

BRIDGED METALLOCENE COMPOUNDS

The invention relates to new metallocene compounds. In particular, the new compounds are metallocenes of the transition metals selected from the group consisting of hafnium, titanium and zirconium. These compounds can be used as the source of the transition metal in an olefin polymerization catalyst.

The compounds of the invention comprise those of formula (V) (E) (W) M-L. Preferred compounds within that formula are compounds of formula IA and IB which are defined below,



The element L is a ligand defined below, M is a metal selected from the group consisting of zirconium, hafnium and titanium, X is the same or different and is halide (chloride, bromide or iodide) or alkyl, preferably methyl, or aryl; and Y is preferably alkyl. The group Cp' is an unsubstituted or substituted cyclopentadienyl group. Compounds of formula IA can be used in combination with alumoxane to polymerize ethylene. Compounds of IB can be used in the zwitterionic form to polymerize ethylene, without an alumoxane component for activation of the transition metal.

The invention relates to transition metal compounds, to their synthesis, and to their use in olefin polymerization, which can be characterized by the formula I', where I' is

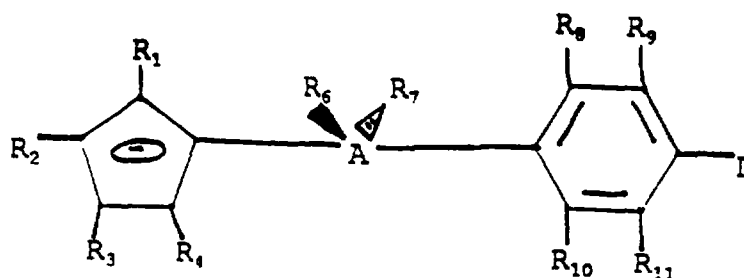


in which M is selected from the group consisting of zirconium, hafnium and titanium;

each of V, E and W is the same or different and is independently alkyl of 1 to 6 carbon atoms, halide, or unsubstituted or substituted cyclopentadienyl,

provided that one, and only one, of said V, E, and W is unsubstituted or substituted cyclopentadienyl; and

in which L is



wherein each of R₁, R₂, R₃ and R₄ is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

5 A is C, Si, Ge; and each of R₆ and R₇ is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

each of R_8 , R_9 , R_{10} , R_{11} , is the same or different, and is
10 fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

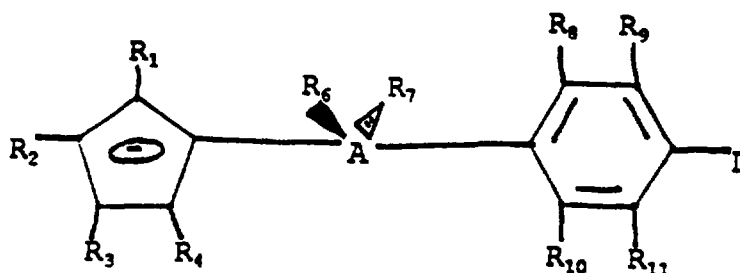
D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal [sodium or lithium]; halogen [chloride or bromide]; alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine; and BG, or AlG₃, in which B is boron (B) or Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

Preferred compounds of I' are the compounds of formula IA and IB.

20	$L-M [X]_2 [Cp']$	IA.
	$L-M[Y] [Cp']^+$	IB.

L refers to a ligand which has the formula



in which each of 1, 2, 3 and 4 is hydrogen, alkyl of 1 to 6 carbon atoms [including methyl, ethyl, propyl, butyl, isobutyl pentyl isomers of pentyl and hexyl and isomers of hexyl], alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties, (such as indenyl);

A is C, Si, Ge,; and each of R₆ and R₇ is the same or different and is alkyl of 1 to 20, preferably 1 to 6, carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

each of R₈, R₉, R₁₀, R₁₁, is the same or different, and is fluorine, hydrogen, or alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal (e.g. sodium or lithium), halogen (chloride or bromide); alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine, and BG₃ or AlG₃ in which B is boron (B) or aluminum (Al),

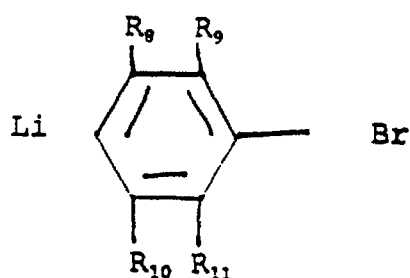
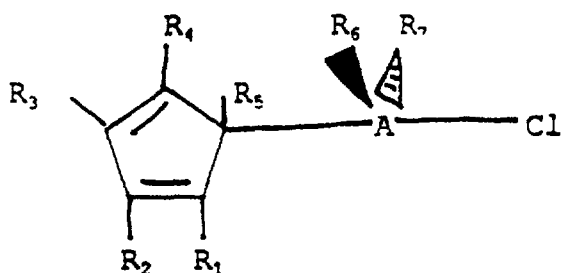
G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms, and M is defined as above.

