

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number
WO 03/000744 A1

- (51) International Patent Classification⁷: **C08F 4/60**, 10/00, C07F 7/18, 17/00
- (74) Agents: **CAMPBELL, Neil** et al.; Frank B. Dehn & Co., 179 Queen Victoria Street, London EC4V 4EL (GB).
- (21) International Application Number: PCT/GB02/02853
- (81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 21 June 2002 (21.06.2002)
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0115370.9 22 June 2001 (22.06.2001) GB
0117629.6 19 July 2001 (19.07.2001) GB
- (71) Applicant (*for all designated States except US*): **BOREALIS TECHNOLOGY OY** [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **EKHOLM, Peter** [FI/FI]; Petkeltie 8 C 62, FIN-20540 Turku (FI). **LUTTIKHEDDE, Hendrik** [NL/FI]; Intolantie 9, FIN-21260 Raisio (FI). **MAARANEN, Janne** [FI/FI]; Heisitie 1 B, FIN-04260 Kerava (FI). **PENNINKANGAS, Antti** [FI/FI]; Asentajankatu 4, FIN-20780 Kaarina (FI). **WILEN, Carl-Eric** [FI/FI]; Pihlajatertuntie 8 B, FIN-2940 Espoo (FI).
- Published:**
— *with international search report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 03/000744 A1

(54) Title: METALLOCENE CATALYSTS CONTAINING AN IDENYL MOIETY SUBSTITUTED AT THE 4-, 5-, 6- OR 7-POSITION BY A SILOXY OR GERMYLOXY GROUP

(57) Abstract: A metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenyloid moiety, characterised in that said moiety is directly or indirectly substituted at the 4-, 5-, 6- or 7-position by a pendant siloxy or germyloxy group.

METALLOCENE CATALYSTS CONTAINING AN INDENYL MOIETY SUBSTITUTED AT THE 4-, 5-, 6
- OR 7-POSITION BY A SILOXY OR GERMYLOXY GROUP

This invention relates to catalysts for olefin
5 polymerisation, in particular to catalysts which
comprise a metal bonded to a pentahapto (η^5)
cyclopentadienyl moiety, fused to at least one 6-
membered ring.

In olefin polymerizations, it has long been known
10 to use as a catalyst system the combination of a
metallocene procatalyst and an alumoxane co-catalyst or
catalyst activator.

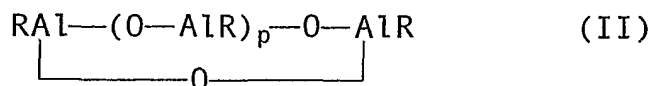
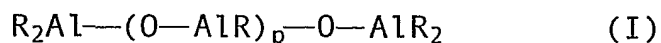
By "metallocene" is meant here a metal complex
which comprises at least one ligand complexed to a metal
15 and having a hapticity of 2 or greater, for example 2 to
5, especially 5. Metallocenes which comprise one or
more pentahapto (η^5) ligands, for example the
cyclopentadienyl ligand, have assumed greatest
importance and the subsequent discussion will focus
20 mainly on but is not limited to this subtype of
multihapto-containing metal-ligand complexes.

The metallocene may for example be a so-called
"open sandwich" or "half sandwich" compound in which the
metal is complexed by a single multihapto η^5 ligand; a
25 "sandwich" compound in which the metal is complexed by 2
or more such ligands; a "handcuff compound" in which the
metal is complexed by a bridged *bis*-multihapto ligand,
for example a *bis*- η^5 -ligand; or a "scorpionate compound"
in which the metal is complexed by a multihapto (e.g. η^5)
30 ligand bridged to a η^1 (for example a σ -bonded) ligand.

Metallocenes have been much used in the
copolymerization of olefins, especially ethylene,
propylene, other α -olefins and higher olefins, in the
presence of a co-catalyst/catalyst activator such as an
35 alumoxane.

Alumoxanes are compounds with alternating aluminium
and oxygen atoms, generally compounds of formula I or II

- 2 -



where each R, which may be the same or different, is a C₁₋₁₀ alkyl group, and p is an integer having a value between 0 and 40). These compounds may be prepared by reaction of an aluminium alkyl with water. The
 5 production and use of alumoxanes is described in the patent literature, especially the patent applications of Texas Alkyls, Albemarle, Ethyl, Phillips, Akzo Nobel, Exxon, Idemitsu Kosan, Witco, BASF and Mitsui.

Traditionally, the most widely used alumoxane is
 10 methylalumoxane (MAO), an alumoxane compound in which the R groups are methyl groups. MAO however is poorly characterised, appears to comprise a range of cage-like structures more complex than the simple linear or cyclic structures of formulae I and II, and is relatively
 15 expensive. Accordingly, efforts have been made to use alumoxanes other than MAO. Thus, for example WO98/32775 (Borealis) proposes the use of metallocene procatalysts with alumoxanes in which R is a C₂₋₁₀ alkyl group, e.g. hexaisobutylalumoxane (HIBAO).

20 The contents of WO98/32775 and all other publications referred to hereafter are hereby incorporated by reference.

Much effort has been expended into the development of improved metallocene-containing catalyst systems on
 25 account of the economic importance of olefin polymers. Of particular relevance are the investigations into indenyl-containing metallocenes in which the 5-membered cyclopentadienyl ring bonds in a η^5 fashion to the metal in the complex. For example WO 97/28170 (Borealis)
 30 discloses investigations into the substitution of the 5-membered ring of the indenyl moiety with alkoxy, siloxy and other groups. US Patent Nos. 5,672,668, 5,504,232 and 5,304,613 (all to Winter *et al.*) disclose, *inter*

5 *alia*, handcuff compounds or other metallocenes comprised of indenyl-based complexes, particularly those in which the 6-membered ring in the indenyl moiety is functionalised with one or more hydrocarbyl or halohydrocarbyl substituents.

US Patent No. 5,483,002 (to Seelert *et al.*) discloses similar types of *bis* indenyl-based metallocenes. Exemplary of such 5,6 fused systems is the indenyl system.

10 Chiral C₂-symmetric *bis*(indenyl) ansa-metallocenes are precursors to highly active catalysts for stereoselective polymerisation of alpha-olefins. The performance characteristics of these systems are different, the variations being induced by size and
15 position of the substituents. For example, dimethylsilylene bridged 2,2'-dimethyl-4,4'-diaryl substituted *bis*(indenyl) zirconocenes developed by Brintzinger and co-workers (*Organometallics* 1994, 13, 964) and Spaleck *et al.* (*Organometallics* 1994, 13, 954),
20 catalyse the production of isotactic polypropylenes with catalyst activities and polymer properties comparable to those obtained with heterogeneous Ziegler-Natta catalysts.

25 Research into electronically altered indenyl and *bis*(indenyl) metallocenes, however, has remained relatively sparse. So too are reports of electronically modified indenyloid and *bis*(indenyloid) ligands. As used herein, the term indenyloid is intended to embrace the general class of anions formed by the deprotonation
30 of any 5,6-fused system whereby to form a cyclopentadienyl η^5 ligand fused to a 6-membered ring. Indenyl itself may be considered as the parent indenyloid but will be referred to as indenyl here. The fluorenyl ligand is an example of an indenyloid ligand.

35 Previously, it has been reported that halogen or alkoxy substitution in the six-membered rings of indenenes reduces the activity of the catalyst system and the

molecular weight of the produced polymer (Consiglio *et al.*, *Organometallics* 1990, 9, 3098; Collins *et al.*, *Organometallics* 1992, 11, 2115). *Bis*(indenyl) zirconocenes with 2-amino functionalised ligands have
5 been reported by several groups (Luttikhedde *et al.*, *Organometallics* 1996, 15, 3092; Plenio and Burth, *J. Organomet. Chem.* 1996, 519, 269; Brintzinger *et al.*, *J. Organomet. Chem.* 1996, 520, 63). The bridged complexes show somewhat lower catalytic activities compared with
10 their unsubstituted *bis*(indenyl) zirconocene analogues.

WO 97/28170 (*supra*) does in some way address this neglected area. However, this publication addresses the issue of electronically modifying, by way of substitution, the 5-membered ring of indenyl and
15 indenylid compounds whereby to produce metallocene compounds in which an oxygen atom is directly bonded to the 2-position of a η^5 indenyl moiety.

However, there have been no reports of metallocenes in which the 6-membered ring of an indenyl or indenylid ring has been electronically modified by substitution by
20 a pendant heteroatom attached group at the 4- or 7-position (i.e. a position adjacent to an atom participating in both the 5- and 6-membered rings).

Surprisingly, however, it has been found that a
25 number of such compounds, *viz* metallocenes coordinated by a η^5 indenyl or indenylid moiety in which a 6-membered ring fused directly or indirectly to the 5-membered ring is substituted by a siloxy or germyloxy group, exhibit advantageous properties. These
30 complexes, when used as procatalysts in α -olefin polymerisation, allow the production of α -olefin homo or copolymers with notably higher molecular weight than achievable with analogous compounds in which the 6-membered ring is not substituted by a siloxy or
35 germyloxy group. Moreover the activity of these complexes in polymerisations is high, as measured by the quantity of polymer produced per unit time against the

quantity of metallocene used; and in copolymerisations, the complexes of the invention result in higher comonomer incorporation than do analogous compounds in which the 6-membered ring is not substituted by a siloxy or germyloxy group.

Viewed from one aspect, therefore the present invention provides a metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position, preferably the 4- or 7-position, by a pendant siloxy or germyloxy group.

As used herein the term metallocene catalyst is intended to embrace the actual catalytic species. This may be the metallocene compound itself or a metallocene procatalyst by which term is meant a compound which may be brought into a catalytically active state (e.g. for catalysis of α -olefin polymerization) by reaction with a co-catalyst or catalyst activator, e.g. an aluminium alkyl or other aluminium compound or a boron compound.

The metal will generally be a transition metal or lanthanide, especially a Group 3 (i.e. including scandium) to Group 7 (i.e. including manganese) transition metal, particularly a Group 4 to 6 metal, in particular Zr, Ti or Hf. For the avoidance of doubt, lanthanide metals herein include lanthanum itself.

Viewed from a further aspect, the invention provides an olefin polymerisation catalyst system comprising or produced by the reaction of:

(i) a metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group; and

(ii) a cocatalyst/catalyst activator, e.g. an

aluminium alkyl compound, in particular an alumoxane, especially an aluminum alkyl compound comprising alkyl groups containing from 1 to 6 carbon atoms.

Alternatively, said aluminum alkyl compound may be one which contains at least two carbon atoms.

Viewed from a still further aspect, the invention provides a process for olefin polymerisation comprising polymerising an olefin in the presence of a metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group.

Viewed from a yet another aspect, the invention provides a process for the preparation of a metallocene catalyst which comprises metallating a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety with a transition metal or lanthanide, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group.

Alternatively, it will be understood that the metallocene catalyst may be produced by the exchange of a metal ion in an existing metallocene for another metal ion through transmetallation.

Viewed from a different aspect, the invention provides an olefin polymer produced in a polymerisation process catalysed by an olefin polymerisation catalyst system comprising or produced by the reaction of

(i) a metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group; and

(ii) a cocatalyst/catalyst initiator, e.g. an aluminium alkyl compound, in particular an alumoxane,

especially an aluminum alkyl compound comprising alkyl groups containing from 1 to 6 carbon atoms.

Alternatively, said aluminum alkyl compound may be one which contains at least two carbon atoms.

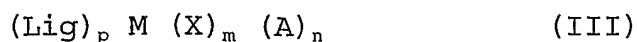
5 Viewed from an alternative aspect, the invention provides the use in olefin polymerisation of a metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said
10 moiety is directly or indirectly substituted at the 4-5-, 6- or 7-position by a pendant siloxy or germyloxy group.

By directly or indirectly is meant that the pendant siloxy or germyloxy group is either directly bonded to
15 one of the carbon atoms at position 4, 5, 6 or 7 (throughout this specification the numbering of carbon atoms is derived from the IUPAC numbering scheme for the indenyl ring) or is attached to one of these atoms, for example, by way of one or more intervening atoms, which
20 may form a fused ring.

For the avoidance of doubt, however, the invention does not relate to metallocene catalysts containing only η^5 cyclopentadienyl ligands which form part of an indenyl or indenylid moiety which contain only one or more
25 directly bonded siloxy or germyloxy substituents at the 1-, 2- or 3- positions and no other siloxy or germyloxy substituents elsewhere.

Thus the catalyst of the invention may for example be a compound of formula (III):

30



in which:

M is a transition metal ion or a lanthanide metal
35 ion;

p is 1 or 2;

m is greater than or equal to 0;

n is greater than or equal to 0;

n+m is equal to the valency of the metal not satisfied by ligand or ligands Lig;

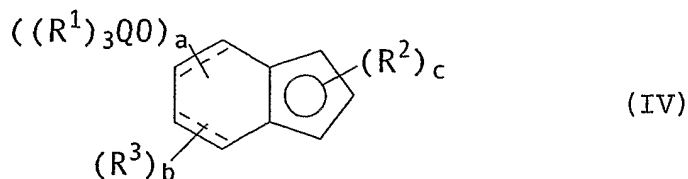
5 X is a ligand which co-ordinates to M (for example a η^5 hydrocarbyl, η^1 hydrocarbyl, halo, hydrocarbyl amino or hydrocarbyl amido ligand);

A is a σ -ligand as defined hereinafter; and

10 each ligand Lig which may be the same or different is a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenyloid moiety, characterised in that said moiety is directly or indirectly substituted at the 4-5-, 6- or 7-position by a pendant siloxy or germyloxy group, for example (Lig)_p, may be one or two of ligands In as defined hereafter.

15 M in the metallocene catalysts of the invention is preferably a group 4 to 6 transition metal, e.g. a metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. However, the metal is preferably Cr, Ti, Zr or Hf, particularly Cr if M is liganded by a single multihapto group or Ti, Zr or Hf if M is η -liganded by one or more multihapto groups.

20 Useful indenyl or indenyloid ligands according to the invention may be represented by symbol "In" wherein In consists of a negatively charged indenyl or indenyloid moiety of the following formula (IV):



wherein one or more of the ring carbon atoms may be replaced by a ring heteroatom;

each Q is either a silicon or a germanium atom;

35 either or both of the bonds shown as ----- may be present or absent;

each R¹ which may be the same or different is a

hydrogen or a C₁₋₂₀ hydrocarbyl especially an alkenyl or alkyl group, especially a C₁₋₈ group, or a η^1 ligand (for example a σ ligand such as a nitrogen-containing group such as amine, at least one R¹ being other than hydrogen;

5 each R² may be hydrogen or a group bonded to the 5-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC) carbon, oxygen, silicon, germanium, nitrogen or sulfur, e.g. C₁₋₂₀ hydrocarbyl, hydrocarbyl siloxy, hydrocarbyloxy,

10 hydrocarbylgermyloxy, hydrocarbyl silyl or hydrocarbylgermyl group particularly an oxygen-, silicon-, germanium- or sulfur-attached hydrocarbyl group;

15 each R³ may be hydrogen or a group bonded to the 6-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC) carbon, oxygen, silicon, germanium, nitrogen or sulfur, e.g. C₁₋₂₀ hydrocarbyl, hydrocarbyl siloxy, hydrocarbyloxy,

20 hydrocarbylgermyloxy, hydrocarbyl silyl or hydrocarbylgermyl group particularly an oxygen-, silicon-, germanium- or sulfur-attached hydrocarbyl group; or

two or more R² and/or two or more R³ groups attached to adjacent ring atoms on the same ring together form a
25 5- to 8-membered fused ring; and optionally

one R² or R³ is -L-Z wherein L is a 1 to 4 atom chain and Z is a second moiety, which may be the same as or different to said first moiety, preferably of formula (IV) and joined to L through one R² or R³, if present in
30 which L is one and the same chain common to both moieties,

a is an integer between 1 and 3,

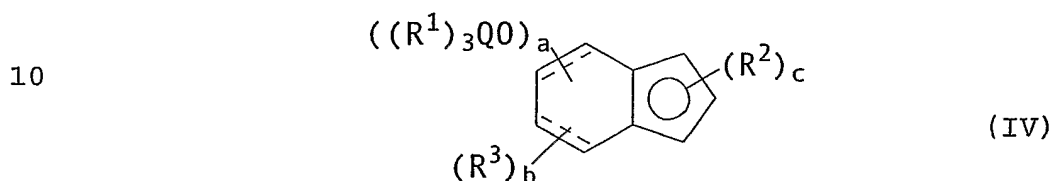
b is an integer between 1 and 3, the sum of a and b being no more than 4,

35 c is an integer between 1 and 3,

with the proviso that no more than one -L-Z group is present in each ligand In.

Preferably L-Z where present is attached to the 5-membered ring, especially at the 1- or 3-positions or less preferably to the 6-membered ring at the 4- or 7 positions.

