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Unexpected Precatalyst σ-Ligand Effects in Phenoxyimine Zr-Catalyzed Ethylene/1-Octene Copolymerizations

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ABSTRACT: Recent decades have witnessed intense research efforts aimed at developing new homogeneous olefin polymerization catalysts, with a primary focus on metal-Cl or metal -hydrocarbyl precursors. Curiously, metal-NR_2 precursors have received far less attention. In this contribution, the Zr-amido complex **FI_2ZrX_2** (FI = 2,4-di-*tert*-butyl-6-((isobutylimino)methyl)phenolate, X = NMe_2) is found to exhibit high ethylene polymerization activity and relatively high 1-octene co-enchainment selectivity (up to 7.2 mol%) after sequential activation with trimethylaluminum, then $Ph_3C^+B(C_6F_5)_4^{\square}$. In sharp contrast, catalysts with traditional X = hydrocarbyl ligands such as benzyl and methyl give low 1-octene incorporation (0 -1.0 mol%). This unexpected selectivity persists under scaled/industrial operating conditions and was previously inaccessible with traditional metal-Cl or -hydrocarbyl precursors. NMR, X-ray diffraction, and catalytic control experiments indicate that in this case an FI ligand is abstracted from **$FI_2Zr(NMe_2)_2$** by trimethylaluminum in the activation process to yield a catalytically active cationic mono-**FIZr**- species. Heretofore this process was believed to serve as only a major catalyst deactivation pathway to be avoided. This work demonstrates the importance of investigating diverse precatalyst monodentate σ-ligands in developing new catalyst systems, especially for group 4 olefin polymerization catalysts.

INTRODUCTION

Since the pioneering research by Ziegler and Natta on heterogeneous olefin polymerizations in the 1950s, polyolefins have become some of the most important industrial materials.[1-2] Over the last three decades, homogeneous polymerization catalyst systems and methodologies have advanced rapidly, with some produced industrially on a world-scale.[3-9] These developments have often focused on the design and modification of ancillary ligands as well as the effects of the identity of the central metal ion. Group 4 metal chloride and hydrocarbyl complexes have primarily been used as catalyst precursors for such systems due to their straightforward synthetic accessibility and the ease with which they are activated (Figures 1A and 1B).[7, 10-11] In contrast, readily accessible dialkylamido complexes, which have predominantly been used only as intermediates in the synthesis of hydrocarbyl and chloride complexes, have been largely overlooked (Figure 1B),[12-13] since these complexes often suffer from low alkylation efficiency[7, 14] and can afford multiple active sites.[12, 15-17] Aluminum alkyl reagents such as $Al(^iBu)_3$ or $Al(^iBu)_2H$ are often used as alkylating agents.[18-20] However, these AlR_3 reagents are also strong reducing reagents, capable of reducing some ancillary ligands (e.g., those with imine moieties).[21-22]

The implementation of phenoxyiminato (FI; Figure 1C) group 4 metal complexes has afforded significant advances in post-metallocene homogeneous olefin polymerization catalysis.[4, 10-11, 23-27] For example, activated $FI_2Zr(alkyl)_2$ complexes are employed to produce the hard block (PE-rich) of Olefin Block Copolymers (OBCs)[28] via chain shuttling polymerizations, a process which has been commercialized by Dow Chemical. However, compared to the chloride and alkyl congeners, the corresponding $FI_2Zr(NMe_2)_2$ complexes have not been used as precatalysts.[7] Here we report a novel strategy for

