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(71) Applicant *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: VAN BEEK, Johannus, Antonius, Maria [NL/NL]; St. Servaasbolwerk 10, NL-6211 NB Maastricht (NL). VAN DOREMAELE, Gerardus, Henricus, Josephus [NL/NL]; Op de Hoef 6, NL-6132 HN Sittard (NL). GRUTER, Gerardus, Johannes, Maria [NL/NL]; Ravelijnstraat 23, NL-6217 LW Maastricht (NL). ARTS, Henricus, Johannes [NL/NL]; Montjoiestraat 4, NL-6151 JD Sittard (NL). EGGELS, Guillaume, Hermanus, Maria, Rene [NL/NL]; Hammermolen 43, NL-6086 BE Roggel en Neer (NL).

(74) Agent: KRIJGSMAN, Willem; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

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(54) Title: CATALYST COMPOSITION AND PROCESS FOR THE POLYMERIZATION OF AN OLEFIN

(57) Abstract

The invention relates to a new catalyst composition which is suitable for the polymerization of an olefin and which comprises a reduced transition metal complex and a co-catalyst. The invention is characterized in that the transition metal complex consists of a reduced transition metal, chosen from groups 4-6 of the Periodic Table of the Elements, with a multidentate monoanionic ligand and with two monoanionic ligands. In particular the reduced transition metal is titanium (Ti).

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CATALYST COMPOSITION AND PROCESS FOR THE POLYMERIZATION OF AN OLEFIN

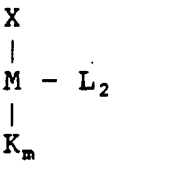
The invention relates to a catalyst composition which is suitable for the polymerization of an olefin and comprises a reduced transition metal complex and a co-catalyst. The invention also relates to a process for the polymerization of an olefin with such a catalyst composition.

Catalyst compositions comprising a reduced transition metal complex and a co-catalyst are known from WO-A-93/19104, which describes complexes of a reduced transition metal of group 4 of the Periodic Table of the Elements, with a bidentate dianionic ligand bonded to it.

The catalyst composition of the present invention is distinguished from that in that the transition metal complex consists of a reduced transition metal chosen from groups 4-6 of the Periodic Table of the Elements combined with a multidentate monoanionic ligand (X) and two monoanionic ligands (L) as well as, optionally, extra ligands (K).

Such a catalyst composition has not been described before, nor applied in a polymerization of an olefin.

The catalyst composition of the invention is characterized in that the transition metal complex has the following structure:



(I)

where X is $(Ar\text{-}R\text{-})_s Y(\text{-}R\text{-}DR'_n)_q$

and the symbols have the following meanings:

M a reduced transition metal from group 4, 5 or 6 of the Periodic Table of the Elements,

X a multidentate monoanionic ligand,

Y a cyclopentadienyl group, an amidino or phosphidino group, bonded to M,

R a connecting group between the Y group and the DR'_n or Ar group,

D an electron-donating hetero atom chosen from group 15 or 16 of the Periodic Table of the Elements,

R' a substituent,

Ar an electron-donating aryl group,

L monoanionic ligand bonded to M, to the exclusion of a cyclopentadienyl group, an amidino or phosphidino group,

K a neutral or anionic ligand bonded to M,

m the number of K groups,

n the number of R' groups bonded to D,

q and s $q + s \geq 1$.

A few examples of transition metal complexes according to the invention are presented in Table 5.

In the following the various components (groups) of the transition metal complex will be discussed in more detail.

a) The transition metal (the M group)

The transition metal in the complex has been chosen from groups 4-6 of the Periodic Table of the Elements (see the new IUPAC notation to be found on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990). More preferably, the transition metal has been chosen from group 4; the highest preference is given to titanium (Ti) as transition metal.

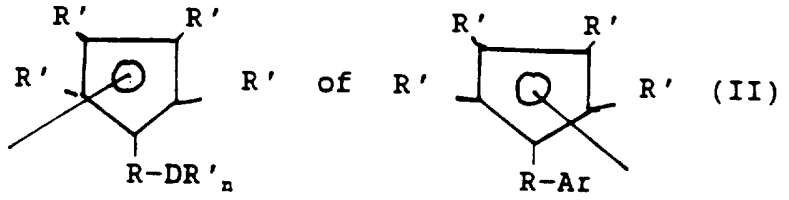
The transition metal is present in reduced form in the complex, which means that the transition metal is in a reduced oxidation state. By 'reduced oxidation state' is meant an oxidation state which is lower than the highest possible oxidation state (at most M^{3+} for a transition metal of group 4, at most M^{4+} for a transition metal of group 5 and at most M^{5+} for a transition metal of group 6).

b) The X group

The X group is a multidentate monoanionic ligand consisting of three components: the Y group (a cyclopentadienyl group, an amidino or phosphidino group), the connecting group (bridge) R and the DR'_n or Ar group (the donor). A multidentate monoanionic ligand is a ligand which is bonded covalently to the transition metal at one site (the anionic site, Y) and may be bonded coordinatively to the transition metal at one (bidentate) other site or at several (tridentate, tetradentate, etc.) sites (via the D or Ar group(s)). Examples of tridentate monoanionic ligands are $Y-R-DR'_{n-1}-R-DR'_n$ and $Y(-R-DR'_n)_2$.

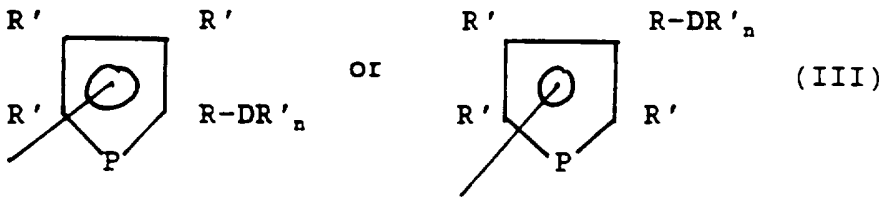
c) The Y group

The Y group may be a substituted cyclopentadienyl group (Cp group), with the possibility of a substitution in the Y group being present in addition to the substitution at the Y group. One or several of the substituents at the ring is the $R-DR'_n$ group or the R-Ar group. Examples of an X group with such a Y group (or ligand) have the following structure (with substituents at the ring):



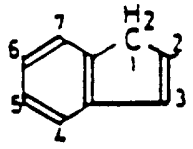
The Cp group may also be a hetero cyclopentadienyl group. Here and in the following a hetero cyclopentadienyl group (in the following also referred to as 'hetero ligand') is understood to be a group that has been derived from a cyclopentadienyl group, but in which at least one of the C atoms in the 5-ring of the cyclopentadienyl has been replaced by a hetero atom, which hetero atom may be chosen from group 14, 15 or 16 of the Periodic Table of the Elements. If there is more than one hetero atom present in the 5-ring of the hetero ligand, these hetero atoms may be either the same or different. More preferably, the hetero atom has been chosen from group 15, while yet more preferably the hetero atom is phosphorus.