5 The ligands in themselves are novel and form a further aspect of the invention. Viewed from this aspect, therefore, there is provided a ligand of formula (IV)



(wherein one or more of the ring carbon atoms may
15 be replaced by a ring heteroatom;

each Q is either a silicon or a germanium atom;

either or both of the bonds shown as ----- may be present or absent;

20 each R¹ which may be the same or different is a hydrogen or a C₁₋₂₀ hydrocarbyl especially an alkenyl or alkyl group, especially a C₁₋₈ group, or a η¹ ligand (for example a σ ligand such as a nitrogen-containing group such as amine, at least one R¹ being other than hydrogen;

25 each R² may be hydrogen or a group bonded to the 5-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC) carbon, oxygen, silicon, germanium, nitrogen or sulfur, e.g. C₁₋₂₀ hydrocarbyl, hydrocarbyl siloxy, hydrocarbyloxy, hydrocarbylgermyloxy, hydrocarbyl silyl or
30 hydrocarbylgermyl group particularly an oxygen-, silicon-, germanium- or sulfur-attached hydrocarbyl group;

35 each R³ may be hydrogen or a group bonded to the 6-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC) carbon, oxygen, silicon, germanium, nitrogen or sulfur, e.g. C₁₋₂₀ hydrocarbyl, hydrocarbyl siloxy, hydrocarbyloxy,

hydrocarbylgermyloxy, hydrocarbyl silyl or hydrocarbylgermyl group particularly an oxygen-, silicon-, germanium- or sulfur-attached hydrocarbyl group; or

5 two or more R^2 and/or two or more R^3 groups attached to adjacent ring atoms on the same ring together form a 5- to 8-membered fused ring; and optionally

one R^2 or R^3 is -L-Z wherein L is a 1 to 4 atom chain and Z is a second moiety, which may be the same as or
10 different to said first moiety, preferably of formula (IV) and joined to L through one R^2 or R^3 , if present in which L is one and the same chain common to both moieties,

a is an integer between 1 and 3,

15 b is an integer between 1 and 3, the sum of a and b being no more than 4,

c is an integer between 1 and 3,

with the proviso that no more than one -L-Z group is present in each ligand In) and salts and complexes
20 thereof.

For the avoidance of doubt, ligands In include homocyclic or heterocyclic indenyl/indenyloid moieties which may be optionally fused to other rings.

By fused or non-fused is meant that the indenyl or
25 indenyloid ligand may have two carbon or heteroatoms also forming part of an additional ring which may itself be fused or an optionally substituted carbocyclic or heterocyclic ring etc. For example the fluorenyl ring is embraced by this invention.

30 By homo- or heterocyclic is meant that any ring of the indenyl ligand or indenyloid ligand may have only carbon ring atoms (i.e. homo or isocyclic) or may have ring atoms other than carbon (heterocyclic). Such ring heteroatoms may for example be, independently from each
35 other, N, S, Se, O, P, B or Si.

The variables a, b and c are all preferably 1 or 2, especially 1.

Preferred ligands In are those in which at least one group of formula $-OQ(R^1)_3$ is a siloxy or germyloxy group directly attached to the 4-position or the 7-position or indirectly attached to the 4-, 5-, 6- or 7-
5 position. Also preferred are ligands In in which one or more of said moiety or moieties of formula (IV) contain 2 groups of formula $(R^1)_3QO-$, for example one such group at position 4 and one at position 7 in the indenyl or indenyloid ring.

10 In one embodiment, one of the groups R^1 is an amine, e.g. alkylamine, bound to the Si or Ge atom via a carbon atom of said amine, wherein the nitrogen atom acts as a σ -ligand coordinating any metal ion present. In such an embodiment it is preferred if L-Z is absent.

15 Especially preferably ligands of In are those in which one group R^2 is of formula $-L-Z$. Particularly preferred are those in which $-L-Z$ is present at the 1-position and/or in which Z is another moiety of formula (IV), preferably attached to L through an R^2 group.

20 In ligands In, including those preferred types as described herein, L is preferably of formula $(C(R^2)_2)_q$ or $Si(R^2)_2$ in which q is one or 2 or more and R^2 is as hereinbefore defined but may not represent a group L-Z but is preferably hydrogen or a hydrocarbyl group.

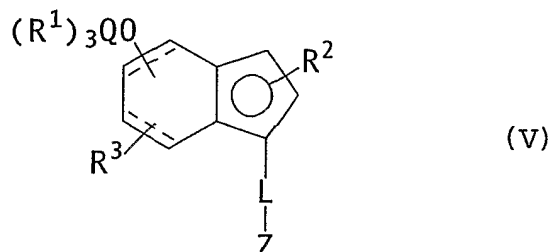
25 Compounds of formula (III) are preferably of formula $(Lig)_2M(A)_n$ wherein M, A and n are as hereinbefore defined; and $(Lig)_2$ is a ligand In in which one group R^2 in said first moiety of formula (IV) is $-L-Z$, where L is preferably of formula $(CR^2)_2$, $((CR^2)_2)_2$ or
30 $Si(R^2)_2$ in which R^2 is as hereinbefore defined but is preferably hydrogen or a hydrocarbyl group and Z is a second moiety preferably of formula (IV) which may or may not be the same as the first moiety of formula (IV) with the proviso that L is attached to the 1-position in
35 said second moiety of formula (IV).

Preferably, in the moiety or moieties of formula (IV) of ligands In there is no other substitution other

than the substituents $\text{OQ}(\text{R}^1)_3$ and R^2 ; i.e. $\text{R}^3 = \text{H}$.

Particularly preferred ligands In used according to the various aspects of the present invention are those of formula (V)

5



10

(wherein R^1 , R^2 , R^3 , Q and L-Z are as hereinbefore defined).

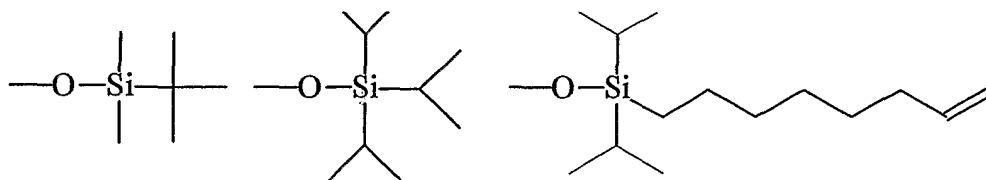
15

Preferably in ligands In, L is preferably of formula $(\text{C}(\text{R}^2)_2)_2$ or $\text{Si}(\text{R}^2)_2$ in which R^2 is as hereinbefore defined (but is not L-Z) and is preferably hydrogen or a hydrocarbyl group, for example methyl.

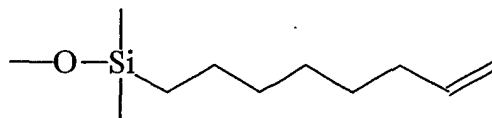
20

Examples of suitable $(\text{R}^1)_3\text{QO}$ groups wherein Q = Si in the metallocene procatalysts of the invention include:

25

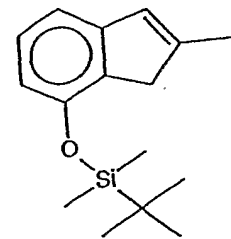
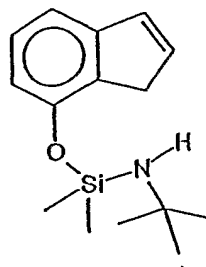
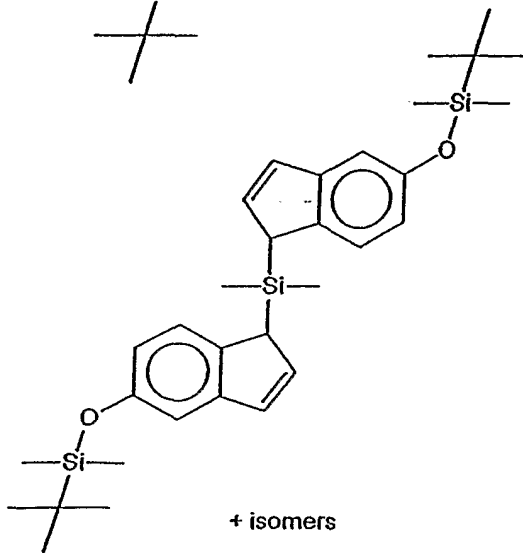
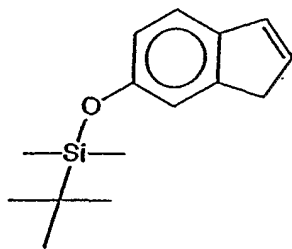
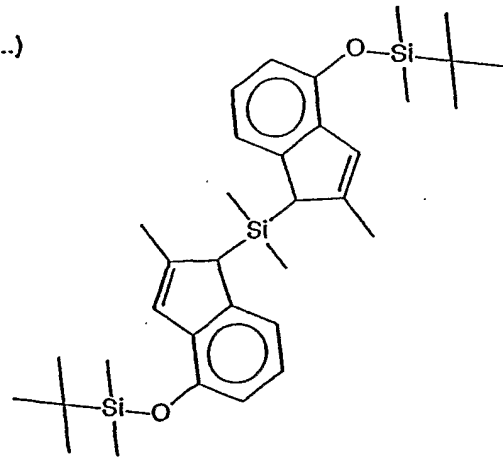
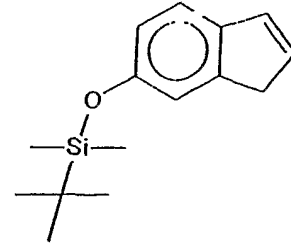
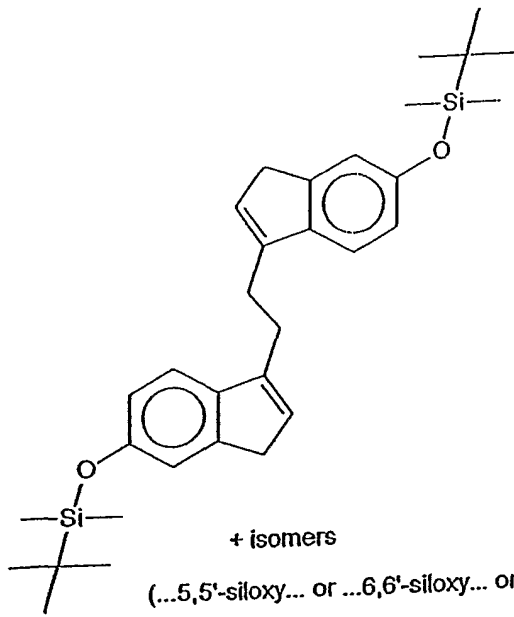


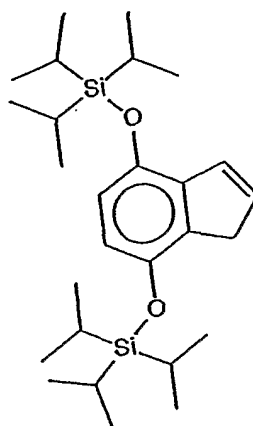
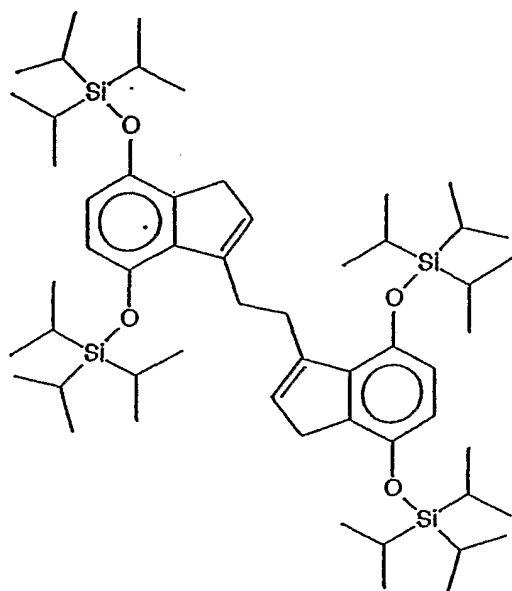
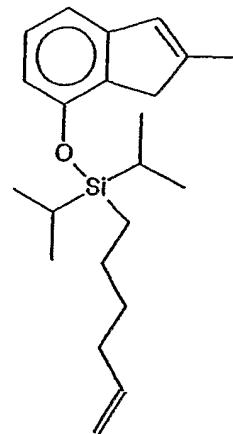
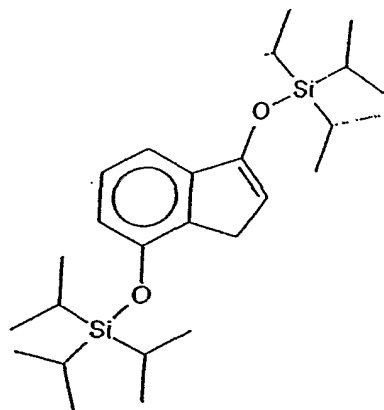
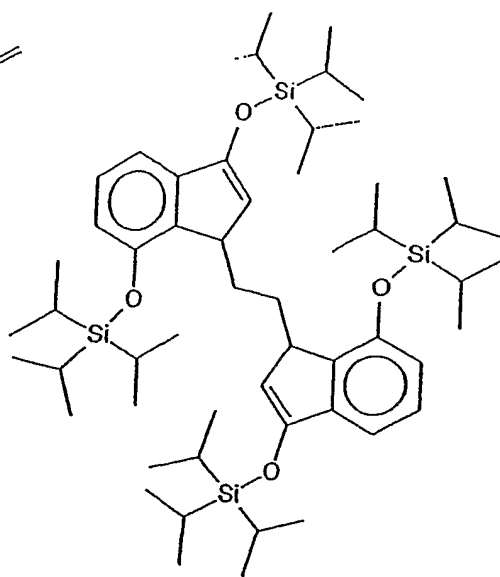
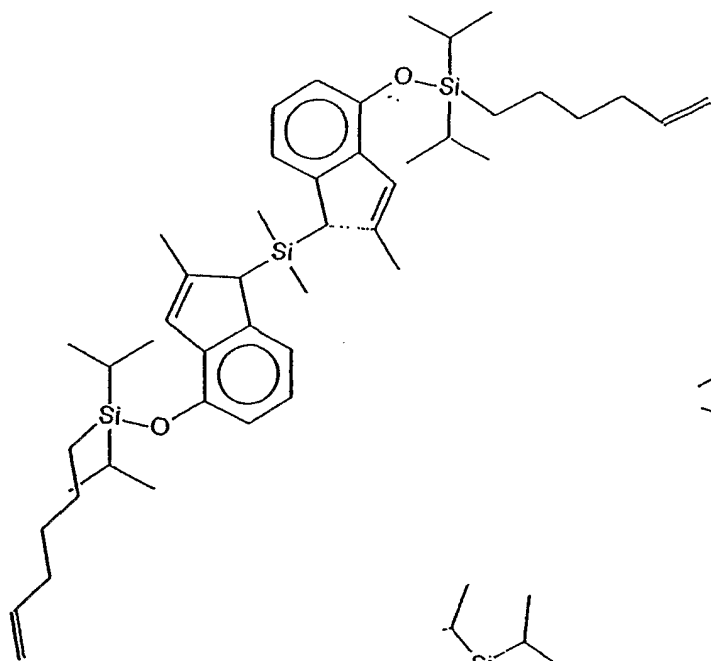
and



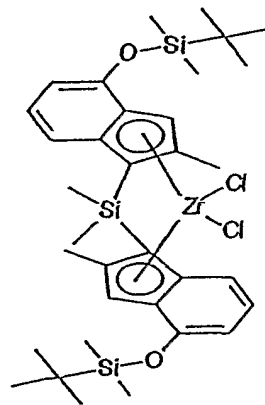
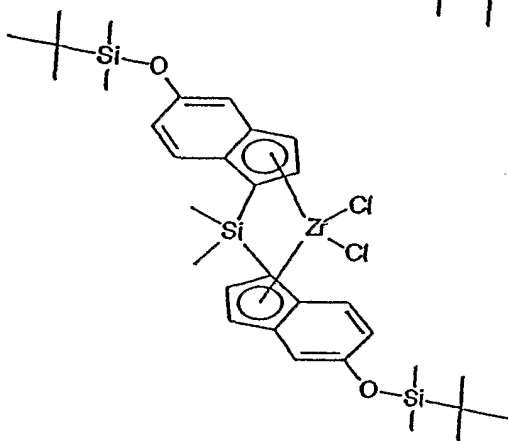
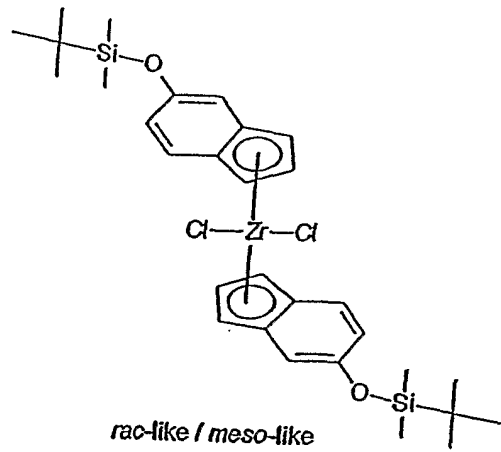
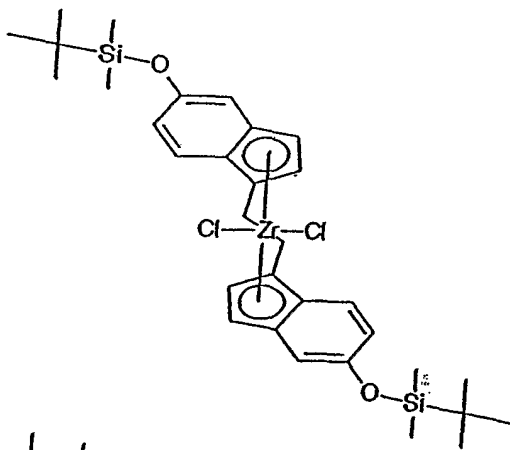
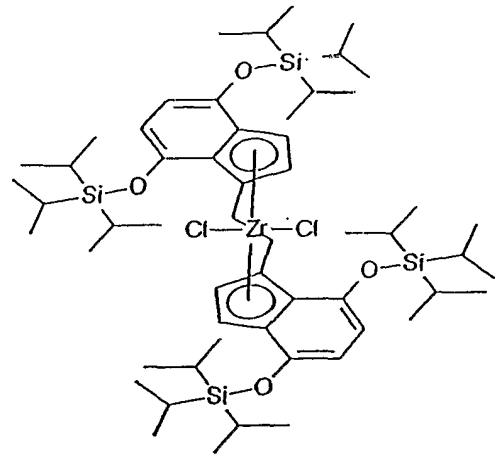
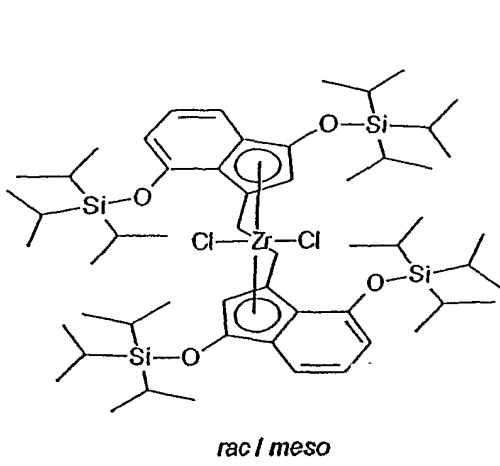
30

