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Catalyst Nuclearity Effects in Olefin Polymerization

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ABSTRACT

Catalyst Nuclearity Effects in Olefin Polymerization

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The new binuclear organo-zirconium and -titanium metal complexes {2,7-di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalenediolato group 4 metal complexes {1,8-(O)₂C₁₀H₄-2,7-[CH=N(2,6-*i*-Pr₂C₆H₃)]₂}Zr₂Cl₆(THF)₂ (**FI²-Zr₂**) and {1,8-(O)₂C₁₀H₄-2,7-[CH=N(2,6-*i*-Pr₂C₆H₃)]₂}Ti₂Cl₆(THF)₂ (**FI²-Ti₂**) are compared to the mononuclear analogues {3-*i*-Bu-2-(O)C₆H₃CH=N(2,6-*i*-Pr₂C₆H₃)}ZrCl₃(THF) (**FI-Zr₁**) and {3-*i*-Bu-2-(O)C₆H₃CH=N(2,6-*i*-Pr₂C₆H₃)}TiCl₃(THF) (**FI-Ti₁**), respectively, in ethylene polymerization and ethylene + olefin copolymerization processes. The comonomers studied include 1-hexene, 1-octene, 1,5-hexadiene (**1,5-HD**), 1,4-pentadiene (**1,4-PD**), and highly hindered 1,1-disubstituted methylenecyclopentane (**MCP**) and methylenecyclohexane (**MCH**). In ethylene + 1-hexene copolymerizations, **FI²-Zr₂** enchains 1.5x more 1-hexene than **FI-Zr₁**, and **FI²-Ti₂** enchains 2.2x more 1-hexene than **FI-Ti₁**. While ethylene + **1,5-HD** and ethylene + **1,4-PD** copolymerizations mediated by **FI²-Zr₂** and **FI-Zr₁** produce ethylene + **1,4-PD** and ethylene + **1,5-HD** copolymers at respectable activities, **FI²-Ti₂** and **FI-Ti₁** are virtually inactive. While **MCP** and **MCH** are efficiently co-enchained with ethylene via a ring-unopened pathway by both **FI²-Ti₂** and **FI-Ti₁**, **FI²-Zr₂** and **FI-Zr₁** produce only polyethylene. These examples represent the first olefin copolymerizations reported for mono-phenoxyiminato group 4 complexes, and in general the bimetallic catalysts incorporate between 1.8x - 3.4x more comonomer in ethylene + olefin copolymerizations than their monometallic counterparts. In comparison to mono- and binuclear

group 4 constrained geometry catalysts (CGCs), the mono- and binuclear **FI** catalysts: 1) enchain significantly greater densities of α -olefins, 2) display enhanced binuclear catalyst polymerization activity versus their mononuclear analogues, and 3) produce predominantly linear polyethylenes as opposed to the branched polyethylenes produced by CGCs.

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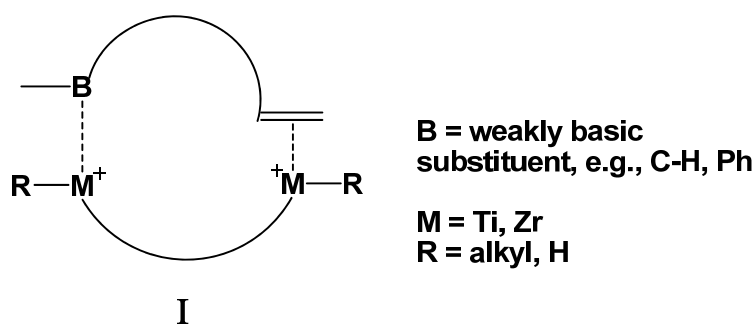
Chapter 1

Enhanced Activity and Comonomer Enchainment in Ethylene + Olefin Copolymerizations Mediated by Bimetallic Group 4 Phenoxyiminato Catalysts

Introduction

Recently, intensive research efforts have been devoted to discovering unique and/or more efficient homogeneous catalytic processes which derive from cooperative effects realizable between proximate active centers in multinuclear metal complexes.¹ In some cases, these complexes mimic the capabilities of enzymes in enforcing conformational control to promote selectivity as well as in enhancing effective local reagent concentrations.² In the area of single-site olefin polymerization catalysis,³ we recently reported that $-\text{CH}_2\text{CH}_2-$ (Figure 1-2, **Ti₂**, **Zr₂**) and $-\text{CH}_2-$ (Figure 1-2, **C1-Ti₂**, **C1-Zr₂**) bridged bimetallic “constrained geometry catalysts” (CGCs)⁴ exhibit pronounced nuclearity effects in terms of enhanced branch formation, α -olefin comonomer enchainment selectivity/activity, and molecular weight enhancement as compared to their mononuclear counterparts (Figure 1-2, **Ti₁**, **Zr₁**).^{3b,5} Secondary interactions between weakly

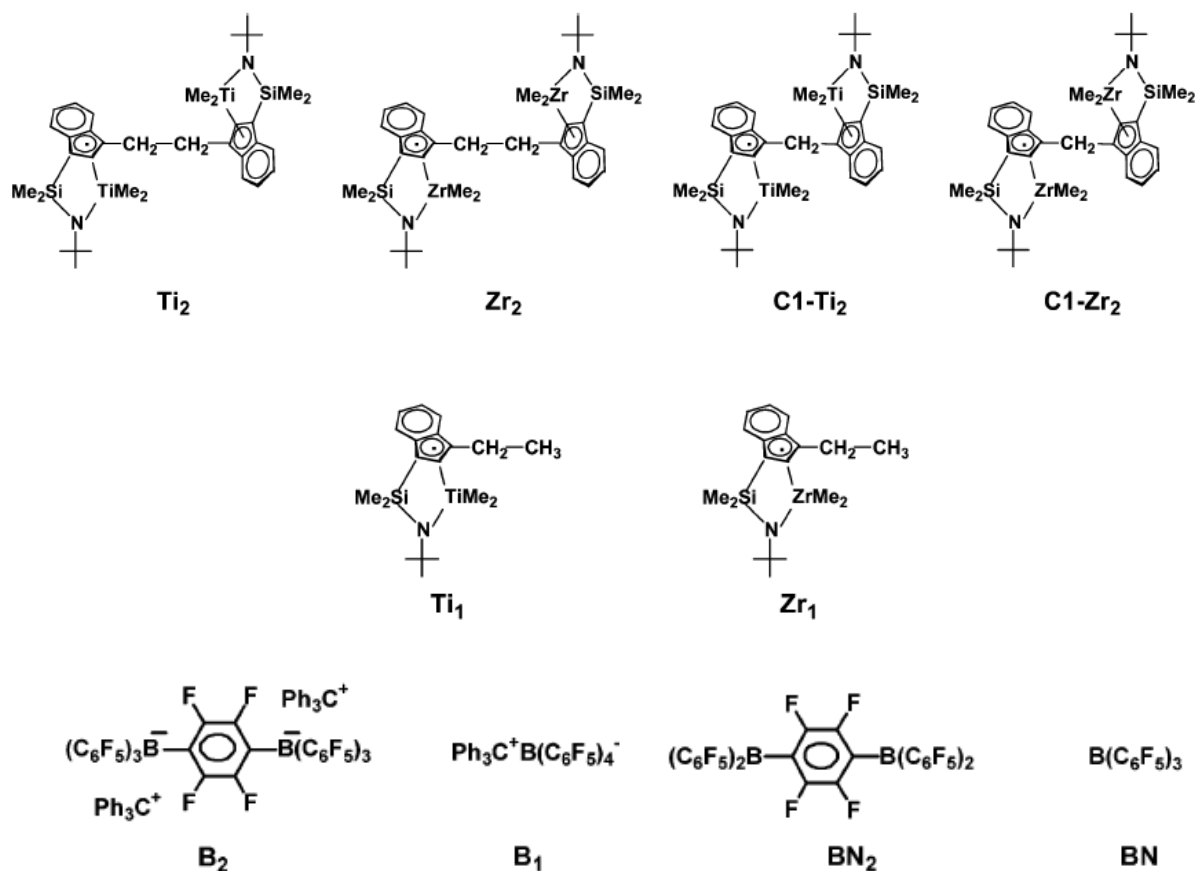
Figure 1-1. Schematic representation of bimetallic effects observed in olefin polymerization



basic monomer substituents (e.g., C-H bonds, Ph groups) and the second metal center appear to play a key role in modifying enchainment and chain transfer kinetics (Figure 1-1, **I**). The shorter linker in the **C1**-bridged catalysts draws the catalytic centers to an approximate, shortest

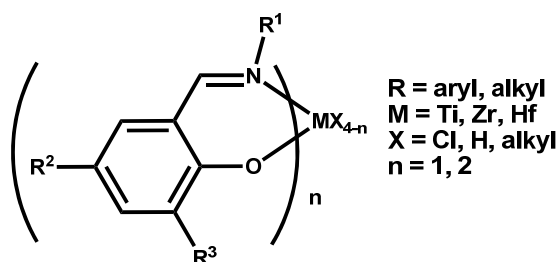
attainable M...M distance of ~ 6.0 Å versus ~ 6.6 Å in **Ti₂** and **Zr₂**.⁶ The result of shortening the M...M distance dramatically increases product M_w and 1-hexene enchainment selectivity in copolymerizations.^{5c,d} Binuclear activators/cocatalysts⁷ **B₂** and **BN₂** have also been implemented in these olefin(co)polymerizations, and have been shown to also enhance cooperativity between catalyst centers (versus mononuclear **B₁** and **BN**) by electrostatically⁸ poisoning the catalyst centers in closer proximity.

Figure 1-2. Binuclear family of ‘constrained geometry catalysts,’ cocatalysts, and their respective mononuclear analogues



In the non-metallocene area of single-site polymerization catalysis,⁹ new families of group 4 bis-¹⁰ and mono-phenoxyiminato¹¹ olefin polymerization catalysts (Figure 1-3) have been studied in several laboratories. Attractions of these catalysts include the ease of preparation, activities competitive with those of group 4 metallocenium catalysts, ability to support living polymerizations, and utility in producing unique polyolefin architectures.¹² A priori, the coordinatively open nature of mono-phenoxyiminato group 4

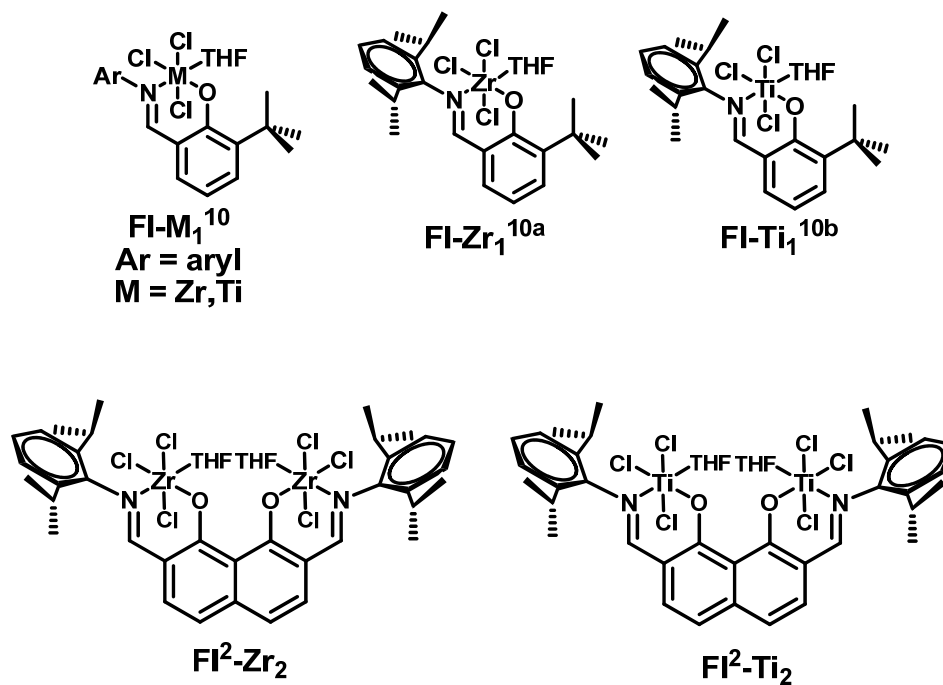
Figure 1-3. Phenoxyiminato group 4 olefin polymerization catalysts



active sites would appear to be conducive to the enchainment of α -olefin comonomers. However, mono-phenoxyiminato group 4 catalysts curiously exhibit limited productivity and comonomer incorporation selectivity in ethylene + α -olefin copolymerizations.¹¹ In light of the aforementioned results in which binuclear CGCs exhibit enhanced homopolymerization activities and copolymerization selectivities, the intriguing question arises as to whether two covalently linked phenoxyiminato group 4 catalytic centers could enhance/modify copolymerization productivity and comonomer enchainment selectivity in such polymerizations. In a preliminary communication, we briefly reported the synthesis and initial observations on the polymerization characteristics of the first binuclear phenoxyiminato group 4 metal complex (**FI**²-**Zr**₂, Figure 1-4).¹³ We designed and synthesized the rigid, planar **FI**² ligand to maximize the

potential for cooperative effects between active phenoxyiminato catalytic centers. The naphthalenic backbone should prevent the metal centers from rotating away from each other during catalytic events which can occur around the flexible alkylene linkers in **Ti₂**, **Zr₂**, **C1-Ti₂**, and **C1-Zr₂**. In addition to conformational rigidity, the minimum attainable M...M proximity was

Figure 1-4. New binuclear family of catalysts synthesized for the current study and their mononuclear analogues



also taken into account in ligand design. The M...M distance in the **FI²** ligand structure is estimated to be 5.4 - 5.9 Å,¹⁴ versus ~6.0 Å for **C1-Zr₂** and ~6.6 Å for **Zr₂**.⁶ In the aforementioned binuclear CGC systems, as noted above, shortening the M...M distance via replacing a two carbon linker (**Zr₂**) with a one carbon linker (**C1-Zr₂**) leads to dramatic

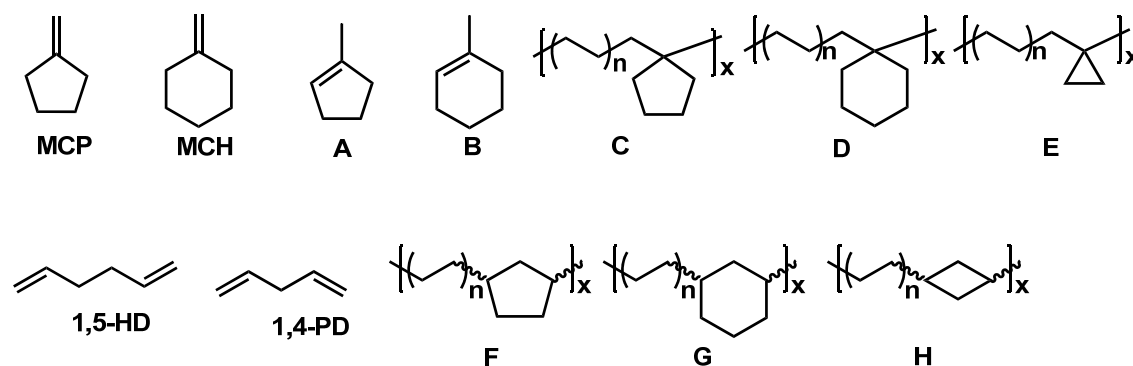
enhancements in polyethylene M_w s and comonomer incorporation densities in the products obtained from **C1-Zr₂** versus **Zr₂**.¹⁵

In general, CGC-Zr catalysts produce low- M_w polyolefins with low activities and with low α -olefin cochainment efficiencies, whereas CGC-Ti catalysts produce high- M_w polyolefins with high activities and high α -olefin cochainment efficiencies.¹⁶ For example, in ethylene homopolymerizations under identical conditions, **Ti₁** produces polyethylenes with M_w s 100x - 700x greater than those produced by **Zr₁**, depending on cocatalyst. Moreover, **Ti₁** displays polymerization activities between 10x - 70x greater than **Zr₁**.¹⁷ These marked differences between Zr and Ti, therefore led us to also investigate the synthesis and properties of **FI-Ti₁**^{11a} and **FI²-Ti₂**.

An additional, informative class of comonomers to examine for cooperative enchainment effects is the highly encumbered methylenecycloalkanes (**MCAs**).^{5b,18} For monomers having little or no ring strain such as methylenecyclopentane (**MCP**) and methylenecyclohexane (**MCH**), isomerization to the thermodynamically more stable internal cycloolefins (Figure 1-5, **A**, **B**) is mediated by a variety of mononuclear d^0/f^n metallocene catalysts.¹⁸ Several methylenecycloalkanes are reported to undergo rapid single-site copolymerization with ethylene via ring-unopened pathways, mediated by neutral Ni-diimine, d^0/f^n metallocene, **Ti₁**, and **Ti₂** catalysts, yielding macromolecules having saturated hydrocarbon rings incorporated in the polyolefin backbone (Figure 1-5, structures **C**, **D**, **E**).^{18b,19} Such substitutions are expected to drastically modify viscoelastic properties, because the bulky rings inhibit the tight coiling effects normally exhibited by polyethylenes. Increasing the average chain length between coils should lessen the tightness of the coiling.²⁰ Saturated ring-functionalized polyolefins are also expected

to have smaller dielectric constants, lower refractive indices, reduced water absorption, and greater optical transparency versus their homopolymer counterparts.²¹ Such polymer

Figure 1-5. Hindered comonomers and α,ω dienes and the corresponding ethylene copolymer microstructures they produce



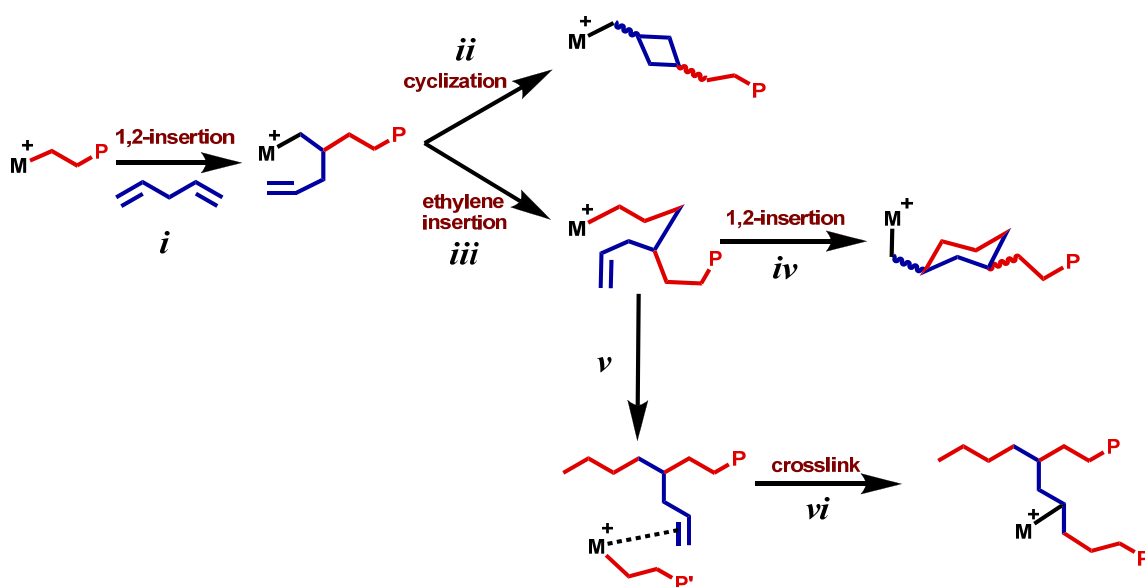
architectures are normally accessed via heterogeneous hydrogenation of polyindenes^{20a} or polystyrenes.^{20b-d} However, the additional hydrogenation step is inefficient, the conditions are relatively harsh, and the products often suffer from incomplete hydrogenation and/or chain scission. Therefore, a single-step homogeneous catalytic polymerization process is an appealing alternative for accessing this useful macromolecular structure class.³

We recently reported that Ti_2 -mediated copolymerization of **MCP** and **MCH** with ethylene leaves the saturated hydrocarbon ring structures intact.^{5b} In contrast to highly ring-strained cyclopropyl substituents, which can potentially compromise product polymer stability, comonomers **MCP** and **MCH** have minimal ring strain (6.5 and 0 kcal/mol for **MCP** and **MCH**, respectively),^{18c,22} and can be incorporated into polyethylene chains in ring-unopened geometries. Since the binuclear catalyst $\text{FI}^2\text{-Zr}_2$ exhibits enhanced selectivity for α -olefin

comonomers, the question also arises as to whether this unusual selectivity pattern can be extended to severely encumbered comonomers, and to $\text{FI}^2\text{-Ti}_2$.

