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(54) Title: ALKENE POLYMERIZATION USING BETA-KETOIMINATO METAL COMPLEXES

(57) Abstract: Group (IV) and (X) metal complexes with ketoiminate ligands are prepared by deprotonation of a ketoimine ligand followed by reaction with the appropriate metal halide. In preferred cases, the compounds are titanium (IV), zirconium (IV) and hafnium (IV), preferred cases, the compounds are titanium (IV), zirconium (IV) and hafnium (IV) complexes with (arylimino-alkyl)-spiro[4,5]decan-6-one ligands. The compounds are useful as catalysts for polymerizing ethylene, C<sub>3</sub>-C<sub>10</sub>-alpha olefins and C<sub>4</sub>-C<sub>10</sub> cyclic alkenes and for copolymerizing ethylene with comonomers.

## Alkene Polymerization using Beta-Ketoiminato Metal Complexes

The invention was made at least in part with United States Government support under National Science Foundation related grant CCMR (Cornell Center for Materials Research) Grant Number DMR 0079992. The United States Government has certain rights in the invention.

### Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Application No. 60/602,320, filed August 18, 2004, the whole of which is incorporated herein by reference.

### Technical Field

This invention is directed to group (IV) and group (X) metal complexes with beta-ketoiminato ligands and to the use of these complexes as catalysts for polymerization of ethylene, C<sub>3</sub>-C<sub>10</sub>-alpha olefins, C<sub>4</sub>-C<sub>10</sub> cyclic alkenes and for the copolymerization of ethylene and comonomers.

### Background of the Invention

Group (IV) and group (X) metal complex catalysts with beta-ketoiminato ligands for use for polymerizing ethylene and alpha olefins are known. See Kim, J., et al, *Journal of Organometallic Chemistry* 620, 1-7 (2001); Li, X.-F., et al, *Organometallics* 23, 1223-1230 (2004); Zhang, D., et al, *Organometallics* 23, 3270-3275 (2004).

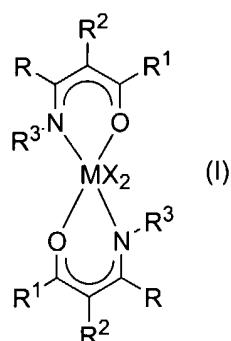
These efforts have focused on complexes with beta-ketoiminato ligands, where carbon alpha to the carbonyl carbon is planar (sp<sup>2</sup>-hybridized) or methyl or trifluoromethyl.

A new family of ligands is important to enrich the pool for catalyst discovery.

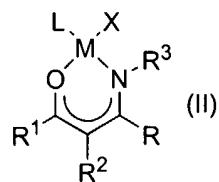
Summary of the Invention

It has been discovered herein that a new family of ligands is available where a carbon alpha to a carbonyl carbon is a tetrahedral carbon, that is a carbon which has four bonds extending in different directions.

In an embodiment of the invention, denoted the first embodiment, there is provided a compound having the structure:

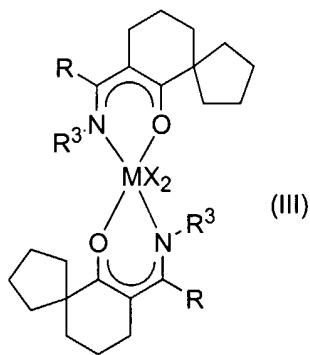


where M is selected from the group consisting of titanium, zirconium and hafnium; where X is selected from the group consisting of halogens, C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> alkoxides and C<sub>1</sub>-C<sub>20</sub> amides; where R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> fluorocarbons (includes, for example, fluoroalkyls and fluoroaryls including those with both H and F substituents) and C<sub>3</sub>-C<sub>20</sub> heterocycles; where R<sup>1</sup> is selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> hydrocarbons bound by a tetrahedral carbon atom, i.e., where carbon alpha to carbonyl carbon, i.e., the carbon bonded to oxygen of ketoimine moiety is a tetrahedral carbon; R<sup>2</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> fluorocarbons (includes, for example, fluoroalkyls and fluoroaryls including those with both H and F substituents) and C<sub>3</sub>-C<sub>20</sub> heterocycles; R<sup>3</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> fluorocarbons (includes, for example, fluoroalkyls and fluoroaryls including those with both H and F substituents) and C<sub>3</sub>-C<sub>20</sub> heterocycles; where two or more of R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> can be bonded together to form a ring; or having the structure:

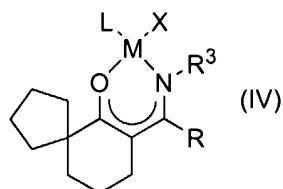


where M is selected from the group consisting of nickel and palladium, L is a neutral two electron donor (i.e., an uncharged group which fulfills the function of filling the coordination valance of M, e.g., an ether, phosphine or nitrile group), X, R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are defined as above and where two or more of R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> can be bonded together to form a ring.

In preferred cases, R<sup>1</sup> and R<sup>2</sup> are bonded together thereby forming (arylimino-alkyl)-spiro[4,5]decane-6-one ligand (two for (I) and one for (II)), i.e., to contain spiro[4,5]decane-6-onato moiety. In this case, the compounds have the structure:



where M is selected from the group consisting of titanium, zirconium, and hafnium, and R and R<sup>3</sup> are defined as above and R and R<sup>3</sup> can be bonded together to form a ring or have the structure:



where M is selected from the group consisting of nickel and palladium and L, R and R<sup>3</sup> are defined as above and R and R<sup>3</sup> can be bonded together to form a ring.

Preferably X is Cl, R is H or CF<sub>3</sub> and R<sup>3</sup> is phenyl or fluorinated phenyl and even more preferably the compound contains at least one fluorine atom.

The compounds (I), (II), (III) and (IV) are useful as catalysts for polymerization of ethylene, C<sub>3</sub>-C<sub>10</sub> alpha olefins, and C<sub>4</sub>-C<sub>10</sub> cyclic alkenes and for copolymerizing ethylene and comonomer selected from the group consisting of C<sub>3</sub>-C<sub>10</sub> alpha olefins, styrene, C<sub>3</sub>-C<sub>10</sub> dienes, C<sub>3</sub>-C<sub>10</sub> alkenyl halides and C<sub>4</sub>-C<sub>10</sub> cyclic alkenes.

In another embodiment of the invention, denoted the second embodiment, ethylene is polymerized in the presence of a catalytically effective amount of activated compound (I), e.g., activated compound (III), to produce polyethylene of M<sub>n</sub> in the range of 1,000 to 3,000,000 and polydispersities (PDI) in the range of 1 to 3.

In still another embodiment of the invention, denoted the third embodiment, C<sub>3</sub>-C<sub>10</sub> alpha olefin is polymerized in the presence of a catalytically effective amount of activated compound (I), e.g., activated compound (III), to produce poly(C<sub>3</sub>-C<sub>10</sub> alpha olefin) of M<sub>n</sub> ranging from 1,000 to 3,000,000 and PDI ranging from 1 to 3.