In the formula, the Cp' group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group can be straight-or branched chain C₁-C₆ alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. The cyclopentadienyl groups and L can be also substituted or bridged by polymethylene or dialkylsilane groups, such as -CH₂-, -CH₂-CH₂-, -CR'R"- and -CR'R"-CR'R"- where R' and R" are short alkyl groups or hydrogen, -Si(CH₃)₂-, Si(CH₃)₂-CH₂-CH₂-Si(CH₃)₂- and similar bridge groups. Suitable groups constituting Cp' include unsubstituted or substituted cyclopentadienyl. Substituted cyclopentadienyls include mono-, di- tri-, tetra- and penta-substituted

cyclopentadienyls in which the substituents are alkyl of 1 to 6 carbon atoms [including methyl, ethyl, propyl, butyl, isobutyl, pentyl, isomers of pentyl, hexyl and isomers of hexyl or alkylene groups of 3 to 10 carbon atoms which form bicyclic and tricyclic alicyclic groups. The cyclopentadienyl ring may be mono-, di-, tri-, tetra or penta-substituted. The substitution may be alkyl of 1 to 6 carbon atoms; and thus includes the methylcyclopentadienyl, dimethylcyclopentadienyl, trimethylcyclopentadienyl, tetramethylcyclopentadienyl, pentamethylcyclopentadienyl, ethylcyclopentadienyl, methylethylcyclopentadienyl, propylcyclopentadienyl, methylpropylcyclopentadienyl, butylcyclopentadienyl, methylbutylcyclopentadienyl, and hexylcyclopentadienyl, and an indenyl group, 4,5,6,7-tetrahydroindenyl group and fluorenyl group. These cyclopentadienyl groups may be substituted by a halogen atom or trialkylsilyl group. The lithium compound may comprise said cyclopentadienyl substituted by a second cyclopentadienyl bonded together via an alkylene group such as ethylene and propylene, an isopropylidene group, a substituted alkylene group such as diphenylmethylene, a silylene group or a substituted silylene group such as dimethylsilylene, diphenylsilylene and methylphenylsilylene. The di-, tri-, tetra or penta-substituted cyclopentadienyl groups can be dialkyl, trialkyl, tetraalkyl or pentaalkyl-substituted cyclopentadienyl in which the alkyl is 1 to 6 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, and isomers of butyl, pentyl, hexyl.

The ligand L can be synthesized from compounds of formula 1.

The initial synthesis step comprises contacting the compound of formula 1 with a compound of formula a,

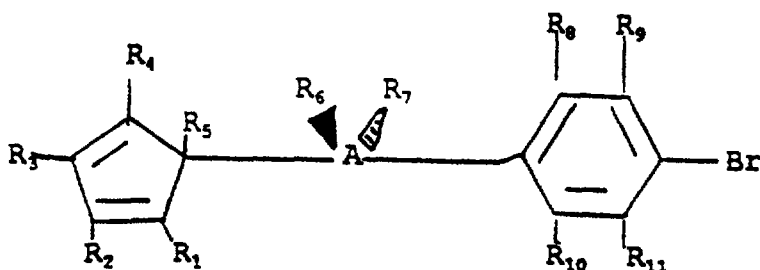


(1)

(a)

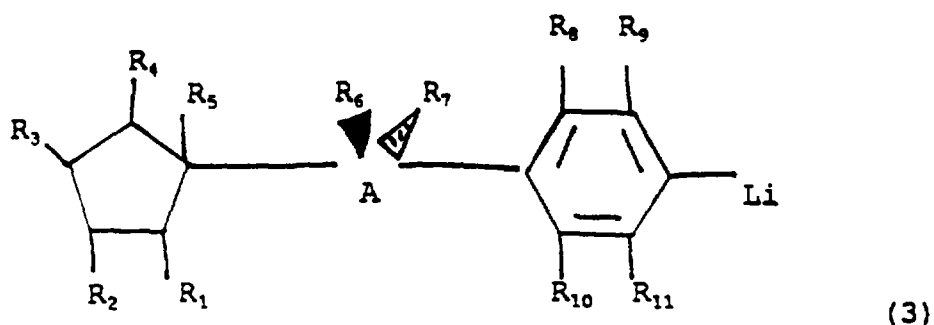
in these compounds of formulae 1 and a, each of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , and R_{11} , and A are as defined above; and R_5 is preferably hydrogen, although it may be GeZ , wherein Ge is germanium and Z is alkyl of 1 to 6 carbon atoms [including methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl and isomers of pentyl and hexyl and isomers of hexyl] or aryl of 6 to 10 carbon atoms. In preferred embodiments, R_5 is hydrogen while each of R_1 - R_4 is methyl; the kinetic inertness of the tetramethylcyclopentadiene proton, when R_5 is hydrogen, allows preferential nucleophilic displacement of the A- C_1 bond in compound 1 as well as lithiation of component 2 resulting in the high yield synthesis of the compound of formula 4, in subsequent steps. Contact of the two compounds can be undertaken at low temperatures, preferably below ambient temperatures in diethyl ether, for extended periods of time. Compounds of formula I in which R_1 - R_4 , R_6 and R_7 are methyl and A is Si (silicon) are readily available. In preferred embodiments herein the compound of formula a is 1,lithium-4,bromo,-2,3,5,6-tetrafluorophenyl.

