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(54) Titre : PROCEDE DE PRODUCTION DE POLYMERES DE POIDS MOLECULAIRE TRES ELEVE AU MOYEN DE
CATALYSEURS METALLOCENES PONTES SPECIAUX
(54) Title: METHOD FOR PRODUCING ULTRA-HIGH MOLECULAR WEIGHT POLYMERS BY MEANS OF SPECIAL
BRIDGED METALLOCENE CATALYSTS

(57) **Abrégé/Abstract:**

The present invention relates to a process to manufacture ultra high molecular weight polymers by means of polymerization and co-polymerization of olefins using novel bridged metallocene catalysts catalysts² as well as their catalyst systems.



TIC 2005/G009

Abstract

- 5 The present invention relates to a process to manufacture ultra high molecular weight polymers by means of polymerization and co-polymerization of olefins using novel bridged metallocene catalysts catalysts² as well as their catalyst systems.

² Translator's note: possible typo in the original?

TIC 2005/G009

Ticona GmbH

Process for Manufacturing Ultra High Molecular Weight Polymers Using Novel Bridged Metallocene Catalysts

5

The invention relates to a process of manufacturing ultra high molecular weight polymers via the polymerization and co-polymerization of olefins using catalysts and their catalyst systems.

- 10 Ultra high molecular weight ethylene polymers refer to a viscosimetrically determined molecular weight of greater than 1×10^6 mol/g. Because of their extraordinary properties, such as higher abrasion resistance and low sliding friction, such polymers have a multitude of uses. Consequently, they are used in materials handling, bulk materials handling, as well as in medical applications such as joint sockets in
- 15 prosthetic joints.

Because of these novel properties, the processing of ultra high molecular weight polyethylene is highly complex. Ram-extrusion and compression molding of powdered raw materials are processes used to produce molded parts, whereby the

20 molded parts manufactured often still exhibit the characteristics of the raw powder. Films and fibers are produced using solution or gel processes, which require a large amount of solvents. An objective is therefore to develop new ultra high molecular weight polyethylenes, which have improved processability.

- 25 According to the present state of technology, ultra high molecular weight polyethylene is manufactured according to the low pressure process using heterogeneous Ziegler catalysts. Such catalysts are, for example, described in the following patent documents: EP186995, DE3833445, EP575840 and US20020045537.

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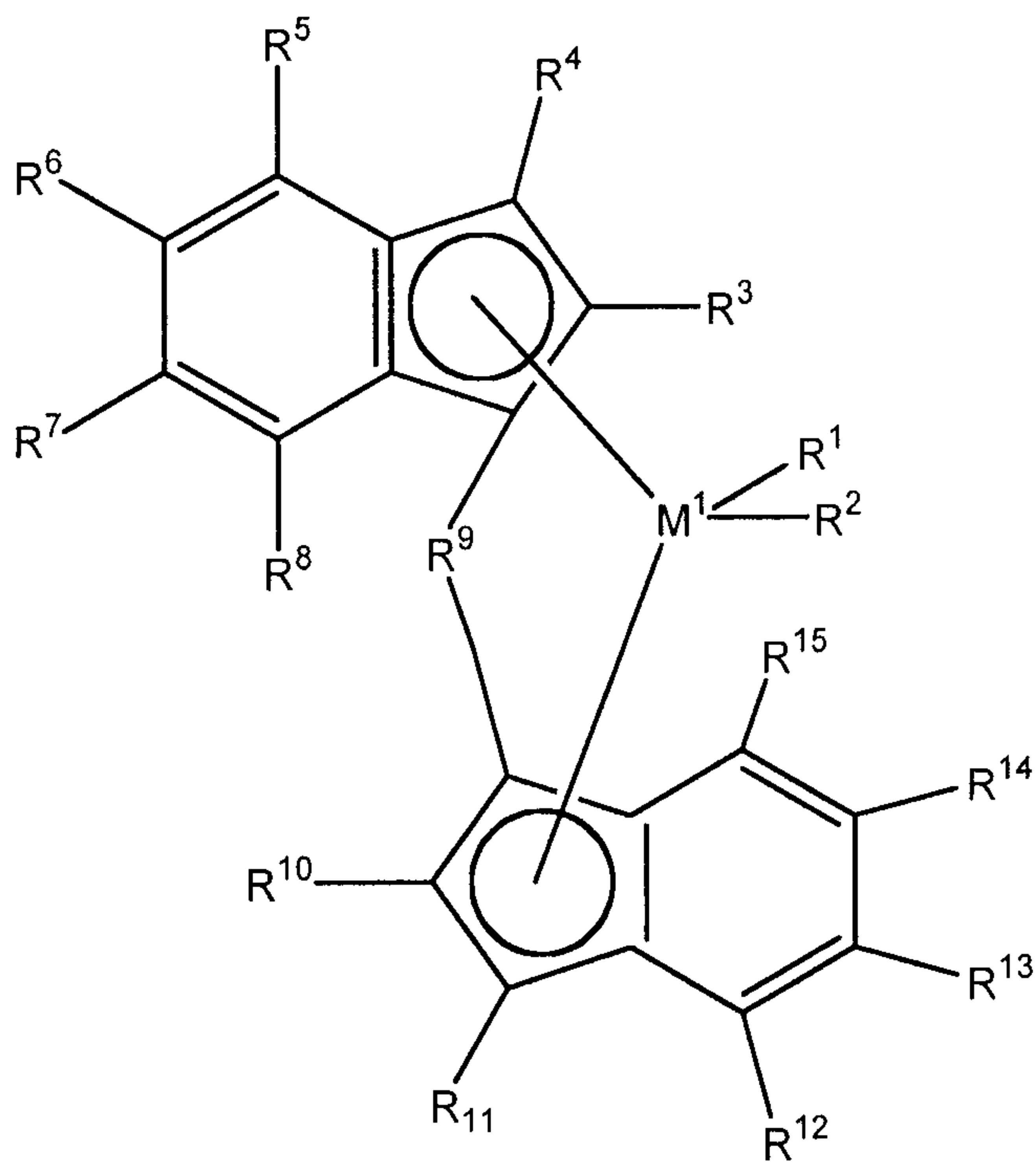
Other known catalysts for olefin polymerization are single site catalysts. According to the present state of technology, ultra high molecular weight polymers are manufactured using these catalysts only in exceptional cases and under

economically unprofitable conditions. Consequently, heterogeneous constrained-geometry catalysts form ultra high molecular weight polyethylene only with moderate activity and increased long chain branching, which can lead to reduced hardness and worse abrasion properties. With so-called phenoxy-imine catalysts, UHMWPE
5 is obtained only at low activity at economically unprofitable temperature levels. Examples of these as well as other metallocenes are described in WO9719959, WO0155231, Adv. Synth. Catal 2002, 344, 477-493, EP0798306 as well as in EP0643078.

10 Surprisingly, bridged single site catalysts with a suitable ligand structure were found, which in connection with aluminoxanes as co-catalysts, not only permitted the manufacture of ultra high molecular weight polyethylenes with a viscosimetrically determined molecular weight of greater than 1×10^6 mol/g, but also produced products with improved processability. The reason for the improved processability,
15 without being bound to a theory, has to do with the narrower molecular weight distribution Mw/Mn of 2 to 6 compared to polymers that were manufactured using Ziegler catalysts and have a molecular weight distribution Mw/Mn of 3 to 30.

The process according to the invention also contradicts the prejudice that
20 economically manufacturing ultra high molecular weight polymers is impossible using aluminoxanes as co-catalysts. Through its novel ligand structure, the catalyst is sterically shielded enough against the primary mechanism for low molecular weight products to result, namely the chain transfer to aluminoxane, without however losing its economically necessary activity to the monomers.

The object of the present invention is a process to manufacture ultra high molecular weight polymers using the compounds of Formula I



Formula I

whereby:

M^1 is a transition metal of the 3rd to 6th group of the periodic table, whose oxidation level does not equal zero, and is preferably Ti, Zr, Hf, V, Mo, Sc, Y, Cr and Nb; and

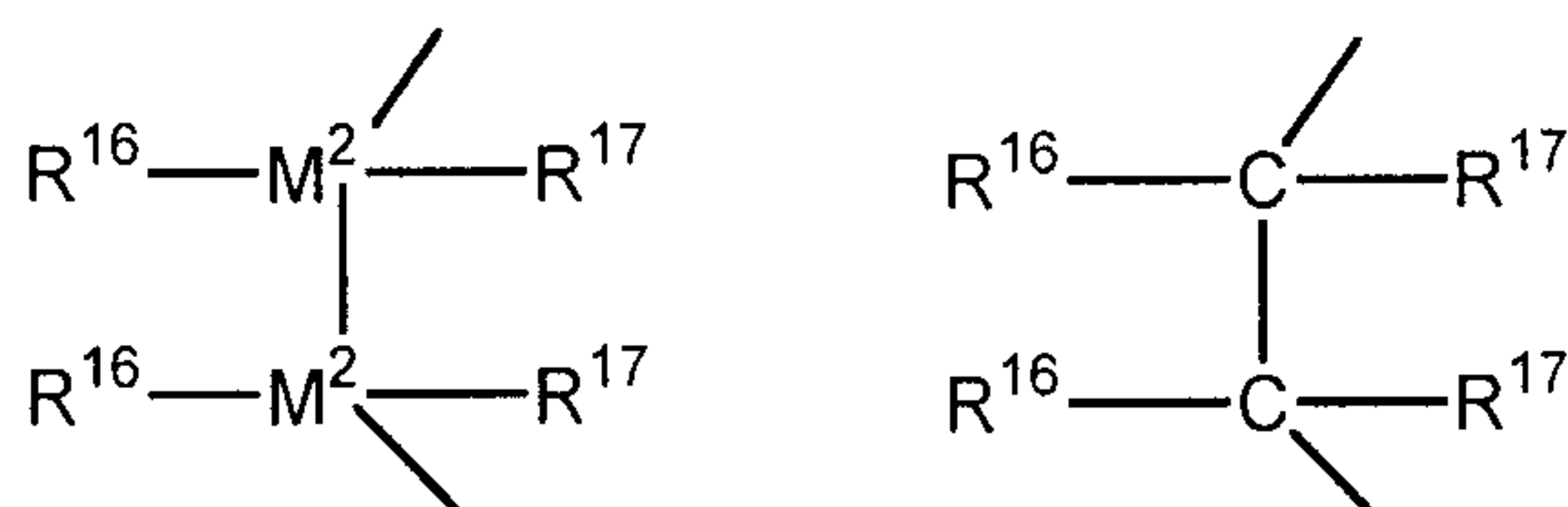
R^1 is hydrogen or a C₁-C₂₀-carbonaceous group or a halogen atom; and

R^2 is hydrogen or a C₁-C₂₀ carbonaceous group or a halogen atom; and

R^3 , R^{10} are each identical or different and are each a C₁-C₂₀ carbonaceous group, provided that at least one radical R^3 or R^{10} is a C₂-C₂₀ carbonaceous group; and

R^4 , R^5 , R^6 , R^7 , R^8 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} are each identical or different and are each hydrogen or a halogen atom or a C₁-C₂₀ carbonaceous group, whereby two or several consecutively can form a cyclic system; and

R^9 forms a bridge between the ligands, which can be shown by the following formulae:



whereby:

- 5 M^2 is either silicon, germanium or tin; and
 R^{16} , R^{17} are each identical or different and equal to hydrogen or a $\text{C}_1\text{-C}_{20}$
carbonaceous group or a halogen atom.

- In the present invention, a $\text{C}_1\text{-C}_{20}$ carbonaceous group is understood to be
10 preferably the radicals
 $\text{C}_1\text{-C}_{20}$ -alkyl, in particular methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, cyclopentyl, n-hexyl, cyclohexyl, n-octyl, or cyclooctyl,
 $\text{C}_1\text{-C}_{20}$ alkenyl, in particular ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, octenyl or cyclooctenyl,
15 $\text{C}_1\text{-C}_{20}$ alkynyl, in particular ethynyl, propynyl, butynyl, pentynyl, hexynyl or octynyl, $\text{C}_6\text{-C}_{20}$ aryl, in particular benzylidene, o-methoxybenzylidene, 2,6-dimethylbenzylidene, phenyl, biphenyl, naphthyl, anthracenyl, triphenylenyl, [1,1',3',1'']-terphenyl-2'-yl, binaphthyl, or phenanthrenyl,
 $\text{C}_1\text{-C}_{20}$ fluoralkyl, in particular, trifluoromethyl, pentafluoroethyl or 2,2,2-trifluoroethyl,
20 $\text{C}_6\text{-C}_{20}$ fluoroaryl, in particular pentafluorophenyl, 3,5-bistrifluoromethylphenyl, pentafluorobenzylidene, 3,5-bistrifluoromethylbenzylidene, tetrafluorophenyl, or heptafluoronaphthyl,
 $\text{C}_1\text{-C}_{20}$ alkoxy, in particular methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, or t-butoxy,
25 $\text{C}_6\text{-C}_{20}$ aryloxy, in particular phenoxy, naphthoxy, biphenyloxy, anthracenyloxy, phenanthrenyloxy,

C₇-C₂₀ arylalkyl, in particular o-tolyl, m-tolyl, p-tolyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-di-i-propylphenyl, 2,6-di-t-butylphenyl, o-t-butylphenyl, m-t-butylphenyl, p-t-butylphenyl,

C₇-C₂₀ alkylaryl, in particular benzyl, ethylphenyl, propylphenyl, diphenylmethyl, triphenylmethyl, or naphthalinylmethyl,

C₇-C₂₀ aryloxyalkyl, in particular o-methoxyphenyl, m-phenoxyethyl, p-phenoxyethyl,

C₁₂-C₂₀ aryloxyaryl, in particular p-phenoxyphenyl, C₅-C₂₀ heteroaryl, in particular 2-pyridyl, 3-pyridyl, 4-pyridyl, chinolyl, isochinolyl, acridinyl, benzochinolyl, or benzoisochinolyl,

C₄-C₂₀ heterocycloalkyl, in particular furyl, benzofuryl, 2-pyrrolidinyl, 2-indolyl, 3-indolyl, 2,3-dihydroindolyl,

C₈-C₂₀ arylalkenyl, in particular o-vinylphenyl, m-vinylphenyl, p-vinylphenyl,

C₈-C₂₀ arylalkinyl, in particular o-ethynylphenyl, m-ethynylphenyl, or p-ethynylphenyl,

C₂-C₂₀ heteroatomic group, in particular carbonyl, benzoyl, oxybenzoyl, benzoyloxy, acetyl, acetoxy, or nitrile, whereby one or more C₁-C₂₀ carbonaceous groups can form a cyclic system.

In the present invention, a C₂-C₂₀ carbonaceous group is understood to be preferably the radicals

C₂-C₂₀ alkyl, in particular ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, cyclopentyl, n-hexyl, cyclohexyl, n-octyl, or cyclooctyl,

C₂-C₂₀ alkenyl, in particular ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, octenyl or cyclooctenyl,

C₂-C₂₀ alkynyl, in particular ethynyl, propynyl, butynyl, pentynyl, hexynyl or octynyl,

C₆-C₂₀ aryl, in particular benzylidene, o-methoxybenzylidene, 2,6-dimethylbenzylidene, phenyl, biphenyl, naphthyl, anthracenyl, triphenylenyl, [1,1',3',1'']-terphenyl-2'-yl, binaphthyl, or phenanthrenyl,

C₂-C₂₀ fluoroalkyl, in particular, 3-trifluoropropyl, 2,2'-trifluoroisopropyl, C₆-C₂₀ fluoroaryl, in particular pentafluorophenyl, 3,5-bistrifluoromethylphenyl, pentafluorobenzylidene, 3,5-bistrifluoromethylbenzylidene, tetrafluorophenyl or heptafluoronaphthyl,

C₂-C₂₀ alkoxy, in particular n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, or t-butoxy,

C₆-C₂₀ aryloxy, in particular phenoxy, naphthoxy, biphenyloxy, anthracenyloxy, phenanthrenyloxy,

C₇-C₂₀ arylalkyl, in particular o-tolyl, m-tolyl, p-tolyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-di-i-propylphenyl, 2,6-di-t-butylphenyl, o-t-butylphenyl, m-t-

5 butylphenyl, p-t-butylphenyl,

C₇-C₂₀ alkylaryl, in particular benzyl, ethylphenyl, propylphenyl, diphenylmethyl, triphenylmethyl, or naphthalinylmethyl,

C₇-C₂₀ aryloxyalkyl, in particular o-methoxyphenyl, m-phenoxyethyl, p-phenoxyethyl,

10 C₁₂-C₂₀ aryloxyaryl, in particular p-phenoxyphenyl,

C₅-C₂₀ heteroaryl, in particular 2-pyridyl, 3-pyridyl, 4-pyridyl, chinolinyl, isochinolinyl, acridinyl, benzochinolinyl, or benzoisochinolinyl,

C₄-C₂₀ heterocycloalkyl, in particular furyl, benzofuryl, 2-pyrrolidinyl, 2-indolyl, 3-indolyl, 2,3-dihydroindolyl,

15 C₈-C₂₀ arylalkenyl, in particular o-vinylphenyl, m-vinylphenyl, p-vinylphenyl,

C₈-C₂₀ arylalkinyl, in particular o-ethynylphenyl, m-ethynylphenyl, or p-ethynylphenyl,

C₂-C₂₀ heteroatomic group, in particular benzoyl, oxybenzoyl, benzoyloxy, whereby one or more C₂-C₂₀ carbon containing groups can form a cyclic system.