Another comonomer class which can introduce saturated hydrocarbon ring structures into polyethylene chains and which may be amenable to cooperative effects is α,ω -dienes,²³ such as 1,5-hexadiene (**1,5-HD**) and 1,4-pentadiene (**1,4-PD**). In ethylene + **1,5-HD** copolymerizations mediated by zirconocenium catalysts,²⁴ 1,3-cyclopentyl fragments (Figure 1-5, structure **F**) are introduced via a diene olefinic group undergoing insertion, followed by rapid cycloinsertion of the second pendant vinyl group. In ethylene + **1,4-PD** copolymerizations mediated by

Scheme 1-1. Insertion pathways for 1,4-pentadiene (**1,4-PD**) copolymerized with ethylene mediated by zirconocene catalysts²⁵



zirconocenium catalysts (Scheme 1-1),²⁵ a 1,3-cyclohexyl unit (Figure 1-5, structure **G**) is

introduced via diene olefinic endgroup insertion (step **i**), followed by insertion of an ethylene monomer (step **iii**), then cyclization (step **iv**). Cycloinsertion to afford 1,3-cyclobutyl groups has also been observed (step **ii**), despite the substantial strain energy introduced (Figure 1-5, structure **H**).^{25a} For **1,5-HD** and **1,4-PD**, the pendant vinyl group may also remain intact as a branch or may undergo insertion at a second propagating catalyst center to create a cross- link.²⁵ The highly open, bifunctional nature of **FI²-Zr₂** and **FI²-Ti₂** led us to also investigate ethylene copolymerizations with these two dienes, mediated by the **FI²-M₂** versus **FI-M₁** catalysts.

Herein we report the synthesis, characterization, and catalytic polymerization/copolymerization properties of the new binuclear phenoxyiminato catalysts/precatalysts **FI²-Zr₂** and **FI²-Ti₂**. We compare their polymerization properties to those of the mononuclear analogues **FI-Zr₁** and **FI-Ti₁**, and to the nuclearity effects previously observed in the CGC catalyst series.^{5,13,15,17} Studies of ethylene homopolymerization are first discussed, followed by ethylene copolymerizations with the α -olefins 1-hexene and 1-octene. Next, the hindered olefins **MCP** and **MCH** are examined in copolymerizations with ethylene. It is found that they are not isomerized to the thermodynamically favored isomers **A** and **B**, but are instead co-enchained with ethylene in a ring-unopened fashion in the presence of **FI-Ti₁** and **FI²-Ti₂**. These results represent the first reports of copolymerizations mediated by mono-phenoxyiminato Ti and Zr catalysts. It will be seen that, compared to the mononuclear catalysts **FI-Zr₁** and **FI-Ti₁**, bimetallic catalysts **FI²-Zr₂** and **FI²-Ti₂** produce copolymers with greater efficiency and with significantly greater comonomer enchainment selectivity. Finally, we compare and contrast these results to those obtained with mononuclear and binuclear Ti and Zr CGC catalyst systems.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum line (10^{-5} Torr), or in a nitrogen-filled MBraun glove box with a high capacity recirculator (<1 ppm O_2). Argon and ethylene (Matheson, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Ether solvents were purified by distillation from Na/K alloy/benzophenone ketyl. Hydrocarbon solvents were distilled under nitrogen from Na/K alloy. All solvents for high-vacuum line manipulations were stored *in vacuo* over Na/K alloy in Teflon-valve sealed bulbs. Deuterated hydrocarbon solvents were obtained from Cambridge Isotope Laboratories (all ≥ 99 atom %D), were freeze pump- thaw degassed, dried over Na/K alloy and were stored in resealable flasks. Other non-halogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from CaH_2 and stored over activated Davison 4A molecular sieves. The reagents 2,6-di-*iso*-propylaniline and trimethylchlorosilane were purchased from Aldrich and used as received. The comonomers methylenecyclopentane, methylenecyclohexane, 1,5-hexadiene, 1,4-pentadiene, 1-hexene, and 1-octene (Aldrich) were dried for a week over CaH_2 and were freshly vacuum-transferred prior to polymerization experiments. The reagent $LiCH_2TMS$ (Aldrich) was sublimed before use. The reagent $TiCl_4$ (Aldrich) was distilled before use. Methylaluminoxane (MAO, obtained as a 10% toluene solution from Aldrich) was dried under high vacuum to remove excess volatile aluminum alkyls before use. The reagents 1,8-bis(methyloxymethoxy)naphthalene,²⁶ $Zr\{3\text{-}^t\text{Bu-2-}$

(O)C₆H₃CH=N(2,6-*i*-Pr₂C₆H₃)}Cl₃(THF) (**FI-Zr₁**),^{11d} TiCl₄(THF)₂,²⁷ and Ti{3-*t*-Bu-2-(O)C₆H₃CH=N(2,6-*i*-Pr₂C₆H₃)}Cl₃(THF) (**FI-Ti₁**)^{11c} were prepared according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on a Varian Inova 400 (FT 400 MHz, ¹H; 100 MHz, ¹³C), Unity- or Mercury-400 (FT, 400 MHz, ¹H; 100 MHz, ¹³C), or Inova-500 (FT, 500 MHz, ¹H; 125 MHz, ¹³C) spectrometer. Chemical shifts(δ) for ¹H and ¹³C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J. Young). ¹³C NMR assays of polymer microstructure were conducted in mixture (1:1 in volume) of 1,2,4-trichlorobenzene (containing 0.1 M Cr(acac)₃ solution as a relaxation agent) and 1,1,2,2-tetrachloroethane-*d*₂ at 130°C. Resonances were assigned according to the literature for ethylene-olefin, ethylene-diene, and ethylene-**MCA** copolymers.^{5b,25,37} Elemental analyses were performed by Midwest Microlabs, LLC, Indianapolis, Indiana. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 10 °C/min. GPC measurements were performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 μm mixed columns was used. Samples were prepared at 160 °C. Molecular weights were determined by GPC using narrow polystyrene standards and are not corrected. Laser desorption mass spectra were obtained with a Perseptive BioSystems time-of-flight MALDI mass spectrometer using a dithranol matrix.

Synthesis of 2,7-diformyl-1,8-bis(methyloxymethoxy)naphthalene (1). The general procedure of Glaser was followed with the following modifications.²⁶ A solution of 1,8-

bis(methyloxymethoxy)naphthalene (4.00 g, 16.1 mmol) in Et₂O (180 mL) was added dropwise over 3 h to a solution of *n*-BuLi (2.5 M, 19.4 mL, 48 mmol) and TMEDA (7.2 mL, 48 mmol) in Et₂O (20 mL) at 0 °C. After stirring the reaction mixture for 5 h at 0 °C, dry DMF (7.5 mL, 48 mmol) was added at 0 °C, and the resulting mixture was warmed to room temperature and stirred overnight. Water (80 mL) was then added, and after the reaction mixture was stirred for 1 h at room temperature, the pH of the reaction solution was raised to 7–8 by addition of dilute HCl. The mixture was next extracted with 125 mL CH₂Cl₂, and the combined organic extracts were washed with water. After drying over sodium sulfate and filtration, the volatiles were removed, leaving an orange oil and an orange solid. This oil/solid mixture was washed with ethanol which removed the oil, leaving a bright-yellow solid which was used in the next step without further purification. The ¹H NMR spectrum was in agreement with that reported by Glaser.²⁶ Yield, 2.5 g (51%).

Synthesis of 2,7-diformyl-1,8-dihydroxynaphthalene (2). The general procedure of Glaser was followed with the following modifications.^{26,28} Under N₂, the reagent 2,7-diformyl-1,8-bis(methyloxymethoxy)naphthalene (**1**, 2.5 g, 8.2 mmol) was dissolved in 60 mL degassed CH₂Cl₂. A degassed solution of 60 mL isopropanol and 15 mL of 12 M HCl was added to the solution of **1** at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. The deprotected, pure product partially precipitated from the reaction solution. A second crop of pure, yellow product was obtained by extracting the reaction mixture with water (5x 100 mL), drying the organic phase with sodium sulfate, and removing the volatiles *in vacuo*. The ¹H NMR spectrum was in agreement with that reported by Glaser.²⁶ Combined yield, 1.7 g (95%).

Synthesis of 2,7-Bis-{[(E)-2,6-diisopropyl-phenylimino]-methyl}-naphthalene-1,8-diol ($\text{H}_2\text{-FI}^2$). Under N_2 , the reagent 2,7-diformyl-1,8-dihydroxynaphthalene (2.15 g, 9.93 mmol) was dissolved in 50 mL dry dichloromethane. Activated molecular sieves (2.0 g) were then added, followed by formic acid (5 drops), and 2,6-diisopropylaniline (8.0 mL, 42 mmol). The reaction was heated under reflux for 3 h during which time the 2,7-diformyl-1,8-dihydroxynaphthalene gradually dissolved, and the reaction mixture color changed from yellow to dark red. The reaction mixture was then cooled and filtered. The volatiles were removed from the filtrate *in vacuo*, and the resulting red oily solid was washed with hexanes (3 x 15 mL) and collected by filtration to afford a pure orange solid. Yield, 4.5 g (86%). X-ray quality single crystals were obtained by slow evaporation of a dichloromethane solution. Spectroscopic and analytical data for $\text{H}_2\text{-FI}^2$ are as follows. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 0°C , 399.447 MHz): δ 14.73 (s, 1H, OH), 13.47 (d, 1H, $\text{HN}=\text{CH}$, $^3J_{\text{H-H}} = 12.7$ Hz), 8.74 (s, 1H, $\text{HC}=\text{N}$), 8.36 (d, C_3 naph, 1H, $^3J_{\text{H-H}} = 7.8$ Hz), 7.75 (d, 1H, $\text{HN}=\text{CH}$, $^3J_{\text{H-H}} = 12.7$ Hz), 6.78-7.40 (m, 9H), 3.06 (d sept, 4H, CHMe_2), 1.22 (dd, 24H, CHMe_2). Anal. Calcd. for $\text{C}_{36}\text{H}_{42}\text{N}_2\text{O}_2$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.84; H, 7.90; N, 5.25.

Synthesis of 2,7-Bis-{[(E)-2,6-diisopropyl-phenylimino]-methyl}-1,8-bis-trimethylsiloxy-naphthalene ($\text{TMS}_2\text{-FI}^2$). The reagents 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene ($\text{H}_2\text{-FI}^2$, 589 mg, 1.10 mmol) and LiCH_2TMS (228.2 mg, 2.424 mmol) were combined in a reaction flask in the glovebox. On the vacuum line, dry THF (25 mL) was added at -78°C and the mixture was stirred for 30 min, followed by stirring for 30 min at 0°C . The volatiles were next removed *in vacuo*, and the resulting solid was dissolved in 20 mL dry dichloromethane. Next, trimethylchlorosilane (0.35 mL, 2.7 mmol) was added with stirring, and

the resulting solution became hazy over a period of 4.5 h. The reaction mixture was then filtered, and volatiles were removed from the filtrate *in vacuo*. Pure orange product was obtained by washing the resulting orange/brown solid with cold pentane (5 mL). Yield, 598 mg (80%). X-ray quality single crystals were obtained by cooling a saturated pentane solution at -10°C. Spectroscopic and analytical data for **TMS₂-FI²** are as follows. ¹H NMR (CDCl₃, 23°C, 499.447MHz): δ 8.762 (s, 2H, HC=N), 8.475 (d, 2H, ³J_{H-H} = 8.457 Hz, naph C3), 7.639 (d, 2H, ³J_{H-H} = 8.641 Hz, naph C4), 7.297 (d, 2H, ³J_{H-H} = 7.537 Hz, dipp *p*), 7.231 (t, 4H, ³J_{H-H} = 7.354 Hz, dipp *m*), 3.152 (sept, 4H, ³J_{H-H} = 6.802 Hz, CHMe₂), 1.307 (s, 24H, CHMe₂), 0.227 (s, 18H, SiMe₃). ¹³C NMR (CDCl₃, 23°C, 100.745 MHz) δ 158.447, 154.442, 150.080, 140.512, 138.032, 125.771, 124.647, 124.214, 123.351, 123.267, 122.460, 28.111, 24.214, 23.564, 0.387. Anal. Calcd. for C₃₆H₄₂N₂O₂: C, 74.28; H, 8.61; N, 4.13. Found: C, 74.26; H, 8.60; N, 4.15.

Synthesis of {2,7-di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalenediolato}bis-[(trichloro)-(tetrahydrofuran)Zr(IV)] (FI²-Zr₂). Under an N₂ atmosphere, the reagent 2,7-di(2,6-diisopropylphenyl)imino-1,8-di(trimethylsiloxy)naphthalene (**TMS₂-FI²**, 484 mg, 0.713 mmol) in 20 mL dry dichloromethane was added dropwise with stirring to a solution of ZrCl₄(THF)₂ (538 mg, 1.43 mmol) in 20 mL dry dichloromethane at -78°C. The solution was then allowed to warm to room temperature and stirred for 1 h before heating to reflux for 24 h. The volatiles were then removed *in vacuo*, and the residue was redissolved in 25 mL dichloromethane and filtered. Next, 20 mL dry toluene was added to the filtrate, and the resulting pure orange product was isolated by filtration. Yield, 762 mg (79%). Attempts at isolating single crystals of **FI²-Zr₂** using standard methods invariably gave powders. Attempts to alkylate Zr with methyl lithium, methyl magnesium bromide, or benzyl magnesium bromide led to an unidentified mixture of

products. Spectroscopic and analytical data for **FI²-Zr₂** are as follows. ¹H NMR (CD₂Cl₂, 23°C, 499.447MHz): δ 12.953 (s, 2H, HC=N), 8.162 (d, 2H, ³J_{H-H}=14.668 Hz, naph C3), 7.620 (d, 2H, ³J_{H-H} = 8.149 Hz, naph C4), 7.501 (t, 2H, ³J_{H-H} = 7.335 Hz, dipp *p*), 7.330 (m, 4H, ³J_{H-H} = 8.964 Hz, dipp *m*), 3.193 (sept, 4H, ³J_{H-H} = 6.520 Hz, CHMe₂), 1.286 (s, 24H, ³J_{H-H} = 6.519 Hz, CHMe₂). ¹³C NMR (CD₂Cl₂, 23°C, 100.745 MHz): δ 171.281, 167.466, 147.524, 144.200, 142.764, 136.481, 134.094, 130.865, 124.656, 119.707, 110.889, 29.032, 23.436. Anal. Calcd. for C₃₆H₄₂N₂O₂: C, 49.29; H, 5.26; N, 2.61. Found: C, 49.68; H, 5.48; N, 2.65. MALDI-TOF-MS: m/z 1074.2 (parent ion calcd 1070.04), 921.9 (-2 THF calcd 925.93), 731.8 (-2 THF and -ZrCl₃ calcd 730.13).

Synthesis of {1,8-(O)₂C₁₀H₄-2,7-[CH=N(2,6-*i*Pr₂C₆H₃)]₂}Ti₂Cl₆(THF)₂ (FI²-Ti₂). Under an N₂ atmosphere, the reagent 2,7-di(2,6-diisopropylphenyl)imino-1,8-di(trimethylsiloxy)naphthalene (TMS₂-FI², 650 mg, 0.713 mmol) in 20 mL dry dichloromethane was added dropwise with stirring to a solution of TiCl₄(THF)₂ (538 mg, 1.43 mmol) in 20 mL dry dichloromethane at -78°C. The reaction mixture became very dark purple as it was allowed to warm to room temperature. After stirring for 1 h, the mixture was heated to reflux for 30 min. After cooling, the mixture was filtered, then the volatiles were removed *in vacuo*. The residue was redissolved in 15 mL dichloromethane, then 15 mL diethyl ether was added and the mixture stored at -10°C overnight. The resulting pure purple product was isolated by filtration. Yield, 660 mg (70%). Attempts at isolating single crystals of **FI²-Ti₂** using standard methods were unsuccessful. Attempts to alkylate Ti with methyl lithium, methyl magnesium bromide, or benzyl magnesium bromide led to an unidentified mixture of products. Spectroscopic and analytical data for **FI²-Ti₂** are as follows. ¹H NMR (CDCl₃, 23°C, 499.447MHz): δ 13.12 (s, 2H, HC=N), 8.08 (d, 2H, ³J_{H-}

$_{\text{H}}=14.93$ Hz, naph C3), 7.56 (d, 2H, $^3J_{\text{H-H}} = 8.497$ Hz, naph C4), 7.46 (t, 2H, $^3J_{\text{H-H}} = 7.72$ Hz, dipp *p*), 7.33-7.24 (m, 4H, $^3J_{\text{H-H}} = 7.98$ Hz, dipp *m*), 3.27 (sept, 4H, $^3J_{\text{H-H}} = 6.78$ Hz, *CHMe*₂), 1.31 (s, 24H, $^3J_{\text{H-H}} = 6.70$ Hz, *CHMe*₂). ¹³C NMR (CDCl₃, 23°C, 100.745 MHz): δ 171.242, 166.524, 147.178, 144.166, 136.150, 134.254, 130.624, 124.542, 119.906, 119.595, 109.446, 28.955, 23.749. Anal. Calcd. for C₄₄H₅₆Cl₆N₂O₄Ti₂: C, 53.63; H, 5.73; N, 2.84. Found: C, 53.44; H, 5.62; N, 2.76. MALDI-TOF-MS: *m/z* 844.8 (parent ion -2 THF calcd 840.02).

Ethylene + Olefin Copolymerization Experiments. On the high vacuum line (10⁻⁵ Torr), ethylene (co)polymerizations were carried out in 250 mL round-bottom three-neck flasks equipped with a large magnetic stirring bar, Morton indentations, and a thermocouple probe. In a typical experiment, the desired amount of comonomer was vacuum-transferred into a graduated flask at -78°C, then the comonomer was injected into a pre-assembled, degassed reactor containing toluene (50 mL) and MAO (500 equiv relative to metal). The mixture was pre-saturated under of ethylene (1.0 atm) and equilibrated at the desired reaction temperature using an external bath. The catalytically-active species was freshly generated in toluene (4.0 mL) and MAO (500 eq relative to metal). After an activation time (~30 min), the catalyst solution was then quickly injected into the rapidly stirred flask using a gas-tight syringe equipped with a flattened spraying needle. The temperature of the toluene solution was monitored in representative experiments using a thermocouple (OMEGA Type K thermocouple with a Model HH21 microprocessor thermometer). The reaction exotherm temperature rise was invariably less than 5°C during these polymerizations. After a measured time interval, the polymerization was quenched by the addition of 2% acidified methanol (15 mL). More methanol (500 mL) was then added, and the polymer was collected by filtration, washed with methanol and 10% aqueous

HCl, and dried on the high vacuum line overnight to a constant weight. Ethylene homopolymerizations were carried out using a similar procedure.

