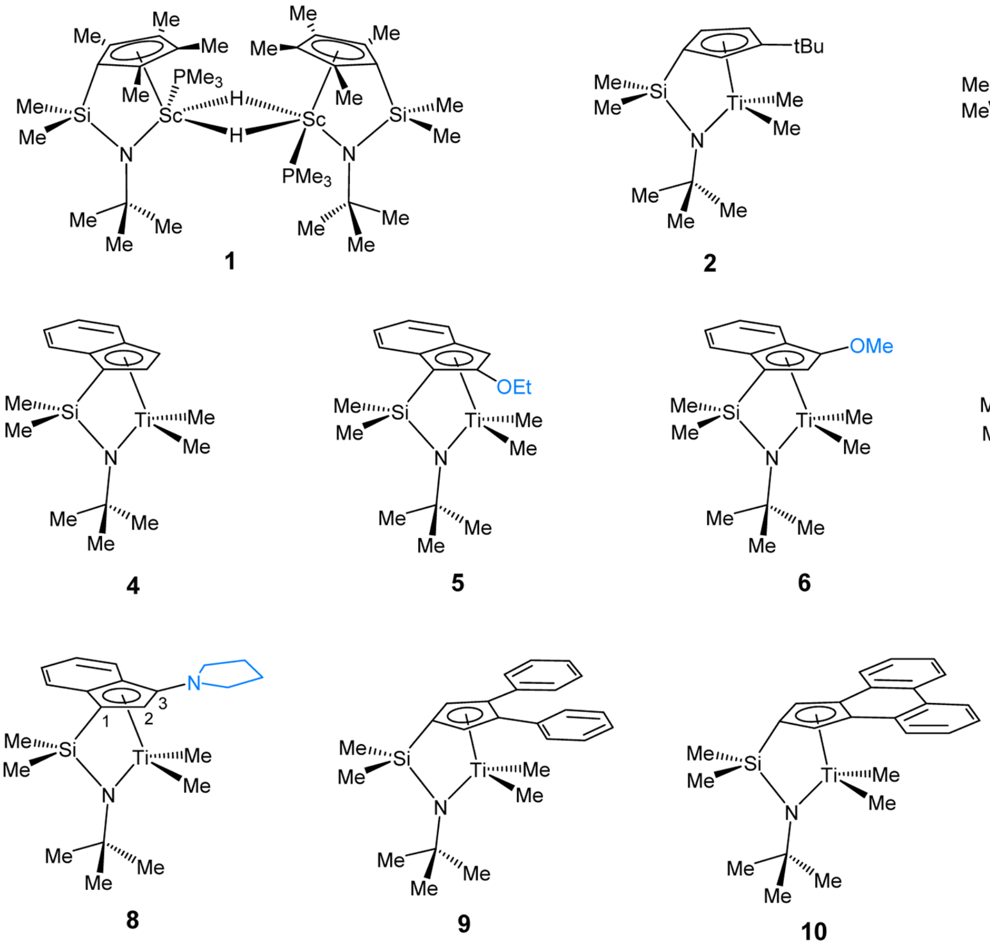


Figure 1. Constrained geometry catalysts (CGCs).

a myriad of products that benefit our society. These polyolefin products have to meet a strict set of requirements for targeted applications and serve various markets such as health and medical, food and specialty packaging, pipes and fittings, consumer and durable goods, and rigid packaging, among others. There are six key variables that define the properties of ethylene-based polymers: (a) polymer molecular weight, (b) molecular weight distribution, (c) short-chain branching (type and amount), (d) short-chain branching distribution, (e) long-chain branching level, and (f) block structure. Commercial olefin polymerization catalysts not only have to produce polymer products with the desired architectures and properties outlined above, but they also must exhibit high catalytic activity and have appropriate reaction rates with chain transfer agents (e.g., H_2, which is commonly used to control molecular weight; alkyl aluminum and zinc compounds) under the desired polymerization conditions. Additionally, precatalysts (neutral, unactivated complexes) need to be thermally stable at and above ambient temperature, as they are often stored for weeks before they are used. The performance of a given catalyst is heavily influenced by the reaction conditions, such as the monomer concentrations and temperature. From this perspective, the solution process, which benefits from being run at temperatures above 120 °C, is especially challenging for catalyst development. At such high reactor temperatures, it is often difficult to maintain high catalyst activity and high molecular weight capability as both attributes almost always decline with an increase of reactor temperature. With a wide range of polyolefin products desired, from high density polyethylene (HDPE) to elastomers (e.g., ethylene-propylene-diene (EPDM)), many different catalysts may be needed, as it is unlikely that a single catalyst will be able to address all the needs for the production of these various products. The strict set of requirements needed for the development of new polyolefin products makes identification of appropriate catalysts for a given product and production process a highly challenging endeavor. Although most polyolefin products are still produced using classical Ziegler–Natta catalysts (Ti, Cr catalysts on solid supports), billions of pounds of polyethylene-based products are currently produced annually using molecular catalysts.[2] The shift from Ziegler–Natta catalysts toward molecular catalysts is motivated by the desire to produce products with improved properties, due to the enhanced control over polymer microstructure that molecular catalysts provide, as well as the ability to produce new products that are very difficult or impossible to manufacture commercially using traditional Ziegler–Natta catalysts. This account describes some of our research on the development of molecular olefin polymerization catalysts employed in the solution process. The main goal of this research was to identify highly active catalysts capable of operating at high reactor temperatures while producing polymers with very high molecular weights and with a range of ethylene/α-olefin reactivity ratios.

2. CONSTRAINED GEOMETRY CATALYSTS

Bis-metallocenes of group IV transition metals were the first class of molecular catalysts that attracted significant attention in the

Table 1. Ethylene-1-Octene Copolymerization Data with Complexes **3**−**8**[12], [a]

precatalyst (amt, μmol)	polymer yield (g)	T (°C)	activity (g polymer/mmol cat)	polymer density (g/mL)	M_w (kg/mol)	PDI
3 (1)	87.5	140	87 500	0.897	78	2.6
4 (1.2)	25.8	140	21 500	0.894	105	2.2
5 (0.8)	58.8	140	73 500	0.897	92.7	2.8
6 (0.8)	27.0	140	33 750	0.894	148	2.1
7 (1.2)	22.5	140	18 750	0.928	98.8	3.5
8 (0.05)	30.1	140	602 500	0.906	280	2.1
3 (1)	45.0	160	45 000	0.902	47.1	2.2
8 (0.05)	18.5	160	369 500	0.908	237	2.9

[a] Polymerization conditions: 2-L Parr reactor; 740 g of Isopar-E; 118 g of octene; ethylene pressure = 500 psi; 5.3 mmol hydrogen; precatalyst/activator = 1:1; activator = $B(C_6F_5)_3$; reaction time = 15 min.

Table 2. Ethylene-Styrene Copolymerization Data with **3**, **9**, and **10**[15], [a]

precatalyst	polymer yield (g)	activity (g polymer/mmol cat)	styrene incorp. (mol %)	aPS (wt %)[b]	M_w (kg/mol)	PDI
3	35.6	11 870	11.0	0.73	11.3	2.36
9	91.5	30 500	21.5	1.48	72.8	4.76
10	149.1	49 700	30.6	0.87	134.1	5.26

[a] Polymerization conditions: 2-L Parr reactor; precatalyst amount = 3 μmol; activator = $B(C_6F_5)_3$; activator amount = 9 μmol; 455 g of styrene; 433 g of toluene; ethylene pressure = 200 psi; run time = 30 min; temperature = 90 °C; H_2 = 10.6 mmol. [b] aPS = atactic polystyrene.