By way of illustration of an X group with such a hetero ligand as Cp group, below the structures are represented of two X groups with hetero ligands containing one phosphorus atom as hetero atom (substitution at and in the Y group):



For clarity's sake it should be pointed out that the M group as a rule is bonded to the Cp group via an η^5 bond. The other R' substituents at the ring of the hetero ligand may be of the same type as those which may be present at the Cp group, as represented in formula (II); the hetero ligand may also be a hetero indenyl, hetero fluorenyl or hetero benzoindenyl group. Preferably, the Cp group according to formula (II) is substituted with four alkyl groups (the Y group is then called a tetraalkyl-cyclopentadienyl group); more preferably, these four alkyl groups are methyl groups.

The numeration of the substitution sites of the indenyl group is in general and in the present description as well based on the IUPAC Nomenclature of Organic Chemistry 1979, rule A 21.1. The numeration of the substituent sites for indene is shown below. This numeration is analogous for an indenyl group:

Indene  (IV)

The Y group may also be an amidino (-NR'-) or a phosphidino (-PR'-) group; in other words, the Y group may also be a group which contains nitrogen (N) or phosphorus (P) and is bonded covalently to the M group as well as to the R group.

d) The R group

The R group, which may also be absent (so that the DR'_n or Ar group is bonded directly to the Y group (the Cp, amidino or phosphidino group)), constitutes the bond between the Y group and the DR'_n or Ar group. The size of the R group is critical to the

extent that it determines the accessibility of the M group relative to the DR'_n or Ar group, which gives the desired intramolecular coordination. If the R group (or bridge) is too short, the donor may not coordinate well due to ring tension. The R groups may each separately be a hydrocarbon group with 1-20 carbon atoms (e.g. alkylidene, arylidene, aryl alkylidene, etc.). Examples of such groups are methylene, ethylene, propylene, butylene, phenylene, whether or not with a substituted side chain. Preferably, the R group has the following structure:

$$(-CR'_2-)_p \qquad (V)$$

where p = 1-4. The R' groups may each separately be as defined hereafter.

Besides carbon, the main chain of the R group may also contain silicon or germanium. Examples of such R groups are: dialkyl silylene, dialkyl germylene, tetra-alkyl disilylene or tetraalkyl silaethylene ($-SiR'_2CR'_2-$). The alkyl groups in such a group preferably have 1-4 carbon atoms and more preferably are a methyl or ethyl group.

e) The DR'_n group

This donor group consists of an electron-donating hetero atom D, chosen from group 15 or 16 of the Periodic Table of the Elements, and one or more substituents R' bonded to D. The number of R' groups is linked up with the nature of the hetero atom D, in the sense that n = 2 if D is from group 15 and n = 1 if D is from group 16. The R' substituent bonded to D is as defined hereafter with the exception that it cannot be H.

The hetero atom D has preferably been chosen from the group comprising nitrogen (N), oxygen (O),

phosphorus (P) and sulphur (S); more preferably, the hetero atom is nitrogen (N) or phosphorus (P). It is further possible for two R' groups in the DR'_n group to be connected with each other to form a ring-shaped structure (so that the DR'_n group can be a pyrrolidinyl group). The DR'_n group can form coordinative bonds with M.

f) The Ar group

The electron-donating group (or donor) used may also be a substituted or non-substituted aryl group ($C_6R'_5$), such as phenyl, tolyl, xylyl, mesitylyl, cumyl, tetramethyl phenyl, pentamethyl phenyl, etc. The coordination of this Ar group in relation to M may vary from η^1 to η^6.

g) The R' group

The R' groups may each separately be hydrogen or a hydrocarbon radical with 1-20 carbon atoms (e.g. alkyl, aryl, aryl alkyl and the like). Examples of such hydrocarbon radicals are methyl, ethyl, propyl, butyl, hexyl, decyl, phenyl and the like. Also, two adjacent hydrocarbon radicals may be connected with each other in a ring system; therefore the Cp group may be an indenyl, a fluorenyl or a benzoindenyl group. Such a group as well may contain one or more R' groups as substituents. R' may also be a substituent which instead of or in addition to carbon and/or hydrogen may comprise one or more hetero atoms of groups 14-16 of the Periodic Table of the Elements. Thus, a substituent may be a Si-containing group.

h) the L group

The transition metal complex contains two ligands L, of a monoanionic nature, which are bonded to the transition metal. Examples of such ligands, which

may be identical or different, are: a hydrogen atom, a halogen atom, an alkyl, aryl or aryl alkyl group, an alkoxy or aryloxy group, a group comprising a hetero atom chosen from group 15 or 16 of the Periodic Table of the Elements, for example:
- a sulphur compound, such as sulphite, sulphate, thiol, sulphinate, thioalkyl,
- a phosphorus compound, such as phosphite, phosphate.
Two L groups may also be connected with each other and so form a dianionic bidentate ring system.

These and other ligands can be tested for their suitability by means of simple experiments by one skilled in the art.

Preferably, L is a halogenide and/or an alkyl or aryl group; more preferably, a Cl group and/or a C_1-C_4 alkyl or a benzyl group. Excluded L groups are a Cp group, an amidino group or a phosphidino group (so L cannot be a Y group).

i) the K group

The K group is a neutral or anionic ligand bonded to M; it may also be absent, on the proviso that if K is monoanionic, the following holds for K_m:
m = 0 for M^{3+}
m = 1 for M^{4+}
m = 2 for M^{5+}

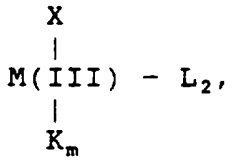
The K group may be a ligand as described for the L group or a (substituted) Cp group ($C_5R'_5$), an amido (NR'_2) or a phosphido group (PR'_2). The K group may also be a neutral ligand such as an ether, an amine, a phosphine, a thioether, etc. Two K groups may also be connected with each other by an R group and so form a bidentate ring system. Thus two K groups may also form together an X group. For each neutral K the value of m is higher by one than the value stated above for a monoanionic K group.

As can also be seen from formula (I) the X group of the transition metal consists of a Y group to which are linked one or more donor groups (the Ar groups), linked via an R group, and/or the DR'_n group(s). The number of donor groups is linked closely to the Y group; it is at least 1 and at most equal to the number of substitution sites that are present at a Y group.

With reference, by way of example, to the structure according to formula (II), one (1) substitution site in such a Cp group has been taken either by an R-Ar group or by an $R-DR'_n$ group ($q + s = 1$). If all R' groups in formula (II) are an R-Ar group and/or an $R-DR'_n$ group, the value of $(q + s)$ is 5.

A special embodiment of the catalyst composition according to the invention comprises a transition metal complex in which a bidentate/monoanionic ligand is present and in which the reduced transition metal has been chosen from group 4 of the Periodic Table of the Elements and has an oxidation state of 3+.

In this case the catalyst composition according to the invention comprises a transition metal complex of the following structure:



(VI)

where the symbols have the same meaning as described above for formula (I) and where M(III) is a transition metal chosen from group 4 of the Periodic Table of the Elements and is in oxidation state 3+.

Such a transition metal complex has no anionic K ligands (for an anionic K, m = 0 in case of M^{3+}).

