Title: METALLOECNE COMPOUNDS

Abstract: A bridged metallocene compound of formula (I) wherein: M is an atom of a transition metal selected from those belonging to group 3, 4, or to the lanthanide or actinide groups in the Periodic Table of the Elements; X, equal to or different from each other, is a hydrogen atom, a halogen atom, a R, OR, OCO₂, OCOR, SR, NR₂ or PR₃ group; L is a divalent bridging group; R¹ and R², equal to each other, are C₁₋₄₀ hydrocarbon radical; R₃ is hydrogen or a C₁₋₄₀ hydrocarbon radical and W is an aromatic 5 or 6 membered ring.
Title: Metallocene compounds

The present invention relates to a new class of metallocene compounds having a particular substitution pattern able to polymerize alpha olefins in high yields to give a polymer having an high molecular weight. The present invention further relates to the catalyst system thereof and the polymerization process therefrom.

Metallocene compounds are well known in the art as catalyst components for the polymerization of olefins. WO04/106351 relates to a class of bis indenyl metallocene compounds substituted in positions 2, 4 and 6. The compounds disclosed have C\textsubscript{i} symmetry i.e. the two indenyl are substituted in a different way, in particular the substituents in position 2 of the indenyl ring are different. This implies that the synthesis of these compounds is quite complicated for the reason that two different indenyl moieties have to be prepared. US 5,840,948 relates to some bis indenyl based metallocene compounds containing 2-metyl, 4,6 diisopropyl moiety and 2,4,6 trimethylindenyl moiety. However the particular substitution pattern of the compounds of the present invention is not suggested.

Thus there still is the need to find a new class of metallocene compounds able to polymerize olefins in higher yields and to produce polymers having very high molecular weight especially when the process is carried out at high temperature.

An object of the present invention is a bridged metallocene compound of formula (I)

![Chemical structure](image)

(I)

wherein:
M is an atom of a transition metal selected from those belonging to group 3, 4, or to the lanthanide or actinide groups in the Periodic Table of the Elements; preferably M is zirconium, titanium or hafnium; X, equal to or different from each other, is a hydrogen atom, a halogen atom, a R, OR, OSO₂CF₃, OCOR, SR, NR₂ or PR₂ group wherein R is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X groups can be joined together to form a group OR'Ο wherein R' is a C₁-C₂₀-alkylidene, C₆-C₂₀-arylidene, C₇-C₂₀-alkylidene, or C₇-C₂₀-arylalkylidene radical; preferably X is a hydrogen atom, a halogen atom or R group; more preferably X is chlorine or a methyl radical;

L is a divalent bridging group selected from C₁-C₂₀ alkylidene, C₃-C₇ cycloalkylidene, C₆-C₂₀ arylidene, C₇-C₂₀ alkylidene, or a C₇-C₂₀ alkylidene radicals, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or it is a silylidene radical containing up to 5 silicon atoms; preferably L is Si(R₁)₂ wherein R₁ is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radical; more preferably L is Si(CH₃)₃ or SiPh₂;

R₁, equal to each other, are C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements such as methyl or ethyl radical; preferably R₁ is a linear C₁-C₂₀-alkyl, such as a methyl, or ethyl radical;

R², equal to or different from each other, are C₃-C₄₀ branched, cyclic or acyclic, alkyl, alkenyl, or alkynyl radicals optionally containing heteroatoms belonging to groups 13-17 of the periodic table of the elements; preferably R², equal to or different from each other, are C(R₁)₂R₃ group;

wherein R₃ is equal to or different from each other, are hydrogen atoms or a C₁-C₄₀ hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R₃ is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R₃ is a linear or branched, C₁-C₂₀ alkyl radical; more preferably R₃ is a methyl or ethyl radical;

R⁴ is a C₁-C₄₀ hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R⁴ is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radical...
radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two $R^1$ radical can join together to form a $C_4-C_6$ membered ring wherein optionally one carbon atom can be substituted with a nitrogen, sulfur or oxygen atom; more preferably $R^1$ is a linear or branched, $C_i-C_4$-alkyl radical; more preferably $R^1$ is a methyl or ethyl radical; examples of group $C(R^{19})_2R^{18}$ are tert-butyl, isopropyl, cyclopentyl, cyclohexyl, 2 furanyl radicals; linear or branched $C_i-C_4$-alkyl radicals, such as methyl, ethyl, isopropyl, trimethylsilyl, or tertbutyl radical; preferably the two $R^2$ groups are the same;

$R^3$, equal to or different from each other, are hydrogen atoms or $C_1-C_{40}$ hydrocarbon radicals belonging to groups 13-17 of the periodic table of the elements; preferably $R^3$ is a hydrogen atom or a linear or branched, cyclic or acyclic, $C_i-C_4$-alkyl, $C_2-C_4$ alkenyl, $C_2-C_4$ alkynyl, $C_6-C_{40}$-aryl, $C_7-C_4$-alkylaryl or $C_7-C_4$-aryllalkyl radicals belonging to groups 13-17 of the periodic table of the elements; more preferably $R^3$, equal to or different from each other, are hydrogen atoms or linear or branched $C_i-C_4$-alkyl radicals, even more preferably $R^3$ are hydrogen atoms.

$W^1$ and $W^2$, equal or different from each other, are aromatic 5 or 6 membered rings that can contain heteroatoms belonging to groups 15-16 of the Periodic Table of the Elements; the valence of each atom of said ring is substituted with hydrogen atom or it can optionally be substituted with $R^5$ groups, wherein $R^5$, equal to or different from each other, are $C_1-C_{40}$ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably $R^5$, are linear or branched, cyclic or acyclic, $C_i-C_{40}$-alkyl, $C_2-C_{40}$ alkenyl, $C_2-C_{40}$ alkynyl, $C_6-C_4$-aryl, $C_7-C_4$-alkylaryl or $C_7-C_4$-aryllalkyl radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

Preferably $W^1$ and $W^2$ are selected from the group comprising the following moieties of formula (Wa), (Wb) and (Wc):

![Diagram](image)

wherein the * represents the point in which the moiety is bonded to the indenyl moiety of the
compound of formula (I);

R^6, R^7, R^8, R^9 and R^{10}, equal to or different from each other, are hydrogen atoms or C_1-C_40 hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^6, R^7, R^8, R^9 and R^{10}, are hydrogen atoms or linear or branched, cyclic or acyclic, C_(4-20)alkyl, C_2-C_40 alkenyl, C_2-C_40 alkynyl, C_6-C_40 aryl, C_7-C_40 alkaryl or C_7-C_40 arylalkyl radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

Z^1 is a nitrogen atom or a CR^{10} group; Z^2 is a nitrogen atom or a CR^5 group; Z^3 is a nitrogen atom or a CR^7 group; Z^4 is a nitrogen atom or a CR^8 group; Z^5 is a nitrogen atom or a CR^9 group; provided that no more than 2 groups among Z^1, Z^2, Z^3, Z^4 and Z^5 are nitrogen atoms, preferably no more than one group among Z^1, Z^2, Z^3, Z^4 and Z^5 is a nitrogen atom;

Z^6 is an oxygen atom, a sulfur atom, a NR^13 group or a CR^13 group; Z^7 is an oxygen atom, a sulfur atom, a NR^14 group or a CR^14 group; Z^8 is an oxygen atom, a sulfur atom, a NR^15 group or a CR^15 group; Z^9 is an oxygen atom, a sulfur atom, a NR^16 group or a CR^16 group;