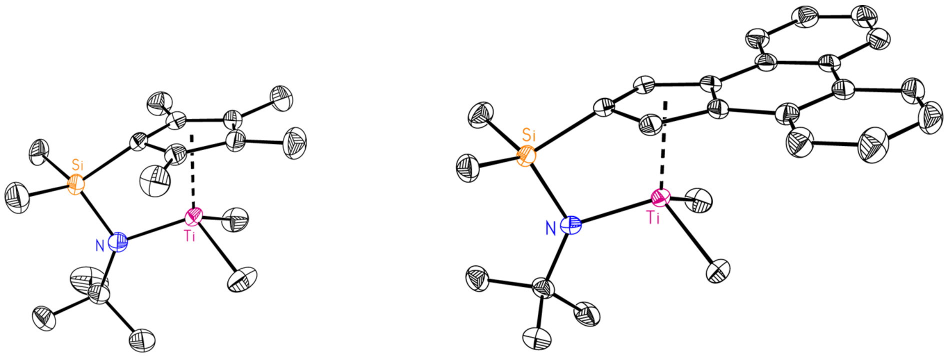


Figure 2. Molecular structures of **3** and **10**.[15]

area of homogeneous olefin polymerization.[3] Not only were very active catalysts identified, but the subsequent detailed mechanistic understanding of olefin polymerization that arose from interest in this area helped to pave the way for future catalyst development. In 1990, Bercaw et al.[4] reported the preparation of scandium complexes (e.g., **1**) (Figure 1) containing a ligand framework composed of cyclopentadienyl linked via a silicon dimethyl fragment to a *t*-butylamido unit. These scandium complexes functioned as α-olefin oligomerization catalysts without a need for an activator. Complexes containing a cyclopentadienyl-silyl-amido ligand scaffold were later named constrained geometry catalysts (CGCs).[5] Soon after, Okuda[6] published the first synthesis of a Ti complex (**2**) containing a CGC ligand. Subsequently, research groups from The Dow Chemical Company[7] and Exxon Chemical Company[8] published patent applications describing the synthesis of Ti complex **3** (Figure 1) that uses Bercaw's ligand as the basis for a highly active catalyst for ethylene/α-olefin copolymerization reactions. Importantly, polymerizations with these catalysts can be conducted at high reactor temperatures when activated with the appropriate cocatalyst. Because **3** was capable of operating at polymerization temperatures at and above 120 °C, CGC catalysts offered the promise of being utilized in a commercial solution process. In addition to being very active at temperatures above 120 °C, **3** was found to be an excellent α-olefin incorporator, allowing for the commercial production of copolymers containing a very high level of α-olefins and with narrow molecular weight distributions. The ethylene/1-octene reactivity ratio, which is a measure of α-olefin incorporating ability, is much lower for **3** ($r_1 \sim 8$ at 140 °C)[9] than that for traditional Ziegler−Natta catalysts ($r_1 \geq 40$). Although the performance of **3** was impressive, this catalyst has limited molecular weight capability when producing ethylene-1-octene copolymers.[10]

Therefore, we were interested in developing CGCs capable of producing copolymers with significantly higher molecular weight than **3**, and which could maintain excellent activities at even higher reaction temperatures. Early work on CGCs suggested[7,11] that catalyst efficiency is related to electron density at the metal center. In an attempt to increase electron density at Ti even further, we prepared complexes containing alkoxy and amino substituents attached to the indenyl fragment of the CGC ligand (**5**−**8**, Figure 1).[12] Electrochemical and NMR studies demonstrated that, indeed, the introduction of heteroatom substituents led to the enhancement of electron density at the metal center, with substituents in the third indenyl position being more effective electron donors than those in the second position. Evaluation of precatalysts **5**−**8** at 140 °C in ethylene-1-octene copolymerization reactions revealed that the alkoxy-substituted precatalysts (**5**, **6**) led to higher catalytic activities than unsubstituted indenyl complex **4** (Table 1) and that precatalysts with 3-substituted heteroatom groups (**6**, **8**) led to higher molecular weight copolymers than those with 2-substituted heteroatom groups (**5**, **7**). Most importantly, we discovered that the 3-pyrrolidine-based CGC complex **8** is not only the most active of all CGC precatalysts that we studied (25 times more active than **4**), but it also produced copolymers with significantly higher molecular weight than any other CGCs. At a reaction temperature of 160 °C, **8** was shown to be eight times more active and to produce copolymers with molecular weights five times higher than **3**. Interestingly, this dramatic effect of adding an amino group seems to be restricted to CGCs, as bis-metallocenes with heteroatom substituents do not perform better than their hydrocarbon analogues.[13,14]

With the discovery of **3** and its exceptional ability to incorporate α-olefins such as propylene and 1-octene, there was an interest in exploring its ability to perform more challenging polymerization reactions, such as a copolymerization of ethylene and styrene, as such copolymers are very difficult to produce using traditional Ziegler–Natta catalysis. Early in our studies, it was found that **3** is indeed capable of copolymerizing ethylene and styrene with moderate catalytic activities, but the ethylene/styrene reactivity ratio was quite high (r_1 = 23 at 70 °C), which necessitated very high styrene concentrations in the reactor to produce high styrene content copolymers. High styrene concentration led to the production of a significant amount of atactic polystyrene, an undesirable side product derived from the thermal polymerization of styrene. Therefore, there was a need to develop a catalyst with much improved catalytic activity for ethylene-styrene copolymerization, along with a significant lowering of the ethylene/styrene reactivity ratio in order to mitigate the formation of atactic polystyrene. Kinetic analysis of an ethylene-styrene copolymerization using **3** revealed a substantial styrene penultimate monomer effect that led to the hypothesis that catalysts bearing aromatic moieties in close proximity to the active site could enhance the styrene reactivity.[15]

Consequently, two new CGC precatalysts, **9** and **10**, were designed, and each showed dramatic improvements in both catalytic activity and styrene reactivity. For example, **10** was found to be about four times more active and to incorporate three times more styrene than does **3** under the same polymerization conditions. Moreover, **10** produced an ethylene-styrene copolymer with a molecular weight over 10 times higher than **3** (Table 2). The ethylene/styrene reactivity ratio for **10** was determined to be significantly lower (r_1 = 4.2 at 70 °C) than that of **3**. Molecular structures of **3** and **10** are shown in Figure 2. The outstanding ethylene-styrene copolymerization attributes of **10**, which include very high polymerization activity, very high copolymer molecular weight capacity, and very low ethylene/styrene reactivity ratio, make this catalyst an excellent candidate for commercial operations.

3. IMINO-AMIDO TYPE CATALYSTS

Group IV complexes supported by bidentate nitrogen-based ligands can give rise to highly active polyolefin catalysts. The core structural motif common to the most active variants is a five-membered metallacycle formed by coordination of the two nitrogen donors to the metal center. Typically, one nitrogen donor is anionic, and the other is neutral (dative). The remainder of the metal coordination sphere of the precatalyst is occupied by alkyl groups (at least two) and, in some cases, by an additional monodentate ligand. The polyolefin catalysts derived from these complexes are notable for their high activities, capacities for producing high molecular weight polymers, and their propensities to engage in reversible chain transfer reactions with suitable organometallic reagents.

Pyridyl-Amide Catalysts

The highly modular nature of the imino-amido core structure (Figure 3) is another attractive feature of this class of catalysts, as many different ligand structures are possible. This variability allows for the tuning of the desired catalyst attributes through ligand design. Some of the early examples within the imino-amido class included catalysts supported by pyridyl-amide ligands (Figure 4). Originally developed at Union Carbide as trimethyl precatalysts (generation 1),[16] these were subsequently elaborated during a joint research collaboration between Symyx Technologies and The Dow Chemical Company,[17] resulting in a series of catalysts comprising an additional cyclometalated aryl moiety linked to the pyridyl core (generation 2).

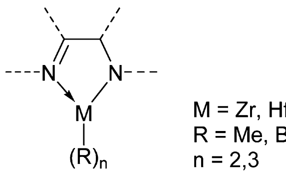
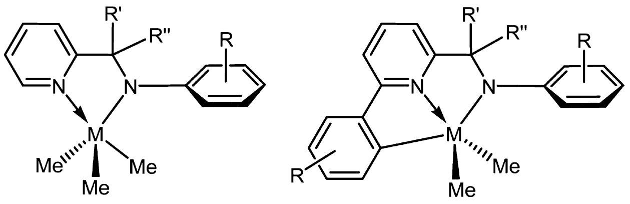


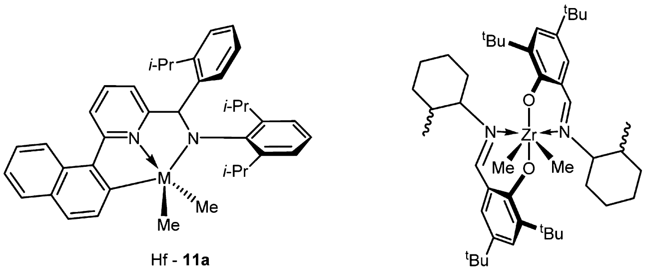
Figure 3. Core structure of imino-amido-type polyolefin catalysts.



generation 1 generation 2

Figure 4. Pyridyl-amide catalysts.