Ethylene + Methylenecycloalkane Copolymerization Experiments. On the high vacuum line (10^{-5} Torr), ethylene + methylenecycloalkane copolymerizations were carried out in 25 mL flasks equipped with a magnetic stirring bar, Morton indentations, and a thermocouple probe. In a typical experiment, in the glove-box, measured amounts of catalyst and cocatalyst were loaded into a 25 mL flask, which was then evacuated on the vacuum line. Freshly distilled comonomer (3 mL) was next syringed into the flask at the desired temperature. The mixture was vigorously stirred for 2 min for activation. Following this procedure, the flask was then exposed to 1.0 atm of ethylene. The temperature of the solution was monitored in representative experiments using a thermocouple (OMEGA Type K thermocouple with a Model HH21 microprocessor thermometer). The reaction exotherm temperature rise was invariably less than 5 °C during these polymerizations. After a measured time interval, the polymerization was quenched by the addition of toluene followed by 1.5 mL 2% acidified methanol. Another 250 mL methanol was then added and the polymer was collected by filtration, washed with methanol, and dried on the high vacuum line overnight to a constant weight.

X-Ray Crystal Structure Determinations of $\text{H}_2\text{-FI}^2$ and $\text{TMS}_2\text{-FI}^2$. Crystals of $\text{H}_2\text{-FI}^2$ suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane solution at room temperature. In air, the crystals were placed on a glass slide and covered with dry Infineum V8512 oil. Crystals of $\text{TMS}_2\text{-FI}^2$ suitable for X-ray diffraction were obtained by slow cooling of a saturated pentane solution to -10 °C. Inside the glovebox, the crystals were placed on a glass slide and covered with dry Infineum V8512 oil. The crystals were then

removed from the box. Suitable crystals of **H₂-FI²** and **TMS₂-FI²** were selected under a microscope using plane-polarized light. The crystals were separately mounted on a glass fiber and transferred to a Bruker SMART 1000 CCD area detector diffractometer in a nitrogen cold stream at 153 (2) K. Diffraction data were obtained with a fine focus, sealed tube Mo K α radiation source ($\lambda = 0.71073$ Å) and a graphite monochromator. Twenty frames (20 s exposures, 0.3° slices) were collected in three areas of space to determine the orientation matrix. The parameters for data collection were determined by the peak intensities and widths from the 60 frames used to determine the orientation matrix. The faces of the crystals were then indexed and data collection was begun. After data collection, the frames were integrated, the initial crystal structures were solved by direct methods, the structure solutions were refined through successive least squares cycles and subjected to face-indexed absorption corrections. For **H₂-FI²**, the refinements were carried to convergence with the hydrogen atoms of the two imine functionalities and the two phenol functionalities located in the electron difference map, while the remaining hydrogen atoms were placed in idealized positions and refined isotropically with fixed U_{eq} under standard riding model constraints. For **TMS₂-FI²**, The refinements were carried to convergence with the hydrogen atoms placed in idealized positions and refined isotropically with fixed U_{eq} under standard riding model constraints. Crystal data, data collection, and refinement parameters are summarized in Table 1 and in the Crystallographic Information File (CIF, see Supporting Information).

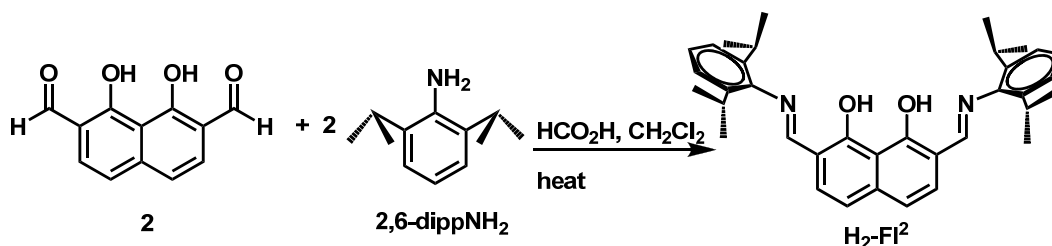
Results

The goal of this study was to investigate the generality and scope of nuclearity and cooperativity effects in binuclear group 4 olefin polymerization catalysis. For this study, we designed and synthesized a new family of *non-cyclopentadienyl* bimetallic group 4 phenoxyiminato complexes to probe the generality of the ‘bimetallic effect’ first identified in CGC-group 4 complexes.^{5,15,17} There, covalently tethered CGC centers (Figure 1-2) exhibit enhanced polymerization activity, selectivity for copolymerization, and product molecular weight. We now sought to assess the consequences of: 1) deleting the cyclopentadienyl ligation, 2) contracting the M···M distance, 3) rigidifying the metal binding, 4) introducing phenoxyimine ligation. The new family of bimetallic complexes we synthesized were the phenoxyiminato group 4 complexes, $\{1,8-(\text{O})_2\text{C}_{10}\text{H}_4-2,7-[\text{CH}=\text{N}(2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)]_2\}\text{Zr}_2\text{Cl}_6(\text{THF})_2$ (Figure 1-4, **FI²-Zr₂**) and the analogous titanium complex $\{1,8-(\text{O})_2\text{C}_{10}\text{H}_4-2,7-[\text{CH}=\text{N}(2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)]_2\}\text{Ti}_2\text{Cl}_6(\text{THF})_2$ (Figure 1-4, **FI²-Ti₂**). It will be seen that increasing the nuclearity of these phenoxyiminato group 4 complexes significantly enhances activity and increases comonomer enchainment selectivity, and that Ti vs. Zr polymerization activities and selectivities are quite different.

I. Synthesis and Characterization of Binucleating Di-phenoxyimine Ligand Precursor 2,7-Di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene (H₂-FI²). The precursor to the present ligand, 2,7-diformyl-1,8-dihydroxynaphthalene (**2**), was synthesized according to the literature procedure²⁶ with some minor modifications. Pure 2,7-diformyl-1,8-bis(methyloxymethoxy)naphthalene (**1**) was obtained by following the procedure outlined by Glaser and coworkers, however, after workup, purification of the orange crude product was

achieved by repeated washing with ethanol to afford the bright yellow product. The binucleating di-phenoxyimine ligand, **H₂-FI²**, was synthesized from **2** following the general condensation methodology outlined by Grubbs and coworkers for mononuclear ligands (Scheme 1-2).²⁹ Under reflux in dichloromethane, condensation of 2,6-diisopropylaniline and **2** in the presence of formic acid as a catalyst and molecular sieves as a water scavenger favors the formation of **H₂-FI²** in good yield. Removal of excess 2,6-diisopropylaniline was accomplished here by repeated washing of the reaction residue with hexanes. The unexpected ¹H NMR spectral characteristics of **H₂-FI²** (see Experimental Section for data) include magnetically inequivalent hydroxyl protons far downfield and a broad, dissymmetric aromatic region. Treatment of **H₂-FI²** with D₂O results in the immediate disappearance of the two resonances in the ¹H NMR spectrum at δ 13.5 and 14.7 ppm, indicating that they are –OH protons. Recording the spectrum over a temperature range (0 °C to 140 °C) reveals a dynamic process (Figure 1-6), and in conjunction with the single crystal X-ray structure, indicates that the structure of **H₂-FI²**

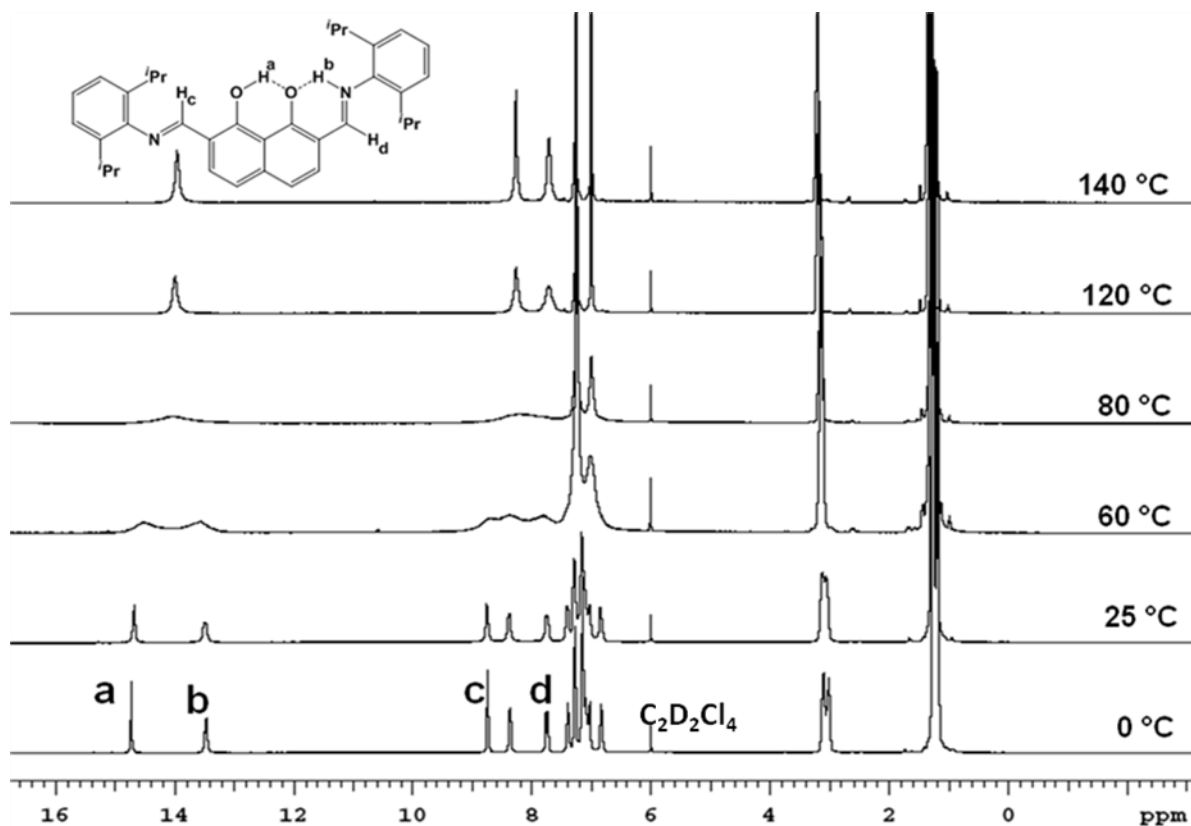
Scheme 1-2. Synthetic route for binucleating ligand precursor **H₂-FI²**

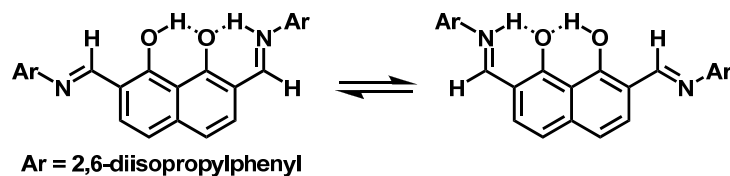


is instantaneously dissymmetric and fluxional in solution (see Scheme 1-3 and Figure 1-8 below), with an imine N being reversibly protonated/deprotonated by the adjacent hydroxyl group. At 0 °C, the proton exchange is slow enough on the NMR time scale that one

dissymmetric species is detected, and the peaks are sharp. This low temperature spectrum may be assigned as a solution structure which is the same as the solid state structure, i.e. where one imine N is protonated by the adjacent hydroxyl group, and the other imine N-aryl group is not protonated and is bent away from the hydroxyl group (see Scheme 1-3 and Figure 1-8 below). The doublet at δ 13.5 ppm is assigned as the hydrogen bound to nitrogen, and it is coupled ($^3J_{\text{H-H}} = 12.7$ Hz) to the doublet at δ 7.8 ppm. The singlets at δ 12.4 and 8.8 ppm are assigned as the hydroxyl proton and the imine C-H proton which is bent away from the naphthyl core, respectively. As the solution is warmed in the NMR spectrometer, a number of peaks

Figure 1-6. Variable-temperature ^1H NMR (400MHz) spectra of ligand **H₂-FI²** in $\text{C}_2\text{D}_2\text{Cl}_4$ solution showing dynamic proton exchange between 0 °C to 140 °C



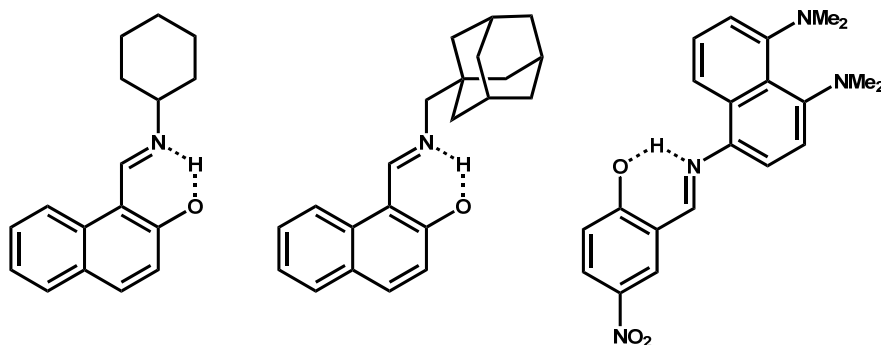
Scheme 1-3. Equilibrium proton exchange observed for ligand **H₂-FI²**

progressively broaden and by ~ 80 °C have coalesced. Above ~ 80 °C, these peaks sharpen as expected for a dynamic process. Above 120 °C, the two signals for the acidic protons have merged to a single peak, the aromatic region has simplified from eight signals to four, and the signals for the isopropyl groups merge to one peak each for the -CH (septet) and -CH₃ (doublet) groups.

II. Molecular Structure of Ligand H₂-FI². A summary of crystal structure data for the ligand **H₂-FI²** is presented in Table 1, selected bond distances and angles for **H₂-FI²** are summarized in Table 1-2, and a drawing is shown in Figure 1-8. The imine and hydroxyl hydrogen atoms of the molecule (Figure 1-8; H1a, H2d, H13, and H24) were located in the difference map, while the remaining hydrogen atoms were placed in idealized positions. As mentioned above, the imino substituents adopt dissymmetric positions relative to the naphthalene core. One imine substituent is protonated, causing it to be drawn proximate to the naphthalene core by a H-bonding interaction with the adjacent deprotonated O atom. This half of the molecule is keto-amine in nature, with the C-O bond being slightly shorter (1.289(2) Å) and having double bond character relative to other phenoxyimine C-O bonds (1.355(2) Å). This type of keto-amine structure in the solid state has been described in at least three other examples of phenoxyimine molecules (Figure 1-7).³⁰ The neighboring imine substituent is not protonated, and

is consequently bent away from the hydroxyl region due to the absence of an available H-bonding interaction. This half of the molecule has bond lengths very similar to other phenoxyimines.³⁰ The naphthalene core and the two imine groups all lie in the same plane, however the N-aryl groups both lie orthogonal to the naphthalene core likely due to the unfavorable non-bonded interactions between the hydroxyl groups and the bulky isopropyl groups.

Figure 1-7. Examples of phenoxyimine compounds which display keto-amine solid state structures³⁰

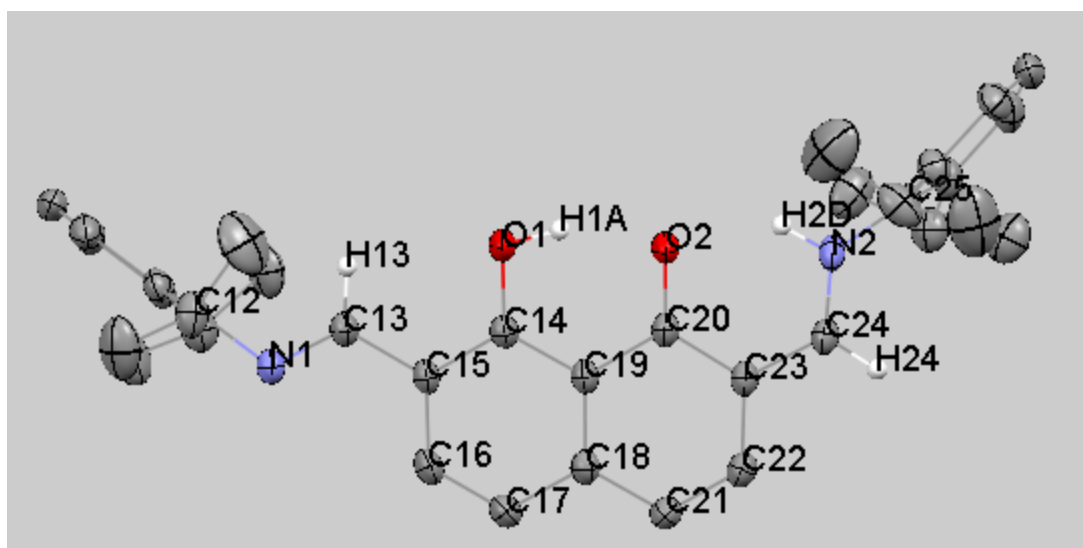


III. Synthesis and Characterization of Binucleating Phenoxyimine Ligand Precursor

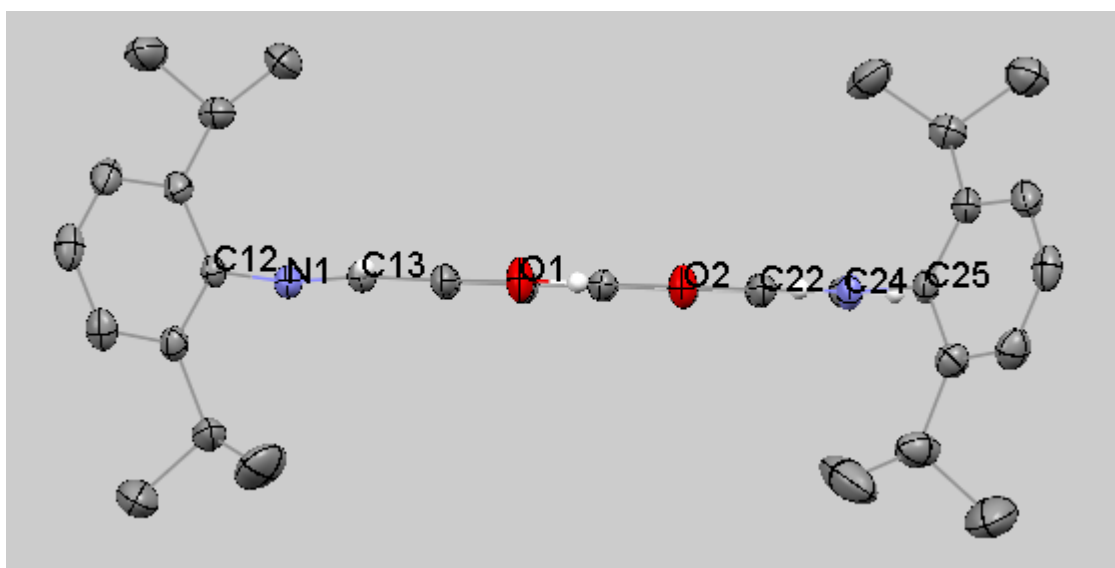
2,7-Di(2,6-diisopropylphenyl)imino-1,8-di(trimethylsiloxy)naphthalene (TMS₂-FI²). Similar to the reported chemistry of mononuclear phenoxyiminato ligands,¹¹ reactions of **H₂-FI²** or **Li₂-FI²** with group 4 metal synthons led to inseparable mixtures of products. In order to improve selectivity in the group 4 metalation reactions, the silylated derivative **TMS₂-FI²** was synthesized by LiCH₂TMS deprotonation and subsequent addition of trimethylchlorosilane

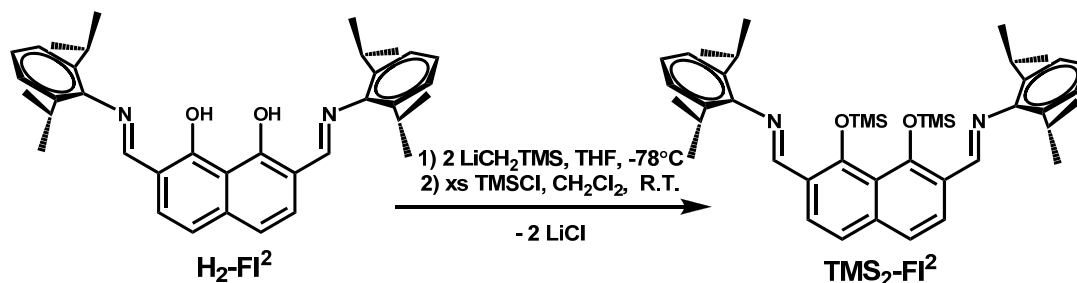
Figure 1-8. The molecular structure and atom numbering scheme for 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene (**H₂-FI²**). Thermal ellipsoids are drawn at the 50% probability level (a) Front side view of naphthyl group, and (b) side view of naphthyl plane

(a)



(b)



Scheme 1-4. Synthetic route for binucleating ligand precursor **TMS₂-FI²**

(Scheme 1-4). In contrast to procedures reported for mononucleating phenoxyiminato ligands,^{11a} heating is not required for complete silylation, and, in our hands, heating decomposes the ligand solutions to form unidentified products. The ¹H NMR spectral characteristics of **TMS₂-FI²** show that the molecule adopts a symmetric geometry as expected due to the introduction of non-H-bonding, bulky trimethylsilyl groups which displace the N-aryl substituents furthest away from the central naphthalene core. The molecular structure of **TMS₂-FI²** is confirmed by a single crystal X-ray structure determination (see Figure 1-9 below). It will be seen that clean group 4 metalations (*vide infra*) are readily accomplished with this reagent.