Z^{10} is a nitrogen atom or a carbon atom that bonds the indenyl moiety of the structure of formula (I); with the proviso that not more than 1 group among Z^6, Z^7, Z^8, Z^9 or Z^{10} is a sulfur atom, an oxygen atom or a nitrogen-containing group atom selected from NR^13, NR^14, NR^15, NR^16, and a nitrogen atom; R^{13}, R^{14}, R^{15} and R^{16}, equal to or different from each other, are hydrogen atoms or C_1-C_40 hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^{13}, R^{14}, R^{15} and R^{16}, are hydrogen atoms or linear or branched, cyclic or acyclic, C_(4-20)alkyl, C_2-C_40 alkenyl, C_2-C_40 alkynyl, C_6-C_40 aryl, C_7-C_40 alkaryl or C_7-C_40 arylalkyl radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R^{13}, R^{14}, R^{15} and R^{16} are hydrogen atoms, C_(4-20)alkyl or C_6-C_40 aryl radicals;

In the moiety of formula (Wa), in a preferred embodiment, R^7 is a Ci-C_40 alkyl radical, preferably a branched Ci-C_40 alkyl radical, more preferably R^7 is a branched Ci-C_40 alkyl radical wherein the carbon atom in position alpha is a tertiary carbon atom such as a tertbutyl radical, and R^5, R^8, R^9 and R^{10} are hydrogen atoms;

In a further preferred embodiment R^{10} and R^8 are Ci-C_40 alkyl radicals, preferably they are linear C_1-C_40 alkyl radicals such as methyl radicals and R^7, R^8 and R^9 are hydrogen radicals:
In a further preferred embodiment R, R7 and R8 are linear or branched Ci-C4-alkyl radicals such as methyl or tertbutyl radicals and R10 and R9 are hydrogen atoms.

In a further preferred embodiment R6, R7, R8, R9 and R10 are hydrogen atoms;

In the moiety of formula (Wb), in a preferred embodiment, Z1 is a nitrogen atom and Z2, Z3, Z4 and Z5 are respectively CR6, CR7, CR8 and CR9 wherein the meaning of R6, R7, R8, and R9 is described above; in a further preferred embodiment Z3 is a nitrogen atom and Z1, Z2, Z4 and Z5 are respectively CR10, CR6, CR8 and CR9 wherein the meaning of R10, R6, R8, and R9 is described above; in a further preferred embodiment Z2 is a nitrogen atom and Z1, Z3, Z4 and Z5 are respectively CR10, CR7, CR8 and CR9 wherein the meaning of R10, R7, R8, and R9 is described above;

In the moiety of formula (Wc) in a preferred embodiment Z6 is an oxygen atom, a sulfur atom, a NR16 group; preferably it is a sulfur atom or a NR16; wherein R16 is preferably a Ci-C4-alkyl radical; more preferably Z6 is a sulfur atom; and Z7, Z8, Z9 and Z10 are respectively a CR14, CR15, CR16 and a carbon atom, wherein R14 is a hydrogen atom or a Ci-C4-alkyl radical such as methyl or ethyl; and R15 and R16 are hydrogen atoms or Ci-C4-alkyl radicals.

In a preferred embodiment of the present invention in the compounds of formula (I) T1 and T4, equal to or different from each other, are an OR2, or a SR2 wherein R2 is described above and T2 and T3, equal to or different from each other, are linear Ci-C4-alkyl alkyl radicals, such as methyl or ethyl radicals.

In a further preferred embodiment T1 and T4, equal to or different from each other, are an OR2, a SR2 or a C(R18)3 group; preferably T1 and T4 are an OR2 or an SR2 groups; and T2 and T3 equal to or different from each other are a C(R18)2R18 group wherein R18 has been described above and R19 is a C1-C4-hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R19 is a linear or branched, cyclic or acyclic, Ci-C4-o-alkyl, C2-C4-alkenyl, C2-C4-alkynyl, C6-C4-o-aryl, C7-C4-o-alkylaryl or C7-C4-o-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two R19 radical can join together to form a C4-C6 membered ring wherein optionally one carbon atom can be substituted with a nitrogen, sulfur or oxygen atom; more preferably R19 is a linear or branched, Ci-C2-o-alkyl radical; more preferably R19 is a methyl or ethyl radical; examples of group C(R19)2R18 are tert-butyl, isopropyl, cyclopentyl, cyclohexyl, 2 furanyl radicals;

A preferred class of the compounds of formula (I) is represented by formula (Ha):
Wherein M, L, X, R_1, R_2, R_3, R_6, R_7, R_8, R_9 and R_10 have the meaning reported above.

A further preferred class of compounds of formula (I) has formula (lib)
Wherein M, L, X, R₁, R₂, R₃, R¹⁴, R¹⁵, R¹⁶ have the meaning reported above.

Examples of compounds having formula (I) are as follows:

racemic-Me₂Si(2-methyl-4-phenyl-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-methyl-4-(tert-butylphenyl)-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-methyl-4-(thiophen-2-yl)-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-methyl-4-(5-methylthiophen-2-yl)-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-methyl-4-(benzothiophen-2-yl)-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-methyl-4-(4-pyridyl)-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-methyl-4-(2,5-dimethylphenyl)-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me₂Si(2-ethyl-4-phenyl-6-tert-butylinden-1-yl)₂ZrCl₂
racemic-Me$_2$Si(2-R-propyl-4-phenyl-6-tert-butylinden-1-yl)$_2$ZrCl$_2$

racemic-anti-Me$_2$Si(2-methyl-4-phenyl-6-tert-butylinden-1-yl)(2-methyl-4-(5-methylthiophen-2-yl)-6-tert-butylinden-1-yl)ZrCl$_2$

and their correspondent dimethyl derivatives and further the corresponding titanium, and hafnium compounds.

Preferably the metalloocene compounds object of the present invention are in their racemic(rac) or anti-racemic form.

For the purpose of the present invention the term "racemic(rac) form" means that the same substituents on the two cyclopentadienyl moieties are on the opposite side with respect to the plane containing the zirconium and the centre of the said cyclopentadienyl moieties, "anti-racemic form" means that the bulkier substituents of the two cyclopentadienyl moieties on the metalloocene compound are on the opposite side with respect to the plane containing the zirconium and the centre of the said cyclopentadienyl moieties as shown in the following compound:

A further object of the present invention is a catalyst system for the polymerization of olefins obtainable by contacting:

a) a metalloocene compound of formula (I);

b) at least an alumoxane or a compound able to form an alkylmetallocene cation; and
c) optionally an organo aluminum compound.

Preferably the metallocene compounds have formulas selected from (Ia), (Ha) or (lib).

Alumoxanes used as component b) in the catalyst system according to the present invention can be obtained by reacting water with an organo-aluminium compound of formula $H_jA1U_{3-j}$ or $H_jA1_2U_{6-j}$, where the U substituents, same or different, are hydrogen atoms, halogen atoms, C1-C20-alkyl, C3-C20-cyclalkyl, C6-C20-aryl, C7-C20-alkylaryl or C7-C20-aryllalkyl radicals, optionally containing silicon or germanium atoms, with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and 100:1.