Importantly, many catalysts within the larger pyridyl-amide family can produce high molecular weight polymers at elevated reaction temperatures. It was noted early on that these catalysts can produce high molecular weight, isotactic polypropylene, which is unusual for C_s/C_1-symmetric catalysts. This early research also revealed that these complexes are similarly useful for producing ethylene-α-olefin copolymers, and can exhibit living behavior under certain reaction conditions.[18] Moreover, these catalysts exhibit a marked propensity to undergo facile chain transfer reactions with some metal alkyl species (e.g., diethylzinc). This behavior has been successfully harnessed to produce novel



Hf - **11a**
Zr - **11b**

12

Figure 5. Precatalysts initially used to make OBCs.

Table 3. Ethylene-1-Octene Copolymerization Data with Generation 2 Pyridyl-Amide Catalysts **11a** and **11b**[20, a]

precatalyst (amt, μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
11a (1.5)	19.9	13 267	1420	3.1	12.1
11b (1.5)	8.4	8 400	867	3.3	8.5
3 (CGC) (0.2)	46.7	233 500	50	2.2	15.6

[a] Polymerization conditions: 2-L Parr reactor; 533 mL of Isopar-E; 250 g of octene; temperature =120 °C; ethylene pressure = 460 psi; 10 mmol hydrogen; precatalyst/activator/MMAO = 1:1.2:10; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; reaction time = 15 min.

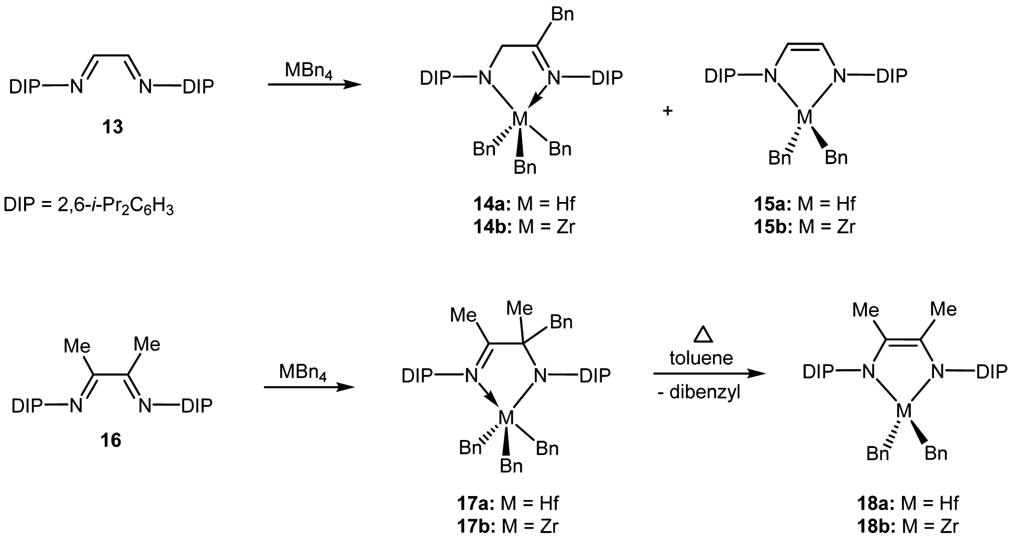


Figure 6. Reactions of bis-imines with group IV tetrabenzyl precursors.

Table 4. Ethylene-1-Octene Copolymerization Data with Bis-Imine Derived Catalysts[22, a]

precatalyst (amt, μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
14a (5)	26.8	5 400	362	8.0	10.2
17a (0.25)	29.5	118 000	238	7.4	13.1
18a (10)	3.3	650	175	25.0	9.2

[a] Polymerization conditions: 2-L Parr reactor; 533 mL of Isopar-E; 250 g of octene; temperature = 120 °C; ethylene pressure = 460 psi; precatalyst/activator = 1:1.1; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; 10 μmol MMAO; reaction time = 15 min.

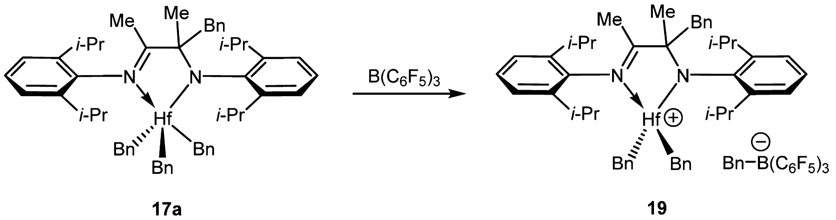


Figure 7. Formation of the ion pair **19**.

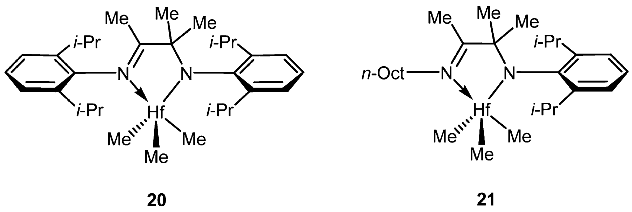


Figure 8. Imino-amido complexes with trimethylethylidene bridging units.

olefin-block copolymers in continuous processes at economically viable conditions (e.g., **11a** in conjunction with **12**, Figure 5).[19] These novel materials display a unique combination of high melting temperatures and low glass-transition temperatures, and can therefore sustain a high degree of elastomeric character at high temperatures.

Apart from the capacity to engage in chain transfer reactions with diethylzinc, the features of **11a** that render it useful and industrially relevant are its ability to produce high polymer molecular weights at elevated temperatures and its propensity to incorporate substantial amounts of α-olefins during copolymerization reactions.[20] Drawbacks of **11a** and **11b** include relatively low catalytic activity and a tendency to produce polymers with broad compositional distributions (Table 3). The polymer compositional issue was seen to arise, at least in part, due to an unexpected activation mechanism in which an olefin inserts into the metal-aryl bond of the *ortho*-metalated naphthyl group.[21]

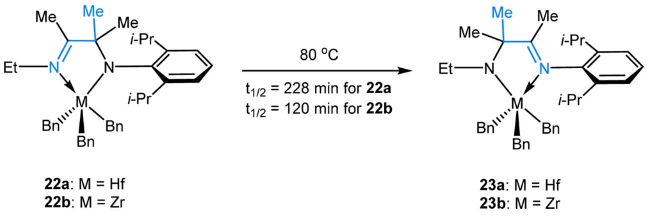


Figure 9. Thermal isomerization of imino-amido complexes containing trimethylethylidene bridges.

Imino-Amido Catalysts

In 2007, we reported new examples of imino-amido catalysts, wherein neutral bis-imine ligands were reacted with group IV metal alkyl precursors to produce the desired complexes via insertion of an imine group into a metal–alkyl bond.[22] When bis-imine **13** was reacted with MBn_4 (M = Zr, Hf), mixtures of the corresponding imino-amido tribenzyl complexes (**14a,b**) and bis-amido dibenzyl complexes (**15a,b**) were obtained (Figure 6). When bis-imine **16** was used, the tribenzyl complexes (**17a,b**)

Table 5. Ethylene-1-Octene Copolymerization Data with Unsymmetrical Imino-Amido Trimethyl Catalysts[26, a]

precatalyst (amt μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
20 (0.7)	26.7	38 100	275	2.3	2.4
21 (0.7)	58.7	83 900	283	2.4	5.5
3 (CGC) (0.2)	39.1	195 500	47	2.3	14.8

[a] Polymerization conditions: 2-L Parr reactor; 533 mL of Isopar-E; 250 g of octene; temperature = 120 °C; ethylene pressure = 460 psi; 10 mmol hydrogen; precatalyst/activator/MMAO = 1:1.2:10; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; reaction time = 10 min.