A compound of formula 2 is the product of the contact of the compound of formula 1 and formula a, which is isolatable as a solid compound. The formula of compound(s) 2 is

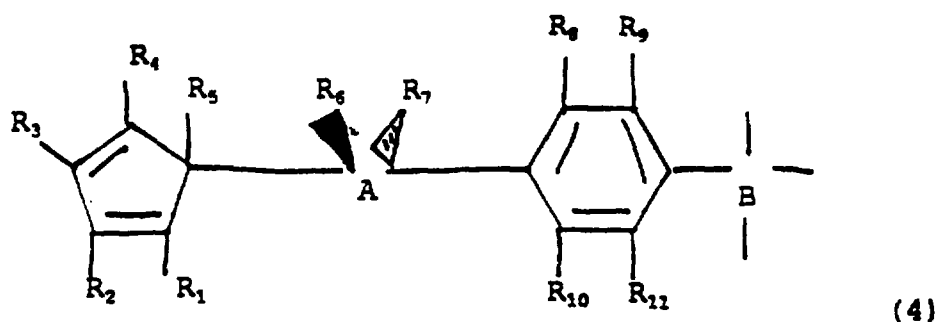


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When D is bromine in compound 2, that compound can be further treated with either an alkyl lithium [n-butyllithium] or a Grignard reagent, and subsequently with $B(C_6F_5)_3$ to produce a compound 4, wherein D is $-[B(C_6F_5)_3]$ anion. The sequence can be illustrated by the reactions to yield compounds of formulae 3 and 4. Reaction of compound 2 with BuLi will produce a compound of formula 3, which has the structure



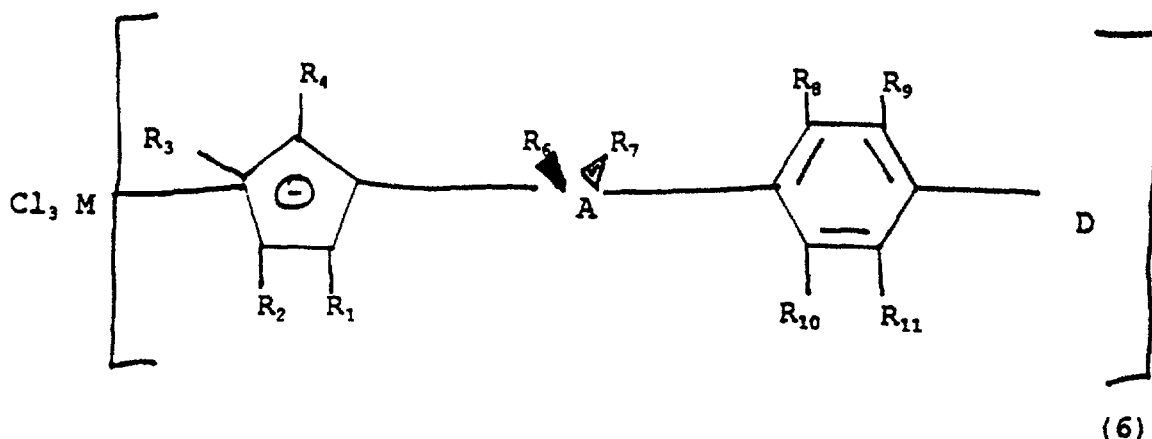
This reaction is undertaken at temperatures below ambient temperature, preferably at -78°C , in diethyl ether. Without isolation, the compound of formula 3 is contacted under substantially the same conditions with $B(C_6F_5)_3$, at -78°C , in diethyl ether for twelve hours to produce the compound of formula 4.



The compound of formula 4 can be converted to a dianion form by abstracting R_5 by treatment with alkyl lithium compounds; this step is conducted in diisopropyl ether, which is essential to facilitate the isolation and purification of the compound 4 when it is a dianion, as for example when D is $-BG_3$ in formula 5 and G is C_6F_5 .