In still another embodiment of the invention, denoted the fourth embodiment, C<sub>4</sub>-C<sub>10</sub> cyclic alkene is polymerized in the presence of a catalytically effective amount of activated compound (I), e.g., activated compound (III), to produce poly(C<sub>4</sub>-C<sub>10</sub> cyclic alkene) of M<sub>n</sub> ranging from 1,000 to 3,000,000 and PDI ranging from 1 to 3.

In still another embodiment of the invention, denoted the fifth embodiment, ethylene and comonomer in a mole ratio of ethylene to comonomer ranging from 1:99 to 99:1 are copolymerized in the presence of a catalytically effective amount of activated compound (I), e.g., activated compound (III), to produce copolymer of ethylene and said comonomer of M<sub>n</sub> ranging from 1,000 to 3,000,000.

Where M is Ti and X is Cl, the polymerizations/copolymerizations are advantageously carried out with the activation being effected by an activating effective amount of methylaluminoxane such that [Al]:[Ti] mole ratio ranges from 100 to 200:1; e.g., 125 to 175:1.

Where M is Zr and X is Cl, the polymerizations/copolymerizations are carried out with the activation being effected by an activating effective amount of methylaluminoxane of compounds of the first embodiment herein such that [Al]:[Zr] mole ratio ranges from 100 to 200:1; e.g., 150:1.

Where M is Hf and X is Cl, the polymerization/copolymerization are advantageously carried out with the activation being effected by an activating effective amount of methylaluminoxane such that [Al]:[Hf] mole ratio ranges from 100 to 200:1; e.g., 150:1.

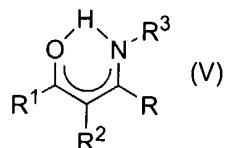
The said polymerizations/copolymerizations can also be carried out in the presence of an activating effective amount of trialkylaluminum/fluorinated borate salts, such as *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> such that [Al]:[B]:[M] mole ratio ranges from 10 to 100:2:1; e.g., 40:2:1.

The molecular weights and polydispersities (PDI) are determined by high temperature gel-permeation chromatography using monodisperse polyethylene standards.

#### Detailed Description

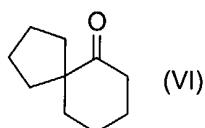
We turn now to the first embodiment of the invention.

We turn now to synthesis of compounds of the structure (I).



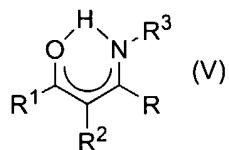
(V) where R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are defined as for structure (I), is deprotonated in solvent, e.g., at -78°C with 1 equivalent of butyllithium followed by reaction with MX<sub>4</sub>. The lithium of BuLi replaces the H in (V) and 2 Lig-Li + MX<sub>4</sub> gives (Lig)<sub>2</sub> MX<sub>2</sub> + 2 LiX.

We turn now to synthesis of the compounds of the structure (III). Spiroketone (VI)



is obtained, for example, through a pinacol rearrangement from [1,1'-bicyclopentyl]-1,1'-diol. This synthesis is described in Kita, Y., et al., Tetrahedron Lett 38, 8315-8318 (1997) and Kita, Y., Tetrahedron 54, 14689-14704 (1998). Where R<sup>3</sup> is C<sub>1</sub>-C<sub>20</sub> hydrocarbon or C<sub>1</sub>-C<sub>20</sub> fluorocarbon, coupling of R<sup>3</sup>N=C(R)Cl with spiroketone generates the corresponding ligand whereupon deprotonation followed by reaction with MX<sub>4</sub> as described above gives compound (III). The compound R<sup>3</sup>N=C(R)Cl is prepared by reacting R<sup>3</sup>NH<sub>2</sub> and RC(O)OH in CCl<sub>4</sub> with Ph<sub>3</sub>P and Et<sub>3</sub>N. Where R is H, the spiroketone (VI) is first formylated using ethyl formate to generate aldehyde which is coupled with R<sup>3</sup>NH<sub>2</sub> under neat conditions in the presence of p-toluenesulfonic acid and phosphorus pentoxide to generate ligand whereupon deprotonation followed by reaction with MX<sub>4</sub> as described above gives compound (III).

We turn now to synthesis of the compounds of the structure (II).



(V) is deprotonated in solvent, e.g., at  $-78^{\circ}\text{C}$  with one equivalent of butyllithium followed by reaction with one equivalent *trans*- $[(\text{L})_2\text{NiX}(\text{Cl})]$ .

We turn now to synthesis of the compounds (IV). Ligand is formed as described above for (III). Deprotonation, followed by reaction with *trans*- $[(\text{L})_2\text{NiX}(\text{Cl})]$  gives (IV).

We turn now to the method embodiments of the invention herein.

The amount of compound (I) or compound (II) per mole of monomer ranges, for example, from 1 to  $1 \times 10^{-6}$  mmol per mole; i.e., this amount can provide catalytically effective amount.

The methylaluminoxane mentioned above is an activator for compounds (I)/(III).

Alternatives for the methylaluminoxane are reaction with a metal alkyl such as  $\text{AlR}_3$  or  $\text{ZnR}_2$  followed by reaction with  $(\text{Ph}_3\text{C})^+(\text{BAr}_4^-)$ ,  $(\text{PhNMe}_2\text{H})^+(\text{BAr}_4^-)$ ,  $\text{Ar}_3\text{B}$  or  $\text{Ar}_3\text{Al}$ , e.g., trialkylaluminum/fluorinated borate salts, e.g.,  $i\text{-Bu}_3\text{Al}/\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_4^-$ .

Activators for compounds (II)/(IV) are Lewis acids such as (1,5-cyclooctadiene) $\text{Ni}$ ,  $\text{Ar}_3\text{B}$  or  $\text{Ar}_3\text{Al}$ .

As used herein, the term “activator” means any compound that reacts with (I) or (II) to generate an active catalytic *species in situ* and the term “activated” means that (I) or (II) has been reacted with activator to convert M of (I) or (II) to cationic form and/or to cause rearrangement of (I) or (II) to a more active or selective form.

Amounts are given above exemplary for methylaluminoxane activating effective amount.

Reaction times typically range from 5 minutes to 1 hour.

Reaction temperatures can range, e.g., from 0 to  $50^{\circ}\text{C}$ .

A suitable solvent for the catalyst for the polymerizations/copolymerizations is toluene.

The invention is illustrated in the following working examples.

Example I

Synthesis of (III) where M is Ti, X is Cl,  
R is CF<sub>3</sub>, R<sup>3</sup> is Ph - Compound 1a.

This synthesis is set forth below. This compound is sometimes designated "CAT" hereinafter.