Table 6. Ethylene-1-Octene Copolymerization Data with Unsymmetrical Imino-Amido Benzyl Catalysts[23, a]

precatalyst (amt, μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
22a (0.25)	35.2	140 800	633	3.1	3.8
23a (1.0)	6.7	6 700	520	5.2	3.3
22b (0.25)	22.9	91 600	782	2.8	1.7
23b (1.0)	5.5	5 500	294	60	2.9
3 (CGC) (0.2)	113.8	569 000	108	2.6	14.9

[a] Polymerization conditions: 2-L Parr reactor; 533 mL of Isopar-E; 250 g of octene; temperature = 120 °C; ethylene pressure = 460 psi; precatalyst/activator/MMAO = 1:1.2:10; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; reaction time = 15 min.

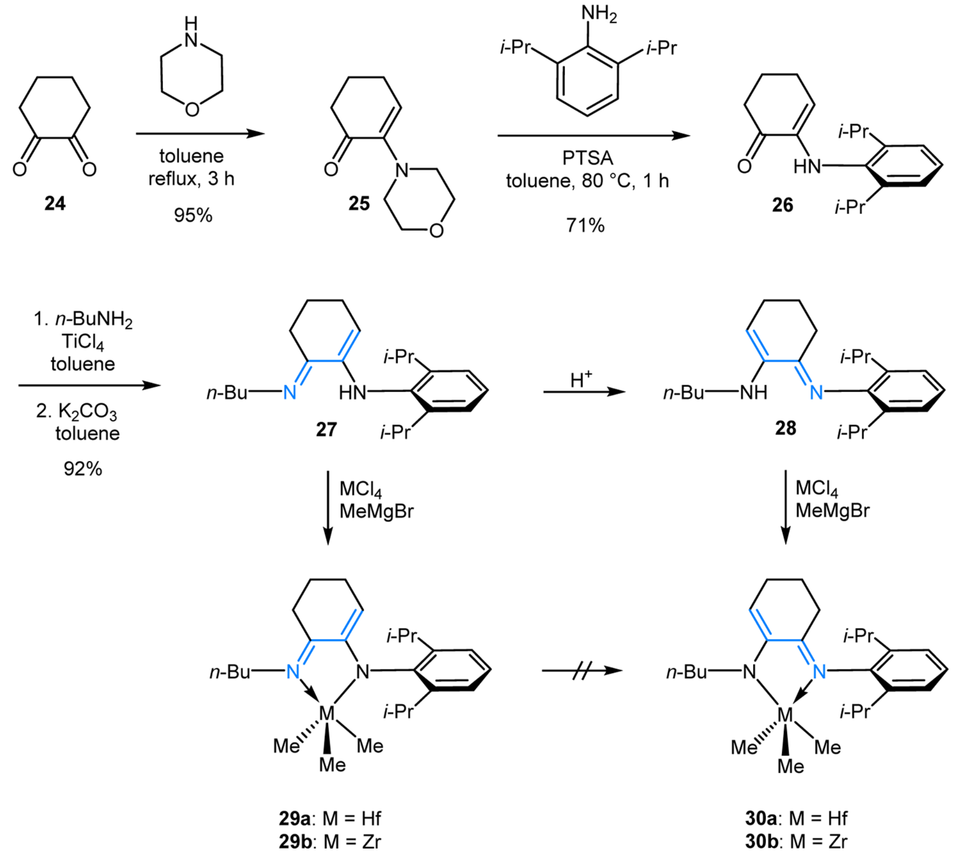


Figure 10. Synthesis of imino-enamido complexes.

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Table 7. Ethylene-1-Octene Copolymerization Data with Imino-Enamido Catalysts[27, a]

precatalyst (amt, μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
29a (0.2)	49.6	248 000	743	3.1	7.2
30a (0.8)	24.8	31 000	641	3.4	2.5
29b (0.2)	11.8	59 000	584	2.5	5.2
30b (0.8)	16.5	20 600	347	2.7	1.3
3 (CGC) (0.3)	82.2	411 000	100	2.2	15.9

[a] Polymerization conditions: 2-L Parr reactor; 533 mL of Isopar-E; 250 g of octene; temperature = 120 °C; ethylene pressure = 460 psi; precatalyst/activator = 1:1.2; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; 10 μmol MMAO; reaction time = 10 min.

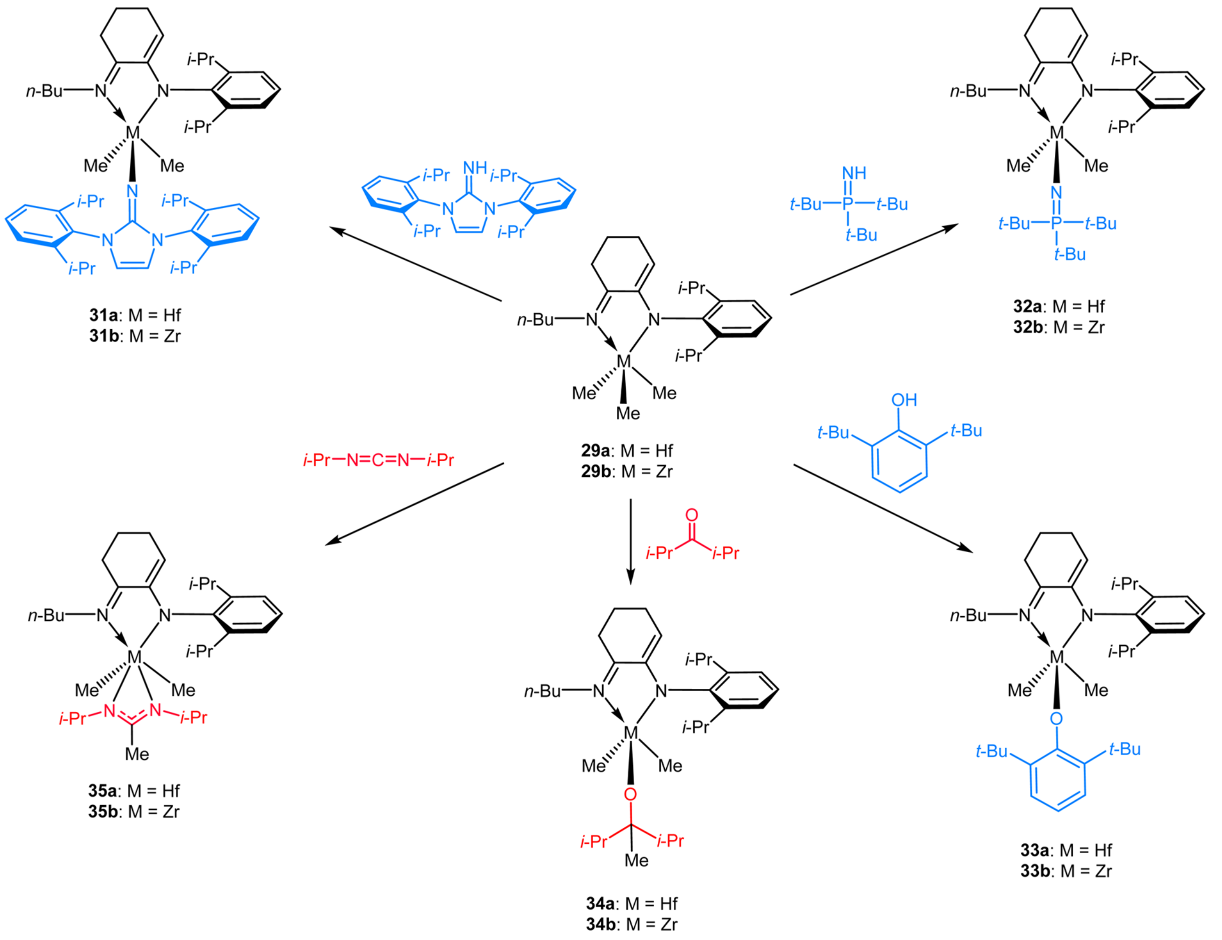


Figure 11. Derivatization reactions with **29a** and **29b**.

were obtained, but at higher temperature they converted quantitatively to bis-amido dibenzyl complexes (**18a**,**b**). The conversion of **17a** to **18a** was studied in detail and was observed to follow first order kinetics, with calculated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 33.3 kcal/mol and 20 eu, respectively. The transformation proceeded with the elimination of dibenzyl as the sole byproduct via a radical pathway.