IV. Molecular Structure of Compound TMS₂-FI². A summary of crystal structure data for **TMS₂-FI²** is presented in Table 1-1, selected bond distances and angles are summarized in Table 1-3, and a drawing is shown in Figure 1-9. Similar to the structure of **H₂-FI²**, **TMS₂-FI²** is planar, however the N-aryl groups are orthogonal to the naphthalene plane, and one trimethylsilyl group is located on either side of the naphthalene plane. The keto-amine metrical parameters observed in **H₂-FI²** are not evident in **TMS₂-FI²**, and all bonds and angles are similar to those in more typical phenoxyimine compounds.³⁰ The lack of intramolecular H-bonding

interactions and the bulky nature of the N-aryl and trimethylsilyl groups forces the imine groups to rotate away from the center of the naphthalene core.

Table 1-1. Summary of the Crystal Structure Data for **H₂-FI²** and **TMS₂-FI²**

Complex	H₂-FI²	TMS₂-FI²
Formula	C ₃₆ H ₄₂ N ₂ O ₂	C ₄₂ H ₅₈ N ₂ O ₂ Si ₂
Formula Weight	534.72	679.08
Crystal Dimensions (mm)	0.506 x 0.326 x 0.186	0.598 x 0.232 x .070
Crystal System	Monoclinic	Monoclinic
<i>a</i> , Å	10.0592(8)	26.914(6)
<i>b</i> , Å	23.0731(18)	9.765(2)
<i>c</i> , Å	13.9928(11)	16.289(4)
α , deg	90	90
β , deg	109.4350(10)	109.311(3)
γ , deg	90	90
<i>V</i> , Å ³	3062.6(4)	4040.1(15)
Space group	P2(1)/n	Cc
<i>Z</i> value	4	4
<i>D</i> _{calc} , mg/m ³	1.160	1.116
Temp K	153(2)	153(2)
μ , mm ⁻¹	0.071	0.123
Radiation	MoK α	MoK α
2 θ range, deg	1.77 to 28.91	1.60 to 28.78
Intensities (unique, (<i>R</i> _{int}))	7436, 0.0299	9137, 0.0828
<i>R</i>	0.0616	0.0462
w <i>R</i> ₂	0.1614	0.1123

Table 1-2. Selected Bond Distances (Å) and Angles (deg) for compound **H₂-FI²**

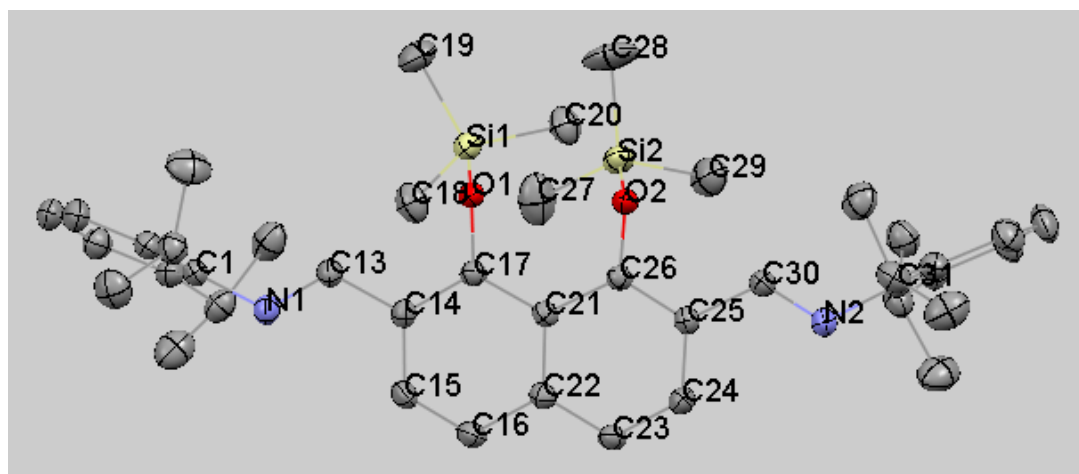
Distances			
O(2)-C(20)	1.289(2)	N(2)-C(25)	1.438(2)
O(1)-C(14)	1.3472(19)	C(18)-C(17)	1.412(2)
C(20)-C(23)	1.436(2)	C(18)-C(21)	1.435(2)
C(20)-C(19)	1.449(2)	C(12)-N(1)	1.4286(19)
C(19)-C(18)	1.414(2)	C(22)-C(21)	1.353(2)
C(19)-C(14)	1.428(2)	C(22)-C(23)	1.426(2)
C(14)-C(15)	1.399(2)	N(1)-C(13)	1.279(2)
C(15)-C(16)	1.408(2)	C(16)-C(17)	1.372(2)
C(15)-C(13)	1.464(2)	C(23)-C(24)	1.409(2)
N(2)-C(24)	1.306(2)		
Angles			
O(2)-C(20)-C(23)	121.84(13)	C(14)-C(15)-C(13)	119.49(14)
O(2)-C(20)-C(19)	120.39(13)	C(16)-C(15)-C(13)	121.77(13)
C(23)-C(20)-C(19)	117.76(14)	C(24)-N(2)-C(25)	128.79(14)
C(18)-C(19)-C(14)	119.48(13)	C(1)-C(12)-N(1)	120.36(14)
C(18)-C(19)-C(20)	120.29(13)	C(8)-C(12)-N(1)	117.93(14)
C(14)-C(19)-C(20)	120.23(14)	C(13)-N(1)-C(12)	116.33(13)
O(1)-C(14)-C(15)	119.10(14)	N(2)-C(24)-C(23)	122.35(14)
O(1)-C(14)-C(19)	120.50(13)	C(26)-C(25)-N(2)	118.65(14)
C(15)-C(14)-C(19)	120.40(14)	C(33)-C(25)-N(2)	117.90(14)
C(14)-C(15)-C(16)	118.74(14)	N(1)-C(13)-C(15)	122.81(15)

Table 1-3. Selected Bond Distances (Å) and Angles (deg) for compound **TMS₂-FI²**

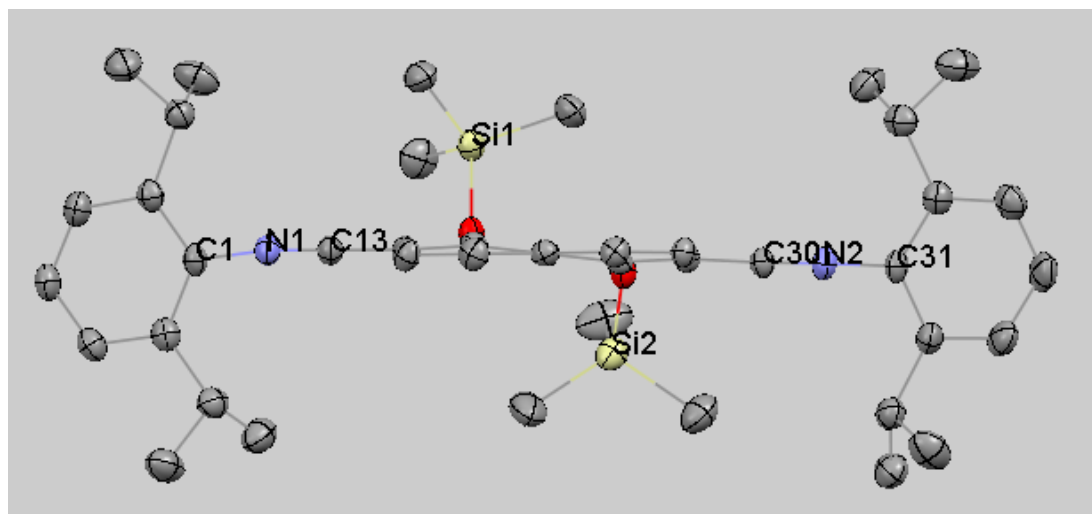
Distances			
C(1)-N(1)	1.421(3)	C(22)-C(23)	1.412(3)
C(13)-N(1)	1.274(3)	C(23)-C(24)	1.367(3)
C(13)-C(14)	1.471(3)	C(24)-C(25)	1.415(3)
C(14)-C(17)	1.396(3)	C(25)-C(26)	1.386(3)
C(14)-C(15)	1.411(3)	C(25)-C(30)	1.470(3)
C(15)-C(16)	1.356(3)	C(26)-O(2)	1.361(2)
C(16)-C(22)	1.417(3)	C(27)-Si(2)	1.857(3)
C(17)-O(1)	1.370(2)	C(28)-Si(2)	1.843(3)
C(17)-C(21)	1.427(3)	C(29)-Si(2)	1.851(3)
C(18)-Si(1)	1.856(2)	C(30)-N(2)	1.262(3)
C(19)-Si(1)	1.846(2)	C(31)-N(2)	1.425(2)
C(20)-Si(1)	1.849(2)	O(1)-Si(1)	1.6822(15)
C(21)-C(22)	1.426(3)	O(2)-Si(2)	1.6765(15)
C(21)-C(26)	1.441(2)		
Angles			
C(9)-C(1)-N(1)	117.48(17)	O(2)-C(26)-C(21)	120.45(17)
C(2)-C(1)-N(1)	120.93(18)	C(25)-C(26)-C(21)	120.67(16)
N(1)-C(13)-C(14)	120.58(18)	N(2)-C(30)-C(25)	121.31(17)
C(17)-C(14)-C(15)	119.24(17)	C(32)-C(31)-C(39)	121.03(17)
C(17)-C(14)-C(13)	121.30(17)	C(32)-C(31)-N(2)	119.48(18)
C(15)-C(14)-C(13)	119.44(17)	C(39)-C(31)-N(2)	119.21(17)
C(16)-C(15)-C(14)	121.30(18)	C(13)-N(1)-C(1)	121.56(18)
C(15)-C(16)-C(22)	120.59(18)	C(30)-N(2)-C(31)	120.28(17)
O(1)-C(17)-C(14)	118.46(17)	C(17)-O(1)-Si(1)	124.56(12)
O(1)-C(17)-C(21)	120.89(16)	C(26)-O(2)-Si(2)	127.82(12)
C(14)-C(17)-C(21)	120.64(17)	O(1)-Si(1)-C(19)	104.29(10)
C(22)-C(21)-C(17)	117.73(16)	O(1)-Si(1)-C(20)	111.42(9)
C(22)-C(21)-C(26)	117.54(17)	C(19)-Si(1)-C(20)	110.55(12)
C(17)-C(21)-C(26)	124.72(17)	O(1)-Si(1)-C(18)	109.54(9)
C(23)-C(22)-C(16)	120.16(17)	C(19)-Si(1)-C(18)	111.01(12)
C(23)-C(22)-C(21)	120.11(17)	C(20)-Si(1)-C(18)	109.92(11)
C(16)-C(22)-C(21)	119.73(18)	O(2)-Si(2)-C(28)	102.82(11)
C(24)-C(23)-C(22)	120.51(18)	O(2)-Si(2)-C(29)	109.12(11)
C(23)-C(24)-C(25)	121.04(18)	C(28)-Si(2)-C(29)	109.70(15)
C(26)-C(25)-C(24)	119.60(17)	O(2)-Si(2)-C(27)	111.30(11)
C(26)-C(25)-C(30)	121.15(16)	C(28)-Si(2)-C(27)	115.21(17)
C(24)-C(25)-C(30)	119.25(17)	C(29)-Si(2)-C(27)	108.49(14)
O(2)-C(26)-C(25)	118.88(16)		

Figure 1-9. Molecular structure and numbering scheme for 2,7-di(2,6-diisopropylphenyl)imino-1,8-di(trimethylsiloxy)naphthalene (**TMS₂-FI²**). Thermal ellipsoids are drawn at the 50% probability level. (a) Top view of naphthyl skeleton, and (b) side view of the naphthyl plane.

(a)



(b)

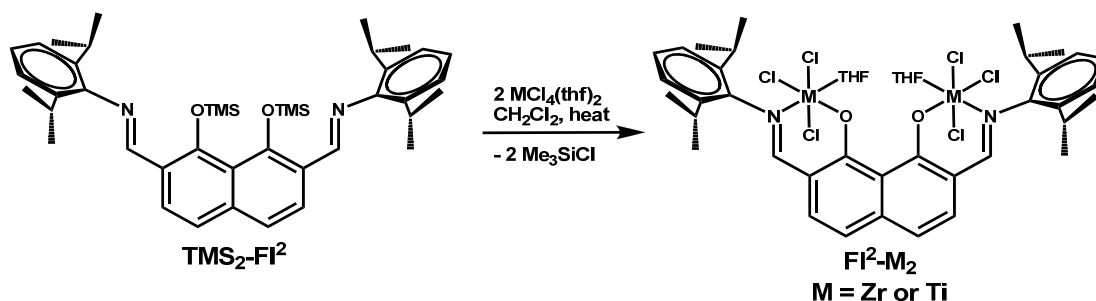


V. Synthesis and Characterization of Bimetallic Phenoxyiminato Group 4 Complexes {1,8-(O)₂C₁₀H₄-2,7-[CH=N(2,6-*i*-Pr₂C₆H₃)]₂}Zr₂Cl₆(THF)₂ (**FI²-Zr₂**) and {1,8-(O)₂C₁₀H₄-2,7-[CH=N(2,6-*i*-Pr₂C₆H₃)]₂}Ti₂Cl₆(THF)₂ (**FI²-Ti₂**). General methodologies for

selectively synthesizing mono-phenoxyiminato group 4 complexes have been reported by several groups.¹¹ Selective addition of a *single phenoxyiminato ligand* to a group 4 metal precursor is best achieved using the trimethylsiloxy derivative of the phenoxyimine ligand and the bis-THF adduct of appropriate the group 4 metal chloride.¹¹ In this way, clean double-metalation of both phenoxyimine functionalities of the **FI**² ligand is accomplished by addition of ZrCl₄(THF)₂ at low temperature, followed by gradual increase in temperature to reflux for 24 hours (Scheme 1-5). The reaction progress can be followed by monitoring the evolution of trimethylchlorosilane in the ¹H NMR spectrum. In the ¹H NMR spectrum, a large displacement of the imine proton resonance from $\delta \sim 8.8$ ppm in **TMS**₂-**FI**² to ~ 13.0 ppm in **FI**²-**Zr**₂ is indicative of Zr coordination. Analytically pure product may be obtained by recrystallization from a mixture of dichloromethane and toluene at -10 °C. Since X-ray quality single crystal growth attempts were unsuccessful, the bimetallic constitution was unambiguously verified by MALDI-TOF MS and elemental analysis. The elemental analysis is consistent with one THF ligand bound to each quasi-octahedral Zr center, in agreement with the MALDI-TOF data indicating that the THF ligands remain bound when the complex is ionized.

In a procedure similar to the synthesis of **FI**²-**Zr**₂, **FI**²-**Ti**₂ was synthesized via the same basic trimethylchlorosilane elimination reaction (Scheme 1-5).¹¹ However, in contrast to the synthesis of **FI**²-**Zr**₂, complete evolution of trimethylchlorosilane occurs in only 30 minutes of reflux for M = Ti, as compared to the 24 hours required for **FI**²-**Zr**₂. Analytically pure product is obtained by recrystallization from a mixture of dichloromethane and diethyl ether. Attempts to isolate X-ray quality single crystals were unsuccessful. However, unambiguous characterization using NMR spectroscopy, elemental analysis, and MALDI-TOF MS confirm the bimetallic

Scheme 1-5. Synthetic route to metal complexes

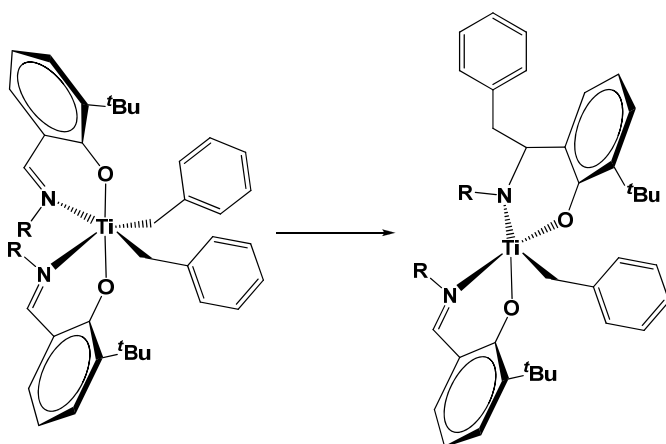


constitution. The elemental analysis is in agreement with one THF ligand being bound to each quasi-octahedral Ti center. The MALDI mass spectrum indicates facile loss of both THF ligands with the major peak appearing at $m/z = 844.8$, which corresponds to the mass of $\text{FI}^2\text{-Ti}_2$ minus the mass of two THF molecules. The ^1H NMR spectrum of $\text{FI}^2\text{-Ti}_2$ indicates a shift of the imine proton resonance from δ 8.8 to 13.1 ppm on coordination of Ti and elimination of trimethylchlorosilane. As in the case of $\text{FI}^2\text{-Zr}_2$, this is consistent with Ti coordination to N.

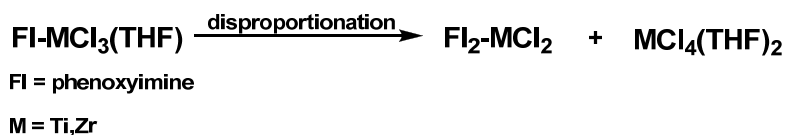
VI. Polymerization Properties of Bimetallic Complexes $\text{FI}^2\text{-Zr}_2$ and $\text{FI}^2\text{-Ti}_2$ Activated with MAO. Activation of $\text{FI}^2\text{-Zr}_2$ and $\text{FI}^2\text{-Ti}_2$ is achieved by vigorously shaking these compounds with a solution of MAO in toluene for 30 minutes. These complexes alone are insoluble in toluene, however they are readily dissolved and activated under these reaction conditions. The polymerization studies were limited to using MAO as the cocatalyst since neither benzyl nor methyl derivatives of $\text{FI}^2\text{-Zr}_2$ and $\text{FI}^2\text{-Ti}_2$ could be obtained cleanly. Group 4 mono- and bis-phenoxyiminato alkyls are prone to decomposition by several identified pathways, including ligand redistribution and nucleophilic attack on the imine carbon center to form phenoxyamides. Phenoxyiminato group 4 complexes bearing methyl or benzyl ligands are known to undergo reaction by either intermolecular or intramolecular pathways to convert the

imine functionality to an amido group (Scheme 1-6)³¹ Mono-phenoxyiminato group 4 complexes are also reported to undergo disproportionation (Scheme 1-7).^{11a,32}

Scheme 1-6. Intramolecular decomposition pathway of bis(phenoxyiminato) group 4 alkyl complexes



Scheme 1-7. Intermolecular ligand rearrangement as a decomposition pathway for mono(phenoxyiminato) group 4 complexes



In the present study, other methods of activation, such as the *in situ* addition of Al^iBu_3 , followed by $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$,^{12b} afforded very low polymerization activity.

