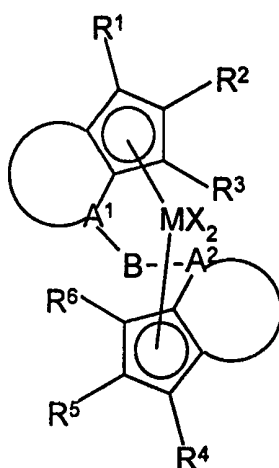




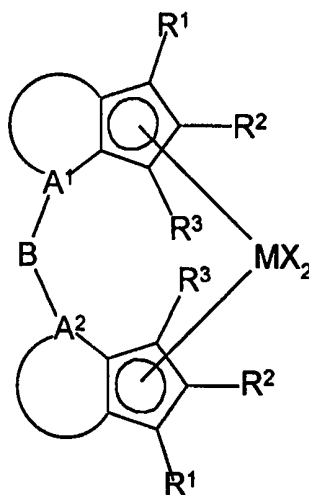
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(21) International Application Number: PCT/KR98/00375 (22) International Filing Date: 24 November 1998 (24.11.98) (30) Priority Data: 1997/62461 24 November 1997 (24.11.97) KR (71) Applicant (for all designated States except US): LG CHEMICAL LTD. [KR/KR]; LG Twin Tower, 20, Youido-dong, Youngdeungpo-ku, Seoul 150-010 (KR). (72) Inventors; and (75) Inventors/Applicants (for US only): OH, Jae-Seung [KR/KR]; Town House, 107, Doryong-dong, Yuseong-ku, Daejeon-city 305-340 (KR). PARK, Jae-Hyeon [KR/KR]; LG-Gooyeonrip, 7, Doryong-dong, 388-11, Yuseong-ku, Daejeon-city 305-340 (KR). PARK, Young-Whan [KR/KR]; LG-Sataek, 6-102, Doryong-dong, 381-42, Yuseong-ku, Daejeon-city 305-340 (KR). (74) Agent: KIM, Won-Ho; 702, Teheran Boulevard, 825-33, Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).	(81) Designated States: CN, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	

(54) Title: POLYMERIZATION CATALYST FOR OLEFIN MONOMERS



(X)



(XI)

(57) Abstract

Transition metal compounds coordinated with bis-cyclopentadienyl type ligands, in which steric hindrance is given to the central metal and the direction of steric hindrance is controlled, not by connection cyclopentadienyl moieties directly with diradical as in previous arts, but by selecting appropriate number of atoms and location of bridge-bonding as shown in formula (X) and (XI) where R¹ - R⁶ are respectively same or different substituent containing 1 - 20 non-hydrogen atoms.

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POLYMERIZATION CATALYST FOR OLEFIN MONOMERS

a) Field of the invention

This invention relates to catalyst for the homo- or co-polymerization of
5 ethylene, α -olefin and cycloolefin. More particularly, this invention related to
the structure of the transition metal compounds which can be used for the
homo- or co-polymerization of ethylene, α -olefin and cycloolefin.

b) Background of the invention

10 In the early 1980s, Prof. Kaminsky reported in DE 3127133 that the
metallocene compound of group IV showed excellent activity in the olefin
polymerization when it was activated with alkylaluminumoxane. Since that, active
research was done to develop the novel catalysts by varying the structure of the
cyclopentadienyl ligands.

15 Metallocene compounds whose two cyclopentadienyl or hydroindenyl
or fluorenyl ligands was connected by bridge (bridged metallocene
compounds) was synthesized and tested for the polymerization to show
characteristic reactivity which could not be seen with unbridged metallocene
compounds.

20 For example, C₂ symmetric bridged metallocene compounds
containing two (hydro)indenyl ligands gave isotactic stereoselectivity in the α -
olefin polymerization (DE 3508887, EP-A-485821, EP-A-485823). However,
the meso-compounds, which have the same composition but have different
symmetry, C_s, was known to give a uniform comonomer composition in the
25 polymer chains when it was used for the copolymerization of cycloolefin and
ethylene or α -olefin (DE 4107682).

The metallocene compound which was derived from bridged ligand of
cyclopentadienyl and fluorenyl showed the syndiotactic stereoselectivity in the
 α -olefin polymerization (EP-A-351392).

30 The bridge connect directly two five membered ring of the
cyclopentadienyl or indenyl or hydroindenyl or fluorenyl ligands via methylene,

ethylene, and dialkylsilylene diradical in the previously known bridged metallocene compounds. R. H. Halterman summarize it in Chemical Review, 92, 659 (1992).

5

BRIEF DESCRIPTION OF THE INVENTION

This invention gives the novel structure of the bridged transition metal compounds in which the bridge connect the two ligands in different way.

The bridge connect indirectly the two cyclopentadienyl rings. That is, 10 the cyclopentadienyl ligands whose two adjacent carbon were connected by triradicals to form annulated cyclopentadienyl ligand containing one radical in a newly formed ring are bridged by connecting each said remaining one radical to bridge. Novel bridged metallocene compounds can be synthesized by this bridged ligands.

15 In previous bridged metallocene compounds, steric hindrance was endowed by the annulated ring of the cyclopentadienyl ligands.

The metallocene compounds described in this invention endow the different steric hindrance from previously known bridged metallocene compounds, and especially the steric hindrance can be controlled by changing 20 the length of bridge and bridging point.