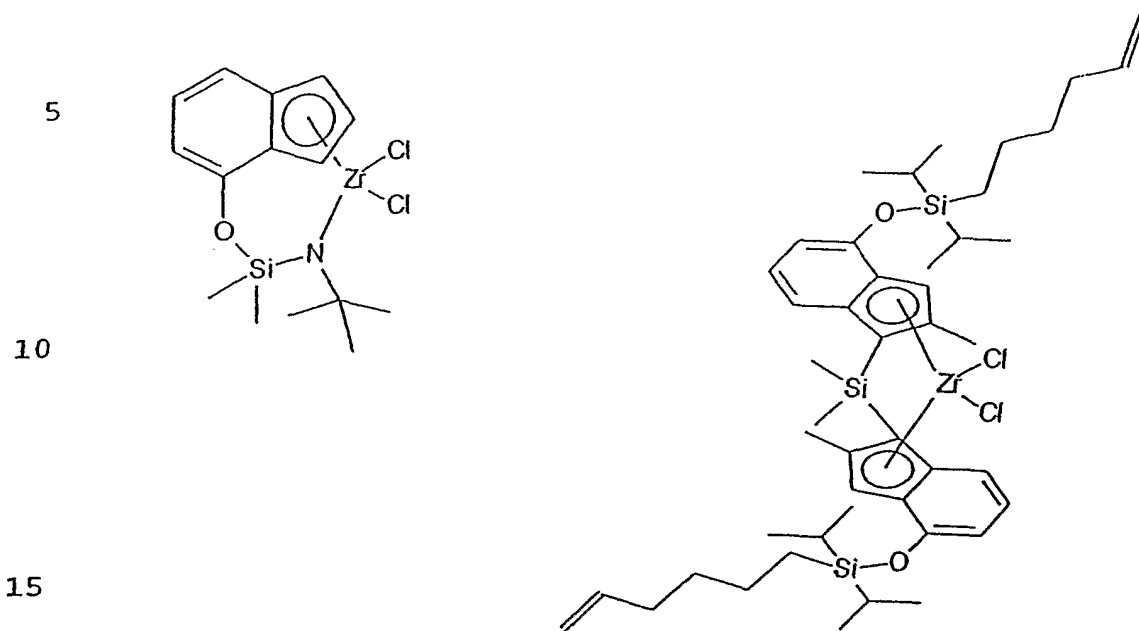
Thus typical examples of ligands of formula In include mono or bisanions of the following mono and bridged bis indenenes:





Typical examples of the metallocene catalysts of the invention thus include:





Examples of particular further η -ligands are well known from the technical and patent literature relating to metallocene olefin polymerization catalysts, e.g. EP-A-35242 (BASF), EP-A-129368 (Exxon), EP-A-206794 (Exxon),

25 WO 97/28170 (Borealis), EP-A-318048, EP-A-643084, EP-A-69951, EP-A-410734, EP-A-128045, EP-B-35242 (BASF), EP-B-129368 (Exxon) and EP-B-206794 (Exxon). These include

30 cyclopentadienyl,
 indenyl,
 fluorenyl,
 octahydrofluorenyl,
 methylcyclopentadienyl,
 35 1,2-dimethylcyclopentadienyl,
 pentamethylcyclopentadienyl,
 pentyl-cyclopentadienyl,

2-dimethyl,tertbutylsiloxy-inden-1-yl,
n-butylcyclopentadienyl,
1,3-dimethylcyclopentadienyl,
4,7-dimethylindenyl,
5 1,-ethyl-2-methylcyclopentadienyl,
tetrahydroindenyl, and
methoxycyclopentadienyl.

By a σ -ligand moiety is meant a group bonded to the
10 metal at one or more places via a single atom, eg a
hydrogen, halogen, silicon, carbon, oxygen, sulphur or
nitrogen atom. Examples of such ligands include:

halogenides (e.g. chloride and fluoride),
15 hydrogen,
triC₁₋₁₂ hydrocarbyl-silyl or -siloxy (e.g.
trimethylsilyl),
triC₁₋₆ hydrocarbylphosphimido (e.g.
triisopropylphosphimido),
20 C₁₋₁₂ hydrocarbyl or hydrocarbyloxy (e.g. methyl, ethyl,
phenyl, benzyl and methoxy),
diC₁₋₆ hydrocarbylamido (e.g. dimethylamido and
diethylamido), and
5 to 7 ring membered heterocyclyl (e.g. pyrrolyl,
25 furanyl and pyrrolidinyl).

The siloxy or germyloxy indenyl or indenylid
ligands used according to the various aspects of the
invention may be prepared by any convenient means, for
30 example by reaction of a corresponding indanone, or
analogue thereof (for example a 9-fluorenone) in which a
6-membered ring fused to the 5-membered ring is directly
or indirectly substituted with a hydroxyl group. Such
compounds (e.g. 2-hydroxy-9-fluorenone and 4- and 5-
35 hydroxy-indanone, which may be purchased from Aldrich)
are commercially available. Alternatively, appropriate
hydroxy-substituted indenenes or other polycyclic

structures containing the indene skeleton and with one or more appropriate hydroxyl groups, may be used as starting materials.

5 These starting materials may be reacted with a compound of formula $(R^1)_3QHal$ wherein R^1 and Q are as defined above and Hal is an appropriate halide, for example chloride, bromide or iodide (chloride being preferred) in a suitable solvent, for example *N,N*-dimethyl formamide (DMF) or dichloromethane.

10 Covalent catalysis may be used to assist in such reactions, e.g. effective quantities of triethylamine, 1,8-diazobicyclo[5,6,0]undec-7-ene (DBU) or imidazole may be employed.

15 Where the starting materials comprise more than one hydroxyl group such reactions permit the formation of mono- or bis-substituted siloxy or germyloxy compounds. Moreover, it is also possible to react an appropriate starting indanone, for example 4-hydroxy-indan-1-one with two equivalents of compound of formula $(R^1)_3QHal$,
20 which may or may not be the same, to afford the corresponding bis ether of 1,4-dihydroxy-ind-1-ene through trapping of the enol tautomer.

The appropriate siloxy or germyloxy compounds may then be converted by, for example, a two-step process
25 involving converting the indanone into a hydrazone (e.g. by reaction with tosyl hydrazine), in the presence of an effective amount of sulfuric acid in methanol; followed by reaction of the so-formed hydrazone with an appropriate base, e.g. an organolithium compound, such
30 as methyllithium or butyllithium. The parent reaction here is commonly known as the Shapiro reaction. Particular bases of use in this regard include *t*-BuLi, *n*-BuLi, lithium diisopropylamide, *t*-BuOK, trialkylamines, dialkyl-magnesium, alkylmagnesium
35 chloride, alkyl CuLi and dialkyl zinc which may be used in conjunction with a suitable solvent. If necessary, a donor such as dimethoxyethane may be added to the

reaction medium containing the hydrazone prior to addition of the base.

Alternatively, the keto group in the indanone may simply be reduced under standard conditions (e.g. sodium borohydride in methanol and/or tetrahydrofuran (THF)) followed by dehydration to form the desired indene or indene skeleton-containing compound.

If the formation of a *bisindenyl* or *bisindenyl*oid ligand (i.e. a "handcuff" ligand as herein before defined) is desirable, two equivalents (which may or may not be the same) of 1*H*- or 3*H*-indene etc. may be reacted with an appropriate base, e.g. an organolithium compound, such as methyl lithium or butyllithium. Particular bases and solvents of use in this regard are as hereinbefore defined. If necessary, a donor such as dimethoxyethane may be added to the reaction medium containing the appropriate 1*H*- or 3*H*-indene etc. prior to addition of the base.

The anion or anions, as appropriate, may be reacted with a molecule of formula LG_1-L-LG_2 (wherein L is as hereinbefore defined and LG_1 and LG_2 represent any appropriate leaving groups which may or may not be the same, for example bromide, tosyl, chloride etc., whereby to form the desired *bisindenyl* ligand. Alternatively, a "handcuff" ligand may be formed by a two step process in which one equivalent of a first indenyl anion is reacted with one equivalent of LG_1-L-LG_2 and the resultant indene or equivalent molecule substituted with $-L-LG_2$ may be reacted with a second molecule anion whereby to form the desired *bis indenyl/bis indenyl*oid ligand.

Alternatively, wherein R^3 is of formula $-L-Z$, the indenyl to indenyl bridging may be achieved using the methods disclosed in WO96/38458 (Montell).

Formation of the desired metallocene is effected by reacting the desired ligand with an appropriate quantity of base, e.g. an organolithium compound, such as methyl lithium or butyllithium (i.e. where formation of a

mono η^5 ligand is desired, one equivalent of base is used and where a *bisindenyl* ligand is being used (i.e. a *bis* η^5 ligand) two equivalents of base may be used.

Particular bases and solvents of use in this regard are as hereinbefore defined. If necessary, a donor such as dimethoxyethane may be added to the reaction medium containing the appropriate 1*H* or 3*H* indene etc. prior to addition of the base.

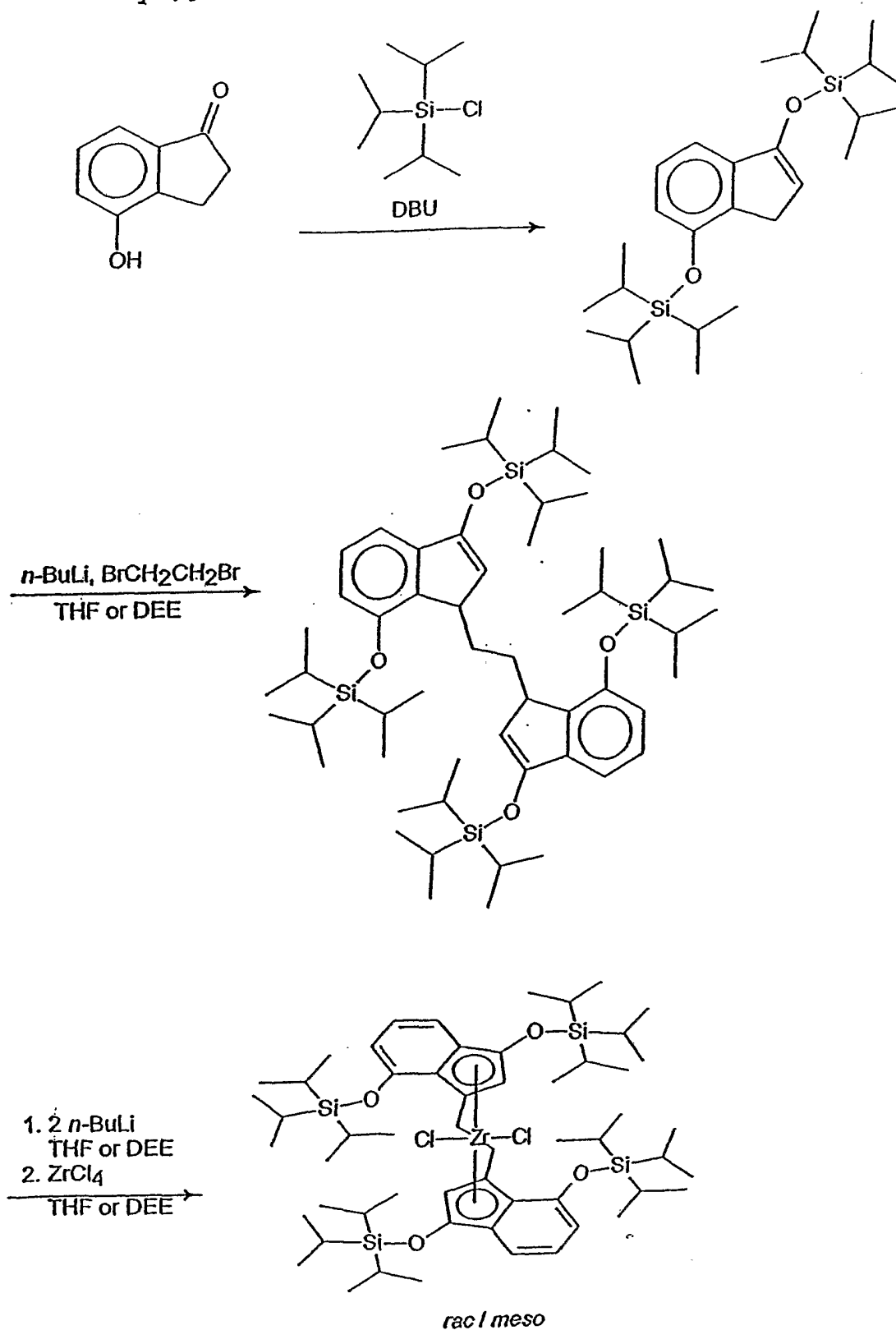
The ligand can be metallated conventionally, e.g. by reaction with a halide of the metal M, preferably in an organic solvent, e.g. a hydrocarbon or a hydrocarbon/ether mixture. Bridged siloxy- or germyloxy cyclopentadienyl ligands may be constructed by reacting a siloxy- or germyloxy monocyclopentadienyl ligand with a bridging agent (e.g. $\text{Si}(\text{CH}_3)_2\text{Cl}_2$) or with a bridging agent and a further η -ligand (e.g. a different cyclopentadienyl ligand or with an indenyl, fluorenyl, etc ligand).

An alternative approach to the complexes is also envisaged where the siloxycyclopentadiene is reacted with $\text{Zr}(\text{NMe}_2)_4$ or $\text{Zr}(\text{CH}_2\text{Ph})_4$ followed by Me_3SiCl to yield the complex directly. Also, trimethylsilyl (siloxy) cyclopentadiene reacts with ZrCl_4 to afford the complex directly.

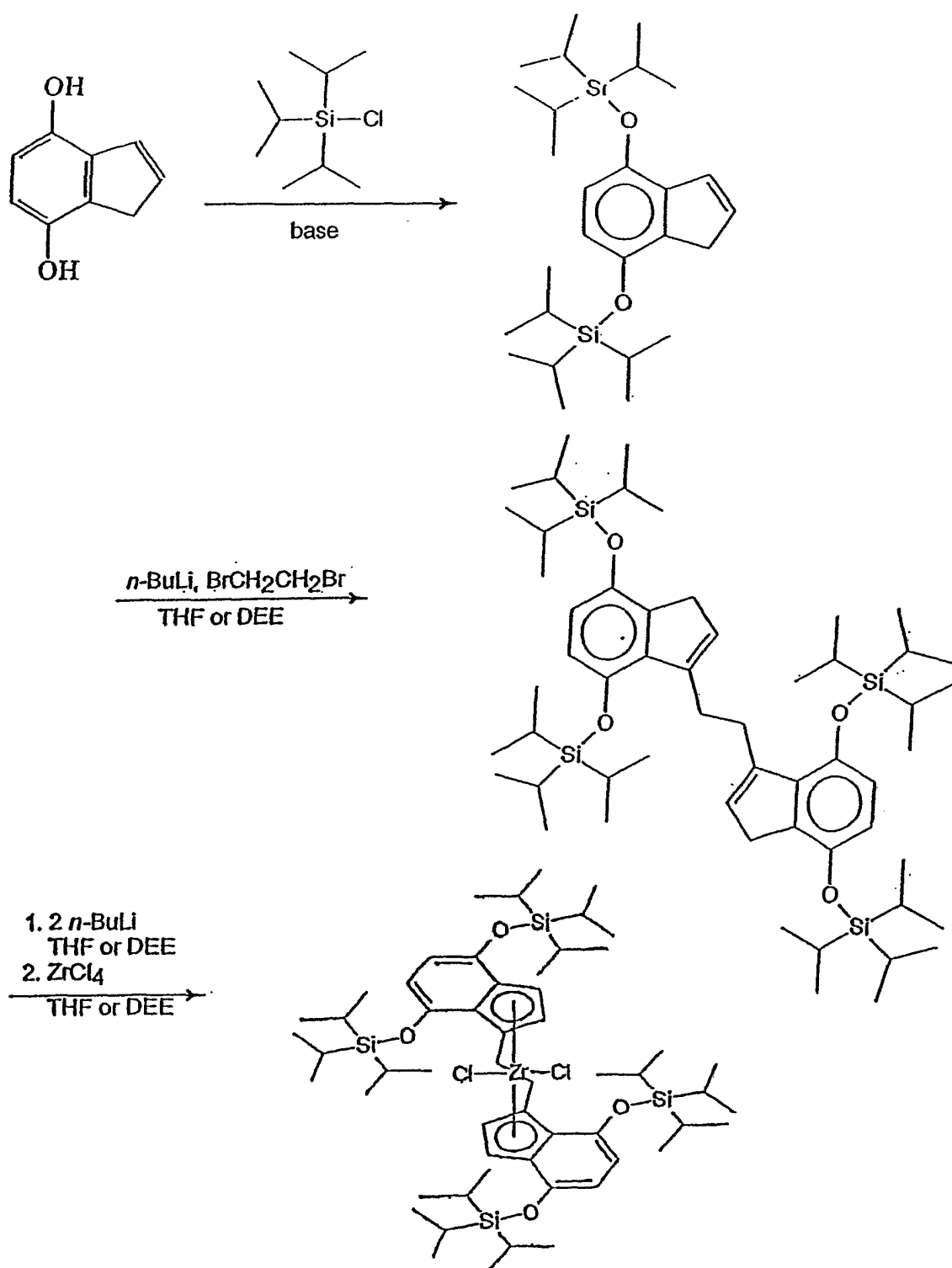
σ -ligands other than chlorine may be introduced by displacement of chlorine from an η -ligand metal chloride by reaction with appropriate nucleophilic reagent (e.g. methyl lithium or methylmagnesium chloride) or using, instead of a metal halide, a reagent such as tetrakisdimethylamidotitanium or metal compounds with mixed chloro and dimethylamido ligands.