It should be pointed out that in WO-A-93/19104 also transition metal complexes are described in which a group 4 transition metal in a reduced oxidation state (3+) is present. The complexes described in WO-A-93/19104 have the general formula:

$$Cp_a(ZY)_bML_c \qquad (VII)$$

The Y group in this formula (VII) is bonded covalently to the transition metal M (see p. 2 of WO-A-93/19104). This means that the Cp-Z-Y group is of a dianionic nature. The X group in the transition metal complex according to the invention is of a monoanionic nature. This changes the nature of the transition metal complex and consequently the nature of the catalyst that is active in the polymerization. Without being committed to it, the following theory is proposed. The transition metal complexes described in WO-A-93/19104 are ionogenic after interaction with the co-catalyst. However, the transition metal complex according to WO-A-93/19104 that is active in the polymerization is of a neutral nature (on the basis of the assumption that the polymerizing transition metal complex comprises, besides M(III), one dianionic ligand and one growing monoanionic polymer chain). By contrast, the polymerization active transition metal complex of the catalyst composition according to the invention is of a cationic nature (on the basis of the assumption that the polymerizing transition metal complex - based on the formula (VI) structure - comprises, besides M(III), only one monoanionic bidentate ligand and one growing monoanionic polymer chain).

Transition metal complexes in which the transition metal is in a reduced oxidation state, but have the following structure:

$$Cp - M(III) - L_2 \qquad (VIII)$$

as a rule are not active in olefin polymerizations. It is precisely the presence, in the transition metal complex, of the DR'_n or Ar group (the donor), bonded to the Y group by means of the R group, that gives a stable transition metal complex suitable for polymerization.

Such an intramolecular donor has been found to form a stable transition metal complex which shows a high catalytic activity. This is surprising since a transmission metal complex with an external donor, although being stable, does not show catalytic activity.

The catalyst composition also contains a co-catalyst. That may be a catalyst on the basis of an organometallic compound. The metal in such a compound has been chosen from group 1, 2, 12 or 13 of the Periodic Table of the Elements. At least one hydrocarbon radical is bonded directly to the metal via a carbon atom. Suitable organometallic compounds are for instance compounds of sodium, lithium, zinc, magnesium and, preferably, aluminium. The hydrocarbon group used in such compounds preferably contains 1-30, more preferably 1-10 carbon atoms. Examples of suitable compounds are amyl sodium, butyl lithium, diethyl zinc, butyl magnesium chloride and dibutyl magnesium. Preference is given to organoaluminium compounds. To be mentioned are the trialkyl aluminium compounds (such as triethyl aluminium, tri-isobutyl aluminium), the alkyl aluminium hydrides (such as di-isobutyl aluminium hydride), alkylalkoxy organoaluminium compound and halogen-containing organoaluminium compounds (such as diethyl aluminium chloride, diisobutyl aluminium

chloride, ethyl aluminium sesquichloride). Preferably, linear or cyclic aluminoxanes are used as organoaluminium compound.

As co-catalyst may also be used, besides or in addition to the organometallic compound, a compound which contains or yields in a reaction with the transition metal complex a non-coordinating or poorly coordinating anion. Such compounds have been described for instance in EP-A-426,637. Such an anion is bonded sufficiently labily to be replaced by an unsaturated monomer during the olefin polymerization. Such compounds are also mentioned in EP-A-277,003 and EP-A-277,004. Such a compound preferably contains a triaryl borane or a tetraaryl borate or an aluminium equivalent thereof. Examples of suitable compounds are:

- dimethyl anilinium tetrakis (pentafluorophenyl) borate $[C_6H_5N(CH_3)_2H]^+ [B(C_6F_5)_4]^-$
- dimethyl anilinium bis (7,8-dicarbaundecaborate)-cobaltate (III)
- tri(n-butyl)ammonium tetraphenyl borate
- triphenylcarbenium tetrakis (pentafluorophenyl) borate
- dimethylanilinium tetraphenyl borate
- tris(pentafluorophenyl) boron.

If this type of non-coordinating or poorly coordinating anions are used, it is preferable for the transition metal complex to be alkylated (that is to say: the L group is an alkyl group). As described for instance in EP-A-500,944, the reaction product of a halogenated transition metal complex and an organometallic compound, such as for instance TEA (= triethyl aluminium), may also be used.

The quantity of co-catalyst on a molar basis relative to the quantity of transition metal complex, in case an organometallic compound is used as co-catalyst, usually is 1 : 1 - 10,000 : 1, preferably 1 :

1 - 2,500 : 1. If a compound containing or yielding a non-coordinating or poorly coordinating anion is used as co-catalyst, the ratio usually is 1 : 100 - 1,000 : 1, preferably 1 : 1 - 250 : 1 an more preferably 1 : 2 - 250 : 1.

The transition metal complex as well as the co-catalyst may be present in the catalyst composition as a single component or as a mixture of several components. This will notably be the case in those situations where there is a need to influence the molecular properties, such as molecular weight and in particular the molecular weight distribution.

The catalyst composition according to the invention can be used by a method known as such as a catalyst component for the polymerization of an olefin. The olefin envisaged in particular is an olefin chosen from the group comprising α-olefin, internal olefin, cyclic olefin and di-olefin. Mixtures of these can also be used.

The invention relates in particular to a process for the polymerization of an α-olefin. The α-olefin is preferably chosen from the group comprising ethene, propene, butene, pentene, heptene, octene and styrene (substituted or non-substituted), mixtures of which may also be used. More preferably, ethene and/or propene is used as α-olefin. The use of such olefins results in the formation of (semi)crystalline polyethene homo- and copolymers, of high as well as of low density (HDPE, LDPE, LLDPE, etc.), and polypropene, homo- and copolymers (PP and EMPP). The monomers needed for such products and the processes to be used are known to the person skilled in the art.

The process according to the invention is also suitable for the preparation of amorphous or rubber-like copolymers based on ethene and another α-olefin. Propene is preferably used as the other α-

olefin, so that EPM rubber is formed. It is also quite possible to use a diene besides ethene and the other α-olefin, so that a so-called EADM rubber is formed, in particular EPDM (ethene propene diene rubber).

The catalyst composition according to the invention can be used supported as well as non-supported. The supported catalysts are used mainly in gas phase and slurry processes. The carrier used may be any carrier known as carrier material for catalysts, for instance SiO_2, Al_2O_3 or $MgCl_2$.

Polymerization of the olefin can be effected in a known manner, in the gas phase as well as in a liquid reaction medium. In the latter case, both solution and suspension polymerization are suitable, while the quantity of transition metal to be used generally is such that its concentration in the dispersion agent amounts to 10^{-8} - 10^{-4} mol/l, preferably 10^{-7} - 10^{-3} mol/l.

The process according to the invention will hereafter be elucidated with reference to a polyethene preparation known per se, which is representative of the olefin polymerizations meant here. For the preparation of other polymers on the basis of an olefin the reader is expressly referred to the multitude of publications on this subject.