**7-(2,2,2-Trifluoro-1-phenylimino-ethyl)-spiro[4,5]decan-6-one.** A procedure similar to that used to make *N*-substituted  $\beta$ -enamino acid derivatives from 2-alkyl-2-oxazolines and *N*-arylimidoyl chloride as described in Fustero, S., et al., J. Org. Chem. 61, 8849-8859 (1996), was used. Thus, to a stirred solution of diisopropylamine (2.8 mL, 20 mmol) in THF (15 mL) at 0°C was added *n*-butyllithium (1.6 M in hexanes, 12.5 mL, 20 mmol) dropwise. After being stirred for an additional 30 min. the solution was cooled to -78°C and spiro[4,5]-decan-6-one (1.52g, 10 mmol) in THF (15 ml) was added. The reaction mixture was stirred for 2 h, then lifted from the dry ice/acetone bath to warm to room temperature (RT) for 20 min. After cooling down to -78°C, a solution of the *N*-phenyl-2,2,2-trifluoroacetimidoyl chloride (2.07g, 10 mmol) in THF (15 mL) was slowly added to the reaction mixture. When TLC analysis showed the disappearance of the starting material, the reaction was quenched by saturated ammonium chloride aqueous solution. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL x 3). The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvents were removed under reduced pressure to furnish the crude product as brown oil. Purification by column chromatography over silica gel (5-7% (v/v) ethyl acetate/hexanes, R<sub>f</sub>=0.5) afforded 1.3g (41%) of pure product as a yellow oil. <sup>1</sup>H NMR (300 MHz):  $\delta$  10.95 (s, 0.5H, OH/CH), 7.24 (m, 2H, ArH), 7.08 (t, J = 7.5, 1H, ArH), 6.95 (d, J = 8.1, 2H, ArH), 5.54 (brs, 0.1H, CH/OH), 2.70 (m, 2H, CH<sub>2</sub>), 2.31-2.03 (m, 2H, CH<sub>2</sub>), 1.86-1.80 (m, 4H, CH<sub>2</sub>), 1.73-1.66 (m, 4H, CH<sub>2</sub>), 1.51-1.39 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz):  $\delta$  208.5, 142.5, 129.2, 128.0, 124.1, 121.7, 119.7, 116.4, 56.2, 40.2, 38.6, 37.1, 35.2, 26.1, 21.7. <sup>19</sup>F NMR (282 MHz):  $\delta$  -68.3.

**Ti complex 1a.** The Ti complex 1a was synthesized following the procedure similar to that reported in literature to make phenoxyimine Ti complex with minor modifications. Thus, to a stirred solution of ligand 7-(2,2,2-trifluoro-1-phenylimino-ethyl)-spiro[4,5]decan-6-one (1.29 g, 3.98 mmol) in 20 mL of diethyl ether (Et<sub>2</sub>O) at -78°C was added *n*-BuLi (1.6

M in hexanes, 2.48 mL, 3.98 mmol) dropwise using a gas tight syringe. This solution was allowed to slowly return to room temperature and stirred for an additional half hour. The solution was then added dropwise *via* cannula to a solution of TiCl<sub>4</sub> (1.0 M in toluene, 2.0 mL, 2.0 mmol) in Et<sub>2</sub>O (15 mL) at -78°C. The resulting deep red solution was allowed to warm naturally to room temperature and stirred for an additional 16 h. After removal of the solvent under vacuum, the residue was taken up in toluene and the precipitated LiCl was removed by filtration over a Celite plug. Removal of solvent *in vacuo* gave a deep red powder that was crystallized from a mixture of toluene/pentane to give the desired complex as a deep red crystalline solid (1.02 g, 67%). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 500 MHz): δ 7.14 (d, J = 7.0, 2H, ArH), 7.03 (t, J = 7.8, 2H, ArH), 6.92 (t, J = 7.2, 2H, ArH), 6.84 (t, J = 7.2, 2H, ArH), 6.72 (d, J = 7.0, 2H, ArH), 2.68 (m, 2H, CH<sub>2</sub>), 2.48 (m, 2H, CH<sub>2</sub>), 1.93 (m, 2H, CH<sub>2</sub>), 1.81 (m, 2H, CH<sub>2</sub>), 1.47-1.32 (m, 16H, CH<sub>2</sub>), 1.11 (m, 2H, CH<sub>2</sub>), 0.77 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 125 MHz): δ 187.4, 159.6 (q, J<sub>CF</sub> = 26.4), 150.2, 126.5, 122.7, 122.5, 120.1, 113.4, 51.3, 40.8, 40.1, 37.5, 27.7, 21.6. <sup>19</sup>F NMR (toluene-*d*<sub>8</sub>, 470 MHz): δ -60.0.

### Example II

Synthesis of (III) where M is Ti, X is Cl,  
R is CF<sub>3</sub>, R<sup>3</sup> is 2,6-F<sub>2</sub>Ph - Compound 1b

This synthesis is set forth below.

***N*-(2,6-Difluoro-phenyl)-2,2,2-trifluoro-acetimidoyl chloride.** The procedure used to make *N*-phenyl analogue was followed. Thus, 2,6-difluoroaniline (5.17 mL, 6.20 g, 48 mmol) was reacted with trifluoroacetic acid (TFA, 3.08 mL, 4.56 g, 40 mmol) and carbon tetrachloride (CCl<sub>4</sub> 38.6 mL, 61.50 g, 400 mmol) in the presence of triphenylphosphine (Ph<sub>3</sub>P, 31.47 g, 120 mmol) and triethylamine (Et<sub>3</sub>N, 6.70 mL, 4.86 g, 48 mmol) under reflux condition for 6 h afforded 3.70 g (38%) of pure product as a colorless oil after vacuum distillation (54°C/240 mTorr). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 6.35 (d, J = 9.1, 2H, ArH-3,5), 6.33 (t, J=9.0, 1H, ArH-4). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz): δ 153.0 (dd, <sup>1</sup>J<sub>CF</sub> = 251.7, <sup>3</sup>J<sub>CF</sub> = 4.2, ArC, *ortho*), 140.3 (N=C), 128.2, 122.4 (t, <sup>3</sup>J<sub>CF</sub> = 16.0, ArC, *para*), 117.5 (q, <sup>1</sup>J<sub>CF</sub> = 278.0, CF<sub>3</sub>), 112.3 (dd, <sup>2</sup>J<sub>CF</sub> = 18.3, <sup>4</sup>J<sub>CF</sub> = 4.6, ArC, *meta*). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 470 MHz): δ -71.8, -121.0.

**7-[1-(2,6-Difluoro-phenylimino)-2,2,2-trifluoro-ethyl]-spiro[4,5]decan-6-one.** The procedure used to make *N*-phenyl analogue was followed. Thus, spiro[4,5]decan-6-one was reacted with diisopropylamine (2.8 mL, 2.02 g, 20 mmol) and *n*-BuLi (1.6 M in hexane, 12.5 mL, 20 mmol) in THF at -78°C, and then *N*-(2,6-difluoro-phenyl)-2,2,2-trifluoro-acetimidoyl chloride (2.44 g, 10 mmol) to afford 0.51 g (15%) of pure product as a yellow oil. <sup>1</sup>H NMR (300 MHz): δ 11.08 (s, 1H, OH/CH), 7.03 (m, 1H, ArH), 6.90 (m, 2H, ArH), 2.65 (brs, 2H, CH<sub>2</sub>), 2.00-1.42(m, 12H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz): δ 222.9, 221.9, 208.9, 125.1, 112.5, 111.8, 111.7, 111.5, 56.0, 38.8, 37.0, 27.1, 26.2, 21.9.

