OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

(12) (19) (CA) **Demande-Application**

(21) (A1) **2,225,014**
(22) 1997/12/16
(43) 1999/06/16

(72) GAO, Xiaoliang, CA
(72) ZORICAK, Peter, CA
(72) WANG, Qinyan, CA
(71) NOVA Chemicals Ltd., CA

(51) Int.Cl.^{6} C07F 17/00, C08F 4/64, C08F 10/02, C07F 5/02

(54) **LIGANDS HETEROCYCLIQUES B-N (BORE-AZOTE)**
(54) **B-N HETEROCYCLIC LIGANDS**

(57) A catalyst component comprising a group 4 metal having a heterocyclic ligand which is pi-bonded to the metal, characterized in that this ligand contains a boron-nitrogen ("B-N") fragment contained in the ring and further characterized in that a dialkyl amido substituent is bonded to the boron atom. Catalyst systems which contained this catalyst component are useful olefin polymerization catalysts, particularly for the preparation of polyethylene. The resulting polyethylenes are characterized by having an extremely broad molecular weight distribution (MWD).

10

20

B-N Heterocyclic Ligands

ABSTRACT OF THE DISCLOSURE

A catalyst component comprising a group 4 metal having a heterocyclic ligand which is pi-bonded to the metal, characterized in that this ligand contains a boron-nitrogen ("B-N") fragment contained in the ring and further characterized in that a dialkyl amido substituent is bonded to the boron atom. Catalyst systems which contained this catalyst component are useful olefin polymerization catalysts, particularly for the preparation of polyethylene. The resulting polyethylenes are characterized by having an extremely broad molecular weight distribution (MWD).

30

B-N Heterocyclic Ligands

FIELD OF THE INVENTION

This invention relates to a catalyst having a unique heterocyclic ligand which is pi-bonded to a group 4 metal. The catalyst is useful for the preparation of ethylene polymers having a broad molecular weight distribution.

BACKGROUND OF THE INVENTION

Professor Natta, co-inventor of the so-called "Ziegler-Natta" catalysts) investigated the use of homogeneous catalysts having pi-bonded cyclic ligands for olefin polymerization. Titanocene (Cp_2TiCl_2) is an example of such a catalyst. This work was not initially successful (from the perspective of developing a commercially useful catalyst).

Professors Kaminsky and Sinn advanced the art of homogeneous olefin polymerization by discovering that alumoxanes are excellent activators for metallocene catalysts. The use of methylalumoxane (MAO) in combination with zirconocene, titanocene or hafnocene catalysts produces a very active olefin polymerization system. The polymers produced by such "Kaminsky/Sinn" catalysts are generally characterized by having very uniform polymer properties (especially narrow molecular weight distribution and, in the case of copolymers - very uniform comonomer incorporation). These uniform polymer properties typically produce excellent strength characteristics but poor "processibility" characteristics. That is, it is difficult to use the polymers on conventional "conversion" equipment (i.e. the equipment

to "convert" the polymers to end products such as plastic film) but the resulting products have excellent strength.

It is generally accepted that the narrow molecular weight distribution of these polymers accounts for the processibility problems. Accordingly, many attempts have been made to provide processes which broaden molecular weight distribution - such as the use of two (or more) catalysts having different termination responses (so as to produce a bimodal distribution); and/or the use of two or more reactors operated under different conditions (e.g. different temperatures; different concentrations of molecular weight control agents; different monomer concentrations).

These prior art methods have been successful in producing polymers having a broader molecular weight, but the economic cost of these methods is undesirable.

SUMMARY OF THE INVENTION

In one embodiment this invention provides a catalyst component defined by the formula:

$$M(L1)_x(L2)_y(L3)_z$$

wherein

M is Zr, Ti or Hf;

L1 is a heterocyclic ligand which is pi-bonded to M, characterized in that L1 contains a heterocyclic B-N fragment and further characterized in that a dialkyl amido substituent is bonded to said B atom;

L2 is a cyclopentadiene-type ligand; and

each L3 is a non-interfering anionic ligand;

with the provisos that:

X is 1 or 2;

Y is 0 or 1;

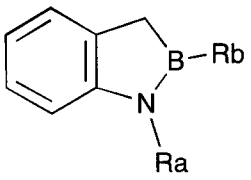
Z is 2 or 3; and

X + Y + Z = 4.

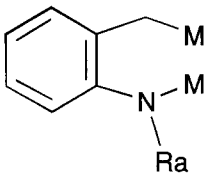
In another embodiment this invention provides the catalyst system having a catalyst component as defined above and wherein a catalyst support selected from silica and silica-alumina is employed to synthesize said supported form.

The invention further provides a method for the synthesis of heterocyclic compounds having both of (a) a B-N fragment; and (b) an aromatic ring which is fused to the heterocycle.

A process for the preparation of a fused ring dihydroazobole defined by the formula:



said process comprising the reaction of:



+ X_2BR_b

wherein:

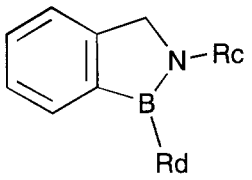
M is selected from Li and MgBr;

X is selected from Cl and Br;

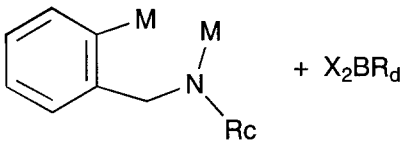
each Ra is a hydrocarbyl having from 1 to 20 carbon atoms; and

Rb is selected from hydrocarbyl having from 1 to 20 carbon atoms and a dialkyl amido.

