PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B01J 31/00, C07F 1/08, C08F 4/64, 10/00 | **A1**

(11) International Publication Number: **WO 98/11986**

(43) International Publication Date: 26 March 1998 (26.03.98)

(21) International Application Number: PCT/US97/16518

(22) International Filing Date: 18 September 1997 (18.09.97)

(30) Priority Data:
60/026,937 19 September 1996 (19.09.96) US

(71) Applicant *(for all designated States except US)*: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: FURTEK, Allan, Brent [-/US]; 45 Casale Drive So., Warren, NJ 07059 (US).

(74) Agents: SCHNELLER, Marina, V. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

(81) Designated States: AU, CA, JP, KR, SG, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METALLOCENES FOR MULTIMETALLIC POLYMERIZATION CATALYSTS

(57) Abstract

The invention relates to new metallocene compounds comprising at least two transition metals.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

METALLOCENES FOR MULTIMETALLIC POLYMERIZATION CATALYSTS

The invention relates to new metallocene compounds comprising at least two transition metals.

Catalysts containing at least two transition metals have been synthesized. These catalysts have been used in olefin polymerization, for example, in ethylene polymerization and copolymerization. The recent literature reports catalysts which have been synthesized to include one or more transition metals, both in the form of metallocene or a combination of metallocene and Ziegler-Natta catalyst. The earlier catalysts containing two transition metals were prepared as physical admixtures, unsupported or supported on a carrier. The interaction between two different sources of transition metal in a single catalyst may affect the ultimate activity and selectivity characteristics of the two transition metals.

The invention relates to a composition which is defined by the general formula

$$(M\ L)_rB$$

In that formula M is a transition metal moiety and each L is a linkage, each of which may be the same or different as illustrated below; the transition metal moiety M and an atom or molecular moiety generically defined by B are linked via the linking group L to form a star molecule. The subscript r is a number no greater than the valence of B. The molecule containing at least two transition metals may be used as a catalyst composition. The transition metal containing molecule can polymerize ethylene or copolymerize ethylene with a second alpha olefin. When used as a catalyst for olefin polymerization the composition may be used alone or contacted with an alumoxane, and/or monomeric Al(III) compound such as the trialkylaluminum or dialkylaluminum halides or hydrides (in each of which the alkyl is methyl, ethyl, butyl, isobutyl) and/or ionic lewis acid activators such as $B(C_6F_6)_3$, $[Ph_3C]^+[B(C_6F_5)_4]$.

In these multimetallic catalysts for olefin polymerization or copolymerization, comprising two or more different catalytic sites, each site is designed to produce a characteristic type of polymer, which differ in molecular weight, molecular weight distribution short chain branching from comonomer incorporation, long chain branching, etc. When two or more of such sites are combined in a single catalyst molecule, a polymer product which is multimodal in molecular weight, branching and other properties, may be produced, and since produced by a single catalyst molecule, these different polymer molecules will be blended thoroughly at the molecular level, thus improving the physical properties of the blended polymer product.

More specifically, the invention relates to a composition which is characterized by the empirical formula

$$(M^1_aL^1_b)_x(M^2_cL^2_d)_y(M^3_eL^3_f)_zW(M^4_gL^4_h)_m$$

wherein, W is silicon, boron, carbon, or nitrogen and derivations thereof;

x, y, z and m are numbers which have numerical values less than the valence of W; and m+x+y+z is equal to the valence of W;

each of M^1, M^2, M^3 and M^4 is the same or different and is $MeX^1X^2X^3$,

wherein Me is a Group IV or V transition metal, preferably hafnium, zirconium or titanium and X^1, X^2 and X^3 may be the same or different and each is independently a halide (iodide, bromide, chloride or fluoride); alkyl of 1 to 6 carbon atoms; or Cp wherein Cp is unsubstituted cyclopentadienyl or cyclopentadienyl substituted with one or more alkyl groups of 1 to 6 carbon atoms straight or branched chain, or saturated or unsaturated alkylene of 1 to 8 carbon atoms, which form bicyclic or tricyclic derivatives of cyclopentadienyl, e.g., substituted or unsubstituted indenyl or fluorenyl; or amide, e.g., NR'R" where R' and R" are alkyl or aryl groups