A. Ethylene Homopolymerization Studies. Ethylene homopolymerizations were carried out under conditions identical³³ to those previously reported for CGC catalysts **Zr₂** and **Ti₂**.⁵ Procedures for all polymerizations were those designed to minimize mass transfer and exotherm

effects.⁵ The activities for **FI²-Ti₂** are modest and are slightly lower than those of **FI²-Zr₂** (Table 1-4, entry 6 versus 2). However, at 40 °C, **FI²-Zr₂** produces polyethylene with an activity ~6.4x that of mononuclear **FI-Zr₁**, and **FI²-Ti₂** produces polyethylene with an activity ~1.9x that of mononuclear **FI-Ti₁**. As reported for other mononuclear phenoxyiminato catalysts,^{11c,d} **FI-Zr₁** and **FI-Ti₁** produce linear, high M_w polyethylenes, however the substantial polydispersities indicate that multiple catalytic sites or conformations may be involved. The binuclear complexes **FI²-Zr₂** and **FI²-Ti₂** also produce very high molecular weight linear polyethylenes at 24 °C, as indicated by the insolubility of the polymeric products. However, increasing the polymerization temperature to 40 °C lowers the product M_w to ~155,000 g/mol for **FI²-Zr₂**-mediated polymerizations. For **FI²-Ti₂**-mediated polymerizations at 40 °C, the polyethylene M_w is lowered to ~297,000 g/mol, slightly lower than the polyethylene derived from **FI-Ti₁** under the same conditions (entry 7 vs. 8). GPC-derived polydispersities are, however, somewhat greater than 2.0 suggesting that multiple active sites or conformations may be present during the polymerization process. As previously reported, broadened polyethylene polydispersities are commonly observed with phenoxyiminato polymerization catalysts.³⁴ The melting points of the ethylene homopolymers were determined by DSC, and the melting point values are indicative of linear polyethylene. The ethylene homopolymers were also analyzed by ¹H and ¹³C NMR spectroscopy which further indicates that the polymers are linear polyethylenes with no detectable branching. The ¹H NMR spectral integrals indicate an approximate ratio of vinylic endgroups to saturated endgroups of ~1:8. Saturated endgroups suggest that the termination pathway is chain transfer to Al (e.g., Scheme 1-8),³⁵ while vinylic endgroups indicate β-hydride elimination (either to metal or to monomer).^{3,4,5} Chain transfer to Al has been identified as the major chain transfer pathway

for a bis-phenoxyiminato zirconium catalyst in ethylene homopolymerization.³⁶ In the present case, a 1:8 ratio of unsaturated to saturated endgroups corresponds to approximately 68% chain transfer to Al and 32% β -hydride elimination since every polyethylene chain terminated by chain

Table 1-4. Ethylene Homopolymerization and Ethylene + α -Olefin Copolymerization Results for Catalysts **FI²-Zr₂**, **FI-Zr₁**, **FI²-Ti₂**, and **FI-Ti₁**^a

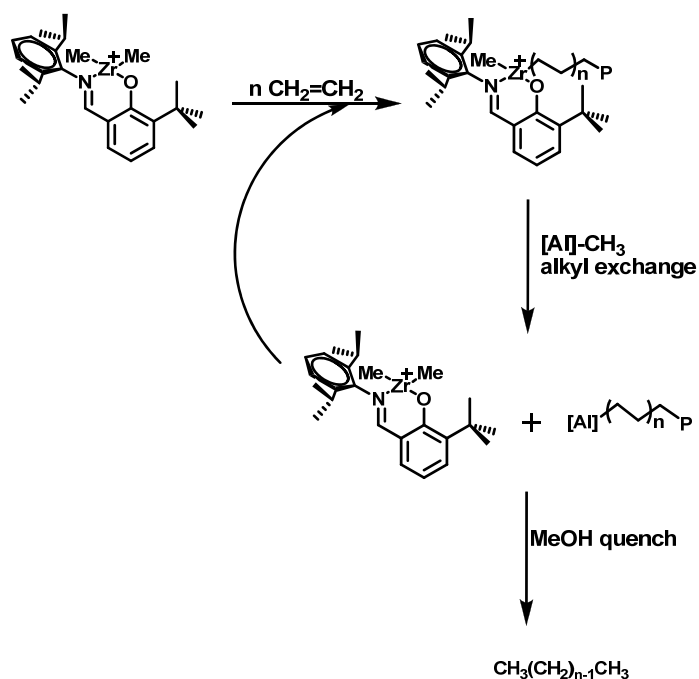
entry	catalyst	co-monomer	temperature (°C)	comonomer conc. (M)	polymer yield (g)	activity ^b (x10 ⁵)	T _m (°C) ^c	10 ³ M _w ^d	M _w /M _n ^d	comonomer incorporation (%) ^e
1	FI-Zr₁	n/a	24	n/a	0.019	2.1	131.8	too insol.	too insol.	n/a
2	FI²-Zr₂	n/a	24	n/a	0.167	16	142.6	too insol.	too insol.	n/a
3	FI-Zr₁	n/a	40	n/a	0.036	3.6	130.3	too insol.	too insol.	n/a
4	FI²-Zr₂	n/a	40	n/a	0.230	23	140.4	155	3.92	n/a
5	FI-Ti₁	n/a	24	n/a	0.025	2.5	135.9	675	23.7	n/a
6	FI²-Ti₂	n/a	24	n/a	0.053	5.3	136.3	too insol.	too insol.	n/a
7	FI-Ti₁	n/a	40	n/a	0.043	4.3	134.8	315	6.55	n/a
8	FI²-Ti₂	n/a	40	n/a	0.082	8.3	135.8	297	4.49	n/a
9	FI-Zr₁	1-octene	40	0.72	0.022	2.2	128.5	22	11.9	4.1
10	FI²-Zr₂	1-octene	40	0.72	0.083	8.3	125.6	105	3.61	7.3
11	FI-Ti₁	1-octene	40	0.72	0.022	2.2	120.3	96	5.46	8.4
12	FI²-Ti₂	1-octene	40	0.72	0.039	3.9	121.7	182	3.33	15.2
13	FI-Ti₁	1-hexene	40	0.72	0.027	2.7	128.6	188	33.6	4.3
14	FI²-Ti₂	1-hexene	40	0.72	0.045	4.5	120.6	76	3.91	9.4
15	FI-Zr₁	1-hexene	40	0.72	0.015	1.0	125.0	21	9.61	7.4
16	FI²-Zr₂	1-hexene	40	0.72	0.150	12	125.8	98	3.31	11.0

^a(Co)polymerizations carried out on a high-vacuum line with 10 μ mol Ti/Zr and MAO as cocatalyst (Al : M⁺ = 1000 : 1) in 50 mL of toluene under 1.0 atm ethylene pressure for 60 to 90 min. ^bGram polymer/[(mol M⁺)·atm·h]. ^cFrom GPC vs polystyrene standards. ^dComonomer incorporation calculated from the ¹³C NMR spectra.³⁷ n/a = not applicable.

transfer to Al has two methyl endgroups, and every polyethylene chain terminated by β -hydride elimination has one methyl and one vinyl endgroup.

Scheme 1-8. Chain Transfer to Aluminum as a Termination Pathway for Ethylene

Polymerization.



B. Ethylene + α -Olefin Copolymerization Studies. Ethylene + 1-hexene and ethylene + 1-octene copolymerization data are presented in Table 1-4. As observed in the ethylene homopolymerizations (*vide supra*), the activities of **FI²-Ti₂** are again slightly lower than those of **FI²-Zr₂** for both ethylene + 1-hexene (Table 1-4, entry 10 vs. 12) and ethylene + 1-octene copolymerizations (Table 1-4, entry 6 vs. 8). However, the activity of **FI²-Ti₂** for both of these copolymerizations is nearly 2x that of **FI-Ti₁** under identical reaction conditions (Table 1-4, entries 7 vs. 8 and 9 vs. 10). While **FI-Zr₁** exhibits extremely low activity for ethylene + 1-hexene copolymerizations and ethylene + 1-octene copolymerizations, note that **FI²-Zr₂** is 12x more active than **FI-Zr₁** for ethylene + 1-hexene copolymerization (Table 1-4, entry 15 vs. 16) and nearly 3x more active than **FI-Zr₁** for ethylene + 1-octene copolymerization (Table 1-4,

entry 10 vs. 9). In regard to selectivity for comonomer enchainment, the selectivity of **FI²-Ti₂** for 1-hexene incorporation is 4.5x that of **FI²-Zr₂** (Table 1-4, entry 10 vs. 11), and 2.2x that of **FI-Ti₁** (Table 1-4, entry 10 vs. 9). The selectivity of **FI²-Zr₂** for 1-hexene incorporation is 1.5x that of **FI-Zr₁** (Table 1-4, entry 16 vs. 15). The selectivity of **FI²-Ti₂** for 1-octene incorporation is 1.8x that of **FI-Ti₁** (Table 1-4, entry 7 vs. 8), and, interestingly, 2.1x that of **FI²-Zr₂** (Table 1-4, entry 8 vs. 6). The selectivity for 1-octene incorporation by **FI²-Zr₂** is 1.8x that of **FI-Zr₁** (Table 1-4, entry 6 versus entry 5). Maximum comonomer incorporation densities are achieved by the Ti catalysts, with 1-octene levels as high as 15.2% achieved for **FI²-Ti₂**. For ethylene + 1-hexene copolymerizations mediated by **FI²-Zr₂**, the copolymer M_w of the copolymer is ~4.7x greater than that mediated by **FI-Zr₁**, however, for those mediated by **FI²-Ti₂**, M_w is nearly half that of **FI-Ti₁**. For the ethylene + 1-octene copolymerizations mediated by **FI²-Zr₂**, the M_w is ~5x than in the same copolymerizations mediated by **FI-Zr₁**. The same trend also holds for the 1-octene copolymerization using **FI²-Ti₂**, although the M_w is only ~2x greater than that of the copolymer obtained using **FI-Ti₁** as catalyst. In all but one case, the PDIs of the polymers derived from binuclear catalysts are narrower than those derived from the mononuclear catalysts. Vinylic endgroups are detected in the ¹H NMR spectra of these copolymers, however accurate determination of the ratio of vinylic to saturated endgroups is not possible due to an overlap of the signals from endgroup methyl groups and butyl branch methyl groups.

C. Ethylene + Methylenecyclopentane (MCP) and Ethylene + Methylenecyclohexane (MCH) Copolymerization Studies. Ethylene + **MCP** and ethylene + **MCH** copolymerization data are presented in Table 1-5. With **MCP** as the solvent, **MCP** is incorporated using the **FI-Ti₁** and **FI²-Ti₂** catalysts at low levels and with moderate polymerization activity. In contrast, **FI²-**

Ti₂ is ~4.5x more active and the copolymer M_w is ~2x greater than the copolymers obtained using **FI-Ti₁** as the catalyst. The low selectivity for comonomer incorporation for both **FI-Ti₁** and **FI²-Ti₂** catalysts (<1%) indicates a substantial barrier for **MCP** insertion. This result is in marked contrast to the ethylene + **MCH** copolymerizations. Under identical reaction conditions, **MCH** is incorporated to a much greater extent for both **FI-Ti₁**- (3.4%) and **FI²-Ti₂** (11.6%) – catalyzed copolymerization. Note also that **FI²-Ti₂** incorporates ~3.4x more **MCH** than does **FI-Ti₁** (Table 1-5, entry 4 vs. 3), and that M_w is ~5x greater for the **FI²-Ti₂**–derived copolymer than for the copolymer obtained with **FI-Ti₁**. The ¹H and ¹³C NMR spectra of the copolymers indicate that **MCP** and **MCH** are incorporated via ring-unopened pathways,^{18a} and the integral ratio of vinylic endgroups to saturated endgroups (~1 : 7) indicates ~65% chain transfer to Al and 35% β-hydride elimination.

It is presumed that the proximate metal center assists in the insertion of comonomers (see more in the Discussion section), and it is likely that the additional methylene group and greater skeletal flexibility of **MCH** versus **MCP**, plays a role in the enhanced comonomer enchainment. Specifically, the geometry of the catalyst/comonomer combination may be more ideal for insertion of **MCH** than for **MCP**. Interestingly, in contrast, the catalysts **FI-Zr₁** and **FI²-Zr₂** do not incorporate measurable quantities of **MCP** or **MCH** under the same polymerization conditions. In fact, polyethylene homopolymer is obtained under these conditions, indicating a marked metal center dependency of the comonomer enchainment selectivity in these types of catalysts.

Table 1-5. Ethylene + **MCA** and Ethylene + α,ω -Diene Copolymerization Results for **FI-Ti₁**, **FI²-Ti₂**, **FI-Zr₁**, and **FI²-Zr₂**.^a

entry	cat	co- monomer	comonomer conc. (M)	polymer yield (g)	activity ($\times 10^3$) ^b	T _m (°C) ^c	10 ³ M _w ^d	M _w /M _n ^d	comonomer incorporation (%) ^e	cis%/trans%
1	FI-Ti₁	MCP	neat	0.025	3.4	128.3	58	20.2	0.4	n/a
2	FI²-Ti₂	MCP	neat	0.115	15	126.4	121	4.01	0.7	n/a
3	FI-Ti₁	MCH	neat	0.080	8.1	124.3	20	13.1	3.4	n/a
4	FI²-Ti₂	MCH	neat	0.096	9.7	124.7	104	3.48	11.6	n/a
5	FI-Zr₁	MCP	neat	0.042	3.3	135.3	n/a	n/a	PE	n/a
6	FI²-Zr₂	MCP	neat	0.026	6.9	134.2	n/a	n/a	PE	n/a
7	FI-Zr₁	MCH	neat	0.031	2.6	130.5	n/a	n/a	PE	n/a
8	FI²-Zr₂	MCH	neat	0.077	6.2	137.9	n/a	n/a	PE	n/a
9	FI-Zr₁	1,5-HD	0.3	0.012	1.0	127.9	34	10.3	7.9	44/56
10	FI²-Zr₂	1,5-HD	0.3	0.151	15	131.5	78	3.22	10.3	60/40
11	FI-Zr₁	1,4-PD	0.3	0.292	29	124.0	73	3.28	2.1	82/18
12	FI²-Zr₂	1,4-PD	0.3	0.742	74	124.0	75	4.81	5.4	69/31
13	FI-Ti₁	1,5-HD	0.3	0.004	0.3	123.8	n/a	n/a	n/a	n/a
14	FI²-Ti₂	1,5-HD	0.3	0.003	0.2	122.6	n/a	n/a	n/a	n/a
15	FI-Ti₁	1,4-PD	0.3	0.008	0.8	123.4	n/a	n/a	n/a	n/a
16	FI²-Ti₂	1,4-PD	0.3	0.007	0.7	121.4	n/a	n/a	n/a	n/a

^aCopolymerizations carried out at room temperature on a high-vacuum line with 10 μ mol Ti/Zr and MAO as cocatalyst (Al : M⁺ = 1000 : 1) under 1.0 atm ethylene pressure. Copolymerizations carried out for 45 to 75 min.

^bGram polymer/[$(\text{mol M}^+) \cdot \text{atm} \cdot \text{h}$]. ^cBy DSC. ^dFrom GPC vs polystyrene standards. ^eComonomer incorporations from

¹³C NMR spectra.^{18a,25a,38} PE = polyethylene (as judged by ¹³C NMR spectroscopy and DSC); n/a = not applicable.

D. Ethylene + 1,5-HD and Ethylene + 1,4-PD Copolymerization Studies. Ethylene + **1,5-HD** and ethylene + **1,4-PD** copolymerization data are presented in Table 1-5. In marked contrast to the **MCA** copolymerizations, **FI-Zr₁** and **FI²-Zr₂** perform far more efficiently than do **FI-Ti₁** and **FI²-Ti₂** in these copolymerizations. For significantly more dilute comonomer concentrations (0.30 M) than employed in the **MCA** copolymerizations above, **1,5-HD** is copolymerized with good incorporation levels (10.3%) and moderate activity using **FI²-Zr₂** as

the catalyst. Compared to **FI-Zr₁**-derived ethylene + **1,5-HD** copolymer, **FI²-Zr₂** enchains 1.3x (Table 1-5, entry 10 vs. 9) more **1,5-HD** at an activity which is 15.3x greater than **FI-Zr₁**. The M_w of the **FI²-Zr₂**-derived copolymer (78,000 g/mol, PDI = 3.22) is 2.3x greater than the M_w of the **FI-Zr₁**-derived copolymer (34,000 g/mol, PDI = 10.3), and the PDI is much less broad for the **FI²-Zr₂**-derived copolymer. In the polymerization process, both **FI²-Zr₂** and **FI-Zr₁** convert all **1,5-HD** units into a mixture of enchaind *cis*- and *trans*-1,3-cyclopentyl fragments (structure C) according to the ¹³C NMR spectra of the copolymers.^{24,25} No signals associated with cross-links are detected in the NMR spectra, however vinylic endgroups (δ 5.1 ppm) and a very small amount of pendant vinylic groups (δ 5.5 ppm) are observed in the ¹H NMR spectra of the copolymers. An approximate ratio of 1:5 was observed for unsaturated to saturated endgroups, corresponding to ~54% chain transfer to Al and 46% β -hydride elimination. The **FI²-Zr₂**-derived copolymer consists of 60% *cis*- and 40% *trans*-1,3-cyclopentyl fragments, while the **FI-Zr₁**-derived copolymer consists of 44% *cis*- and 56% *trans*-1,3-cyclopentyl fragments according to the ¹³C NMR spectroscopic assay.^{24,25} A plausible explanation for this selectivity difference is presented in the Discussion section.

Ethylene + **1,4-PD** copolymerizations proceed with good comonomer incorporation levels and moderate activities using both **FI-Zr₁** and **FI²-Zr₂** catalyst systems. **FI²-Zr₂** turns over with an activity ~2.5x greater than does **FI-Zr₁**, and the **1,4-PD** comonomer is incorporated to ~2.6x greater density using **FI²-Zr₂** as compared to **FI-Zr₁** (Table 1-5, entry 12 vs. 11). The GPC-derived M_w of the **FI²-Zr₂**-derived copolymer (75,000 g/mol, PDI = 4.81) is nearly the same as the **FI-Zr₁**-derived copolymer (73,000 g/mol, PDI = 3.28). According to the ¹³C NMR spectra of the copolymers,²⁵ all **1,4-PD** units are converted to a mixture of *cis*- and *trans*-1,3-

cyclohexyl fragments. No signals associated with cross-links are detected in the NMR spectra, however vinylic endgroups (δ 5.1 ppm) and a small amount of pendant vinylic groups (δ 5.5 ppm) are observed in the ^1H NMR spectra of the copolymers. As in the ethylene + **1,5-HD** copolymers, an approximate ratio of 1:5 was observed for unsaturated to saturated endgroups, corresponding to ~54% chain transfer to Al and 46% β -hydride elimination. The **FI²-Zr₂**-derived copolymer consists of 69% *cis*- and 31% *trans*-1,3-cyclohexyl fragments, and the **FI-Zr₁**-derived copolymer consists of 82% *cis*- and 18% *trans*-1,3-cyclopentyl fragments according to the ^{13}C NMR spectra of the copolymers. Under identical reaction conditions, **FI-Ti₁** and **FI²-Ti₂** produce less than 10 mg of copolymer in these ethylene + α,ω -diene copolymerizations.