20 In a preferred embodiment of the invention, for Formula 1:

M¹ shall be a transition metal of the 4th group of the periodic table, whose oxidation level does not equal zero, and is preferably Ti, Zr or Hf; and

R¹ shall be hydrogen or a C₁-C₂₀-carbonaceous group or a halogen atom; and

25 R² shall be hydrogen or a C₁-C₂₀ carbonaceous group or a halogen atom; and

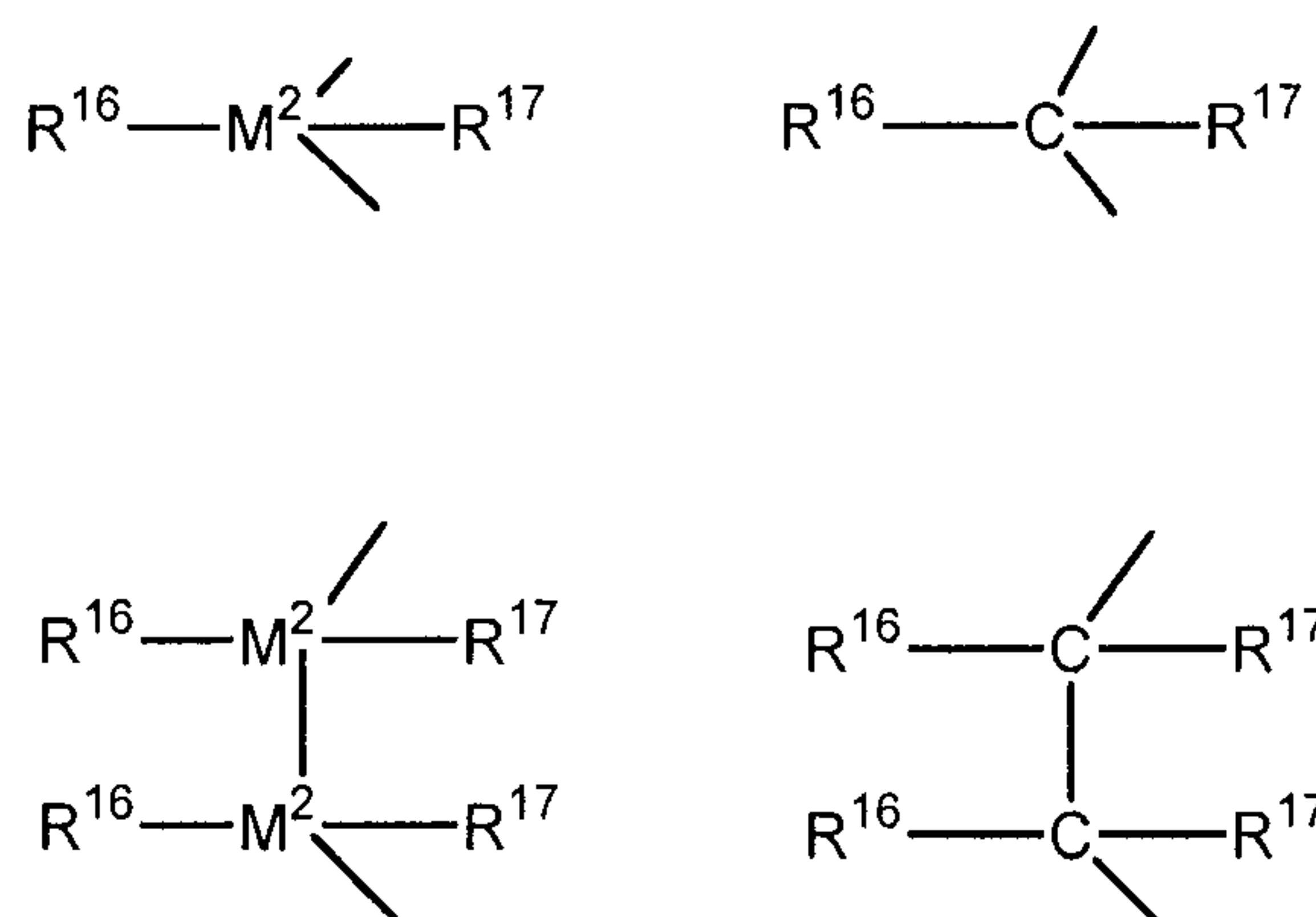
R³ shall be a C₂-C₂₀ carbonaceous group, preferably one cyclized in an α - or β -position or one in an α - or β - position branched carbonaceous group; and

R¹⁰ shall be a C₁-C₁₀ carbonaceous group; and

R⁴, R⁶, R⁷, R⁸, R¹⁰, R¹¹, R¹³, R¹⁴, R¹⁵ shall each be equal to hydrogen; and

30 R⁵, R¹² shall each be identical or different and shall be a C₁-C₂₀ carbonaceous group, of which two or several consecutively can form a cyclic system; and

R⁹ shall form a bridge between the ligands, which can be shown by the following formulae:



Whereby:

- 5 M^2 is silicon; and
 R^{16} , R^{17} are each identical or different and are each hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom.

In another embodiment of the invention, for Formula 1:

10

- M^1 shall be zirconium; and
 R^1 , R^2 shall be equal and stand for chlorine, methyl or phenolate; and

15

- R^3 shall be an isopropyl-, isobutyl-, cyclopentyl-, cyclohexyl-, tert-butyl-, or a phenyl group; and

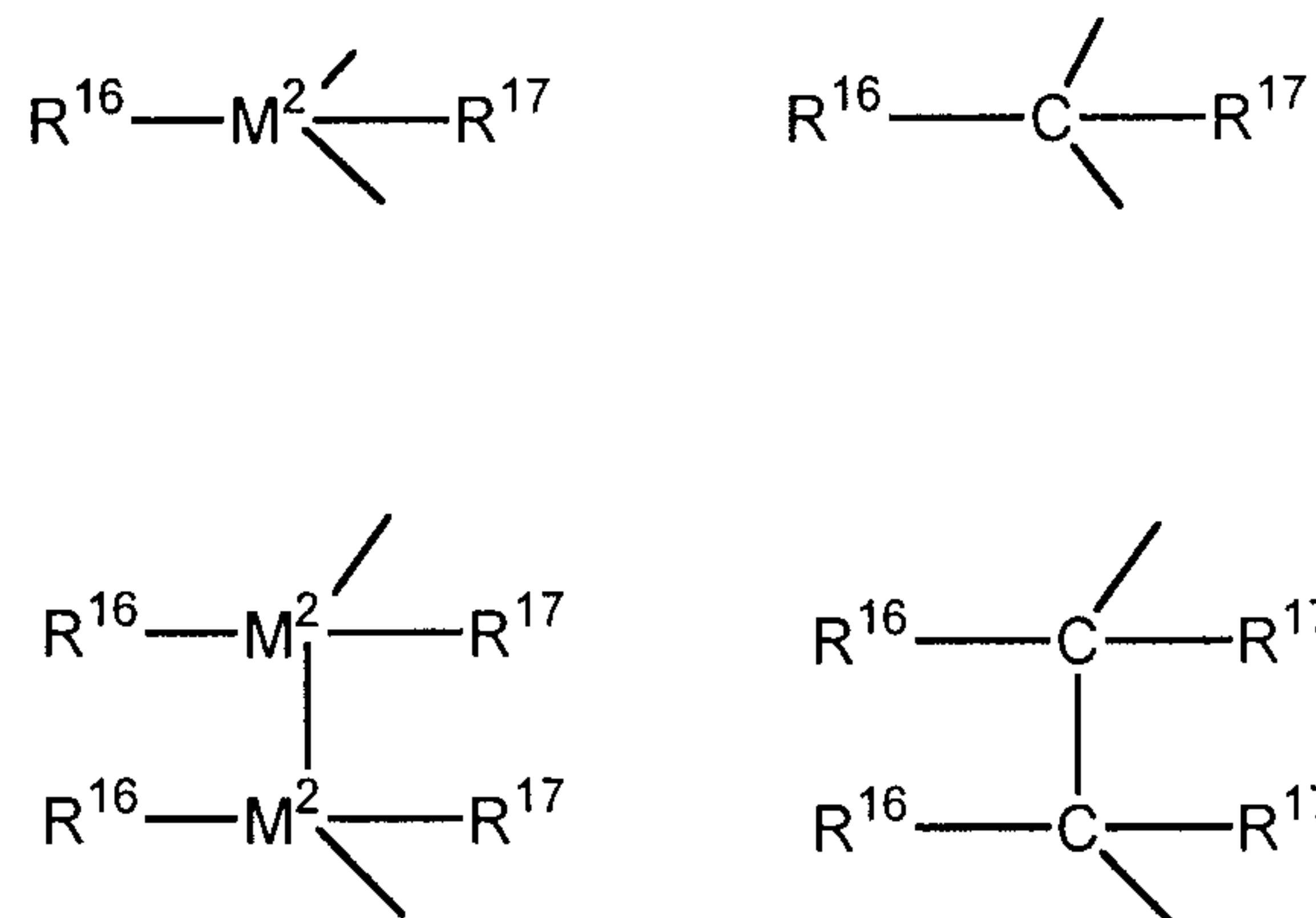
- R^{10} shall be a C_1 - C_6 carbonaceous group and an alkyl group; and

- R^4 , R^6 , R^7 , R^8 , R^{10} , R^{11} , R^{13} , R^{14} , R^{15} shall each be hydrogen; and

- R^5 , R^{12} shall be identical and a phenyl group which supports a C_1 - C_4 alkyl group in para-position; and

20

- R^9 shall form a bridge between the ligands, which can be shown by the following formulae:



Whereby:

M^2 is silicon; and

- 5 R^{16} , R^{17} are each identical or different and are hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom.

Illustrative but non-limiting examples for compounds of Formula I are:

Dimethylsilandiyl-(2-isopropyl-4-(p-isopropyl-phenyl)indenyl)(2-methyl-4-(p-isopropyl-phenyl)indenyl)-zirconium dichloride,

- 10 Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2-methyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2,7-dimethyl-4-(p-tert.-butyl-phenyl) indenyl)-zirconium dichloride,

- 15 Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2,5,6,7-tetramethyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-6-methyl-4-(p-tert.-butyl-phenyl)indenyl)(2,6-dimethyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-sec.-butyl-phenyl)indenyl)(2-methyl-4-(p-sec.-butyl-phenyl)indenyl)-zirconium dichloride,

- 20 Dimethylsilandiyl-(2-isopropyl-4-(p-cyclohexyl-phenyl)indenyl)(2-methyl-4-(p-cyclohexyl-phenyl)indenyl)- zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-trimethylsilyl-phenyl)indenyl)(2-methyl-4-(p-trimethylsilyl-phenyl)indenyl)- zirconium dichloride,

- 25 Dimethylsilandiyl-(2-isopropyl-4-(p-adamantyl-phenyl)indenyl)(2-methyl-4-(p-adamantyl-phenyl)indenyl)- zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-tris(trifluoromethyl)methyl-phenyl)indenyl)(2-methyl-4-(p-tris(trifluoromethyl)methyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-phenyl-indenyl)(2-methyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2-methyl-4-phenyl-indenyl)-zirconium dichloride,

5 Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2,7-dimethyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2,5,6,7-tetramethyl-4-phenyl-indenyl)-zirconium dichloride,

10 Dimethylsilandiyl-(2-isopropyl-6-methyl-4-(p-tert.-butyl-phenyl)indenyl)(2,6-dimethyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-phenyl-indenyl)(2,7-dimethyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-phenyl-indenyl)(2,5,6,7-tetramethyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

15 Dimethylsilandiyl-(2-isopropyl-6-methyl-4-phenyl-indenyl)(2,6-dimethyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-isopropyl-4-(p-tert.-butyl-phenyl)indenyl)(2-methyl-4-(4-naphthyl)-indenyl)indenyl)-zirconium dichloride,

20 Dimethylsilandiyl-(2-isopropyl-4-(4-naphthyl)-indenyl)indenyl)(2-methyl-4-(p-tert.-butyl-phenyl)indenyl)-zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-[4,5]-benzo-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(1-naphthyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(2-naphthyl)-indenyl)zirconium dichloride,

25 Dimethylsilandiyl-bis(2-isopropyl-4-phenyl-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-tert.-butyl-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-isopropyl-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-ethyl-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-acenaphth-indenyl) zirconium dichloride,

30 Dimethylsilandiyl-bis(2,4-diisopropyl-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-methyl-indenyl)zirconium dichloride

Dimethylsilandiyl-bis(2,4,6-triisopropyl-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2,4,5-triisopropyl-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-5-isobutyl-indenyl) zirconium dichloride

Dimethylsilandiyl-bis(2-isopropyl-5-*t*-butyl-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*tert*-butyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,

5 Dimethylsilandiyl-bis(2-isopropyl-4-(4'-ethyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-trifluoromethyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-methoxy-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*tert*-butyl-phenyl)-indenyl)zirconium dimethyl,

10 Dimethylsilandiyl-bis(2-isopropyl-4-(4'-methyl-phenyl)-indenyl)zirconium dimethyl,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-ethyl-phenyl)-indenyl) zirconium dimethyl,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-trifluoromethyl-phenyl)indenyl) zirconium dimethyl,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-methoxy-phenyl)-indenyl) zirconium dimethyl,

15 Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*tert*.-butyl-phenyl)-indenyl)hafnium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*tert*.-butyl-phenyl)-indenyl)titanium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*n*-propyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*n*-butyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-hexyl-phenyl)-indenyl)zirconium dichloride,

20 Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*sec*-butyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-methyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-ethyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*n*-propyl-phenyl)-indenyl)zirconium dichloride,

25 Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*n*-butyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-hexyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-pentyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-(4'-cyclohexyl-phenyl)-indenyl)zirconium

dichloride, Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*sec*-butyl-phenyl)-indenyl)zirconium

30 dichloride, Dimethylsilandiyl-bis(2-isopropyl-4-(4'-*tert*.-butyl-phenyl)-indenyl)

zirconium dichloride, Dimethylsilandiyl-bis(2-*n*-propyl-4-phenyl-indenyl)zirconium

dichloride,

Dimethylsilandiyl-bis(2-*n*-propyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-*n*-propyl-4-(4'-ethyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-propyl-4-(4'-iso-propyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-propyl-4-(4'-n-butyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-n-propyl-4-(4'-hexyl-phenyl)-indenyl) zirconium dichloride,

5 Dimethylsilandiyl-bis(2-n-propyl-4-(4'-cyclohexyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-n-propyl-4-(4'-sec-butyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-propyl-4-(4'-tert. -butyl-phenyl)-indenyl) zirconium

dichloride, Dimethylsilandiyl-bis(2-n-butyl-4-phenyl-indenyl)zirconium dichloride,

10 Dimethylsilandiyl-bis(2-n-butyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-ethyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-n-propyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-iso-propyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-n-butyl-phenyl)-indenyl) zirconium dichloride,

15 Dimethylsilandiyl-bis(2-n-butyl-4-(4'-hexyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-cyclohexyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-sec-butyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-n-butyl-4-(4'-tert.-butyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-phenyl-indenyl) zirconium dichloride,

20 Dimethylsilandiyl-bis(2-hexyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-ethyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-n-propyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-iso-propyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-n-butyl-phenyl)-indenyl) zirconium dichloride,

25 Dimethylsilandiyl-bis(2-hexyl-4-(4'-n-hexyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-cyclohexyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-sec-butyl-phenyl)-indenyl)zirconium dichloride,

Dimethylsilandiyl-bis(2-hexyl-4-(4'-tert. -butyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-phenyl-4-phenyl-indenyl)zirconium dichloride,

30 Dimethylsilandiyl-bis(2-phenyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-phenyl-4-(4'-ethyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-phenyl-4-(4'-n-propyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-phenyl-4-(4'-iso-propyl-phenyl)-indenyl) zirconium dichloride,

Dimethylsilandiyl-bis(2-phenyl-4-(4'-n-butyl-phenyl)-indenyl) zirconium dichloride,

- Dimethylsilandiyl-bis(2-phenyl-4-(4'-n-hexyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-bis(2-phenyl-4-(4'-cyclohexyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-bis(2-phenyl-4-(4'-sec-butyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-bis(2-phenyl-4-(4'-tert.-butyl-phenyl)-indenyl) zirconium dichloride,
5 Dimethylsilandiyl-bis(2-isopropyl-4-(4'-tert.-butyl-phenyl)-indenyl)zirconiumbis(dimethylamine),
Dimethylsilandiyl-bis(2-isopropyl-4-(4'-tert.-butyl-phenyl)-indenyl)zirconium dibenzyl,
Dimethylsilandiyl-bis(2-ethyl-4-(4'-tert.-butyl-phenyl)-indenyl)zirconium dichloride,
Dimethylsilandiyl-bis(2-isopropyl-4-(4'-tert.-butyl-phenyl)-indenyl) zirconium dimethyl,
10 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-5-azapentalene)(2-isopropyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-6-azapentalene)(2-isopropyl-4-(4'-methyl-phenyl)-indenyl) zirconium dichloride,
15 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-ethyl-phenyl)indenyl)zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-(4'-n-propyl-phenyl)-indenyl)zirconium dichloride,
20 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-isopropyl-phenyl)-indenyl)zirconium dichloride,
Dimethylsilandiyl-(2-methyl-6-azapentalene)(2-isopropyl-4-(4'-isopropyl-phenyl)-indenyl)zirconium dichloride,
Dimethylsilandiyl-(2,5-dimethyl-6-thiapentalene)(2-isopropyl-4-(4'-isopropyl-phenyl)-indenyl)-zirconium dichloride,
25 Dimethylsilandiyl-(2-methyl-6-oxapentalene)(2-isopropyl-4-(4'-isopropyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-6-azapentalene)(2-isopropyl-4-(4'-n-butyl-phenyl)-indenyl)-
30 zirconium dichloride,
Dimethylsilandiyl-(2-methyl-5-thiapentalene)(2-isopropyl-4-(4'-n-butyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-oxapentalene)(2-isopropyl-4-(4'-n-butyl-phenyl)-indenyl) zirconium dichloride,

- Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-(4'-s-butyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-oxapentalene)(2-isopropyl-4-(4'-s-butyl-phenyl)-indenyl) zirconium dichloride,
- 5 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-tert. -butyl-phenyl)-indenyl)-zirconium dichloride,
Dimethylsilandiyl-(2-methyl-6-azapentalene)(2-isopropyl-4-(4'-tert.-butyl-phenyl)-indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-n-pentyl-phenyl)-
- 10 indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2-methyl-N-phenyl-6-azapentalene)(2-isopropyl-4-(4'-n-pentyl-phenyl)-indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-oxapentalene)(2-isopropyl-4-(4'-n-pentyl-phenyl)-indenyl) zirconium dichloride,
- 15 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-n-hexyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-(4'-n-hexyl-phenyl)-indenyl) zirconium dichloride,
Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropyl-4-(4'-n-hexyl-phenyl)-
- 20 indenyl) zirconium dichloride,
Dimethylsilandiyl-(2, 5-Dimethyl-4-thiapentalene)(2-isopropyl-4-(4'-n-hexyl-phenyl)-indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2, 5-Dimethyl-6-thiapentalene)(2-isopropyl-4-(4'-n-hexyl-phenyl)-indenyl)-zirconium dichloride,
- 25 Dimethylsilandiyl-(2,5-dimethyl-6-thiapentalene)(2-isopropyl-4-(4'-cyclohexyl-phenyl)-indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-trimethylsilyl-phenyl)-indenyl)-zirconium dichloride,
Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-(4'-tri methylsilyl-phenyl)-
- 30 indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2-methyl-5-thiapentalene)(2-isopropyl-4-(4'-trimethylsilyl-phenyl)-indenyl)- zirconium dichloride,
Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropyl-4-(4'-trimethylsilyl-phenyl)-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2,5-Dimethyl-4-azapentalene)(2-isopropyl-4-(4'-adamantyl-phenyl)-indenyl)- zirconium dichloride,

Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-(4'-adamantyl-phenyl)-indenyl)-zirconium dichloride,

5 Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropyl-4-(4'-adamantyl-phenyl)-indenyl)- zirconium dichloride,

Dimethylsilandiyl-(2, 5-dimethyl-4-thiapentalene)(2-isopropyl-4-(4'-adamantyl-phenyl)-indenyl)-zirconium dichloride,

10 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-(4'-tris(trifluoromethyl)-methyl-phenyl)-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2,5-Dimethyl-4-azapentalene)(2-isopropyl-4-(4'-tris(trifluoromethyl)methyl-phenyl)-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-(4'-tris(trifluoromethyl)methyl-phenyl)-indenyl)-zirconium dichloride,

15 Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropyl-4-(4'-tris(trifluoromethyl)-methyl-phenyl)-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-N-phenyl-6-azapentalene)(2-isopropyl-4-(4'-tert-butyl-phenyl)-indenyl)-zirconium dichloride,

20 Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropylindenyl) zirconium dichloride,

Dimethylsilandiyl-(2-methyl-N-phenyl-4-azapentalene)(2-isopropylindenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropylindenyl)zirconium dichloride,

Dimethylsilandiyl-(2-methyl-5-thiapentalene)(2-isopropylindenyl)zirconium dichloride,

25 Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropylindenyl) zirconium dichloride,

Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

30 Dimethylsilandiyl-(2-methyl-5-azapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-6-azapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-N-phenyl-4-azapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-N-phenyl-5-azapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

5 Dimethylsilandiyl-(2-methyl-5-thiapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

10 Dimethylsilandiyl-(2-methyl-4-oxapentalene)(2-isopropyl-4-phenyl-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-4-azapentalene)(2-isopropyl-4, 5-benzo-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-N-phenyl-4-azapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

15 Dimethylsilandiyl-(2-methyl-N-phenyl-5-azapentalene)(2-isopropyl-4,5-benzo-indenyl)- zirconium dichloride,

Dimethylsilandiyl-(2-methyl-N-phenyl-6-azapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

20 Dimethylsilandiyl-(2-methyl-4-thiapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-5-thiapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-6-thiapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

25 Dimethylsilandiyl-(2-methyl-4-oxapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

Dimethylsilandiyl-(2-methyl-5-oxapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

30 Dimethylsilandiyl-(2-methyl-6-oxapentalene)(2-isopropyl-4,5-benzo-indenyl)-zirconium dichloride,

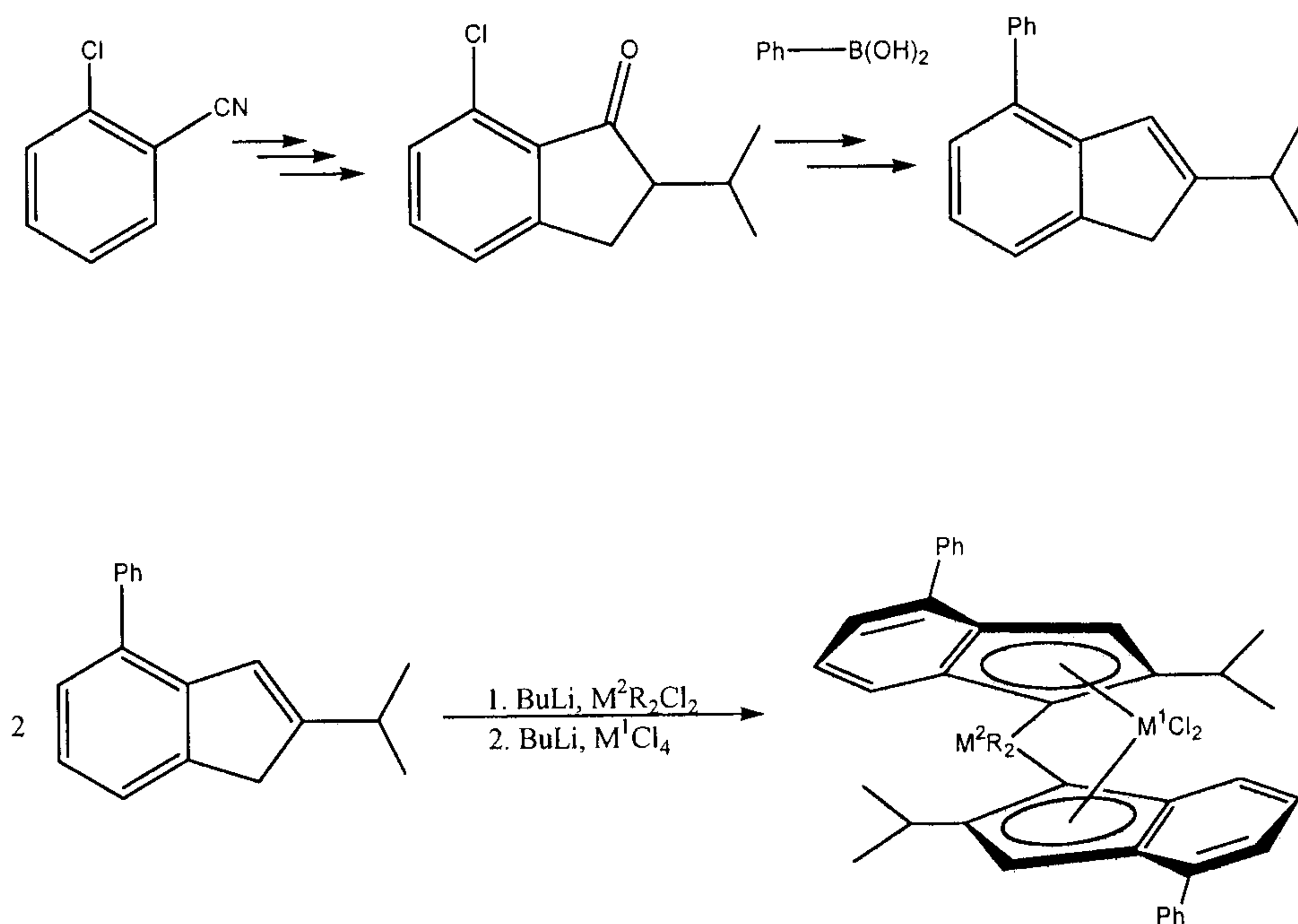
Dimethylsilandiyl-bis(2-isopropyl-4-azapentalene)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-N-phenyl-4-azapentalene)zirconium dichloride,

Dimethylsilandiyl-bis(2-isopropyl-4-thiapentalene)zirconium dichloride,

as well as the corresponding titanium and hafnium compounds and also various bridges of dimethylsilandiyl according to Formula I such as dimethylmethandiyl, diphenylmethandiyl, ethandiyl, 1,2-dimethylethandiyl, dipropylsilandiyl, dibutylsilandiyl, dipentylsilandiyl, dihexylsilandiyl, diheptylsilandiyl, dioctylsilandiyl, 5 dinonylsilandiyl, didecylsilandiyl, diundecylsilandiyl, didodecylsilandiyl.

The synthesis of the compounds of Formula I according to the invention can be conducted according to processes known to one skilled in the art. An example therefor is set forth in the following.



10

The compounds of Formula I according to the invention are particularly suited to be components of catalyst systems to manufacture polyolefins through the polymerization of at least one olefin in the presence of a catalyst that contains at least one co-catalyst and at least one compound of Formula I according to the 15 invention.

15

Ethylene is preferred as the olefin. In a preferred embodiment of the invention, ethylene is polymerized using the catalysts according to the invention, whereby polymerization is understood to be both the homo-polymerization of ethylenes as 20 well as the co-polymerization of ethylene with other olefins. The ethylene used in the process can, if desired, contain still other olefins that are selected from the group that is formed by

20

1-olefin with 2-20, preferably 2 to 10 C atoms, such as propene, 1-butene, 1-pentene, 1-hexene, 1-decene, 4-methyl-1-pentene or 1-octene, styrene, dienes such as 1,3-butadiene, 1,4-hexadiene, vinyl norbornene, norbornadiene, ethyl norbornadiene and cyclo-olefins such as norbornene, cyclopentadiene, tetracyclododecene or methyl norbornenes as well as mixtures of same. Particular preference is given to co-polymerizing the ethylene used with one or more 1-olefins with 2 to 8 C atoms such as propene, 1-butene, 1-pentene, 1-hexene, styrene or butadiene.

10 A co-monomer fraction of 0.1 to 10%, is preferred, preferably 0.5 to 9% and in particular 2 to 5%.

Particular preference is given to the co-polymerization of ethylene with the co-monomer propene.

15 Further preference is given to the process according to the invention whereby the ethylene used is homo-polymerized or co-polymerized with propene.

Particular preference is given to the process according to the invention whereby the ethylene used is homo-polymerized.

20

The ethylene polymers and co-polymers manufactured with the process according to the invention are ultra high molecular weight, since they have a viscosimetrically determined molecular weight of greater than 1×10^6 mol/g.

25 Preference is also given to polyethylenes with a molecular weight of greater than 1×10^6 mol/g that can be obtained using the process according to the invention.

The viscosimetric measurements are made in Decalin at 135°C and a concentration of 0.1g (polymer)/1 l (Decalin). The molecular weight can be derived from the viscosity number.

30

The polymerization is conducted at a temperature of -20 to 300°C, preferably 0 to 200°C, most especially preferred at 20 to 100°C. The pressure is from 0.5 to 2000

bar, preferably 1 to 64 bar. The polymerization can be conducted in solution, in bulk, in suspension or in emulsion, continuously or in batches, in one or more stages. Suitable solvents for the polymerization are, for example, aliphatic hydrocarbons such as pentane, hexane and the like or aromatic hydrocarbons such as benzene, toluene, xylene and the like, or ethers such as diethyl ether, dibutyl ether, methyl-tert-butyl ether, tetrahydrofuran, dioxane, anisole, diphenyl ether and ethyl-phenyl ether, as well as halogenated solvents such as dichloromethane, trichloromethane, chlorobenzene, bromobenzene and the like. Mixtures of various solvents in various proportions can also be used according to the invention.

Ultra high molecular weight ethylene polymers and co-polymers are obtained through the polymerization of at least one olefin in the presence of catalyst systems of at least one compound of Formula I and one co-catalyst.

In a preferred embodiment of the invention, the catalyst system used in the process according to the invention contains at least one co-catalyst.

The co-catalyst that, together with at least one transition metal compound of Formula I, forms the catalyst system, contains at least one aluminoxane compound, or another Lewis acid, or an ionic compound, which reacts with the transition metal compound to convert it into a cationic compound.

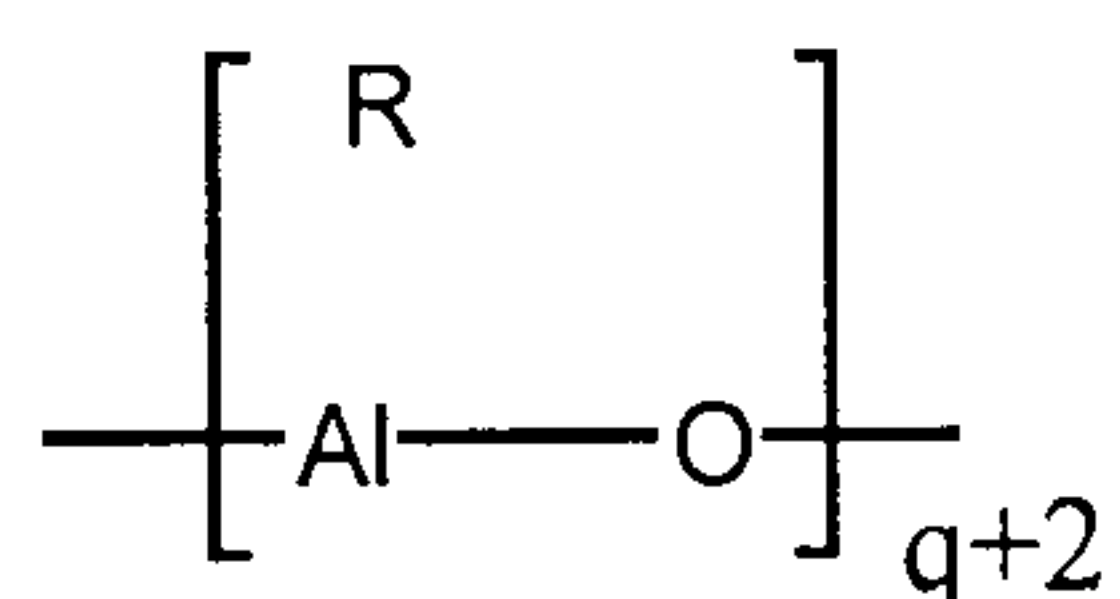
Particular preference is given to catalyst systems that contain at least one Lewis acid as co-catalyst.

As aluminoxane, preference is given to using a compound of the general Formula II.



Formula II

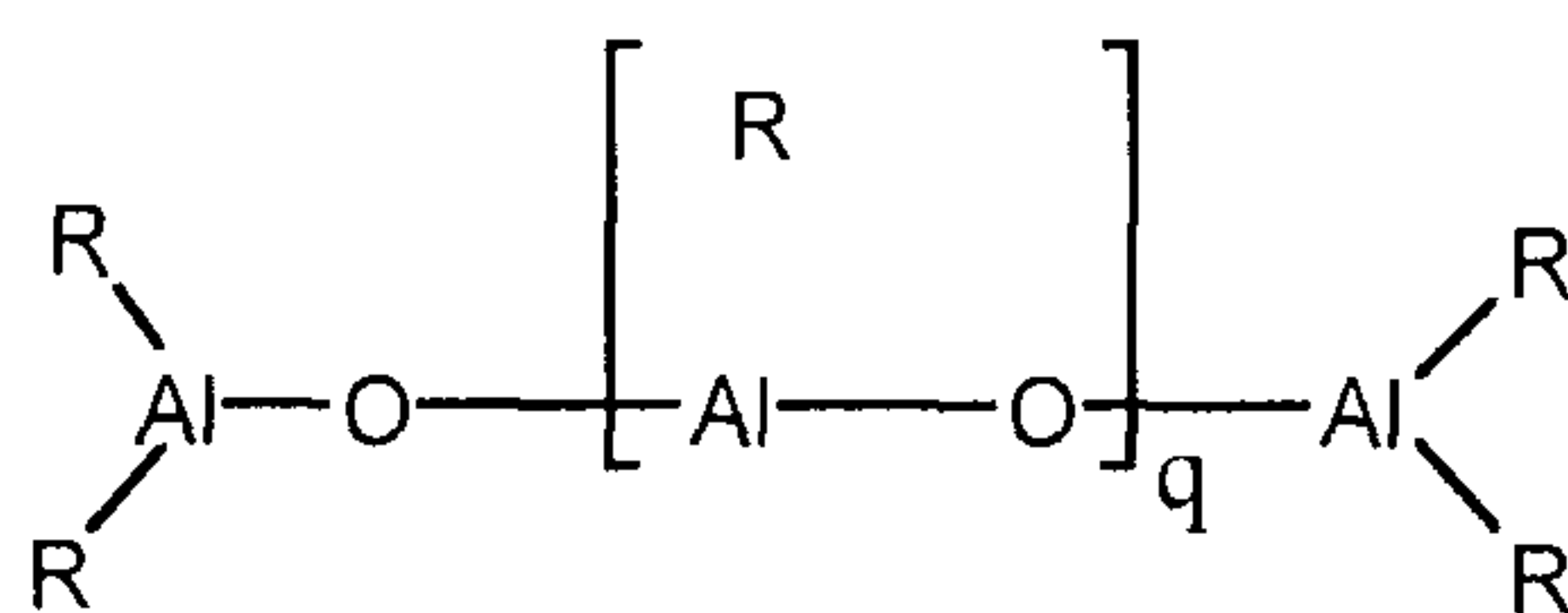
Other suitable aluminoxanes could, for example, be cyclic as in Formula III