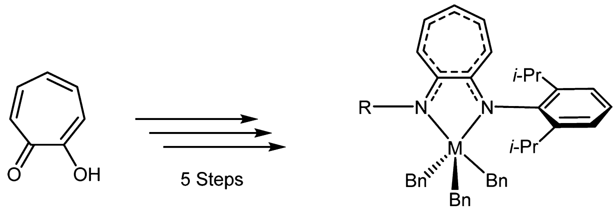
Ethylene-1-octene copolymerization reactions carried out at 120 °C demonstrated that alkyl substitution on the imine backbone imparted favorable qualities to the resulting catalyst, as **17a** was an order of magnitude more active than **14a** (Table 4). The bis-amido complex **18a** gave rise to a very poor catalyst. Notably, however, all of the precatalysts produced copolymers with relatively high molecular weights in spite of their varying efficiencies. Additionally, the polydispersity indices (PDIs) were broad in all cases, which is indicative of multisite behavior. In light of this, an NMR experiment was conducted in which **17a** was treated with $B(C_6F_5)_3$, resulting in clean formation of the ion-separated pair **19** (Figure 7). The selective formation of **19**, along with its high stability at room temperature, suggested that the observed catalyst multisite behavior was due to either its decomposition at higher temperatures or to its side reactions with alkylaluminum species that are commonly used as impurity scavengers in polymerization reactions.

While **17a** exhibited encouraging catalytic characteristics, its lack of thermal stability limits its commercial utility due to the associated storage and handling problems. In an attempt to design catalysts with improved thermal stability, ligands comprising a trimethylethylidene bridging unit were prepared based on the hypothesis that the radical pathway involving homolytic cleavage of a benzyl group would be suppressed if the benzyl group were exchanged for a methyl group (Figure 8).[23] Both symmetrical and unsymmetrical Hf trimethyl complexes were prepared; the former contained a 2,6-diisopropylphenyl substitution at both the imino and the amido N atoms (**20**),

Table 8. Ethylene-1-Octene Copolymerization Data with 29a, 29b, and Their Derivatives[28, a]

precatalyst (amt, μmol)	M center/X ligand	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
29a (0.15)	Hf/methyl	19.3	128 667	647	2.8	7.2
31a (0.4)	Hf/imidazol-imine	10.1	25 250	317	2.9	0.6
32a (0.15)	Hf/phosphinimide	36.7	244 667	704	2.7	1.3
33a (6.0)	Hf/phenoxy	35.8	5 970	100	3.5	4.1
34a (0.2)	Hf/alkoxy	15.7	78 500	128	3.4	5.6
35a (10)	Hf/amidinate	0.8	80	199	9.3	6.3
29b (0.2)	Zr/methyl	11.1	55 500	584	2.5	5.2
31b (0.2)	Zr/imidazol-imine	4.5	22 500	596	3.2	0.5
32b (0.08)	Zr/phosphinimide	10.7	133 750	991	2.3	1.8
33b (1.0)	Zr/phenoxy	18.6	18 600	73	5.2	5.3
34b (0.40)	Zr/alkoxy	33.0	82 500	77	2.9	6.9
35b (8.5)	Zr/amidinate	5.0	588	187	4.2	7.9
3 (CGC) (0.2)		70.1	350 500	102	2.3	15.2

[a] Polymerization conditions: 2-L Parr reactor; 533 mL of Isopar-E; 250 g of octene; temperature = 120 °C; ethylene pressure = 460 psi; precatalyst/activator = 1:1.2; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; 10 μmol MMAO; reaction time = 10 min.

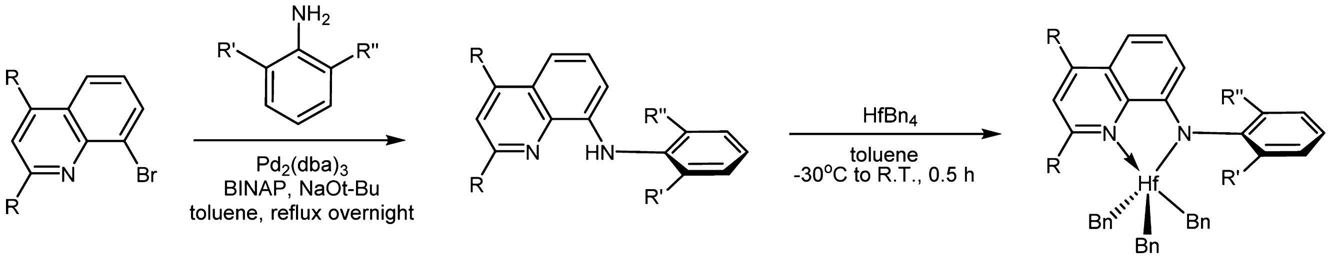


36

37a: M = Hf, R = nBu
37b: M = Zr, R = nBu
38a: M = Hf, R = NMe_2
38b: M = Zr, R = NMe_2

Figure 12. Aminotroponiminato complexes.

analogous to **17a**, while the unsymmetrical variant featured an *n*-octyl substituent on the imino N atom (**21**).[24] Complex **21** proved to be the superior catalyst, exhibiting substantially higher activity than **20** along with improved 1-octene incorporation (Table 5). Both **20** and **21** produced relatively high molecular weight copolymers with narrow PDIs. They were also shown to undergo very efficient chain shuttling polymerization with **11a** to produce olefin block copolymers.[25] However, thermal instability was still an issue with precatalyst **21** despite the use of a methyl group in the ligand bridge. Experimental and computational studies on the related, unsymmetrical complexes **22a** and **22b** showed that a thermally induced isomerization occurs in which the ligand backbone rearranges via a 1,2-methyl shift (Figure 9). For both Zr- and Hf-based catalysts, the resulting isomeric complexes (**23a** and **23b**) gave rise to poorer catalysts. The catalysts derived from **22a** and **22b**, however, were very active and produced polymers with low PDIs. While both catalysts had



39 : R = H
40 : R = Me

41 : R = H, R' = R" = *i*-Pr (38%)
42 : R = H, R' = R" = Me (57%)
43 : R = H, R' = *i*-Pr, R" = H (73%)
44 : R = Me, R' = R" = Me (46%)

45 : R = H, R' = R" = *i*-Pr (80%)
46 : R = H, R' = R" = Me (71%)
47 : R = H, R' = *i*-Pr, R" = H (74%)
48 : R = Me, R' = R" = Me (85%)

Figure 13. Preparation of hafnium complexes bearing amidoquinoline ligands.

Table 9. Ethylene-1-Octene Copolymerization Data with Hf Amidoquinoline Catalysts[30, a]

precatalyst (amt, μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (wt %)
22a (0.75)	18.3	24 339	391	3.3	9.8
53a (0.75)	23.5	31 352	604	4.2	18.3
45 (0.75)	19.2	25 599	280	2.8	13.4
46 (0.75)	30.9	41 165	404	3.5	16.5
47 (0.75)	10.6	14 049	160	2.9	6.9
48 (0.75)	28.3	37 715	632	3.0	14.9

[a] Polymerization conditions: 1-Gal reactor; 1350 mL of Isopar-E; 250 g of octene; temperature = 120 °C; ethylene pressure = 425 psi; 20 mmol hydrogen; precatalyst/activator = 1:1.2; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; 22.5 μmol MMAO; reaction time = 10 min.