each of L^1, L^2, L^3 and L^4 is unsubstituted cyclpentadienyl; cyclopentdienyl substituted with alkyl of 1 to 6 carbon atoms (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc.); alkyl of 1 to 6 carbon atoms or alkylene of 1 to 6 carbon atoms (e.g. methylene); aryl (phenyl or benzyl) of 6 to 18 carbon atoms, unsubstituted or substituted by F, alkyl of 1 to 10 carbon atoms; diynyl $(-C\equiv C-C\equiv C-)_n$, wherein n is 1 to 4; alkylsilyl groups or by alkylene groups;

each of b, d, f and h is 0, 1 or 2; and

each of a, c, e and g is 0 or 1, as long as a+c+e+g = at least 2.

W is silicon, boron, nitrogen or carbon, and compounds, including organic derivatives, thereof.

The composition may be used alone or with a support as a catalyst. Accordingly, unsupported and supported catalysts can be made in accordance with the invention. Preferably, the carrier or support, used interchangeably herein, is selected from the group consisting of silica, alumina or silica/ alumina. In preferred embodiments, the silica bears OH (hydroxyl) groups. As a result of its hydroxyl content the compound may become bound to the carrier via reaction or bonding of W with surface hydroxyl group. The composition may be used as a catalyst, with or without an activator.

The compositions may be synthesized by various methods. The method of synthesis of compounds in which at least two of the group comprising L^1, L^2, L^3 and L^4 is cyclopentadienyl unsubstituted or substituted can be prepared as follows: unsubstituted cyclopentadiene or substituted derivatives thereof, which contain acidic hydrogens on the ring itself are contacted with sodium or butyl lithium to form the alkali metal salt of the unsubstituted or substituted cyclopentadiene. Formation of the alkali metal salt may be undertaken in a suitable solvent, for example, ether or hydrocarbon solvents, at temperatures from -78°C to +30°C. The salt may be isolated. Thereafter the alkali metal salt can be contacted with trichloromethylsilane ($MeSiCl_3$), in a molar ratio of of at least three (3) moles of alkali metal salt to

one mole, of silane to form a triscylopentadienyl compound, e.g. tris(cyclopentadienyl)-methyl-silane. The silane compound in which the precursor chloro groups (of the trichloromethylsilane) have been replaced by cyclopentadienyl groups may then be deprotonated by reaction with one, two, three or more equivalents of a suitable base, for example butyl lithium, then contacted with one or more transition metal salts. The salts of the transition metal can be the halides (chlorine or bromine, e.g. $TiCl_4$ or $ZrCl_4$). Alternatively, the transition metal salts can be halide or alkyl transition metal salts consisting at least one cyclopentadienyl group, unsubstituted or substituted with alkyl of 1 to 6 carbon atoms or alkylene groups of 1 to 6 carbon atoms. Separation of the desired compound is via recrystallization, sublimation or other suitable means. The transition metals of the transition metal salt can be zirconium, hafnium or titanium, and admixtures thereof. When the X^1, X^2 or X^3 of $MeX^1X^2X^3$ is a cyclopentadienyl, the group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group can be preferably straight-chain or branched C_1-C_6 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, and each of X^1, X^2 and X^3 may be the same or different. The cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as $-CH_2-$, $-CH_2-CH_2-$, -CR'R"- and -CR'R"-CR'R"- where R' and R" are short alkyl groups or hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-CH_2-Si(CH_3)_2-$ and similar bridge groups. The alkyl groups are preferably straight-chain or branched C_1-C_8 alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl. Suitable cyclopentadienyl groups include indenyl cyclopentadienyl,pentamethylcyclopentadienyl,

n-butylcyclopentadienyl, iso-butylcyclopentadienyl, dimethylcyclopentadienyle,indenyl), 4,5,6,7-tetrahydro-1-indenyl) and ethylene-(bis(4,5,6,7-tetrahydro-1-indenyl))

The ethylene resin, homopolymer or copolymer, produced in the presence of a composition containing or derived from $(M^1_aL^1_b)_x(M^2_cL^2_d)_y(M^3_eL^3_f)_zW(M^4_gL^4_h)_m$ will contain residues of that composition. It will contain 0.01 to 4500 ppm transition metals (provided by M^1, M^2, M^3 and M^4). Copolymers of ethylene will contain as a comonomer at least one olefin which contains 3 to 10 carbon atoms, preferably 1-butene, 1-hexene or 1-octene.