**Ti complex 1b.** The Ti complex **1b** was synthesized following the procedure to make **1a**. Thus, ligand 7-[1-(2,6-difluoro-phenylimino)-2,2,2-trifluoro-ethyl]-spiro[4,5]decan-6-one (0.57 g, 1.59 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 0.99 mL, 1.59 mmol) and then TiCl<sub>4</sub> (1.0 M in toluene, 0.8 mL, 0.8 mmol) to give a deep red powder that was crystallized from a mixture of toluene/pentane to give the desired complex as a deep red crystalline solid (0.15g, 23%). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz): δ 6.55 (m, 4H, ArH), 6.40 (m, 2H, ArH), 2.80-0.80 (m, 28H, CH<sub>2</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 100 MHz): δ 189.2, 127.8, 122.3, 119.4, 113.1, 112.5, 112.3, 111.6, 51.6, 40.9, 39.9, 37.4, 27.0, 21.4. <sup>19</sup>F NMR (toluene-*d*<sub>8</sub>, 376 MHz): δ -60.8, -113.2, -116.4. Anal Calcd for C<sub>36</sub>H<sub>34</sub>Cl<sub>2</sub>F<sub>10</sub>N<sub>2</sub>O<sub>2</sub>Ti: C, 51.76; H, 4.10; N, 3.35. Found: C, 51.59; H, 4.17; N, 3.10.

### Example III

Synthesis of (III) where M is Ti, X is Cl, R is H and R<sup>3</sup> is Ph - Compound **1c**

This synthesis is set forth below.

**6-Oxo-spiro[4,5]decane-7-carbaldehyde.** The procedure similar to that reported in Lopez-Alvarada, P., et al., Eur. J. Org. Chem. 2002, 1702-1707 for formylation under basic conditions was followed. A solution of spiro[4,5]decan-6-one(2.70 g, 17.74 mmol) in dry toluene (40 mL) was added dropwise by a gas tight syringe at room temperature to a suspension of sodium methoxide (4.29 g, 75.44 mmol) in dry toluene (75 mL). The reaction mixture turned from white to pale yellow and was cooled to 0°C. After 20 min, ethyl formate (6.12 mL, 5.61 g, 75.73 mmol) was added dropwise by a gas tight syringe, and the reaction

mixture was stirred at room temperature overnight. Diethyl ether (80 mL) was then added, and the suspension was washed with water (40 mL x 2) and was titrated to pH = 6 by 2N HCl (aq.). The ethereal solution was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to yield 3.04 g (95%) product as a light yellow oil. <sup>1</sup>H NMR (300 MHz):  $\delta$  14.79 (d, J = 3.3, 1H, OH/CH), 8.62 (d, J = 3.3, 1H, CHO), 2.33 (t, J = 6.2, 2H, CH<sub>2</sub>), 2.12-1.42(m, 12H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz):  $\delta$  191.4, 187.8, 108.1, 48.9, 39.3, 36.2, 26.5, 24.1, 20.7.

**7-Phenyliminomethyl-spiro[4,5]decan-6-one.** A 150 mL round bottom flask was charged with spiroaldehyde (1.00 g, 5.55 mmol), aniline (0.65 g, 6.93 mmol) and the mixture was stirred for ca 10 min to achieve total dissolution. *p*-Toluenesulfonic acid (*p*-TSA, 50 mg) and phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>, 50 mg) were added, and then the stirred mixture was heated to 110°C (oil bath) for 2 h under nitrogen. After cooling down to room temperature, CH<sub>2</sub>Cl<sub>2</sub> (180 mL) was added to dissolve the brown slurry and the solution was washed by water (60 mL x 2), brine and then dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel (10% (v/v) EtOAc/hexanes) to give 1.24 g (88%) of red oil. <sup>1</sup>H NMR (400 MHz):  $\delta$  11.89 (d, J = 11.6, 1H, OH/CH), 7.23 (m, 2H, ArH-*ortho*), 7.10 (dt, J = 12.0, 1.0, 1H, CHN), 6.98-6.93 (m, 3H, ArH-*para* + ArH-*meta*), 2.45-2.42 (m, 2H, CH<sub>2</sub>), 2.04-2.00 (m, 2H, CH<sub>2</sub>), 1.78-1.61 (m, 8H, CH<sub>2</sub>), 1.47-1.41 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz):  $\delta$  206.0, 142.1, 140.6, 129.5, 122.6, 115.7, 104.6, 53.5, 39.3, 36.7, 28.9, 26.2, 21.4.

**Ti complex 1c.** The Ti complex **1c** was synthesized following the procedure to make **1a**. Thus, ligand 7-phenyliminomethyl-spiro[4,5]decan-6-one (1.24 g, 4.86 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 3.03 mL, 4.86 mmol) and then TiCl<sub>4</sub> (1.0 M in toluene, 2.43 mL, 2.43 mmol) to give a deep red powder (81 mg, 6%). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz):  $\delta$  7.02-6.84 (m, 12H, CHN+ArH), 2.39 (m, 2H, CH<sub>2</sub>), 1.92 (m, 2H, CH<sub>2</sub>), 1.80 (m, 4H, CH<sub>2</sub>), 1.46-1.02 (m, 18H, CH<sub>2</sub>), 0.70 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 100 MHz):  $\delta$  182.2, 165.0, 154.6, 128.3, 125.8, 123.9, 112.3, 48.9, 40.1, 37.7, 36.9, 27.7, 26.6.

#### Example IV

Synthesis of (III) where M is Ti, X is Cl,  
R is H and R<sup>3</sup> is 2,6-F<sub>2</sub>Ph - Compound **1d**

The synthesis of Compound **1d** is set forth below.

**7-[2,6-Difluoro-phenylimino)-methyl]-spiro[4,5]decan-6-one.** The procedure to make *N*-phenyl analogue was followed. Thus, spiroaldehyde (0.72 g, 4.01 mmol) was reacted with 2,6-difluoroaniline (0.62 g, 4.81 mmol) in the presence of *p*-toluenesulfonic acid (40 mg) and P<sub>2</sub>O<sub>5</sub> (50 mg) to afford 1.04 g (89%) of pure product as a yellow oil after column chromatography over silica gel (10% (v/v) EtOAc/hexanes). <sup>1</sup>H NMR (300 MHz):  $\delta$  11.88 (d, *J* = 11.3, 1H, OH/CH), 7.30 (d, *J* = 11.5, 1H, CHN), 6.87-6.79 (m, 3H, ArH), 2.42 (t, *J* = 5.4, 2H, CH<sub>2</sub>), 2.09-2.00 (m, 2H, CH<sub>2</sub>), 1.79-1.60 (m, 8H, CH<sub>2</sub>), 1.48-1.40 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz):  $\delta$  207.0, 153.8, (dd, *J*<sub>CF</sub> = 246.2, 5.8), 144.3 (t, *J*<sub>CF</sub> = 6.4), 121.6 (t, *J*<sub>CF</sub> = 9.7), 119.3 (t, *J*<sub>CF</sub> = 12.6), 112.3 (dd, *J*<sub>CF</sub> = 16.0, 7.7), 106.6, 54.1, 39.4, 36.8, 29.2, 26.4, 21.5. <sup>19</sup>F NMR (282 MHz):  $\delta$  -126.2.