Aspects of these synthetic strategies are illustrated in the following schemes which are for illustrative purposes only:

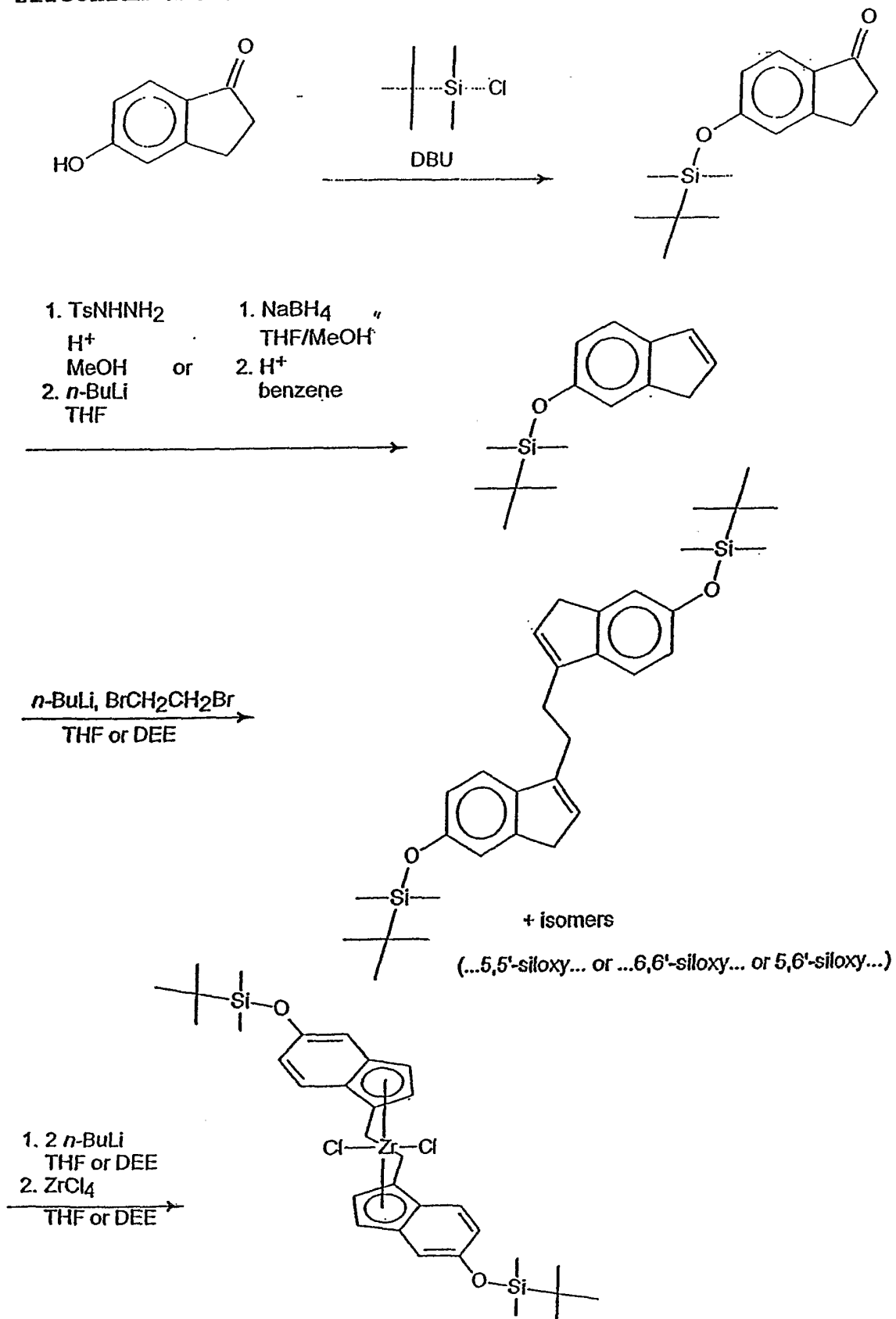
Scheme 1 - Strategy for the synthesis of *rac/meso*-[ethylenebis(3,7-di(tri-isopropylsiloxy)inden-1-yl)]zirconium dichloride



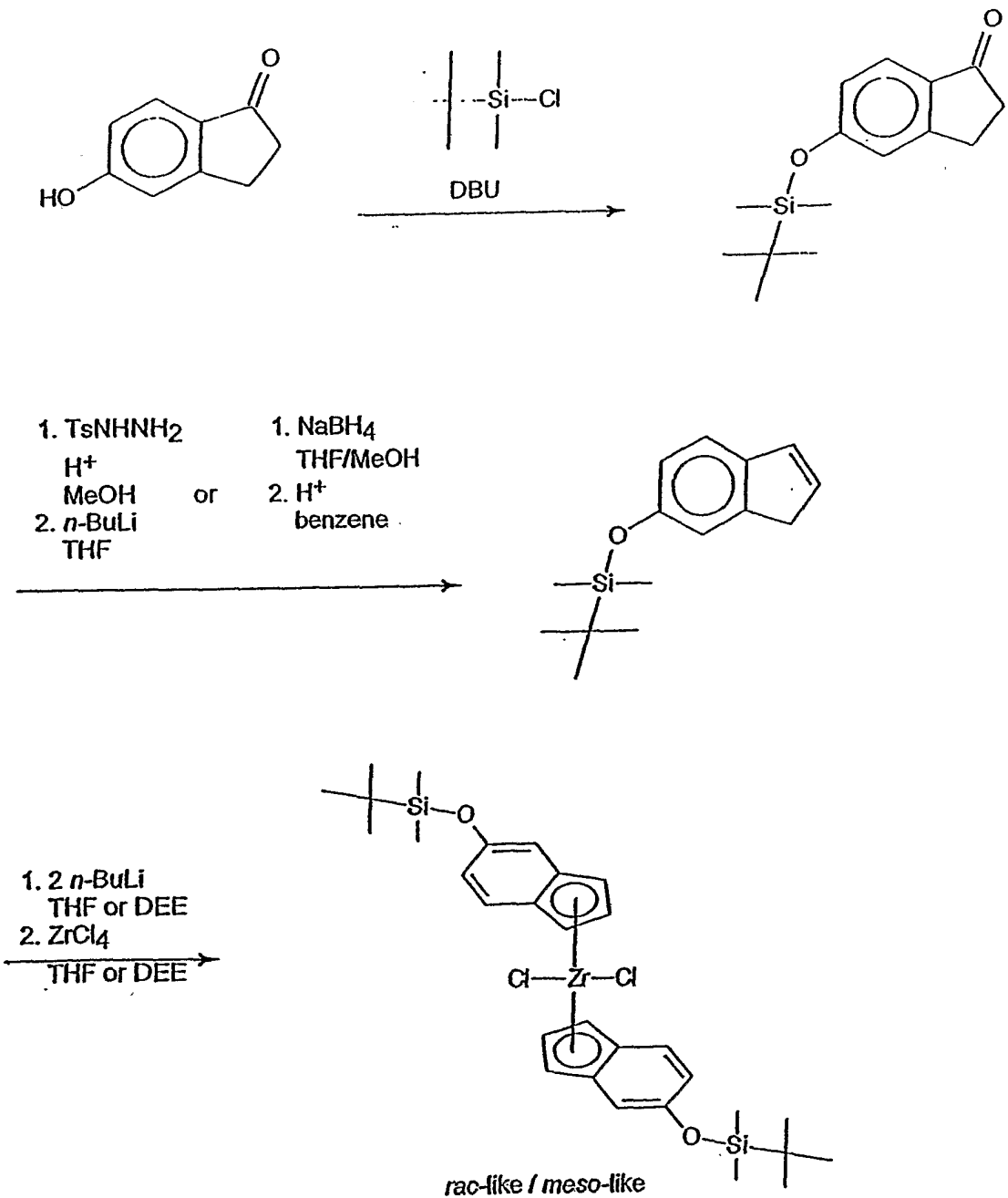
Scheme 2 - Strategy for the synthesis of rac/meso-[ethylenebis(4,7-di(tri-isopropylsiloxy)inden-1-yl)]zirconium dichloride



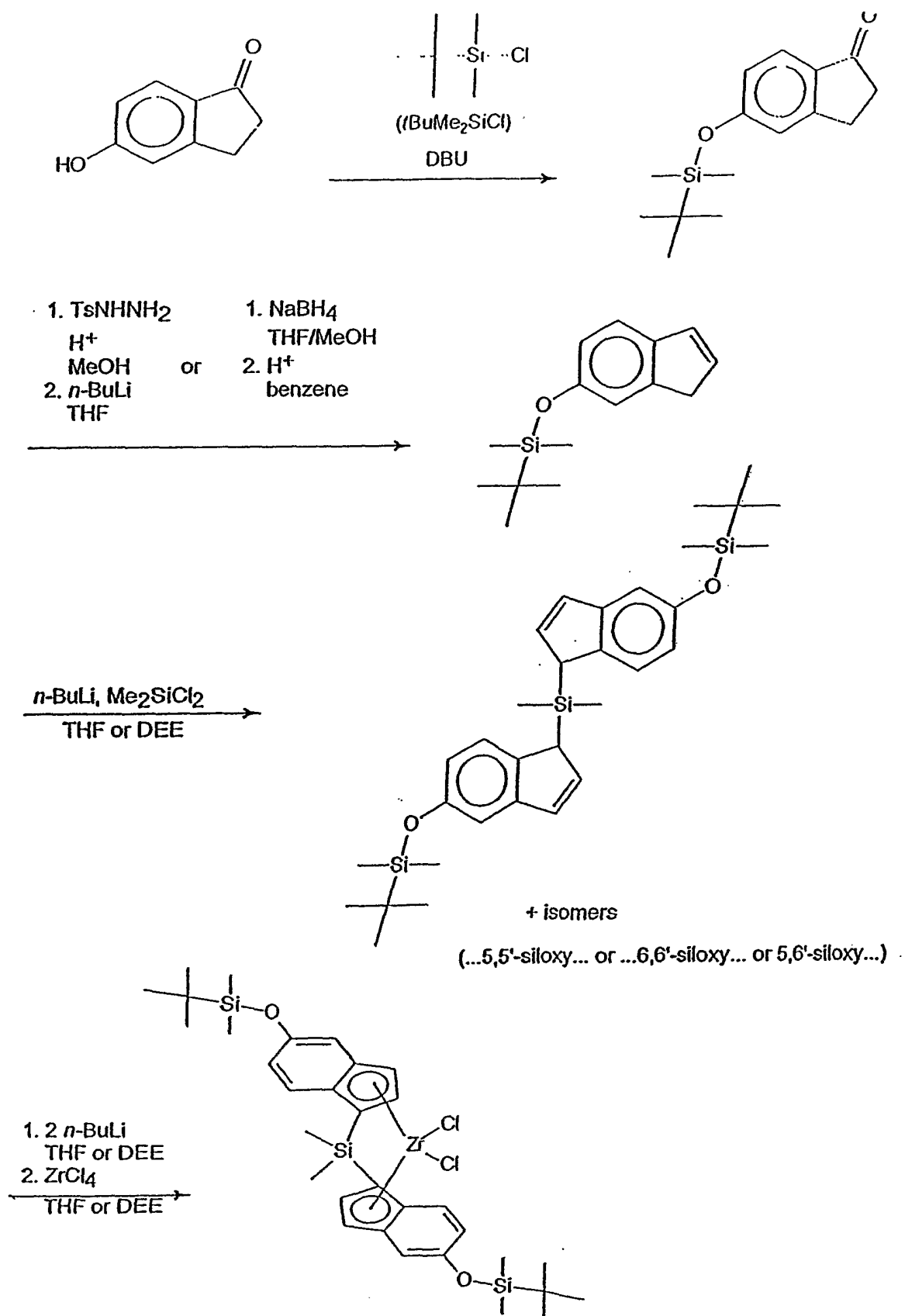
Scheme 3 - Strategy for the synthesis of *rac/meso*-[ethylenebis(5-(*tert*-butyldimethylsiloxy)indenyl)]-zirconium dichloride



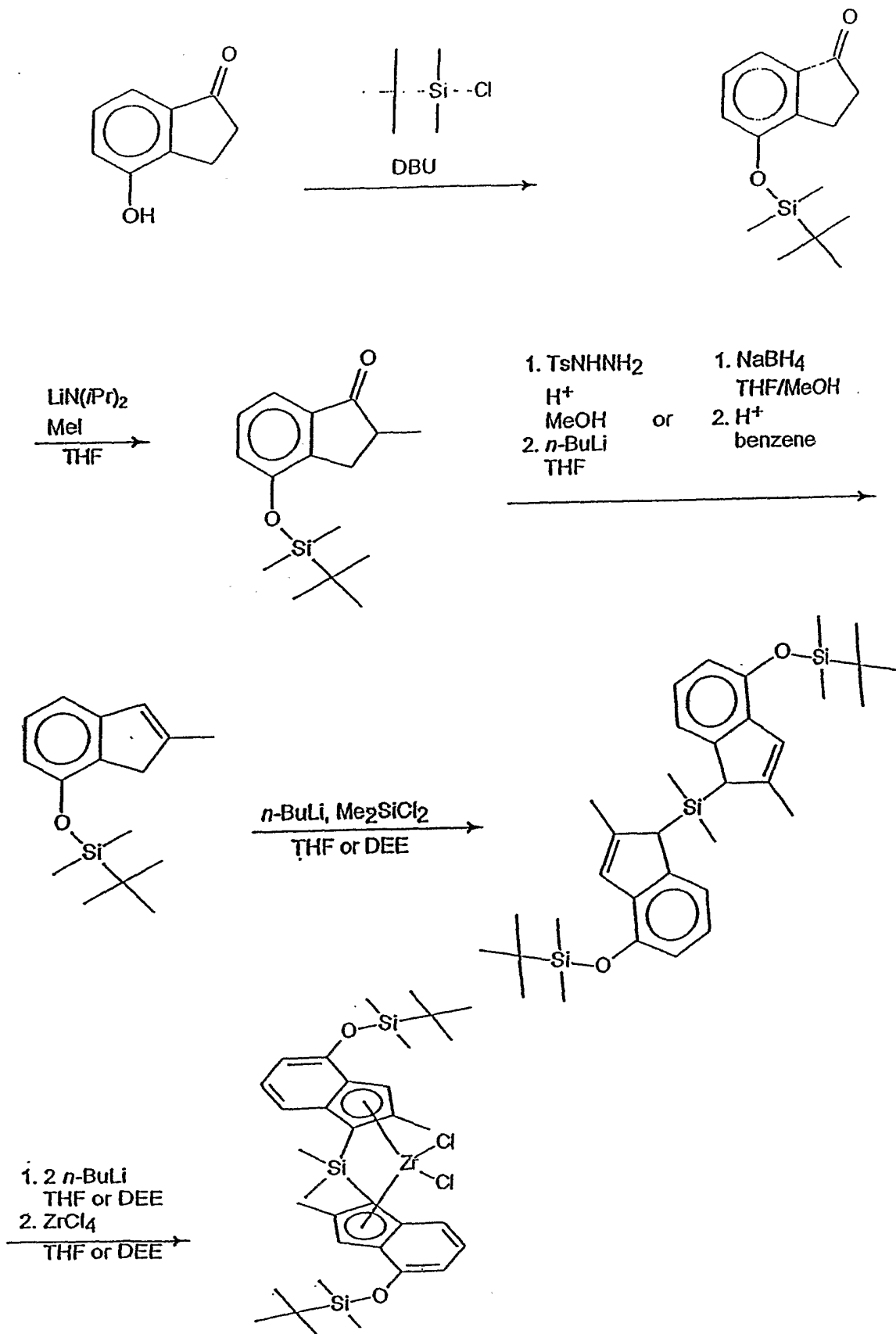
Scheme 4 - Strategy for the synthesis of bis-(5-(tert-butylidimethylsiloxy)-indenyl)zirconium dichloride