After formation of the of the compound 5, it is contacted with a transition metal chloride, in which the

transition metal M is titanium, zirconium or hafnium (III or IV), for example, the tetrahalide or tetrachloride of zirconium, hafnium or titanium. The reaction results in production of a transition metal compound of formula 6



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Reaction of the compound of formula 6 with a lithium cyclopentadienyl derivative [in which cyclopentadienyl is denoted by Cp'], in methylene chloride at below ambient temperatures [at -78°C] results in production of transition metal compound containing two cyclopentadienyl groups which is the compound of formula IA, above.

The cyclopentadienyl moiety in the lithium compound used to convert compound of formula 6, to the compound of formula IA can be unsubstituted or substituted; if substituted, the cyclopentadienyl ring may be mono-, di-, tri-, tetra or penta-substituted. The substitution may be alkyl; and thus includes the methylcyclopentadienyl, dimethylcyclopentadienyl, trimethylcyclopentadienyl, tetramethylcyclopentadienyl, pentamethylcyclopentadienyl, ethylcyclopentadienyl, methylethylcyclopentadienyl, propylcyclopentadienyl, methylpropylcyclopentadienyl, butylcyclopentadienyl, methylbutylcyclopentadienyl, and hexylcyclopentadienyl, and an indenyl group, 4,5,6,7-tetrahydroindenyl group and fluorenyl group. These cyclopentadienyl groups may be substituted by a halogen atom or trialkylsilyl group. The lithium compound may comprise said cyclopentadienyl substituted by a second cyclopentadienyl bonded together via

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an alkylene group such as ethylene and propylene, an isopropylidene group, a substituted alkylene group such as diphenylmethylene, a silylene group or a substituted silylene group such as dimethylsilylene, diphenylsilylene and methylphenylsilylene. The di-, tri, tetra or penta-substituted cyclopentadienyl groups can be dialkyl, trialkyl, tetraalkyl or pentaalkyl-substituted cyclopentadienyl in which the alkyl is 1 to 6 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, and isomers of butyl, pentyl, hexyl. Lithium cyclopentadienyl derivatives are readily commercially available.

Reaction of compound of formula IA with a Grignard reagent or an alkyl lithium reagent results in displacement of the halides by alkyl groups to produce compounds of formula IA in which X is alkyl, provided by the Grignard.

Compounds of formula IA can be converted to compounds of formula IB by contacting the alkylated (wherein X is alkyl of 1 to 6 carbon atoms) IA materials with a borane compound including but not limited to $B(C_6F_5)_3$, $Ph_3C^+B(C_6F_5)_4^-$ or $HNR_2Ph^+B(C_6F_5)_4^-$ to abstract an alkyl X group and convert the transition metal compound to a zwitterion for use in polymerization without alumoxane activation. The zwitterion compounds of formula IB may be exemplified by the expression (V)(E)(L)M⁺ or (V)(W)(L)M⁺ or (E)(W)(L)M⁺, in which L includes the group D which is BG_3 or AlG_3 in which B is boron (B) or aluminum (Al), sodium lithium or halogen and G is selected from the group consisting of pentafluorophenyl, bistrifluoromethylphenyl, hydrogen and alkyl of 1 to 6 carbon atoms. In a catalyst composition the transition metal compounds of IA can be combined with an alumoxane, to activate the compound IA; the amount of alumoxane provides an Al[alumoxane]: transition metal ratio of 50 to 10,000.

Aluminoxanes, e.g. methylalumoxane (MAO), have been used as co-catalyst with metallocene catalysts. The class of alumoxanes (used interchangeably hereinafter with

"aluminoxane") comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula: $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and $(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C1-C8 alkyl group and preferably methyl.

Methylalumoxane is commonly produced by reacting trimethylaluminum with water or with hydrated inorganic salts, such as $CuSO_4 \cdot 5H_2O$ or $Al_2(SO_4)_3 \cdot 5H_2O$. Methylalumoxane can be also generated in situ in polymerization reactors by adding trimethylaluminum and water or water-containing inorganic salts. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of 1200. MAO is typically kept in solution in toluene.

Conditions for the polymerization and copolymerization of ethylene

The process of the invention may be undertaken in gas phase, in fluid bed gas phase, or in slurry. The catalyst of the invention, allows for the production of linear low density polyethylene in the gas phase or in a slurry polymerization. The products from both the gas phase (e.g. fluid bed) and slurry have a high bulk density, which allows for increased throughput of product per weight of catalyst.