Formula III

5

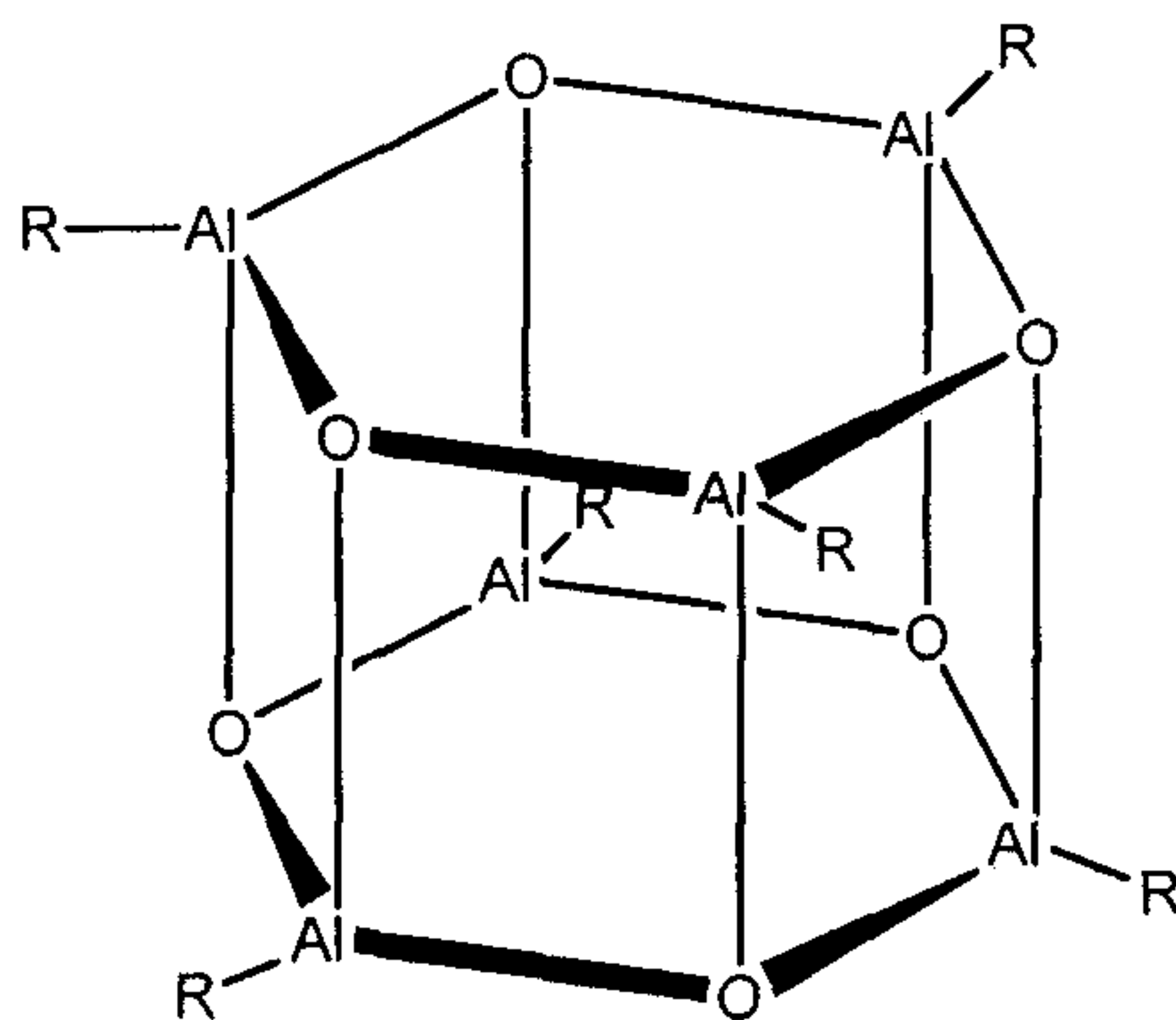
or linear as in Formula IV



Formula IV

or of a cluster type as in Formula V.

10



Formula V

Such aluminosiloxanes are, for example, described in JACS 117 (1995), 6465-74,
15 Organometallics 13 (1994), 2957-2969.

The radical R in the Formulae II, III, IV and V may be identical or different and are each a C₁-C₂₀-hydrocarbon group such as a C₁-C₆ alkyl group, a C₆-C₁₈ aryl group, benzyl or hydrogen, and q stands for an integer of 2 to 50, preferably 10 to 35.

20 Preferably, the radicals R are identical and are each methyl, isobutyl, n-butyl, phenyl or benzyl, in particular methyl.

If the radicals R are different, they are preferably methyl and hydrogen, methyl and isobutyl, or methyl and n-butyl, containing hydrogen or isobutyl or n-butyl preferably
25 up to 0.01-40% (number of radicals R).

The aluminoxane can be manufactured in various ways according to known processes. One of the methods is, for example, reacting an aluminum hydrocarbon compound and/or a hydridoaluminum hydrocarbon compound with water (gaseous, solid, liquid or bound—for example as water of crystallization) in an inert solvent (such as toluene).

To prepare an aluminoxane having different alkyl groups R, two different aluminum trialkyls ($\text{AlR}_3 + \text{AlR}'_3$), corresponding to the desired composition and reactivity, are reacted with water (see S. Pasynkiewicz, Polyhedron 9 (1990) 429 and EP-A-0,302,424).

Regardless of the type of preparation, a variable content of unreacted aluminum feed compound, present in free form or as an adduct, is common to all aluminoxane solutions.

As Lewis acid, preference is given to using at least one boron or organoaluminum compound containing $\text{C}_1\text{-C}_{20}$ carbonaceous groups, such as branched or unbranched alkyl or haloalkyl groups, such as methyl, propyl, isopropyl, isobutyl, trifluoromethyl, unsaturated groups such as aryls, or haloaryls, such as phenyl, tolyl, benzene groups, p-fluorophenyl, 3,5-difluorophenyl, pentachlorophenyl, pentafluorophenyl, 3,4,5 trifluorophenyl and 3,5 di(trifluoromethyl)phenyl.

Examples of Lewis acids are trimethylaluminum, triethylaluminum, triisobutylaluminum, tributylaluminum, trifluoroborane, triphenylborane, tris(4-fluorophenyl)borane, tris(3,5-difluorophenyl)borane, tris(4-fluoromethylphenyl)borane, tris(pentafluorophenyl)borane, tris(tolyl)borane, tris(3,5-dimethylphenyl)borane, tris(3,5-difluorophenyl)borane, and/or tris(3,4,5-trifluorophenyl)borane. Particular preference is given to tris(pentafluorophenyl)borane.

As ionic cocatalysts, preference is given to using compounds that contain a noncoordinating anion, such as tetrakis(pentafluorophenyl)borate, tetraphenylborate, SbF_6^- , CF_3SO_3^- or ClO_4^- .

As cationic counterions, use is made of protonated Lewis bases such as, for example, methyl amine, aniline, N,N-dimethylbenzylamine, as well as their derivatives, N,N-dimethylcyclohexylamine and its derivatives, dimethylamine, diethylamine, N-methylaniline, diphenylamine, N,N-dimethylaniline, trimethylamine, triethylamine, tri-n-butylamine, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, triethylphosphine, triphenylphosphine, diphenylphosphine, tetrahydrothiophene, or triphenylcarbenium.

- Examples of such ionic compounds are
- Triethylammoniumtetra(phenyl)borate,
 - Tributylammoniumtetra(phenyl)borate,
 - Trimethylammoniumtetra(tolyl)borate,
 - Tributylammoniumtetra(tolyl)borate,
 - Tributylammoniumtetra(pentafluorophenyl)borate,
 - Tributylammoniumtetra(pentafluorophenyl)aluminate,
 - Tripropylammoniumtetra(dimethylphenyl)borate,
 - Tributylammoniumtetra(trifluoromethylphenyl)borate,
 - Tributylammoniumtetra(4-fluorophenyl)borate,
 - N,N-Dimethylaniliniumtetra(phenyl)borate,
 - N,N-Diethylaniliniumtetra(phenyl)borate,
 - N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,
 - N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,
 - Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,
 - Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,
 - Triphenylphosphoniumtetrakis(phenyl)borate,
 - Triethylphosphoniumtetrakis(phenyl)borate,
 - N,N-Dimethylcyclohexylammoniumtetrakis(pentafluorophenyl)borate
 - N,N-Dimethylbenzylammoniumtetrakis(pentafluorophenyl)borate
 - Diphenylphosphoniumtetrakis(phenyl)borate,
 - Tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,
 - Tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,
 - Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,
 - Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,

Triphenylcarbeniumtetrakis(phenyl)aluminate,
 Ferroceniumtetrakis(pentafluorophenyl)borate and/or
 Ferroceniumtetrakis(pentafluorophenyl)aluminate.

Preference is given to triphenylcarbeniumtetrakis(pentafluorophenyl)borate and/or

5 N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate.

Mixtures of at least one Lewis acid and at least one ionic compound can also be used.

10 Further suitable cocatalyst components are borane or carborane compounds such as

7,8-dicarbaundecaborane(13),

Undecahydride-7,8-dimethyl-7,8-dicarbaundecaborane,

Dodecahydride-1-phenyl-1,3-di-carbanonaborane,

15 Tri(butyl)ammoniumundecahydride-8-ethyl-7,9-dicarbaundecaborate,

4-carbanonaborane(14)bis(tri(butyl)ammonium)nonaborate,

Bis(tri(butyl)ammonium)undecaborate,

Bis(tri(butyl)ammonium)dodecaborate,

Bis(tri(butyl)ammonium)decachlorodecaborate,

20 Tri(butyl)ammonium-1-carbadecaborate,

Tri(butyl)ammonium-1-carbadodecaborate,

Tri(butyl)ammonium-1-trimethylsilyl-1-carbadecaborate

Tri(butyl)ammoniumbis(nonahydride-1,3-di-carbonnonaborate)cobaltate(III),

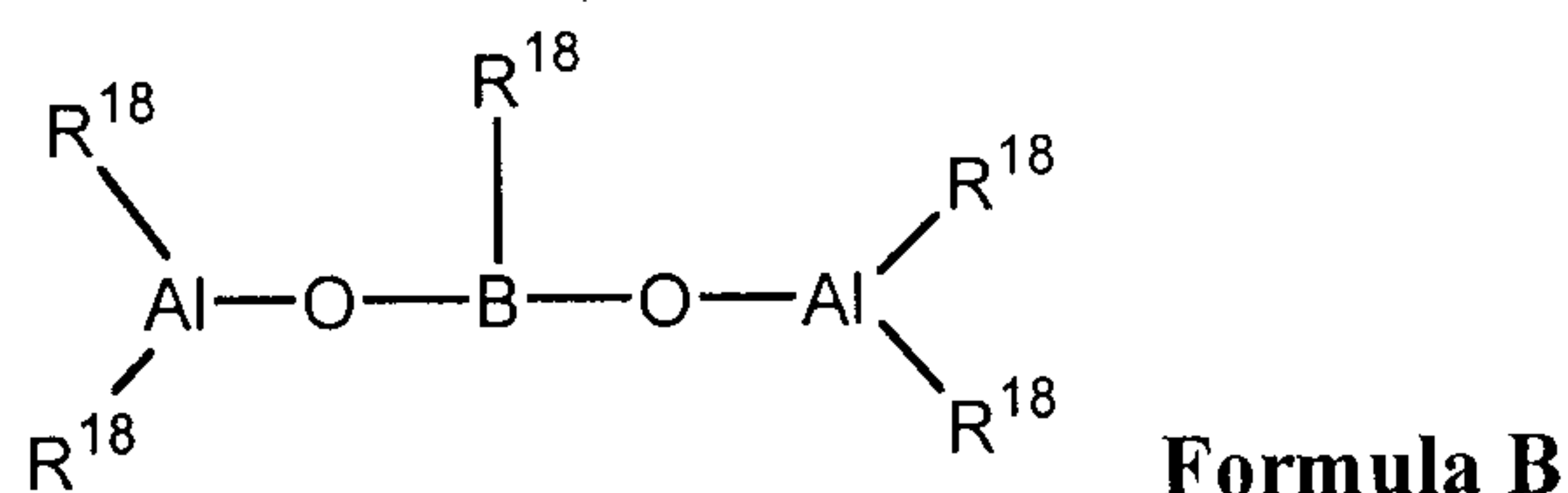
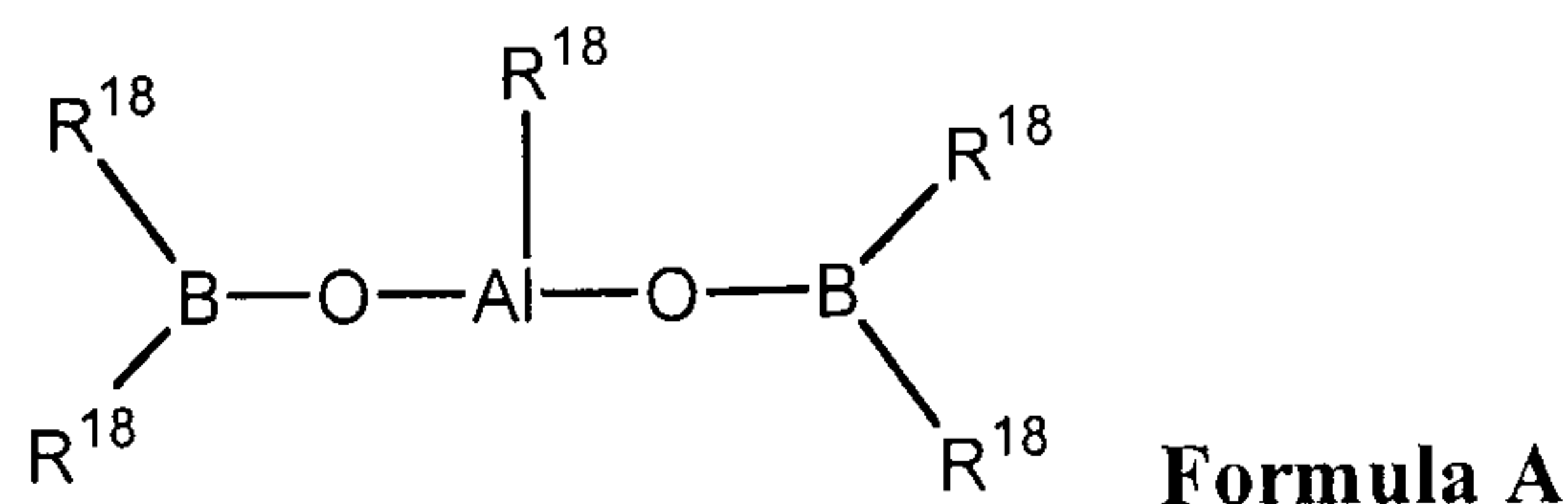
Tri(butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)ferrate(III).

25

Further useful co-catalyst systems are combinations of at least one of the
 aforementioned amines and if desired, a support with organoelement compounds, as
 they are described in patent WO 99/40129.

30 The supports with organoelement compounds named in WO 99/40129 are also
 components of this invention.

Preferred components of these co-catalyst systems are the compounds of Formulae A and B,



whereby

R^{18} [is¹] a hydrogen atom, a halogen atom, a $\text{C}_1\text{-C}_{20}$ carbonaceous group, in particular $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_1\text{-C}_{20}$ haloalkyl, $\text{C}_1\text{-C}_{10}$ alkoxy, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_6\text{-C}_{20}$ haloaryl, $\text{C}_6\text{-C}_{20}$ aryloxy, $\text{C}_7\text{-C}_{20}$ arylalkyl, $\text{C}_7\text{-C}_{40}$ haloarylalkyl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ haloalkylaryl. R^{18} can also be an OSiR_3 group, whereby R is identical or different and has the same meaning as R^{18} .

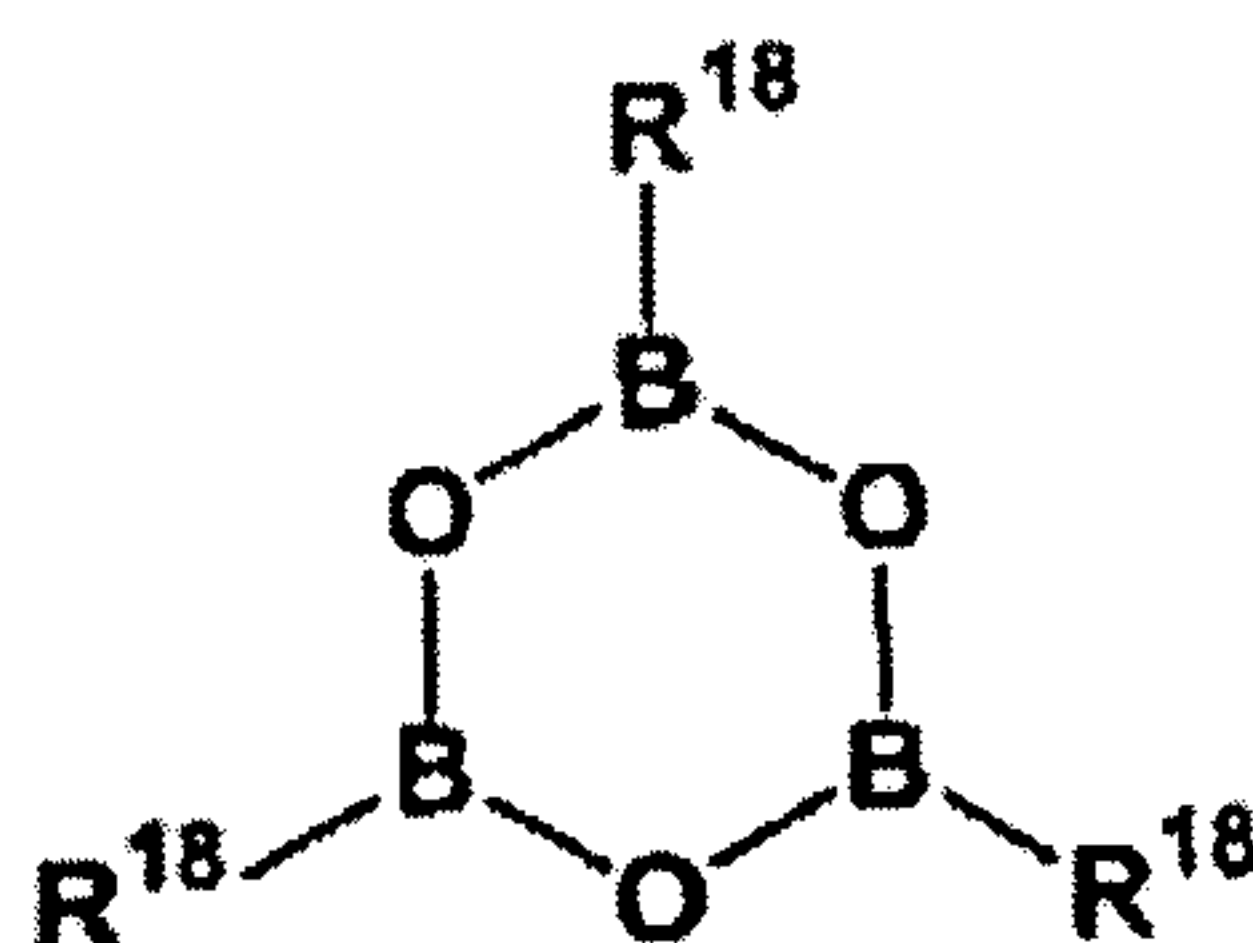
Further preferred co-catalysts are general compounds that are formed by the reaction of at least one compound of Formula C and/or D and/or E with at least one compound of formula F.