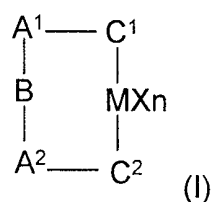
In rac-ethylenebis(indenyl)zirconium dichloride, there is two conformational fluxional motion, δ -form and λ -form (Organometallics, 14, 1256 (1995)). This motion was known to decrease the stereoselectivity in the α -olefin polymerization at high temperature (Metallocenes '95 proceedings 25 403f and references cited therein). A bridged metallocene depicted in this invention, for example, rac-metallocene compound in which two indenyl ligand was connected by ethylene through 6 position of the indenyl ring cannot have such a conformational fluxional motion.

It has been impossible to prepare exclusively meso-compound in the 30 synthesis of the previously known bridged compounds. For example, S. Collins and R. B. Raush reported respectively in Journal of Organometallic

Chemistry, vol. 342, 21 (1998) and Organometallics, vol. 10, 1501 (1991) that the rac- and meso-compounds are almost always obtained as a mixture and tedious separation step is necessary. Furthermore, because the meso-compound is usually minor isomer, it is not suitable to use meso isomer in industry. In this invention are disclosed novel structures of bridged ligands that give only meso isomers due to their stereochemistry and their novel bridged metallocene compounds.

DETAILED DESCRIPTION OF THE INVENTION

This invention related to the transition metal compounds represented general structure (I):



Where

M is a transition metal selected from of Group 3 or 4 or 5 or 6.

A^1 and A^2 are respectively and independently hydrocarbyl triradical consisted of more than two carbon atoms which are bonded to the cyclopentadienyl ring in covalently, or 0 - 10 carbon atoms including one or more of B, N, P, S, O, or Si atom, in which the triradical may have same or different substituents containing 1 - 20 non-hydrogen atoms.

B is hydrocarbyl diradical containing 1 - 20 carbon atoms or substituted hydrocarbyl diradical containing 0 - 20 carbon atoms, B, N, P, S, O, or Si atoms in which the diradical may have same or different substituents containing 1 - 20 non-hydrogen atoms and the radicals joined to C^1 and C^2 to form bridge by covalent bonds.

C^1 and C^2 are respectively and independently triradical of cyclopentadienyl moiety which is covalently bonded to two radical sites of A^1 and A^2 and one radical site of M, in which the triradical may have same or different substituents containing 1 - 20 non-hydrogen atoms and the

substituent may be hydrocarbyl radical with 1 - 20 carbon atoms or radical containing one or more of B, N, P, S, O, or Si atoms and 1 - 20 carbon atoms.

X is respectively and independently ligand of halogen, hydrocarbyl containing 1 - 20 carbon atoms, alkoxy, aryloxy, amide, arylamide, phosphide, arylphosphide, sulfide, or arylsulfide.

n is integer of 0 - 4 which depends on the oxidation state of M.

In above general formula (I), M can be, particularly, Ti, Zr, Hf, Sc, Cr, V, W and, more particularly, Ti, Zr, Hf. Illustrative but not limiting example of bridged cyclopentadienyl ligands ($R^1-A^1-B-A^2-R^2$) are bis(4-indenyl)methane, bis(5-indenyl)methane, bis(7-indenyl)methane, bis(1-fluorenyl)methane, bis(2-fluorenyl)methane, bis(3-fluorenyl)methane, bis(4-fluorenyl)methane, bis(4-(2-indenyl)methane, bis(5-(2-indenyl)methane, bis(5-(2-indenyl)methane, bis(6-(2-indenyl)methane, bis(7-(2-indenyl)methane, bis(4-(1-indenyl)methane, bis(5-(1-methyl)indenyl)methan, bis(6-(1-methyl)indenyl)methan, bis(7-(1-methyl)indenyl)methan, bis(4-(3-methyl)indenyl)methan, bis(5-(3-methyl)indenyl)methan, bis(6-(3-methyl)indenyl)methan, bis(7-(3-methyl)indenyl)methan, bis(4-(5-methyl)indenyl)methan, bis(5-(6-methyl)indenyl)methan, bis(6-(5-methyl)indenyl)methan, bis(7-(5-methyl)indenyl)methan, bis(4-(6-methyl)indenyl)methan, bis(5-(4-methyl)indenyl)methan, bis(6-(4-methyl)indenyl)methan, bis(7-(4-methyl)indenyl)methan, bis(4-(6-methyl)indenyl)methan, bis(5-(7-methyl)indenyl)methan, bis(6-(7-methyl)indenyl)methan, bis(7-(6-methyl)indenyl)methan, bis(4-(7-methyl)indenyl)methan, (4-(7-methyl)indenyl)(7-(4-methyl)indenyl)methan, (4-(7-methyl)indenyl)(5-(4-methyl)indenyl)methan, (4-(7-methyl)indenyl)(6-(4-methyl)indenyl)methan, bis(4-(2,5-dimethyl)indenyl)methan, bis(4-(2,6-dimethyl)indenyl)methan, bis(4-(2,7-dimethyl)indenyl)methan, bis(4-(1,5-dimethyl)indenyl)methan, bis(4-(1,6-dimethyl)indenyl)methan, bis(4-(1,2-dimethyl)indenyl)methan, bis(4-(2,3-dimethyl)indenyl)methan, bis(4-(5,6-dimethyl)indenyl)methan, bis(4-(5,7-dimethyl)indenyl)methan, bis(4-(6,7-dimethyl)indenyl)methan, bis(7-(2,5-