Preferably, the polymerization (copolymerization) is undertaken at a temperature and/or pressure below the sintering temperature of the polymer particles. Most preferably, the process is undertaken in the fluid bed gas phase or in a slurry reactor. The high activity of the catalysts herein allow for efficacious low pressure fluid bed gas phase and/or slurry process product production. Much lower activity catalysts than those described herein are employed in high pressure processes at pressures which exceed 400 psi, such as solution and high pressure slurry polymerizations. For the production of ethylene copolymers in the

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process of the present invention an operating temperature of 30° to 115°C is preferred, and a temperature of 70° to 106°C is most preferred. Temperatures of 75° to 90°C are used to prepare products having a density of 0.91 to 0.92, and
5 temperatures of 80° to 100°C are used to prepare products having a density of 0.92 to 0.94, and temperatures of 90° to 115°C are used to prepare products having a density of 0.94 to 0.96.

In the gas phase, linear low density production is
10 conducted at 85°C and high density product is formed at 105°C. In slurry polymerization, linear low density production is conducted at 70°C and high density production is conducted at 90°C.

In polymerizations described herein, pressures are below
15 10000 psi, preferably below 1000 psi. The fluid bed reactor is operated at pressures of up to 1000 psi, and is preferably operated at a pressure of from 150 to 350 psi, with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat
20 capacity of the gas.

Examples

Preparation of $(C_5(CH_3)_4H-Si(CH_3)_2-p-C_6F_4Br)$ (1):n-BuLi (16.8 mL, 1.6M in hexanes) was carefully injected over a 5 minute period to a -78°C Et_2O (100 mL) suspension of 1,4-
25 dibromo 2,3,5,6 tetrafluorobenzene ($C_6Br_2F_4$) (12.9 g) and stirred for 10 min. (Caution: n-BuLi addition must be slow and the solution must be kept cold to prevent formation of benzyne and LiF). A Et_2O (15 mL) solution of chlorodimethylsilyl tetramethyl cyclopentadiene $(CH_3)_4(C_5)Si(CH_3)_2-$
30 $Cl)H$ (8.97 g) was then cannulated over a 7-8 minute period into the flask containing LiC_6F_4Br . A yellow solution formed immediately. The solution was left stirring at -78°C for 1 hour and then warmed to -50°C for an additional ~10 hours.

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After this time, the reaction was allowed to warm to room temperature overnight. Stirring was then stopped, to let the salts settle over a one hour period. The remaining yellow solution was separated by cannula filtration. Removal of solvent from the filtrate left an orange oily solid. Recrystallization from pentane at -78°C left a pale yellow oily solid. Yield 15.0 g, 88%.

Preparation of $(\text{C}_5(\text{CH}_3)_4\text{H}-\text{Si}(\text{CH}_3)_2-\text{p}-\text{C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}(\text{Et}_2\text{O})_4)$ (2): $n\text{-BuLi}$ (1.56 mL, 2.5 M in hexanes) was slowly syringed into a -78°C Et_2O (~20 mL) solution of 1 (1.6 g) and stirred for 10 min. This mixture was then quickly added via cannula to a -78°C Et_2O (~40 mL) solution of $\text{B}(\text{C}_6\text{F}_5)_3$. Immediately upon addition a yellow solution formed. The flask was stirred at -78°C for an additional 14 hours and then left to warm to room temperature overnight. The product formed a yellow solution. Solvent was removed under vacuum and the product was washed 2x with ~20 mL pentane. After pumping dry, a white crystalline solid was isolated. Yield 3.2 g, 81%. Note: This reaction does not proceed if pentane is used instead of diethylether (Et_2O) as the solvent.

Preparation of $(\text{C}_5(\text{CH}_3)_4-\text{Si}(\text{CH}_3)_2-\text{p}-\text{C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}_2(\text{i-Pr}_2\text{O})_4)$ (3): $n\text{-BuLi}$ (1.15 mL, 2.5 M in hexanes) was syringed into a stirred -78°C isopropyl ether (~40 mL) solution of 2 and then warmed to room temperature on its own. Stirring was continued overnight and left a white solid suspended in solution. The isopropyl ether was removed via cannula filtration to leave a white crystalline solid which was then washed 1x with pentane (20 mL) and pumped dry. Yield 2.54 g, 77%. Note: Removal of the Cp methine proton does not proceed to completion in either Et_2O or THF due to the formation of an oily layer at the bottom, possibly a calathrate. Longer reaction times (2.5 days) produces no difference in the recovered yield of 3. Use of greater than 1 equivalent of $n\text{-BuLi}$ is also ineffective. Use of a smaller alkyl lithium

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such as methyl lithium (MeLi) does not work either. A mixture of unidentified products is recovered in this case. The use of lithium dimethyl amide ($\text{LiN}(\text{CH}_3)_2$) produces results similar to that when 1.1 equivalent of n-BuLi is used (i.e. ~ 50% conversion to 3).