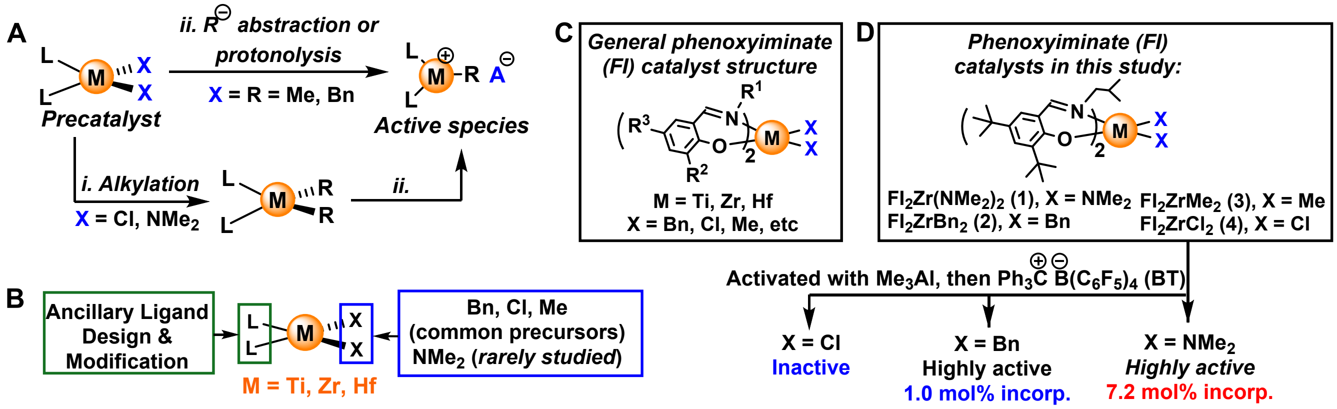


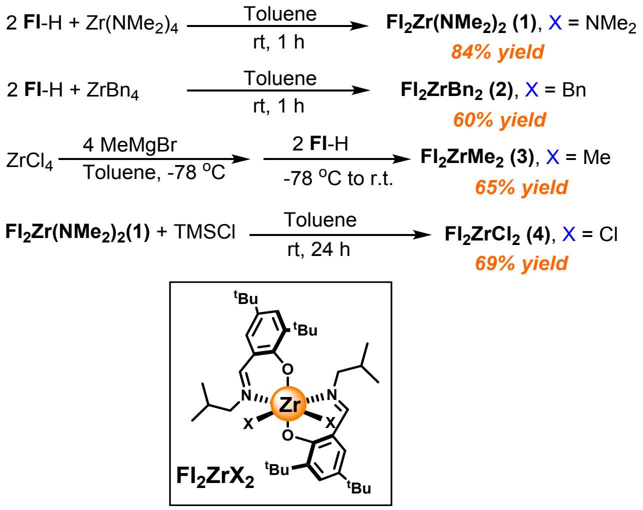
Figure 1. A. Group 4 precatalysts with various monodentate X σ-ligands and their activation pathways for olefin polymerization. **B**. Common design approaches to new olefin polymerization catalysts. **C**. General phenoxyimine catalyst structures. **D**. This study

the activation of $FI_2Zr(NMe_2)_2$ complexes to afford highly active catalysts for ethylene/1-octene copolymerization, giving 1-octene incorporation of up to 7.2 mol%. This result stands in sharp contrast to the benzyl or methyl analogues, which achieve only 0-1.0 mol% 1-octene incorporation under the same reaction conditions. Both advanced NMR spectroscopy and X-ray diffraction, combined with control experiments argue that ancillary ligand transfer from Zr to Al occurs during trimethylaluminum (TMA) alkylation. Heretofore this process was believed to only serve as a major catalyst deactivation pathway and should be avoided. Instead we report here the generation and characterization of a mono-FI-Zr catalyst capable of high comonomer incorporation levels with minimal loss in polymerization activity.

RESULTS AND DISCUSSION

Phenoxyimine Zr precatalysts $\mathbf{FI_2Zr(NMe_2)_2}$ (**1**), $\mathbf{FI_2ZrBn_2}$ (**2**), $\mathbf{FI_2ZrMe_2}$ (**3**), and $\mathbf{FI_2ZrCl_2}$ (**4**) were synthesized in good yields as shown in Scheme 1. Note that **3** is synthesized by reacting the free phenoxyimine ligand FI-H (FI-H = 2,4-di-*tert*-butyl-6-((isobutylimino)methyl)phenol) with *in situ* generated $ZrMe_4$. This is a more straightforward and efficient method than the previously reported approach involving the reaction of FI-MgBr with *in situ* generated Me_2ZrCl_2.[26, 29] Single crystals suitable for X-ray diffraction were obtained via the slow cooling of toluene/*n*-hexane for **1**, and toluene for **3** and **4**. The Zr centers in all structures (Figure 2) adopt distorted octahedral geometries with *trans*-O, *cis*-N_{imine}, and *cis*-X (X = NMe_2, Me, or Cl) configurations around the Zr center. This likely reflects both steric and electronic factors, with the Zr-O bond length shorter than the Zr-N_{imine} distance (2.04 Å vs. 2.44 Å in **1**, 2.00 Å vs. 2.40 Å in **3**, and 1.99 Å vs. 2.32 Å in **4**, see SI).[7, 30] To the best of our knowledge, the X-ray structure of **3** represents the first example of the crystallographic characterization of an FI_2ZrMe_2 complex.

Scheme 1. Synthesis of Zr Precatalysts.



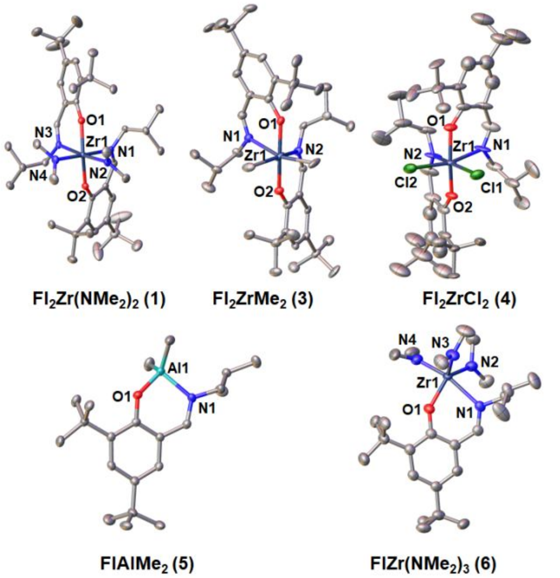


Figure 2. Molecular structures of complexes **1**, **3**, **4**, **5,** and **6**. Hydrogen atoms are omitted for clarity.