A process for the preparation of a fused ring dihydroazobole defined by the formula:



said process comprising the reaction of:



wherein:

each Rc is a hydrocarbyl having from one to 20 carbon atoms;

X is selected from Cl and Br; and

Rd is selected hydrocarbyl having from one to 20 carbon atoms and dialkyl amido.

Catalysts according to this invention may be used to polymerize polyethylene having a broad molecular weight distribution.

DETAILED DESCRIPTION

Part 1: Novel Catalyst Component

The novel catalyst components of this invention are defined by the formula:

$$M(L1)_x(L2)_y(L3)_z$$

wherein

M is a group 4 metal (preferably Ti, Zr or Hf);

L1 is a heterocyclic ligand (described in detail below);

L2 is a cyclopentadienyl-type ligand (described below);

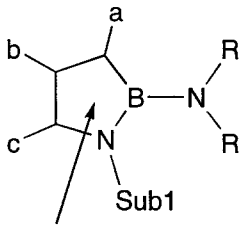
L3 is a simple anionic ligand (described below);

X is 1 or 2;

Y is 0 or 1 (i.e. the use of the cyclopentadienyl-type ligand is optional; and

Z is 2 or 3.

L1: Heterocyclic Ligand



formula (I)

The heterocyclic ligand is characterized by three features:

1. The B-N "heterocyclic fragment" (i.e. boron-nitrogen in the ring, bonded to each other);
2. The dialkyl amido substituent on the B atom; and

3. (π) pi-bonding to the group 4 metal (indicated by the arrow ($\rightarrow$) in formula (I)).

The dialkyl amido substituent is preferably dimethyl amido (i.e. in formula (I), both R groups are methyl). Exemplary, alternative R groups include other alkyl groups having from 2 to 10 carbon atoms and silyl substituents.

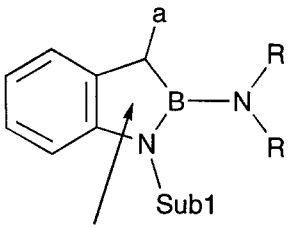
The ligand contains optional substituents a, b, and c. (a, b, and c are hydrogen if not substituted.)

An illustrative list of the (optional) substituents a, b, and c includes C_1-C_{20} hydrocarbyl radicals; substituted C_1-C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an alkoxy radical or a radical containing a Lewis acidic or basic functionality; substituted C_1-C_{20} hydrocarbyl radicals wherein the substituent contains an atom selected from the group 14 of the Periodic Table of Elements (where group 14 refers to IUPAC nomenclature); and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkyborido radicals, or a radical containing Lewis acidic or basic functionality; or a ring in which two adjacent R-groups are joined forming C_1-C_{20} ring to give a saturated or unsaturated polycyclic ligand.

It is preferred that the substituents b and c form a ring as shown in formula II below.

Referring to formula (I), "Sub 1" refers to a substituent which satisfies the third valence of the N atom. Examples of Sub 1 substituents include H, CH_3 and $Si(Me)_3$.

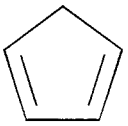
The preferred form of L1 is shown in formula II:



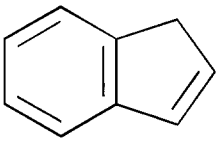
formula II

L2: Cyclopentadiene-Type Ligand

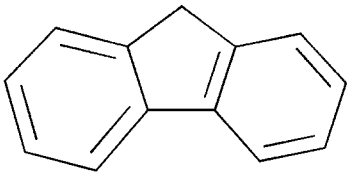
L2 is a cyclopentadiene-type ligand. As used herein, this term is meant to convey its conventional meaning and to include indene and fluorene ligands. The simplest (unsubstituted) cyclopentadiene, indene and fluorene structures are illustrated below.



cyclopentadiene



indene



fluorene

The arrows (→) indicate pi-bonding formed by these ligands with the group 4 metal.

It will be readily appreciated by those skilled in the art that the hydrogen atoms shown in the above formula may be replaced with substituents to provide the "substituted" analogues. Thus, in the broadest sense, the inventive organometallic complexes may contain a cyclopentadienyl-type structure which may be an unsubstituted cyclopentadienyl, unsubstituted indenyl, substituted indenyl, unsubstituted fluorenyl or substituted fluorenyl. A description of permissible substituents on these cyclopentadienyl type structures is provided in United States Patent 5,324,800 (Welborn).

An illustrative list of such substituents for cyclopentadienyl groups includes C_1-C_{20} hydrocarbyl radicals; substituted C_1-C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or a radical containing a Lewis acidic or basic functionality; substituted C_1-C_{20} hydrocarbyl radicals wherein the substituent contains an atom selected from the group 14 of the Periodic Table of Elements (where group 14 refers to IUPAC nomenclature); and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkyborido radicals, or a radical containing Lewis acidic or basic functionality; or a ring in which two adjacent R-groups are joined forming C_1-C_{20} ring to give a saturated or unsaturated polycyclic ligand.

L3: Non-Interfering Anionic Ligand

Any simple anionic ligand which may be bonded to an analogous metallocene catalyst component (i.e. where the analogous metallocene catalyst component is defined by the formula $Cp_2M(L3)_2$,

where Cp is a cyclopentadiene-type ligand; M is a group 4 metal; and L3 is as defined herein) may also be used with the catalyst components of this invention.

"Non-interfering" means that this ligand doesn't interfere (deactivate) the catalyst.