- dimethyl)indenyl)methan, bis(7-(1,5-dimethyl)indenyl)methan, bis(7-(1,6-dimethyl)indenyl)methan, bis(7-(1,2-dimethyl)indenyl)methan, bis(7-(2,3-dimethyl)indenyl)methan, bis(7-(5,6-dimethyl)indenyl)methan, bis(7-(4,5-dimethyl)indenyl)methan, bis(7-(4,6-dimethyl)indenyl)methan, (4-(2,7-dimethyl)indenyl)(7-(2,4-dimethyl)indenyl)methan, 1,2-bis(4-indenyl)ethane, 1,2-bis(5-indenyl)ethane, 1,2-bis(7-indenyl)ethane, bis(4-(7-methyl)indenyl)ethane, (4-(7-methyl)indenyl) (7-(4-methyl)indenyl)ethane, (4-(7-methyl)indenyl) (5-(4-methyl)indenyl)ethane, (4-(7-methyl)indenyl) (6-(4-methyl)indenyl)ethane, bis(4-(2-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(5-(2-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(6-(2-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(7-(2-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(4-(1-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(5-(1-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(6-(1-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(7-(1-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(4-(3-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(5-(3-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(6-(3-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(7-(3-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(4-(5-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(5-(6-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(6-(5-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(7-(5-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(4-(6-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(4-(2-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(5-(4-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(6-(4-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(7-(4-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(4-(6-methyl)-4,5,6,7-tetrahydroindenyl)methane, bis(5-(7-methyl)-4,5,6,7-tetrahydroindenyl)methane,

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|----|--|-------------------------------|
| | tetrahydroindenyl)methane, | bis(6-(7-methyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(6-methyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(2,5-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(2,6-dimethyl)-4,5,6,7- |
| 5 | tetrahydroindenyl)methane, | bis(4-(2,7-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(1,5-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(1,6-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(1,2-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(2,3-dimethyl)-4,5,6,7- |
| 10 | tetrahydroindenyl)methane, | bis(4-(5,6-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(5,7-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(4-(6,7-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(2,5-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(2,6-dimethyl)-4,5,6,7- |
| 15 | tetrahydroindenyl)methane, | bis(7-(2,4-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(1,5-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(1,6-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(1,2-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(2,3-dimethyl)-4,5,6,7- |
| 20 | tetrahydroindenyl)methane, | bis(7-(5,6-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(4,5-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, | bis(7-(4,6-dimethyl)-4,5,6,7- |
| | tetrahydroindenyl)methane, 1,2-bis(4--4,5,6,7-tetrahydroindenyl)ethane, 1,2- | |
| | bis(5--4,5,6,7-tetrahydroindenyl)ethane, | 1,2-bis(6--4,5,6,7- |
| 25 | tetrahydroindenyl)ethane, 1,2-bis(7--4,5,6,7-tetrahydroindenyl)ethane, 1,3- | |
| | bis(1-fluorenyl)propane, 1,2-bis(2-fluorenyl)ethane, 1,2-bis(3-fluorenyl)ethane, | |
| | 1,2-bis(4-fluorenyl)ethane, 1,2-bis(4-(2-methyl)indenyl)ethane, 1,2-bis(5-(2- | |
| | methyl)indenyl)ethane, 1,2-bis(6-(2-methyl)indenyl)methane, 1,2-bis(7-(2- | |
| | methyl)indenyl)ethane, 1,2-bis(4-(1-methyl)indenyl)ethane, 1,2-bis(5-(1- | |
| 30 | methyl)indenyl)methane, 1,2-bis(6-(1-methyl)indenyl)methane, 1,2-bis(7-(1- | |
| | methyl)indenyl)ethane, 1,2-bis(4-(3-methyl)indenyl)ethane, 1,2-bis(5-(3- | |

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 1,2-bis(5-(1,4-dimethyl)indenyl)ethane, 1,2-bis(5-(2,3-dimethyl)indenyl)ethane,
 15 1,2-bis(5-(4,6-dimethyl)indenyl)ethane, 1,2-bis(5-(4,7-dimethyl)indenyl)ethane,
 1,2-bis(5-(3,6-dimethyl)indenyl)ethane, 1,2-bis(5-(3,7-dimethyl)indenyl)ethane,
 1,2-bis(6-(2,5-dimethyl)indenyl)ethane, 1,2-bis(6-(2,4-dimethyl)indenyl)ethane,
 1,2-bis(6-(2,3-dimethyl)indenyl)ethane, 1,2-bis(6-(1,5-dimethyl)indenyl)ethane,
 1,2-bis(6-(1,3-dimethyl)indenyl)ethane, 1,2-bis(6-(1,2-dimethyl)indenyl)ethane,
 20 1,2-bis(6-(5,7-dimethyl)indenyl)ethane, 1,2-bis(6-(4,5-dimethyl)indenyl)ethane,
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 (1,3,5-trimethyl)indenyl)methane, 1,2-bis-(5-(1,2,4-trimethyl)indenyl)methane,
 30 1,2-bis-(6-(1,2,3-trimethyl)indenyl)methane, 1,2-bis-(7-(4,5,6-
 trimethyl)indenyl)methane, 1,3-bis-(4-(5,6,7-trimethyl)indenyl)propane, 1,2-bis-

- (6-(4,5,7-trimethyl)indenyl)ethane, 1,2-bis-(5-(4,6,7-trimethyl)indenyl)ethane,
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 bis-(7-(1,2,3,4-tetramethyl)indenyl)methane,
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 1,2-bis(4-(6-methyl)-4,5,6,7-tetrahydroindenyl)ethane, 1,2-bis(5-(4-methyl)-4,5,6,7-tetrahydroindenyl)ethane,
 1,2-bis(6-(4-methyl)-4,5,6,7-tetrahydroindenyl)ethane,