Preparation of $(\text{ZrCl}_3, (\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}(\text{i-Pr}_2\text{O})_4)$ (4): 0.708 g of 3 was suspended in i-Pr₂O (~10 mL) and cooled to -78 C. 1.1 equiv. of ZrCl₄ (144 mgs) was then added slowly via side arm addition funnel. Upon addition, a yellow oil formed but the reaction was allowed to warm to room temperature and stirred overnight. The solution was concentrated and when the stirring was stopped a yellow oil layer was deposited at the bottom of the flask. The excess (iPr)₂O was cannulated off, then pumped dry. The product was then dissolved in ~30 mL CH₂Cl₂ and left to let the salts settle. The supernatant was then filtered through medium porosity filter paper. The CH₂Cl₂ was removed to leave a yellow crystalline solid. Successive recrystallization from CH₂Cl₂ /pentane left a yellow oily solid which became crystalline after vacuum was applied. Yield .790 g, 52%.

Note: Mixing 3 and ZrCl₄ in a 1:1 ratio together before adding cold i-Pr₂O produces similar results. Likewise, vacuum transferring i-Pr₂O onto 3 and ZrCl₄ also gives 4. In all cases, the product needs to be washed with a little i-Pr₂O to remove any 2 which is formed in the reaction. Use of only .95 equiv. of ZrCl₄ in any reaction leaves traces of 3 which cannot be removed easily. If the reaction is done in CH₂Cl₂ some decomposition of the ligand is observed.

Preparation of $(\text{Zr}(\text{CH}_2\text{Ph})_3, (\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}(\text{Et}_2\text{O})_4)$ (5): 0.200 g of 4 was suspended in ~10 mL of Et₂O and cooled to -78°. BzMgCl (161 µL, 3.2 eq) was syringed in and the reaction was allowed to warm to room temperature. A bright yellow solution formed immediately and

was left stirring for 8 hrs. Solvent was stripped and the product dissolved in CH_2Cl_2 to separate the salts. The solution was cannula filtered and dried under vacuum to leave a bright yellow solid. Yield not established. Note: This reaction does not proceed well in $i\text{-Pr}_2\text{O}$.

Preparation of $(\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{Si}(\text{CH}_3)_3)(\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3\text{Li}(i\text{-Pr}_2\text{O})_4)$ (6): .475 g of 4 was mixed with .045 g of LiCp-SiMe_3 (base free). ~10 mL of cold (-78°C) CH_2Cl_2 was cannulated onto the two solids and stirred at room temperature for 2 hrs. A yellow solution formed. Stirring was stopped, the salts were allowed to settle and the solution was collected via cannula filtration. Successive CH_2Cl_2 /pentane recrystallizations left a yellow crystalline solid. Yield is quantitative by $^1\text{HNMR}$.

Preparation of $(\text{Zr}(\text{CH}_3)_2(\eta^5\text{-C}_5\text{H}_4)\text{Si}(\text{CH}_3)_3)(\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3\text{Li}(i\text{-Pr}_2\text{O})_4)$ (7): .175 g of (6) was suspended in ~10 mL of Et_2O and cooled to -78°C . 2.5 equiv. CH_3MgBr was syringed in and the reaction kept cold for 1 hr. It was then warmed to room temperature and stirred for 5 hrs. The resulting solution was filtered and then solvent was removed under vacuum to leave a yellow solid.

In situ generation of $[\text{Zr}(\text{CH}_3)(\text{THF})(\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3)(\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3)]$; 0.33 g of (7) was dissolved in THF_{d-8} and cooled to -10°C . One equivalent of tris-pentafluorophenyl boron was then added via spatula to the sample and warmed to room temperature immediately. A $^1\text{HNMR}$ spectrum was recorded within 10 minutes and exhibited resonances consistent with the formation of the compound. Spectroscopic data: $^1\text{HNMR}$ δ -0.22 (s, 3H, Zr-CH_3); δ 0.63 (br s, 6H, $\text{Si}(\text{CH}_3)_2$); δ 0.30 (2, 9H, $-\text{Si}(\text{CH}_3)_3$); δ 1.79 (s, 3H, Cp-CH_3); δ 1.88 (2, 3H, Cp-CH_3); δ 1.99 (s, 3H, Cp-CH_3); δ 1.99 (s, 3H, Cp-CH_3); δ 5.72 (br s, 1H, TMS-Cp); δ 5.95 (br s, 1H, TMS-Cp); δ 6.40 (br

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s, 1H, TMS-Cp); δ 6.50 (br s, 1H, TMS-Cp).

CATALYST PREPARATION

All procedures were performed under a dry nitrogen atmosphere. All liquids/solvents were anhydrous.

5 Catalyst A, 15 mg (0.0097 mmol) of $(Zr(Cl_2[\{\eta^5-C_5H_4\}(Si(CH_3)_3)](\eta^5-C_5(CH_3)_4)-Si(CH_3)_2-p-C_6F_4B(C_6F_3)]\cdot Li(O-i-Pr_2O)_4\}$ were dissolved in 2.0 g of a MAO/toluene solution (13 weight percent aluminum, 9.63 mmol Al, Al/Zr=1000) at room temperature. The catalyst was used immediately after
10 preparation.