The olefin polymerization may be undertaken in solution, slurry or gas phase. When ethylene polymerization or copolymerization of ethylene with an alpha olefin of 3 to 10 carbon atoms is undertaken in the gas phase, for example, in a fluid bed, it is essential to operate the fluid bed reactor at a temperature below the sintering temperature of the polymer particles. To insure that sintering will not occur, operating temperatures below the sintering temperature are desired. For the production of ethylene copolymers in the process of the present invention an operating temperature of 60° to 115°C is preferred, and a temperature of 75° to 95°C is most preferred.

The fluid bed reactor is operated at pressures of about 150 to 350 psig, with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

A "diluent" gas may be employed in the polymerizations. It is nonreactive under the conditions in the polymerization reactor. The diluent gas can be nitrogen, argon, helium, methane, ethane, and the like.

In fluidized bed reactors, the superficial gas velocity of the gaseous reaction mixture through the bed must exceed the minimum flow required for fluidization, and preferably is at least 0.2 feet per second above the minimum flow. Ordinarily the superficial gas velocity does not exceed 5.0 feet per second, and most usually no more than 2.5 feet per

second is sufficient. The feed stream of gaseous monomer, with or without inert gaseous diluents, is fed into the reactor which operates at a space time yield of about 2 to 20 pounds/hour/cubic foot of bed volume.

For film production, the products may contain any of various additives conventionally added to polymer compositions such as lubricants, microtalc, stabilizer, antioxidants, compatibilizers, pigments, etc. These reagents can be employed to stabilize the products against oxidation. For example, additive packages comprising 400-1200 ppm hindered phenol(s); 700-2000 ppm phosphites; 250-1000 ppm antistats and 250-1000 ppm stearates, for addition to the resin powders, can be used for pelletization. The polymers can be added directly to a blown film extruder, e.g., a Sterling extruder, to produce films having a thickness of about 0.5 TO 5 mils.

The resins produced using the multimetallic catalysts described here may also be used for many other purposes, for example, blow molding, injection molding or rotomolding applications. By designing the sites of the multimetallic catalysts to produce polymer molecules with desired properties (e.g., molecular weight, molecular weight distribution, short chain or long chain branching from comonomer, etc.) the type of resins produced by the catalyst may be tailored for specific uses. This would provide a significant advantage over the current technology.

CLAIMS:

1. A homopolymer or copolymer of ethylene with one or more comonomers containing the residues of a composition of the formula

$$(M^1_aL^1_b)_x(M^2_cL^2_d)_y(M^3_eL^3_f)_zW(M^4_gL^4_h)_m$$

wherein W is silicon, boron, carbon or nitrogen;

m, x, y, and z are numbers which have numerical values less than the valence of W; and m+x+y+z is equal to the valence of W;

each of M^1, M^2, M^3 and M^4 is the same or different and is $MeX^1X^2X^3$,

wherein Me is a transition metal, preferably hafnium, zirconium or titanium and each of X^1, X^2 and X^3 may be the same or different and each is independently a halide; or alkyl of 1 to 6 carbon atoms; or Cp wherein Cp is unsubstituted cyclopentadienyl or cyclopentadienyl substituted by at least one alkyl of 1 to 6 carbon atoms straight or branched chain, or unsaturated or saturated alkylene of 1 to 8 carbon atoms, which form bicyclic or tricyclic derivatives of cylcopentadienyl

each of L^1, L^2, L^3 and L^4 is unsubstituted cyclopentadienyl; cyclopentdienyl substituted with one or more alkyl groups of 1 to 6 carbon atoms (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc.); alkyl of 1 to 6 carbon atoms or alkylene of 1 to 6 carbon atoms (e.g. methylene); aryl (phenyl or benzyl) of 6 to 18 carbon atoms, unsubstituted or substituted by fluorine, alkyl of 1 to 10 carbon atoms; diynyl $(-C\equiv C-C\equiv C-)_n$, wherein n is 1 to 4 alkylsilyl groups or by alkylene groups;

each of b, d, f and h is 0, 1 or 2; and

each of a, c, e and g is 0 or 1, as long as a+c+e+g = at least 2.