An illustrative list includes hydrogen, hydrocarbyl having up to 10 carbon atoms, halogen, amido and phosphido (with each L3 preferably being chlorine, for simplicity).

Part 2: Polymerization

The polymerization process of this invention is conducted in the presence of a catalyst component according to the aforedefined $M(L1)_x(L2)_y(L3)_z$ formula and an "activator or cocatalyst". The terms "activator" or "cocatalyst" may be used interchangeably and refer to a catalyst component which combines with the organometallic complex to form a catalyst system that is active for olefin polymerization.

Preferred cocatalysts are the well known alumoxane (also known as aluminoxane) and ionic activators.

The term "alumoxane" refers to a well known article of commerce which is typically represented by the following formula:

$$R_2'AlO(R'AlO)_mAlR_2'$$

where each R' is independently selected from alkyl, cycloalkyl, aryl or alkyl substituted aryl and has from 1-20 carbon atoms and where m is from 0 to about 50 (especially from 10 to 40). The preferred alumoxane is methylalumoxane or "MAO" (where each of the R' is methyl).

Alumoxanes are typically used in substantial molar excess compared to the amount of metal in the catalyst. Aluminum:transition metal molar ratios of from 10:1 to 10,000:1 are preferred, especially from 50:1 to 500:1.

As used herein, the term "ionic activator" is meant to refer to the well known cocatalyst systems which are described, for example, in United States Patent 5,198,401 (Hlatky and Turner), and the carbonium, sulfonium and oxonium analogues of such ionic activators which are disclosed by Ewen in United States Patent 5,387,568. In general, these ionic activators form an anion which only weakly coordinates to a cationic form of the catalyst. Such "ionic cocatalysts" may or may not contain an active proton (e.g. trimethyl ammonium, tributylammonium; N,N-dimethyl anilinium, carbonium, oxonium or sulfonium). They do contain a labile substantially non-coordinating anion (such as tetraphenyl borate or tetrakis(pentafluorophenyl) borate). The preferred of these ionic activators are tris(pentafluorophenyl) borane (which can generate the borate upon reaction with the organometallic catalyst complex), [triphenyl methyl][tetrakis(pentafluorophenyl) borate] and [N,N-dimethyl anilinium][tetrakis(pentafluorophenyl) borate]. In commercial practice, the triphenyl methyl (or "carbonium") salts may be preferred.

These ionic activators are typically used in approximately equimolar amounts (based on the transition metal in the catalyst) but lower levels may also be successful and higher levels also generally

work (though sub-optimally with respect to the cost-effective use of the expensive activator).

In addition to the catalyst and cocatalyst, the use of a "poison scavenger" may also be desirable. As may be inferred from the name "poison scavenger", these additives may be used in small amounts to scavenge impurities in the polymerization environment. Aluminum alkyls, for example triisobutyl aluminum, are suitable poison scavengers. (Note: some caution must be exercised when using poison scavengers as they may also react with, and deactivate, the catalyst.)

Polymerizations according to this invention may be undertaken in any of the well known olefin polymerization processes including those known as "gas phase", "slurry", "high pressure" and "solution".

The use of a supported catalyst is preferred for gas phase and slurry processes whereas a non-supported catalyst is preferred for the other two.

When utilizing a supported catalyst, it may be preferable to initially support the cocatalyst, then the catalyst (as will be illustrated in the Examples).

The polymerization process according to this invention uses at least one olefin monomer (such as ethylene, propylene, butene, hexene) and may include other monomers which are copolymerizable therewith (such as other alpha olefins, preferably butene, hexene or octene, and under certain conditions, dienes such as hexadiene

isomers, vinyl aromatic monomers such as styrene or cyclic olefin monomers such as norbornene).

It is especially preferred that the polymerization process utilize a major portion of ethylene monomer and a minor portion of an alpha olefin comonomer selected from butene, hexene and octene so as to produce a linear low density polyethylene ("LLDPE") product.

The most preferred polymerization process of this invention encompasses the use of the novel catalysts (together with a cocatalyst) in a medium pressure solution process. As used herein, the term "medium pressure solution process" refers to a polymerization carried out in a solvent for the polymer at an operating temperature from 100 to 320°C (especially from 120 to 220°C) and a total pressure of from 3 to 35 mega Pascals. Hydrogen may be used in this process to control (reduce) molecular weight. Optimal catalyst and cocatalyst concentrations are affected by such variables as temperature and monomer concentration but may be quickly optimized by non-inventive tests.

Further details concerning the medium pressure polymerization process (and the alternative gas phase, slurry and high pressure processes) are well known to those skilled in the art (and widely described in the open and patent literature).

EXAMPLES

The invention will now be illustrated in further detail by way of the following non-limiting examples. For clarity, the Examples have been divided into two parts, namely Part A (Catalyst Component

Synthesis), Part B (Solution Polymerization) and Part C (Gas Phase Polymerization).

PART A1: Catalyst Component Synthesis

Synthesis of 4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Methylazaborole

Step 1 Preparation of dimethylaminoboron dibromide

Dimethylamine (4.611 grams (g) (102 millimoles (mmol)) was condensed into a well stirred hexane (100 milliliters (mL)) solution of boron tribromide (9.67 mL, 102 mmol), in 100 mL of hexane cooled to -78°C. Immediately white precipitate of dimethylamine-boron tribromide began to separate. To the slurry was then added triethylamine (14.25 mL, 102 mmol) dissolved in 100 mL of hexane with constant stirring and cooling. After 16 hours the white precipitate of triethylamine hydrobromide was filtered off and washed with 50 mL of hexane. From the filtrate, all hexane was distilled off at ambient pressure and the resulting colorless liquid was distilled under slight vacuum collecting the fraction between 85-95°C. Yield, 9.63 g. Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 2.51 (peak area = 6 protons (6H).