The alumoxanes used in the catalyst system according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

$$\text{U}$$

\[
A\text{l} - O - (A\text{l} - O)^n_{1} - A\text{l}
\]

wherein the substituents U, same or different, are defined above.

In particular, alumoxanes of the formula:

$$\text{U}$$

\[
A\text{l} - O - (A\text{l} - O)^n_{2} - A\text{l}
\]

can be used in the case of linear compounds, wherein $n^1$ is 0 or an integer of from 1 to 40 and the substituents U are defined as above; or alumoxanes of the formula:

$$(A\text{l} - O)^n_{2}$$

can be used in the case of cyclic compounds, wherein $n^2$ is an integer from 2 to 40 and the U substituents are defined as above.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TD MBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TT MBAO).

Particularly interesting cocatalysts are those described in WO 99/21899 and in WO 01/21674 in which the alkyl and aryl groups have specific branched patterns.
Non-limiting examples of aluminium compounds that can be reacted with water to give suitable alumoxanes (b), described in WO 99/21899 and WO01/21674, are:

- tris(2,3,3-trimethyl-butyl)aluminium
- tris(2,3-dimethyl-hexyl)aluminium
- tris(2,3-dimethyl-pentyl)aluminium
- tris(2,3-dimethyl-heptyl)aluminium
- tris(2-methyl-3-ethyl-pentyl)aluminium
- tris(2-methyl-3-ethyl-hexyl)aluminium
- tris(2-methyl-3-ethyl-heptyl)aluminium
- tris(2-methyl-3-propyl-hexyl)aluminium
- tris(2-ethyl-3-methyl-butyl)aluminium
- tris(2-propyl-3-methyl-butyl)aluminium
- tris(2-isopropyl-3-methyl-butyl)aluminium
- tris(2-isobutyl-3-methyl-pentyl)aluminium
- tris(2,3,3-trimethyl-pentyl)aluminium
- tris(2,3,3-trimethyl-hexyl)aluminium
- tris(2-ethyl-3,3-dimethyl-butyl)aluminium
- tris(2-ethyl-3,3-dimethyl-pentyl)aluminium
- tris(2-ethyl-3,3-dimethyl-butyl)aluminium
- tris(2-ethyl-3,3-dimethyl-pentyl)aluminium
- tris(2-phenyl-butyl)aluminium
- tris(2-phenyl-propyl)aluminium
- tris(2-(4-fluoro-phenyl)-propyl)aluminium
- tris(2-(4-chloro-phenyl)-propyl)aluminium
- tris[2-(3-isopropyl-phenyl)-propyl]aluminium
- tris(2-phenyl-butyl)aluminium
- tris(3-methyl-2-phenyl-butyl)aluminium
- tris(2-phenyl-pentyl)aluminium
- tris[2-(pentafluorophenyl)-propyl]aluminium
- tris[2,2-diphenyl-ethyl]aluminium and tris[2-phenyl-2-methyl-propyl]aluminium, as well as the corresponding compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen atom, and those wherein one or two of the hydrocarbyl groups are replaced with an isobutyl group.

Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBA), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA), tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetalloocene cation are compounds of formula D+E-, wherein D+ is a Bronsted acid, able to donate a proton and to react irreversibly with a substituent X of the metalloocene of formula (I) and E- is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be removed by an olefinic monomer. Preferably, the anion E- comprises one or more boron atoms. More preferably, the anion E- is an anion of the formula BAr4(E-), wherein in the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred compound, as described in WO 91/02012. Moreover, compounds of formula BAr3 can be conveniently used.
Compounds of this type are described, for example, in the International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula BAr₃P wherein P is a substituted or unsubstituted pyrrol radical. These compounds are described in WO01/62764. Compounds containing boron atoms can be conveniently supported according to the description of DE-A-19962814 and DE-A-19962910. All these compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2:1; more preferably about 1:1.

Non limiting examples of compounds of formula D⁺E⁻ are:
- Tributylammoniumtetakis(pentafluorophenyl)borate,
- Tributylammoniumtetakis(pentafluorophenyl)aluminate,
- Tributylammoniumtetakis(trifluoromethylphenyl)borate,
- Tributylammoniumtetakis(4-fluorophenyl)borate,
- Dimethylbenzylammoniumtetakis(pentafluorophenyl)borate,
- Dimethylhexylammoniumtetakis(pentafluorophenyl)borate,
- N,N-Dimethylanilinium tetrakis(pentafluorophenyl)borate,
- N,N-Dimethylanilinium tetrakis(pentafluorophenyl)aluminate,
- Dimethylbenzylammoniumtetakis(pentafluorophenyl)borate,
- Dimethylhexylammoniumtetakis(pentafluorophenyl)borate,
- Di(propyl)ammoniumtetakis(pentafluorophenyl)borate,
- Di(cyclohexyl)ammoniumtetakis(pentafluorophenyl)borate,
- Triphenylcarbenium tetrais(pentafluorophenyl)borate,
- Triphenylcarbenium tetrais(pentafluorophenyl)aluminate,
- Ferrocenium tetrakis(pentafluorophenyl)borate,
- Ferrocenium tetrakis(pentafluorophenyl)aluminate.

Organic aluminum compounds used as compound c) are those of formula H₃AlU₃⁺ or H₃Al₃U₆⁻ as described above.

The catalysts of the present invention can also be supported on an inert carrier. This is achieved by depositing the metallocene compound a) or the product of the reaction thereof with the component b), or the component b) and then the metallocene compound a) on an inert support. The support can be a porous solid such as talc, a sheet silicate, an inorganic oxide or a finely divided polymer powder (e.g. polyolefin). Suitable inorganic oxides may be found among the oxides of elements of groups 2,
3, 4, 5, 13, 14, 15 and 16 of the Periodic Table of the Elements. Examples of oxides preferred as supports include silicon dioxide, aluminum oxide, and also mixed oxides of the elements calcium, aluminum, silicon, magnesium or titanium and also corresponding oxide mixtures, magnesium halides, styrene/divinylbenzene copolymers, polyethylene or polypropylene. Other inorganic oxides which can be used alone or in combination with the abovementioned preferred oxidic supports are, for example, MgO, ZrO₂, TiO₂ or B₂O₃.

A suitable class of supports which can be used is that constituted by porous organic supports functionalized with groups having active hydrogen atoms. Particularly suitable are those in which the organic support is a partially crosslinked styrene polymer. Supports of this type are described in European application EP-633 272.

Another class of inert supports particularly suitable for use according to the invention is that of polyolefin porous prepolymers, particularly polyethylene.

A further suitable class of inert supports for use according to the invention is that of porous magnesium halides such as those described in International application WO 95/32995.

The support materials used preferably have a specific surface area in the range from 10 to 1 000 m²/g, a pore volume in the range from 0.1 to 5 ml/g and a mean particle size of from 1 to 500 µm. Preference is given to supports having a specific surface area in the range from 50 to 500 m²/g, a pore volume in the range from 0.5 to 3.5 ml/g and a mean particle size in the range from 5 to 350 µm. Particular preference is given to supports having a specific surface area in the range from 200 to 400 m²/g, a pore volume in the range from 0.8 to 3.0 ml/g and a mean particle size of from 10 to 300 µm.