Formula C

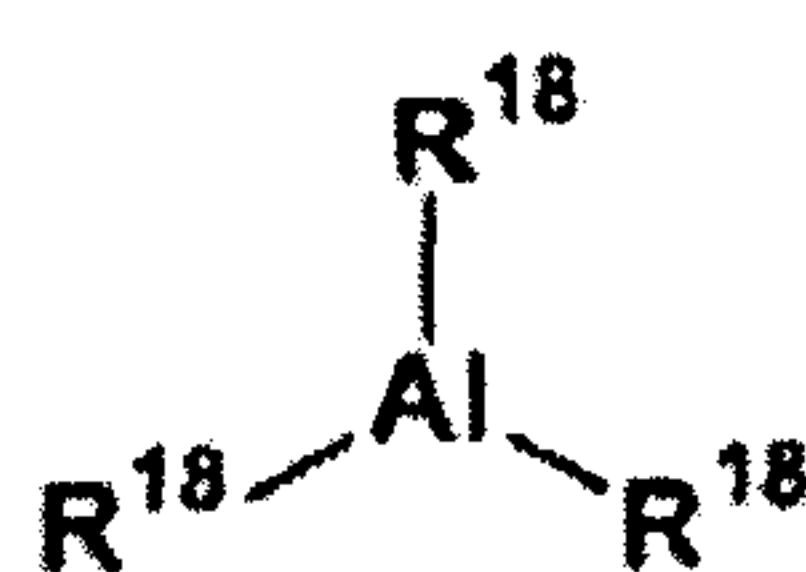


Formula D



Formula E

¹ Translator's Note: The verb is missing in the original.

**Formula F**

5

whereby:

R^{18} has the same meaning as mentioned above; and

R^{19} can be a hydrogen atom or a boron free $\text{C}_1\text{-C}_{20}$ carbonaceous group such as $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ arylalkyl, $\text{C}_7\text{-C}_{20}$ alkylaryl; and

10 X^1 is an element of the 16th group of the periodic table or an NR group, whereby R is a hydrogen atom or a $\text{C}_1\text{-C}_{20}$ hydrocarbon radical such as $\text{C}_1\text{-C}_{20}$ -Alkyl or $\text{C}_1\text{-C}_{20}$ Aryl; and

L is an element of the 16th group of the periodic table or an NR group, whereby R is a hydrogen atom or a $\text{C}_1\text{-C}_{20}$ hydrocarbon radical such as $\text{C}_1\text{-C}_{20}$ -alkyl or

15 $\text{C}_1\text{-C}_{20}$ aryl;

f is an integer from 0 to 3;

g is an integer from 0 to 3, whereby $z + y$ cannot equal 0;

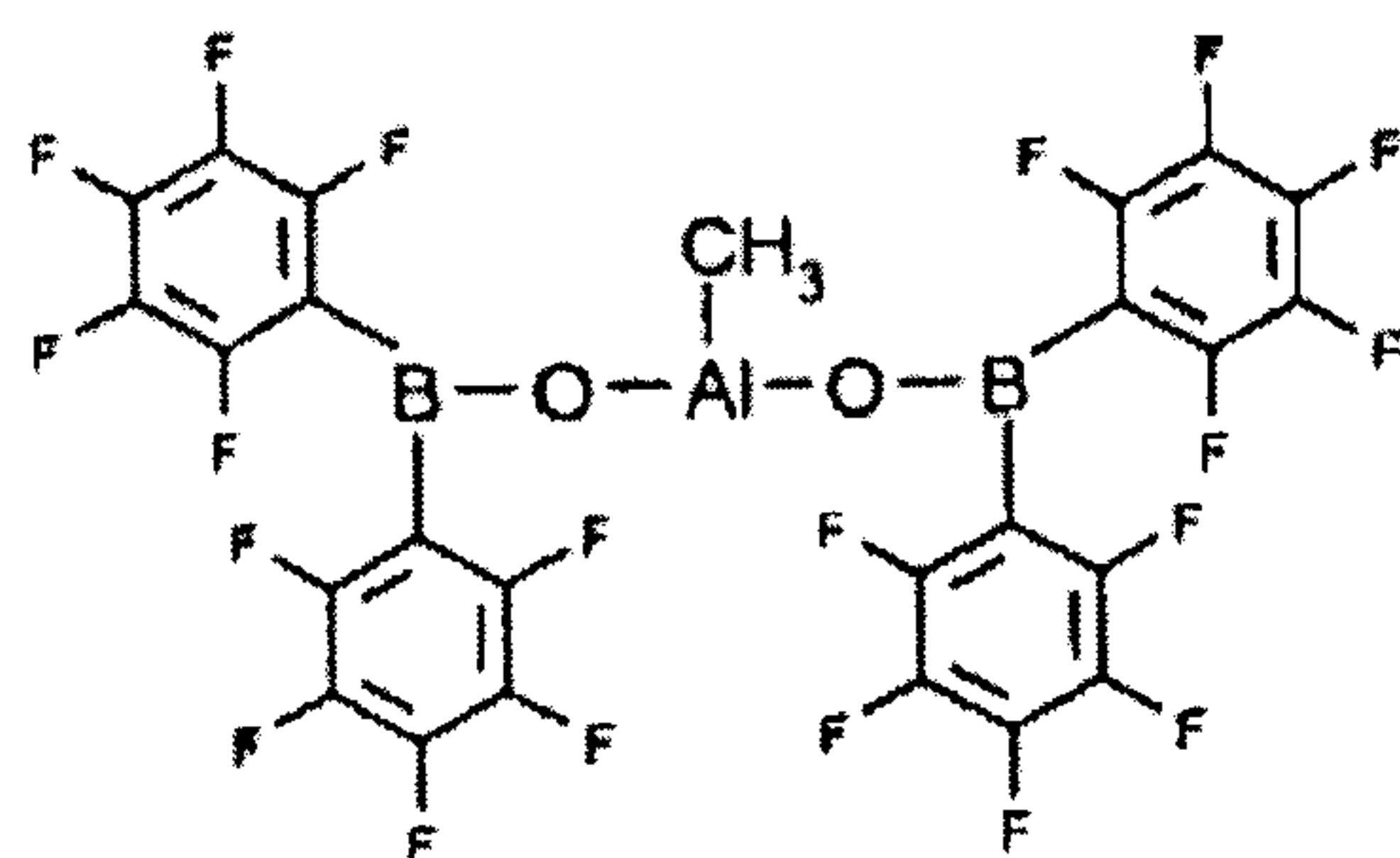
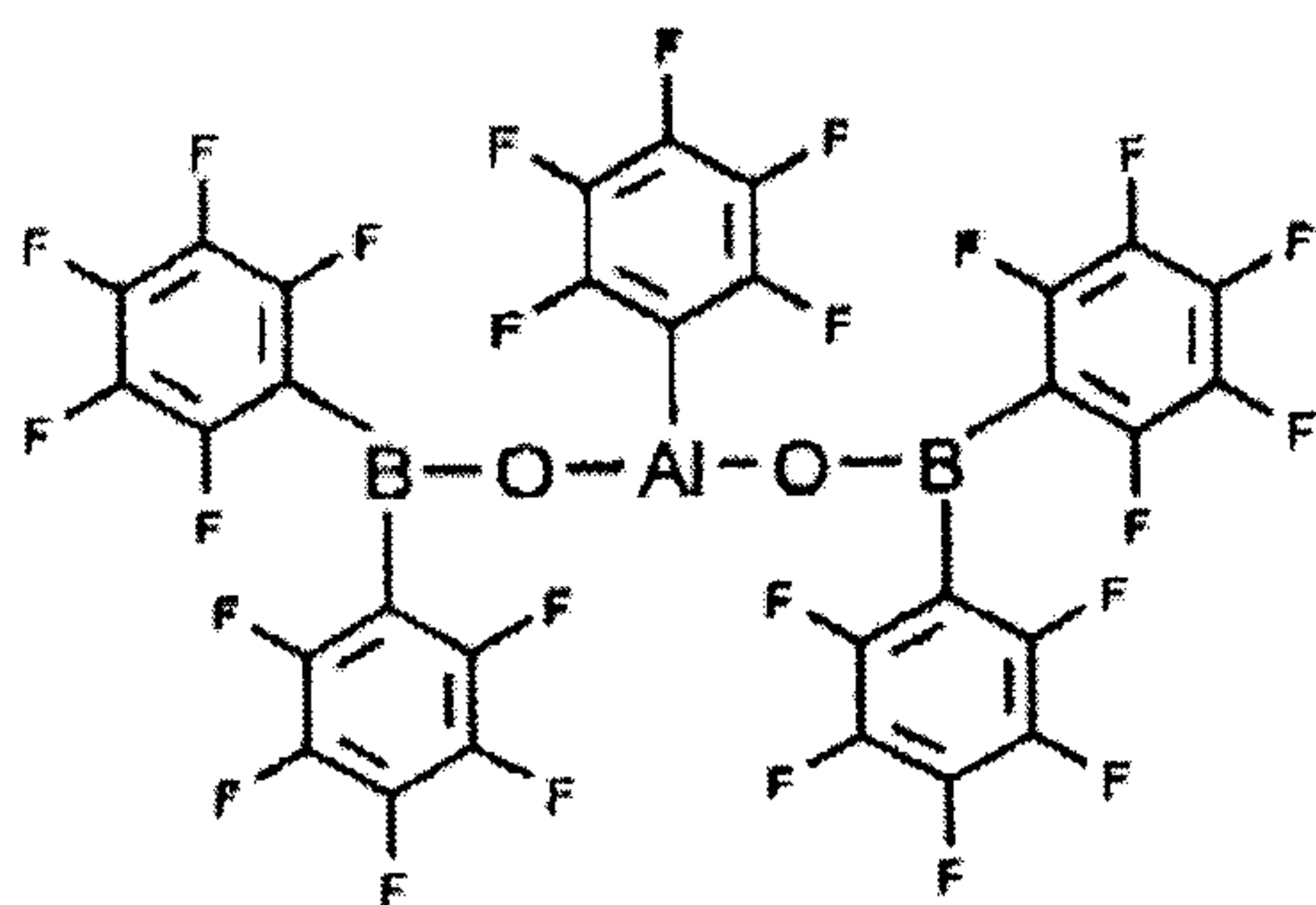
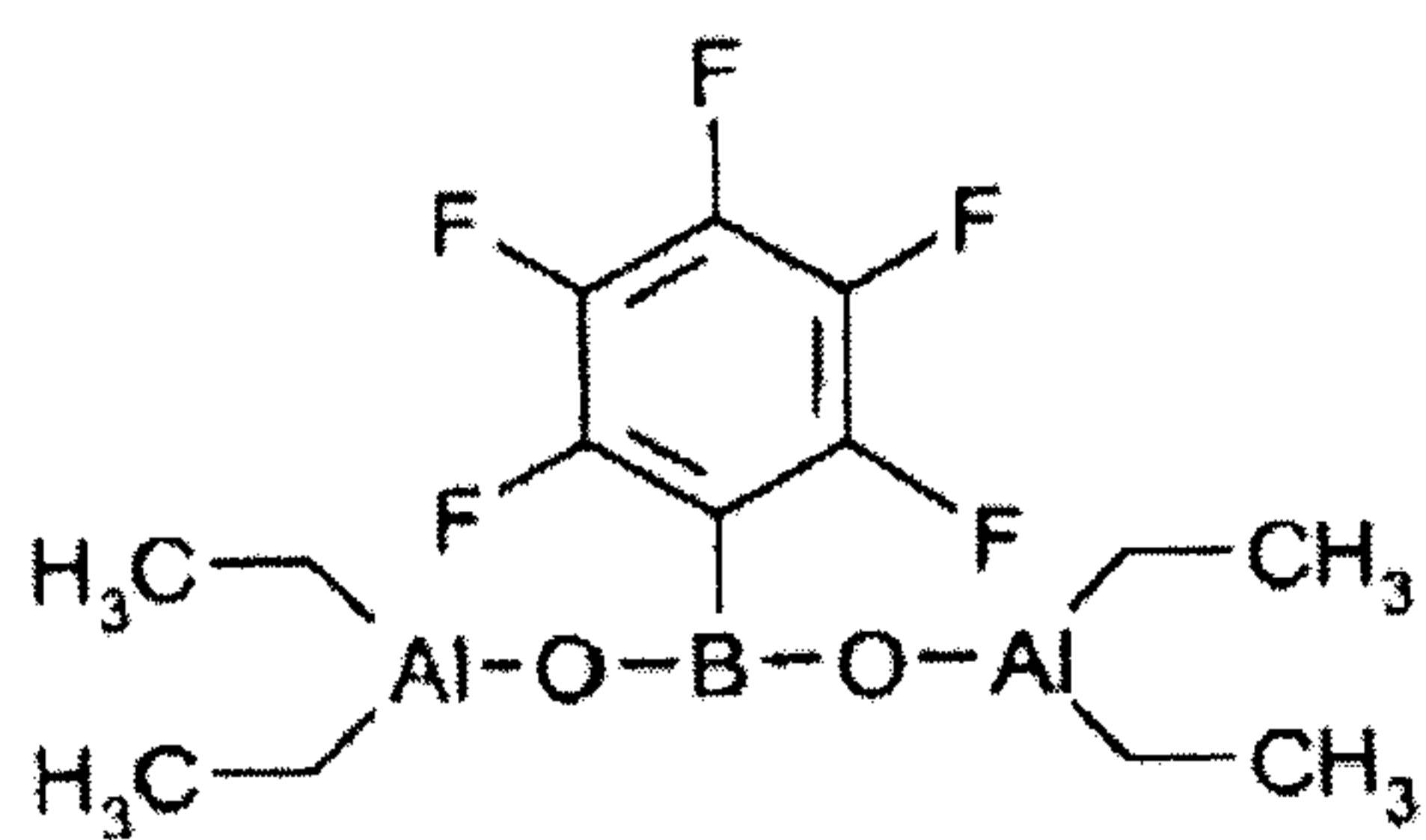
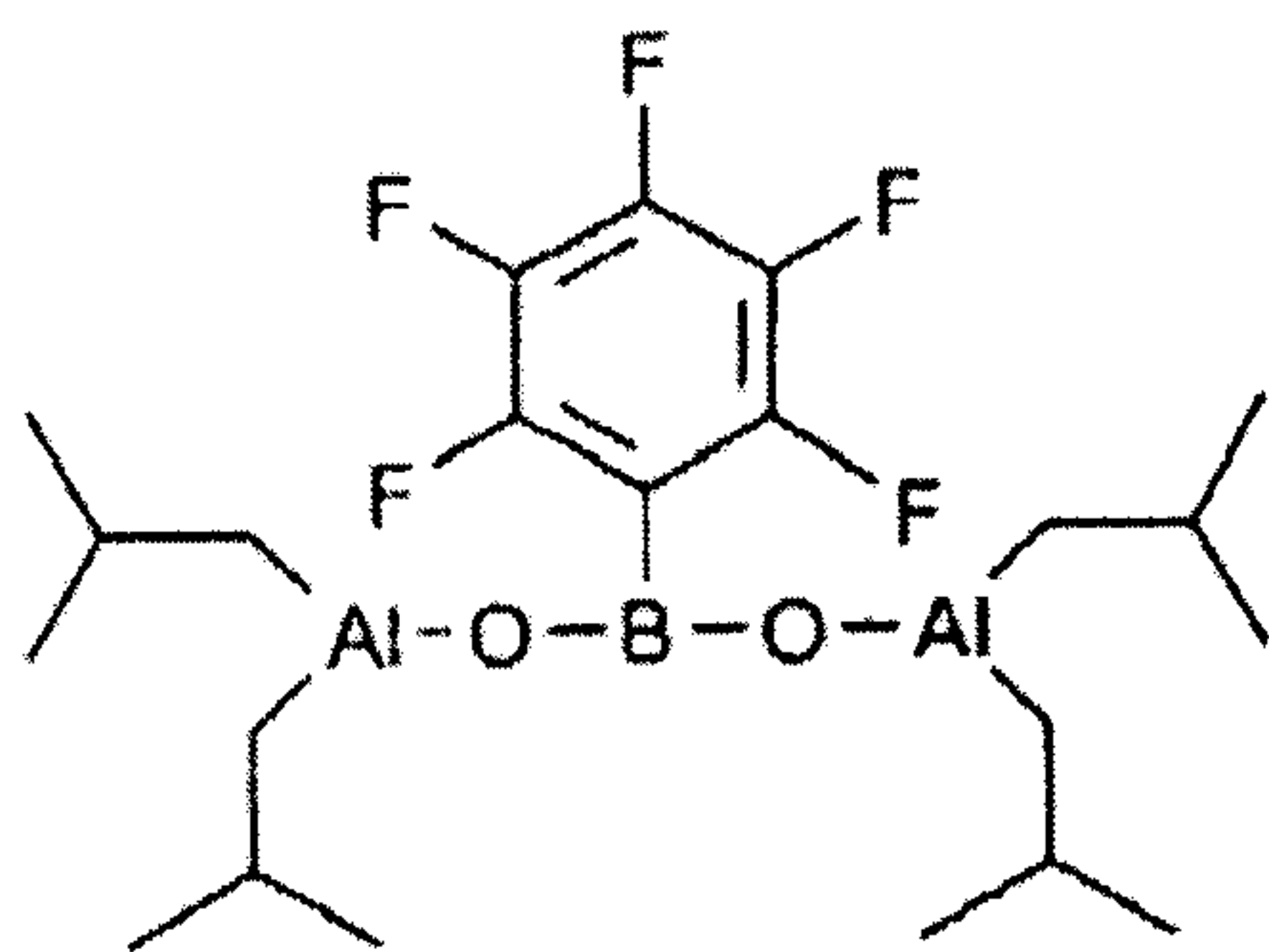
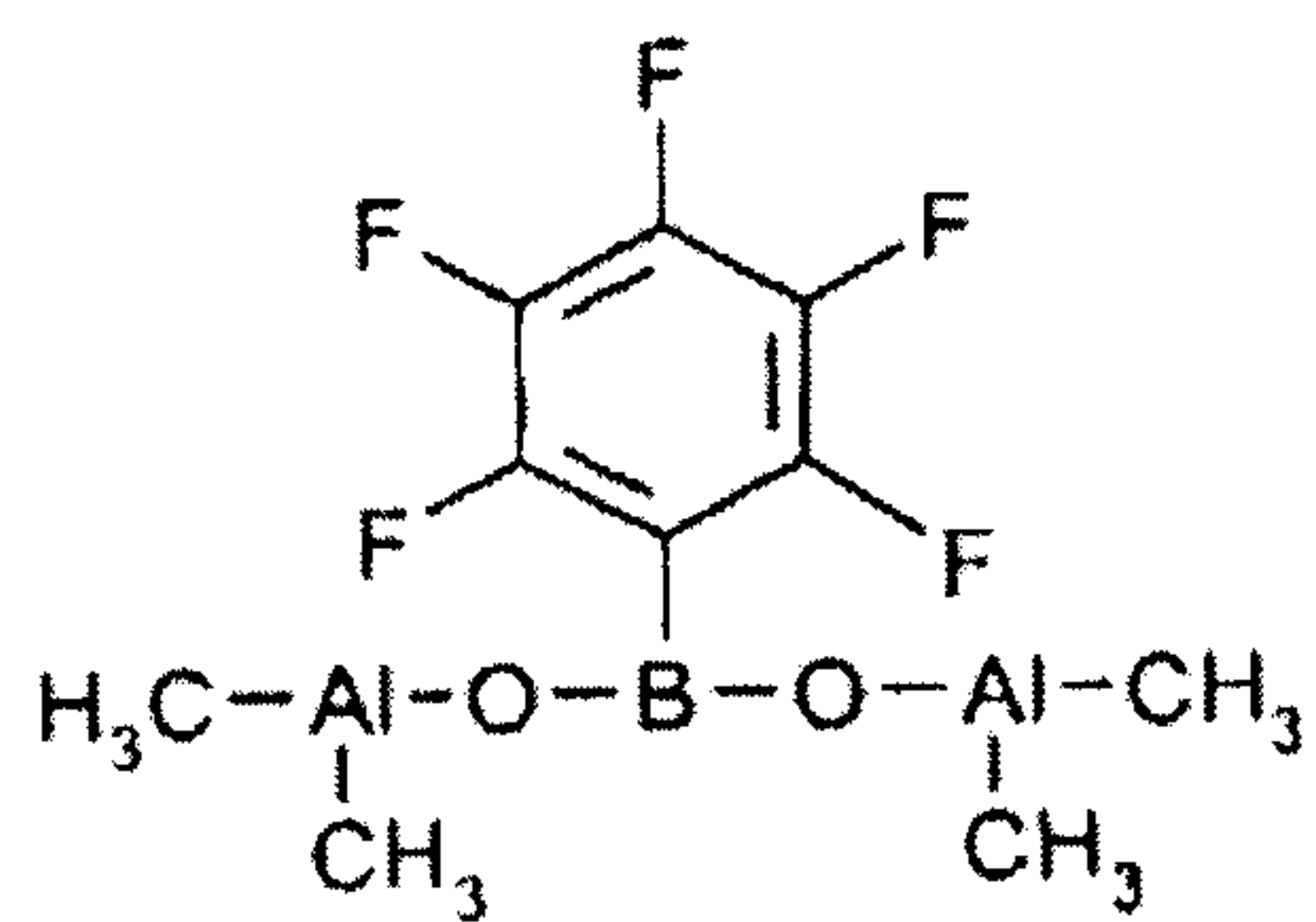
h is an integer from 1 to 10.