Step 2 Preparation of dilithio-N-trimethylsilyl-*o*-toluidine

n-Butyl lithium (1.6 molar (M), 122.3 mL, 196 mmol) was added dropwise to *o*-toluidine (20.968 g, 196 mmol) dissolved in 300 mL of diethyl ether, at 0°C. The solution was the stirred for 20 minutes while warming to room temperature. The solution was the cooled to -78°C and chlorotrimethylsilane (24.83 mL, 196 mmol) was added slowly with

a syringe. Solution was warmed to room temperature over 1 hour and then all diethyl ether was removed under reduced pressure. To the remaining slurry was added 50 mL of hexane and then filtered to remove lithium chloride. Hexane was removed under reduced pressure and remaining liquid was distilled at 90°C/200 microns to give N-trimethylsilyl-*o*-toluidine. Yield, 22.991 g. Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 7.05 (2H), 6.8 (2H), 3.08 (1H), 1.89 (3H), 0.18 (9H).

To a solution of N-trimethylsilyl-*o*-toluidine (22.991 g, 128 mmol) in 220 mL of hexane was added n-butyl lithium (1.6 M, 102.6 mL, 256 mmol) from a dropping funnel over 1 hour with continuous stirring. The solution was then refluxed for 40 hours giving an orange precipitate which was filtered and washed with hexane. Yield, 24.32 g. Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated tetrahydrofuran (C_4D_8O): 6.8-5.8 (4H), 0.05 (9H), -2.01 (2H).

Step 3 Preparation of 4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Trimethylsilylazaborole

Dilithio-N-trimethylsilyl-*o*-toluidine (5.857 g, 30.5 mmol) was slurried in 500 mL of ether and cooled to -100°C. To the slurry was added quickly dimethylaminoboron dibromide (6.539 g, 30.5 mmol) dissolved in 100 mL of tetrahydrofuran. The solution was then allowed to reach room temperature while stirring for 16 hours. All solvent was removed under reduced pressure and the remaining viscous oil was distilled, collecting the fraction at 91°C/600 microns. Yield, 3.15 g.

Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 7.2-6.8 (4H), 2.47 (6H), 1.97 (2H), 0.29 (9H).

Step 4 Preparation of 4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Methylazaborole

4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Trimethylsilylazaborole (1.05 g, 4.5 mmol) was dissolved in 100 mL of diethyl ether and cooled to -78°C. To this solution was added condensed HCl gas (4.5 mmol) and then allowed to warm to room temperature while stirring for 4 hours. All diethyl ether and chlorotrimethylsilane was removed under reduced pressure leaving a white crystalline solid (4,5-benzo-2,3-didhydro-2-dimethylaminoazaborole) (in quantitative yield). Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 7.2-6.5 (4H), 4.5 (1H), 2.43 (3H), 2.28 (3H), 1.92 (2H).

To a solution of 4,5-benzo-2,3-didhydro-2-dimethylaminoazaborole (0.17 g, 1.06 mmol) in 25 mL of tetrahydrofuran and cooled to -78°C, was added lithium diisopropylamine (0.114 g, 1.06 mmol) in 20 mL of tetrahydrofuran. The solution was then stirred for 30 minutes while warming to room temperature. Tetrahydrofuran and diisopropylamine were then removed under reduced pressure. Remaining solid was redissolved in 30 mL of diethyl ether and cooled to -78°C. To this solution was added methyl trifluoromethylsolphonate (0.12 mL, 1.06 mmol) from a syringe and the solution was allowed to warm to room temperature while stirring for 1 hour. Diethyl ether was removed under reduced pressure

and 30 mL of hexane was added to precipitate lithium trifluoromethylsulphonate which was removed by filtration. Hexane was removed under reduced pressure from the filtrate leaving a pale yellow oil (4,5-benzo-2,3-dihydro-2-dimethylamino-1-methylazaborole). Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 7.2-6.5 (4H), 2.79 (3H), 2.51 (6H), 1.88 (2H).

Synthesis of Cyclopentadienyl(4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Methyl-η^5–azaborolinyl) Zirconium Dichloride

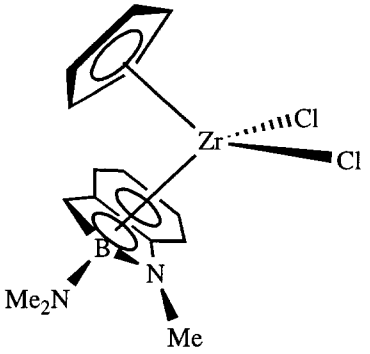
Step 1 Preparation of 4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Methylazaborolinyllitium

To a solution of 4,5-benzo-2,3-dihydro-2-dimethylamino-1-methylazaborole (0.204 g, 1.172 mmol) in 20 mL of tetrahydrofuran was added lithium 2,2,6,6-tetramethylpiperidide (0.173 g, 1.172 mmol) in 20 mL of tetrahydrofuran, at -78°C. The solution was then allowed to warm to room temperature over 30 minutes with constant stirring. Tetrahydrofuran was removed under reduced pressure and 15 mL of *o*-xylene was added and then also removed under reduced pressure along with 2,2,6,6-tetramethylpiperidine leaving a pale yellow solid (4,5-benzo-2,3-dihydro-2-dimethylamino-1-methylazaborolinyllitium) in quantitative yield. Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated tetrahydrofuran (C_4D_8O): 6.45-5.95 (4H), 3.27 (3H), 3.15 (1H), 2.73 (6H).