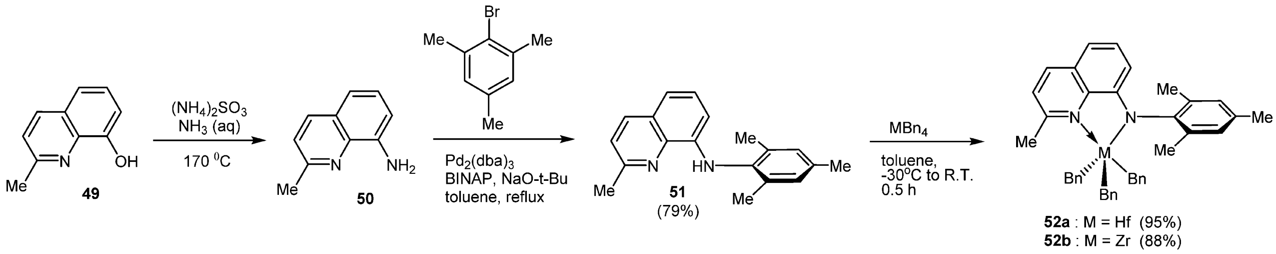


Figure 14. Improved preparation of amidoquinoline complexes from inexpensive materials.

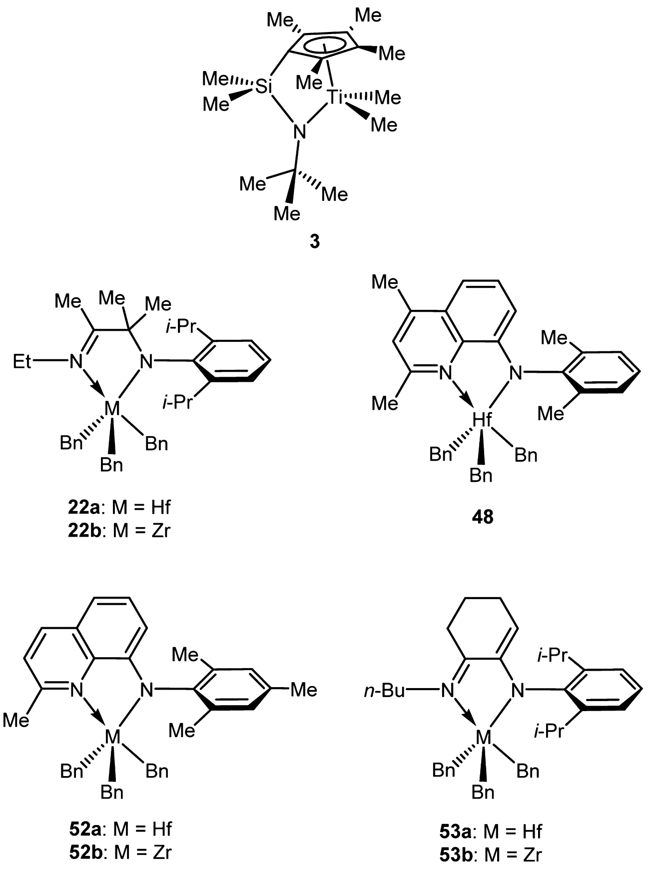


Figure 15. Structures of catalysts tested in batch reactor ethylene-1-octene copolymerizations at 140 °C.

relatively low α-olefin incorporation, Hf-based catalyst **22a** had higher incorporation of 1-octene than did Zr-based catalyst **22b** (Table 6). Note that, in comparison to a CGC (**3**), these imino-amido catalysts have significantly higher polymer molecular weight building capacity and a significantly lower ability to incorporate α-olefins into a growing polymer chain.

Imino-Enamido Catalysts

The studies on imino-amido catalysts produced two key findings that are relatively general for the larger catalyst family: (1) unsymmetrical ligands with alkyl substitution on the imino donor and aryl substitution on the amido donor are preferred and (2) Hf catalysts incorporate α-olefins more effectively and produce higher M_W copolymers than their Zr analogues do. Unfortunately, the thermodynamically favored and kinetically accessible isomers (**23a** and **23b**) are inferior catalysts, thus prompting further research in this area. We envisioned that analogous catalysts containing a cyclohex-2-enylidene fragment would be resistant to both of the aforementioned rearrangements.[26] The desired ligand (**27**) was prepared in three steps from commercial materials (Figure 10). Synthetic protocols were developed to produce **27** cleanly, though typically a few percent of **28** was also formed via acid-catalyzed rearrangement. Upon metalation, the resulting isomeric imino-enamido complexes (Hf, **29a** and **30a**; Zr, **29b** and **30b**; Figure 10) do not interconvert and they are more robust than the previously described imino-amido precatalysts. The imino-enamido catalysts display the same overall trends as seen for the imino-amido (acyclic) analogues (**22a**,**b** and **23a**,**b**): catalysts with arylamido/alkylimino substitution (**29a**, **29b**) perform substantially better than their isomeric counterparts **30a** and **30b**, and the Hf catalysts (**29a**, **30a**) incorporate α-olefins more effectively than their Zr analogues (**29b**, **30b**) do (Table 7). The catalyst derived from **29a** is among the best reported in this family, exhibiting excellent activity, ultrahigh molecular weight building capacity, and improved α-olefin incorporation relative to the acyclic analogue **22a**. As such, we developed a practical and economic large scale synthesis of **29a**, which was accomplished in 57% overall yield in four steps, starting from cyclohexa-1,2-dione (**24**).[27]

Derivatization Reactions of Triakyl Imino-Enamido Complexes

In contrast to the more widely known metallocene and CGC catalyst families, bidentate imino-amido-type precatalysts have a coordination sphere that contains three alkyl groups bound to the metal center. The active catalyst is accessed by removal of one of the alkyl groups with a suitable cocatalyst, generating a cationic species with a vacant coordination site and two remaining alkyl groups. While the precise details of the polymerization mechanism for this type catalyst are unknown, two distinct possibilities exist: (1) the resulting active catalyst grows two polymer chains, or (2) one of the original alkyl groups (e.g., Me, CH_2Ph) is not initiated and is merely a spectator ligand during the polymerization reaction. Consequently, we considered catalyst modification whereby one of the alkyl groups is replaced by a different monoionic ligand. This new ligand, then, is a spectator during catalysis, and therefore, can influence the steric and electronic environment at the metal center, and thus the polymerization outcome. By employing such a strategy, it is possible to modify a trialkyl precatalyst (LMR_3) to form a large number of new dialkyl precatalysts (LMR_2X).

This approach was used to modify **29a** and **29b** via protonolysis reactions with various protic precursors and insertion reactions with various unsaturated organic precursors (Figure 11).[28] The evaluation of the resulting precatalysts for polymerization (Table 8) demonstrated the efficacy of this approach, as the nature of the newly introduced anionic ligand X was seen to have a dramatic impact on the catalysts. This is evidenced by the marked variation in both the catalytic activities

Table 10. Ethylene-1-Octene Copolymerization Data with Various Catalysts Bearing Bidentate Amido Ligands[31, a]

precatalyst (amt μmol)	polymer yield (g)	activity (g polymer/mmol cat)	M_W (kg/mol)	PDI	octene incorp (mol %)
3 (CGC) (0.3)	36.1	100 278	23	2.5	25.3
22a (0.5)	14.3	23 833	65	2.0	7.4
22b (0.7)	16.1	19 167	114	8.4	4.8
48 (0.6)	28.6	39 722	400	3.2	12.0
52a (0.6)	33.6	46 667	460	3.4	13.3
52b (2.5)	18.3	6 100	285	3.7	10.4
53a (0.6)	39.9	55 417	237	2.4	13.3
53b (2.0)	20.6	8 583	233	7.1	9.8

[a] Polymerization conditions: 2-L reactor; 605 mL of Isopar-E; 300 g of octene; temperature = 140 °C; ethylene pressure = 288 psi; precatalyst/activator = 1:1.2; activator = $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; 10 μmol MMAO; reaction time = 10 min.