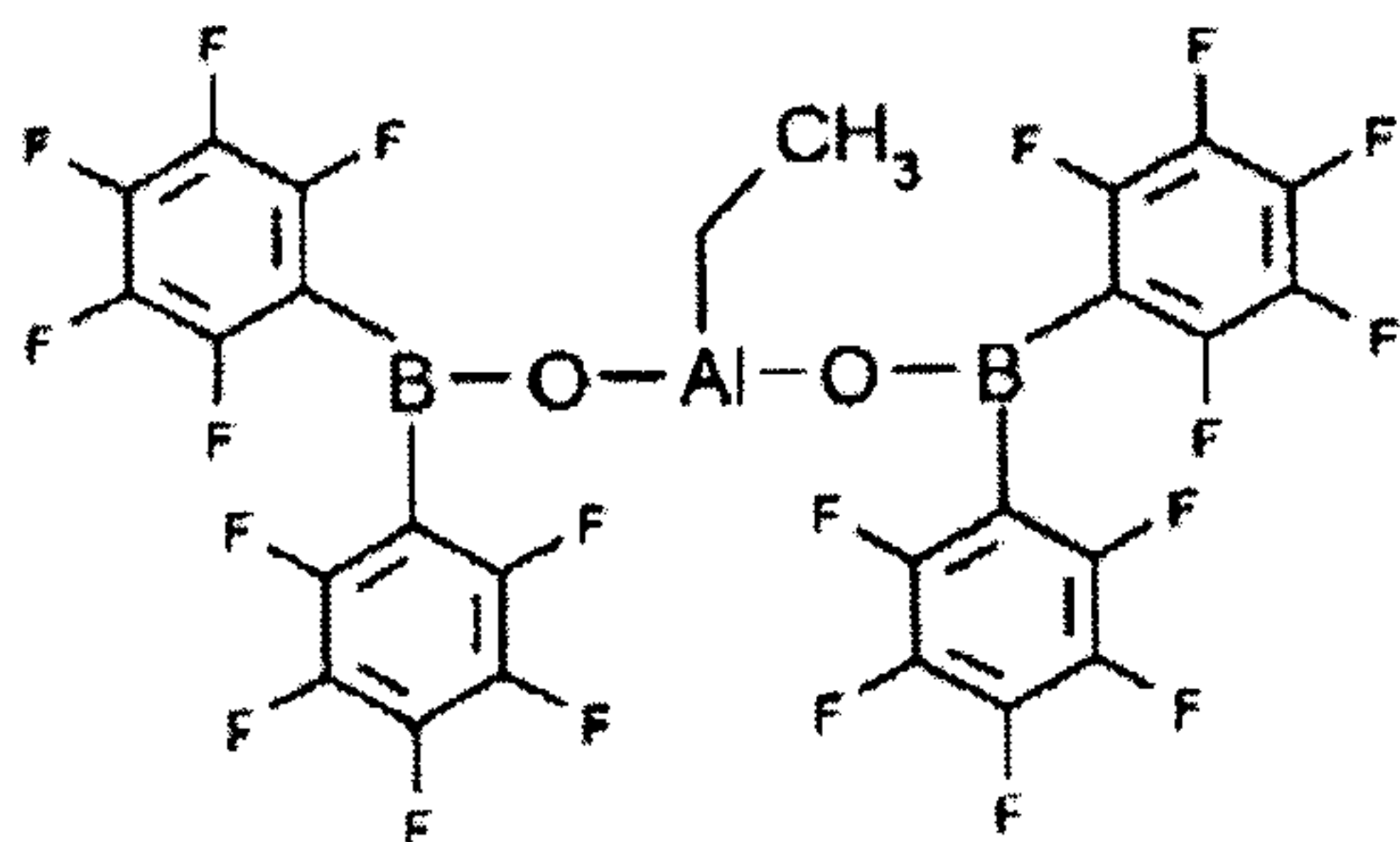
20 If desired, the organoelement compounds are combined with an organometallic compound of Formulae II to V and/or VI,

$[\text{M}^3\text{R}^{20}_r]_k$ **Formula VI**

25 whereby M^3 is an element of the 1st, 2nd, and 13th group of the periodic table, R^{20} is identical or different and is a hydrogen atom, a halogen atom, a $\text{C}_1\text{-C}_{40}$ carbonaceous group, in particular a $\text{C}_1\text{-C}_{20}$ alkyl, a $\text{C}_6\text{-C}_{20}$ aryl, a $\text{C}_7\text{-C}_{20}$ aryl-alkyl, or a $\text{C}_7\text{-C}_{20}$ alkyl-aryl group, r is an integer from 1 to 3 and k is an integer of 1 to 4.

30 Examples for the co-catalytically effective compounds of Formulae A and B are:





The organometallic compounds of Formula F are preferably uncharged Lewis acids, whereby M^2 stands for lithium, magnesium and/or aluminum, in particular aluminum.

- 5 Examples of preferred organometallic compounds of Formula F are trimethylaluminum, triethylaluminum, triisopropylaluminum, trihexylaluminum, trioctylaluminum, tri-n-butylaluminum, tri-n-propylaluminum, triisoprenealuminum, dimethylaluminum monochloride, diethylaluminum monochloride, diisobutylaluminum monochloride, methylaluminum sesquichloride, ethylaluminum sesquichloride,
- 10 dimethylaluminum hydride, diethylaluminum hydride, diisopropylaluminum hydride, dimethylaluminum(trimethylsiloxide), dimethylaluminum(triethylsiloxide), phenylalane, pentafluorophenylalane, and o-tolylalane.

- Further co-catalysts, which may be in unsupported or supported form, are the
- 15 compounds mentioned in EP-A-924223, DE-A-19622207, EP-A-601830, EP-A-824112, EP-A-824113, EP-A-811627, WO9711775 and DE-A-19606167.

Moreover, the catalysts according to the invention can be homogeneously as well as well as heterogeneously supported.

20

In a preferred embodiment, it is claimed that the compound of Formula I used in the process according to the invention is used in the form of a catalyst system in supported form.

- 25 The support component of the catalyst system can be any organic or inorganic, inert solid, in particular a porous support such as talc, inorganic oxides and finely divided polymer powder (e.g., polyolefin).

Suitable inorganic oxides may be found in the groups 2, 3, 4, 5, 13, 14, 15, and 16 of the periodic table. Examples for the oxides preferred as supports include silicon dioxide, aluminum oxide, and also mixed oxides of the elements calcium, aluminum, silicon, magnesium, titanium and corresponding oxide mixtures as well as

5 hydrotalcite. Other inorganic oxides that can be used either alone or in combination with the aforementioned preferred oxidic supports, are e.g. MgO, ZrO₂, TiO₂ or B₂O₃, to name a few.

The support materials used have a specific surface area in the range from 10 to
10 1000 m²/g, a pore volume in the range from 0.1 to 5 ml/g and a mean particle size of 1 to 500 µm. Preference is given to supports with a specific surface area in the range of 50 to 500 µm, a pore volume in the range from 0.5 to 3.5 ml/g and a mean particle size in the range of 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
15 the range from 0.8 to 3.0 ml/g, and a mean particle size of 10 to 200 µm.

If the support material used naturally exhibits a low moisture content or residual solvent content, the dehydration or drying before use can be omitted. If this is not the case, as when using silica gel as support material, dehydration or drying is
20 advisable. Thermal dehydration or drying of the support material can be carried out under a vacuum and a simultaneous blanketing with inert gas (e.g., nitrogen). The drying temperature is in the range from 100 to 1000 °C, preferably from 200 to 800°C. The pressure is not critical in this instance. The drying process can last from 1 to 24 hours. Shorter or longer drying times are possible, provided that
25 establishment of equilibrium with the hydroxyl groups on the support surface can take place under the conditions chosen, which normally takes from 4 to 8 hours.

Dehydration or drying of the support material can also be carried out by chemical means, by reacting the adsorbed water and the hydroxyl groups on the surface with
30 suitable passivating agents. Reaction with the passivating reagent can convert all or part of the hydroxyl groups into a form which does not lead to any adverse interaction with the catalytically active centers. Suitable passivating agents are, for example, silicon halides and silanes, e.g. silicon tetrachloride, chlortrimethylsilane, dimethylamino trichlorosilane, or organometallic compounds of aluminum, boron and

magnesium, for example trimethylaluminum, triethylaluminum, triisobutylaluminum, triethylborane, dibutylmagnesium. Chemical dehydration or passivation of the support material is carried out, for example, by reacting a suspension of the support material in a suitable solvent with the passivating reagent either in pure form or as a solution in a suitable solvent in the absence of air and moisture. Suitable solvents are, for example, aliphatic or aromatic hydrocarbons such as pentane, hexane, heptane, toluene or xylene. Passivation is carried out at from 25°C to 120°C, preferably from 50 to 70°C. Higher and lower temperatures are possible. The reaction time is from 30 minutes to 20 hours, preferably from 1 to 5 hours. After the chemical dehydration is complete, the support material is isolated by filtration under inert conditions, washed one or more times with suitable inert solvents as described above and subsequently dried in a stream of inert gas or under reduced pressure.

Organic support materials such as finely divided polyolefin powders (e.g., polyethylene, polypropylene or polystyrene) can also be used and should likewise be freed of adhering moisture, solvent radicals or other impurities by appropriate purification and drying operations prior to use.

To prepare the supported catalyst system, at least one of the above-described compounds of Formula I is brought in contact with at least one co-catalyst component in a suitable solvent, preferably giving a soluble reaction product, an adduct or a mixture.

The preparation so obtained is then mixed with the dehydrated or passivated support material, the solvent removed and the resulting supported catalyst system dried, to ensure that all or most of the solvent is removed from the pores of the support materials. The supported catalyst is obtained as a free flowing powder.

Another object of the present invention is a process to depict a free flowing and, if desired, pre-polymerized supported catalyst system comprising the following steps:

- a) preparation of a mixture of at least one compound of Formula I and at least one co-catalyst in a suitable solvent or suspension medium;
- b) application of the mixture obtained from Step a) to a porous, preferably inorganic, dehydrated support;

- c) removal of most of the solvent from the resulting mixture;
- d) isolation of the supported catalyst system;
- e) if desired, a pre-polymerization of the supported catalyst system obtained using one or several olefinic monomer(s), to obtain a pre-polymerized supported catalyst system.

Preferred solvents in step a) are hydrocarbons and hydrocarbon mixtures that are liquid at the reaction temperature chosen and in which the individual components are preferably dissolved. The solubility of the individual components is, however, not a prerequisite, as long as the reaction product from the compound of Formula I and the co-catalyst is soluble in the solvent chosen. Examples for the suitable solvents include alkanes such as pentane, isopentane, hexane, heptane, octane, and nonane; cycloalkanes such as cyclopentane and cyclohexane; and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene. Very particular preference is given to toluene.

The amounts of aluminoxane and compound of Formula I used in the preparation of the supported catalyst system can be varied over a wide range. Preference is given to a molar ratio of aluminum to transition metal in the compound of Formula I of 10 : 1 to 1000 : 1, very particularly preferably from 50 : 1 to 500 : 1.

In the case of methylaluminoxane preference is given to using 30% strength toluene solutions; the use of 10% strength solutions is, however, also possible. To carry out the preactivation, the compound of Formula I in the form of a solid is dissolved in a solution of the aluminoxane in a suitable solvent. It is also possible to dissolve the compound of Formula I separately in a suitable solvent and then to combine this solution with the aluminoxane solution. Preference is given to using toluene.

The preactivation time is from 1 minute to 200 hours.

The preactivation can take place at room temperature (25°C). The use of higher temperatures can, in certain cases, shorten the time required for the preactivation and produce an additional increase in activity. In this case, a higher temperature means a range from 50 to 100°C.

The pre-activated solution or the mixture is then combined with an inert support material, usually silica gel, which is in the form of a dry powder or as a suspension in one of the aforementioned solvents.

- 5 Preference is given to using the support material as powder. The order of addition is immaterial. The preactivated metallocene co-catalyst solution or the metallocene co-catalyst mixture can be added to the support material or else the support material can be introduced to the solution.
- 10 The volume of the preactivated solution or the metallocene co-catalyst mixture can exceed 100% of the total pore volume of the support material used or else can be up to 100% of the total pore volume.

- The temperature at which the preactivated solution or the metallocene co-catalyst mixture is brought in contact with the support material can vary in the range from 0 to 15 100°C. Lower or higher temperatures are, however, also possible.