2. A process for production of polymers or copolymers of ethylene comprising contacting a feed comprising ethylene, under ethylene polymerization conditions, with a composition comprising

$$(M^1_aL^1_b)_x(M^2_cL^2_d)_y(M^3_eL^3_f)_zW(M^4_gL^4_h)_m$$

wherein, W is silicon, boron, carbon, nitrogen or derivatives thereof;

m, x, y, and z is a number which has a numerical value less than the valence of W; and m+x+y+z is equal to the valence of W;

each of M^1, M^2, M^3 and M^4 is the same or different and is $MeX^1X^2X^3$,

wherein Me is is a transition metal, preferably hafnium, zirconium or titanium and each of X^1, X^2 and X^3 may be the same or different and each is independently a halide; alkyl of 1 to 6 carbon atoms; Cp wherein Cp is unsubstituted cyclopentadienyl or cyclopentadienyl substituted by at least one alkyl of 1 to 6 carbon atoms straight or branched chain, or alkylene of 1 to 8 carbon atoms, which form bicyclic or tricyclic derivatives of cyclopentadienyl

each of L^1, L^2, L^3 and L^4 is unsubstituted cyclopentadienyl; cyclopentdienyl substituted with one or more alkyl groups of 1 to 6 carbon atoms (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc.); alkyl of 1 to 6 carbon atoms or saturated or unsaturated alkylene of 1 to 6 carbon atoms (e.g. methylene); aryl (phenyl or benzyl) of 6 to 18 carbon atoms, unsubstituted or substituted by F, alkyl of 1 to 10 carbon atoms; diynyl $(-C\equiv C-C\equiv C-)_n$, wherein n is 1 to 4; alkylsilyl groups or by alkylene groups;

each of b, d, f and h is 0,1 or 2; and

each of a, c, e and g is 0 or 1, as long as a+c+e+g = at least 2.

3. A product produced by the process of Claim 2.

4. A catalyst or catalyst precursor composition comprising

$$(M^1_aL^1_b)_x(M^2_cL^2_d)_y(M^3_eL^3_f)_zW(M^4_gL^4_h)_m$$

wherein, W is silicon, boron, carbon, nitrogen or derivatives thereof;

m, x, y, and z is a number which has a numerical value less than the valence of W; and m+x+y+z is equal to the valence of W;

each of M^1, M^2, M^3 and M^4 is the same or different and is $MeX^1X^2X^3$,

wherein Me is is a transition metal, preferably hafnium, zirconium or titanium and each of X^1, X^2 and X^3 may be the same or different and each is independently a halide; alkyl of 1 to 6 carbon atoms; or Cp wherein Cp is unsubstituted cyclopentadienyl or cyclopentadienyl substituted by at least one alkyl of 1 to 6 carbon atoms straight or branched chain, or alkylene of 1 to 8 carbon atoms, which form bicyclic or tricyclic derivatives of cylcopentadienyl

each of L^1, L^2, L^3 and L^4 is unsubstituted cyclopentadienyl; cyclopentdienyl substituted with one or more alkyl groups of 1 to 6 carbon atoms (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc.); alkyl of 1 to 6 carbon atoms or alkylene of 1 to 6 carbon atoms (e.g. methylene); aryl (phenyl or benzyl) of 6 to 18 carbon atoms, unsubstituted or substituted by F, alkyl of 1 to 10 carbon atoms; diynyl $(-C\equiv C-C\equiv C-)_n$, wherein n is 1 to 4 alkylsilyl groups or by alkylene groups;

each of b, d, f and h is 0, 1 or 2; and

each of a, c, e and g is 0 or 1, as long as a+c+e+g = at least 2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/16518

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 31/00; C07F 1/08; C08F 4/64, 10/00
US CL :502/103, 117, 202; 526/134, 160, 170; 556/7, 8, 11, 51, 53
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)

U.S. : 502/103, 117, 202; 526/134, 160, 170; 556/7, 8, 11, 51, 53

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,372,980 A (DAVIS) 13 December 1994, see entire document.	1-4
X	US 5,214,173 A (JORDAN et al) 25 May 1993, see examples 3, 4, 9 and 10.	1-4
X	EP 0,366,290 B1 (CHISSO CORPORATION) 02 May 1990, see claims.	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier document published on or after the international filing date	"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
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 04 DECEMBER 1997	Date of mailing of the international search report 23 DEC 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BERNARD LIPMAN Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)★