The preparation of polyethene relates to a process for homopolymerization or copolymerization of ethene with one or more α-olefins having 3-12 carbon atoms and optionally one or more non-conjugated dienes. The α-olefins that are suitable in particular are propene, butene, hexene and octene. Suitable dienes are for instance 1,7-octadiene and 1,9-decadiene. It has been found that the catalyst composition of the present invention is especially suitable for solution or suspension polymerization of ethene.

Any liquid that is inert relative to the catalyst system can be used as dispersion agent in the polymerization. One or more saturated, straight or branched aliphatic hydrocarbons, such as butanes, pentanes, hexanes, heptanes, pentamethyl heptane or mineral oil fractions such as light or regular petrol, naphtha, kerosine or gas oil are suitable for that purpose. Aromatic hydrocarbons, for instance benzene and toluene, can be used, but because of their cost as well as on account of safety considerations, it will be preferred not to use such solvents for production on a technical scale. In polymerization processes on a technical scale, it is preferred therefore to use as solvent the low-priced aliphatic hydrocarbons or mixtures thereof, as marketed by the petrochemical industry. If an aliphatic hydrocarbon is used as solvent, the solvent may yet contain minor quantities of aromatic hydrocarbon, for instance toluene. Thus, if for instance methyl aluminoxane (MAO) is used as co-catalyst, toluene can be used as solvent in order to supply the MAO in dissolved form to the polymerization reactor. Drying or purification is desirable if such solvents are used; this can be done without problems by the average person skilled in the art.

Such a solution polymerization is preferably carried out at temperatures between 150°C and 250°C; in general, a suspension polymerization takes place at lower temperatures, preferably below 100°C.

The polymer solution resulting from the polymerization can be worked up by a method known per se. In general the catalyst is de-activated at some point during the processing of the polymer. The de-activation is also effected in a manner known per se, e.g. by means of water or an alcohol. Removal of the catalyst residues can mostly be omitted because the quantity of catalyst in the polymer, in particular the

content of halogen and transition metal is very low now owing to the use of the catalyst system according to the invention.

Polymerization can be effected at atmospheric pressure, but also at an elevated pressure of up to 500 MPa, continuously or discontinuously. If the polymerization is carried out under pressure the yield of polymer can be increased additionally, resulting in an even lower catalyst residue content. Preferably, the polymerization is performed at pressures between 0.1 and 25 MPa. Higher pressures, of 100 MPa and upwards, can be applied if the polymerization is carried out in so-called high-pressure reactors. In such a high-pressure process the catalyst according to the present invention can also be used with good results.

The polymerization can also be performed in several steps, in series as well as in parallel. If required, the catalyst composition, temperature, hydrogen concentration, pressure, residence time, etc. may be varied from step to step. In this way it is also possible to obtain products with a wide molecular weight distribution.

The invention also relates to a polyolefin that can be obtained by means of a polymerization process with utilization of the catalyst composition according to the invention.

The invention will now be elucidated by means of the following non-restrictive examples.

All tests in which organometallic compounds were involved were carried out in an inert nitrogen atmosphere, using standard Schlenk equipment. A method for synthesis of (dimethylaminoethyl)-tetramethyl cyclopentadienyl was published by P. Jutzi et al., Synthesis 1993, 684.

$TiCl_3$, the esters used and the lithium reagents, 2-bromo-2-butene and 1-chlorocyclohexene came from

Aldrich Chemical Company. $TiCl_3 \cdot 3THF$ was obtained by heating $TiCl_3$ for 24 hours in THF with reflux. (THF stands for tetrahydrofurane). In the following 'Me' means 'methyl', 'iPr' means 'isopropyl, 'Bu' means 'butyl', 'iBu' means 'isobutyl', 'tertBu' means 'tertiary butyl' 'Ind' means 'indenyl', 'Flu' means 'fluorenyl', 'Ph' means 'phenyl'.
Pressures mentioned are absolute pressures.

Synthesis of bidentate monocyclopentadienyl complexes

Example I

Synthesis of (dimethylaminoethyl)tetramethyl-cyclopentadienyltitanium(III)dichloride ($C_5Me_4(CH_2)_2NMe_2TiCl_2$).

a) Preparation of 4-hydroxy-4-(dimethylamino-ethyl)-3,5-dimethyl-2,5-heptadiene

2-bromo-2-butene (108 g; 0.800 mol) was added to 10.0 g of lithium (1.43 mol) in diethyl ether (300 ml) in about 30 minutes with reflux. After stirring overnight (17 hours), ethyl-3-(N,N-dimethylamino)propionate (52.0 g; 0.359 mol) was added to the reaction mixture in about 15 minutes. After stirring for 30 minutes at room temperature 200 ml of water was added dropwise. After separation the water phase was extracted two times with 50 ml of CH_2Cl_2. The organic phase was reduced by evaporation and the residue was distilled at reduced pressure. The yield was 51.0 g (67%).

b) Preparation of (dimethylaminoethyl)tetramethyl-cyclopentadiene

The compound (21.1 g; 0.10 mol) prepared as described under a) was added in a single portion to p-toluenesulphonic acid.H_2O (28.5 g; 0.15 mol), dissolved

in 200 ml of diethyl ether. After stirring for 30 minutes at room temperature the reaction mixture was poured out in a solution of 50 g of $Na_2CO_3 \cdot 10H_2O$ in 250 ml of water. After separation the water phase was extracted two times with 100 ml of diethyl ether. The combined ether layer was dried (Na_2SO_4), filtered and evaporated. Then the residue was distilled at reduced pressure. The yield was 11.6 g (60%).

c. Preparation of (dimethylaminoethyl)tetramethyl-cyclopentadienyltitanium(III)dichloride

1.0 equivalent of n-BuLi (1.43 ml; 1.6 M) was added (after cooling to -60°C) to a solution of the $C_5Me_4H(CH_2)_2NMe_2$ of b) (0.442 g; 2.29 mmol) in THF (50 ml), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -100°C and then $TiCl_3.3THF$ (0.85 g; 2.3 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at reduced pressure. After addition of special boiling point gasoline the complex (a green solid) was purified by repeated washing of the solid, followed by filtration and backdistillation of the solvent. It was also possible to obtain the pure complex through sublimation.