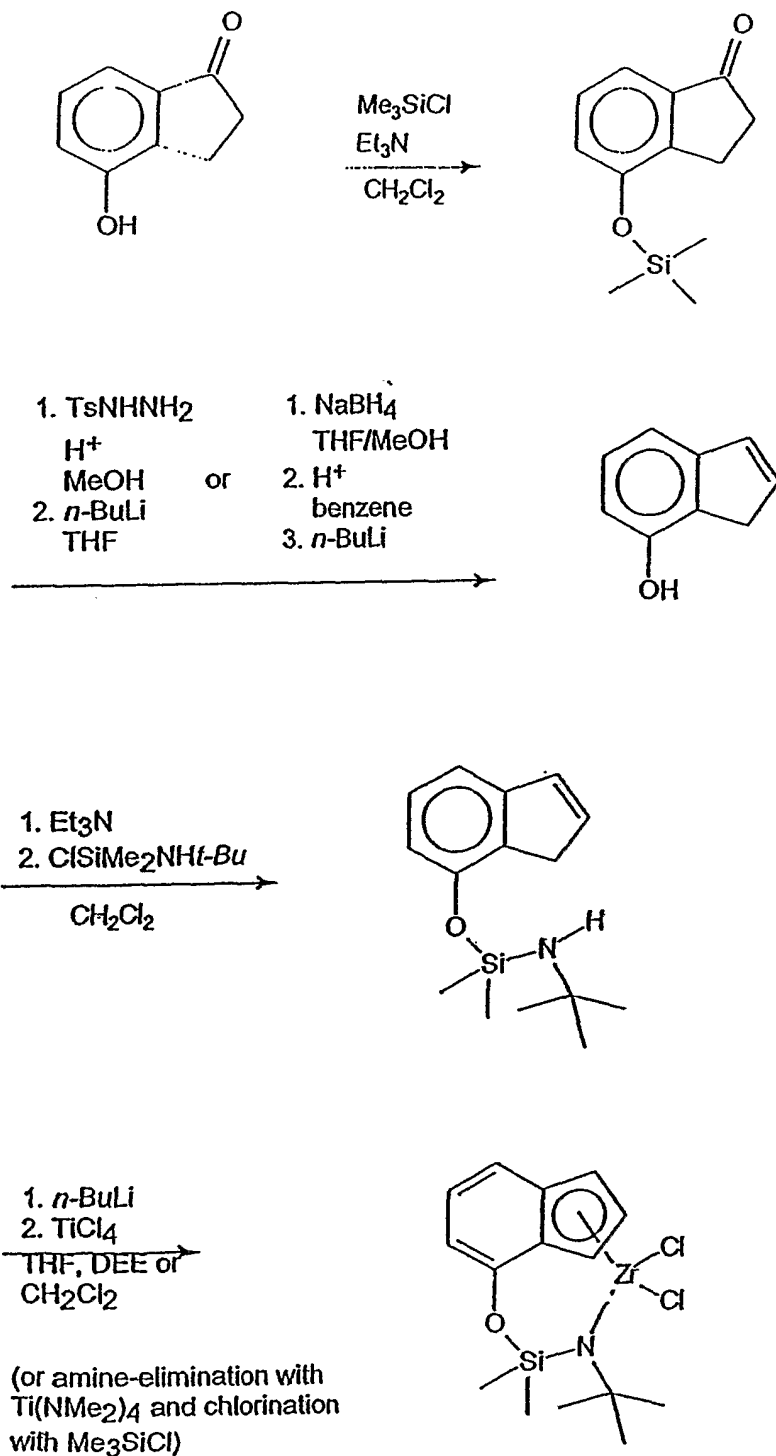
Scheme 5 - Strategy for the synthesis of rac/meso-[dimethylsilylenebis(5-(tert-butyl dimethylsiloxy)-indenyl)]zirconium dichloride



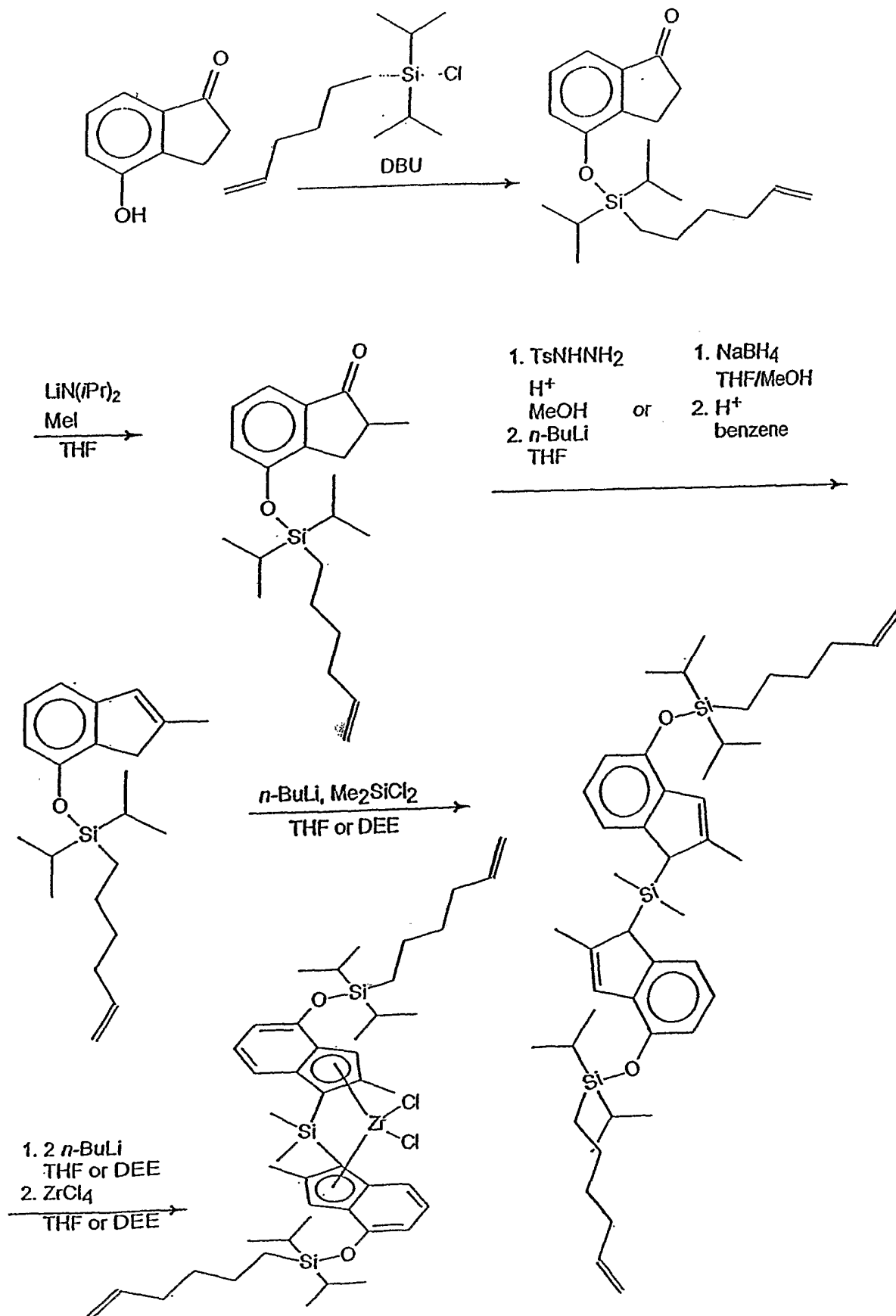
Scheme 6 - Strategy for the synthesis of rac/meso-[dimethylsilylenebis(4-(tert-butyl dimethylsiloxy)-2-methylindenyl)]zirconium dichloride



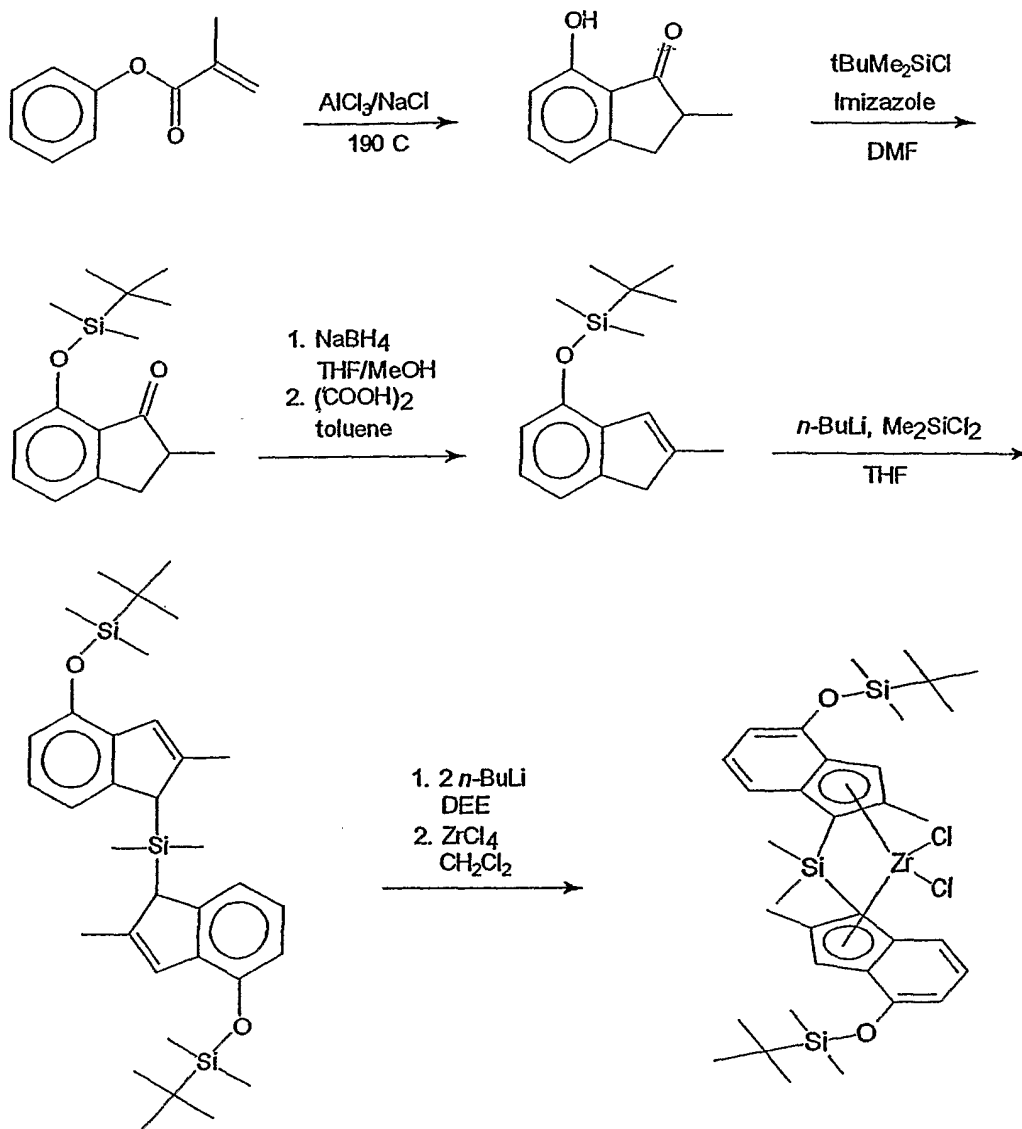
Scheme 7 - Strategy for the synthesis of (N-tert-butylamido) (dimethyl) (η^5 -inden-4-yloxy) silanetitanium dichloride



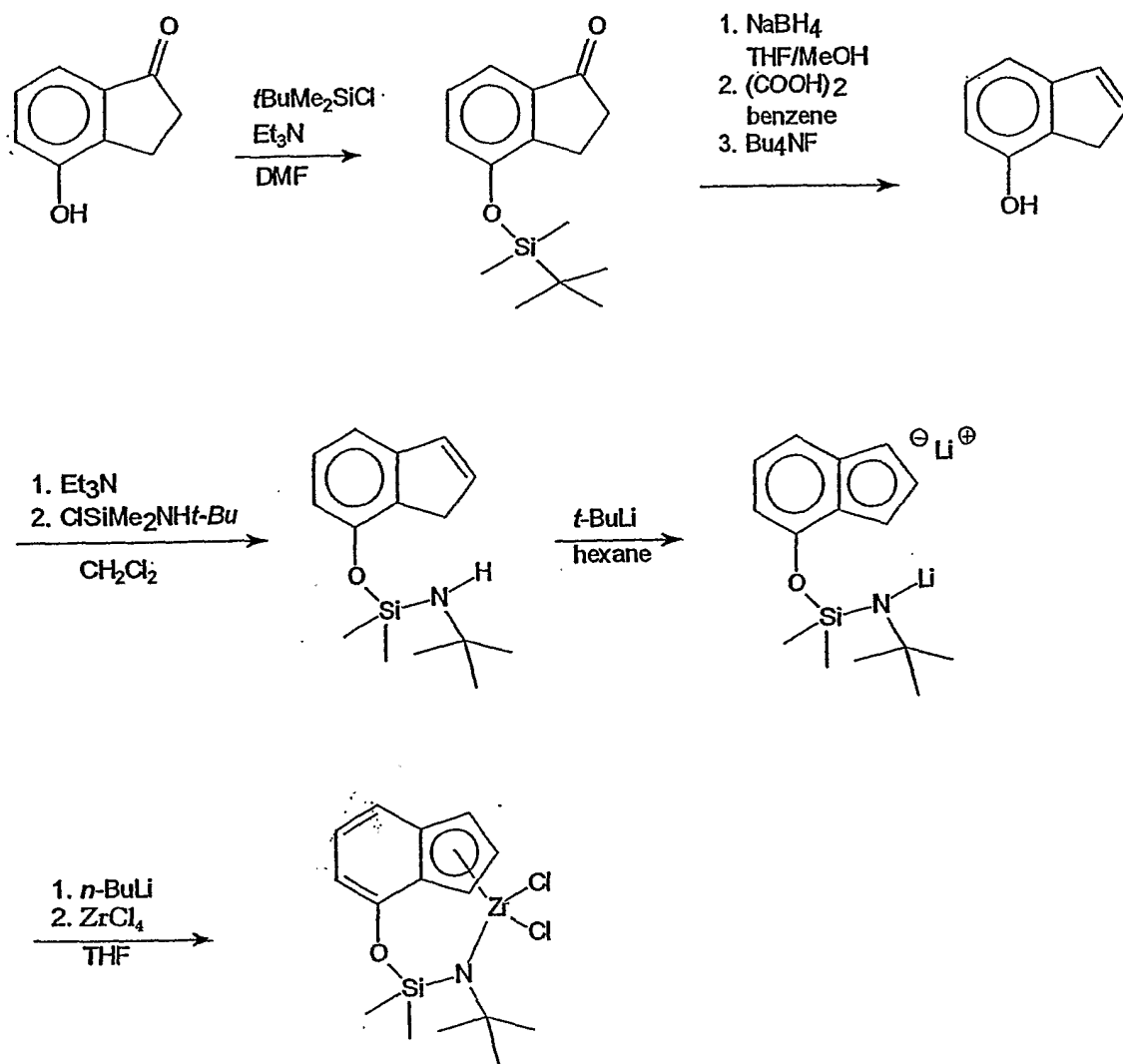
Scheme 8 - Strategy for the synthesis of rac/meso-[dimethylsilylenebis(4-(diisopropylhexenylsiloxy)-2-methylindenyl)]zirconium dichloride



Scheme 9 - Strategy for the synthesis of rac-[dimethylsilylenebis(4-(tert-butyldimethylsiloxy)-2-methylindenyl)]zirconium dichloride



Scheme 10 - Strategy for the synthesis of (N-tert-butylamido) (dimethyl) (η^5 -inden-4-yloxy) silanezirconium dichloride



The cocatalyst of scheme 6 is particularly suitable in the preparation of isotactic polypropylene and the cocatalyst of scheme 7 is particularly suitable in high temperature production of polypropylenes.

5 The metallocene catalyst and cocatalyst may be introduced into the polymerization reactor separately or together or, more preferably they are pre-reacted and their reaction product is introduced into the polymerization reactor.

10 As mentioned above, the olefin polymerisation catalyst system of the invention comprises (i) a metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said
15 moiety is substituted in the 4- or 7-position by a pendant siloxy or germyloxy group; and normally (ii) an aluminium alkyl compound (or other appropriate cocatalyst), or the reaction product thereof.

20 While the aluminium alkyl compound may be an aluminium trialkyl (e.g. triethylaluminium (TEA)) or an aluminium dialkyl halide (e.g. diethyl aluminium chloride (DEAC)), it is preferably an alumoxane, either MAO or an alumoxane other than MAO, such as an isobutylalumoxane, e.g. TIBAO (tetraisobutylalumoxane)
25 or HIBAO (hexaisobutylalumoxane). Alternatively, however, the alkylated (e.g. methylated) metallocene catalysts of the invention may be used with other cocatalysts, e.g. boron compounds such as $B(C_6F_5)_3$, $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$, $(C_6H_5)_3C:B(C_6F_5)_4$ or $Ni(CN)_4[B(C_6F_5)_3]_4^{2-}$.

30 However, when the metal in the catalyst is a group 3 transition metal, i.e. Sc, Y, La or Ac, no co-activator is required since such catalyst species are already in an active form, e.g. compounds of formula In_2ScH wherein In is as hereinbefore defined and
35 comprises 2 moieties of formula (IV).