Step 2 Preparation of Cyclopentadienyl(4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Methyl-η^5–azaborolinyl) Zirconium Dichloride

To a solution of cyclopentadienyl zirconium trichloride bis(tetrahydrofuran) (0.496 g, 1.172 mmol) in 30 mL of tetrahydrofuran

was added 4,5-benzo-2,3-dihydro-2-dimethylamino-1-methylazaborolinyllitium (1.172 mmol) in 20 mL of tetrahydrofuran, at -78°C. The solution was then allowed to reach room temperature while stirring for 16 hours. Tetrahydrofuran was removed under reduced pressure and 30 mL of toluene was added to precipitate lithium chloride which was removed by filtration. The filtrate was concentrated to 5 mL and 30 mL of hexane was added to precipitate the complex. Yield, 0.244 g. Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 6.6-5.95 (4H), 5.85 (5H), 3.19 (1H), 2.83 (3H), 2.59 (6H). The structure is shown below. (In this structure and elsewhere in this specification, the term "Me" refers to a methyl group.)

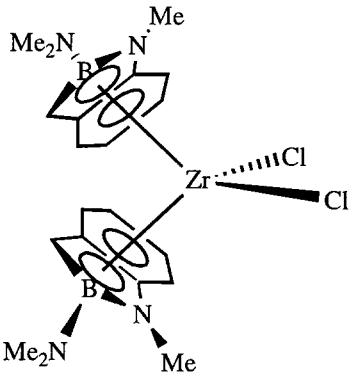


Synthesis of Bis(4,5-Benzo-2,3-Dihydro-2-Dimethylamino-1-Methyl-η^5–azaborolinyl) Zirconium Dichloride

Step 1 Preparation of bis(4,5-benzo-2,3-dihydro-2-dimethylamino-1-methyl-η^5–azaborolinyl) zirconium dichloride

To a solution of zirconium tetrachloride bis(tetrahydrofuran) (0.399 g, 1.06 mmol) in 25 mL of toluene was added 4,5-benzo-2,3-dihydro-2-dimethylamino-1-methylazaborolinyllitium (2.12 mmol) in

20 mL of tetrahydrofuran, at -78°C. The solution was then allowed to reach room temperature while stirring for 16 hours. Toluene solution was filtered to remove lithium chloride and the solid washed with toluene (2 x 15 mL) to extract most of the poorly soluble complex. The orange toluene solution was concentrated to 5 mL causing precipitation of microcrystalline orange powder. Yield, 0.212 g. Proton nuclear magnetic resonance spectrum (^{1}H-NMR) in deuterated toluene (C_7D_8): 7.1-6.98 (4H), 3.14 (3H), 2.69 (1H), 2.36 (6H). The structure is shown below.



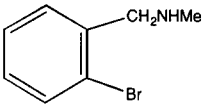
PART A2: Preparation Of Dihydroazaboroles Having Fused Rings

The subject dihydroazaboroles have fused ring structures.

Preparation of 2-bromobenzylmethylamine

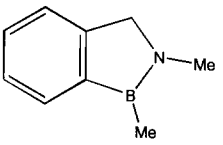
A solution of 2-bromobenzylbromide (10g, 40 mmol) in ethanol (60 mL) was added to a tetrahydrofuran (THF) solution of methylamine (240 mmol) at -78°C. The reaction mixture was stirred while it was slowly warmed to room temperature, which was them pumped to remove the reaction solvents and the excess of methyl amine. The residue was then treated with water and the solution was extracted

with ether. The ether solution was dried over sodium sulfate and was pumped to dryness. The product was distilled under vacuum (150 microns, b.p. 54°C, 7.0 g, 87%). ^{1}H NMR (C_6D_6, δ): 7.6 - 7.05 (m, 4H, C_6H_4), 3.87 (s, 2H, CH_2), 2.41 (s, 3H, N-CH_3), 1.41 (br.s, 1H, N-H).



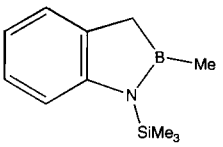
Preparation of 2,5 - Dihydro-1,2 - Dimethyl - 3,4 - Benzoazaborole

To a solution of 2 - bromobenzylmethylamine (17.55 g, 87.71 mmol) in THF (200 mL) at 0°C was added slowly MeMgBr (87.71 mmol) in ether. After the reaction mixture was stirred for 10 minutes, a small portion of the solution was transferred onto activated magnesium (3 g) turnings. After the reaction started, the rest of the solution was gradually transferred over. The mixture was refluxed for 3 more hours and the THF solution was transferred into a two-necked flask containing 800 ml of hexane. The slurry was cooled in a solid CO_2 acetone bath and a THF solution of $MeBBr_2$ (16.3 g, 87.7 mmol) was added. The reaction mixture was stirred overnight while the cold bath slowly warmed to room temperature. The solvent was pumped off and the residue was extracted with hexane. The product was distilled under vacuum after hexane was removed (450 microns, b.p. 44 -51^{0}C, 7.1 g, 56% yield). ^{1}H NMR (C_6D_6, δ): 7.1 - 7.8 (m, 4 H, C_6H_4), 3.72 (s, 2H, CH_2), 2.71 (s, 3H, N-CH_3), 0.66 (s, 3H, B-CH_3). M^+: 145.