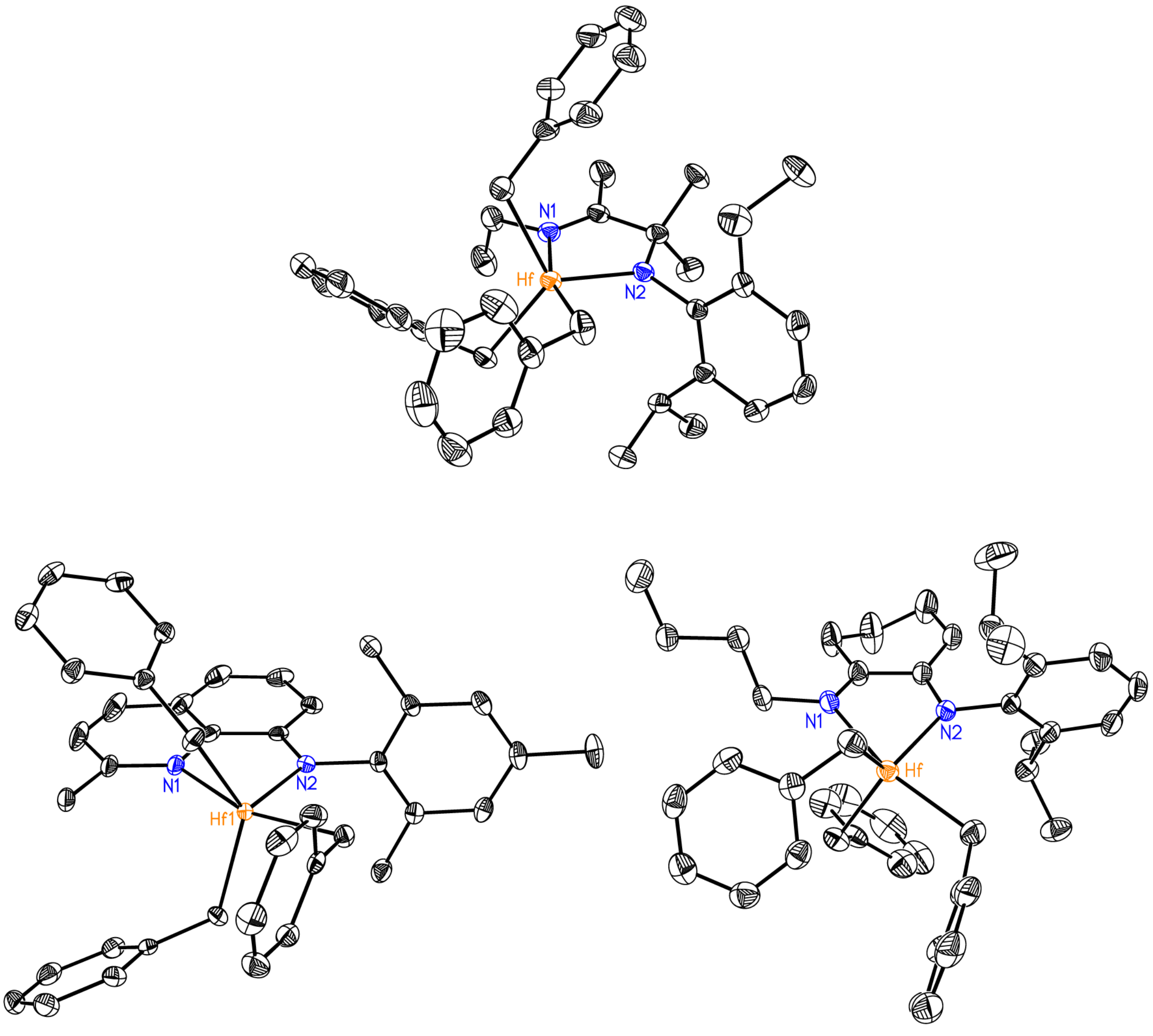


Figure 16. Molecular structures of **22a**,[23] **52a**,[31] and **53a**.[26]

in the series (ranging from 80 to 244 667 g polymer/mmol of metal), as well as the resulting copolymer compositions (molecular weights ranging from 73 000 to 991 000 g/mol, and 1-octene incorporation ranging from 0.5 to 7.9 mol %). Of the new catalysts, those derivatized with a phosphinimine ligand (complexes **32a** and **32b**) were particularly noteworthy, exhibiting excellent activities, extremely high molecular weight capacities, and high ethylene selectivity as evidenced by the comparatively low octene contents in the resulting copolymers (Table 8).

Aminotroponiminato Catalysts

Following the success of the imino-enamido catalysts, and with an aim of preparing species that were resistant to all the isomerization pathways observed in the previous systems, aminotroponiminato complexes (**37a**,**b** and **38a**,**b**) were prepared in five steps from tropolone (**36**, Figure 12).[29] Complete delocalization of the imine bond through the N−C−C−N fragment of the metallacycle was apparent for all the complexes reported; therefore, isomerization was a nonissue. Unfortunately, these aminotroponiminato complexes led to low catalytic activities in polymerization reactions and produced polymers with broad PDIs indicative of multisite behavior.

Amidoquinoline Catalysts

In another attempt to design a ligand system stable to isomerization, a series of Hf complexes supported by amidoquinoline ligands (**45**−**48**) were prepared (Figure 13).[30] Importantly, both of the ligand precursors and the precatalysts themselves are thermally and chemically robust, as they are not susceptible to any of the aforementioned isomerization pathways available to the imino-amido precatalysts.

Polymerization evaluations showed that the best of the amidoquinolines (**46** and **48**) displayed excellent catalytic properties, comparing well against **22a** and **29a**. For both, high catalytic activities, ultrahigh molecular weight building capacities, and moderate levels of *α*-olefin enchainment were observed (Table 9). Methyl substitution in the position *ortho* to the quinoline nitrogen resulted in a significant increase in the catalyst molecular weight building capacity, and was therefore deemed to be an important structural feature. This series (**45**−**47**) also highlighted the marked impact of the arylamido substitution. While the only change across this series is the *ortho* substitution on the arylamido moiety, 1-octene incorporation varied from 6.9 to 16.5%, the copolymer molecular weights varied from 160 000 to 404 000 g/mol, and the activities ranged from 14 to 41 kg polymer/mol catalyst.

Following the encouraging results obtained with **46** and **48**, the development of a more cost-effective synthetic route became a focus of our efforts, as the synthesis originally involved the use of expensive 8-bromoquinolines **39** and **40** (Figure 13). A less expensive starting material was found in 8-hydroxyquinaldine (**49**, Figure 14), which is widely available and inexpensive, and maintains methyl substitution *ortho* to the quinoline nitrogen.[31] The desired aminoquinoline ligands can be accessed in two steps (Figure 14). Ligand **51** containing a mesitylamido substituent was prepared, and subsequently used to prepared Hf and Zr trialkyl complexes (**52a** and **52b**), respectively. Molecular structures of imino-amido (**22a**), imino-enamido (**53a**), and aminoquinoline (**52a**) Hf precatalysts are shown in Figure 16.

The new amidoquinoline complexes were evaluated as catalysts in high temperature (140 °C) ethylene-1-octene copolymerization reactions, along with selected catalysts from the imino-amido and imino-enamido groups (Figure 15). This data set (Table 10) provides a good comparison of several of the best performing catalysts from the various subsets of the larger family of catalysts supported by bidentate amido ligands, and also includes a CGC (**3**). The Hf-based catalyst (**52a**) bearing the new amidoquinoline ligand was among the best tested, exhibiting the highest molecular weight building capacity, along with good activity and the highest propensity toward 1-octene incorporation apart from CGC.