Catalyst B, 4 mg (0.0099 mmol) of $(\eta^5-C_5H_4-n-Bu)_2ZrCl_2$ were dissolved in 2.0 g of a MAO/toluene solution (13 wt.% aluminum, 9.63 mmol Al, Al/Zr = 1000) at room temperature.

POLYMERIZATION

15 Ethylene/1-hexene copolymers were prepared by these catalysts under identical polymerization procedures, described below:

A 1 gallon stainless steel autoclave at room temperature was charged with 1500 mL heptane and 150 mL 1-hexene. 1.0 mL
20 of 14 weight percent tri-iso-butylaluminum in hexane were added. The reactor was closed, and the temperature was brought to 70°C. 50 mg of catalyst B was introduced with ethylene pressure. Ethylene was replenished on demand to keep reactor pressure constant at 135 psi. After 60 minutes,
25 the reactor was vented and cooled to room temperature. 42.1 gm polymer were collected.

	Catalyst	A	B
	Activity		
	kg/gZr/hr	170	1870
30	I ₂ (g/10 min.)	0.07	0.04
	MFR	17.3	18.1
	Density (g/cc)	0.916	0.917
	Mole % C ₆	2.1	1.0
	Melting Pt. (°C)	111.2	118.5

CLAIMS:

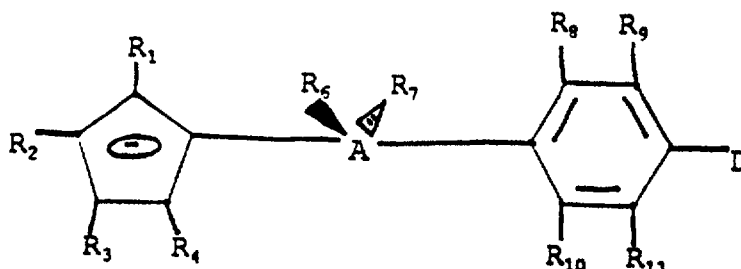


1. A compound of the formula

(V) (E) (W) M-L

in which M is selected from the group consisting
5 of zirconium, hafnium and titanium;

in which each of V, E, W is the same or different
and each is alkyl of 1 to 6 carbon atoms, halide, or
unsubstituted or substituted cyclopentadienyl provided that
one, and only one, of V, E, and W, is unsubstituted or
10 substituted cyclopentadienyl; and in which L is



wherein each of R_1 , R_2 , R_3 , R_4 , is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

A is C, Si, Ge; and each of R_6 and R_7 is the same or
15 different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

each of R_8 , R_9 , R_{10} , R_{11} , is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

20 D is hydrogen, alkyl of 1 to 6 carbon atoms, sodium, lithium, halogen, BG_3 or AlG_3 in which B is boron (B) and Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

25 2. The compound of Claim 1, wherein D is BG_3 .



3. The compound of Claim 2, wherein G is pentafluorophenyl.

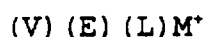
4. The compound of Claim 1, wherein each of R_1 , R_2 , R_3 , and R_4 , is methyl.

5. The compound of Claim 1, wherein A is Si.

6. The compound of Claim 5, wherein each of R_6 and R_7 is alkyl of 1 to 6 carbon atoms.

7. The compound of claim 6, wherein G is pentafluorophenyl.

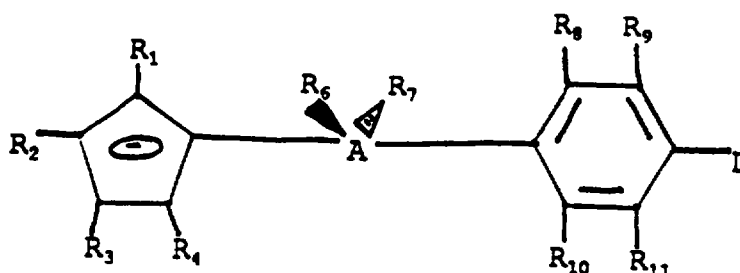
8. A compound of the empirical formula



in which M is selected from the group consisting of zirconium, hafnium and titanium;

5 in which each of V and E is the same or different and each is alkyl of 1 to 6 carbon atoms, halide, or unsubstituted or substituted cyclopentadienyl provided that one, and only one, of V, and E is unsubstituted or substituted cyclopentadienyl;

10 and in which L is



wherein each of R_1 , R_2 , R_3 , R_4 , is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;



A is C, Si, or Ge; and each of R_6 and R_7 is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

5 each of R_8 , R_9 , R_{10} , R_{11} is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms; sodium; lithium; halogen; alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine; or BG_3 or
10 AlG_3 in which B is boron (B) and Al is aluminum (Al),

G is selected from the group consisting of pentafluorophenyl, trifluoromethyl, phenyl, hydrogen and alkyl of 1 to 6 carbon atoms.