For polymerization studies, the "alkylation" of amido complex **1** ($\mathbf{FI_2Zr(NMe_2)_2}$) was performed by adding a trimethylaluminum (TMA) solution in toluene to a solution of the precatalyst in toluene at 25□C. The reaction mixture was then stirred for 30 min (determined as optimum empirically) before adding the cocatalyst/activator $Ph_3C^+B(C_6F_5)_4$□ (BT). Notably, a stirring period of 30 min is critical to effective alkylation, and shorter alkylation times result in little or no polymer. Ethylene/1-octene copolymerization reactions were next carried out under rigorously anhydrous and anerobic conditions at 40 °C in a 350 mL glass, semi-batch reactor under a constant ethylene pressure of 4 atm ethylene, 3.56 g of 1-octene, and 45 mL of toluene, which gives an ethylene/1-octene molar ratio of 1:1.7 in the liquid phase. Polymerization times and polymer yields were adjusted to minimize the influence of exotherm and mass transfer limitations, as well as significant 1-octene depletion.[31-32] Polymerization results are summarized in Table 1. All product polymers are monomodal with narrow Đ values (<2.9), characteristic of well-defined single-site behavior. As expected, there is no activity when no TMA is present for alkylation (Table 1, entry 1). Surprisingly, however, when **1** is activated by TMA, then BT, it exhibits both high activity and significantly greater 1-octene incorporation (7.2 mol%) than TMA, then BT-activated **2** and **3**, which, under identical polymerization conditions, yield 1.0 mol% and 0.9 mol% 1-octene incorporation, respectively (Table 1, entries 2 vs 5 and 8). Interestingly, catalysis with dibenzyl precatalyst **2** or dimethyl precatalyst **3** yields products with 1-octene incorporation levels all below 1.5 mol% (Table 1, entries 4-9). Together these results argue that activation of amido precatalyst **1** with TMA, then BT leads to a different active species than do precatalysts **2** and **3**. Note again that the polymers produced in all these experiments are monomodal with narrow Đ, characteristic of well-defined single-site behavior.

The effects of TMA loading on the polymerization characteristics were also studied, and strong detrimental effects of excess TMA on both polymerization activity and 1-octene incorporation are observed for **1**. By increasing the TMA loading from 40 (Table 1, entries 3 vs. 2) to 120 equiv, the polymerization activity is reduced by 5.8x for **1**; by increasing the TMA loading from 0.0 (see Table 1) to 120 equiv, the polymerization activity is reduced by 6.2x for **2**, and 2x for **3**. Additionally, 1-octene incorporation is depressed by 2.7x for **1** (Table 1, entry 3 vs. 2); interestingly, however, the 1-octene incorporation changes are small for **2** and **3** by increasing the TMA loading from 0.0 to 120 equiv (Figures 3A and 3B, and Table 1). Note that dichloride complex **4** exhibits no polymerization activity following reaction with TMA (40 equiv), then BT, likely reflecting the known poor alkylation efficiency of Zr-Cl moieties.[33-34]

The detrimental effects of TMA on polymerization activity may reflect catalyst decomposition induced by large amounts of TMA or a strong coordination of TMA to the FI_2Zr- center presumably via μ-Me bonding. The resulting Zr···Al adducts are thought to act as important intermediates in alkyl/polymeryl chain transfer.[9, 25, 35-39] However, the adducts may become less active, or even inactive dormant species,[34, 40-43] if the coordination is too strong (Figure 4A). In this study, a Zr···Al adduct, characteristic of a $FI_2Zr(\mu\text{-}Me)_2AlMe_2$ moiety, is confirmed by NMR spectroscopy. NMR studies of FI_2MX_2 activation chemistry have proven challenging for a number of reasons, including that alkylation can modify the ancillary ligand structure and strong, multiple Al coordination modes to the Zr catalyst,[9, 25, 34-43] as well as the general fluxional nature of such FI-based complexes.[21, 45-47] Using the preformed, well-defined precatalyst **3** (**FI_2ZrMe_2**), in reaction with cocatalyst/activator BT, yields a clean NMR spectrum, which stands in contrast to previous alkylation studies using FI_2ZrCl_2 and MAO,[47-49] and provides a better understanding of the activation process via first generating a well-defined $FI_2ZrMe^+B(C_6F_5)_4^-$ species (see SI). The ^{13}C NMR chemical shift of the Zr-*Me*⁺ moiety here is at δ 59.5 ppm (Figure 4B), which then experiences an upfield shift to δ 23.5 ppm upon the addition of 5 equiv of TMA (Figure 4C, see SI), indicating formation of μ-methyl groups.[50-52] With increasing TMA concentrations, the rate of chain propagation, and thus catalytic activity, is depressed or eliminated for many group 4 catalysts.[10, 34, 53-54] Note in the present study that the product polymer M_w falls with increasing TMA concentrations (Figure 3C) under all studied conditions, and that terminal double bonds are detected for all the product polymer samples by ^1H NMR (see SI). Thus, chain transfer to Al and β-H elimination/transfer are both operative chain termination pathways here (Figure 4A). Note that rapid Zr-polymeryl chain transfer between Zr and main group metal alkyls is a key component of the Dow chain shuttling polymerization process.[28]

Table 1. Data for ethylene/1–octene copolymerizations mediated by the indicated precatalysts[a]