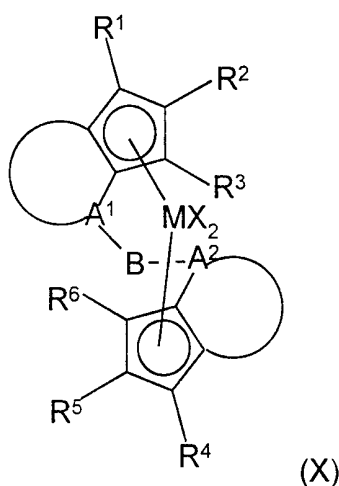
	tetrahydroindenyl)ethane,		1,2-bis(7-(4-methyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-	bis(4-(6-methyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(7-methyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(6-(7-methyl)-4,5,6,7-
5	tetrahydroindenyl)ethane,	1,2-	bis(7-(6-methyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(4-(2,5-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(4-(2,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-	bis(4-(2,7-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(4-(1,5-dimethyl)-4,5,6,7-
10	tetrahydroindenyl)ethane,		1,2-bis(4-(1,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-	bis(4-(1,2-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,3-bis(4-(2,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(4-(5,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-	bis(4-(5,7-dimethyl)-4,5,6,7-
15	tetrahydroindenyl)ethane,		1,2-bis(4-(6,7-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(2,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(2,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(2,4-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(1,2-dimethyl)-4,5,6,7-
20	tetrahydroindenyl)ethane,		1,2-bis(5-(1,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(1,4-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(2,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(4,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(5-(4,7-dimethyl)-4,5,6,7-
25	tetrahydroindenyl)ethane,		1,2-bis(5-(3,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(6-(2,5-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(6-(2,4-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(6-(2,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(6-(1,5-dimethyl)-4,5,6,7-
30	tetrahydroindenyl)ethane,		1,2-bis(6-(1,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,		1,2-bis(6-(1,2-dimethyl)-4,5,6,7-

	tetrahydroindenyl)ethane,	1,2-bis(6-(2,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(6-(5,7-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(6-(4,5-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(6-(1,4-dimethyl)-4,5,6,7-
5	tetrahydroindenyl)ethane,	1,2-bis(7-(2,5-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(2,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(2,4-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(1,5-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(1,6-dimethyl)-4,5,6,7-
10	tetrahydroindenyl)ethane,	1,2-bis(7-(1,2-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(2,3-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(5,6-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(4,5-dimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(7-(4,6-dimethyl)-4,5,6,7-
15	tetrahydroindenyl)ethane,	bis(4-(1,2,4-trimethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	bis(7-(1,2,4-trimethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	1,2-bis(7-(1,2,4-trimethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	bis(4-(1,2,7-trimethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	bis(4-(1,3,5-trimethyl)-4,5,6,7-
20	tetrahydroindenyl)methane,	1,2-bis(5-(1,2,4-trimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(6-(1,2,3-trimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,3-bis(5-(5,6,7-trimethyl)-4,5,6,7-
	tetrahydroindenyl)propane,	1,2-bis(-(4,5,7-trimethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	1,2-bis(5-(13,6,7-trimethyl)-4,5,6,7-
25	tetrahydroindenyl)ethane,	1,2-bis(4-(5,6,7-trimethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	bis(4-(1,2,3,5-tetramethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	bis(7-(1,2,3,4-tetramethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	1,2-bis(7-(1,2,3,4-tetramethyl)-4,5,6,7-
	tetrahydroindenyl)ethane,	bis(4-(2,5,6,7-tetramethyl)-4,5,6,7-
30	tetrahydroindenyl)methane,	bis(4-(1,3,5,6-tetramethyl)-4,5,6,7-
	tetrahydroindenyl)methane,	1,2-bis(5-(1,2,3,4-tetramethyl)-4,5,6,7-

- tetrahydroindenyl)ethane, 1,2bis(6-(1,2,3,4-tetramethyl)-4,5,6,7-
 tetrahydroindenyl)ethane, 1,2-bis(7-(2,4,5,6-tetramethyl)-4,5,6,7-
 tetrahydroindenyl)ethane, 1,2-bis(4-(2,5,6,7-tetramethyl)-4,5,6,7-
 tetrahydroindenyl)ethane, 1,2-bis(6-(3,4,5,7-tetramethyl)-4,5,6,7-
 5 tetrahydroindenyl)ethane, 1,2-bis(5-(1,4,6,7-tetramethyl)-4,5,6,7-
 tetrahydroindenyl)ethane, 1,2-bis(4-(1,5,6,7-tetramethyl)-4,5,6,7-
 tetrahydroindenyl)ethane, (4--4,5,6,7-tetrahydroindenyl)(4-(1-methyl)-4,5,6,7-
 tetrahydroindenyl)methane, bis(4--4,5,6,7-tetrahydroindenyl)methylmethane,
 bis(4-(2-methyl)-4,5,6,7-tetrahydroindenyl)dimethylmethane, (4-fluorenyl)(4--
 10 4,5,6,7-tetrahydroindenyl)methan, 1,2-bis(5-4,5,6,7- tetrahydroindenyl)-1,2-
 dimethylethane, 1,3-bis(4-indenyl)propane

Bridged cyclopentadienyl ligands of this invention are not restricted by
 above examples. This invention include all compounds represented by general
 formula (I) by the variation of the substituents of the ligands, M, X and n.

- 15 An example of the structure of the rac-metallocene compounds
 prepared according to this invention is depicted in general formula (X).

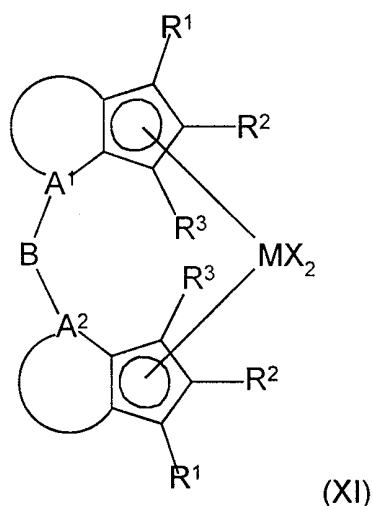


- where M, X, A¹, A², and B are same as described above and R¹ - R⁶ is are
 respectively same or different substituent containing 1 - 20 non-hydrogen
 20 atoms.