4. END GROUP ANALYSIS

Understanding termination reactions is important to catalyst development, particularly when catalysts capable of producing very high molecular weight polymers are targeted. End group analysis data allows for the evaluation of various chain termination events taking place during polymerization. For example, the presence of vinyl groups (V) indicates chain termination after an ethylene insertion, whereas the presence of vinylenes (Vy1, Vy2) and vinylidenes (Vd) in the polymer is a signature of chain termination following *α*-olefin insertion (2,1- and 1,2-insertion, respectively). End groups can directly impact the resulting polymer architecture; for example, vinyl groups are directly related to the formation of long chain branches. The level of end group unsaturation is inversely proportional to polymer molecular weight and can be used to validate GPC data. Figure 17 shows fragments of ^{1}H NMR spectra of polymers generated from three different catalysts. From these spectra, it is evident that imino-amido catalyst **21** leads to much more frequent termination following 1-octene compared to the imino-enamido catalyst **53a**. Interestingly, the ^{1}H NMR spectrum for the copolymer produced by CGC complex **3** (Figure 17) shows high levels of internal unsaturations (Vy3 and T) in addition to the expected polymer end groups.[10]

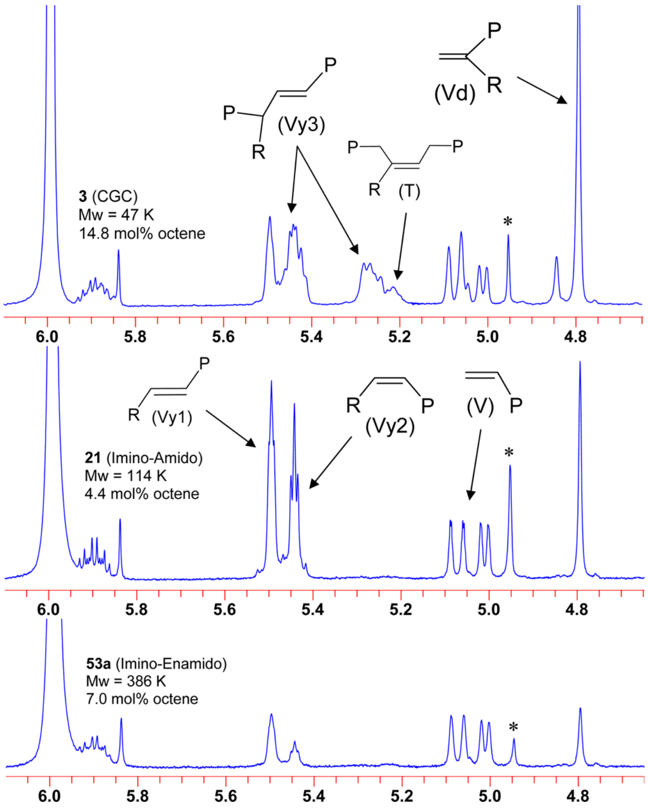


Figure 17. Fragments of the olefin region of ^{1}H NMR spectra of selected copolymers. Asterisk denotes resonance originating from antioxidant.

5. ACTIVATORS FOR OLEFIN POLYMERIZATION

Impressive advances in olefin polymerization mediated by molecular catalysts would not be possible if not for the development of robust and effective activators[32] that transform neutral transition metal precatalysts into cationic, highly Lewis acidic species. The most important attribute of well-defined activators is the weakly coordinating nature of the anion, as it is important that the anion does not interact strongly with the cationic metal center. Perhaps the most well-known among well-defined activators in the field of olefin polymerization catalysis are tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, and $[Q]^+[B(C_6F_5)_4]^-$, Q = Ph_3C, HNR_3. $B(C_6F_5)_3$ is a powerful Lewis acid capable of abstracting alkyl groups from a transition metal center. This borane can also react quite rapidly with main group (e.g., Al, Ga) alkyls at room temperature in hydrocarbons, leading to complete alkyl/aryl group exchange.[33] This is an easy and reliable way to produce tris(pentafluorophenyl)alane and galane compounds. Interestingly, when this reaction is conducted in coordinating solvents such as diethyl ether or THF, a

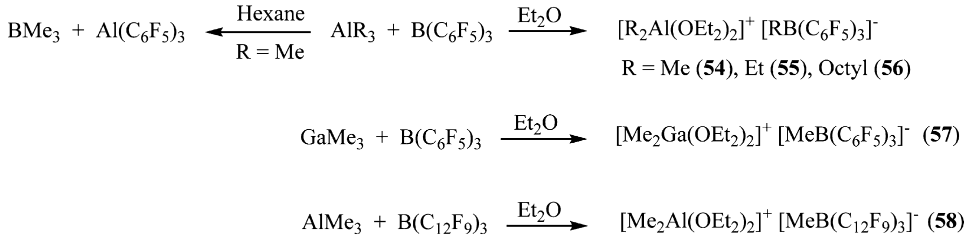


Figure 18. Reactivity of aluminum and gallium alkyls with perfluoroaryl boranes.

very different reaction outcome is observed. Instead of alkyl/aryl group exchange, $B(C_6F_5)_3$ abstracts an alkyl group from Al or Ga alkyls to generate ion pairs (**54**–**58**) (Figure 18).[33] These alumenium borates were found to be very effective activators for CGC precatalysts.

In an attempt to further delocalize the negative charge within the anion portion of the activator, we prepared activators in which the monoanion is composed of two Lewis acids linked by an imidazole group (**59**–**62**).[34] Such anions can be prepared either by the reaction of potassium imidazolate with two equivalents of $M(C_6F_5)_3$ (M = B, Al), followed by metathesis of the resulting salt with ammonium chloride derivatives, or by the direct reaction in toluene of two equivalents of $M(C_6F_5)_3$ (M = B, Al) with one equivalent of imidazole and one tertiary amine (Figure 19). Molecular structure of activator **61** is presented in Figure 20. Activators **59** and **60** were evaluated with CGC **3** at 140 °C and were shown to lead to higher catalytic activities than the catalyst derived from **3** and the activator $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$ when evaluated under the same reaction conditions.

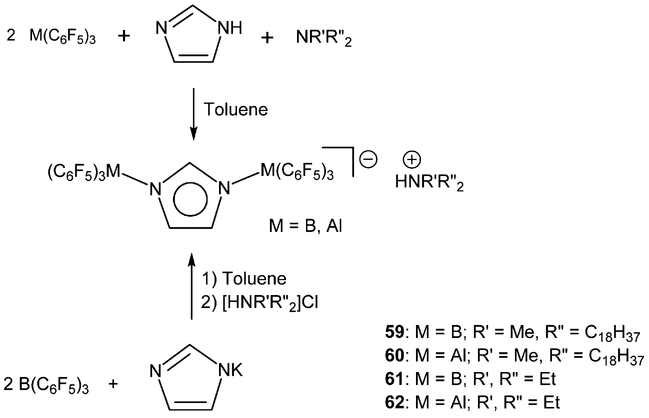


Figure 19. Synthesis of expanded borate and aluminate activators.

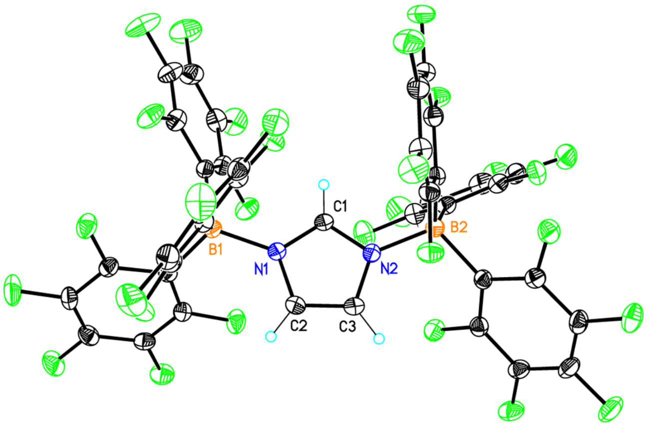


Figure 20. Molecular structure of the anion of activator **61**.[34]

6. CONCLUSIONS

Olefin polymerization mediated by molecular catalysts is a mature field; however, research in this area will undoubtedly continue for many years due to the continued need to develop new and valuable polyolefin products. There is no single catalyst that can fulfill all the process and product requirements for the increasingly broad range of polyolefin products needed today. Although tremendous advancements in catalyst development have been achieved, significant opportunities to design and develop new catalysts that would enable the production of these new polyolefin materials still remain. What hinders the pace of catalyst development is the lack of understanding of factors that control catalyst behavior, such as catalyst attributes that control polymer molecular weight and comonomer incorporation. Future research directed at understanding these fundamental questions can perhaps lead to the development of catalysts with programmable and predictable polymerization performance.

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The authors declare no competing financial interest.

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