Discussion

In the case of the binuclear CGCs (Figure 1-2), it was proposed that when the olefinic bond of an alkene comonomer binds to the first metal center, the second highly electrophilic d^0 metal center can engage in secondary, possibly agostic interactions,³⁹ leading to enhanced comonomer binding affinity and activating ability, thereby modifying relative enchainment and chain transfer rates (Figure 1-1 I and Scheme 1-9). Density functional theory (DFT/B3LYP) calculations on **C1-Zr₂** show that the agostic interaction contributes ~2 kcal/mol stabilization to the coordinated bimetallic α -olefin complex in which the alkyl chain is proximate to the adjacent metal center (Figure 1-10).⁴⁰ It is found that the C7-H bond in structure **II** is elongated by ~0.02 Å, and the effective charge on Zr2 in structure **II** (+1.83) is substantially lower than that of Zr2 in structure **III** (+1.93), further indicating an agostic interaction with Zr2. This agostic stabilization is reasonably associated with the selectivity for olefin comonomer enchainment which is observed

Scheme 1-9. Proposed mechanistic scenario for enhanced α -olefin enchainment by bimetallic CGC catalysts

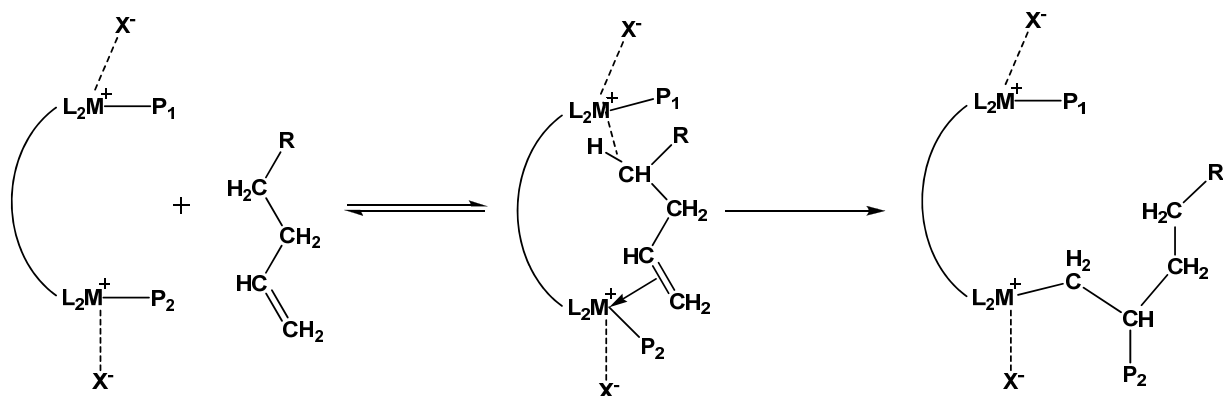
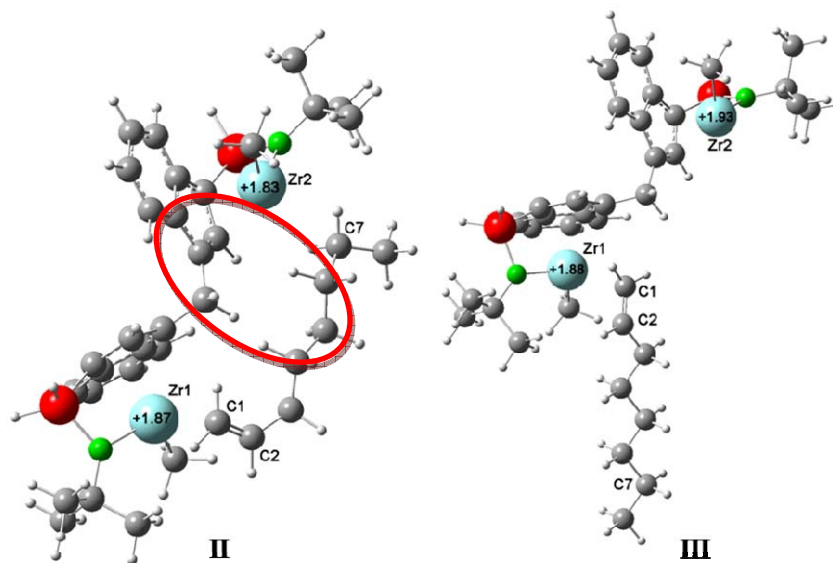


Figure 1-10. Density functional theory (DFT/B3LYP) results show that the π -complex of 1-octene with **C1-Zr₂** in which the alkyl chain interacts with the proximate Zr-center (**II**) is more stable than if the alkyl chain is bent away from the proximate Zr-center (**III**). From reference 39



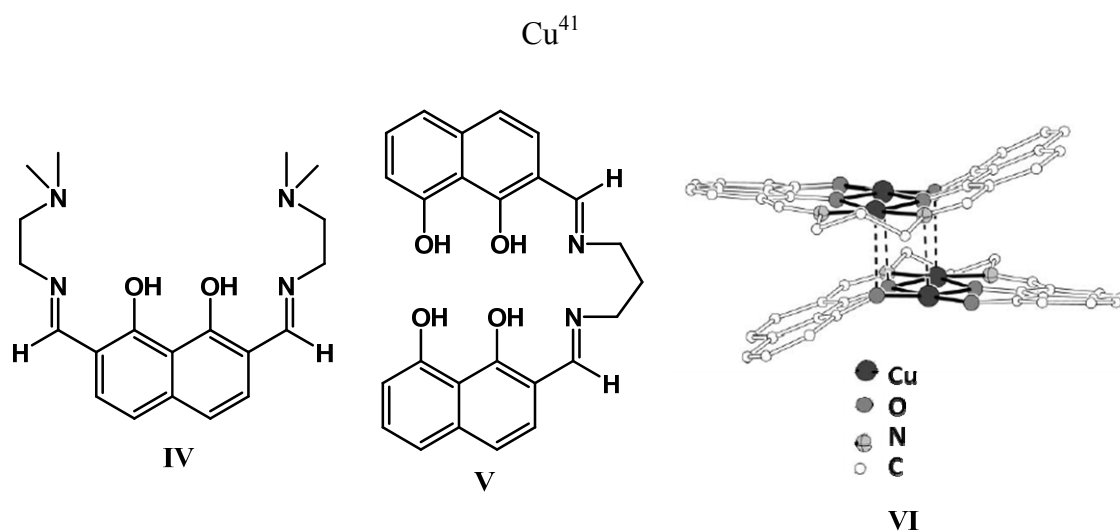
for bimetallic catalysts relative to their mononuclear analogues. Therefore, introducing rigid ligation and contracting the distance between metal centers should favor cooperative enchainment processes. The next important question is whether and how these binuclear enchainment effects are operative in the present family of binuclear phenoxyiminato catalysts, how they vary with group 4 metal, and whether the comonomer scope may be broadened.

The results of the present investigation indicate that as the nuclearity of the phenoxyiminato group 4 catalysts is increased, polymerization properties are dramatically altered both in terms of activity as well as selectivity for bulky olefinic comonomer incorporation. Overall productivities are significantly increased in all cases for the binuclear versus the mononuclear catalysts (Tables 1-4 and 1-5), indicating enhanced rates of not only ethylene homopolymerization but also comonomer enchainment relative to ethylene enchainment. In previous studies of binuclear CGC-based catalysts, olefinic comonomers were observed to depress polymerization activity, presumably due to competition for coordination sites, although selectivities for comonomer incorporation were substantially greater than for mononuclear CGC catalysts.^{5,15} In the sections that follow, we discuss the origins of the effects observed and the polymers produced.

I. Structural Design Considerations for Ligand FI². When we set out to synthesize a new family of binuclear transition metal catalysts, we sought to maximize the potential for metal-metal cooperativity during polymerization while using metal-ligand sets conducive to rapid olefin activation and enchainment. The first characteristic to enhance versus earlier **Ti₂**, **Zr₂**, **C1-Ti₂**, and **C1-Zr₂** CGC structures was the positional rigidity of the metal centers. A rigid ligand structure would prevent the metal centers from rotating away from each other as is

possible in **C1-Ti₂** and **Ti₂** (Figure 1-2). While **Ti₂** has a negligible barrier to rotation, **C1-Ti₂** has an estimated barrier for 360° rotation of ~65 kcal/mol,^{3b} but still possesses substantial conformational mobility. In contrast, the **FI²** ligand design ‘locks’ the metal centers such that they are always disposed with the shortest possible inter-metal distance (5.4 - 5.9 Å estimated¹⁴). Whereas the catalytic centers in the **C1-Ti₂** and **Ti₂** CGCs may rotate in solution away from a shortest estimated M···M distances of ~6.0 Å and ~6.6 Å, respectively, the rigid naphthalene backbone prevents this type of rotation. Although the crystal structures of **FI²-Zr₂** and **FI²-Ti₂**

Figure 1-11. Multi-nucleating ligands similar to **H₂-FI²**. Structure **VI** shows an X-ray diffraction crystal structure of a **IV**-Cu complex, revealing that half of the ligand lies in the same plane as



are not available, the molecular structures can be estimated to be near-planar with respect to the naphthalene core and the metal centers, with a metal - metal distance estimated to be ~5.4 to 5.9 Å.¹⁴ We introduced *o,o'* solubilizing groups on the N-aryl substituents in order to maintain good solubility. The ligand structure chosen is similar to two ligands reported by Glaser in multi-nucleating Cu systems designed for applications as magnetic materials (Figure 1-11).⁴¹ The

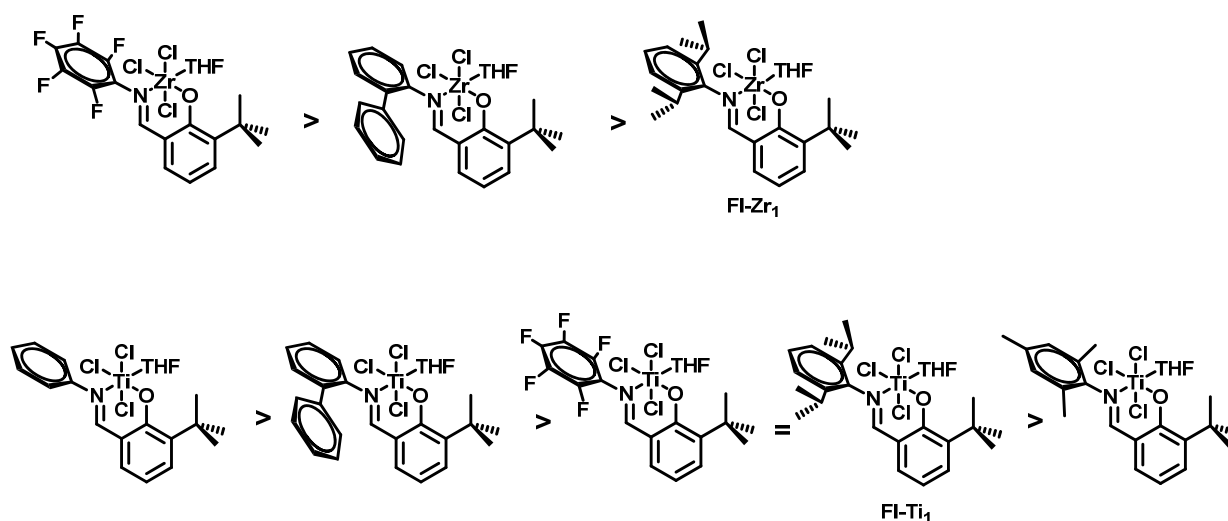
reported Cu complexes were characterized by single-crystal XRD, and in some cases, the structures are planar with respect to the metal centers and the naphthyl moiety.

II. Ethylene Homopolymerizations. Bochmann reported that a series of mono-phenoxyiminato Zr and Ti complexes (Figure 1-12) produces very high M_w linear polyethylenes when activated with MAO.^{11a,b} When the polymerization experiments were carried out at 60 °C, M_w was substantially decreased.^{11a} These characteristics are also observed in the present study for both **FI²-Zr₂** and **FI²-Ti₂** activated with MAO. Under room temperature polymerization conditions, the polyethylene products are completely insoluble. However, at elevated polymerization temperatures (40 °C), product M_w s are sufficiently depressed to obtain soluble polymers, informative NMR spectra, and good GPC traces, although the polydispersities are still somewhat greater than 2.0, suggesting multiple active sites or conformations. As previously mentioned, phenoxyiminato group 4 complexes are prone to decomposition via ligand rearrangement processes and/or nucleophilic attack on the imine functionality, which could, in principle, create additional catalytic species.

In previous work,^{11a,b} well-defined ligand substituent activity trends (such as ligand electron-donating/withdrawing effects) could not be discerned for the mononuclear phenoxyiminato mononuclear group 4 catalysts. However, there are nevertheless large activity variations observed within the series (Figure 1-12), depending on the N-aryl substituent. For example, the strongly electron-withdrawing N-pentafluorophenyl substituent afforded the highest ethylene homopolymerization activity in this series.^{11a} However, an intermediate electron-withdrawing tendency N-phenyl substituent afforded the highest activity Ti catalyst in the same study. Note also that the most active Zr complex is ~3x more active than the most active Ti

complex. Overall, the characteristics of these catalysts are very sensitive to ligand substituents, with 100-fold activity variations arising from ligand substituents.

Figure 1-12. The family of mono-phenoxyimine zirconium and titanium complexes and their relative activities towards ethylene homopolymerization.^{11a,b}

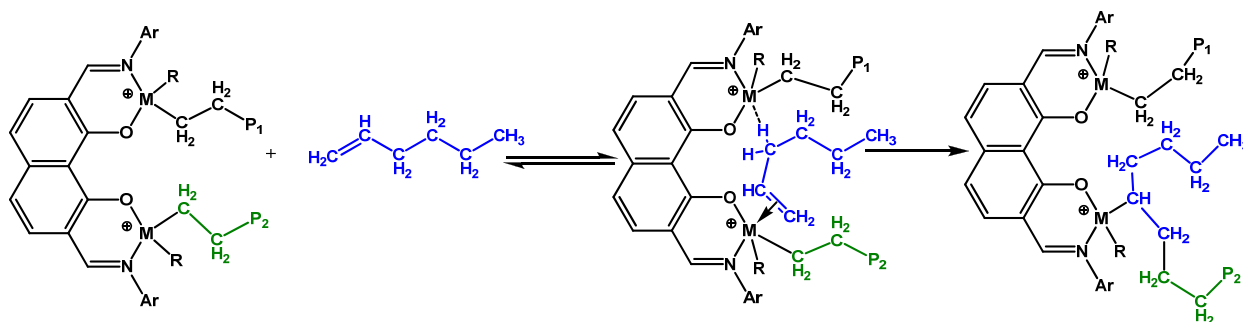


A broad survey of ligand N-substituent effects in the present binuclear complexes was not conducted due to the restriction that the imine substituent must contain bulky alkyl groups to retain useful solubility. For example, an N-*p*-tolyl substituted ligand was also synthesized, however, the resulting bimetallic complex was too insoluble in common solvents for meaningful studies. Nevertheless, the present binuclear catalysts display substantially higher ethylene polymerization activities than their mononuclear analogues. At the two reaction temperatures examined, **FI²-Zr₂** displays an average polymerization activity of ~7x greater than that of **FI-Zr₁**, and **FI²-Ti₂** displays an average activity of ~2x greater than that of **FI-Ti₁**.

III. Ethylene + α -Olefin Copolymerizations. Both the present ethylene + 1-hexene and ethylene + 1-octene copolymerization data indicate that, compared to typical experimental olefin polymerization conditions at low catalyst concentration levels (10^{-4} to 10^{-8} M), the close enforced contact between the two catalytic centers leads to significantly greater extents of comonomer enchainment. It is likely that coordination/activation of the α -olefin to one cationic metal center is stabilized by a secondary, possibly agostic interaction with the proximate cationic metal center, which may facilitate/stabilize α -olefin capture/binding at the metal center and enhance the subsequent enchainment probability (Scheme 1-10 and Figure 1-10). In the case of the binuclear versus mononuclear CGC catalysts, dramatic comonomer enchainment selectivity is observed along with substantial branching in ethylene homopolymerizations.^{5c,d,f,15} However, *reduced* overall polymerization activities are observed for the binuclear CGC catalysts versus the mononuclear CGC analogues. For example, in ethylene + 1-octene copolymerizations with **Ti₂** and **Ti₁** as the catalysts and **B₁** as the cocatalyst, **Ti₁** produces copolymer with an activity which is 2x that of **Ti₂**. It was postulated that this is possibly due to the α -olefin partially blocking or competing for ethylene activation and enchainment sites.^{5f} However, for the present phenoxyiminato catalysts in the current study, an enhancement in activity is observed, albeit modest in some cases.

In this study, the bimetallic catalysts exhibit significantly greater activity than the monometallic complexes in *all* analogous cases (i.e., where the only experimental variable is monometallic vs. bimetallic catalyst and reaction conditions are identical). We hypothesize that this is a result of a cooperativity between the two activated catalyst centers during the polymerization which creates an advantageous coordination environment around the linked

Scheme 1-10. Proposed scenario for enhanced α -olefin enchainment by bimetallic catalysts (M = Ti, Zr; Ar = 2,6-diisopropylphenyl; R = alkyl, H; anion omitted for clarity)



catalysts, thereby increasing the enchainment efficiency during both ethylene polymerizations and ethylene + olefin copolymerizations.