Example II

Synthesis of 9-(dimethylaminoethyl)octahydro-fluorenyltitanium(III)dichloride (H_8-$Flu(CH_2)_2NMe_2TiCl_2$).

a. Preparation of (dimethylaminoethyl)bis(1-cyclohexenyl)-methanol

1-chloro-1-cyclohexene (5.8 g; 0.049 mol) was added to lithium (1.1 g; 0.049 mol) in diethyl ether (50 ml) in a single portion. After stirring overnight at room temperature, stirring was continued for 7 more hours with reflux. After cooling, ethyl-3-(N,N-

dimethylamino)propionate (3.0 g; 0.021 mol) was added and as a result of the exothermic reaction refluxing occurred. After cooling to room temperature and stirring for another 30 minutes 100 ml of water was added. The water layer was separated off and extracted with diethyl ether. The combined ether layer was dried (K_2CO_3), filtered and evaporated. The yield was 4.5 g (83%).

b. Preparation of 9-(dimethylaminoethyl)octahydrofluorene

The compound (3.95 g; 0.015 mol) prepared as described under a) was added to p-toluenesulphonic acid.H_2O (4.0 g; 0.021 mol) in diethyl ether (100 ml), followed by stirring for 1 hour (temperature rising to reflux temperature). After cooling, 25 ml of water and 6.0 g of $Na_2CO_3 \cdot 10H_2O$ (0.021 mol) were added. After separation the water phase was extracted two times with a diethyl ether/pentane mixture (1/1, v/v). The combined organic layers were dried with K_2CO_3, filtered and reduced by evaporation. The residue was dissolved in diethyl ether (25 ml), after which a 25 ml n-BuLi solution (1.6 M in hexane; 0.040 mol) was added dropwise. The precipitate was filtered off, washed with diethyl ether (25 ml) and hydrolized with methanol. After acidifying with 1N HCl the methanolic layer was extracted 3 times with 25 ml of pentane. The combined pentane layers were washed twice with water, dried with K_2CO_3, filtered and evaporated. The yield was 1.5 g (41%).

c. Preparation of 9-(dimethylaminoethyl)octahydro-fluorenyltitanium(III)dichloride

1.0 equivalent of n-BuLi (0.97 ml; 1.6 M) was added (after cooling to -60°C) to a solution of the $C_{13}H_{17}(CH_2)_2NMe_2$ of b) (0.380 g; 1.55 mmol) in THF (50

ml), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -100°C and then $TiCl_3.3THF$ (0.58 g; 1.55 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at sub-atmospheric pressure. The purification was done as in example I.

Example III

Synthesis of (dibutylaminoethyl)tetramethyl-cyclopentadienyltitanium(III) dichloride ($C_5Me_4(CH_2)_2NBu_2TiCl_2$).

a. Preparation of ethyl 3-(N,N-di-n-butylamino)propionate

Ethyl 3-bromopropionate (18.0 g; 0.10 mol) was added carefully to di-n-butylamine (25.8 g; 0.20 mol), followed by stirring for 2 hours. Then diethyl ether (200 ml) and pentane (200 ml) were added. The precipitate was filtered off, the filtrate was evaporated and the residue was distilled at sub-atmospheric pressure. The yield was 7.0 g (31%).

b. Preparation of bis(2-butenyl)(di-n-butylaminoethyl)-methanol

2-Lithium-2-butene was prepared from 2-bromo-2-butene (16.5 g; 0.122 mol) and lithium (2.8 g; 0.4 mol) as in example I. To this, the ester of a) (7.0 g; 0.031 mol) was added with reflux in approx. 5 minutes, followed by stirring for about 30 minutes. Then was (200 ml) was carefully added dropwise. The water layer was separated off and extracted twice with 50 ml of CH_2Cl_2. The combined organic layer was washed once with 50 ml of water, dried with K_2CO_3, filtered and evaporated. The yield was 9.0 g (100%).

c. Preparation of (di-n-butylaminoethyl)tetramethyl-cyclopentadiene)

4.5 g (0.015 mol) of the compound of b) was added dropwise to 40 ml of concentrated sulphuric acid of 0°C, followed by stirring for another 30 minutes at 0°C. Then the reaction mixture was poured out in a mixture of 400 ml of water and 200 ml of hexane. The mixture was made alkaline with NaOH (60 g) while being cooled in an ice bath. The water layer was separated off and extracted with hexane. The combined hexane layer was dried with K_2CO_3, filtered and evaporated. The residue was distilled at sub-atmospheric pressure. The yield was 2.3 g (55%).

d. Preparation of (di-n-butylaminoethyl)tetramethyl-cyclo-pentadienyltitanium(III)dichloride

1.0 equivalent of n-BuLi (0.75 ml; 1.6 M) was added (after cooling to -60°C) to a solution of the $C_5Me_4H(CH_2)_2NBu_2$ of c) (0.332 g; 1.20 mmol) in THF (50 ml), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -100°C and then $TiCl_3.3THF$ (0.45 g; 1.20 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at sub-atmospheric pressure. The purification was done as in example I.

Example IV

Synthesis of dimethylaminomethyl)tetra-methyl-cyclopentadienyltitanium(III) dichloride ($C_5Me_4CH_2NMe_2TiCl_2$).

a. Preparation of 4-hydroxy-4-(dimethylaminomethyl)-3,5-dimethyl-2,5-heptadiene

Analogously to example I, this compound was prepared from N,N-dimethyl glycine ethyl ester (6.6 g;

0.050 mol) with a yield of 7.7 g (78%).

b. Preparation of (dimethylaminomethyl)tetramethyl-cyclopentadiene

At 0°C the compound of a) (7.7g; 0.039 mol) was added dropwise to concentrated sulphuric acid (30 g), followed by stirring for 30 minutes at 0°C. The reaction mixture was poured out in water (400 ml) and made alkaline with sodium hydroxide. After extraction with CH_2Cl_2 the organic layer was evaporated and the residue was distilled at sub-atmospheric pressure. The resulting product was dissolved in a mixture of hexane (50 ml) and diethyl ether (10 ml), after which n-butyl lithium (20 ml 1.6 M in hexane; 0.032 mol) was added dropwise. The precipitate was filtered off, washed with hexane and hydrolyzed with water. After extraction with CH_2Cl_2 the organic layer was evaporated and the residue was distilled at sub-atmospheric pressure. The yield was 1.9 g (27%).

c. Preparation of (dimethylaminomethyl)tetramethyl-cyclo-pentadienyltitanium(III)dichloride

1.0 equivalent of n-BuLi (2.90 ml; 1.6 M) was added (after cooling to -60°C) to a solution of the $C_5Me_4HCH_2NMe_2$ of b) (0.829 g; 4.63 mmol) in THF (50 ml), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -100°C and then $TiCl_3.3THF$ (1.71 g; 4.6 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at sub-atmospheric pressure. The purification was done as in example I.

Example V

Synthesis of (dimethylaminopropyl)tetra-methyl-cyclo-pentadienyltitanium(III) dichloride ($C_5Me_4(CH_2)_3NMe_2TiCl_2$)

a. Preparation of 4-hydroxy-4-(3-bromopropyl)-3,5-dimethyl-2,5-heptadiene

Analogously to example I, 2-lithium-2-butene was prepared from 2-bromo-2-butene (15.0 g; 0.11 mol) and lithium (2.8 g; 0.26 mol). To the product obtained, ethyl 4-bromobutanoate (11.0 g; 0.056 mol) was added dropwise and with reflux at -40 - -20°C, followed by stirring for 30 minutes at -20°C. Water (200 ml) and subsequently pentane (100 ml) were slowly added dropwise at -20°C. After separation of the layers the water layer was washed two times with 100 ml of pentane/ether (1/1, v/v), after which the combined organic layers were washed with water (50 ml). The organic layer was dried (K_2CO_3), filtered and evaporated. The yield was 14.0 g (96%).

b. Preparation of 4-hydroxy-4-(3-dimethylaminopropyl)-3,5-dimethyl-2,5-heptadiene