Entry	Precat.	TMA equiv	Time (min)	Poly. (g)	Act.[b]	Mw[c]	Ð[c]	1-Octene Incorp.[d]
1	**$FI_2Zr(NMe_2)_2$ (1)**	0[e]	2.0	0	0	-	-	-
2	**$FI_2Zr(NMe_2)_2$ (1)**	40	2.0	3.79	2846	6	1.5	7.2
3	**$FI_2Zr(NMe_2)_2$ (1)**	120	2.0	0.66	495	4	1.4	2.7
4	**FI_2ZrBn_2 (2)**	0[e]	0.5	2.37	7097	14	2.0	1.5
5	**FI_2ZrBn_2 (2)**	40	0.5	1.88	5649	5	1.3	1.0
6	**FI_2ZrBn_2 (2)**	120	2.0	1.53	1144	4	1.3	0
7	**FI_2ZrMe_2 (3)**	0[e]	0.5	2.19	6572	13	2.2	1.3
8	**FI_2ZrMe_2 (3)**	40	0.5	1.31	3932	4	1.3	0.9
9	**FI_2ZrMe_2 (3)**	120	0.5	1.03	3099	2	1.2	0.1
10	**FI_2ZrCl_2 (4)**	40	1.0	0	0	-	-	-
11	**$FIAlMe_2$ (5)**	0[e]	6.0	0	0	-	-	-
12	**$FIZr(NMe_2)_3$ (6)**	0[e]	2.0	0	0	-	-	-
13	**$FIZr(NMe_2)_3$ (6)**	40	2.0	2.42	1812	9	1.3	6.3
14	**$FIZr(NMe_2)_3$ (6)**	120	2.0	0.88	660	8	2.9	3.2
15	**FI_2ZrMe_2 (3)**	0[f]	5	0	0	-	-	-
16	**FI_2ZrMe_2 (3)**	40[f]	0.5	1.24	3720	2	1.3	0.5

[a] Conditions: precatalyst: 10 μmol; trimethylaluminum (TMA) alkylating agent; $Ph_3C^+B(C_6F_5)_4^-$ (BT), 12 μmol; 1-octene, 3.58 g (5 mL); toluene, 45 mL; ethylene, 4 atm, 40 °C; each entry performed in duplicate. [b] Units kg/(mol·h·atm). [c] M_w in units kg/mol; Ð, dispersity; determined by triple–detection GPC versus polystyrene standards. [d] In mol%, by ^{13}C NMR, calculated according to literature.[44] [e] BT directly added to the precatalyst solution without TMA. [e] $Al_2(NMe_2)_2Me_4$ (10 μmol) was added to toluene solution of precatalyst (entry 15) or precatalyst+40 equiv TMA (entry 16) and stirred for 30 min before BT addition.

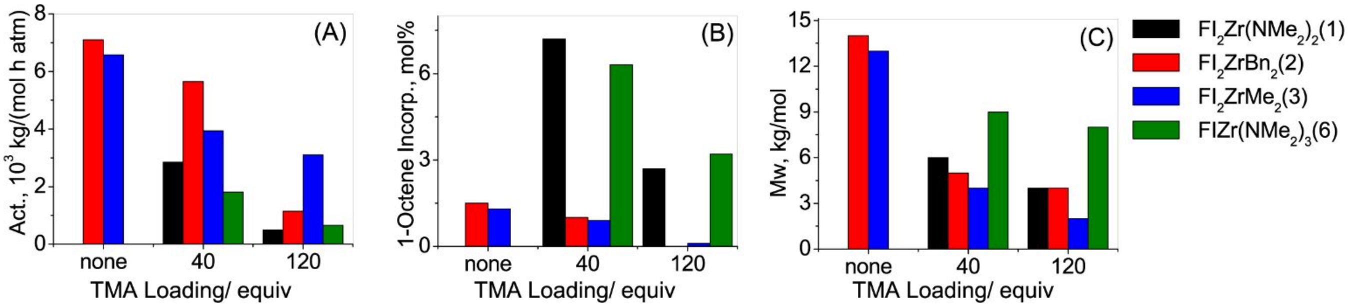


Figure 3. Effects of TMA loading (equiv/Zr) on activity (**A**), 1-octene incorporation (**B**), and M_w (**C**) in FI_2ZrX_2-catalyzed ethylene/1-octene copolymerization.

As noted above, unexpected precatalyst monodentate σ-ligand effects (i.e., enhanced 1-octene incorporation) are observed when using **FI$_2$Zr(NMe$_2$)$_2$** (**1**) + TMA compared to the **2** and **3** analogs. FI$_2$ZrX$_2$ (X = Bn, Cl, etc)-type precatalysts are known to exhibit very low α-olefin enchainment selectivity in the presence of ethylene, especially for FI ligands having sterically bulky substituents.[6-7, 55-56] Thus, for **1** + TMA + BT it appears likely that a new active species is formed that exhibits enhanced 1-octene incorporation selectivity.[55] It will be seen below that ancillary ligand transfer occurs during alkylation of **1** by TMA. Ti and Zr complexes having bidentate monoanionic ligands, including those having phenoxyimine ligands, have previously been reported to undergo ancillary ligand transfer reactions with trimethylaluminum (TMA),[57-61] forming bidentate monoanionic ligand coordinated Al complexes along with unidentified group 4 species. Such processes have been previously associated with catalyst deactivation pathways (Figure 5B).[11, 48, 57-60, 62-65] Here, the proposed ancillary ligand abstraction scenario is confirmed by *in situ* NMR spectroscopy, precatalyst X-ray diffraction, and catalytic control experiments.