Preparation of 4,5-Benzo-2,3-Dihydro-2-Methyl-1-Trimethylsilylazaborole

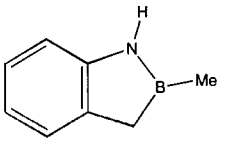
The dilithio salt (38.1 g, 198.2 mmol) prepared above was dissolved in ether (1 liter) and the orange solution was cooled in a liquid nitrogen slush bath (-100°C). A THF solution (~100 mL) of $MeBBr_2$ (carefully prepared by the slow addition of THF (dropwise first!) into $MeBBr_2$ at -78°C) was quickly transferred into the vigorously stirred solution of the dilithio salt. The reaction flask was let stay in the cold bath while it was slowly warmed up to room temperature overnight. The solvents were stripped off under vacuum and the residue was treated with hexane (~50mL). The mixture was well mixed and was pumped to dryness. The residue was extracted with hexane (~200 mL) and was filtered. The filtrate was pumped to dryness and the residue was distilled under vacuum (b.p. 56°C, 150 microns). Yield 20.3g, 50.4%. ^1H NMR (C_7D_8, δ): 7.4 - 7.0 (m, 4H, C_6H_4), 2.07 (s, s,2H, CH_2), 0.65 (s, 3H, B-CH_3), 0.30 (s, 9H, $SiMe_3$). M+ = 203.



Preparation of 4,5-Benzo-2,3-Dihydro-2-Methylazaborole

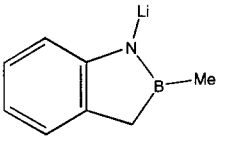
HCl(g) (535 mL at 1 atm. and 23°C, 22 mmol) was condensed under vacuum onto a frozen solution of 4,5-Benzo-2,3-Dihydro-2-

Methyl-1-Trimethylsilylazaborole (4.1 g, 22 mmol) in ether (~100 mL). The mixture was vigorously stirred while it was warmed up to room temperature. A white slurry formed after the mixture thawed, which became clear at near room temperature. The clear solution turned cloudy again and the slurry was stirred overnight to produce an almost colorless solution. Proton NMR of a small portion of the solution showed the product formed almost quantitatively. The solution was pumped to dryness and the residue was distilled under vacuum. The product solidified at about 0°C. (b.p. 31-33°C, at 200 microns.) Yield, 2.1 g, 80%. ^{1}H NMR (C7D8, δ): 7.4 - 6.6 (m, 4H, C_6H_4), 5.6 (br.s, 1H, NH), 2.07 (s, 2H, CH_2), 0.53 (s, 3H, BCH_3). M^+ = 131.



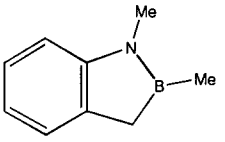
Preparation of Lithium(4,5-Benzo-2,3-Dihydro-2-Methylazaborolide)

The corresponding azaborole (0.415g, 3.17 mmol) in ether at -78°C was treated with a slurry of Li(TMP) (0.468 g, 3.17 mmol). A clear solution formed, which was warmed up to room temperature and was stirred for a further hour. The solution was pumped to dryness and hexane (~10 ml) was added. The resultant slurry was pumped to dryness. The process was repeated one more time and more hexane (~30 mL) was added. The slurry was filtered and the white solid over the frit was dried under vacuum. Yield: Quantitative. ^{1}NMR (THF-d8, δ): 7.1 - 6.2 (m, 4H, C_6H_4), 1.77 (s, 2H, CH_2), 0.51 (s, 3H, BCH_3).



Preparation of 4,5-Benzo-2,3-Dihydro-2, 3-Dimethylazaborole

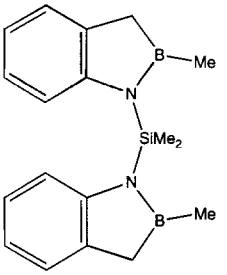
Lithium(4,5-Benzo-2,3-Dihydro-2-Methylazaborolide) (3.77 mmol) prepared from the corresponding N-H compound was dissolved in ether (~30 mL) and the solution was cooled in a solid CO_2 acetone bath. Methyltriflate (3.70 mmol) was added dropwise via a syringe. The solution was warmed up to room temperature slowly and was stirred for a further hour. Proton NMR spectrum of a portion of the solution showed the reaction was almost quantitative. Ether was removed carefully under vacuum and the product was vacuum transferred at 23°C and 160 microns with a bath temperature of 50°C. ^1H NMR (C_7D_8, δ): 7.4 - 6.2 (m, 4H, C_6H_4), 2.66 (s, 3H, NCH_3), 2.01 (s, 2H, CH_2), 0.46 (s, 3H, BCH_3).



Preparation of Dimethylsilylbis(4,5-Benzo-2,3-Dihydro-2-Methylazaborolide)

To an ethereal solution of Lithium(4,5-Benzo-2,3-Dihydro-2-Methylazaborolide) (3.168 mmol) at -78°C was added an ethereal solution of Me_2SiCl_2 (1.584 mmol, 0.204g). The cold bath was removed and the solution was slowly warmed to room temperature. A

white slurry formed, which was stirred for 2 hours at room temperature and was pumped to dryness. Hexane was added and the slurry was filtered. The filtered slurry was pumped to dryness and a colorless oil was obtained, which solidified at room temperature in about 2 hours. Yield: quantitative. ^{1}H NMR (C7D8, δ): 6.9 - 7.3 (m, 8H, C6H4), 2.12 (s, 4H, CH2), 0.62 (s, 6H, BCH3), 0.577 (s, 6H, SiMe2). $M^+ = 318$.