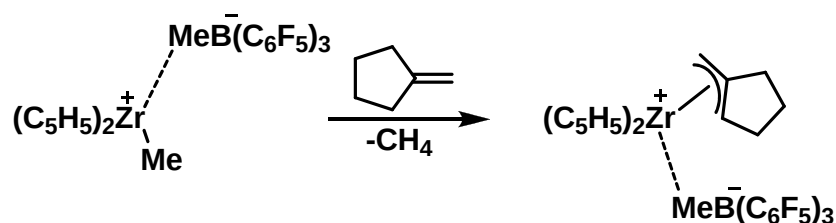
IV. Sterically Encumbered MCA Copolymerizations. In accord with previous observations on CGCTi-mediated ethylene + **MCA** copolymerizations,¹⁸ **MCP** and **MCH** are incorporated via ring-unopened pathways using **FI²-Ti₂** and **FI-Ti₁** as the catalysts to yield macromolecular products **C** and **D** (Figure 1-5). However, under identical reaction conditions, **FI²-Zr₂** and **FI-Zr₁** yield only ethylene homopolymer. The minimal ring strain energy associated with these comonomers likely has a strong influence on their enchainment pathways in that copolymerizations proceed without ring-opening, which is thermodynamically unfavorable. For comonomers **MCP** and **MCH**, different catalytic pathways are in principle accessible, depending on the particular group 4 catalyst. For example, $(C_5H_5)_2ZrMe^+MeB(C_6F_5)_3^-$ reacts with **MCP** to form an η^3 -allyl complex without enchainment (Scheme 1-11).⁴² It was also reported that, with $(C_5H_5)_2ZrMe^+MeB(C_6F_5)_3^-$ as the catalyst, **MCP** and **MCH** are ultimately converted to the

thermodynamically favored internal olefins **A** and **B** (Figure 1-5), again without enchainment.^{18c}

The same isomerization reactions occur when $\text{CGCZrMe}^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ catalysts are employed.^{18b}

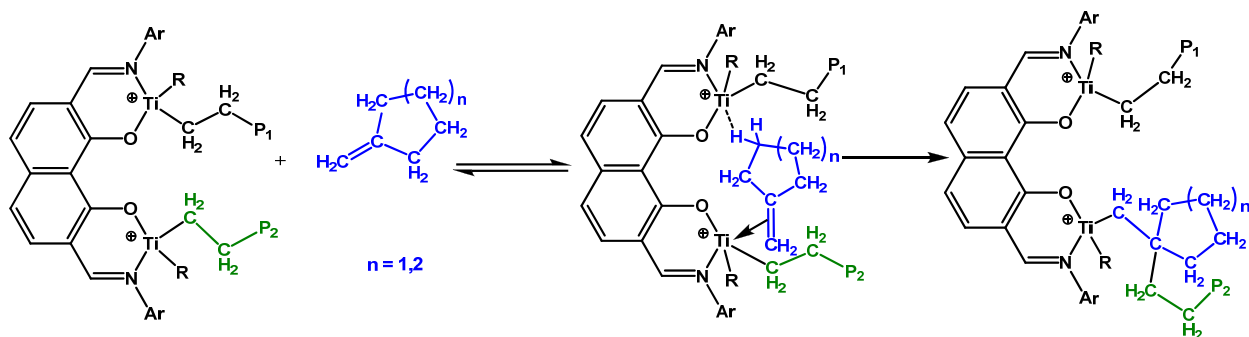
While neither $(\text{C}_5\text{H}_5)_2\text{ZrMe}^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ nor $\text{CGCZrMe}^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ catalysts are capable of

Scheme 1-11. Isomerization mechanism for strained methylenecycloalkanes



incorporating **MCH** and **MCP** into the polyethylene backbone, $\text{CGCTiMe}^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ catalysts enchain **MCH** and **MCP** into ethylene copolymers to form polymer structures **C** and **D**, respectively. An appealing explanation is that tighter ion pairing in $\text{CGCZrMe}^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ versus $\text{CGCTiMe}^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ structures leads to lower bulky comonomer enchainment selectivity.^{18a,43} A similar scenario may be operative in the present **FI** catalyst series. Thus, while **FI**²-**Ti**₂ and **FI**-**Ti**₁ incorporate **MCH** and **MCP** into ethylene copolymers with moderate

Scheme 1-12. Proposed Mechanistic Scenario for Enhanced **MCA** Enchainment by Bimetallic Catalyst **FI**²-**Ti**₂



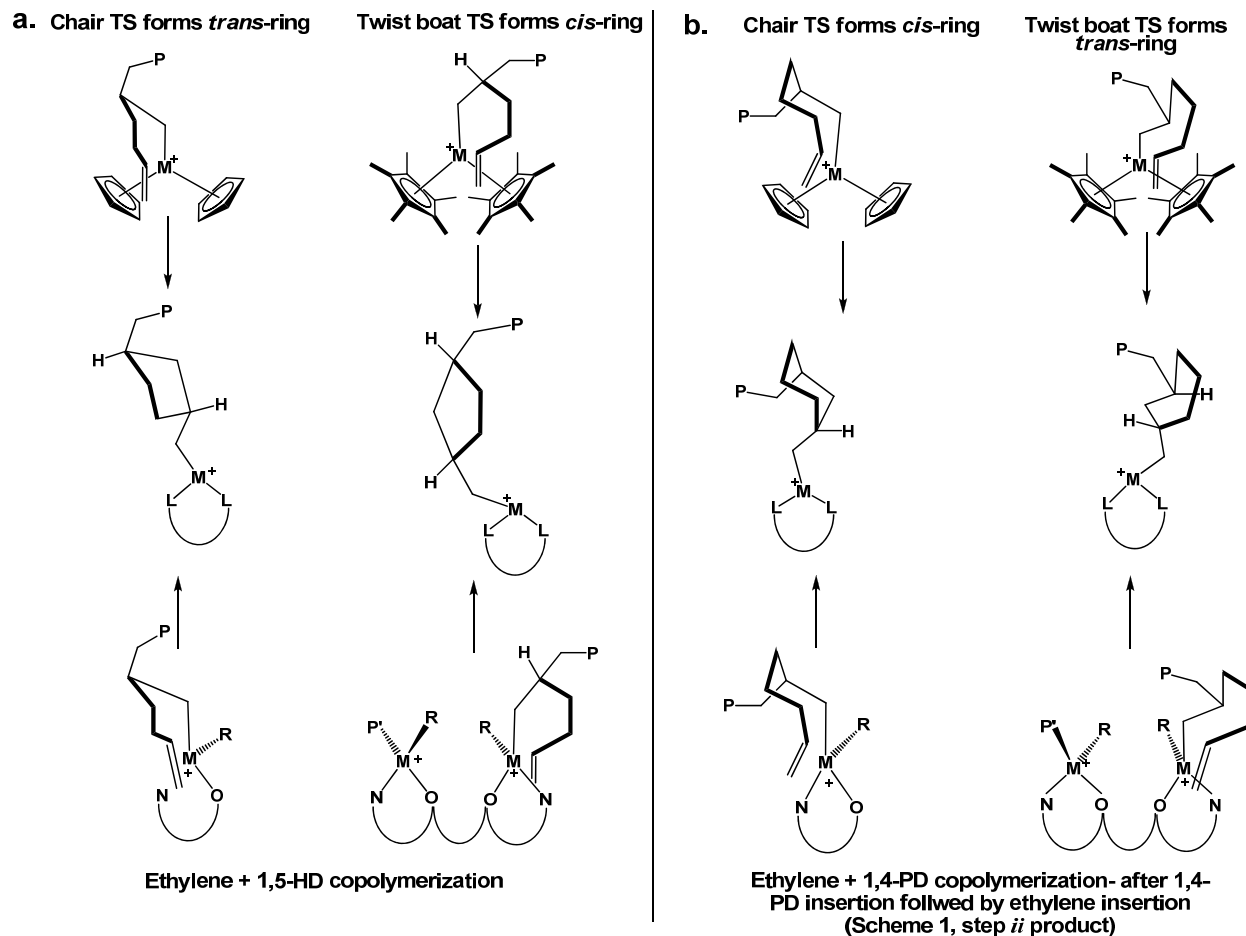
activities as noted above, **FI²-Zr₂** and **FI-Zr₁** produce exclusively polyethylene homopolymer under the same reaction conditions. Tighter ion pairing between the Zr cation and the associated MAO anion may raise the barrier to coordination and insertion of the very bulky methylenecycloalkanes. For **FI²-Ti₂**, it appears that one electrophilic Ti center assists the proximate Ti center in inserting the bulky **MCA** comonomers (Scheme 1-12). While **MCP** is incorporated in a very low percentage, **MCH** is incorporated to 11.6%, which is ~3.4x the enchainment achieved by **FI-Ti₁**.

V. Ethylene + α,ω -Diene Copolymerizations. It is reasonable to assume that the copolymerizations of ethylene + **1,4-PD** and ethylene + **1,5-HD** follow essentially similar pathways to ethylene + α -olefin copolymerizations with respect to the observed enhanced incorporation of comonomer (Scheme 1-10). In the case of **FI²-Zr₂**- and **FI-Zr₁**-catalyzed copolymerization of ethylene + **1,4-PD**, 1,3-cyclohexyl units are incorporated in polymer structure **G** (Figure 1-5) with 69% *cis*- and 82% *cis*-1,3-cyclohexyl group selectivity, respectively. In the case of **FI²-Zr₂** and **FI-Zr₁** catalyzed copolymerization of ethylene + **1,5-HD**, 1,3-cyclopentyl units are enchainment to form polymer structure **F** (Figure 1-5) with 65% *cis*- and 44% *cis*-1,3-cyclohexyl group selectivity, respectively. No detectable cross-linked polymers are found in any of the product polymers. Interestingly, under identical reaction conditions, **FI²-Ti₂** and **FI-Ti₁** yield only trace amounts of copolymer. Regarding the differences in the *cis/trans* ratios in the polymer products obtained from **FI²-Zr₂** and **FI-Zr₁**, it is plausible that the proximate metal center in **FI²-Zr₂** plays a role in directing the ring closure stereochemistry. Waymouth and Resconi⁴⁴ analyzed the transition states for **1,5-HD** homopolymerization mediated by various zirconocenium catalysts differing in the bulkiness of the cyclopentadienyl

ligands. They found, both in experiment and theory, that bulkier cyclopentadienyl ligands induce greater diastereoselectivity for *cis*-ring closure. They proposed that the selectivity for *trans*-ring formation reflects a preference for a chair-like transition state in which the polymer chain occupies an equatorial position (Figure 1-13a). However, as the ancillary ligand steric encumbrance increases, the chair-like transition-state is destabilized by the cyclopentadienyl ligand substituents, with an alternative twist-boat transition-state having the polymer chain in an equatorial position leading to *cis*-1,3-cyclopentyl closure. Theoretical studies on the insertion pathways in CpTiCl₃-derived catalysts, which are a closer comparison to the **FI-M₁** and **FI²-M₂** structures and coordination spheres, suggest similar pathways for insertion of dienes.⁴⁵ Comparing these proposed pathways with the present results leads us to suggest that the proximate metal in the bimetallic catalyst **FI²-Zr₂** serves as a bulky substituent which, in combination with possible agostic stabilization similar to that proposed for ethylene + olefin copolymerizations above (Scheme 1-10), leads to the greater *cis*-ring formation selectivity in the ethylene + **1,5-HD** copolymerizations versus **FI-Zr₁** which is less sterically encumbered, hence less selective for *cis*-ring closure.

Applying the same diastereoselection mechanism to the ethylene + **1,4-PD** copolymerizations reported by Longo and coworkers,²⁵ **1,4-PD** insertion followed by ethylene insertion and cyclization should follow the same preferred pathway, i.e. a chair-like transition state with the polymer chain occupying an equatorial position. However, this transition state leads to *cis*-1,3-cyclohexyl ring closure (Figure 1-13b). If bulky ancillary ligands destabilize the chair-like transition state, a twist-boat transition state would then be preferred, forming a *trans*-1,3-cyclohexyl fragment. This opposite *cis/trans* selectivity relative to **1,5-HD** reflects the extra

Figure 1-13. Transition states for cyclization of (a) **1,5-HD** and (b) **1,4-PD** catalyzed by metallocenium catalysts and by phenoxyiminato catalysts (ligand structures abbreviated for clarity; M = Ti, Zr; P = polymer chain; L = Cp, Me₄Cp, **FI**, or **FI**²; R = alkyl, H)



methylene unit involved in the ring closure. Hence, in Longo's study, the more encumbered *rac*-[CH₂(3-*tert*-butyl-1-indenyl)₂]ZrMe⁺MeMAO⁻ zirconocenium catalyst displays greater selectivity for *trans*-1,3-cyclohexyl ring formation than does Cp₂ZrMe⁺MeMAO⁻ (Cp = cyclopentadienyl).²⁵ In the case of **FI**²-Zr₂- and **FI**-Zr₁-catalyzed ethylene + **1,4-PD** copolymerization, 1,3-cyclohexyl units are enchainned to form polymer structure **G** (Figure 1-5)

with 31% and 18% *trans*-1,3-cyclohexyl group selectivity, respectively. Following the trend that more encumbered catalysts lead to greater *trans*-1,3-cyclohexyl group selectivity, the proximate metal in **FI²-Zr₂** may serve as a bulky group in the cycloinsertion process, in combination with stabilizing agostic interactions, leading to *trans*-1,3-cyclohexyl selectivity.

Interestingly, in both the mononuclear and the binuclear phenoxyiminato systems, the Zr catalysts exhibit much greater activity in ethylene + α,ω -diene copolymerizations than do the corresponding Ti catalysts, which have an activity < 1 g polymer/[(mol M⁺)·atm·h]. In contrast, the ethylene + **MCA** copolymerizations follow the same trend as the CGC-**Zr₂** and -**Ti₂** catalysts in that **FI²-Zr₂** and **FI-Zr₁** do not enchain MCAs, while **FI²-Ti₂** and **FI-Ti₁** enchain MCAs to levels of 0.4% and 11.6%, respectively. If **FI²-Zr₂** is involved in stronger ion pairing than **FI²-Ti₂** (following the CGC-Zr and CGC-Ti trend⁴³), it is then plausible that the determining factor for diene copolymerization is that the catalyst be sufficiently coordinatively/sterically open. It is also plausible that the larger ionic radius of Zr(IV) versus Ti(IV) is required for diene co-enchainment. Taken together, these two factors can explain why **FI²-Ti₂** and **FI-Ti₁** do not efficiently enchain dienes. In fact, to our knowledge, there are only two reports of a single-site Ti catalyst, $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\text{N}^t\text{Bu})]\text{TiCl}_2$, incorporating a non-conjugated diene into an ethylene copolymer, and in neither case is the diene cyclized.⁴⁶

VI. Comparison of Mono- and Bimetallic CGC Catalysts to Phenoxyiminato Mono- and Bimetallic Catalysts. The new family of bimetallic **FI²-M₂** phenoxyiminato group 4 catalysts exhibit both similarities and differences versus the bimetallic CGC group 4 catalysts studied earlier. Table 1-6 summarizes these similarities and differences. Most notably, both families of bimetallic catalysts display dramatic selectivity effects in enhancing comonomer enchainment

levels vs. their monometallic analogues. In ethylene + α -olefin copolymerizations mediated by **FI²-M₂**, between 1.5-fold and 2.2-fold increases are achieved vs. the copolymerizations mediated by **FI-M₁**. These increases are relatively modest in comparison to the 12-fold increase in 1-octene incorporation achieved for **Ti₂/B₂** vs. **Ti₁/B₁**.^{5e} However, the percentage of 1-octene enchainment in the **Ti₂/B₂** case is 7.0%, while the percentage of 1-octene co-enchainment for **FI²-Zr₂** is 7.3% and that for **FI²-Ti₂** is 15.2% under conditions only marginally more concentrated in 1-octene (0.72 M vs. 0.64 M). This dramatic difference in comonomer incorporation is reasonably due to the nature of the **FI-M₁** moiety which can facilitate the incorporation of sterically-demanding olefin comonomers. This factor, in combination with the proposed agostic interactions involved between the alkyl chain of the olefin and the proximate metal, lead to high enchainment levels of 1-octene. In the ethylene + **MCA** copolymerizations mediated by both families of catalysts, only the Ti catalysts are competent to copolymerize **MCAs** with ethylene. As mentioned above, we tentatively attribute this to tighter ion pairing between the Zr cation and the associated MAO counteranion, which retards entry, coordination, and enchainment of bulky comonomers.^{18,43}

An important difference between the CGC and **FI** families of catalysts is the general trend observed for the bimetallic CGC catalysts to display *lower* polymerization activities than their mononuclear analogues, while the bimetallic **FI²-M₂** catalysts display *higher* polymerization activities than their monometallic analogues. For example, ethylene + 1-hexene copolymerizations mediated by **Zr₂/B₁** display an activity 1.5x lower than that of **Zr₁/B₁**,^{5g} while, in contrast, **FI²-Zr₂** displays 12x greater activity than that of **FI-Zr₁** for ethylene + 1-hexene copolymerizations. It was concluded that the decrease in activities observed for the

Table 1-6. Comparison of CGC Catalyst Properties^{5,15,17} Versus **FI** Catalyst Properties (Present Study) for Ethylene Homo- and Copolymerizations. Unless Otherwise Noted, the Polymerization Conditions Compared within Each Entry are Identical. Catalyst Structures are Given in Figures 1-2 and 1-4.

	CGC catalysts	FI catalysts
activity	Ti: very high; Zr: moderate	Ti/Zr: moderate, with Zr being slightly greater
activity of mononuclear vs binuclear	Ti/Zr: bimetallics slightly less active than monometallics	Ti/Zr: bimetallics more active than monometallics
ethylene + α -olefin enchainment selectivity	~0.6 % to 15% incorporation of α -olefins (0.6 - 0.8 M comonomer)	~4.0% to 15% enchainment of α -olefins (0.72 M comonomer)
ethylene + α -olefin enchainment mononuclear vs binuclear	Ti₂ enchains ~3 - 7x more α -olefin than Ti₁ ; Zr₂/C1-Zr₂ enchain ~3 - 12x more α -olefin than Zr₁	FI²-Ti₂/FI²-Zr₂ enchain 1.5 - 2.2x more α -olefin than FI-Ti₁/FI-Zr₁
M _w of ethylene + α -olefin product (10 ³ g/mol)	Ti: 147 - 161; Zr: 0.24 - 380; Ti/Zr: M _w increases with increasing nuclearity	Ti: 76 - 188; Zr: 21 - 105; FI²-Zr₂ yields higher M _w than FI-Zr₁
polyethylene M _w (10 ³ g/mol)	Ti: M _w = 121 - 171; Zr: M _w = 0.61 - 268; M _w increases as catalyst nuclearity increases	Ti: 297 - 675; Zr: 155 and higher
polyethylene microstructure	Ti₂/Zr₂ : ethyl branching; Ti₁ : linear with vinylic endgroups; Zr₁ : long-chain branching with vinylic endgroups	Ti/Zr: linear with saturated and vinylic endgroups
ethylene + MCA enchainment selectivity	Ti₂ enchains ~2x more MCA more than Ti₁ ; Zr inactive for MCA copolymerization	FI²-Ti₂ enchains 2 - 3x more MCA than FI-Ti₁ ; Zr inactive for MCA copolymerization
ethylene + MCA M _w (10 ³ g/mol)	M _w = 158 - 320; Ti₂ gives slightly lower M _w	M _w = 20 - 121; FI²-Ti₂ yields ~2 - 5x higher M _w
predominant chain transfer mechanism	Ti₂/Zr₂/C1-Zr₂ : β -hydride transfer to ethylene; Ti₁/Zr₁ - β -hydride elimination with borane/borate cocatalysts	~50 - 70% chain transfer to Al and ~30 - 50% β -hydride elimination
catalyst stability	very stable/long-lived	multiple active sites formed, then long-lived

bimetallic CGCs is due to the α -olefin blocking/competing for active sites, especially for the higher nuclearity sites.^{5g} A plausible argument for the observed *increase* in activity for the bimetallic **FI**²-**M**₂ catalysts is the coordinatively open nature of the active site. It may be that, in combination with the agostic interactions involving the proximate metal center, the **FI**²-**M**₂ coordination sphere is sufficiently open to avoid activity loss due to competition for enchainment sites.

Another major difference between the CGC and FI catalyst systems is the M_w of the (co)polymers produced by each family of catalysts. While CGC-Zr catalysts tend to form low M_w polymers, this characteristic can be substantially modified by proper choice of cocatalyst. Using MAO as the cocatalyst dramatically increases the product polymer M_w in **C1-Zr**₂-mediated ethylene homopolymerizations and ethylene + 1-hexene copolymerizations.^{3c5b,d} In the case of the **FI** catalyst family, molecular weights greater than 20,000 g/mol are obtained in all cases.

Branched polyethylene microstructures are also obtained in CGC-mediated ethylene homopolymerizations. Specifically, substantial ethyl branch densities are present in **Ti**₂-, **Zr**₂-, and **C1-Zr**₂-derived ethylene homopolymers and are proposed to arise from β -hydride transfer from the growing polymer directly to metal-bound ethylene, followed by rapid reinsertion of olefin-terminated macromonomer. Also, **Zr**₁ produces long-chain branched polyethylene by reinsertion of olefin-terminated macromonomers.^{5d} In contrast, the **FI**-family of catalysts produces essentially branch-free, linear polyethylenes where ~68% of the polymer chains are terminated by chain transfer to Al (Scheme 1-8) and ~32% of the polymer chains are terminated by β -

hydride elimination. Long-chain branches arising from macromonomer reinsertion are not detected in the ^1H and ^{13}C NMR spectra.

A last major difference in the two families of catalysts concerns the stabilities of their active sites. The CGCs are stable and long-lived even at higher temperatures,⁵ whereas the **FI**-catalysts show broadened PDIs indicative of multiple active sites. These different active sites may arise from either of the ligand reaction or ligand rearrangement reactions mentioned above (Schemes 1-6 and 1-7). A stable catalytic species should in theory have $\text{PDI} = 2.0$, however the PDIs of the (co)polymers in the current study range from 3.22 to 33.6.