The structure represented by general formula (X) is very different from
 that of previously well-known rac-metallocene compounds where bridge is
 directly connected with the carbon atoms of the cyclopentadienyl ring.
 Furthermore, the bridge B and the position of A¹ and A² can be freely

controlled. While there is conformational fluxional motion in well-known rac-ethylenebis(1-indenyl)zirconium dichloride, the rac-bridged metallocenes depicted in formula (X) have not such a conformational fluxional motion due to the rigidity of the structure.

5 Structure of the meso-metallocene compounds prepared according to this invention is depicted in general formula (XI).



Where M , X , A^1 , A^2 , $R^1 - R^6$ are same as described above.

There have not been reasonable way to synthesize exclusively meso-
10 compounds but this invention gives way to synthesize exclusively meso-
compounds by controlling the position of A¹ and A² and length of B so that it
may impossible to form rac-compounds.

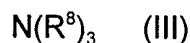
For example, (substituted) bis(5-indenyl)methane or (substituted) 1,2-bis(5-indenyl)ethane cannot form rac-complexes when they are transformed to
15 metallated complexes.

Compounds depicted general formula (I) can be used for the olefin polymerization or copolymerization with cocatalysts represented by general formula (II) or (III) or (IV):

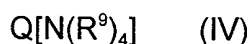


where R⁷ is halogen radical, hydrocarbonyl radical containing 1 - 20 carbon atoms, hydrocarbonyl radical containing 1 - 20 carbon atoms substituted with

halogen, m is integer more than 2, each of R^7 is different or same.



- 5 where N is aluminum or boron atom, R^8 is same as described for R^7 , each R^8 is same or different.



- 10 where Q is inorganic or organic cation charged with +1, N is aluminum or boron, R^9 is same described for R^7 , and each R^9 is same or different. Alkylaluminum compounds depicted general formula (II) can be exist as linear or cyclic or net form, each of which can be used as a single compound or a mixture.

- 15 Examples of alkylaluminum compounds represented by above general formula (II) are methylaluminum, ethylaluminum, isobutylaluminum, butylaluminum, hexylaluminum, octylaluminum, etc.

- Examples of alkylmetal compounds represented by above general formula (III) are trimethylaluminum, triethylaluminum, triisobutylaluminum, tripropylaluminum, tributylaluminum, dimethylchloroaluminum, dimethylisobutylaluminum, dimethylethylaluminum, diethylchloroaluminum, triisopropylaluminum, tri-sec-butylaluminum, tricyclopentylaluminum, triphenylaluminum, triisopentylaluminum, trihexylaluminum, trioctylaluminum, ethyldimethylaluminum, methyl-diethylaluminum, triphenylaluminum, tri-p-
25 tolylaluminum, dimethylaluminummetoxide, trimethylboron, triethylboron, triisobutylboron, tripropylboron, tributylboron, etc.

- Examples of ionic compound represented by the above general formula (IV) are triethylammoniumtetraphenylboron, tributylammoniumtetraphenylboron, tripropylammoniumtetraphenylboron, trimethylammonium(p-tolyl)boron, tripropylammoniumtetra(p-tolyl)boron, triethylammoniumtetra(o,p-dimethylphenyl)boron,
30

- trimethylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, trimethylammoniumtetra(p-trichloromethylphenyl)boron, tributylammoniumtetrapentafluorophenylboron, N,N-diethylanilinumtetraphenylboron, N,N-diethylanilinumtetraphenylboron,
- 5 N,N-diethylanilinumtetrapentafluorophenylboron, diethylammoniumtetrapentafluorophenylboron, triphenylphosphoniumtetraphenylboron, triphenylphosphoniumtetraphenylboron, triethylammoniumtetraphenylaluminum,
- 10 tributylammoniumtetraphenylaluminum, trimethylammoniumtetraphenylaluminum, tripropylammoniumtetraphenylaluminum, trimethylammoniumtetra(p-tolyl)aluminum, tripropylammoniumtetra(p-tolyl)aluminum, triethylammoniumtetra(o,p-dimethylphenyl)aluminum,
- 15 trimethylammoniumtetra(p-trichloromethylphenyl)aluminum, tributylammoniumtetra(p-trichloromethylphenyl)aluminum, tributylammoniumtetrapentafluorophenylaluminum, N,N-diethylanilinumtetraphenylaluminum, N,N-diethylanilinumtetraphenylaluminum, N,N-diethylanilinumtetrapentafluorophenylaluminum,
- 20 diethylammoniumtetrapentafluorophenylaluminum, triphenylphosphoniumtetraphenylaluminum, trimethylphosphoniumtetraphenylaluminum, trimethylphosphoniumtetraphenylaluminum, triethylammoniumtetraphenylboron, tributylammoniumtetraphenylboron,
- 25 trimethylammoniumtetraphenylboron, tripropylammoniumtetraphenylboron, trimethylammoniumtetra(p-tolyl)boron, tripropylammoniumtetra(p-tolyl)boron, triethylammoniumtetra(o,p-dimethylphenyl)boron, trimethylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, trimethylammoniumtetra(p-trifluoromethylphenyl)boron,
- 30 tributylammoniumtetrapentafluorophenylboron, N,N-diethylanilinumtetraphenylboron, N,N-

diethylaniliniumtetrapentafluorophenylboron,
diethylammoniumtetrapentafluorophenylboron,
triphenylphosphoniumtetraphenylboron, triphenylcarboniumtetraphenylboron,
triphenylcarboniumtetraphenylboron, triphenylcarboniumtetraphenylaluminum,
5 triphenylcarboniumtetra(p-trifluoromethylphenyl)boron,
triphenylcarboniumtetrapentafluorophenylboron etc.