The inorganic support can be subjected to a thermal treatment, e.g. to remove adsorbed water. Such a drying treatment is generally carried out at from 80 to 300ºC, preferably from 100 to 200ºC, with drying at from 100 to 200ºC preferably being carried out under reduced pressure and/or a blanket of inert gas (e.g. nitrogen), or the inorganic support can be calcined at from 200 to 1 000ºC to produce the desired structure of the solid and/or set the desired OH concentration on the surface. The support can also be treated chemically using customary desiccants such as metal alkyls, preferably aluminum alkyls, chlorosilanes or SiCl₄, or else methylaluminoxane. Appropriate treatment methods are described, for example, in WO 00/31090.

The inorganic support material can also be chemically modified. For example, treatment of silica gel with (NEt)₂SiFe leads to fluorination of the silica gel surface, or treatment of silica gels with silanes
containing nitrogen-, fluorine- or sulfur-containing groups leads to correspondingly modified silica gel surfaces.

Organic support materials such as finely divided polyolefm powders (e.g. polyethylene, polypropylene or polystyrene) can also be used and are preferably likewise freed of adhering moisture, solvent residues or other impurities by means of appropriate purification and drying operations before use. It is also possible to use functionalized polymer supports, e.g. supports based on polystyrene, via whose functional groups, for example ammonium or hydroxy groups, at least one of the catalyst components can be immobilized. The solid compound obtained by supporting the catalyst system object of the present invention on a carrier in combination with the further addition of the alkylaluminium compound either as such or prereacted with water if necessary, can be usefully employed in the gas-phase or slurry polymerization.

The catalyst system of the present invention can be used also in a solution polymerization process. For the purpose of the present invention the term solution polymerization means preferably that the polymer is fully soluble in the polymerization medium at the polymerization temperature used, and in a concentration range of at least 5% by weight; more preferably from 5 to 50 % by weight.

In order to have the polymer completely soluble in the polymerization medium, a mixture of monomers for copolymers or only one monomer for homopolymers in the presence of an inert solvent can be used. This solvent can be an aliphatic or cycloaliphatic hydrocarbon such as hexane, heptane isooctane, cyclohexane and methylcyclohexane. It is also possible to use mineral spirit or a hydrogenated diesel oil fraction. Also aromatic hydrocarbons can be used such as toluene. Preferred solvents to be used are cyclohexane and methylcyclohexane. In case propylene is used as monomer for the obtainment of propylene copolymers in solution polymerization process, the propylene content in the liquid phase of the polymerization medium preferably ranges from 5% to 60% by weight; more preferably from 20% to 50% by weight.

The catalyst system comprising the metallocene compound of formula (I) can be used for polymerizing olefins, in particular alpha-olefins in high yields to give polymers having high molecular weight. Therefore a further object of the present invention is a process for preparing a alpha-olefin polymer comprising contacting under polymerization conditions one or more alpha-olefins of formula CH2=CHA wherein A is hydrogen or a C1-C20 alkyl radical, in the presence of a catalyst system as described above.
Non limitative examples of alpha-olefins of formula CE^=CHA are: ethylene, propylene, 1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene, preferred alpha olefins are ethylene, propylene and 1-butene.

The metallocene compounds of formula (I) object of the present invention are particularly suitable for the homo and copolymerization of propylene. In fact, the metallocene-based catalyst system of the present invention when used for homo or copolymerizing propylene are able to give polymers having a high molecular weight in high yields also at high temperatures rendering thus possible to use it in the industrial plants that use polymerization temperatures higher than 50° C and that can be comprised between 60° and 200° C, preferably between 80° C and 120° C.

As said above, the metallocene compounds of formula (I) are particularly suitable for the copolymerization of propylene, therefore a further object of the present invention is a process for the preparation of propylene copolymers comprising the step of contacting, under polymerization conditions, propylene with ethylene or one or more alpha olefins of formula CH_i=CHA^1 wherein A^1 is a C2-C20 alkyl radical, in the presence of a catalyst system described above. This process is preferably carried out in solution as described above.

Examples of alpha olefins of formula CH_i=CHA^1 are ethylene, 1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene, preferred alpha olefins are ethylene and 1-butene; more preferred alpha olefin is ethylene.

The content of alpha-olefins derived units in the propylene copolymer object of the present invention ranges from 0.1 to 90% by mol; preferably it ranges from 5% by mol to 70% by mol; more preferably it ranges from 10% by mol to 60% by mol.

The metallocene compounds of the present invention are also particularly suitable for the preparation of copolymers of ethylene and higher alpha olefins, such as propylene, 1-butene, 1-hexene, 1-octene. The copolymers have a comonomer content ranging from 5 to 50% by mol. Particularly preferred are ethylene/1-butene copolymer having a content of 1-butene derive units ranging from 5 to 50% by mol.

As explained above the process for the polymerization of olefins according to the invention can be carried out in the liquid phase in the presence or absence of an inert hydrocarbon solvent, such as in in slurry, or in the gas phase. The hydrocarbon solvent can either be aromatic such as toluene, or aliphatic such as propane, hexane, heptane, isobutane or cyclohexane.

As a general rule, the polymerization temperature is generally comprised between -100° C and +200° C.
preferably comprised between 60° and 200°C, more preferably between 80°C and 120°C. The polymerization pressure is generally comprised between 0.5 and 100 bar.

The lower the polymerization temperature, the higher are the resulting molecular weights of the polymers obtained.

The polymerization yields depend on the purity of the metallocene compound of the catalyst. The metallocene compounds obtained by the process of the invention can therefore be used as such or can be subjected to purification treatments.

Further object of the present invention is a ligand of formula (III)

or its double bond isomers

wherein L, R₁, R², R³ W¹ and W² have the meaning reported above.

Preferred ligands have formulas (IIa) or (IIb):
or their double bond isomers
wherein L, R₁-R₁₆ have the meaning reported above.

The metallocene compounds of formula (I) can be obtained with a process comprising the steps of reacting the dianion with a suitable transition metal source such as metal tetrahalide as for example zirconium tetrachloride. The dianion can be obtained for example by the deprotonation of the ligand of formula (III), for example by using an organolithium compound such as butyl or methyl lithium. The above processes are preferably carried out in an aprotic solvent, either polar or apolar. Said aprotic solvent is preferably an aromatic or aliphatic hydrocarbon, optionally halogenated, or an ether; more preferably it is selected from benzene, toluene, pentane, hexane, heptane, cyclohexane, dichloromethane, diethylether, tetrahydrofurane and mixtures thereof. The above process is carried out at a temperature ranging from -100°C to +80°C, more preferably from -20°C to +70°C.
The following examples are given to illustrate and not to limit the invention.

Examples

The following examples are given to illustrate and not to limit the invention.

Examples

General characterization

**Intrinsic viscosity (LV.) in tetrahydronaphthalene**

The intrinsic viscosity (LV.) was measured in tetrahydronaphthalene (THN) at 135°C.

Melting temperature ($T_m$)

Calorimetric measurements were performed by using a differential scanning calorimeter DSC Mettler. The instrument is calibrated with indium and tin standards. The weighted sample (6-8 mg), was sealed into aluminum pans, heated to 200°C at a rate of 20°C/min and kept at that temperature for 5 minutes. Successively, after cooling at 20°C/min to 5°C and standing for 5 minutes at 5°C, the sample was heated to 200°C at a rate of 20°C/min. In this second heating run, the peak temperature was assumed as melting temperature ($T_m$) and the area as the global melting enthalpy ($\Delta H$).