The metallocene catalyst and cocatalyst may be introduced into the polymerization reactor separately or

- 33 -

together or, more preferably they are pre-reacted and their reaction product is introduced into the polymerization reactor.

If desired the catalyst, catalyst/cocatalyst
5 mixture or a catalyst/cocatalyst reaction product may be used in unsupported form, e.g. metallocene and MAO can be precipitated without an actual carrier material and used as such. The metallocene catalyst or its reaction product with the cocatalyst may also be introduced into
10 the polymerization reactor in supported form, e.g. impregnated into a porous particulate support.

The particulate support material used is preferably an organic or inorganic material, e.g. a polymer (such as for example polyethylene, polypropylene, an ethylene-
15 propylene copolymer, another polyolefin or polystyrene or a combination thereof). Such polymeric supports may be formed by precipitating a polymer or by a prepolymerization, e.g. of monomers used in the polymerization for which the catalyst is intended.
20 However, the support is especially preferably a metal or metalloid oxide such as silica, alumina or zirconia or a mixed oxide such as silica-alumina, in particular silica, alumina or silica-alumina.

Especially preferably the support is a porous
25 material so that the metallocene may be loaded into the pores of the support, e.g. using a process analogous to those described in WO94/14856 (Mobil), WO95/12622 (Borealis) and WO96/00243 (Exxon). The particle size is not critical but is preferably in the range 5 to 200 μm ,
30 more preferably 20 to 80 μm .

Before loading, the particulate support material is preferably calcined, i.e. heat treated, preferably under a non-reactive gas such as nitrogen. This treatment is preferably at a temperature in excess of 100°C, more
35 preferably 200°C or higher, e.g. 200-800°C, particularly about 300°C. The calcination treatment is preferably effected for several hours, e.g. 2 to 30 hours, more

preferably about 10 hours.

The support may be treated with an alkylating agent before being loaded with the metallocene. Treatment with the alkylating agent may be effected using an alkylating agent in a gas or liquid phase, e.g. in an organic solvent for the alkylating agent. The alkylating agent may be any agent capable of introducing alkyl groups, preferably C₁₋₆ alkyl groups and most especially preferably methyl groups. Such agents are well known in the field of synthetic organic chemistry. Preferably the alkylating agent is an organometallic compound, especially an organoaluminium compound (such as trimethylaluminium (TMA), dimethyl aluminium chloride, triethylaluminium) or a compound such as methyl lithium, dimethyl magnesium, triethylboron, etc.

The quantity of alkylating agent used will depend upon the number of active sites on the surface of the carrier. Thus for example, for a silica support, surface hydroxyls are capable of reacting with the alkylating agent. In general, an excess of alkylating agent is preferably used with any unreacted alkylating agent subsequently being washed away.

Following treatment of the support material with the alkylating agent, the support is preferably removed from the treatment fluid and any excess treatment fluid is allowed to drain off.

The optionally alkylated support material is loaded with the catalyst. This loading may be effected by using a solution of the catalyst in an organic solvent therefor, e.g. as described in the patent publications referred to above. Preferably, the volume of catalyst solution used is from 50 to 500% of the pore volume of the carrier, more especially preferably 80 to 120%. The concentration of catalyst compound in the solution used can vary from dilute to saturated depending on the amount of metallocene active sites that it is desired be loaded into the carrier pores.

The active metal (i.e. the metal of the catalyst) is preferably loaded onto the support material at from 0.1 to 4%, preferably 0.5 to 3.0%, especially 1.0 to 2.0%, by weight metal relative to the dry weight of the support material.

After loading of the catalyst onto the support material, the loaded support may be recovered for use in olefin polymerization, e.g. by separation of any excess catalyst solution and if desired drying of the loaded support, optionally at elevated temperatures, e.g. 25 to 80°C.

Alternatively, a cocatalyst, e.g. an alumoxane or an ionic catalyst activator (such as a boron or aluminium compound, especially a fluoroborate) may also be mixed with or loaded onto the catalyst support material. This may be done subsequently or more preferably simultaneously to loading of the catalyst, for example by including the cocatalyst in the solution of the catalyst, by contacting the catalyst loaded support material with a solution of the cocatalyst or catalyst activator, e.g. a solution in an organic solvent, or by first impregnating the cocatalyst with a support and then contacting the cocatalyst impregnated support with a solution of the catalyst or neat catalyst (e.g. as described in WO96/32423). Alternatively however any such further material may be added to the catalyst-loaded support material in the polymerization reactor or shortly before dosing of the catalyst material into the reactor.

In this regard, as an alternative to an alumoxane it may be preferred to use a fluoroborate catalyst activator for the alkylated catalysts, especially a $B(C_6F_5)_3$ or more especially a $^{\circ}B(C_6F_5)_4$ compound, such as $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$ or $(C_6H_5)_3C:B(C_6F_5)_4$. Other borates of general formula $(cation)_a (borate)_b$ where a and b are positive numbers, may also be used.

As an alternative to the loading of the optionally

alkylated support material with a solution of the procatalyst in an organic solvent, loading of the catalyst may be effected by mixing it with the optionally alkylated support material in the absence of solvents with said carrier at a temperature of at least 50°C but less than the vaporisation temperature of the metallocene compound. The particular features of this method are disclosed in WO 96/32423 (Borealis). If use of a cocatalyst/catalyst activator in such process is desired, this may be impregnated into the optionally alkylated support material prior to loading of the catalyst.

Where such a cocatalyst or catalyst activator is used, it is preferably used in a mole ratio to the metallocene of from 0.1:1 to 10000:1, especially 1:1 to 50:1, particularly 1:2 to 30:1. More particularly, where an alumoxane cocatalyst is used, then for an unsupported catalyst the aluminium:metallocene metal (M) molar ratio is conveniently 2:1 to 10000:1, preferably 50:1 to 1000:1. Where the catalyst is supported the Al:M molar ratio is conveniently 2:1 to 10000:1 preferably 50:1 to 400:1. Where a borane cocatalyst (catalyst activator) is used, the B:M molar ratio is conveniently 2:1 to 1:2, preferably 9:10 to 10:9, especially 1:1. When a neutral triarylboron type cocatalyst is used the B:M molar ratio is typically 1:2 to 500:1, however some aluminium alkyl would normally also be used. When using ionic tetraaryl borate compounds, it is preferred to use carbonium rather than ammonium counterions or to use B:M molar ratio 1:1.

Where the further material is loaded onto the catalyst loaded support material, the support may be recovered and if desired dried before use in olefin polymerization.

The olefin polymerized in the method of the invention is preferably ethylene or an alpha-olefin or a mixture of ethylene and an α -olefin or a mixture of

alpha olefins, for example C₂₋₂₀ olefins, e.g. ethylene, propene, n-but-1-ene, n-hex-1-ene, 4-methyl-pent-1-ene, n-oct-1-ene etc. The olefins polymerized in the method of the invention may include any compound which includes unsaturated polymerizable groups. Thus for example 5 unsaturated compounds, such as C₆₋₂₀ olefins (including cyclic and polycyclic olefins (e.g. norbornene)), and polyenes, especially C₆₋₂₀ dienes, may be included in a comonomer mixture with lower olefins, e.g. C₂₋₅ α-olefins. Diolefins (i.e. dienes) are suitably used for 10 introducing long chain branching into the resultant polymer. Examples of such dienes include α,ω linear dienes such as 1,5-hexadiene, 1,6-heptadiene, 1,8-nonadiene, 1,9-decadiene, etc.

15 In general, where the polymer being produced is a homopolymer it will preferably be polyethylene or polypropylene. Where the polymer being produced is a copolymer it will likewise preferably be an ethylene or propylene copolymer with ethylene or propylene making up 20 the major proportion (by number and more preferably by weight) of the monomer residues. Comonomers, such as C₄₋₆ alkenes, will generally be incorporated to contribute to the mechanical strength of the polymer product.

25 Usually metallocene catalysts yield relatively narrow molecular weight distribution polymers; however, if desired, the nature of the monomer/monomer mixture and the polymerization conditions may be changed during the polymerization process so as to produce a broad 30 bimodal or multimodal molecular weight distribution (MWD) in the final polymer product. In such a broad MWD product, the higher molecular weight component contributes to the strength of the end product while the lower molecular weight component contributes to the 35 processability of the product, e.g. enabling the product to be used in extrusion and blow moulding processes, for example for the preparation of tubes, pipes, containers,

etc.

A multimodal MWD can be produced using a catalyst material with two or more different types of active polymerization sites, e.g. with one such site provided by the metallocene on the support and further sites being provided by further catalysts, e.g. Ziegler catalysts, other metallocenes, etc. included in the catalyst material.

Polymerization in the method of the invention may be effected in one or more, e.g. 1, 2 or 3, polymerization reactors, using conventional polymerization techniques, e.g. gas phase, solution phase, slurry or bulk polymerization.

In general, a combination of slurry (or bulk) and at least one gas phase reactor is often preferred, particularly with the reactor order being slurry (or bulk) then one or more gas phase.

For slurry reactors, the reaction temperature will generally be in the range 40 to 110°C (e.g. 85-110°C), the reactor pressure will generally be in the range 5 to 80 bar (e.g. 50-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerization may if desired be effected under supercritical conditions.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen together with monomer (e.g. ethylene).

For solution phase reactors, the reaction temperature used will generally be in the range 130 to 270°C, the reactor pressure will generally be in the

range 20 to 400 bar and the residence time will generally be in the range 0.005 to 1 hour. The solvent used will commonly be a hydrocarbon with a boiling point in the range 80-200°C.

5 Generally the quantity of catalyst used will depend upon the nature of the catalyst, the reactor types and conditions and the properties desired for the polymer product. Conventional catalyst quantities, such as described in the publications referred to herein, may be
10 used.

The invention will now be illustrated by reference to the following non-limiting Examples:

Ligand and complex synthesis

15 All operations are carried out under an argon or nitrogen atmosphere using standard Schlenk, vacuum and drybox techniques. Ether, tetrahydrofuran (THF) and toluene solvents were dried with potassium benzophenone
20 ketyl and distilled under argon prior to use. Other solvents were dried using 13X+13Å molecular sieves. All other chemicals were used as commercially available.

NMR spectra were recorded using a JEOL JNM-EX270
25 MHz FT-NMR spectrometer with tetramethylsilane (TMS) as an internal reference.

Direct inlet mass spectra were recorded using a VG TRIO 2 quadruple mass spectrometer in electron impact ionization mode (70eV).

30 GC-MS analysis was performed using a Hewlett Packard 6890/5973 Mass Selective Detector in electron impact ionization mode (70eV), equipped with a silica capillary column (30m x 0.25 mm i.d).

EXPERIMENTAL; Complex Synthesis

35

General Considerations. All reactions with organometallic reagents were carried out in an argon

atmosphere using standard Schlenk techniques. Solvents were dried and distilled under argon prior to use. Merck Silica 60 (0.1 % Ca) was employed in chromatographic purifications.

5 **Preparation of *rac*-[ethylenebis(4-(*tert*-butyldimethylsiloxy)-indenyl)]-zirconium dichloride (5)**

10 **4-(*tert*-Butyldimethylsiloxy)-1-indanone (1).** To a solution of 4-hydroxy-1-indanone (25.0 g, 169 mmol) and imidazole (28.7 g, 422 mmol) in DMF (500 ml) was added *tert*-butyldimethylchlorosilane. The reaction mixture was stirred overnight at room temperature and treated with water (500 ml) and extracted with diethyl ether (500 ml). The organic phase was collected and dried
15 over sodium sulfate. Evaporation gave a yellow oil which was distilled under reduced pressure to give indanone (1) (35.44 g, 135 mmol, 79.9%) as a colourless oil (120-121°C/0.1 mbar).

20 **4-(*tert*-Butyldimethylsiloxy)-1-indanone tosylhydrozone (2).** To a solution of indanone (1) (30.0 g, 114 mmol) in methanol (1000 ml) was added *p*-toluenesulfonylhydrazide (21.29 g, (114 mmol) and 10 drops of concentrated sulfuric acid. The reaction mixture was
25 then heated under reflux for 3 hours, whereafter the solution was concentrated and a crystallization followed overnight at room temperature. The crystalline tosylhydrozone (2) (40.38 g, 93.8 mmol, 82.2%) was isolated by filtration.

30 **4-(*tert*-Butyldimethylsiloxy)-indene (3).** To a solution of tosylhydrozone (2) (34.87 g, 81 mmol) in THF (350 ml) at 0°C was added dropwise *n*-butyllithium (99 ml, 247 mmol, 2.5 M solution in hexane). After the addition was
35 complete the solution was stirred at room temperature overnight. The reaction solution was then treated with ice water (400 ml) and acidified with hydrochloric acid

(5% solution). The acidic solution was extracted with diethyl ether (3 x 250 ml), the organic fractions were combined and washed successively with aqueous sodium bicarbonate solution and brine, and dried over sodium sulfate. The solvents were removed by evaporation and the remaining yellow oil was distilled under reduced pressure to give indene (3) (6.94g, 28.2 mmol, 34.8%) as a pale yellow oil (82-83°C/0.2 mbar) as a mixture of two doublebond (1H and 3H) isomers.

10

Bis(4-(tert-butyldimethylsiloxy)-1-indenyl)ethane (4).

To an ice cooled solution of indene (3) (8.5 g, 34.5 mmol) in THF (50 mL) was added *n*-BuLi (15.2 ml, 37.9 mmol, 2.5 M solution in hexane) and the reaction mixture stirred for two hours at room temperature. The solution was then cooled to -80°C and a solution of dibromoethane (3.24 g, 17.3 mmol) in THF (15 ml) was added dropwise. After addition was complete, the temperature of the reaction solution was slowly allowed to rise to room temperature and stirred overnight. The resulting solution was washed with saturated ammonium chloride solution (100 ml) and extracted with diethyl ether (2 x 100 ml). The organic fractions were combined and dried over sodium sulfate. Solvents were evaporated and the remaining oil was dissolved in a methanol/acetone mixture (3:1), cooling to -30°C gave (4) (0.68g, 7.6%) as a yellowish crystalline solid.

15

20

25

30

35

Rac-[ethylenebis(4-(tert-butyldimethylsiloxy)-indenyl)]-zirconium dichloride (5). To a solution of (4) (0.68 g, 1.3 mmol) in THF (25 mL) at 0°C was added dropwise *n*-BuLi (1.05 ml, 2.63 mmol, 2.5 M solution in hexane), and the reaction mixture was stirred for three hours at room temperature. The resulting solution was added dropwise to a suspension of ZrCl₄ (0.39 g, 1.7 mmol) in THF (25 mL) at -80°C. The reaction mixture was gradually warmed to room temperature and stirred overnight. The

solvents were evaporated, the remaining solid was extracted with CH_2Cl_2 (100 ml) and filtrated through Celite to remove lithium chloride. The solvent was evaporated and the crude product was extracted with diethyl ether (200 ml) and filtrated through Celite. Concentration and cooling to -30°C gave (5) (50 mg, 5.6%) as yellow microcrystals.

This reaction sequence is depicted in Diagram 1 below.

10

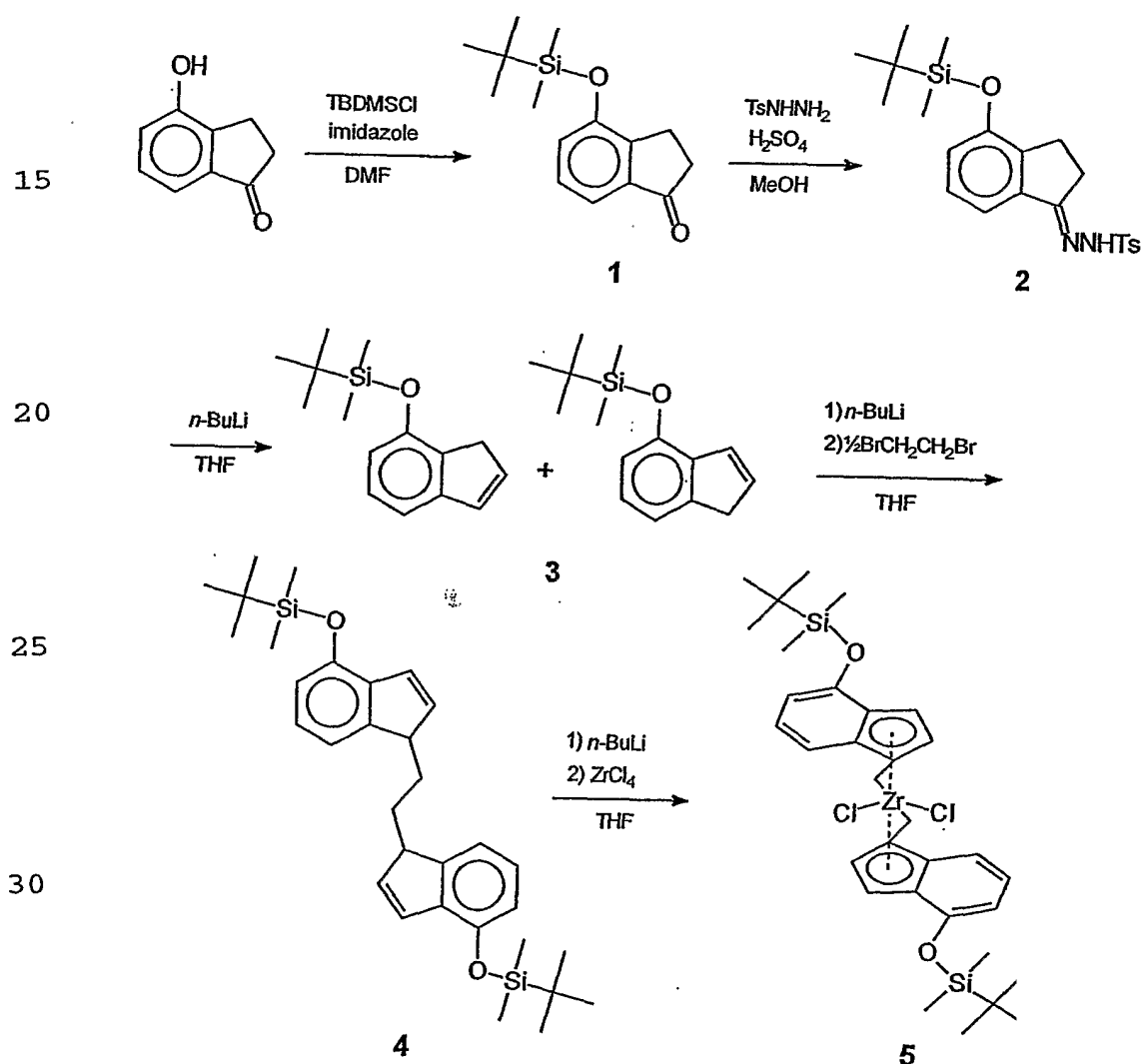


Diagram 1. Synthesis of *rac*-[ethylenebis(4-(*tert*-butyldimethylsiloxy)-indenyl)]-zirconium dichloride.