9. The compound of Claim 8, wherein A is Si.

10. The compound of Claim 9, wherein each of R_6 and R_7 is alkyl of 1 to 6 carbon atoms.

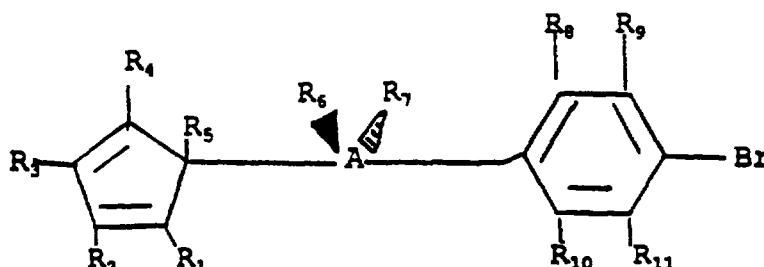
11. The compound of claim 10, wherein G is pentafluorophenyl.

12. A process for olefin polymerization comprising contacting ethylene with a transition metal catalyst, under olefin polymerization conditions, in which the source of transition metal is the compound of Claim 1.

13. A process for olefin polymerization comprising contacting ethylene with a transition metal catalyst, under olefin polymerization conditions, in which the source of transition metal is the zwitterion of Claim 8.



14. A process for forming the compound of Claim 1 comprising contacting a compound of the formula

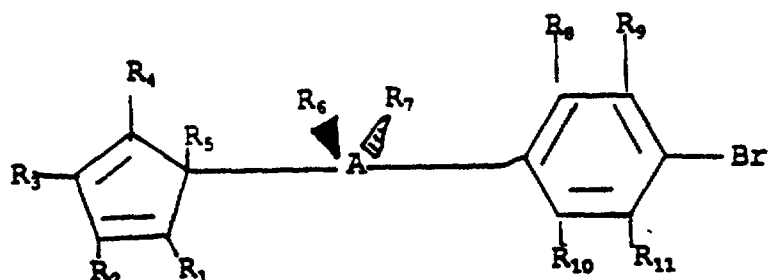


with a reagent effective to abstract the R_5 group to form an intermediate and contacting the intermediate with a transition metal halide, in which the transition metal is selected from the group consisting of zirconium, hafnium and titanium, to form a trihalide transition metal salt of the intermediate.

15. The process of claim 14, which further comprises the step of contacting the trihalide transition metal salt with a compound which is a lithium salt of cyclopentadienyl compound which comprises an unsubstituted or substituted cyclopentadienyl ring which is mono, di-, tri, tetra or penta-substituted cyclopentadienyl, in which the substitution is monoalkyl, dialkyl, trialkyl, tetraalkyl or pentaalkyl-substituted cyclopentadienyl in which the alkyl is 1 to 6 carbon atoms.



16. A salt in which the anion is characterized by the formula



wherein each of R_1 , R_2 , R_3 , R_4 is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

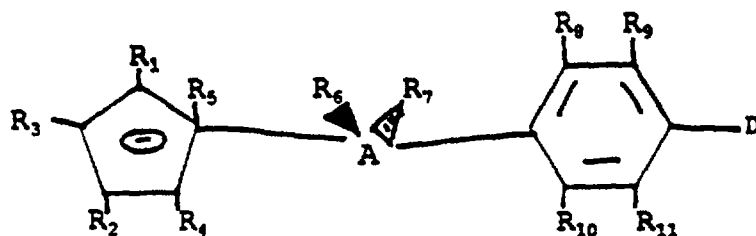
A is C, Si, Ge; and each of R_6 and R_7 is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

each of R_8 , R_9 , R_{10} , R_{11} , is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal [sodium or lithium]; halogen [chloride or bromide]; alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine; and BG_3 or AlG_3 in which B is boron (B) or Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

17. A compound of the formula





wherein each of R_1 , R_2 , R_3 , R_4 is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

5 R_5 is hydrogen or GeZ_3 , wherein Ge is germanium and Z is hydrogen or all alkyl of 1 to 6 carbon atoms;

A is C, Si, Ge; and each of R_6 and R_7 is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

10 each of R_8 , R_9 , R_{10} , R_{11} , is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal [sodium or lithium]; halogen [chloride or bromide]; alkyl halide in which the alkyl has 1 to 6 carbon atoms and
15 halide is chlorine or bromine; and BG_3 or AlG_3 in which B is boron (B) or Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

18. The compound of Claim 17, wherein D is Br.

20 19. The compound of Claim 17, wherein D is Li.