The compound of a) (4.5 g; 17 mmol) was added to 30 g of 40% dimethyl amine in water (0.27 mol), followed by stirring overnight at room temperature and subsequently for 1 hour at 60°C. After addition of Na_2CO_3 (5 g) the water layer was extracted with CH_2Cl_2. The organic layer was evaporated and the residue was added to a mixture of pentane (100 ml) and 1M HCl (300 ml). After separation the water layer was made alkaline with NaOH (16 g) and extracted three times with CH_2Cl_2 (50 ml). The combined organic layers were dried with K_2CO_3, filtered and evaporated. The yield was 2.1 g (54%).

c. Preparation of (dimethylaminopropyl)tetramethyl-cyclopentadiene

The compound of b) (2.1 g; 9.3 mmol) was dissolved in diethyl ether (30 ml), after which p-toluene sulphonic acid.H_2O (3.0 g; 15.8 mmol) was

added, followed by stirring for 1 hour at room temperature. $Na_2CO_3 \cdot 10H_2O$ (5 g) and water (25 ml) were added to the reaction mixture. After separation the water layer was extracted twice with CH_2Cl_2 and the combined organic layers were evaporated. The residue was dissolved in hexane (50 ml)/diethyl ether (10 ml), after which n-butyl lithium (20 ml 1.6 M; 32 mmol) was added dropwise. The precipitate was filtered off, washed with hexane and hydrolyzed with water. After extraction with CH_2Cl_2 the organic layer was dried (K_2CO_3), filtered and evaporated. The yield was 0.6 g (31%).

d. Preparation of (dimethylaminopropyl)tetramethyl-cyclo-pentadienyltitanium(III)dichloride ($C_5Me_4(CH_2)_3NMe_2TiCl_2$)

1.0 equivalent of n-BuLi (1.31 ml; 1.6 M) was added (after cooling to -60°C) to a solution of the $C_5Me_4(CH_2)_3NMe_2$ of c) (0.435 g; 2.1 mmol) in THF (50 ml), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -100°C and then $TiCl_3.3THF$ (0.78 g; 2.1 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at sub-atmospheric pressure. The purification was done as in example I.

Example VI

Synthesis of (N-pyrrolidinylethyl)tetra-methyl-cyclopentadienyltitanium(III)dichloride ($C_5Me_4(CH_2)_2NC_4H_8TiCl_2$)

a. Preparation of ethyl 3-(N-pyrrolidinyl)propionate

Ethyl acrylate (110.0 g; 1.1 mol) was dissolved in THF (250 ml). To this a solution of pyrrolidine (71.5 g; 1.0 mol) in THf (100 ml) was added dropwise in 75 minutes, after which stirring was

continued for 3½ hours at room temperature. The reaction mixture was evaporated by means of a rotary evaporator. The yield was 161.8 g (94%).

b. Preparation of 4-hydroxy-4-(2-N-pyrrolidinylethyl)-3,5-dimethyl-2,5-heptadiene

Analogously to example I, 2-lithium-2-butene was prepared from lithium (2.7 g; 0.39 mol) and 2-bromo-2-butene (21.4 g; 0.16 mol). To this a solution of the amino ester of a) (9.5 g; 0.055 mol) in diethyl ether (30 ml) was added dropwise in about 30 minutes. Stirring was continued for 30 minutes, after which 50 ml of water was very carefully added dropwise. After addition of another 100 ml of water and 100 ml of diethyl ether the layers were separated. The water layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with 50 ml of water, dried ($MgSO_4$), filtered and evaporated. The yield was 12.2 g (93%).

c. Preparation of (N-pyrrolidinylethyl)tetramethyl-cyclopentadiene

A solution of the crude compound (10.3 g; 43.5 mmol) of b) in 40 ml of diethyl ether was added dropwise in 15 minutes to a solution of p-toluene sulphonic acid.H_2O (10.5 g; 0.055 mol) in diethyl ether (100 ml). After stirring for 3 hours at room temperature the reaction mixture was poured out in a solution of $Na_2CO_3 \cdot 10H_2O$ (16.5 g) in 500 ml of water. After separation the water layer was extracted twice with diethyl ether. The combined ether layers were dried ($MgSO_4$), filtered and evaporated. The residue (10.1 g) was distilled at sub-atmospheric pressure. The yield was 6.0 g (50%).

d. Preparation of (N-pyrrolidinylethyl)tetra-methylcyclo-pentadienyltitaniumdichloride $(C_5Me_4(CH_2)_2NC_4H_8)TiCl_2$

A solution of the $C_5Me_4(CH_2)_2NC_4H_8$ (2.3 g; 10.5 mmol) of c) was dissolved in THF (50 ml). After cooling to -60°C 1.0 equivalent of n-BuLi was added (6.6 ml, 1.6 M), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -80°C and then 10.3 mmol (3.8 g) of $TiCl_3.3THF$ was added in a single portion. After stirring for 2 hours at room temperature the THF was removed under vacuum. The purification was done as in example I.

Polymerizations under solution conditions at 160°C

Examples VII-XIV and comparative example A

400 ml of pentamethyl heptane (abbreviation: PMH) and ethylene was supplied to a 1.3-litre reactor, with heating to polymerization temperature (160°C); the pressure was 2 MPa. Optionally a certain quantity of comonomer (1-octene) was added. Next, the required amount of a methyl aluminoxane (MAO) dissolved in toluene (Witco; 1.6 M) and the catalyst solution or slurry were premixed at room temperature for 1 minute and then supplied to the reactor. The catalyst supply vessel was rinsed out with 100 ml of PMH. The pressure in the reactor was kept constant by supplying ethylene. By cooling the reactor the temperature deviation from the setting (160°C) was limited to a maximum of 5°C. After 10 minutes the polymerization was stopped and the polymer was worked up by draining the solution and bthe solvent was evaporated under reduced pressure 50°C. The results are shown in table 1.

Table 1 Polymerization results at 160°C

[Ti] = concentration of Ti in the reactor (mmol/l)
Al/Ti = molar ratio Al/Ti
ml C_8 = number of ml of 1-octene supplied to the reactor
yield = number of grams of ethylene used to keep the pressure in the reactor constant
MI = melt index at the weight stated in brackets in the table
n.d. = not determined

Example	Transition metal complex	[Ti]	Al/Ti	ml C_8	yield	MI
VII	$(Me_4C_5(CH_2)_2NMe_2)TiCl_2$	0.02	800	0	7.5	9.0 (10 kg)
VIII	"	0.02	1600	0	7	n.d.
IX	"	0.02	400	0	6	n.d.
X	"	0.02	800	15	7	18 (1.2 kg)
XI	$(Me_4C_5(CH_2)_2NBu_2)TiCl_2$	0.02	800	0	10.5	10.3 (10 kg)
XII	"	0.02	800	15	11.5	11.9 (10 kg)
XIII	$(H_8\text{-}Flu(CH_2)_2NMe_2)TiCl_2$	0.02	800	0	2	n.d.
XIV	"	0.04	400	0	3	n.d.
A	For comparison: $TiCl_3.3THF$	0.04	800	0	0	n.d.