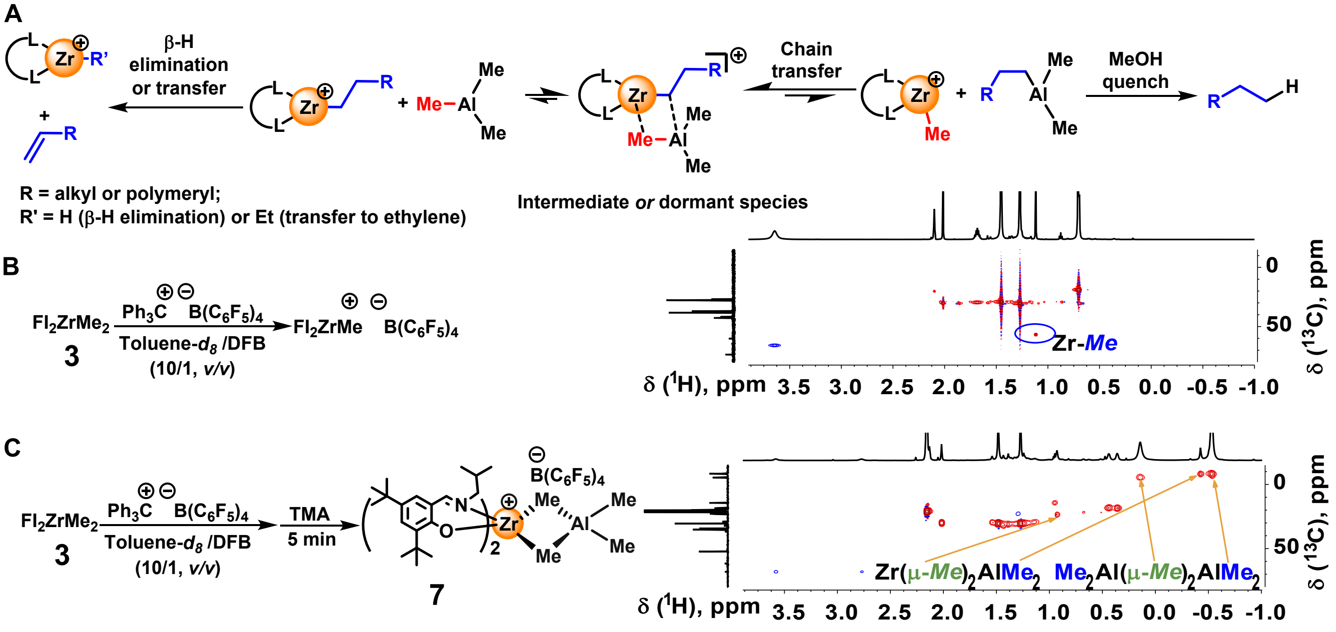


Figure 4. A. FI catalyst chain transfer, termination, and Al coordination processes. B(C$_6$F$_5$)$_4^-$ is omitted for clarity. **B** and **C**. A section of the ^{1}H-^{13}C HSQC spectrum of FI$_2$ZrMe$^+$B(C$_6$F$_5$)$_4^-$ (25 °C) (**B**) and FI$_2$Zr$^+$(μ-Me)$_2$AlMe$_2$ B(C$_6$F$_5$)$_4^-$ (**7**) (-50 °C) (**C**).

In the reaction of **FI$_2$Zr(NMe$_2$)$_2$** (**1**) with TMA, a major set of new ^{1}H NMR resonances corresponding to **FIAlMe$_2$ (5)** is observed (Figure S22), which suggests ancillary ligand transfer to Al is a major pathway during the alkylation process (Figure 5C). It is important to note that **5**, synthesized and isolated independently, is not an active polymerization catalyst (Table 1, entry 11). Note also that the reaction of **1** + TMA does not afford either **FI$_2$ZrMe$_2$** (**3**) or a **3**-TMA adduct based on the following observations: *i*) the ^{1}H NMR features of **3** + TMA do not match those of **1** + TMA (Figure S23); *ii*) **3**, after activation with BT/TMA, forms a cationic FI$_2$Zr species (Figure 4C, see SI), which is a poor 1-octene incorporator (0.9 mol%) vs. **1**, which, as already noted, exhibits increased 1-octene incorporation (7.2 mol%) (Table 1, entries 8 vs. 2); *iii*) complex **3** also undergoes a slow ancillary ligand abstraction in the presence of 5 equiv of TMA, with ca. 59% conversion to **FIAlMe$_2$** (**5**) after 1 day at room temperature (Figure 5C, also see SI). Using the solution, **3** + TMA (40 equiv), reacted at r.t. for 1 day, followed by BT addition, as a polymerization catalyst under otherwise identical conditions to entry 8 of Table 1, shows significantly decreased activity, 1088 vs. 5433 kg/(mol·h·atm), and similarly very low 1-octene incorporation (~0 mol% vs. 0.9 mol%). Thus, **7**, which derives from activation of **3** with BT in the presence of TMA, is likely the active species (Figure 4C); in contrast, the slow ancillary ligand transfer in the reaction of **3** + TMA ultimately affords an inactive catalyst structure which is currently unknown,[11, 48, 57-60, 62-65] instead of the formation of a mono-FI-Zr complex observed in the analogous reaction with **1**, which leads to high activity and 1-octene incorporation.