All or the major part of the solvent is subsequently removed from the supported catalyst system, whereby the mixture can be stirred and, if necessary, also heated.

- 20 Preference is given to removing both the visible portion of the solvent as well as the portion in the pores of the support material. The removal of the solvent can be carried out in a conventional fashion with application of vacuum and/or flushing with inert gas. In the drying process, the mixture can be heated until the free solvent has been removed, which usually takes from 1 to 3 hours at a preferred temperature of 25 from 30 to 60°C. The free solvent is the visible portion of solvent in the mixture. In this context, residual solvent is the portion which is enclosed in the pores. As an alternative to complete removal of the solvent, it is also possible for the supported catalyst system to be dried only to a particular residual solvent content, with the free solvent having been completely removed. The supported catalyst system can 30 subsequently be washed with a low-boiling hydrocarbon such as pentane or hexane and dried again.

The supported catalyst system can either be used directly for the polymerization of olefins or can be prepolymerized using one or more olefinic monomers prior to use in

a polymerization process. An example of the prepolymerization of supported catalyst systems is described in WO 94/28034.

5 A small amount of an olefin, preferably an α -olefin (for example vinyl cyclohexane, styrene or phenyldimethylvinylsilane) as modifying component or an anti-static can be added as additive during or after the preparation of the supported catalyst system. The molar ratio of additive to Metallocene components (compound according to Formula I) is preferably from 1:1000 to 1000:1, very particularly preferably from 1:20 to 20:1.

10

Another object of the invention is the use of the catalyst systems according to the invention, containing at least one compound according to Formula I and at least one co-catalyst to manufacture ultra high molecular weight ethylene homo- or co-polymers.

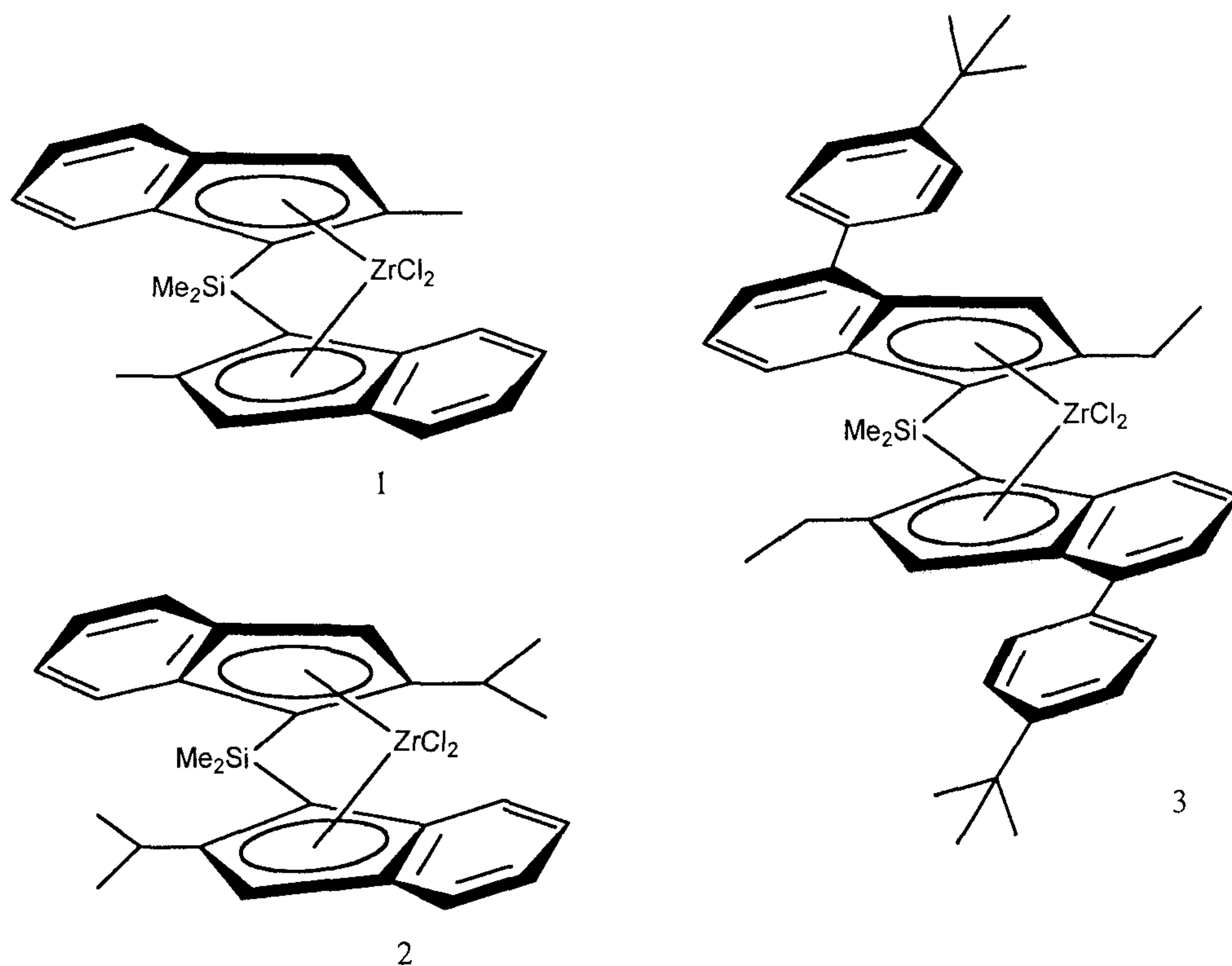
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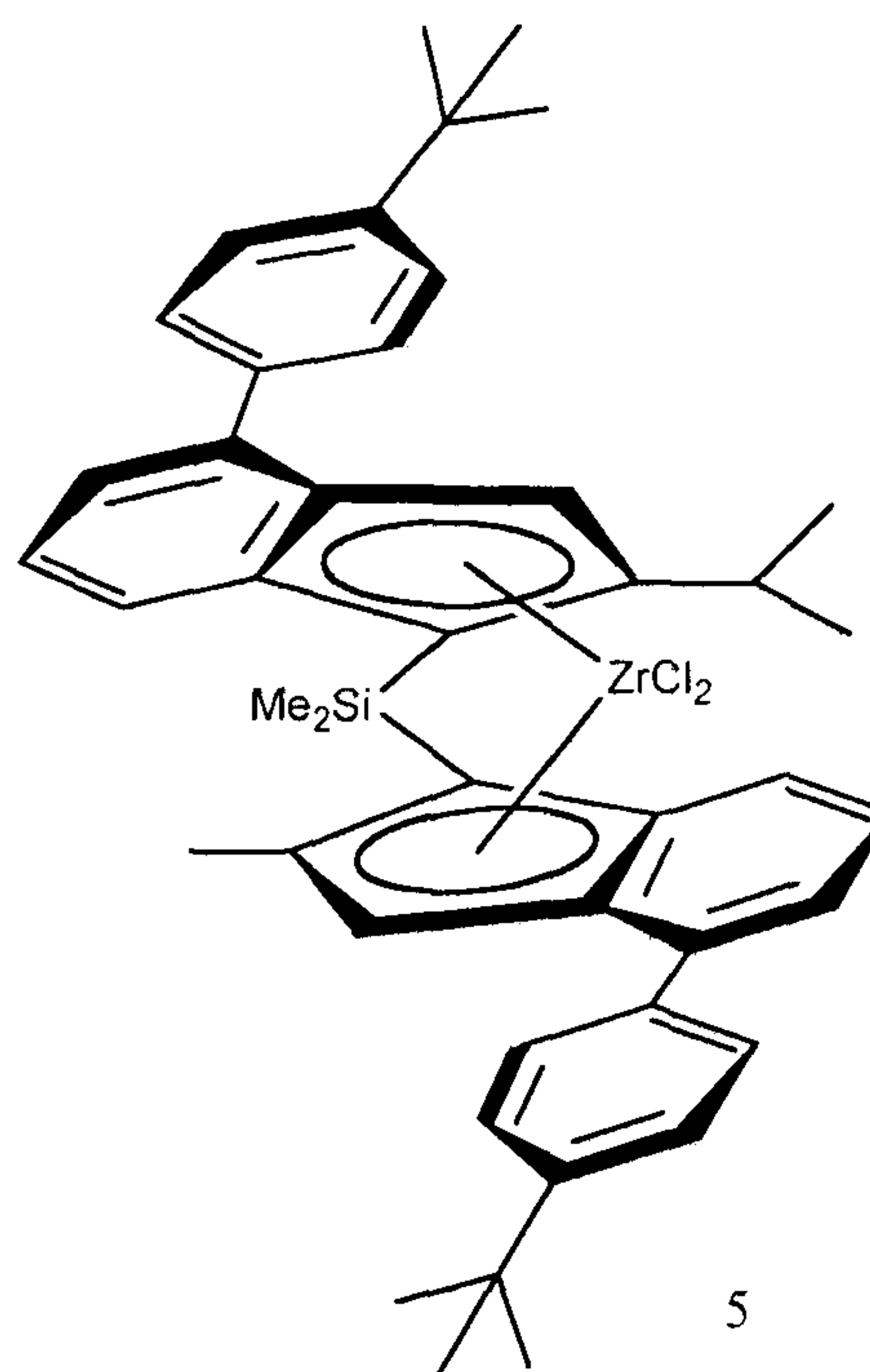
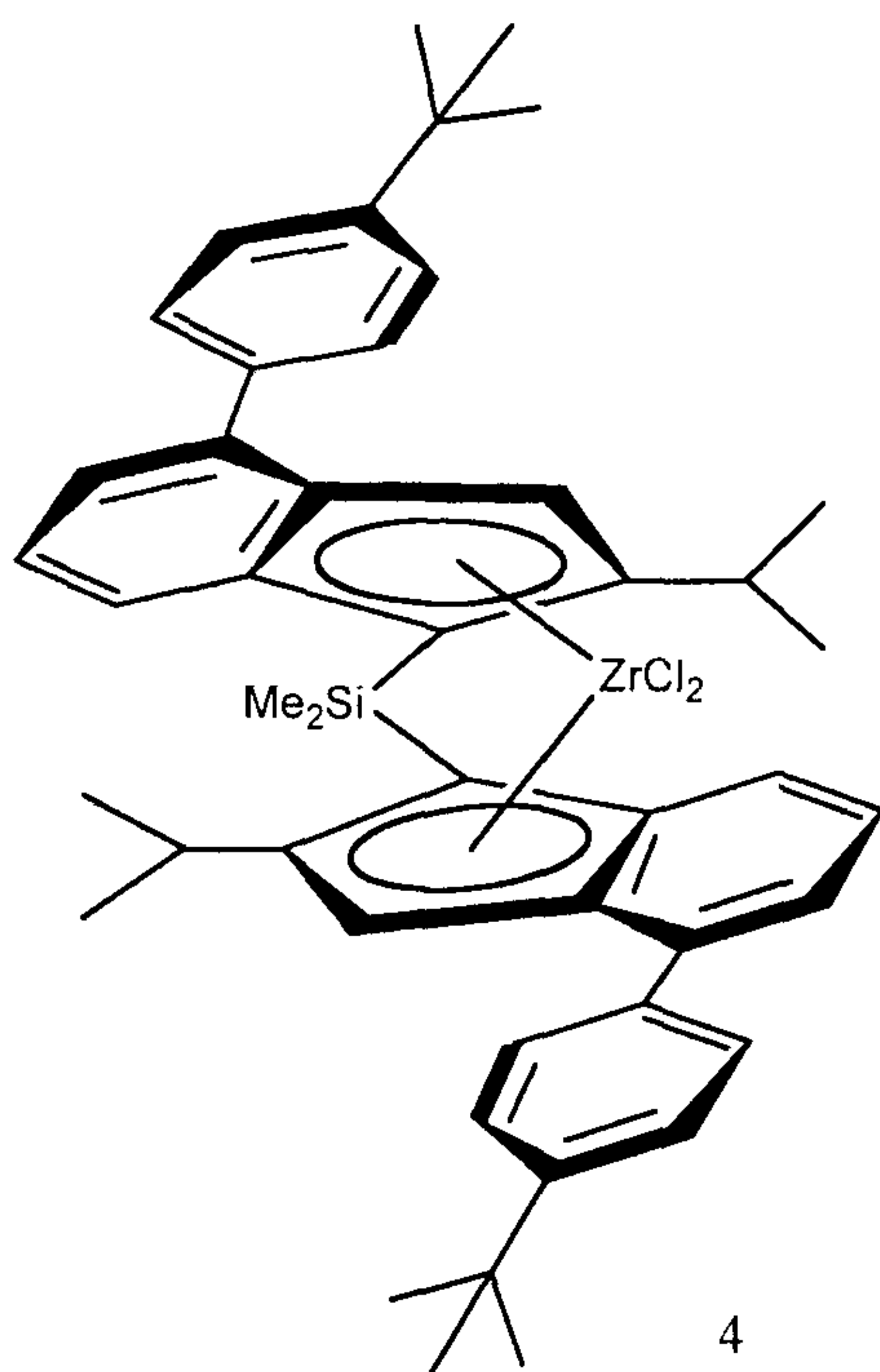
Particular preference is given to the catalyst system being present in supported form.

The invention is depicted through the following examples that, however do not limit the invention.

General information: preparation and handling of organometallic compounds were carried out in the absence of air and moisture under argon (Schlenk technique or glove box). All solvents required were purged with argon and dried over molecular sieves before use.

The following catalysts are used in the examples:





Example 1:

5 Depiction of the supported catalysts

1. Activation:

In an annealed flask under inert gas 0.128 mmol catalyst is dissolved in 20 ml toluene and mixed with 6 ml (28.8 mmol, 1.672 g) MAO (30% in toluene). The mixture is stirred for one hour at room temperature.

2. Supporting:

In an annealed flask under inert gas 6 g SiO₂ (Grace XPO 2107, dried) is placed and suspended with 30 ml abs. toluene. A suspension that can be slightly stirred results, to which the activated catalyst (from 1.) is then added. It is stirred for 10 min and then the solvent is removed in a vacuum to up to no more than 5% residual moisture.

Examples 2-6:

Homopolymerization of ethylene

20 In a 2 l steel autoclave 1.5 l Exxsol is placed and mixed with 15 mmol of an aluminum alkyl (e.g., tri-isobutylaluminum). The reactor is then brought to the desired temperature and an ethylene pressure of 7-15 bar is built up. At the start of

the polymerization 9 μmol of the relevant catalyst (see table 1) suspended in Exxsol is added. It is polymerized for one hour and the reaction is stopped when the ethylene pressure degrades. The polymer is filtered and dried in a vacuum at 80°C. Finally, the yield and the molecular weight are determined.

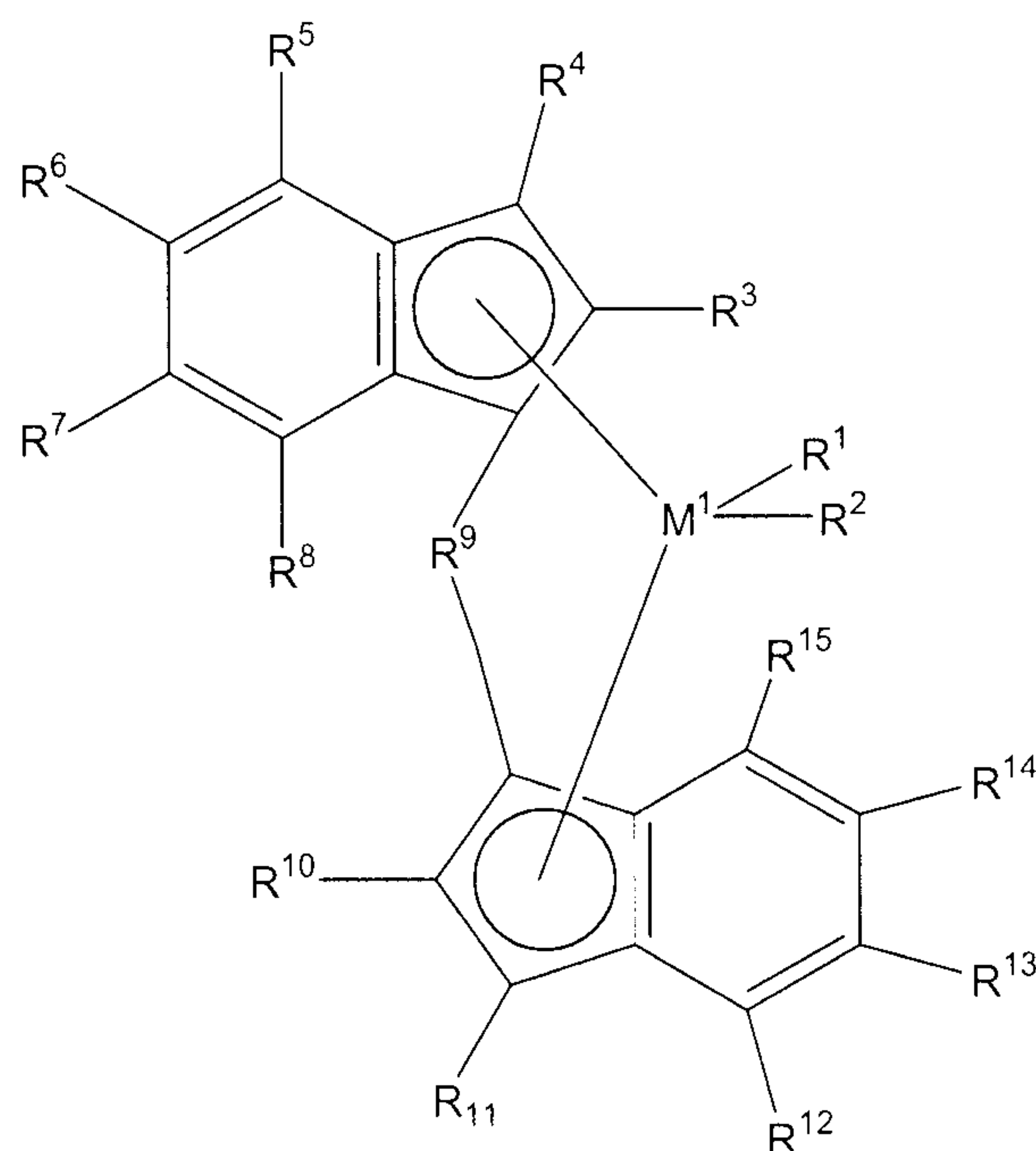
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Example	Catalyst	Pressure C2	Temperature	Yield	M_v
2 (comparison)	1	10 bar	70° C	70 g	0.7×10^6 g/mol
3	2	10 bar	70° C	61 g	2.2×10^6 g/mol
4	3	10 bar	70° C	64 g	1.1×10^6 g/mol
5	4	10 bar	70° C	98 g	1.8×10^6 g/mol
6	5	10 bar	70° C	114 g	2.7×10^6 g/mol

It therefore shows that ultra high molecular weight products are formed only when the bridged metallocene catalysts are used.