Gel permeation chromatography (GPC)

Gel permeation chromatography was carried out at 135°C in 1,2,4-trichlorobenzene using a Waters 150C GPC apparatus.

$^{13}$C-NMR measurement

The polymer microstructure was investigated by $^{13}$C-NMR analysis. The samples were dissolved with a 8% wt/v concentration in 1,1,2,2-tetrachloroethane-$\text{d}_2$ at 120 °C. The $^{13}$C-NMR spectra were acquired at 120°C on a Bruker DPX400 spectrometer operating at 100.61 MHz. Each spectrum was acquired with a 90° pulse, 12 seconds of delay between pulses and CPD (WALTZ 16) to remove $^1$H-$^{13}$C coupling. About 1500 transients were stored in 32K data points using a spectral window of 6000 Hz.

In the case of isotactic polypropylene, the $\text{mmm}$ peak at 21.8 ppm was used as internal reference, and the pentad distribution and amounts of regioerrors were determined as described in Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* 2000, *100*, 1253

In the case of ethylene-propylene copolymers, the assignments of the peaks were made according to Randall[1] and Tritlo[2] and the triad distribution and copolymer compositions was determined according to Kakugo.[3]
The $\delta_S$ peak at 29.9 ppm (nomenclature according to reference 4) was used as internal reference. The product of reactivity ratios $r_{1r_{2}}$ was calculated from the triads according to Carman. [4]


Chemicals and characterization.

All chemicals were handled using standard Schlenk techniques.

Methylalumoxane (MAO) was received from Albemarle as a 30% wt/wt toluene solution and used as such.

Racemic-dimethylsilylbis(2-methyl-4-phenyl-inden-1-yl)dichlorozirconium (Cl) was prepared according to EP 576970;

Racemic-dimethylsilylbis(2-methyl-4-(4-tert-butylphenyl)-inden-1-yl)dichlorozirconium (C2) was prepared according to WO 98/4033 1 (example 65).

Synthesis of rac-dimethylsilyl(2-methyl-4(4-tert-butylphenyl)-6-tert-butylinden-1-yl)dichlorozirconium (Al)

3-(2-Bromo-4-tert-butylphenyl)-2-methylpropanoic acid

N-Bromosuccinimide (98 g, 0.55 mol) and 0.5 g benzoyl peroxide were added to solution of 2-bromo-4-tert-butyl-l-methylbenzene (113.5 g, 0.5 mol) in CCl$_4$ (500 ml). The resulting mixture was refluxed for 6 h, cooled to $20^\circ$C and filtered. The resulting filtrate was evaporated and used without
further purification. A solution of sodium diethylmethylmalonate, prepared from 104.5 g (0.6mol)
diethylmethylmalonate and 40.8g of sodium ethylate in 500ml abs. ethanol was treated dropwise
with 2-bromo-1-(bromomethyl)-4-tert-butylbenzene (0.5 mol). The resulting mixture was refluxed
for 4 h, treated with a solution of NaOH (50 g, 1.25mol) in water (60ml) and refluxed for 2h, then
poured into water (11), and finally washed with toluene (2x100ml). The aqueous solution was
treated with 130ml of 35% HCl. The resulting mixture was extracted with chloroform (4x250ml),
the organic phase was dried over MgSO₄ and evaporated. The residue was heated to 160-170 °C for
15 min yielding the product (92 g, total yield from 1-tert-butyl-4-methylbenzene 60%).

4-Bromo-6-tert-butyl-2-methyl-1-indanone

A mixture of 3-(2-bromo-4-tert-butylphenyl)-2-methylpropanoic acid (46 g, 150 mmol) and SOCl₂
(18 ml, 220 mmol) was stirred for 1 h at 40°C. The excess of SOCl₂ was removed in vacuo. The
residue was dissolved in CH₂Cl₂ (50 ml) and added at 0°C to a suspension of 20 g AlCl₃ in CH₂Cl₂
(200 ml). The reaction mixture was stirred overnight, poured into ice/water (500g) containing 50 ml
of cone. HCl. The organic phase was collected, washed with water, dried over MgSO₄ and
 evaporated. The residue was distilled at 125-130 °C/0.5torr giving 32 g (76%) of product.

1H NMR (CDCl₃, 200°C) δ: 7.83 (d, IH); 7.75 (d, IH); 3.32 (q, IH); 2.77 (m, IH); 2.64 (dd, IH);
1.36 (s, 9H); 1.35 (d, 3H).

13C NMR (CDCl₃, 200°C) δ: 208.78; 153.29; 150.33; 138.00; 135.06; 121.68; 119.37; 42.26; 35.34;
34.89; 31.14; 16.18

6-tert-butyl-4-(4-tert-butylphenyl)-2-methyl-1-indanone

Pd(OAc)₂ (0.3 g, 3 mol %) and PPI13 (0.7 g, 3 mol %) were added to a well stirred mixture 4-bromo-
6-tert-butyl-2-methyl-1-indanone (12.65 g, 45 mmol), tert-butylphenylboronic acid (11.2 g, 63
mmol) and Na₂CO₃ (13.4 g, 126 mmol) in DME (170 ml) - H₂O (56 ml). The resulting mixture was
refluxed with stirring for 6 h, cooled, and poured into water. CHCl₃ (300 ml) was added, the organic
layer was separated, washed with water, dried over MgSO₄, evaporated and purified by gradient
column chromatography (hexane/chloroform from 4:1 to 1:1). The yield was 10.84 g (72 %).

1H NMR (CDCl₃, 200°C) δ: 7.83 (d, IH); 7.71 (d, IH); 7.55 (d, 2H); 7.46 (d, 2H); 3.43 (q, IH); 2.79
(m, 2H); 1.43 (s, 9H); 1.42 (s, 9H); 1.35 (d, 3H).

13C NMR (CDCl₃, 200°C) δ: 209.75; 151.35; 150.38; 148.34; 139.44; 136.63; 132.59; 128.05;
125.37; 119.03; 42.41; 34.77; 34.48; 34.43; 31.27; 31.23; 16.15

5-tert-butyl-2-methyl-7-tert-butylphenyl-1H-indene
5-tert-Butyl-7-(4-tert-buty1phenyl)-2-methyl-1-indanone (10.37 g, 31 mmol) in Et₂O (150 ml) was added dropwise at 0°C to LiAlH₄ (0.6 g, 16 mmol) in Et₂O (100 ml). After 1 h of stirring, 5% HCl (50 ml) was added, the organic phase was separated, the water layer was extracted in Et₂O (2x50 ml). The combined organic phase was washed with aq. Na₂CO₃, dried over MgSO₄ and evaporated. The residue was dissolved in benzene (500 ml), p-TSA (1 g) was added, the resulting mixture was refluxed for 10 min, cooled, washed with water, dried over MgSO₄, evaporated and dried in vacuo. The yield was 9.9 g (near quantitative); yellow viscous oil.

¹H NMR (CDCl₃, 200°C) δ: 7.61 (m, 4H); 7.43 (d, 1H); 7.32 (d, 1H); 7.64 (q, 1H); 3.48 (s, 2H); 2.24 (d, 3H); 1.51 (s, 18H).