The polymerization of the present invention can be conducted in a conventional manner. For example, a suitable amount of an inert organic solvent and a small amount of cocatalyst are added to a glass reactor. At this
10 stage, if a liquid monomer is to be employed, it is introduced into the reactor together with a suitable solvent. In case of a gaseous monomer, it is charged to the reactor to a preset pressure. Then, a catalyst solution is added thereto e. g., by employing a syringe to initiate the polymerization.

The polymerization may be conducted at a temperature ranging from 0
15 to 500 °C under a pressure ranging from 10 to 500 psig. The cocatalyst may be used in an amount ranging 1 to 100,000 molar equivalents based on the metallocene catalyst. Contacting order or introducing order of catalyst, cocatalyst, solvent, olefin monomer or comonomer is not limited. After polymerization for a suitable time, the polymerization reaction was quenched
20 by adding ethanol containing hydrochloric acid. The polymer can be obtained by filtering and washing with methanol. The polymer was dried in vacuum oven.

The following examples are intended to illustrate the present invention more specifically, without limiting the scope of the invention.

25 In the examples, organic reagents and solvent used in the preparation of the catalysts and polymerization were provided from Aldrich, Strem, Sigma, Acros, B & J, Lancaster, Merck and then purified in accordance with a standard method (D. D. Perrin, "Purification of Laboratory Chemicals" 3rd ed., Pergamon Press plc: Oxford, 1988). Air sensitive compounds were prepared
30 and handled according to the standard Shlenk technique or in a glove box under purified nitrogen or argon (D. F. Shriver, "The manipulation of air-

sensitive compounds" 2nd ed., John & Wiley: New York, 1986). The alkyl aluminum compounds were purchased from Akzo and Witco. The comparative metallocene compounds were purchased from Aldrich and used without further purification. High purity gaseous monomers from Applied Gas Technology were passed through moisture and oxygen traps. Liquid monomers from Aldrich were used after a standard purification. In all steps of catalyst preparation and polymerization, air and moisture were blocked from reaction system in order to increase the reproducibility of the experiments.

The structures of catalyst synthesized were confirmed by using 270 MHz FR-NMR (Jeol Co.). The molecular weight of a polymer was measured with High Temperature Gel Permeation Chromatography (GPC) (150CV, Waters in U.S.A) and trichlorobenzene as a solvent at a temperature of 140°C.

Example 1

15

Step1 : synthesis of 1,2-di(p-tolyl)ethane

Method 1

Two moles of 4-methyl benzyl bromide were coupled by a modification of the Burtz coupling reaction (J. March, Advanced Organic Chemistry, 449-451, 4th ed., 1992, A Wiley-Interscience). Into a 250ml schlenk flask were added 12.5g of sodium, 50g of α -bromo xylene dissolved in 150ml tetrahydrofuran and then the reaction mixture were reacted 7days at argon atmosphere. Alcohol was added to quench the reaction. After water was added, the product was extracted with diethyl ether. The organic layer was collected and dried with anhydrous magnesium sulfate. After filtering to remove the magnesium sulfate, all solvent were removed by evaporation with rotary evaporator. The pure compound was obtained by recrystalization in ethanol. Yield was 26.92g (94.8 %).

¹H NMR (300MHz: DMSO-d₃): δ 7.10 (s, 8H), 2.87 (s, 4H), 2.33 (s, 6H)

Method 2

This was prepared by a modification of the known method (J.H.Gerdner and P. Borgstrom, Journal of American Chemical Society, 51, 3375.1929). 20g of 4-methyl benzyl chloride was added dropwise to 3.8g of magnesium in 100ml of tetrahydrofuran and the reaction mixture was stirred to make Grignard reagent. This Grignard reagent was added to the same mole of silver bromide slurry in fresh dried tetrahydrofurane. After reflux for 1 hour, the reaction mixture was cooled to room temp. All solids were removed by filtration. After water and diethyl ether were added, the organic layer was collected. After drying with anhydrous magnesium sulfate and all solvent was removed at reduced pressure. The product was purified by column chromatography. The yield was 21g (70 %).

Method 3

20g of 4-methyl benzyl chloride is added dropwise to schlenk flask containing 3.8g of magnesium and 100ml of tetrahydrofuran to make Grignard reagent. This Grignard reagent was added to the Schlenk flask containing the same mole of 4-methyl benzylchloride in fresh dried tetrahydrofurane. After the reaction mixture was refluxed for 3 hours, it was cooled to room temperature. Aqueous saturated ammonium chloride solution was poured, and the product was extracted with diethyl ether. The organic layer was collected and dried with anhydrous magnesium sulfate. After filtering to remove the magnesium sulfate, all solvent were removed by evaporation with rotary evaporator. The pure compound was obtained by column chromatography. Yield was 9.1 g (30 %).

Step 2: Synthesis of 1,2-bis(7-2,4-dimethyl)indanonyl)ethan

1,2-di(p-tolyl)ethan and 2-bromoisbutyryl bromide reacted to give 1,2-(7-(2,5-dimethyl)indanonyl)ethan by reported procedure (Stehling et al. Organometallics, 13, 968 (1994)). Pure compound was obtained by recrystallization in petroleum ether.