Note that one additional factor must be considered when comparing the differences between the **FI$_2$Zr(NMe$_2$)$_2$** (**1**) and **FI$_2$ZrMe$_2$** (**3**) derived polymerization catalysts. It is known that Al$_2$(NMe$_2$)Me$_5$ and Al$_2$(NMe$_2$)$_2$Me$_4$ will be present, produced as by-products when TMA is used as a Zr-NMe$_2$ catalyst alkylating agent.[66] In a control experiment, Al$_2$(NMe$_2$)$_2$Me$_4$ was prepared using a modified literature procedure (see SI)[67] and introduced into the polymerization solution of **FI$_2$ZrMe$_2$ (3)** in the presence of 0.0 and 40 equiv of TMA, followed by the cocatalyst BT (Table 1, entries 15 and 16). Note that when no TMA is present, there is no polymerization activity, presumably reflecting poisoning effects of Lewis basic Al$_2$(NMe$_2$)$_2$Me$_4$. However, when 40 equiv of TMA is present, the **FI$_2$ZrMe$_2$** mediated polymerization proceeds similarly to that without Al$_2$(NMe$_2$)$_2$Me$_4$ present, in terms of activity, product M$_w$, Đ, and 1-octene incorporation (Table 1, entry 16 vs. 8). This control experiment strongly suggests that the presence of Al$_2$(NMe$_2$)Me$_5$ and Al$_2$(NMe$_2$)$_2$Me$_4$ alkylation by-products cannot account for the observed 1-octene incorporation differences between **FI$_2$Zr(NMe$_2$)$_2$ (1)** and **FI$_2$ZrMe$_2$ (3)** under these conditions.

Based on the above observations, it is reasonable to propose that the other product resulting from ancillary ligand transfer to Al in the case of **1** is a cationic mono-FI Zr complex, most likely in the form of an AlMe$_3$ adduct[34, 41, 54, 62, 65] (*vide supra*). **[Zr⋯Al]** (**8**) is the likely structure containing one coordinated TMA[51, 62, 68] (Figure 5C). Considering the complexity of this system, however, varied types of AlM$_3$ adducts[40, 50, 69-71] may be present to stabilize the cationic mono-FI Zr moiety. All spectroscopic attempts to clarify the exact structure of the catalyst were unsuccessful due to the complexity.[62, 65] Regarding the possible reason for the different ligand transfer tendencies, i.e., much faster FI ligand abstraction for **$FI_2Zr(NMe_2)_2$** (**1**) than for **FI_2ZrMe_2** (**3**), we hypothesize that this may involve the basic nature of the neighboring -NMe_2 ligand helping to preorganize the TMA abstraction process.

We next focused on the synthesis of mono-FI-Zr-alkyl complexes, i.e., $FIZrMe_3$ or $FIZrBn_3$, which would be ideal models for comparative studies. However, all attempts to prepare such complexes were unsuccessful, likely due to their instability.[72-74] Changing the substituent on the FI imine N from less bulky aliphatic isobutyl to more bulky aromatic 2,6-diisopropylphenyl enables preparation of the corresponding more stable FI"$ZrBn_3$ complex,[75] however, when activated, this complex gives negligible olefin polymerization activity, making it a poor control precatalyst for this study (see SI for more details). Thus, we turned to other mono-FI-Zr precatalysts. Fortunately, **$FIZr(NMe_2)_3$** (**6**) is straightforwardly synthesized (Figure 5A) and characterized spectroscopically and by single crystal XRD (Figure 2). Activation of **6** with TMA (40 equiv) +