¹³C NMR (CDCl₃, 200°C) δ: 150.02; 149.59; 146.34; 146.19; 138.80; 137.89; 136.49; 128.00; 127.24; 125.15; 121.47; 115.84; 42.37; 34.64; 34.44; 31.61; 31.33; 16.67

Bis(6-tert-butyl-2-methyl-4-tert-buty1phenyl)-H-inden-l-yl)(dimethyl)silane

A solution of 5-tert-butyl-2-methyl-7-tert-buty1phenyl-H-indene (5.0 g, 15.7 mmol) in Et₂O (70 ml) was cooled to -40°C, and n-BuLi in hexane (1.6M, 9.81 ml, 15.7 mmol) was added. The resulting mixture was allowed to warm to room temperature, stirred for 3 h, cooled to -60°C. CuCN (42 mg, 0.47 mmol) and SiMe₂Cl₂ (0.95 ml, 7.85 mmol) in Et₂O (20 ml) were added. The resulting mixture was allowed to warm to room temperature, and stirred for 16 h. H₂O (20 ml) and benzene (150 ml) were added, the organic phase was separated, dried over MgSO₄, passed through silica gel and evaporated. The residue was dried in vacuo (pale-yellow solid) and used in the next step without further purification.

¹H NMR (CDCl₃, 200°C) δ: 7.62-7.40 (group of m, 12H, C₂H-C); 6.91 (bs); 6.88 (bs) {2H, -CH=}; 3.86 (s); 3.82 (s) {2H, -CH=}; 2.31 (bs); 2.25 (bs) {6H, -C-CH₃}; 1.49 (s); 1.47 (s); 1.46 (s); 1.45 (s) {36H, -C(CH₃)₃}; -0.06 (bs); -0.10 (bs); -0.1 (s) {6H, Si-CH₃}.

Synthesis of rac-dimethylsilyl(2-methyl-4(4-tert-buty1phenyl)-6-tert-butylinden-1-yl)dichlorozirconium

The bis(6-tert-butyl-2-methyl-4-tert-buty1phenyl)-H-inden-l-yl)(dimethyl)silane (7.85 mmol) obtained above was dissolved in Et₂O (80 ml), cooled to -40°C, and n-BuLi (1.6M in hexane, 10.4 ml, 16.7 mmol) was added. The reaction mixture was allowed to warm to room temperature, stirred for 3 h, and evaporated. The resulting yellow-brown solid was suspended in pentane (200 ml), cooled to -60°C, and ZrCl₄ (1.94 g, 8.33 mmol) was added. After 5 min Et₂O (1 ml) was added. The resulting mixture was allowed to warm to room temperature, stirred for additional 16 h, and filtered.
The residue was extracted with evaporation by pentane/CH$_2$Cl$_2$ (2:1) giving a mixture of isomers (1.12 g, 16.7%). This mixture was recrystallized from pentane/CH2Cl2 (5:1) yielding pure rac-form (0.11 g, 3.3%).

$^1$H NMR (CDCl$_3$, 200 Hz) δ: 7.57 (bs, 2H); 7.56 ("d", 4H); 7.47 ("d", 4H); 7.46 (bs, 2H) [C$_{Ar}$H]: 6.87 (s, 2H, H of C$_5$ ring); 2.25 (s, 6H, C-CH$_3$); 1.35 (s, 6H, Si-CH$_3$); 1.33 (s, 18H, -C(CH$_3$)$_3$); 1.32 (s, 18H, -C(CH$_3$)$_3$);

**Preparation of the** catalyst systems.

**Catalyst system SIA1**

9.9 mL of TIBA/cyclohexane solution (1.13 g/L) were mixed with 2.4 mL of MAO/toluene solution to obtain a MAO/TIBA molar ratio of 2:1. The solution was stirred for 1 h at room temperature and transferred into a 50 mL Schlenk flask containing 20.8 mg of Al. This solution was diluted with 23.5 mL of cyclohexane to reach a concentration of 50 gτoτ/L and 0.582 gmetallocene/L.

**Catalyst system S2C1**

39.1 mL of TIBA/isododecane solution (90 g/L) were mixed with 7.4 mL of MAO/toluene solution to obtain a MAO/TIBA molar ratio of 2:1. The solution was stirred for 1 h at room temperature and transferred into a 50 mL Schlenk flask containing 55.8 mg of Cl. The resulting mixture was diluted with 9.8 mL of isododecane to give a cloudy orange solution of concentration 100 gτoτ/L and 0.99 gmetallocene/L.

**Catalyst system S3C1**

39.1 mL of TIBA/cyclohexane solution (1.13 g/L) were mixed with 2.8 mL of MAO/toluene solution to obtain a MAO/TIBA molar ratio of 2:1. The solution was stirred for 1 h at room temperature and transferred into a 50 mL Schlenk flask containing 21.1 mg of Cl. This solution was diluted with 6.78 mL of cyclohexane to give an orange solution of concentration 100 gτoτ/L and 0.99 gmetallocene/L.

**Catalyst system S4C2**

8.1 mL of TIBA/isododecane solution (1.10 g/L) were mixed with 1.9 mL of MAO/toluene solution to obtain a MAO/TIBA molar ratio of 2:1. The solution was stirred for 30 minutes at room temperature. Then, 25 mg of C2 were added to give a clear solution, which was diluted with 4.4 mL of toluene to reach a concentration of 100 gτoτ/L and 1.74 gmetallocene/L.
Propylene polymerization examples
The polymerization procedure and conditions for each test are described below in detail, and also collected in Table 1.
The results from the analysis performed on the polymer samples are collected in Table 2.

Example 1
A 4.4 L jacketed stainless-steel autoclave, equipped with a mechanically driven stirrer and a 35-mL stainless-steel vial and connected to a thermostat for temperature control, was previously purified by washing with an Al(Z-Bu)_3 solution in hexane and dried at 50°C in a stream of nitrogen.
6 mmol of Al(Z-Bu)_3 (as a 100 g/L solution in hexane), 629 g of cyclohexane and 732 g of propylene were charged at room temperature, and the autoclave was then thermostated at 100°C (the polymerization temperature). Under these conditions, the liquid composition, at 100°C, is calculated as being 50/50 %wt propylene/cyclohexane.
4 mL of the catalyst system S1Al was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. Propylene was continuously fed for 30 minutes to maintain a pressure of 32 bar-g: 53 g of propylene were consumed.
Then the bottom discharge valve of the autoclave was opened and the polymer was discharged into a heated steel tank containing water at 70°C. The tank heating was switched off and a flow of nitrogen at 0.5 bar-g was fed. After cooling at room temperature, the steel tank was opened and the wet polymer collected. The wet polymer was dried in an oven under reduced pressure at 70°C. The polymerization data are reported in table 1 and the characterization of the polymer obtained is reported in table 2.

Comparative Example 2
The procedure of example 1 was repeated, with the difference that 5 mL of the catalyst system S2C1 containing the catalyst/cocatalyst mixture (0.99 mg metallocene/mL solution) was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. Propylene was continuously fed for 30 minutes to maintain a pressure of 31.5 bar-g for a total consumption of 43.7 grams of propylene.
The polymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 1 and the characterization of the polymer obtained is reported in table 2.
Activity in kg of polymer per gram of metallocene averaged over 30 minutes.

Table 1

<table>
<thead>
<tr>
<th>Ex</th>
<th>Catalyst System</th>
<th>metallocene (mg)</th>
<th>P (bar-g)</th>
<th>T (min)</th>
<th>Absorbed Propylene (g)</th>
<th>Activity kgmol/gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S1Al</td>
<td>2.33</td>
<td>32</td>
<td>30</td>
<td>53</td>
<td>24.3</td>
</tr>
<tr>
<td>2*</td>
<td>S2C1</td>
<td>4.95</td>
<td>31.5</td>
<td>40</td>
<td>43.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>

* Comparative example

Table 2. Analytical data on the i-VV samples.