PART B: Solution Polymerization

All the compounds are oxygen and moisture sensitive. Manipulations were therefore carried out under nitrogen using a glovebox or under argon using Schlenk-line techniques. Anhydrous toluene was purchased from Aldrich and used without further purification. The catalysts $Cp(C_7H_5BNMe_2NMe)ZrCl_2$ (**1**), $(C_7H_5NSiMe_3BNMe_2)_2ZrCl_2$ (**2**), $(C_7H_5NMeBNMe_2)_2ZrCl_2$ (**3**), and $Cp(C_7H_5BMeNMe)ZrCl_2$ (**4**) were synthesized as described in Part A. The comparison catalyst Cp_2ZrCl_2 (**5**) was purchased from Witco. The catalysts were dissolved in Toluene. The catalyst concentrations were between 2.3 - 3.2 mg/mL.

The solution semi-batch reactor (SBR) was used in the polymerization experiments. The SBR uses a programmable logical

control (PLC) system with software sold under the name Wonderware 5.1 for process control. Ethylene (99.5%), polymer grade, Matheson) and cyclohexane was purified by absorption before use. PMAO-IP was purchased from Akzo-Nobel. Ethylene polymerizations were performed in a 500 mL Autoclave Engineers reactor equipped with an air driven stirrer and an automatic temperature control system. The experiments were first carried out as follows:

Cyclohexane	228 mL
Catalyst Concentration	65 µmol/L (initial); 32.5 µmol/L (increment)
Cocatalyst	PMAO-IP; AL/Zr = 300 mol/mol
Reaction Temperature	160°C
Reactor Pressure	140 psig total
Stirring Speed	2000 rpm

All of the catalysts showed low activity under the above conditions. Thus, the experiments were continued by the addition of a second increment of the catalyst and PMAO-IP at a concentration 5 times higher. The polymerization time was 10 min. in each case. The reaction was terminated by adding 5 mL of methanol to the reactor and the polymer recovered by evaporation of the cyclohexane.

Polymer molecular weights and molecular weight distributions were measured by GPC (Waters 150-C) at 140°C in 1,2,4-trichlorobenzene calibrated using polyethylene standards.

Table 1

Polymerization Activity

Example	Catalyst	Polymerization Activity g PE/mMolcat*hr[1]
1	$Cp(C_7H_5BNMe_2NMe)ZrCl_2$	276.0
2	$(C_7H_5NSiMe_3BNMe_2)_2ZrCl_2$	50.1
3	$(C_7H_5NMeBNMe_2)_2ZrCl_2$	48.1
4	$Cp(C_7H_5BMeNMe)ZrCl_2$	294.6
5	Cp_2ZrCl_2	877.0

[1] The calculation of polymerization activity is based on the ethylene uptake.

Table 2

Polymer Properties

Example	Catalyst	Mw($*10^{-3}$)	Mw/Mn
1	$Cp(C_7H_5BNMe_2NMe)ZrCl_2$	7.5	8.1
2	$(C_7H_5NSiMe_3BNMe_2)_2ZrCl_2$	16	16.0
3	$(C_7H_5NMeBNMe_2)_2ZrCl_2$	118	42.6
4	$Cp(C_7H_5BMeNMe)ZrCl_2$	573.5	99.9
5	Cp_2ZrCl_2	8.0	3.0

PART C: Gas Phase Polymerization

Gas phase copolymerizations of ethylene and butene-1 were completed in a 2 liter reactor. The butene-1 concentration was 0.019 M and the ethylene concentration was 0.490 M. The monomers were added in a premixed form via a pressure control system which maintained pressure at 1275 kPa at 90°C for 60 minutes. Triisobutyl aluminum (TIBAL) was used as a poison scavenger. The aiming point for the catalyst concentration was 2.5 μ mol and the amount of TIBAL used was 200/1 (aiming point, on an Al/Zr molar basis).

Table 3 shows the catalysts used and the observed activities.

Table 3

Ex.	Catalyst Formula	Polymerization Activity g PE/g Zr
3-1	$[C_6H_4N(Me)B(NMe_2)_2CH]ZrCl_2$	28,000
3-2	$Cp[C_6H_4N(Me)B(NMe_2)CH]ZrCl_2$	62,000
3-3	$[C_6H_4N(SiMe_3)B(NMe_2)CH]_2ZrCl_2$	8,900
3-4	$[C_6H_4N(Me)B(NMe_2)CH]ZrCl_3$	3,500
3-5	$Me_2Si[C_6H_4N(Me)B(NMe_2)CH]N(tBu)ZrCl_2$	2,600

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A catalyst component defined by the formula:

$$M(L1)_x(L2)_y(L3)_z$$

wherein:

M is Zr, Ti or Hf;

L1 is a heterocyclic ligand which is pi-bonded to M, characterized in that L1 contains a heterocyclic B-N fragment and further characterized in that a dialkyl amido substituent is bonded to said B atom;

L2 is a cyclopentadiene-type ligand; and

each L3 is a non-interfering anionic ligand;

with the provisos that:

X is 1 or 2;

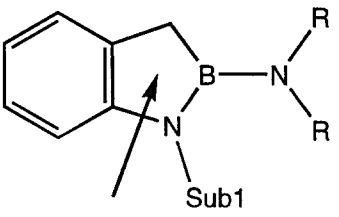
Y is 0 or 1;

Z is 2 or 3; and

$X + Y + Z = 4$.