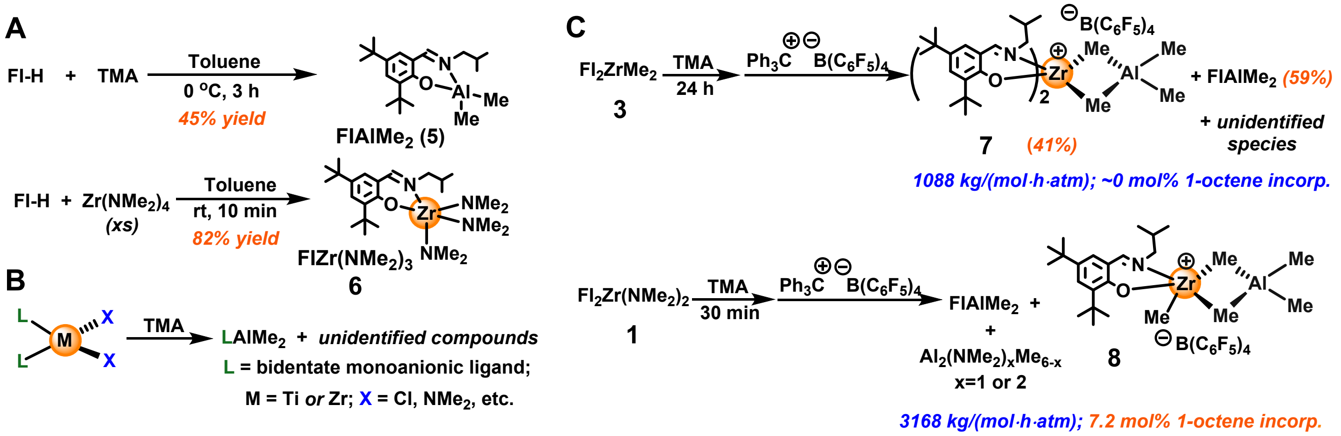


Figure 5. **A.** Synthesis of key complexes relevant to trimethylaluminum (TMA) alkylation studies. **B.** Previously reported ancillary ligand transfer from Ti or Zr to Al as a common catalyst deactivation pathway.[48, 57-60, 63-65] **C.** Reactions of precatalysts **3** and **1** with TMA, and proposed cationic active catalysts.

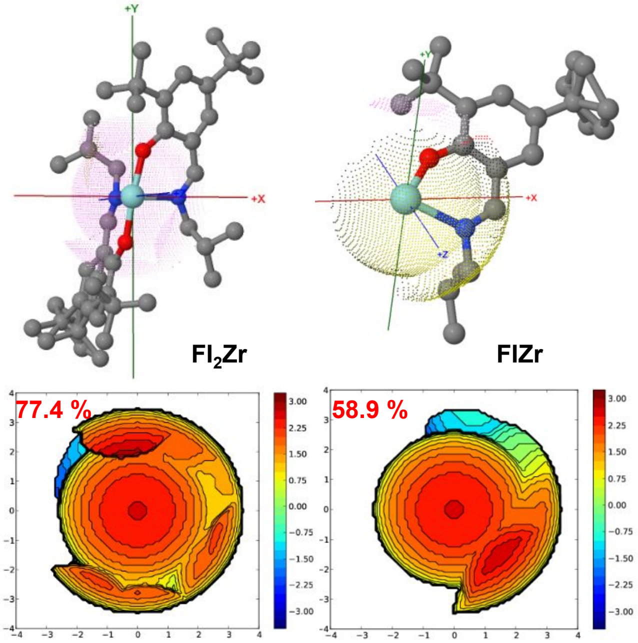


Figure 6. Steric crowding maps from buried volume calculations[76] for **$FI_2Zr(NMe_2)_2$ (1)** and **$FIZr(NMe_2)_3$ (6)** (see SI).

BT gives activity and 1-octene incorporation statistically indistinguishable from that of **1** activated the same way, 6.3 and 7.2 mol%, respectively (Table 1, entries 13 vs. 2). The two precatalysts also behave similarly when 120 equiv of TMA is used (Figure 3).[77] These catalytic results strongly argue that both bis-FI **$FI_2Zr(NMe_2)_2$** (**1**) and mono-FI **$FIZr(NMe_2)_3$** (**6**) precatalysts form similar if not identical cationic mono-FI-Zr catalytic species, reducing the ancillary ligand-engendered steric bulk, reasonably responsible for the enhanced comonomer enchainment. Furthermore, buried volume calculations also confirm the significant differences in percentage buried volume (%VBur), a measure of steric encumbrance, for the backbones of FI_2Zr- and FIZr- catalysts within a radius of 3.5 Å around the Zr center, 77.4 % vs. 58.9 %, respectively (Figure 6). This indicates that the FIZr- center is less sterically congested than the analogous FI_2Zr center. Note that the FI ligand remains intact in both complexes **1** and **6** during TMA-alkylation, since hydrolysis, recovery, and analysis of the resulting organic mixture gives only FI-H ligands without imine reduction (see SI).[74, 78]

The above catalysts were also investigated under conditions more relevant to industrial processes. Ethylene/1-octene copolymerization reactions were carried out at 120 °C in 2L semi-batch reactors under 18.4 atm of ethylene (46 g ethylene in the liquid phase), 300 g of 1-octene, and 609 g of mixed alkanes solvent (Isopar E) which gives ethylene/1-octene molar ratio of 1:2 in the liquid phase. Ethylene was fed on demand to maintain steady concentration. Two different alkylation procedures were employed – method [e] (see Table 2) involved premixing the precatalyst with TMA for 30 min followed by BT addition and injection of the resulting catalyst mixture into the reactor. In method [f] TMA was only mixed with precatalyst for less than 1.0 min. Control experiments with no alkylation step (TMA equiv = 0) also were performed in which precatalyst was mixed with BT and added to the reactor within 5 min. Polymerization trends similar to the effects described above at lower reaction temperatures and pressures (Table 1) are observed under these conditions. The activities of precatalysts **2** and **3** are reduced by mixing the precatalysts with TMA (40 equiv)/BT prior to catalyst addition to the reactor (Table 2, entries 4, 5, 7 and 8) regardless of the TMA premixing method as compared to runs containing no TMA (entries 3 and 6). Similarly, the comonomer incorporation for **2**- and **3**-catalyzed polymerizations remains low, even with 40 equiv of TMA, while the dimethylamido precatalyst, **1**, incorporates 4x more 1-octene (10 mol%, entry 2) than does **2** (2.5 mol%, entry 4) and **3** (3.1 mol%) under identical polymerization conditions and behaves very similarly to mono-FI precatalyst **6** which incorporates 12.3 mol% 1-octene (entry 10). As expected, **1** and **6** do not produce polymer when TMA is not contacted with the precatalyst for a longer period of time. For example, when TMA is mixed with **6** for less than 2 min, no polymer is produced (Table 2, entry 11). To verify the experimental protocol, a **CGCTiMe$_2$** precatalyst (CGC = [(η^5-C_5Me_4-$SiMe_2$-N-*t*-Bu)]$TiMe_2$) was evaluated under the same polymerization conditions and shows 1-octene incorporation of 33 mol% as expected with respect to FI catalysts. These results argue that the unique alkylation/activation chemistry of the **FI$_2$Zr(NMe$_2$)$_2$** precatalyst is maintained under scaled/industrial operating conditions.