<table>
<thead>
<tr>
<th>Example</th>
<th>L.V. (dL/g)</th>
<th>T_m (°C)</th>
<th>mmmm (%)</th>
<th>mrrm (%)</th>
<th>2,1 (%)</th>
<th>3,1 (%)</th>
<th>M_p (IQ^3)</th>
<th>M_w (IQ^3)</th>
<th>M_w/M_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.1</td>
<td>150.1</td>
<td>96.1</td>
<td>0.14</td>
<td>0.5</td>
<td>0.17</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>2*</td>
<td>1.5</td>
<td>154.6</td>
<td>96.6</td>
<td>0.30</td>
<td>0.3</td>
<td>0.11</td>
<td>109</td>
<td>246</td>
<td>2.3</td>
</tr>
</tbody>
</table>

n.a. not available

Propylene/ethylene copolymerization examples

Example 3

The procedure of example 1 was repeated feeding 720 g of cyclohexane, 35 g of ethylene and 654 g of propylene. 4 mL of solution of catalyst system S1Al was injected into the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.

A mixture of ethylene/propylene 10/90 % wt was continuously fed for 30 minutes to maintain the pressure of 35 bar-g: 103.4 g of propylene and 11.6 g of ethylene were consumed.

The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3

Example 4
The procedure of example 1 was repeated feeding 716 g of cyclohexane, 61 g of ethylene and 631 g of propylene. 3 mL of solution of catalyst system SlAl was injected into the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.

A mixture of ethylene/propylene 17/83 % wt was continuously fed for 30 minutes to maintain the pressure of 37 bar-g: 85.1 g of propylene and 17.9 g of ethylene were consumed.
The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.

Example 5

The procedure of example 1 was repeated feeding 676 g of cyclohexane, 72 g of ethylene and 647 g of propylene. 2.5 mL of solution of catalyst system SlAl was injected into the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.

A mixture of ethylene/propylene 21/79 % wt was continuously fed for 30 minutes to maintain the pressure of 39 bar-g: 30.5 g of propylene and 8 g of ethylene were consumed.
The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.
Comparative example 6
The procedure of example 1 was repeated feeding 720 g of cyclohexane, 35 g of ethylene and 654 g of propylene. 3 mL of solution of catalyst system S3C1 was injected into the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.
A mixture of ethylene/propylene 10/90 % wt was continuously fed for 30 minutes to maintain the pressure of 34 bar-g: 40 g of propylene and 4.4 g of ethylene were consumed.
The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.

Comparative example 7
The procedure of example 1 was repeated feeding 716 g of cyclohexane, 61 g of ethylene and 631 g of propylene. 4 mL of solution of catalyst system S3C1 was injected into the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.
A mixture of ethylene/propylene 17/83 % wt was continuously fed for 20 minutes to maintain the pressure of 37 bar-g: 103.7 g of propylene and 21.2 g of ethylene were consumed.
The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.

Comparative example 8
The procedure of example 1 was repeated feeding 676 g of cyclohexane, 72 g of ethylene and 647 g of propylene.
2.5 mL of solution of catalyst system S3C1 was injected into the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.
A mixture of ethylene/propylene 21/79 % wt was continuously fed for 30 minutes to maintain the pressure of 38 bar-g: 78.4 g of propylene and 21 g of ethylene were consumed.
The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.
**Comparative example 9**

The procedure of example 1 was repeated feeding 958g of cyclohexane, 31 g of ethylene and 500 g of propylene in order to obtain a liquid composition at 90°C, 21 bar-g, corresponding to a liquid composition of 5/95%wt ethylene/propylene.

4 mL of solution of the catalyst system S4C2 was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.

A mixture of ethylene/propylene 11/89 % wt was continuously fed for 30 minutes to maintain the pressure of 21 bar-g: 33.7 g of propylene and 4.1 g of ethylene were consumed.

The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.

**Comparative example 10**

The procedure of example 1 was repeated feeding 958g of cyclo-hexane, 50 g of ethylene and 484 g of propylene in order to obtain a liquid composition at 90°C, 24 bar-g, corresponding to a liquid composition of 8/92%wt ethylene/propylene.

4 mL of solution of the catalyst system S4C2 was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial.

A mixture of ethylene/propylene 16/84 % wt was continuously fed for 30 minutes to maintain the pressure of 24 bar-g: 31.2 g of propylene and 5.9 g of ethylene were consumed.

The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.

**Comparative example 11**

The procedure of example 1 was repeated feeding 958g of cyclo-hexane, 64 g of ethylene and 473 g of propylene in order to obtain a liquid composition at 90°C, 26 bar-g, corresponding to a liquid composition of 10/90%wt ethylene/propylene.

4 mL of solution of the catalyst system S4C2 was injected in the autoclave by means of 4 mL of c-hexane through the stainless-steel vial.

A mixture of ethylene/propylene 20/80 % wt was continuously fed for 30 minutes to maintain the pressure of 26 bar-g: 86.5 g of propylene and 21.6 g of ethylene were consumed.
The copolymer was discharged according to the procedure described in example 1. The polymerization data are reported in table 3.

Table 3.

<table>
<thead>
<tr>
<th>Ex</th>
<th>Cat. System</th>
<th>mg of zirconium compound</th>
<th>P (bar·g)</th>
<th>Activity kg eq./g.cat</th>
<th>Ethylene content % mol</th>
<th>I.V. (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>S1A1</td>
<td>2.3</td>
<td>34-35</td>
<td>95.1</td>
<td>7.9</td>
<td>1.82</td>
</tr>
<tr>
<td>4</td>
<td>S1A1</td>
<td>1.8</td>
<td>37</td>
<td>99.4</td>
<td>13.9</td>
<td>1.68</td>
</tr>
<tr>
<td>5</td>
<td>S1A1</td>
<td>1.5</td>
<td>39</td>
<td>48.2</td>
<td>15.8</td>
<td>1.76</td>
</tr>
<tr>
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Activity in kg of polymer per gram of metallocene averaged over 30 minutes.
*Comparative
Claims

1. A bridged metallocene compound of formula (I)

\[
\text{(I)}
\]

wherein:

- \(M\) is an atom of a transition metal selected from those belonging to group 3, 4, or to the lanthanide or actinide groups in the Periodic Table of the Elements;
- \(X\), equal to or different from each other, is a hydrogen atom, a halogen atom, a \(\text{R}, \text{OR}, \text{OSO}_2\text{CF}_3, \text{OCOR}, \text{SR}, \text{NR}_2\) or \(\text{PR}_2\) group wherein \(\text{R}\) is a linear or branched, cyclic or acyclic, \(\text{C}_1\text{-C}_4\text{o-alkyl}, \text{C}_2\text{-C}_4\text{o-alkenyl, C}_6\text{-C}_4\text{o-aryl, C}_7\text{-C}_4\text{o-alkylaryl or C}_7\text{-C}_4\text{o-arylalkyl radical;}
- optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two \(X\) groups can be joined together to form a group \(\text{OR'O}\) wherein \(\text{R}'\) is a \(\text{C}_1\text{-C}_2\text{o-alkylidene, C}_6\text{-C}_2\text{o-arylidene, C}_7\text{-C}_2\text{o-alkylarylidene, or C}_7\text{-C}_2\text{o-arylalkylidene radical;}
- \(L\) is a divalent bridging group selected from \(\text{C}_1\text{-C}_20\) alkylidene, \(\text{C}_3\text{-C}_20\) cycloalkylidene, \(\text{C}_6\text{-C}_20\) arylidene, \(\text{C}_7\text{-C}_20\) alkylarylidene, or a \(\text{C}_7\text{-C}_20\) arylalkylidene radicals, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or it is a silylidene radical containing up to 5 silicon atoms;
- \(\text{R}^1\), equal to each other, are \(\text{C}_1\text{-C}_4\text{o-hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;}