^1H NMR(300MHz: DMSO- d_3): δ 7.19-7.01(dd, 4H), 3.19-3.09(m, 2H). 2.90(s, 4H), 2.59(s, 6H), 2.61-2.31(m, 4H), 1.24-1.20(q, 6H)

Step 3: synthesis of 1,2-bis(7-(2,4-dimethyl)indenyl)ethan

To a flask was added successively 1,2-bis(7-(2,4-dimethyl)indanonyl)ethan and 40ml of tetrahydrofuran and 40ml of ethanol solution 3.5g of sodium borohydride at 0 °C. After stirring for 16 hours, 100g of ice was added. HCl was added until pH of the solution was about 1. The product was extracted with diethyl ether three times. The combined diethyl ether was washed with aqueous sodium bicarbonate. The organic layer was collected and dried with anhydrous magnesium sulfate. After filtering to remove the magnesium sulfate, all solvent were removed by evaporation with rotary evaporator to give residue, 1,2-bis(1-(2,4-dimethyl)indanolyl)ethan, which was used without further purification. To the flask containing the residue was added toluene and 0.2 g of mono hydrated p-toluenesulfonic acid. The reaction mixture was refluxed for 2 hours. The mixture was washed with aqueous sodium bicarbonate. The organic layer was dried with anhydrous magnesium sulfate and the solvent was removed with rotary evaporator. The product was purified by column chromatography. Yield was 92.5 % (4.16 g).

^1H NMR (300MHz: CDCl_3): δ 7.01-6.98(dd, 4H), 6.58(s, 2H), 3.19(s, 4H), 2.92(s, 4H), 2.37(s, 6H), 2.16(s, 6H)

Step 4: synthesis of ethylenebis(7-(2,4-dimethyl)indenyl)zirconium dichloride.

To a Schlenk flask containing 1.36g of 1,2-bis(7-(2,4-dimethyl)indenyl)ethan was added 20ml of freshly dried hexane, 2.5M n-butyl lithium 3.5ml in argon atmosphere. After stirring for 17 hours, 1 g of zirconium tetrachloride was added at room temp. The mixture was stirred for 18 hours. Dark gray solid was isolated by decantation of the solvent. This solid was extracted with 20ml of dichloromethan three times. The obtained yellow solution was evaporated under reduced pressure to become about 20 ml. To

the solution was added hexane to recrystallize the product. Orange solid of title compound was obtained. The yield was 0.5 g.

^1H NMR (300MHz: CD_2Cl_2): δ 6.89-6.33(m, 4H), 3.39-3.19(m, 2H), 2.33-2.30(d, 6H)

5

Step 5: polymerization of ethylene

To a 400 ml of glass reactor was added 200 ml hexane, 4.0 ml methylaluminumoxan (MAO, toluene solution, 6.4 w% Al). At 80 °C, 0.008 mmole of ethylene bis(7-(2,4-dimethyl)indenyl)zirconium dichloride dissolved in 0.5ml
10 toluene was added. Ethylene was fed continuously for 10 minutes under the pressure of 40 psig with vigorous stirring. 20ml of ethanol was added to finish the polymerization. 10% HCl methanol solution was poured. The solid product was collected and washed with methanol. The polymer was dried at 60 °C vacuum over. Yield was 7.45 g. Activity of catalyst was 1.9 Kg(PE) /
15 mmol(Zr)h.

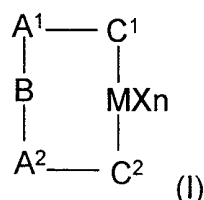
Example 2

Ethylene and nobornene copolymerization was done using the same catalyst made in step 4 of example 1.

20 To a 400 ml of glass reactor was added 250 ml of hexane solution of nobornene (30 g), and 4.0 ml of methylaluminumoxan (MAO, toluene solution, 6.4 w % Al). At 80 °C, 0.008 mmole of ethylene bis(7-(2,4-dimethyl)indenyl)zirconium dichloride dissolved in 0.5 ml toluene was added. Ethylene was fed continuously for 10 minutes under the pressure of 40 psig
25 with vigorous stirring. 20ml of ethanol was added to finish the polymerization. 10% HCl methanol solution was poured. The solid product was collected and washed with methanol. The polymer was dried at 60 °C vacuum oven. Yield was 14.5 g. Activity of catalyst was 7.25 Kg(PE) / mmol(Zr)h.

WHAT IS CLAIMED IS:

1. The compounds represented by general formula (I):



5 where

M is a transition metal selected from of Group 3 or 4 or 5 or 6.

A^1 and A^2 are respectively and independently hydrocarbyl triradical consisted of more than two carbon atoms which are bonded to the cyclopentadienyl ring in covalently, or 0 - 10 carbon atoms including one or
 10 more of B, N, P, S, O, or Si atom, in which the triradical may have same or different substituents containing 1 - 20 non-hydrogen atoms.

B is hydrocarbyl diradical containing 1 - 20 carbon atoms or substituted hydrocarbyl diradical containing 0 - 20 carbon atoms, B, N, P, S, O, or Si atoms in which the diradical may have same or different substituents
 15 containing 1 - 20 non-hydrogen atoms and the radicals joined to C^1 and C^2 to form bridge by covalent bonds.

C^1 and C^2 are respectively and independently triradical of cyclopentadienyl moiety which is covalently bonded to two radical sites of A^1 and A^2 and one radical site of M, in which the triradical may have same or
 20 different substituents containing 1 - 20 non-hydrogen atoms and the substituent may be hydrocarbyl radical with 1 - 20 carbon atoms or radical containing one or more of B, N, P, S, O, or Si atoms and 1 - 20 carbon atoms.