**Ti complex 1d.** The Ti complex **1d** was synthesized following the procedure to make **1a**. Thus, ligand 7-[(2,6-difluoro-phenylimino)-methyl]-spiro[4,5]decan-6-one (1.03 g, 3.54 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 2.21 mL, 3.54 mmol) and then TiCl<sub>4</sub> (1.0 M in toluene, 1.77 mL, 1.77 mmol) gave a deep red powder that was crystallized from toluene to give the desired complex as a deep red crystalline solid (0.83g, 67%). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz):  $\delta$  7.07 (s, 2H, CHN), 6.55 (m, 4H, ArH), 6.38 (m, 2H, ArH), 2.20-0.80 (m, 28H, CH<sub>2</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 100 MHz):  $\delta$  184.7, 169.7, 127.1, 112.2, 112.0, 111.9, 111.0, 49.4, 40.1, 37.7, 36.9, 27.7, 26.6. <sup>19</sup>F NMR (toluene-*d*<sub>8</sub>, 376 MHz):  $\delta$  -116.1, -118.2. Anal Calcd for C<sub>34</sub>H<sub>36</sub>Cl<sub>2</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Ti: C, 58.39; H, 5.19; N, 4.01. Found: C, 58.45; H, 4.98; N, 3.79.

### Example V

Synthesis of (III) where M is Ti, X is Cl, R is H, R<sup>3</sup> is 3,5-F<sub>2</sub>Ph - Compound 1e

The synthesis of Compound **1e** is set forth below.

**7-[3,5-Difluoro-phenylimino)-methyl]-spiro[4,5]decan-6-one.** The procedure to make *N*-phenyl analogue was followed. Thus, spiroaldehyde (1.04 g, 5.77 mmol) was reacted with 3,5-difluoroaniline (0.91 g, 6.92 mmol) in the presence of *p*-toluenesulfonic acid (50 mg) and P<sub>2</sub>O<sub>5</sub> (50 mg) to afford 1.35 g (81%) of pure product as a light yellow oil after column chromatography over silica gel (10% (v/v) EtOAc/hexanes). <sup>1</sup>H NMR (400 MHz):  $\delta$

11.72 (d,  $J = 11.6$ , 1H,  $CH/OH$ ), 6.87 (dt,  $J = 11.6$ , 1.1, 1H,  $CHN$ ), 6.39 (dd,  $J = 9.0$ , 2.2, 2H,  $ArH$ -*ortho*), 6.30 (tt,  $J = 8.9$ , 2.2, 1H,  $ArH$ -*para*), 2.82 (t,  $J = 5.6$ , 2H,  $CH_2$ ), 1.97-1.92 (m, 2H,  $CH_2$ ), 1.72-1.56 (m, 8H,  $CH_2$ ), 1.41-1.36 (m, 2H,  $CH_2$ ).  $^{13}C$  NMR (100 MHz):  $\delta$  207.4, 165.4, 162.9, 143.5, 140.1, 106.7, 98.7, 97.5, 54.1, 39.4, 36.8, 29.2, 26.4, 21.5.  $^{19}F$  NMR (376 MHz):  $\delta$  -108.9.

**Ti complex 1e.** The Ti complex **1e** was synthesized following the procedure to make **1a**. Thus, ligand 7-[(3,5-difluoro-phenylimino)-methyl]-spiro[4.5]decan-6-one (0.68 g, 2.33 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 1.46 mL, 2.33 mmol) and then  $TiCl_4$  (1.0 M in toluene, 1.17 mL, 1.17 mmol) to give a deep red powder that was crystallized from toluene to give the desired complex as a deep red crystalline solid (0.088 g, 11%).  $^1H$  NMR (toluene-*d*<sub>8</sub>, 400 MHz):  $\delta$  6.74 (s, 2H,  $CHN$ ), 6.46 (dd,  $J = 8.7$ , 1.9, 4H,  $ArH$ ), 6.34 (tt,  $J = 9.0$ , 2.3, 2H,  $ArH$ ), 2.36 (m, 2H,  $CH_2$ ), 2.10-1.76 (m, 8H,  $CH_2$ ), 1.49-1.13 (m, 16H,  $CH_2$ ), 0.85 (m, 2H,  $CH_2$ ).  $^{13}C$  NMR (toluene-*d*<sub>8</sub>, 100 MHz):  $\delta$  184.2, 165.6, 164.2, 161.7, 156.3, 113.1, 107.9, 101.3, 49.4, 40.3, 37.6, 36.8, 27.8, 26.6.  $^{19}F$  NMR (toluene-*d*<sub>8</sub>, 376 MHz):  $\delta$  -109.51.

#### Example VI

**Synthesis of (III) where M is Ti, X is Cl, R is H and R<sup>3</sup> is F<sub>5</sub>Ph - Compound 1f**

The synthesis of Compound **1f** is set forth below.

**7-(Pentafluorophenylimino-methyl)-spiro[4,5]decan-6-one.** The procedure to make *N*-phenyl analogue was followed. Thus, spiroaldehyde (0.66 g, 3.66 mmol) was reacted with 2,3,4,5,6-pentafluoroaniline (0.81 g, 4.42 mmol) in the presence of *p*-toluenesulfonic acid (40 mg) and  $P_2O_5$  (50 mg) to afford 1.10 g (87%) of pure product as light yellow crystals after column chromatography over silica gel (10% (v/v) EtOAc/hexanes).  $^1H$  NMR (500 MHz):  $\delta$  11.84 (d,  $J = 11.0$ , 1H,  $CH/OH$ ), 7.16 (d,  $J = 11.3$ , 1H,  $CHN$ ), 2.44 (m, 2H,  $CH_2$ ), 2.06-2.00 (m, 2H,  $CH_2$ ), 1.78-1.75 (m, 2H,  $CH_2$ ), 1.73-1.66 (m, 6H,  $CH_2$ ), 1.49-1.43 (m, 2H,  $CH_2$ ).  $^{13}C$  NMR (125 MHz):  $\delta$  208.2, 142.3, (t,  $J = 6.1$ ), 140.0-139.4 (m), 138.1-136.9 (m), 135.2-134.9 (m), 117.7 (td,  $J = 10.7$ , 4.1), 108.5, 54.5, 39.4, 36.7, 29.3, 26.4, 21.4.  $^{19}F$  NMR (376 MHz):  $\delta$  -156.24 (d,  $J_{FF} = 21.4$ ), -163.07 (td,  $J_{FF} = 21.4$ , 4.6), -166.08 (tt,  $J_{FF} = 21.4$ , 4.6). Anal Calcd for  $C_{17}H_{16}F_5NO$ : C, 59.13; H, 4.67; N, 4.06. Found: C, 59.18; H, 4.60; N, 3.96.