Preparation of *rac*-[dimethylsilylenebis(4-(*tert*-butyldimethylsiloxy)-2-methyl-indenyl)]-zirconium dichloride (10)

5 7-hydroxy-2-methyl-1-indanone (6) was prepared according to the procedure described by Bringmann and Jansen (Liebigs Ann. Chem. 1985, 2116-2125).

10 7-(*tert*-butyldimethylsiloxy)-2-methyl-1-indanone (7). To a solution of 7-hydroxy-2-methyl-1-indanone (6) (10.2 g, 37 mmol) and imidazole (3.02 g, 44 mmol) dissolved in DMF (200 ml) was added *tert*-butyldimethylchlorosilane (6.11 g, 41 mmol) in DMF (50 ml). The reaction mixture was stirred overnight at room temperature and treated
15 with water (200 ml) and extracted with diethylether (2 x 200 ml). The combined organic phases were washed with aqueous NH₄Cl (300 ml), brine (100 ml) and dried over sodium sulfate. Evaporation gave (7) as a yellow oil which was used without further purification.

20 7-(*tert*-butyldimethylsiloxy)-2-methyl-1-indene (8). To a solution of 7 (13.0 g, 47.1 mmol) in THF/methanol (2:1, 500 ml) was added sodium borohydride (3.67 g, 94 mmol) in several portions. The reaction mixture was stirred
25 at room temperature overnight. The clear colorless solution was diluted with diethylether (300 ml), washed with 5% HCl (2 x 300 ml), saturated aqueous NaHCO₃ (300 ml), brine (200 ml) and dried over anhydrous Na₂SO₄. Evaporation of volatiles gave brownish oil which was
30 used without further purification.

The oil (11.2 g) was dissolved in toluene (300 ml) and anhydrous oxalic acid (10.8 g, 120 mmol) was added. The mixture was heated at 100°C for 1 hour and allowed to
35 cool to room temperature. After decanting the solution on water it was diluted with diethyl ether (400 ml). The organic phase was washed with water (300 ml), 5% HCl (2

- 44 -

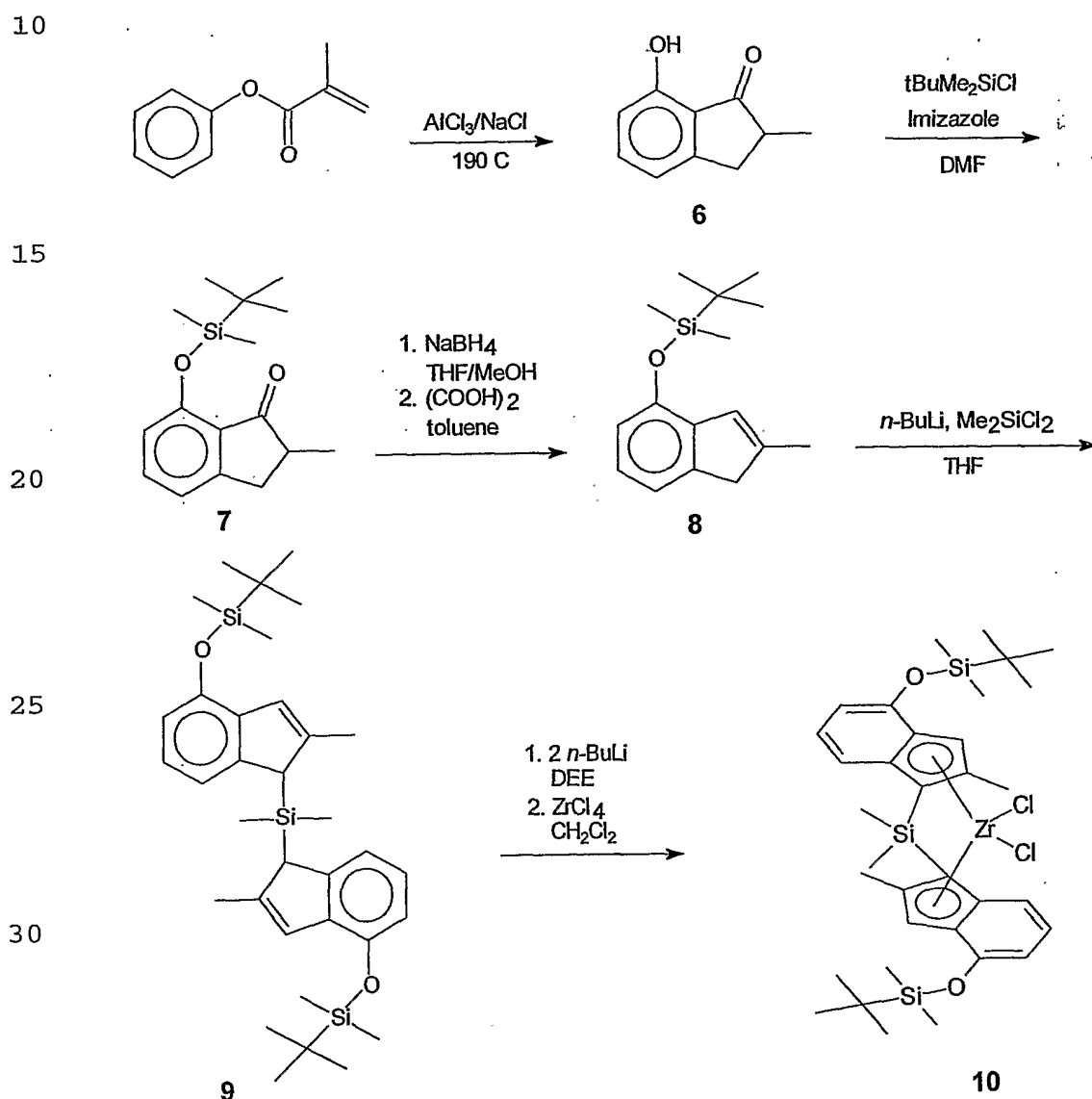
x 300 ml), saturated aqueous NaHCO₃ (300 ml), brine (200 ml) and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure to give brown oil. The crude product was purified by flash chromatography (99%
5 hexane/1% ethyl acetate) to yield **8** (3.1 g) as a colorless oil.

Bis(4-(tert-butyldimethylsiloxy)-2-methyl-1-indenyl)dimethylsilane (9). To an ice cooled solution of
10 **8** (2.70 g, 10.4 mmol) in THF (50 mL) was added *n*-BuLi (4.2 ml, 10.5 mmol, 2.5 M solution in hexane) dropwise. The ice bath was removed 5 minutes after completion of the addition of *n*-BuLi and the reaction mixture was stirred for 40 minutes at room temperature. The orange
15 solution was then cooled to 0°C and a solution of dichlorodimethylsilane (0.67 g, 5.2 mmol) in THF (5 ml) was dropwise added. The reaction mixture was slowly allowed to attain room temperature and stirred overnight. The resulting solution was washed with
20 saturated ammonium chloride solution (100 ml) and extracted with diethyl ether (2 x 100ml). The organic fractions were combined and dried over sodium sulfate. The solvents were evaporated and the remaining oil was purified by flash chromatography (99% pentane/1% diethyl
25 ether) to yield a mixture of rac- and meso-**9** (1.91 g, 64 %) as a yellow oil.

Rac-[dimethylsilylenebis(4-(tert-butyldimethylsiloxy)-2-methyl-indenyl)]-zirconium dichloride (10). To a pale
30 yellow solution of **9** (0.42 g, 0.73 mmol) in Et₂O (15 mL) at -40°C was added dropwise *n*-BuLi (0.60 ml, 1.50 mmol, 2.5 M solution in hexane) and the reaction mixture was stirred for 15 minutes at -40°C and then at room temperature for 1.5 hours. The solvent was removed *in vacuo* and the resulting yellowish powder was mixed with
35 ZrCl₄ (0.17 g, 0.73 mmol). Precooled CH₂Cl₂ (-80°C, 50 ml) was added at -80 °C. The resulting red suspension

was gradually warmed to room temperature and stirred overnight. The resulting red solution was filtered through Celite to remove lithium chloride and the solvent was evaporated. The crude product was extracted with Et₂O, concentrated and cooled to -30°C to give 10 as an orange powder.

This reaction sequence is depicted in Diagram 2 below.



Preparation of [(N-*tert*-butyl-amido)-dimethyl-(η^5 -inden-4-yloxy)-silane]-titanium dichloride (15)

5 4-(*tert*-Butyldimethylsiloxy)-1-indanone (1). To a solution of 4-hydroxy-1-indanone (25.0 g, 169 mmol) in DMF (500 ml) was triethylamine (22.2 g, 220 mmol) added, to the resulting solution was *tert*-butyldimethylchlorosilane (28.0 g, 186 mmol) added. The
10 reaction mixture was stirred overnight at room temperature and treated with water (500 ml) and extracted with diethyl ether (500 ml). The organic phase was collected and dried over sodium sulfate. Evaporation gave a yellow oil which was distilled under reduced
15 pressure to give the indanone (36.68 g, 140 mmol, 82.7%) as a colourless oil (120-121°C/0.1 mbar).

4-Hydroxyindene (11). To a solution of 4-(*tert*-butyldimethylsiloxy)-1-indanone (35.0 g, 133 mmol) in
20 methanol/THF (100ml:200ml) was NaBH₄ (7.57 g, 200 mmol) added in portions at 0 °C. The reaction mixture is stirred overnight. The resulting solution is poured on ice, acidified with concentrated hydrochloric acid to pH = 1 and extracted with diethyl ether (2 x 200 ml). The
25 organic fractions were combined and washed with brine, water and dried over sodiumsulfate. The solvents were evaporated and the remaining oil (siloxyindanol) was dissolved in toluene (300 ml). To this solution was oxalic acid (24.0 g, 267 mmol) added. The mixture was
30 heated under reflux for 3 hours, whereafter the reaction mixture was washed with a 10 % aqueous solution of NaHCO₃ and dried over sodiumsulfate. The solvent was removed by evaporation. The remaining yellow oil was dissolved in
35 THF (300 ml) and treated with tetra-*n*-butylammonium fluoride (69.6 g, 266 mmol) at 0 °C and stirred for 30 min at room temperature. The reaction solution was treated with a saturated NH₄Cl solution (200 ml) and

extracted with diethyl ether (2 x 200 ml). The organic phase was collected, evaporation of solvent left a solid which was recrystallized from methanol to give a pale yellow solid (11.45 g, 86.6 mmol, 65.1%).

5

N-(tert-Butyl)-N-(1-(1H-4-indenyloxy)-1,1-dimethylsilyl)amine (12). 4-Hydroxyindene (9.25 g, 70 mmol) was dissolved in methylenechloride (200 ml) and the solution was cooled to 0 °C. To this solution was triethylamine (10.7 g, 105 mmol) added. The reaction mixture was stirred for 1 h and then N-(tert-butyl)-N-(1-chloro-1,1-dimethylsilyl)amine (13.95 g, 84 mmol) added. The mixture was stirred for 2 h at 0 °C and then the flask was warmed to room temperature and stirred overnight. The solvent was then removed by evaporation and the residue was extracted with hexane (2 x 40 ml) and filtered. Solvent was removed under reduced pressure leaving 14.6 g (56 mmol, 79.8 %) of the silylamine as a yellow liquid.

15
20

N-(tert-Butyl)-N-(1-(1H-4-indenyloxy)-1,1-dimethylsilyl)amine dilithium salt (13). To a solution of N-(tert-Butyl)-N-(1-(1H-4-indenyloxy)-1,1-dimethylsilyl)amine (13.6 g, 52 mmol) in hexane (200 ml) at 0°C was added dropwise t-butyllithium (86 ml, 129 mmol, 1.5 M solution in pentane). The reaction mixture was stirred overnight at room temperature. The resulting off-white precipitate was collected via filtration, washed with hexane (100 ml) and dried under reduced pressure to give 9.8 g (36 mmol, 69.2 %) of the dilithium salt as an off-white solid.

25
30

[(N-tert-butylamido)-dimethyl-(η^5 -inden-4-yloxy)-silane]-titanium dichloride (14). $\text{TiCl}_3(\text{THF})_3$ (7.1g, 19.1 mmol) was suspended in THF (50 ml). To this solution was a solution of N-(tert-butyl)-N-(1-(1H-4-indenyloxy)-1,1-dimethylsilyl)amine dilithium salt (5.2 g, 19.1 mmol) in

35

THF (200 ml) added. The reaction solution was stirred for 1 h. To the resulting solution was PbCl_2 (3.45 g, 12.4 mmol) added and the solution was stirred for 1 h. The solvent was removed under reduced pressure. The residue was then extracted with toluene (50 ml), the solution was filtered, and the toluene was removed under reduced pressure. The residue was then titrated with hexane (50 ml) and the precipitate was collected via filtration, washed with hexane and dried under vacuum to give the titanium dichloride (3.72 g, 9.9 mmol, 51.6%) as an orange solid.

This reaction sequence is depicted in Diagram 3 below.

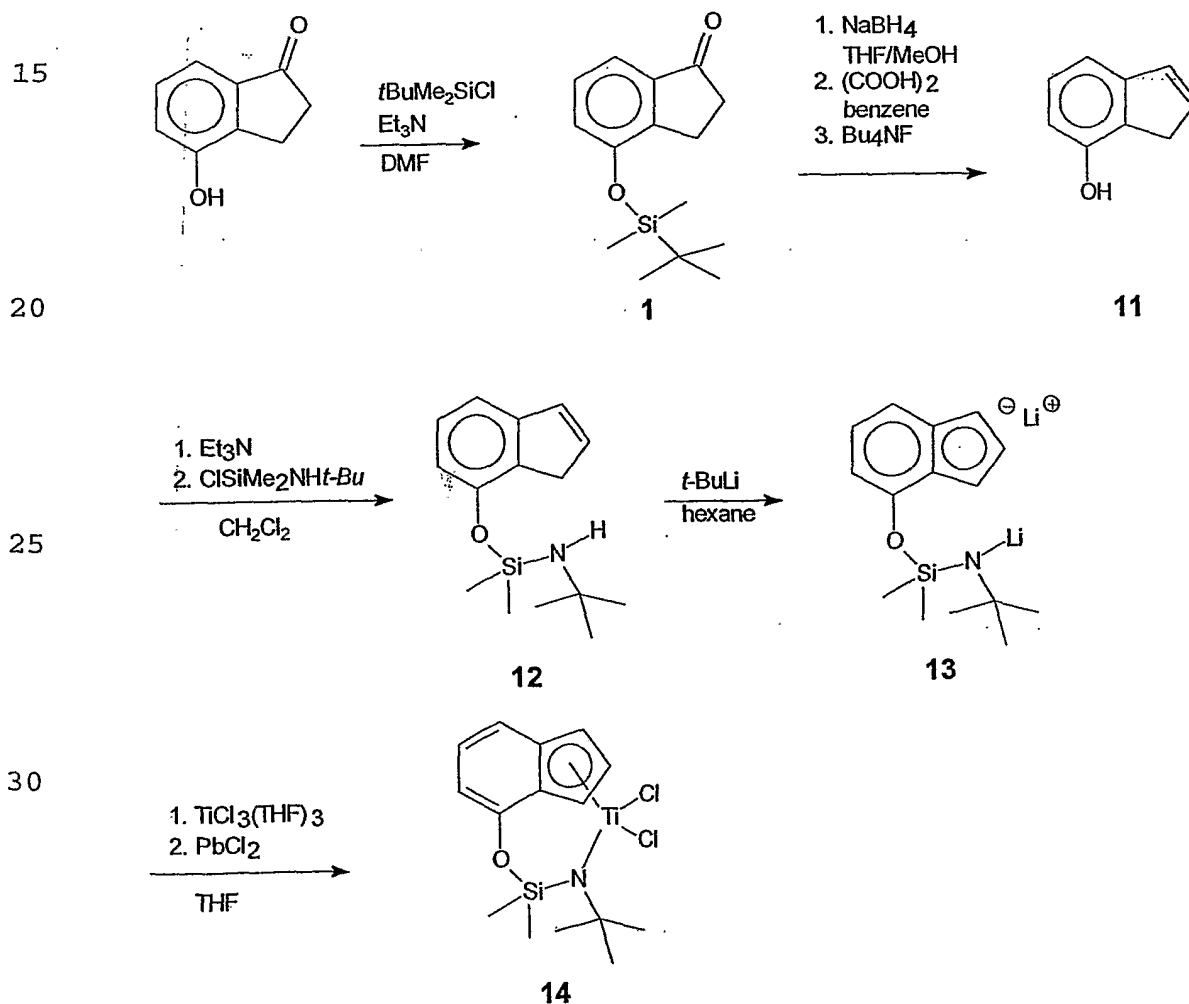


Diagram 3. Synthesis of [(N-tert-butylamido)-dimethyl-(η^5 -inden-4-yloxy)-silane]-titanium dichloride.