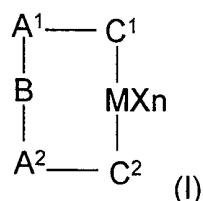
X is respectively and independently ligand of halogen, hydrocarbyl containing 1 - 20 carbon atoms, alkoxy, aryloxy, amide, arylamide, phosphide,
 25 arylphosphide, sulfide, or arylsulfide.

n is integer of 0 - 4 which depends on the oxidation state of M.

2. The method for the preparation of homopolymers or copolymers of

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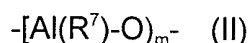
ethylene, α -olefin, or cycloolefin by using the compounds represented by general formula (I) as catalyst and one or more of aluminum or boron compounds as cocatalyst.



5 (where M, A¹, A², C¹, C², B, X, n are same as described in claim 1)

3. The method of claim 2, wherein cocatalyst is represented by general formula (II) which can exist as linear or cyclic or netty form.

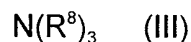
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where R⁷ is halogen radical, hydrocarbyl radical containing 1 - 10 carbon atoms, or hydrocarbyl radical containing 1 - 10 carbon atoms substituted with halogen, m is integer greater than 2, each of R⁷ is different or
15 same.

4. The method of claim 2, wherein cocatalyst is represented by general formula (III).

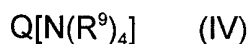
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where N is aluminum or boron atom, R⁸ is halogen radical, hydrocarbyl radical containing 1 - 10 carbon atoms, hydrocarbyl radical containing 1 - 10 carbon atoms substituted with halogen, and each of R⁸ is same or different.

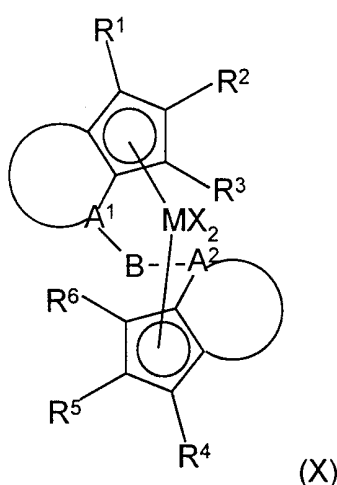
25

5. The method of claim 2, wherein cocatalyst is represented by general formula (VI).



where Q is inorganic or organic cation charged with +1, N is aluminum or boron, R^9 is halogen radical, hydrocarbyl radical containing 1 - 10 carbon atoms, hydrocarbyl radical containing 1 - 10 carbon atoms substituted with halogen, each R^9 is same or different.

6. The compounds represented by general formula (X):



10 where

M is a transition metal selected from Group 3, 4, 5, or 6.

A^1 and A^2 are respectively and independently hydrocarbyl triradical consisted of more than two carbon atoms which are bonded to the cyclopentadienyl ring in covalently, or 0 - 10 carbon atoms including one or more of B, N, P, S, O, or Si atom, in which the triradical may have same or different substituents containing 1 - 20 non-hydrogen atoms.

B is hydrocarbyl diradical containing 1 - 20 carbon atoms or substituted hydrocarbyl diradical containing 0 - 20 carbon atoms, B, N, P, S, O, or Si atoms in which the diradical may have same or different substituents containing 1 - 20 non-hydrogen atoms and the radicals joined to C^1 and C^2 to form bridge by covalent bonds.

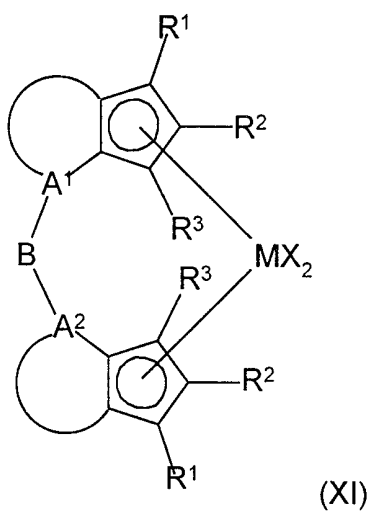
R^1 - C^6 are respectively same or different substituent containing 1- 20 non-hydrogen atoms.

X is respectively and independently ligand of halogen, hydrocarbyl

containing 1 - 20 carbon atoms, alkoxy, aryloxy, amide, arylamide, phosphide, arylphosphide, sulfide, or arylsulfide.

7. The compounds represented by general formula (X):

5



where M, A1, A2, B, R¹ - R⁶, and X is same as described in claim 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 98/00375

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 08 F 4/642; C 07 F 17/00; C 08 F 10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 07 F; C 08 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 145 819 A (WINTER et al.) 08 September 1992 (08.09.92), totality.	1-7
A	US 5 672 668 A (WINTER et al.) 30 September 1997 (30.09.97), totality.	1-7
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A	US 5 532 396 A (WINTER et al.) 02 July 1996 (02.07.96), totality.	1-7

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

„E“ earlier application or patent but published on or after the international filing date

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„O“ document referring to an oral disclosure, use, exhibition or other means

„P“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

„&“ document member of the same patent family

Date of the actual completion of the international search

29 January 1999 (29.01.99)

Date of mailing of the international search report

02 March 1999 (02.03.99)

Name and mailing address of the ISA/AT

Austrian Patent Office

Kohlmarkt 8-10; A-1014 Vienna

Facsimile No. 1/53424/535

Authorized officer

Pusterer

Telephone No. 1/53424/311

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 98/00375

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 702 030 A1 (HOECHST AKTIENGESELLSCHAFT) 20 March 1996 (20.03.96), totality.	1-7
A	EP 0 653 433 A1 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 17 May 1995 (17.05.95), totality.	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 98/00375

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