Examples XV-XXXI and comparative examples B-F

Polymerizations at lower temperatures

700 ml of PMH and the required quantity of octene were supplied to a 1.5-litre reactor. The ethylene pressure was 0.8 MPa and the temperature was 50, 80, 115 or 120°C. The catalyst slurry or solution were premixed in a catalyst vessel at room temperature for 1 minute with a solution of methyl aluminoxane (MAO) in toluene (Witco; 1.6 M) in such a way that Al/Ti = 2000 and then supplied to the reactor. The catalyst vessel was rinsed out with 50 ml of PMH. The pressure in the reactor was kept constant by supplying ethylene.

After 5 to 10 minutes of polymerization the product was collected and dried under vacuum at 60°C. The results are given in table 2a and table 2b. In a few cases a GPC (a gel permeation chromatogram) was made in order to determine the molecular weight Mw (weight average molecular weight).

Table 2a Polymerizations at lower temperatures

Example	Transition metal catalyst	concentration $*10^{-5}$ M/l	Temp. °C	C_8 grams	polymer yield kg/g Ti/ 5 min.	Mw kg/mol
XV	$(C_5Me_4(CH_2)_2NBu_2)TiCl_2$	0.67	115	0	23	
XVI	"	0.67	115	10.8	23	230
XVII	"	0.67	80	0	23	
XVIII	"	0.67	80	10.8	44	450
XIX	$(C_5Me_4(CH_2)_2NMe_2)TiCl_2$	1.33	115	0	12	
XX	"	1.33	115	10.8	15	
XXI	"	1.33	80	0	32	66
XXII	"	0.67	80	10.8	32	350
XXIII	$(C_5Me_4(CH_2)_3NMe_2)TiCl_2$	1.33	80	0	5	
XXIV	"	1.33	50	0	8	
XXV	$(H_8\text{-}Flu(CH_2)_2NMe_2)TiCl_2$	1.33	115	0	6	
XXVI	"	1.33	80	0	14	
XXVII	"	1.33	80	10.8	14	28
XXVIII	"	1.33	50	10.8	5	
XXIX	$(C_5Me_4(CH_2)_2NC_4H_8)TiCl_2$	1.33	115	0	8	
XXX	"	1.33	80	0	3	
XXXI	"	1.33	80	10.8	4	265
	For comparison:					
B	$TiCl_3.3THF$	2.7	80	0	2	
C	"	2.7	80	10.8	<0.1	
D	$(C_5Me_5)TiCl_2.THF$	1.33	80	10.8	<0.5	
E	$(C_5Me_5)Ti(IV)Cl_3$	2.7	80	10.8	1	
F	$(Cp)Ti(IV)Cl_3$	2.7	80	10.8	1	

Table 2b Polymerizations at lower temperatures (continued)

Examples XXXII-XLVIII and comparative examples G-I

The catalysts given in table 2b have been prepared in an analogous manner as decribed in the previous

examples out of the Li compounds of the ligands and $TiCl_3.3THF$.

The polymerizations were performed according to the procedure described in examples XV-XXXI. However, in the examples XXXII-VLIII gasoline was used in stead of PMH.

Examples	Transition metal catalyst	concentration $*10^{-5}$ M/l	Temp. °C	C_8 grams	polymer yield kg/g Ti/ 5 min.	Mw kg/mol
XXXII	$(C_5Me_4(CH_2)_2N(C_{10}H_{21})_2)TiCl_2$	0.67	80	18	15	
XXXIII	"	0.67	50	18	2	
XXXIV	$(C_5H_2{}^{tert}Bu_2(CH_2)_2NMe_2)TiCl_2$	0.67	80	18	50	
XXXV	"	1.33	120	18	6	
XXXVI	$(C_5H_2(SiMe_3)_2(CH_2)_2NMe_2)TiCl_2$	0.10	80	18	589	
XXXVII	"	0.10	120	18	20	
XXXVIII	$(C_5H_3(^{tert}Bu)(CH_2)_2NMe_2)TiCl_2$	0.67	80	18	178	
XXXIX	"	1.33	120	18	10	
XL	$(C_5H(^{i}Pr)_3(CH_2)_2NMe_2)TiCl_2$	0.13	80	18	90	
XLI	"	0.13	120	18	21	
XLII	$(C_5Me_4(CH_2)_2P^{i}Pr_2)TiCl_2$	0.33	120	18	130	32
XLIII	$(C_5Me_4Me_2SiP^{i}Pr_2)TiCl_2$	0.26	80	18	395	
XLIV	"	0.26	120	18	240	
XLV	$(C_5Me_4Me_2SiCH_2PPh_2)TiCl_2$	0.13	80	18	219	
XLVI	"	0.13	120	18	25	
XLVII	$(C_5Me_4(CH_2)_2P^{i}Bu_2)TiCl_2$	0.33	80	18	98	
XLVIII	"	0.33	120	18	112	16
	For comparison:					
G	$(Ind)Ti(IV)Cl_3$	2.67	80	18	0	
H	"	1.33	120	18	0	
I	$(C_5H_2(SiMe_3)_2(CH_2)_2NMe_2)Ti(IV)Cl_3$	0.26	80	18	9	
	"	0.26	120	18	2	

Example XLIX

Ethylene/propene copolymerizations (method 1)

The batch copolymerization experiments were carried out in a stirred 1.5-litre glass reactor. 3.125 mmol of Witco MAO (1.6 M in toluene) was supplied to the reactor as well as 500 ml of heptane which was saturated with ethylene and propene at a pressure of

0.8 MPa and a temperature of 70°C (the C2/C3 ratio in the gas phase was 2). 0.005 mmol of the $(C_5Me_4(CH_2)_2NBu_2)TiCl_2$ of example III was pre-mixed with 3.125 mmol of Witco MAO for 1 minute, after which the mixture was injected into the reactor. The polymerization time was 20 minutes. 16 g of a clear polymer was obtained. The proportion of C3 incorporated was 60% (determined by means of IR measurement) and the Hoekstra value was 38.

Examples L- LIV

Ethylene/propene copolymerizations (method 2)

The batch copolymerization experiments were carried out in a stirred 1.5-litre glass reactor. 500 ml of PMH which was saturated with ethylene and propene at a pressure of 1.0 MPa was supplied to the reactor at temperature of 80°C (the C2/C3 ratio in the gas phase was 0.5). 0.01 mmol of the Ti compound was pre-mixed with 10 mmol of Witco MAO (1.6 M in toluene) for 1 minute, after which the mixture was injected into the reactor. The polymerization time was 10 minutes. The proportion of C3 incorporated was determined by means of IR measurement.