**Ti complex 1f.** The Ti complex **1f** was synthesized following the procedure to make **1a**. Thus, ligand 7-[(pentafluorophenylimino)-methyl]-spiro[4,5]decan-6-one (1.08 g, 3.13 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 1.96 mL, 3.13 mmol) and then TiCl<sub>4</sub> (1.0 M in toluene, 1.57 mL, 1.57 mmol) to give a deep red powder that was crystallized from toluene to give the desired complex as a deep red crystalline solid (0.80 g, 63%). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz):  $\delta$  6.91(s, 2H, CHN), 2.31-2.25 (m, 2H, CH<sub>2</sub>), 2.07-1.95 (m, 2H, CH<sub>2</sub>), 1.75-1.69 (m, 2H, CH<sub>2</sub>), 1.59-1.56 (m, 2H, CH<sub>2</sub>), 1.34-1.10 (m, 2H, CH<sub>2</sub>), 0.88-0.83 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 100 MHz):  $\delta$  187.0, 170.2, 112.7, 49.8, 40.2, 37.4, 36.5, 27.6, 26.4, 26.1. <sup>19</sup>F NMR (376 MHz):  $\delta$  -145.6, -146.9, -158.9, -159.9, -162.6. Anal Calcd for C<sub>34</sub>H<sub>30</sub>Cl<sub>2</sub>F<sub>10</sub>N<sub>2</sub>O<sub>2</sub>Ti: C, 50.58; H, 3.75; N, 3.47. Found: C, 50.66; H, 3.52; N, 3.21.

#### Example VII

Synthesis of (III) where M is Zr, X is Cl, R is CF<sub>3</sub> and R<sup>3</sup> is Ph - Compound 1g

Compound **1g** is synthesized as follows: The ligand 7-(2,2,2-trifluoro-1-phenylimino-ethyl)-spiro[4,5]decane-6-one is synthesized as described in Example I. A solution of the ligand in toluene is added to a solution of tetrakis(dimethylamino) zirconium in toluene solvent at room temperature, leading to an immediate color change from light yellow to orange, and then dark red. The resulting solution is stirred overnight to afford after solvent removal the complex L<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub>. Then the complex L<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> is dissolved in methylene chloride, and an excess (ca. 10 equivalent) of chlorotrimethylsilane is added. After stirring overnight at 22°C, the solvent is removed under vacuum. The dark red residue is triturated with pentane to afford a yellow solid.

#### Example VIII

Synthesis of (III) where M is Hf, X is Cl, R is CF<sub>3</sub> and R<sup>3</sup> is Ph – Compound 1h

Compound **1h** is synthesized as follows: The ligand 7-(2,2,2-trifluoro-1-phenylimino-ethyl)-spiro[4,5]decane-6-one is synthesized as described in Example I. A solution of the ligand in toluene is added to a solution of tetrakis(dimethylamino) hafnium in toluene solvent at room temperature, leading to an immediate color change. The resulting

solution is stirred overnight to afford after solvent removal the complex  $L_2Hf(NMe_2)_2$ . Then the complex  $L_2Hf(NMe_2)_2$  is dissolved in methylene chloride, and an excess (ca. 10 equivalent) of chlorotrimethylsilane is added. After stirring overnight at 22°C, the solvent is removed under vacuum. The residue is triturated with pentane to afford compound **1h** as a solid.

#### Example IX

Synthesis of (IV) where L is  $Ph_3P$ , X is Ph, M is Ni, R is  $CF_3$  and  $R^3$  is Ph - Compound **1i**

Compound **1i** is synthesized as follows: The ligand 7-(2,2,2-trifluoro-1-phenyliminoethyl)-spiro[4,5]decane-6-one is synthesized as set forth in Example I. The ligand is deprotonated in toluene solvent with one equivalent *n*-butyllithium at -78°C. Then one equivalent of *trans*-[( $Ph_3P$ )<sub>2</sub>NiPh(Cl)] in toluene is added. After stirring overnight at 22°C, the suspension is filtered to remove LiCl. Upon concentration of the toluene, crystals of Compound **1i** are grown and isolated after decanting the mother liquor.

#### Example X

##### Polymerization of Ethylene

Polymerizations of ethylene were carried out with **1a**, **1b**, **1c**, **1d**, **1e** and **1f** upon activation with methylalumininoxane (MAO). The polymerization conditions are as follows: 10 psi ethylene, 0.01 mmol catalyst, 80 ml toluene, 1.5 mmol MAO. Results obtained are set forth in said Table 1 below.

Table 1

Polymerization of Ethylene with 1a – 1f / PMAO

Catalyst	R	Ar (R <sup>3</sup> )	Temp. (°C)	Time (min)	Yield (mg)	Activity (mol E/(mol Ti h))	M <sub>n</sub> (g/mol)	PDI	M <sub>n</sub> (Calcd) (g/mol)	T <sub>m</sub> (°C)
1a	CF <sub>3</sub>	Ph	0	10	850	18 200	104 200	1.12	85 000	134.8
1a	CF <sub>3</sub>	Ph	25	10	794	17 000	119 500	1.12	79 400	134.2
1a	CF <sub>3</sub>	Ph	50	10	410	8 780	89 290	1.54	41 000	133.1
1b	CF <sub>3</sub>	2,6-F <sub>2</sub> Ph	0	10	620	13 300	66 600	1.11	62 000	134.0
1b	CF <sub>3</sub>	2,6-F <sub>2</sub> Ph	25	10	762	16 350	77 640	1.10	76 200	134.0
1b	CF <sub>3</sub>	2,6-F <sub>2</sub> Ph	50	10	454	9 740	66 240	1.22	45 400	134.0
1c	H	Ph	0	20	158	1 690	11 500	1.10	15 800	133.7
1c	H	Ph	25	10	80	1 710	8 940	1.05	8 000	130.8
1c	H	Ph	50	10	200	2 140	21 940	1.14	20 000	132.8
1d	H	2,6-F <sub>2</sub> Ph	0	10	8	200	N/D			
1d	H	2,6-F <sub>2</sub> Ph	25	10	5	125	N/D			
1d	H	2,6-F <sub>2</sub> Ph	50	10	36	900	2 090	1.04	3 600	130.6
1e	H	3,5-F <sub>2</sub> Ph	0	10	255	5 460	29 700	1.10	25 500	133.3
1e	H	3,5-F <sub>2</sub> Ph	25	10	405	8 660	35 710	1.10	40 500	133.2
1e	H	3,5-F <sub>2</sub> Ph	50	10	548	11 720	36 870	1.44	54 800	132.9
1f	H	F <sub>5</sub> Ph	0	10	49	1 100	5 000	1.05	4 900	130.4
1f	H	F <sub>5</sub> Ph	25	10	67	1 510	6 300	1.08	6 700	130.3
1f	H	F <sub>5</sub> Ph	50	10	133	2 990	8 740	1.36	13 300	131.1

Conditions: 0.01 mmol catalyst; 80 mL toluene; 1.5 mmol PMAO, [Al]:[Ti] = 150, 10 psi ethylene.