Table 2. Ethylene/1–octene copolymerizations at higher temperature and pressure[a]

Entry	Precat.	Loading (μmol)	TMA equiv	Time (min)	Poly. (g)	Act.[b]	M$_w$[c]	Đ[c]	1-Octene Incorp.[d]
1	**FI$_2$Zr(NMe$_2$)$_2$ (1)**	1.0	0	10	0	0	-	-	-
2	**FI$_2$Zr(NMe$_2$)$_2$ (1)**	1.0	40[e]	10	7.2	2315	11	4.3	10.0
3	**FI$_2$ZrBn$_2$ (2)**	0.5	0	6	18.5	19829	9	2.2	2.3
4	**FI$_2$ZrBn$_2$ (2)**	0.5	40[e]	10	3.8	2444	9	2.6	2.5
5	**FI$_2$ZrBn$_2$ (2)**	0.5	40[f]	10	10.4	6688	12	3.5	2.6
6	**FI$_2$ZrMe$_2$ (3)**	2.0	0	8	17.4	3497	9	2.5	2.5
7	**FI$_2$ZrMe$_2$ (3)**	2.0	40[e]	10	1.2	193	10	2.3	2.4
8	**FI$_2$ZrMe$_2$ (3)**	2.0	40[f]	10	10.3	1656	17	5.8	3.1
9	**FIZr(NMe$_2$)$_3$ (6)**	1.0	0	10	0	0	-	-	-
10	**FIZr(NMe$_2$)$_3$ (6)**	1.0	40[e]	10	14.2	4566	30	6.9	12.3
11	**FIZr(NMe$_2$)$_3$ (6)**	1.0	40[f]	10	0	0	-	-	-
12	**CGCTiMe$_2$**	0.5	0	10	44.2	28426	38	2.5	32.9

[a] Conditions: $Ph_3C^+B(C_6F_5)_4^-$ (BT), 1.2 equiv; 2 L Parr reactor, 120 °C, 18.4 atm, 300 g 1-octene, 609 g Isopar E, 46 g ethylene. [b] Units kg/(mol·h·atm). [c] M$_w$ in units kg/mol; Đ, dispersity; determined by GPC versus polystyrene standards. [d] In mol% determined by compositional GPC with IR5 detector [e] Trimethylaluminum (TMA) mixed with a solution of precatalyst for 30 min. at room temperature followed by addition of BT activator and transfer to the reactor. [f] TMA added to precatalyst solutions followed by activator and the product added to the reactor within 5 min. **CGCTiMe$_2$** = [(η^5-C_5Me_4-$SiMe_2$-N-*t*-Bu)]$TiMe_2$.

CONCLUSIONS

A new phenoxyimine Zr dimethylamido precatalyst is reported for ethylene/1-octene copolymerizations. By changing the identity of the precatalyst monodentate σ-ligands, as opposed to modifying ancillary ligand structure or changing the identity of the central metal, the catalyst exhibits unexpected variations in reactivity in terms of comonomer incorporation selectivity, without the loss of activity. When activated with TMA, then BT, mono-FI **FIZr(NMe$_2$)$_3$** and bis-FI **FI$_2$Zr(NMe$_2$)$_2$** dimethylamido complexes are shown to incorporate significantly higher levels of 1-octene than the corresponding **FI$_2$ZrMe$_2$** and **FI$_2$ZrBn$_2$** derivatives. Detailed investigation suggests that the distinctive precatalyst monodentate σ-ligand effects originate in FI ligand abstraction reactions, which were previously thought to be major catalyst deactivation pathways. Preliminary studies suggest that *in situ* generated mono-FIZr catalysts, which are often inaccessible through alkyl or chloride precursors, likely account for such distinctive catalytic properties. Polymerization studies under scaled/industrial operating conditions also show high catalytic efficiency and reflect the unique alkylation/activation chemistry of the **FI$_2$Zr(NMe$_2$)$_2$** precatalyst. This report demonstrates the importance of screening varied precatalyst monodentate σ-ligands in optimizing new catalysts, especially for group 4 catalysts in olefin polymerizations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Synthesis of ligand and complexes; crystal structures (cif.), polymerization procedures; characterizations of ligand, complexes and polymer products.

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Notes

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