2. The catalyst component of claim 1 wherein each L3 is independently selected from hydrogen, halogen, hydrocarbyl having up to 10 carbon atoms, amido and phosphido.

3. The catalyst component according to claim 1 wherein L1 is:

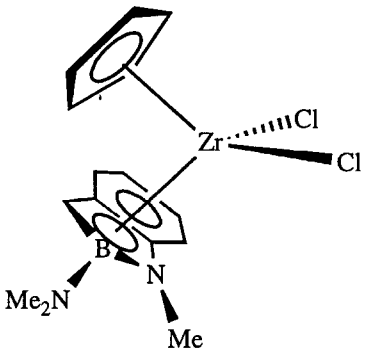


wherein:

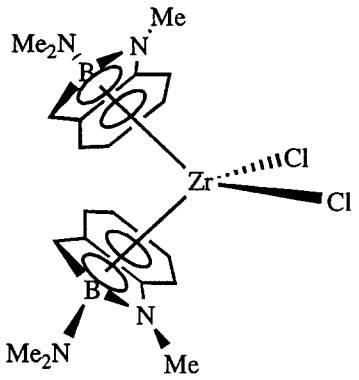
R is selected from Me and $SiMe_3$; and

Sub 1 is selected from H, CH_3 and $SiMe_3$.

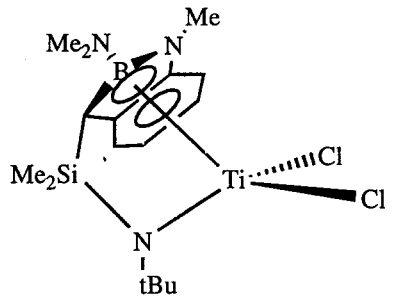
4. The catalyst component according to claim 1 defined by the formula:



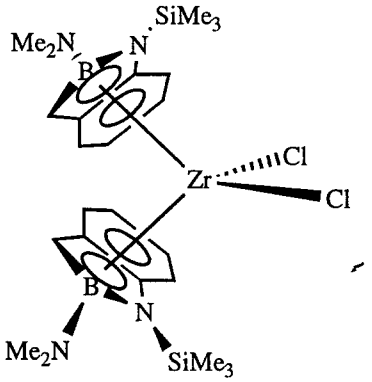
5. The catalyst component according to claim 1 defined by the formula:



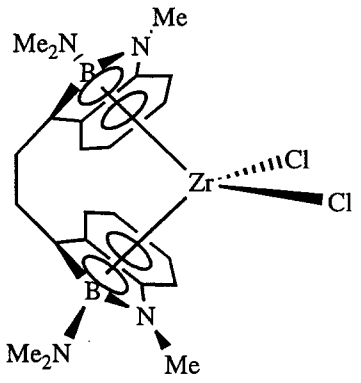
6. The catalyst component according to claim 1 defined by the formula:



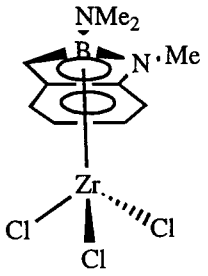
7. The catalyst component according to claim 1 defined by the formula:



8. The catalyst component according to claim 1 defined by the formula:



9. The catalyst component according to claim 1 defined by the formula:



10. A catalyst system for olefin polymerization comprising:

(a) a catalyst component according to claim 1; and

(b) an activator.

11. The catalyst system according to claim 10 which further contains a poison scavenger.

12. The catalyst system according to claim 10 wherein said activator is an alumoxane.

13. The catalyst system according to claim 10 in supported form.

14. The catalyst system according to claim 12 in supported form.

15. The catalyst system according to claim 13 wherein a catalyst support selected from silica and silica-alumina is employed to synthesize said supported form.

16. A process for the polymerization of ethylene and, optionally, at least one additional alpha olefin characterized in that said process is conducted in the presence of a catalyst system comprising:

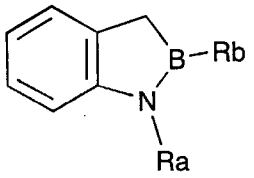
(a) a catalyst component according to claim 1; and

(b) an activator.

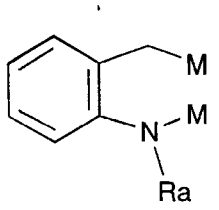
17. The process according to claim 16 wherein said catalyst system is in supported form.

18. The process according to claim 16 characterized in that said polymerization is conducted under medium pressure solution polymerization conditions.

19. A process for the preparation of a fused ring dihydroazobole defined by the formula:



said process comprising the reaction of:



+ X_2BR_b

wherein:

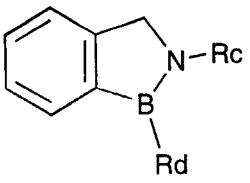
M is selected from Li and MgBr;

X is selected from Cl and Br;

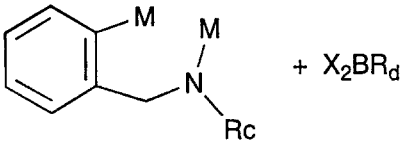
each Ra is a hydrocarbyl having from 1 to 20 carbon atoms; and

Rb is selected from hydrocarbyl having from 1 to 20 carbon atoms and a dialkyl amido.

20. A process for the preparation of a fused ring dihydroazobole defined by the formula:



said process comprising the reaction of:



wherein:

each Rc is a hydrocarbyl having from one to 20 carbon atoms;

X is selected from Cl and Br; and

Rd is selected hydrocarbyl having from one to 20 carbon atoms and dialkyl amido.