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R², equal to or different from each other, are branched, cyclic or acyclic, alkyl, alkenyl, or alkynyl radicals containing from 3 to 40 carbon atoms, optionally containing heteroatoms belonging to groups 13-17 of the periodic table of the elements; R³, equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals belonging to groups 13-17 of the periodic table of the elements;

W¹ and W², equal or different from each other, are aromatic 5 or 6 membered rings that can contain heteroatoms belonging to groups 15-16 of the Periodic Table of the Elements; the valence of each atom of said ring is substituted with hydrogen atom or it can optionally be substituted with R⁵ groups, wherein R⁵, equal to or different from each other, are C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

2. The bridged metallocene compound according to claim 1 wherein M is zirconium, titanium or hafnium; X is a hydrogen atom, a halogen atom, a OR’O or R group; L is Si(R¹¹)₂ wherein R¹¹ is a linear or branched, cyclic or acyclic, C₁-C₄₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀ aryl, C₇-C₄₀ alkyaryl or C₇-C₄₀ arylalkyl radical;

3. The bridged metallocene compound according to claims 1 or 2 wherein R₂, equal to or different from each other, are C(R¹⁸)₂R¹⁸ group; wherein R¹⁸ equal to or different from each other, are hydrogen atoms or a C₁-C₄₀ hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; R¹⁹ is a C₁-C₄₀ hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

4. The bridged metallocene compound according to anyone of claims 1-3 wherein W₁ and W₂ are selected from the group comprising the following moieties of formula (Wa), (Wb) and (Wc):
wherein the * represents the point in which the moiety bounds the indenyl moiety of the compound of formula (I);

R⁶, R⁷, R⁸, R⁹ and R¹⁰, equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;
Z¹ is a nitrogen atom or a CR¹⁰ group; Z² is a nitrogen atom or a CR⁵ group; Z³ is a nitrogen atom or a CR⁷ group; Z⁴ is a nitrogen atom or a CR⁸ group; Z⁵ is a nitrogen atom or a CR⁹ group; provided that no more than 2 groups among Z¹, Z², Z³, Z⁴ and Z⁵ are nitrogen atoms;
Z⁶ is an oxygen atom, a sulfur atom, a NR¹³ group or a CR¹³ group; Z⁷ is an oxygen atom, a sulfur atom, a NR¹⁴ group or a CR¹⁴ group; Z⁸ is an oxygen atom, a sulfur atom, a NR¹⁵ group or a CR¹⁵ group; Z⁹ is an oxygen atom, a sulfur atom, a NR¹⁶ group or a CR¹⁶ group;
Z¹⁰ is a nitrogen atom or a carbon atom that bonds the indenyl moiety of the structure of formula (I); with the proviso that not more than 1 group among Z⁶, Z⁷, Z⁸, Z⁹ or Z¹⁰ is a sulfur atom, an oxygen atom or a nitrogen-containing group atom selected from NR¹³, NR¹⁴, NR¹⁵, NR¹⁶, and a nitrogen atom;
R¹³, R¹⁴, R¹⁵ and R¹⁶, equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.

5. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wa), R⁷ is a Ci-C₄₀-alkyl radical, and R⁵, R⁸, R⁹ and R¹⁰ are hydrogen atoms;

6. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wa), R¹⁰ and R⁸ are Ci-C₄₀-alkyl radicals, and R⁷, R⁵ and R⁹ are hydrogen radicals:
7. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wa), R^6, R^7 and R^8 are linear or branched C1-C4-alkyl radicals and R^10 and R^9 are hydrogen atoms.

8. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wa), R^6, R^7, R^8, R^9 and R^10 are hydrogen atoms.

9. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wb), Z^1 is a nitrogen atom and Z^2, Z^3, Z^4 and Z^5 are respectively CR^6, CR^7, CR^8 and CR^9 wherein the meaning of R^6, R^7, R^8, and R^9 is described in claim 4.

10. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wb) Z^3 is a nitrogen atom and Z^1, Z^2, Z^4 and Z^5 are respectively CR^10, CR^6, CR^8 and CR^9 wherein the meaning of R^10, R^6, R^8, and R^9 is described in claim 4.

11. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wb) Z^2 is a nitrogen atom and Z^1, Z^3, Z^4 and Z^5 are respectively CR^10, CR^7, CR^8 and CR^9 wherein the meaning of R^10, R^7, R^8, and R^9 is described in claim 4.

12. The bridged metallocene compound according to claim 5 wherein in the moiety of formula (Wc) Z^6 is an oxygen atom, a sulfur atom, a NR^16 group.

13. The bridged metallocene compound according to anyone of claims 1-11 having formula (Ha)
wherein

M, L, X, R¹, R², R³, R⁶, R⁷, R⁸, R⁹ and R¹⁰ have the meaning described in claim 1.

14. The bridged metallocene compound according to anyone of claims 1-11 having formula (lib)
Wherein M, L, X, R^1, R^2, R^3, R^{14}, R^{15}, R^{16} have the meaning described in claim 1.

15. A catalyst system for the polymerization of olefin obtainable by contacting:
   a) a metallocene compound of formula (I) as described in claims 1-13;
   b) at least an alumoxane or a compound able to form an alkylmetallocene cation; and
   c) optionally an organo aluminum compound.

16. A process for preparing an alpha-olefin polymer comprising contacting under polymerization conditions one or more alpha-olefins of formula CE^\alpha=CHA wherein A is hydrogen or a C1-C20 alkyl radical, in the presence of a catalyst system of claim 14.

17. A process according to claim 15 wherein propylene is (co)polymerized.

18. A process according to claim 16 wherein propylene is copolymerized with ethylene.

19. A ligand of formula (III)
or its double bond isomers

wherein L, R¹, R², R³, T¹, T², T³, T⁴ and W have the meaning reported in claim 1.
INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/052056

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F17/00 C07F7/08 C08F10/00 C08F4/62

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F C08F

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 practical, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>IZMER, VYACHESLAV V. ET AL; &quot;Palladium-Catalyzed Pathways to Aroyl-Substituted Indenes: Efficient Synthesis of Ligands and the Respective ansa-Zirconocenes&quot; ORGANOMETALLICS 25(5), 1217-1229 CODEN: ORGND7; ISSN: 0276-7333, 2006, XP002432930 the whole document, in particular compound 77</td>
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See patent family annex.

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Date of the actual completion of the international search
10 May 2007

Date of mailing of the international search report
21/05/2007

Name and mailing address of the ISA
European Patent Office, P.B 5818 Patentlaan 2 NL 2280 HV Rijswijk
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Authorized officer
Rinkel, Bert
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