Polymerization Reactions

Ethylene (>99.95%), nitrogen (>99.999%) and n-pentane (> 97%) were used. 1-Hexene was purified by refluxing over sodium and distillation under an atmosphere of nitrogen.

Catalysts were prepared by mixing the co-catalyst (30 wt% MAO in toluene or 70 wt% HIBAO in toluene, both from Albemarle) in toluene to reach the desired Aluminium: M (Metal) molar ratio.

A feeding vessel in a glove box was charged with an appropriate amount of catalyst and transferred to a stirred (400 min⁻¹) Büchi 2.0/3.0 L stirred autoclave reactor. The reactor was purged with nitrogen and charged with n-pentane at ambient temperature. The reactor temperature was adjusted to +80°C and the feed of ethylene into the reactor begun. The partial pressure of ethylene (10⁶ Pa (10.0 bar)) and total pressure (1.3 x 10⁶ Pa (13 bar)) were held constant by continuously feeding in monomer. After 30 minutes the reactor was vented and the polymer isolated.

When 1-hexene was used as comonomer its addition to the reactor was simultaneous with ethylene.

Table 1 below provides details of the polymerisations conducted. The catalysts used were either compound (5) (*infra*) or *rac*-[ethylenebis(2-(*tert*butyldimethylsiloxy)-indenyl)]zirconium dichloride which is disclosed in WO97/28170 (*infra*).

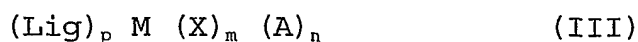
Table 1

Polymer type	HDPE	HDPE	LLDPE	LLDPE	HDPE	HDPE
Complex	Comparative example	Compound (5) of example	Comparative example	Compound (5) of example	Comparative example	Compound (5) of example
5 Catalyst amount	0.25 μmol	0.52 μmol	0.27 μmol	0.5 μmol	0.25 μmol	1.27 μmol
Polymer amount (g)	108	130	165	225	52	47
Polymerisation time (Min)	30	60	30	30	30	60
10 Cocatalyst	MAO	MAO	MAO	MAO	HIBAO	HIBAO
Aluminium/Metal ratio	1000	900	900	900	1000	916
Activity of metal (KgPol/g met h)	9472	2766	13399	9855	4560	433
15 Comonomer	-	-	1-hexene	1-hexene	-	-
Comonomer amount (ml)	-	-	50.0	30.0	-	-
Comonomer amount (w-%)	-	-	2.4	3.3	-	-
20 Medium	PENTANE	^z ISOBUTANE	PENTANE	ISOBUTANE	PENTANE	ISOBUTANE
Medium amount (ml)	1200	1800	1200	1800	1200	1800

Monomer	ETHENE	ETHENE	ETHENE	ETHENE	ETHENE	ETHENE
Pressure tot (bar)	14	23	13	23	14	23
Temperature (°C)	80	80	80	95	80	80
5 CRYSTALLINITY (%)	67	64	53	43	71	-
MELTING TEMP (°C)	135	134	122	116	133	-
MFR ₂ (g/10 min)	n.a.	<0.1	1.4	n.a.	1.32	-
MFR ₂₁ (g/10 min)	7.5	1.20	46.20	0.10	47.50	-
BD (kg/m ³)	70.00	-	178	-	190	-
10 T-VINYLENE (C=C/1000C)	0.01	0.04	0.00	0.04	0.01	-
VINYL (C=C/1000C)	0.50	0.34	0.53	0.17	0.62	-
VINYLDENE (C=C/1000C)	0.02	0.04	0.03	0.06	0.01	-
M _n	44300	63600	35200	143000	35700	-
M _w	145000	270000	86600	477000	88700	-
15 MWD	3.3	4.2	2.5	3.3	2.5	-

Claims:

1. A metallocene catalyst in which the metal is coordinated by a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group.
2. A catalyst as claimed in claim 1 of formula (III)



in which:

- M is a transition metal ion or a lanthanide metal ion;
- p is 1 or 2;
- m is greater than or equal to 0;
- n is greater than or equal to 0;
- n+m is equal to the valency of the metal not satisfied by ligand or ligands Lig;
- X is a ligand which co-ordinates to M selected from a η^5 hydrocarbyl, η^1 hydrocarbyl, halo, hydrocarbyl amino or hydrocarbyl amido ligand;
- A is a σ -ligand; and
- each ligand Lig which may be the same or different is a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group
3. A catalyst as claimed in claim 1 or 2 wherein M is a group 4 to 6 transition metal.
4. A catalyst as claimed in claim 3 wherein said metal is Cr, Ti, Zr or Hf.

5. A catalyst as claimed in anyone of claims 2 to 4 wherein p is 2 and m is zero.

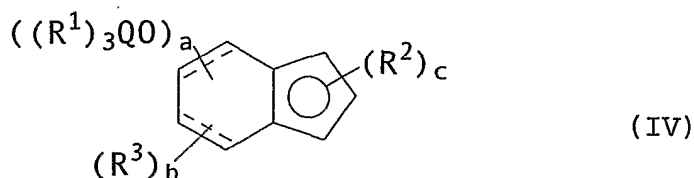
6. A catalyst as claimed in any one of claims 2 to 5 wherein each A is a halo, amido or C₁₋₁₂-hydrocarbyl ligand.

7. A catalyst as claimed in claim 6 wherein each A is a chloro ligand.

10

8. A catalyst as claimed in any one of claims 2 to 7 wherein each Lig is independently a negatively charged indenyl or indenyloid moiety of the following formula (IV):

15



20

wherein one or more of the ring carbon atoms may be replaced by a ring heteroatom;

each Q is either a silicon or a germanium atom;

25 either or both of the bonds shown as ----- may be present or absent;

each R¹ which may be the same or different is a hydrogen or a C₁₋₂₀ hydrocarbyl or a η¹ ligand, at least one R¹ being other than hydrogen;

30 each R² is a hydrogen or a group bonded to the 5-membered ring through a carbon, oxygen, silicon, phosphorus, germanium, nitrogen or sulfur atom;

35 each R³ is a hydrogen or a group bonded to the 6-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC) carbon, oxygen, silicon, germanium, nitrogen, phosphorus or sulfur atom; or

two or more R² and/or two or more R³ groups attached to adjacent ring atoms on the same ring together form a

- 5- to 8-membered fused ring; and optionally
one R^2 or R^3 is -L-Z wherein L is a 1 to 4 atom
chain and Z is a second moiety of formula (IV) and
joined to L through one R^2 or R^3 , if present in which L
5 is one and the same chain common to both moieties,
a is an integer between 1 and 3,
b is an integer between 1 and 3, the sum of a and b
being no more than 4,
c is an integer between 1 and 3,
10 with the proviso that no more than one -L-Z group
is present in each ligand.
9. A catalyst as claimed in claim 8 wherein all the
ring atoms are carbon atoms.
15
10. A catalyst as claimed in claim 8 or 9 wherein both
---- bonds are present.
11. A catalyst as claimed in any one of claim 8 to 10
20 wherein Q is Si.
12. A catalyst as claimed in any one of claims 8 to 11
wherein each R^1 is independently a C_{1-8} hydrocarbyl or C_{1-8}
alkylamine.
25
13. A catalyst as claimed in any one of claims 8 to 12
wherein R^3 is a group bonded to the 6-membered ring
through a carbon, oxygen, silicon, germanium, nitrogen,
phosphorus or sulfur atom.
30
14. A catalyst as claimed in any one of claim 8 to 13
wherein each R^2 or R^3 is independently a C_{1-20} hydrocarbyl,
 C_{1-20} hydrocarbyl siloxy, C_{1-20} hydrocarbyloxy, C_{1-20}
hydrocarbyl silyl group.
35
15. A catalyst as claimed in claim 14 wherein each R^2 or
 R^3 is independently a C_{1-8} hydrocarbyl group or C_{1-20}

hydrocarbylsiloxy group attached to the ring via the oxygen atom.

5 16. A catalyst as claimed in any one of claims 8 to 15 wherein R^3 is H.

10 17. A catalyst as claimed in any one of claims 8 to 16 wherein a group L-Z is present at the 1 or 3 position of formula (IV).

18. A catalyst as claimed in claim 17 wherein L is SiR^2_2 or $(CR^2_2)_q$ in which q is 1 to 3 and R_2 is as hereinbefore defined.

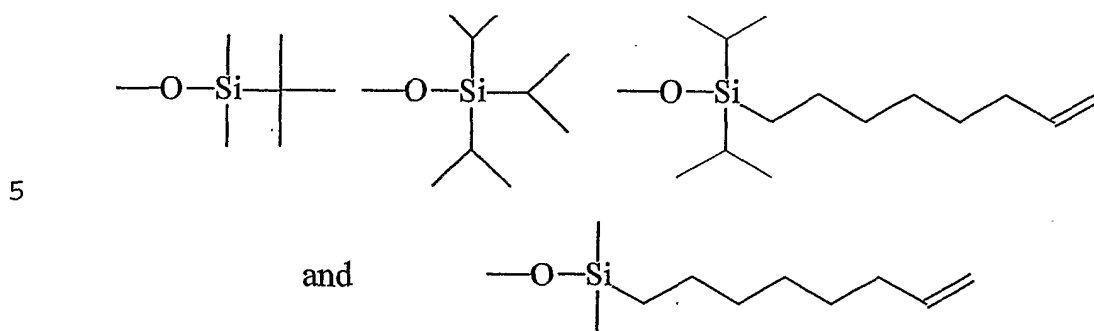
15 19. A catalyst as claimed in claim 18 wherein L is $(CH_2)_q$ or $Si(CH_3)_2$.

20 20. A catalyst as claimed in any of claims 8 to 19 wherein at least one group $-OQ(R^1)_3$ is a siloxy or germyloxy group directly attached to the 4-position or 7-position.

25 21. A catalyst as claimed in any one of claims 8 to 20 where a, b and c are 1.

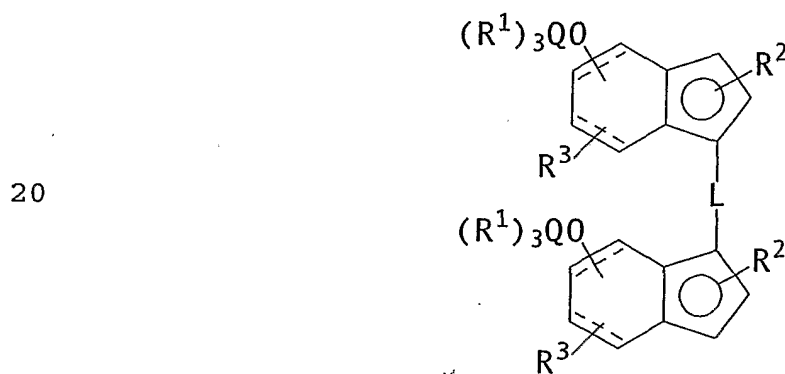
22. A catalyst as claimed in any one of claims 8 to 20 wherein at least two groups $-OQ(R^1)_3$ are present, one at position 4, one at position 7 of formula (IV).

30 23. A catalyst as claimed in any one of claims 8 to 22 wherein $(R^1)_3OQ-$ is selected from the group consisting of $OSi(CH_3)_2N(C_{1-6}\text{-alkyl})H$,



10 24. A catalyst as claimed in any one of claims 8 to 23 wherein Z is present and both moieties of formula (IV) are identical.

15 25. A catalyst as claimed in claim 2 wherein Lig is of formula



wherein R^1 , R^2 , R^3 , Q and L are as hereinbefore defined.

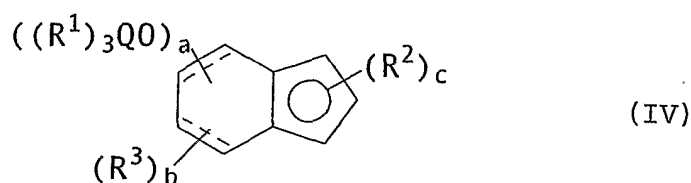
26. An olefin polymerisation catalyst system comprising or produced by the reaction of:

- 30 (i) a metallocene catalyst as claimed in any one of claims 1 to 25; and
 (ii) a cocatalyst/catalyst activator.

35 27. A process for olefin polymerisation comprising polymerising an olefin in the presence of a metallocene catalyst as claimed in claim 1 to 25.

28. A process for the preparation of a metallocene catalyst as claimed in any one of claim 1 to 25 which comprises metallating a η^5 cyclopentadienyl ligand which forms part of an indenyl or indenylid moiety with a transition metal or a lanthanide, characterised in that said moiety is directly or indirectly substituted at the 4- 5-, 6- or 7-position by a pendant siloxy or germyloxy group.

10 29. A compound of formula (IV)



15

(wherein one or more of the ring carbon atoms may be replaced by a ring heteroatom;

each Q is either a silicon or a germanium atom;

20 either or both of the bonds shown as ----- may be present or absent;

each R^1 which may be the same or different is a hydrogen or a C_{1-20} hydrocarbyl or a η^1 ligand example a σ ligand at least one R^1 being other than hydrogen;

25 each R^2 may be hydrogen or a group bonded to the 5-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC) carbon, oxygen, silicon, germanium, nitrogen or sulfur;

30 each R^3 may be hydrogen or a group bonded to the 6-membered ring through an atom of groups 14, 15 or 16 of the periodic table (IUPAC); or

two or more R^2 and/or two or more R^3 groups attached to adjacent ring atoms on the same ring together form a 5- to 8-membered fused ring; and optionally

35 one R^2 or R^3 is -L-Z wherein L is a 1 to 4 atom chain and Z is a second moiety of formula (IV) and joined to L through one R^2 or R^3 , if present in which L is one and the same chain common to both moieties,

- 58 -

a is an integer between 1 and 3,
b is an integer between 1 and 3, the sum of a and b
being no more than 4,
c is an integer between 1 and 3,
5 with the proviso that no more than one -L-Z group
is present in each ligand In) and salts and complexes
thereof.

INTERNATIONAL SEARCH REPORT

In International Application No
PC I/GB 02/02853

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F4/60 C08F10/00 C07F7/18 C07F17/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C07F

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

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LINNOLAHTI, MIKKO ET AL: "Theoretical Study on the Factors Controlling the Accessibility of Cationic Metal Centers in Zirconocene Polymerization Catalysts" MACROMOLECULES (2000), 33(25), 9205-9214, XP002187589	1-12, 16-19, 21, 25-27, 29
Y	page 9210, column 1, paragraph 6 page 9210, column 2, paragraph 1 example S14 page 9211; example S14; table 3 page 9211, column 1, paragraph 2 page 9212, column 2, paragraphs 2, 3 page 9207, column 1, paragraph 4 --- -/--	28

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

27 September 2002

Date of mailing of the international search report

10/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/02853

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	LUTTIKHEDDE H J G ET AL: "Bis(triisopropylsiloxyindenyl) zirconocenes" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 555, no. 1, 25 March 1998 (1998-03-25), pages 127-134, XP004128622 ISSN: 0022-328X page 128; figure 1	28
X	WO 93 11258 A (BIOXYTECH) 10 June 1993 (1993-06-10) example 4	29
X	TANAKA, KIYOSHI ET AL: "Synthetic studies on a picrotoxane sesquiterpene, coriamyrtin. II. An effective stereocontrolled synthesis of the picrotoxane skeleton except for a C1 unit at the C9 position and functionalization of the five-membered ring" CHEM. PHARM. BULL. (1983), 31(6), 1958-71 ' XP001108954 page 1963, column 1; example 30	29
X	US 6 160 184 A (MCMORRIS TREVOR C) 12 December 2000 (2000-12-12) figure 3; example 40	29

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/GB 02/02853

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9311258	A	10-06-1993	FR 2684378 A1	04-06-1993
			FR 2687664 A1	27-08-1993
			AU 3259393 A	28-06-1993
			DE 69212334 D1	22-08-1996
			DE 69212334 T2	09-01-1997
			EP 0625209 A1	23-11-1994
			WO 9311258 A1	10-06-1993
			JP 7506331 T	13-07-1995
			US 5543298 A	06-08-1996

US 6160184	A	12-12-2000	US 5723632 A	03-03-1998
			US 2001029303 A1	11-10-2001
			AU 3744397 A	25-02-1998
			EP 0918776 A1	02-06-1999
			JP 2000515552 T	21-11-2000
			WO 9805669 A1	12-02-1998
			US 6252093 B1	26-06-2001
			US 5856580 A	05-01-1999