Conclusions

The binucleating phenoxyimine ligand **H₂-FI²** and the corresponding bimetallic group 4 complexes $\{1,8-(\text{O})_2\text{C}_{10}\text{H}_4-2,7-[\text{CH}=\text{N}(2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)]_2\}\text{Zr}_2\text{Cl}_6(\text{THF})_2$ (**FI²-Zr₂**) and $\{1,8-(\text{O})_2\text{C}_{10}\text{H}_4-2,7-[\text{CH}=\text{N}(2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)]_2\}\text{Ti}_2\text{Cl}_6(\text{THF})_2$ (**FI²-Ti₂**) have been synthesized and characterized. The catalyst design focused on maximizing interactions between the two metal centers. We compared and contrasted the polymerization properties of these two catalysts with those of their mononuclear analogues, **FI-Ti₁** and **FI-Zr₁**, in ethylene homopolymerizations, ethylene + α -olefin copolymerizations, ethylene + **MCA** copolymerizations, and ethylene + α,ω -diene copolymerizations. To our knowledge, this study represents first report of copolymerizations achievable with mono-phenoxyiminato group 4 catalysts and the second report of significant incorporation of **MCAs** into polyethylene backbones via a coordination polymerization process. Substantial increases in catalytic activity and comonomer enchainment

efficiency into the polyethylene microstructure are observed for all comonomers versus the respective mononuclear catalyst analogues. It is also found that distinct comonomer selectivity differences are displayed for the Zr versus Ti catalysts. Thus, the Zr catalysts enchain α,ω -dienes efficiently while the Ti catalysts are inactive for ethylene + α,ω -diene copolymerization. Conversely, the Ti catalysts enchain **MCAs** efficiently while the Zr catalysts are unable to enchain **MCAs**.

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⁴⁶ Santos, J. M.; Ribeiro, M. R.; Portela, M. F.; Cramail, H.; Deffieux, A.; Antiñolo, A.; Otero,

A.; Prashar, S. *Macromol. Chem. Phys.* **2002**, 203, 139-145. (b) Santos, J. M.; Ribeiro, M. R.;

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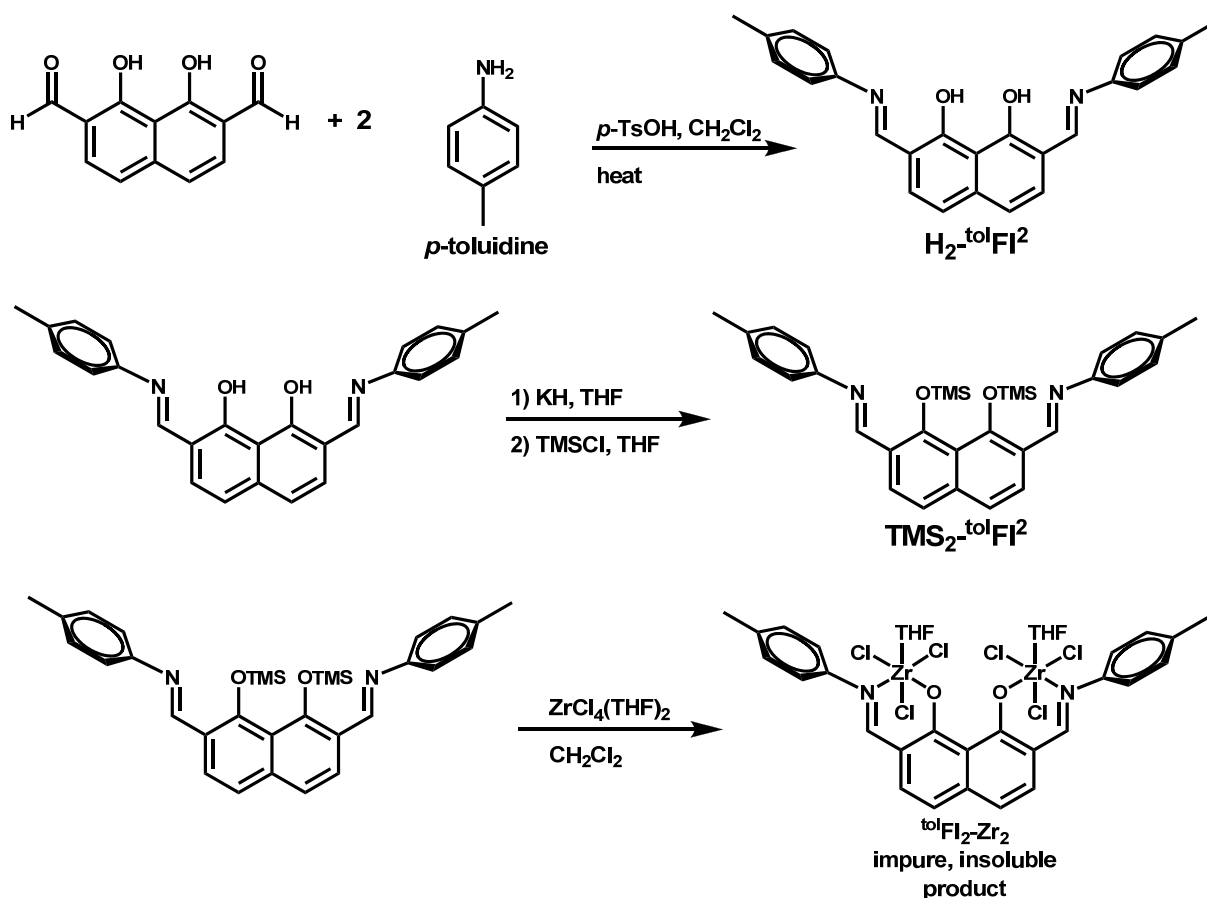
Appendix

Prior to the successful synthesis of $\text{FI}^2\text{-Zr}_2$ and $\text{FI}^2\text{-Ti}_2$, a slightly different binucleating phenoxyiminato ligand was designed. The ligand synthetic scheme was the same as the successful synthesis of $\text{H}_2\text{-FI2}$, however *p*-toluidine was chosen for reaction with 2,7-diformyl-1,8-naphthalenediol (Scheme A-1). This ligand and the corresponding bis(trimethylsiloxy)-derivative were successfully obtained by the methods described in the sections to follow. However, metalation attempts under conditions similar to those used for $\text{FI}^2\text{-Zr}_2$ yielded solid products from the reaction of $\text{TMS}_2\text{-}^{\text{tol}}\text{FI}^2$ and $\text{ZrCl}_4(\text{thf})_2$ which were not pure, and $^{\text{tol}}\text{FI}^2\text{-Zr}_2$ and could not be dissolved in any common solvents. The solvents attempted to dissolve the metalation reaction product included 1,2,4-trichlorobenzene, chloroform, dichloromethane, tetrahydrofuran, toluene, diethyl ether, pentane, acetonitrile, carbon tetrachloride, and 1,1,2,2-tetrachlorethane. Elemental analysis of the solid did not match any molecular formula likely to be the product of the reaction, indicating an impure product.

Synthesis of 2,7-Bis-[(E)-*p*-tolylimino]-methyl}-naphthalene-1,8-diol ($\text{H}_2\text{-}^{\text{tol}}\text{FI}^2$). Under N_2 , the reagent 2,7-diformyl-1,8-dihydroxynaphthalene (0.924 g, 4.28 mmol) was dissolved in 25 mL dry dichloromethane. Activated molecular sieves (2.0 g) were then added, followed by *p*-toluenesulfonic acid (5 mg), and *p*-toluidine (1.008 g, 9.4 mmol) dissolved in 10 mL of dichloromethane. The reaction mixture was heated under reflux for 30 min during which time the 2,7-diformyl-1,8-dihydroxynaphthalene gradually dissolved, and the reaction mixture color changed from yellow to dark red. The reaction mixture was then cooled and filtered. The

volatiles were removed from the filtrate *in vacuo*, and the resulting red oily solid was washed with 10 mL of pentane and collected by filtration to afford a red solid. ^1H NMR (CDCl_3 , 23°C ,

Scheme A-1. Synthetic scheme for the attempted synthesis of $^{\text{tol}}\text{FI}^2\text{-Zr}_2$.



400.637 MHz): δ 15.0 (s), 13.8 (s), 9.47 (s), 8.74 (d), 6.3-7.4 (m), 2.07 (s). LCQ-MS: parent ion-395.34 g/mol.

Synthesis of 2,7-Bis-{[(E)-*p*-tolylimino]-methyl}-1,8-bis-trimethylsiloxy-naphthalene ($\text{TMS}_2\text{-}^{\text{tol}}\text{FI}^2$). The reagents 2,7-bis-{[(E)-*p*-tolylimino]-methyl}-naphthalene-1,8-diol ($\text{H}_2\text{-FI}^2$, 510 mg, 1.29 mmol) and KH (414 mg, 10.4 mmol) were combined in a reaction flask in the

glovebox. On the vacuum line, dry THF (40 mL) was added at 0 °C, and the mixture was stirred for 45 min. The mixture was filtered, then TMS-Cl (1.32 mL, 14.3 mmol) was added to the filtrate. The volatiles were next removed *in vacuo*, and the resulting solid was dissolved in 20 mL dry dichloromethane. The reaction mixture was then filtered, the volatiles were removed from the filtrate *in vacuo*, and the resulting product was pure by NMR and elemental analysis. Spectroscopic and analytical data for **TMS₂-^{tol}FI²** are as follows. ¹H NMR (CD₂Cl₂, 23°C, 400.637 MHz): δ 8.93 (s, 2H, HC=N), 8.22 (d, 2H, ³J_{H-H} = 8.0 Hz), 7.50 (d, 2H, ³J_{H-H} = 8.4 Hz), 7.23 (mult, 4H), 7.17 (t, 4H), 2.38 (s, 6H, *p*-tol Me), 0.167 (s, 18H). Anal. Calcd. for C₃₆H₄₂N₂O₂: C, 71.33; H, 7.11; N, 5.20. Found: C, 71.36; H, 7.12; N, 5.06.

Synthesis of {2,7-Bis-{[(E)-*p*-tolylimino]-methyl}-1,8-bis-trimethylsiloxy-naphthalenediolato}bis-[(trichloro)-(tetrahydrofuran)Zr(IV)]. Under an N₂ atmosphere, the reagent 2,7-bis-{[(E)-*p*-tolylimino]-methyl}-1,8-bis-trimethylsiloxy-naphthalene (**TMS₂-^{tol}FI²**, 768 mg, 1.43 mmol) in 20 mL dry dichloromethane was added dropwise with stirring to a solution of ZrCl₄(THF)₂ (1.08 g, 2.86 mmol) in 20 mL dry dichloromethane at -78°C. The solution was then allowed to warm to room temperature and stirred for 24 h. A red solid appeared, and the mixture was filtered. Yield: 1.35 g.

Crystal structure data (.cif files) for **H₂-FI²**.

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C3 0.0471(10) 0.0289(9) 0.0263(8) 0.0016(6) 0.0051(7) -0.0045(7)
C32 0.0366(9) 0.0296(9) 0.0418(10) 0.0077(7) 0.0090(8) 0.0065(7)
C31 0.0355(9) 0.0225(8) 0.0567(11) -0.0003(7) 0.0218(8) 0.0011(7)
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C34 0.0549(12) 0.0463(11) 0.0312(9) 0.0034(8) 0.0100(8) 0.0163(9)
C29 0.0577(13) 0.0546(13) 0.0368(10) -0.0036(9) 0.0112(9) -0.0116(10)

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All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
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Crystal structure data (.cif files) for **TMS₂-FI²**.

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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

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C3 C -0.21923(8) 0.1881(2) 0.83103(13) 0.0317(4) Uani 1 1 d . . .
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C29 C 0.16851(9) 0.5852(3) 1.03464(18) 0.0477(6) Uani 1 1 d . . .
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H29C H 0.1944 0.5281 1.0775 0.072 Uiso 1 1 calc R . .
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 C37 C 0.24635(9) 1.0946(3) 0.84670(16) 0.0429(6) Uani 1 1 d . . .
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 H38 H 0.2847 1.0498 0.9724 0.048 Uiso 1 1 calc R . .
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 C40 C 0.21491(8) 0.9699(2) 1.04530(14) 0.0326(4) Uani 1 1 d . . .
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 C41 C 0.25995(9) 0.8675(3) 1.08360(16) 0.0402(5) Uani 1 1 d . . .
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 H41B H 0.2538 0.7855 1.0469 0.060 Uiso 1 1 calc R . .
 H41C H 0.2614 0.8420 1.1425 0.060 Uiso 1 1 calc R . .
 C42 C 0.22498(13) 1.0987(3) 1.10163(17) 0.0506(6) Uani 1 1 d . . .
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 H42C H 0.2301 1.0734 1.1621 0.076 Uiso 1 1 calc R . .
 N1 N -0.13999(6) 0.32194(18) 0.97939(11) 0.0271(3) Uani 1 1 d . . .
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 O1 O -0.01897(5) 0.41151(13) 0.88908(8) 0.0241(3) Uani 1 1 d . . .
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 Si1 Si -0.04163(2) 0.37862(6) 0.78168(3) 0.02739(12) Uani 1 1 d . . .
 Si2 Si 0.10867(2) 0.48300(6) 0.98066(4) 0.03137(14) Uani 1 1 d . . .

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 C2 0.0294(9) 0.0266(10) 0.0307(10) -0.0014(8) 0.0147(8) -0.0006(8)
 C3 0.0334(10) 0.0320(11) 0.0308(10) 0.0007(8) 0.0120(8) -0.0020(9)
 C4 0.0635(16) 0.0571(17) 0.0325(12) 0.0031(11) 0.0221(11) 0.0113(13)
 C5 0.0366(11) 0.0493(15) 0.0444(13) 0.0071(11) 0.0096(10) 0.0038(11)
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 C7 0.0344(10) 0.0241(10) 0.0422(12) 0.0010(8) 0.0185(9) -0.0043(8)

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Si1 0.0302(3) 0.0243(3) 0.0291(3) -0.0022(2) 0.0118(2) -0.0019(2)
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Education:**•Northwestern University**

Evanston, IL

Ph.D. Department of Chemistry June 2008. Thesis: Catalyst Nuclearity Effects in Olefin Polymerization.

•University of Illinois at Urbana-Champaign

Urbana, IL

B.S. in Chemistry, High Distinction, May 2002. Performed research in a synthetic inorganic chemistry group resulting in a thesis.

Research Experience:

- Northwestern University Department of Chemistry

Evanston, IL

Advisor: Tobin J. Marks

Dissertation: Enhanced Activity and Comonomer Enchainment in Ethylene + Olefin Copolymerizations Mediated by Bimetallic Group 4 Phenoxyiminato Catalysts

Designed and synthesized new bimetallic catalysts for olefin polymerization which improved efficiency in producing desirable polymer materials properties. Work involves organic and organometallic synthesis and characterization, catalytic polymer synthesis and characterization.

- University of Illinois at Urbana-Champaign

Urbana, IL

Advisor: Thomas B. Rauchfuss

Synthesized new sulfur based ligands for metal complexes. The metal complexes have desirable electronic properties and applications to catalytic hydrodesulfurization.

Awards

Phi Lambda Upsilon conference travel award (2007 and 2006), Northwestern Graduate School conference travel award (2007 and 2006), Marvel Award for outstanding undergraduate research (2002), Dean's List (2000).

Industrial Experience

- Wyeth-Ayerst, 2001:

Developed the scale-up procedure for a newly developed drug candidate. Synthesized 1 kilogram of a drug precursor allowing submission of the drug for FDA trials. Identified a mechanism for a key intermediate in the drug synthesis. Observed the development of a drug at a large pharmaceutical company. Presented results at a symposium for all interns

- BASF Aktiengesellschaft

112th International Summer Course, Ludwigshafen, Germany.

Attended the highly selective course on BASF's business and technological philosophies. Business lectures included the 'Verbund' system, innovation, and marketing. Science lectures included green and white biotechnology, site tours, and nanotechnology. Learned about the importance of new innovations and technologies for a chemical company. Observed a chemical company operating a highly integrated network of production facilities

Teaching Experience

- Northwestern University, Department of Chemistry
Advanced General Chemistry, Teaching Assistant.

Supervised laboratory portion of course. Provided short lectures detailing the laboratory experiment and equipment. Tutored students during office hours. Organized review sessions for exams. Graded exams and laboratory reports. (2002-2003).

Advanced Inorganic Laboratory, Teaching Assistant.

Organized and supervised laboratory experiments. Lectured the inorganic chemistry concepts of the experiments. Graded formal laboratory reports. Tutored students during office hours (2002-2003).

- Tutoring

Tutored a high-school student in advanced placement chemistry. Provided supplemental lecturing and problem set experience. Discussed chemistry concepts and provided extra practice for exams, quizzes, and experiments (2004-2005).

Tutored an undergraduate student in introductory organic chemistry. Discussed problems and provided supplemental chemistry concepts to help in understanding organic chemistry concepts. Provided assistance in understanding lecture and exam material (2000-2001).

Publications

- Salata, M. R.; Marks, T. J. Catalyst nuclearity effects in olefin polymerization. Enhanced Activity and Comonomer Enchainment in Ethylene + Olefin Copolymerizations Mediated by Bimetallic Group 4 Phenoxyiminato Catalysts. manuscript submitted.
- Salata, M. R.; Marks, T. J. Synthesis, characterization, and marked polymerization selectivity characteristics of binuclear phenoxyiminato organozirconium catalysts. *J. Am. Chem. Soc.* 2008, 130, 12-13.
- Letizia, J. A.; Salata, M. R.; Tribout, C. M.; Facchetti, A.; Ratner, M. A.; Marks, T. J. Interplay of solubilizing substituents, crystal packing, and field-effect transistor charge carrier sign in bithiophene-imide polymer semiconductors and their application in high-mobility FETs. manuscript submitted.
- McCain, M. N.; Schneider, S.; Salata, M. R.; Marks, T. J. Tris(phosphino)borate silver complexes as precursors for metallic silver deposition. *Inorg. Chem.* 2008, 47, 2534-2542.
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- Stahl, N. G.; Salata, M. R.; Marks, T. J. B(C₆F₅)₃- vs. Al(C₆F₅)₃-derived metallocenium ion pairs. Structural, thermochemical, and structural dynamic divergences. *J. Am. Chem. Soc.* 2005, 127, 10898-10909.
- Salata, M. R. Synthesis and reactivity of tetrathiooxalate. Undergraduate Honors Thesis, UIUC, 2002.
- Ramesh, M.; Holloway, G. A.; Salata, M. R.; Rauchfuss, T. B. Improved synthesis of C₄S₆2-. Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, USA, August 26-30, 2001.

Technical Skills

- Analytical Skills: single crystal x-ray diffractometry, NMR spectroscopy, infrared spectroscopy, mass spectrometry, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis
- Synthetic Skills: organic, inorganic, polymer, separations
- Computer Skills: MS Office, Bruker AXS Shelxtl single crystal solving program, ChemDraw

Presentations

- ACS Advances in Polyolefins, Santa Rosa, CA
- Catalysis Club of Chicago Symposium, Chicago and Naperville, IL
- Northwestern University Industrial Associates, Evanston, IL
- 112th International Summer Course of BASF, Ludwigshafen, Germany
- Gordon Research Conference in Organometallic Chemistry, Newport, RI
- Northwestern University Chemistry Symposium, Evanston, IL
- Wyeth Internship Symposium, Pearl River, NY

Affiliations

- Catalysis Club of Chicago (2002-present)
- American Association for the Advancement of Science (2006-present)
- Phi Lambda Upsilon Honorary Chemical Society (2003-present)
- American Chemical Society (2002-present)