Patent Claims

1. Process to manufacture ultra high molecular weight olefin polymers comprising predominantly polyethylene, wherein the process comprises reacting ethylene in the presence of a catalyst system which includes a compound of Formula I to produce a polymer having a viscosimetrically determined molecular weight of greater than 1×10^6 g/mol



Formula I

whereby:

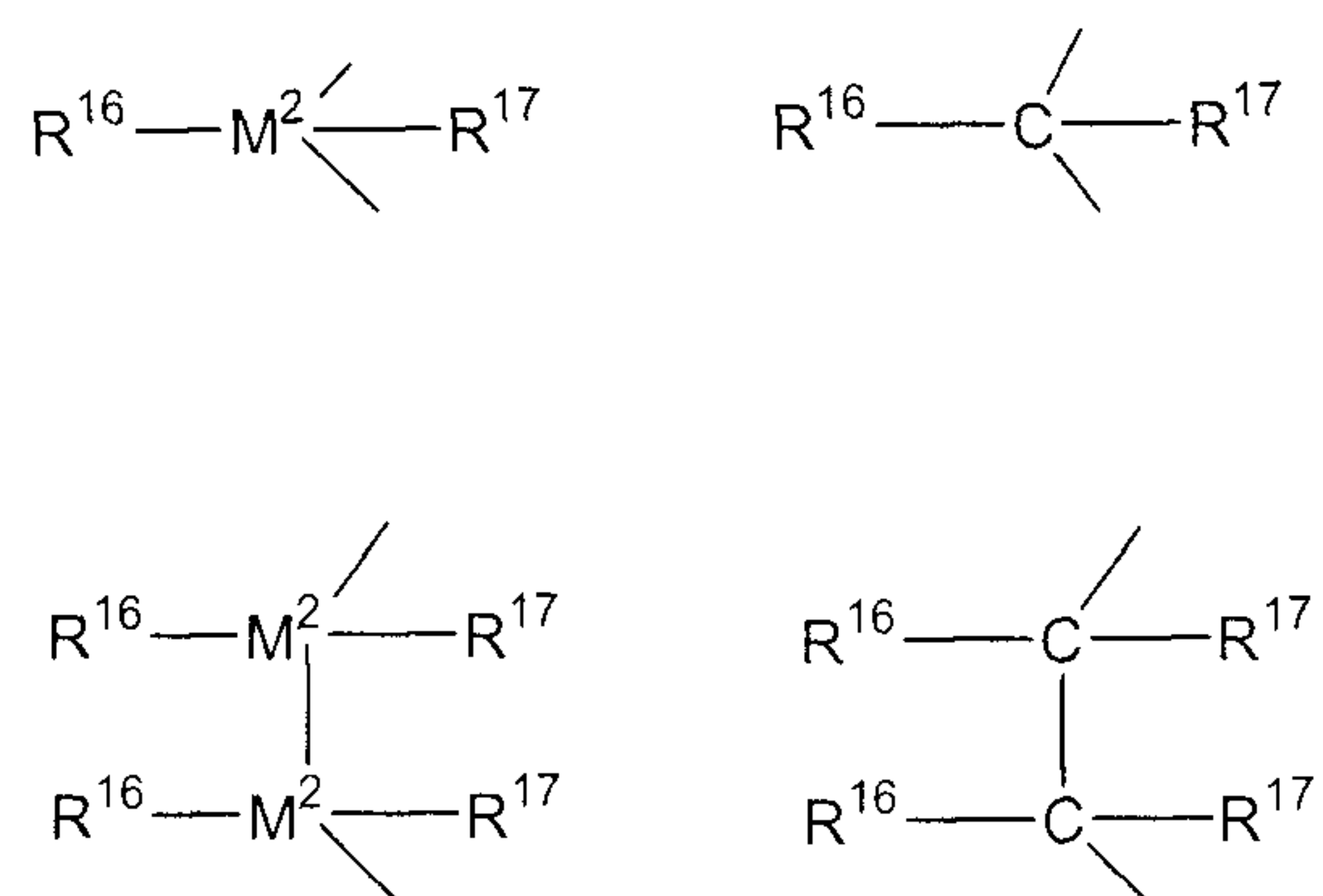
M^1 is a transition metal of the 3rd to 6th group of the periodic table, whose oxidation level does not equal zero; and

R^1 is equal to hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom; and

R^2 is equal to hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom; and

R^3 , R^{10} are each identical or different and are a C_1 - C_{20} carbonaceous group, provided that at least one radical R^3 or R^{10} is a C_2 - C_{20} carbonaceous group; and

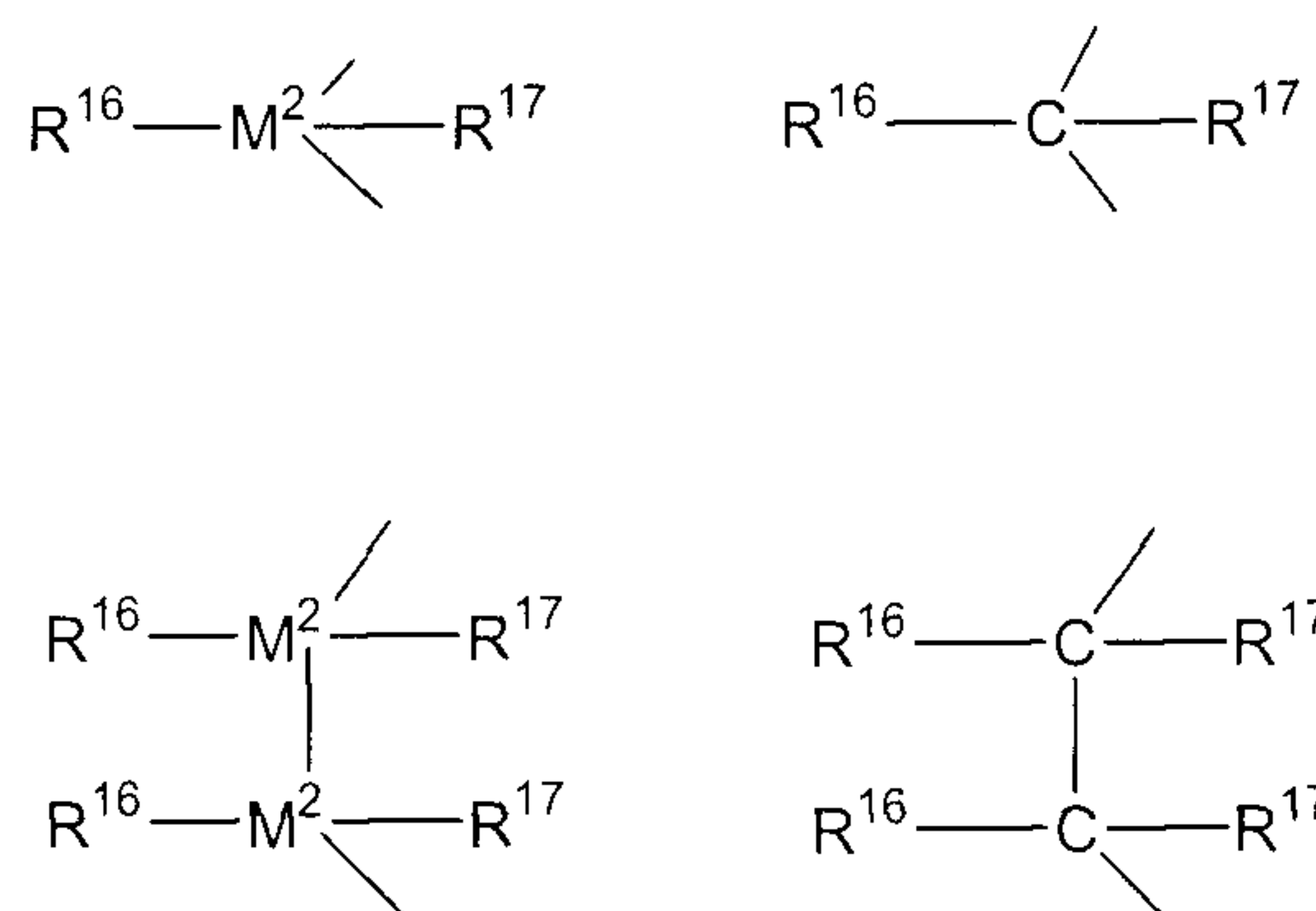
$R^4, R^5, R^6, R^7, R^8, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$ are each identical or different and are a hydrogen or a halogen atom or a C_1 - C_{20} carbonaceous group, whereby two or several consecutively can form a cyclic system; and R^9 forms a bridge between the ligands, which can be formed by the following formulae:



M^2 is either silicon, germanium or tin; and

R^{16}, R^{17} are each identical or different and are each hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom.

2. Process according to Claim 1, wherein the compound of Formula I:
 - M^1 is a transition metal of the 4th group of the periodic table, whose oxidation level does not equal zero; and
 - R^1 is hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom; and
 - R^2 is hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom; and
 - R^3 is a C_2 - C_{20} carbonaceous group; and
 - R^{10} is a C_1 - C_{10} carbonaceous group; and
 - $R^4, R^6, R^7, R^8, R^{11}, R^{13}, R^{14}, R^{15}$ are each hydrogen; and
 - R^5, R^{12} are each identical or different and are a C_1 - C_{20} carbonaceous group, of which two or several consecutively can form a cyclic system; and
 - R^9 forms a bridge between the ligands, which can be formed by the following formulae:



whereby:

M^2 is silicon; and

R^{16} , R^{17} are each identical or different and equal to hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom.

3. Process according to claim 2, wherein R^3 is cyclized in a α - or β -position or in an α - or β -position branched carbonaceous group.

4. Process according to Claim 1, wherein for the compound of Formula I:

M^1 is zirconium; and

R^1 , R^2 are identical and are each chlorine, methyl or phenolate; and

R^3 is an isopropyl-, isobutyl-, cyclopentyl-, cyclohexyl-, tert-butyl-, or a phenyl group;

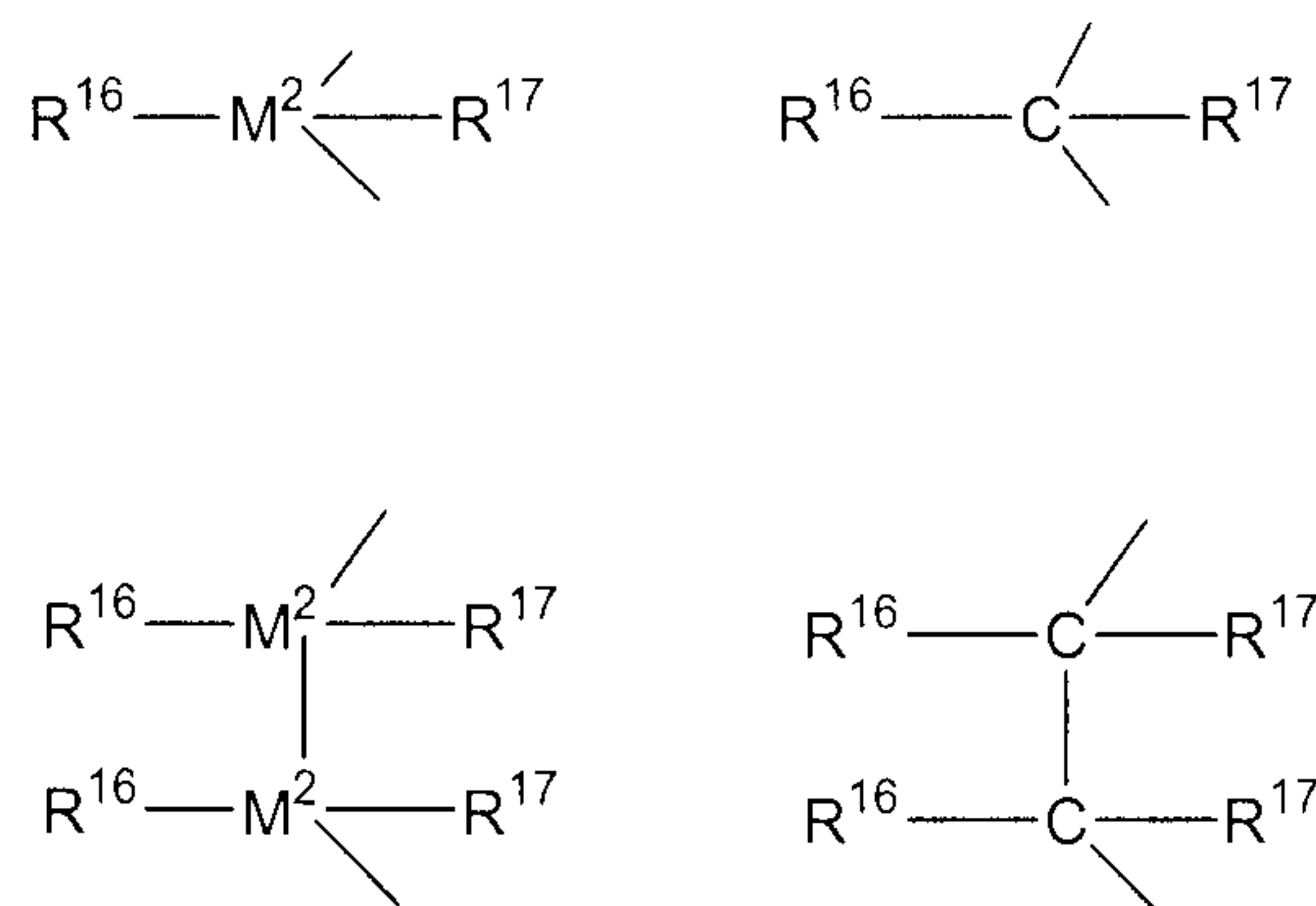
and

R^{10} is a C_1 - C_{10} carbonaceous group and is an alkyl group; and

R^4 , R^6 , R^7 , R^8 , R^{11} , R^{13} , R^{14} , R^{15} are each hydrogen; and

R^5 , R^{12} are identical and a phenyl group which supports a C_1 - C_4 -alkyl group in para position; and

R^9 forms a bridge between the ligands, which can be formed by the following formulae:



whereby:

M^2 is silicon; and

R^{16} , R^{17} are each identical or different and are hydrogen or a C_1 - C_{20} carbonaceous group or a halogen atom.

5. Process according to any one of Claims 1 to 4, whereby ethylene is used as olefin.
6. Process according to any one of claims 1 through 5, whereby the ethylene used contains one or more additional 1-olefins with 2-20 C atoms.
7. Process according to any one of claims 1 through 6, whereby the ethylene used is copolymerized with one or more 1-olefins selected from the group consisting of propene, 1-butene, 1-pentene, 1-hexene, styrene and butadiene.
8. Process according to any one of claims 1 through 7, whereby the ethylene used is homopolymerized or co-polymerized with propene.
9. Process according to any one of claims 1 through 8, whereby the ethylene used is homopolymerized.
10. Process according to any one of claims 1 through 9, whereby the catalyst system contains at least one co-catalyst.

11. Process according to claim 10, whereby the catalyst system contains at least one Lewis acid as co-catalyst.
12. Process according to any one of claims 1 through 11, whereby the compounds of Formula I used are used in the form of a supported catalyst system.
13. Process to produce a supported catalyst system, according to claim 12, comprising the steps:
- a) manufacture of a mixture of at least one compound of the Formula I and at least one co-catalyst in a suitable solvent or suspension medium;
 - b) applying the mixture obtained from Step a) on to a porous inorganic dehydrated support;
 - c) removal of the major portion of solvent from the resulting mixture;
 - d) isolation of the supported catalyst system; and optionally
 - e) prepolymerization of the supported catalyst system obtained with one or several olefin monomer(s) in order to obtain a prepolymerized supported catalyst system.
14. Use of a catalyst system containing at least one compound of Formula I according to claims 1 through 4 and at least one co-catalyst to produce ultra high molecular weight ethylene homo- or co-polymers.
15. The use according to claim 14, whereby the supported catalyst system is present.
16. The process according to claim 1, wherein M^1 is selected from the group consisting of Ti, Zr, Hf, V, Mo, Sc, Y, Cr and Nb.
17. The process according to claim 2 or 3, wherein M^1 is selected from the group consisting of Ti, Zr and Hf.

18. The process according to any one of claims 1 through 6, wherein the additional olefin is selected from the group consisting of propene, 1-butene, 1-pentene, 1-hexene, 1-decene, 4-methyl-1-pentene, 1-octene, styrene, 1,3-butadiene, 1,4-hexadiene, vinyl norbornene, norbornadiene, ethyl norbornadiene, norbornene, cyclopentadiene, tetracyclododecene, methylnorbornene and mixtures of same.

19. The process according to any one of claims 1 through 8, wherein the polyethylene is a copolymer and the comonomer fraction is 0.1 to 10%.