Table 3

Example	transition metal complex	
L	$(C_5Me_4(CH_2)_2N(C_{10}H_{21})_2)TiCl_2$	7.7 grams clear rubber with 63% C_3
LI	$(C_5Me_4(CH_2)_2N^iBu_2)TiCl_2$	3.1 grams clear rubber
LII	$(C_5H(^iPr)_3(CH_2)_2NMe_2)TiCl_2$	10.0 grams rubber
LIII	$(C_5Me_4Me_2SiCH_2PPh_2)TiCl_2$	20.4 grams rubber with 14 % C_3
LIV	$(C_5H_3(^{tert}Bu)(CH_2)_2NMe_2)TiCl_2$	9.0 grams rubber with 15 % C_3

Examples LV and LVI

Continuous polymerizations at 160°C

Continuous ethylene/octene copolymerizations were performed using the methylated catalyst of example I with $[PhMe_2NH][B(C_6F_5)_4]$ as activator and TEA as scavenger. The autoclave (2L, 9.0 MPa) was completely filled with gasoline. In example LV the H_2 feed was 0.4 nL/hr and in example LVI no H_2 was used.

The catalyst given in example I was methylated with MeLi in diethylether using standard procedures.
The results are presented in table 4.

Table 4

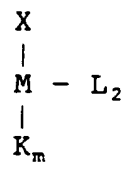
Example	activity Kg/mol Ti	D23 density	MI	Mw/Mn	MFR I21/I2	C8/C2 (m/m)
LV	6672	912	0.5	2.3	46.5	0.2
LVI	6960	887	17	2.5	26.5	0.59

Table 5 Examples of transition metal complexes according to the invention (see formulas I and VI)

M	L	Y	R	D	R'	K
Ti	Cl	C_5H_4	dimethylsilyl	N	methyl	L
Zr	F	C_5Me_4	diethylsilyl	P	ethyl	Y-R'
Hf	Br	Indenyl	dipropylsilyl	As	propyl	X
V	I	Fluorenyl	dibutylsilyl	Sb	n-butyl	diethyl ether
Nb	methyl	benzofluorenyl	methylamido	O	n-pentyl	tetrahydrofuran
Ta	methoxy	octahydrofluorenyl	dimethylgermanyl	S	methoxy	trimethylamine
Cr	ethoxy	C_5H_3(N-Bu)	diethylgermanyl	Se	ethoxy	triethylamine
Mo	hydride	tetrahydroindenyl	diethylpropylene		Cl	trimethylphosphine
W	isopropyl octyl propoxy phenoxy benzyl methylthio	$C_5H_3(SiMe_3)$ methylamido phenylphosphido	tetramethyldisiloxane diphenylsilyl tetramethylsilaethylene methylene diethylmethylene ethylene dimethylethylene ethylphosphidino phenylphosphidino		F Br I phenoxy benzyl H	triethylphosphine triphenylphosphine dimethylsulphide dimethylaniline

C L A I M S

1. Catalyst composition which is suitable for the polymerization of an olefin and comprises a reduced transition metal complex and a co-catalyst, characterized in that the transition metal complex has the following structure:



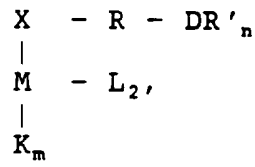
where X is $(Ar-R-)_s Y(-R-DR'_n)_q$
and the symbols have the following meanings:

M a reduced transition metal from group 4, 5 or 6 of the Periodic Table of the Elements,
X a multidentate monoanionic ligand,
Y a cyclopentadienyl group, an amidino or phosphidino group, bonded to M,
R an optional connecting group between the Y group and the DR'_n or Ar group,
D an electron-donating hetero atom chosen from group 15 or 16 of the Periodic Table of the Elements,
R' a substituent,
Ar an electron-donating aryl group,
L monoanionic ligand bonded to M, to the exclusion of a cyclopentadienyl group, an amidino or phosphidino group,
K a neutral or anionic ligand bonded to M,
m the number of K groups,
n the number of R' groups bonded to D,
q and s

$$q + s \geq 1.$$

2. Catalyst composition according to claim 1,

characterized in that the transition metal complex has the following structure:



where:
M is a transition metal from group 4 of the Periodic Table of the Elements in oxidation state 3+.

3. Catalyst composition according to any one of claims 1-2, characterized in that the transition metal is titanium (Ti).

4. Catalyst composition according to any one of claims 1-3, characterized in that the electron-donating hetero atom D is nitrogen (N) or phosphorus (P).

5. Catalyst composition according to any one of claims 1-4, characterized in that the R' group in the DR'_n group is an n-alkyl group.

6. Catalyst composition according to any one of claims 1-5, characterized in that the R group has the following structure:
$(-CR'_2-)_p$, $(-SiR'_2)_p$ or $(-SiR'_2-CR'_2-)_p$
where p = 1-4.

7. Catalyst composition according to any one of claims 1-6, characterized in that L is a halogenide, an alkyl group or a benzyl group.

8. Catalyst composition according to any one of claims 1-7, characterized in that the Y group is a substituted cyclopentadienyl group.

9. Catalyst composition according to any one of claims 1-8, characterized in that the co-catalyst contains a linear or cyclic aluminoxane or a

triaryl borane or triaryl borate.

10. Process for the polymerization of an olefin under the influence of a catalyst system, characterized in that the olefin is polymerized under the influence of a catalyst composition according to any one of claims 1-9.

11. Process according to claim 10, characterized in that the olefin has been chosen from the group comprising α-olefin, internal olefin, cyclic olefin and di-olefin or mixtures of these.

12. Process according to claim 11, characterized in that the α-olefin has been chosen from the group comprising ethene, propene, butene, pentene, heptene, octene, styrene or mixtures of these.

13. Process according to any one of claims 10-12, characterized in that a polymer is prepared on the basis of ethene and/or propene.

14. Process according to any one of claims 10-12, characterized in that a rubber-like polymer is prepared on the basis of ethene, α-olefin and optionally a diene.

15. Polyolefin to be obtained by a process according to any one of claims 10-14 or by polymerization of an olefin under the influence of a catalyst composition according to any one of claims 1-9.

16. Catalyst composition, process and polyolefin as described substantially and by means of the examples.

INTERNATIONAL SEARCH REPORT

Inten ıal Application No
PCT/NL 95/00372

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/64

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 6 C08F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 12112 (EXXON CHEMICALS PATENTS INC.) 23 July 1992 see claims 20,30-32 see examples 11,12 see page 16, line 4 - line 31	1,3,6,7, 11,12
X	WO,A,92 12117 (EXXON CHEMICALS PATENTS INC.) 23 July 1992 see claims 4-8,17 see page 10, line 20 - page 11, line 36 see page 14, line 8 - line 33	1,2,4
A	EP,A,0 608 054 (BP CHEMICALS) 27 July 1994 see claims 1,3 see figure 1	1

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[X] Further documents are listed in the continuation of box C.

[X] 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

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

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

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

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

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"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
31 January 1996	12 FEBRUARY 1996

Name and mailing address of the ISA	Authorized officer
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	Fischer, B

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INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/NL 95/00372

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 365 974 (HOECHST AKTIENGESELLSCHAFT) 2 May 1990 see claim 1 see page 4, line 15 - line 20 see page 5, line 28 - line 32 ---	1
A	WO,A,93 19104 (THE DOW CHEMICAL COMPANY) 30 September 1993 cited in the application see claims 1-4,6 see page 3, line 25 - page 4, line 3 -----	1

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter ial Application No
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