When activated with MAO, these complexes are active for the polymerization of ethylene at 0 to 50 °C (Table 1). The activity of compound 1a was found to be higher than that of the analogous phenoxyketimine catalyst.

As shown in Table 1, living polymerization was obtained with all the complexes in the range of 0 to 25 °C including the CF<sub>3</sub> substituted ketimine catalysts 1a and 1b.

The polymerization results for Compound 1b and 1e with various reaction times are shown in Tables 2 and 3 below, respectively.

**Table 2**Polymerization of Ethylene with 1b / PMAO

Cat. (mg)	Time (min.)	Yield (mg)	M <sub>n</sub> (Calcd)	M <sub>n</sub> (PE Vis)	PDI
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12.6	1	87	5750	6530	1.08
12.6	2	188	12450	13270	1.09
12.6	4	386	25560	26940	1.09
12.6	6	579	38340	39060	1.11
12.6	12	958	63440	61650	1.12

**Table 3**Polymerization of Ethylene with 1e / PMAO

Cat. (mg)	Time (min.)	Yield (mg)	$M_n$ (Calcd)	$M_n$ (PE Vis)	PDI
4.4	2	36	5700	5704	1.07
4.4	4	72	11540	12863	1.08
4.4	6	139	22360	20047	1.05
4.4	8	144	23145	26038	1.07
4.4	10	165	26495	32061	1.06
4.4	12	212	34044	37137	1.07
4.4	20	323	51772	60630	1.07

All the polyethylene products exhibited melting points in the range of 131 to 135°C. The  $^{13}\text{C}$  NMR analysis indicates that these PE samples have linear structures with non-detectable branching.

Example XIPolymerization of Propylene

Polymerization of propylene was carried out with **1a**, **1b**, **1d**, **1e** and **1f**. When  $\text{R}^3$  in the ligand was unsubstituted phenyl (ligand (**1c**)), the catalyst was not active for propylene polymerization. Conditions and results are shown in Table 4 below.

**Table 4**Polymerization of Propylene with 1a – 1f / PMAO

Catalyst	R	Ar	$[\text{Al}]/[\text{Ti}]$	Yield (mg)	Activity (Kg PP/(mol Ti h))	$M_n$ (GPC) (g/mol)	PDI	Tacticity
<b>1a</b>	$\text{CF}_3$	Ph	300	248	2.07	963,000	1.59	atactic
<b>1b</b>	$\text{CF}_3$	2,6-F <sub>2</sub> Ph	300	75 <sup>a</sup>	1.88	218,900	3.52	atactic

1c	H	Ph	150	N/A <sup>b</sup>				
1d	H	2,6-F <sub>2</sub> Ph	300	120	1.00	119,700	2.13	atactic
1e	H	3,5-F <sub>2</sub> Ph	150	165	1.38	3,700	1.25	syndio-enriched
1f	H	F <sub>5</sub> Ph	300	19	0.16	585,700	1.43	iso-enriched

Conditions: 0.02 mmol catalyst (Ti complex), 0°C, 6h, 80 mL toluene, 30 psi propylene.

a) 0.01 mmol cat., 4 hours. B) Not active.

Fluorine atoms at the *ortho* position of *N*-aryl of R<sup>3</sup> (**1b** and **1d**) led to production of atactic polypropylene while fluorine atoms at *meta* positions of *N*-aryl of R<sup>3</sup> (**1e**) led to syndio-enriched polypropylene ([rrrr] = 0.40). Pentafluoro substituted *N*-aryl catalyst (**1f**) generated iso-enriched polypropylene ([mmmm] = 0.20).

Polymerization of propylene was carried out with **1g** by using two different activators. When methylaluminoxane (MAO) was used, atactic polypropylene was produced (Turnover Frequency (TOF): 30.4 mol P/mol Zr·h; M<sub>n</sub> = 508 600, PDI = 1.69). When *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> was used as activator, iso-enriched polypropylene was generated (TOF = 129.8 mol P/mol Zr·h; bimodal GPC trace, PDI = 2.86).

### Example XII

#### Polymerization of Cyclopentene

Polymerization is conducted in a 3-ounce Lab-Crest™ pressure reaction vessel equipped with a magnetic stir bar. The reactor is first conditioned under dynamic vacuum and high temperature and then charged with a 3 mmol of PMAO in toluene and 5 mL of cyclopentene under nitrogen. Then 20 mmol of CAT is dissolved in toluene (3 mL) at room temperature under nitrogen. The solution is then added to the reactor using a syringe. Finally, the reactor is adjusted at 70°C. After 16 h, the reactor contents are poured into methanol/HCl and polymer is isolated by filtration.

### Example XIII

#### Polymerization of Norbornene

Polymerization is conducted in a 3-ounce Lab-Crest™ pressure reaction vessel equipped with a magnetic stir bar. The reactor is under dynamic vacuum and high temperature and then charged with a 3 mmol of PMAO in toluene and 5 mL of norbornene under nitrogen. Then 20 mmol of CAT is dissolved in toluene (3 mL) at room temperature under nitrogen. The solution is then added to the reactor using a syringe. Finally, the reactor

is adjusted at 70°C. After 16 h, the reactor contents are poured into methanol/HCl and polymer is isolated by filtration.

Example XIV  
Cyclopentene/Ethylene Copolymerization

Polymerization is conducted in a 3-ounce Lab-Crest™ pressure reaction vessel equipped with a magnetic stir bar. In a typical polymerization experiment, the reactor is charged with 6 mmol of PMAO in toluene under nitrogen. Then 13.2 mL of cyclopentene is introduced. CAT is dissolved in toluene (5 mL) at room temperature under nitrogen. The solution is then added to the reactor via syringe, such that the fixed [Al]/[M] ratio is 150. Finally, the reactor is pressurized with ethylene gas and adjusted to the desired pressure and temperature. After the desired period of time, the reactor is vented. The polymer is precipitated from methanol/HCl, filtered, and then dried *in vacuo* to constant weight.

Example XV  
Propylene/Ethylene Copolymerization

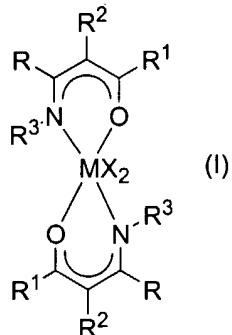
A 6-ounce Lab-Crest™ pressure reaction vessel equipped with a magnetic stir bar is first conditioned under dynamic vacuum and high temperature and then charged with PMAO (0.31 g, 5.3 mmol) and toluene (100 mL). The reactor is then equilibrated at 0°C. At this point, the reactor atmosphere is exchanged with propylene three times, and then the solution is saturated under propylene pressure (30 psi). An overpressure of ethylene (33 psi) is then introduced to the reactor and a toluene solution (4 mL) of CAT (0.01 mmol, [Al]/[M] = 500), is added via syringe. After 1 h, the reactor is vented and the polymer is precipitated in methanol/HCl, filtered, washed with methanol, and then dried *in vacuo* to constant weight.

Variations

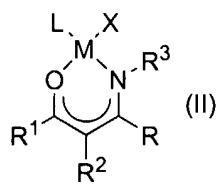
The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. Compound having the structure :



where M is selected from the group consisting of titanium, zirconium and hafnium; where X is selected from the group consisting of halogens, C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> alkoxides and C<sub>1</sub>-C<sub>20</sub> amides; where R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> fluorocarbons and C<sub>3</sub>-C<sub>20</sub> heterocycles; where R<sup>1</sup> is selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> hydrocarbons bound by a tetrahedral carbon atom, i.e., where carbon alpha to carbonyl carbon, i.e., the carbon bonded to oxygen of ketoimine moiety, of ketoimine moiety is a tetrahedral carbon; R<sup>2</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> fluorocarbons and C<sub>3</sub>-C<sub>20</sub> heterocycles; R<sup>3</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>20</sub> hydrocarbons, C<sub>1</sub>-C<sub>20</sub> fluorocarbons and C<sub>3</sub>-C<sub>20</sub> heterocycles; where two or more of R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> can be bonded together to form a ring; or having the structure:



where M is selected from the group consisting of nickel and palladium, L is a neutral two electron donor (i.e., an uncharged group which fulfills the function of filling the coordination valance of M, e.g., an ether, phosphine or nitrile group), X, R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are defined as above and where two or more of R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> can be bonded together to form a ring.

2. The compound of Claim 1 having the structure (I) where M is titanium.
3. The compound of Claim 1 where R<sup>1</sup> and R<sup>2</sup> are bonded together to form spiro[4,5]decan-6-onato.

4. The compound of Claim 3 where M is titanium or zirconium, X is selected from the group consisting of halogens and C<sub>1</sub>-C<sub>20</sub> hydrocarbons, and R<sup>3</sup> is selected from the group consisting of phenyl and fluorinated aryl.

5. The compound of Claim 4 where X is Cl and R is hydrogen or CF<sub>3</sub>.

6. The compound of Claim 4 which contains at least one fluorine atom.

7. The compound of Claim 1 having the structure (II) where R<sup>1</sup> and R<sup>2</sup> are bonded together to form spiro[4,5]decane-6-onato.

8. The compound of Claim 7 where X is Cl, R is hydrogen or CF<sub>3</sub> and R<sup>3</sup> is selected from the group consisting of phenyl and fluorinated phenyl.

9. A method for the polymerization of ethylene, comprising the step of polymerizing ethylene in the presence of a catalytically effective amount of activated compound of Claim 1, thereby producing polyethylene of M<sub>n</sub> in the range of 1,000 to 3,000,000 g/mol and PDI in the range of 1 to 3.

10. A method for the polymerization of ethylene, comprising the step of polymerizing ethylene in the presence of a catalytically effective amount of compound of Claim 5 activated by an activating effective amount of methylaluminoxane, thereby to produce polyethylene of M<sub>n</sub> in the range of 1,000 to 3,000,000 g/mol and PDI in the range of 1 to 3.

11. A method for polymerization of a C<sub>3</sub>-C<sub>10</sub> alpha olefin, comprising the step of polymerizing the C<sub>3</sub>-C<sub>10</sub> alpha-olefin in the presence of a catalytically effective amount of activated compound of Claim 1, thereby producing poly(C<sub>3</sub>-C<sub>10</sub> alpha olefin) of M<sub>n</sub> in the range of 1,000 to 3,000,000 g/mol and PDI in the range of 1 to 3.

12. The method of Claim 11 where said compound contains at least one fluorine atom.

13. A method for the polymerization of a C<sub>3</sub>-C<sub>10</sub> alpha olefin, such method comprising the step of polymerizing the C<sub>3</sub>-C<sub>10</sub> alpha-olefin in the presence of a catalytically effective amount of the compound of Claim 6 activated by an activating effective amount of methylaluminoxane, thereby to produce poly(C<sub>3</sub>-C<sub>10</sub> alpha olefin) of M<sub>n</sub> in the range of 1,000 to 3,000,000 g/mol and PDI in the range of 1 to 3.

14. A method for the polymerization of a C<sub>4</sub>-C<sub>10</sub> cyclic alkene, comprising the step of polymerizing C<sub>4</sub>-C<sub>10</sub> cyclic alkene in the presence of a catalytically effective amount of activated compound of Claim 1, thereby to produce poly(C<sub>4</sub>-C<sub>10</sub> cyclic alkene) having M<sub>n</sub> ranging from 1,000 to 3,000,000 g/mol.

15. A method for polymerization of a C<sub>4</sub>-C<sub>10</sub> cyclic alkene comprising the step of polymerizing C<sub>4</sub>-C<sub>10</sub> cyclic alkene in the presence of a catalytically effective amount of compound of Claim 5 activated by an activating effective amount of methylalumininoxane, thereby to produce poly(C<sub>4</sub>-C<sub>10</sub> cyclic alkene) having M<sub>n</sub> ranging from 1,000 to 3,000,000 g/mol.

16. A method for copolymerizing ethylene and a comonomer selected from the group consisting of C<sub>3</sub>-C<sub>10</sub> alpha olefin, styrene, C<sub>3</sub>-C<sub>10</sub>-diene, C<sub>2</sub>-C<sub>10</sub> alkenyl chloride and C<sub>4</sub>-C<sub>10</sub> cyclic alkene, comprising the step of copolymerizing ethylene and said comonomer in a mole ratio of ethylene to comonomer ranging from 1:99 to 99:1, in the presence of a catalytically effective amount of activated compound of Claim 1, thereby to produce copolymer of ethylene and said comonomer having M<sub>n</sub> ranging from 1,000 to 3,000,000 g/mol.

17. The method of Claim 16 where when the comonomer comprises C<sub>3</sub>-C<sub>10</sub> alpha olefin, said compound contains at least one fluorine atom.

18. A method for copolymerizing ethylene and a comonomer selected from the group consisting of C<sub>3</sub>-C<sub>10</sub> alpha olefin, styrene, C<sub>3</sub>-C<sub>10</sub> diene, C<sub>2</sub>-C<sub>10</sub> alkenyl halide and C<sub>4</sub>-C<sub>10</sub> cyclic alkene, comprising the step of copolymerizing ethylene and said comonomer in a mole ratio of ethylene to comonomer ranging from 1:99 to 99:1, in the presence of a catalytically effective amount of compound of Claim 5 activated by an activating effective amount of methylalumininoxane, thereby to produce copolymer of ethylene and said comonomer having M<sub>n</sub> ranging from 1,000 to 3,000,000 g/mol.

19. The method of Claim 18 where when the comonomer comprises C<sub>3</sub>-C<sub>10</sub> alpha olefin, said compound contains at least one fluorine atom.