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(54) Title: CYCLOPENTADIENE COMPOUND WITH A NON-COORDINATING ANION (57) Abstract Precursor for a catalyst, comprising a transition metal or lanthanide with a ligand system in which at least one Cp derivative is present and in which the precursor contains a non-coordinating anion A ⁻ , which can stabilize a catalyst obtained by the activation of the precursor and which is bound to a cationic group of the Cp derivative or is bound to a cationic group forming part of or being bound to a bridge bound to the Cp derivative within the precursor, the cationic group containing a subgroup which is capable of reacting with a metal-bound alkyl, benzyl or phenyl group and a process for the polymerization of olefins in the presence of a catalyst prepared by contacting such a precursor with an alkylating compound.		

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CYCLOPENTADIENE COMPOUND WITH A NON-COORDINATING ANION

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The invention relates to a precursor for a catalyst, comprising a transition metal or lanthanide with a ligand system in which at least one Cp derivative is present.

Such precursors are generally known within the relevant field of the technology for the preparation of catalysts for the polymerization of α -olefins, diolefins and other ethylenically unsaturated monomers. Chemistry & Industry, 7 November 1994, pages 857-862, lists these precursors and describes how they are activated to yield catalysts. This activation involves contacting the precursors with an alkylating compound and an activator or, if the metal already contains several alkyl groups as ligands, only with an activator. It is generally assumed that this results in the formation of active ion pair, of which the cation is the actual, active catalyst. This activation generally takes place in situ in the polymerization unit. From US-A-5.198.401 it is known to activate in particular precursors with ligand systems in which two Cp derivatives are present, yielding a catalyst in which the anion is a labile, non-coordinating anion. This anion fed to the polymerization unit is combined with a cation.

A disadvantage of the known precursors is that their activation in the way described above may result in byproducts being formed that may have an adverse effect on the polymerization process or, if they exhibit catalytic activity themselves, may give rise to the formation of undesired byproducts.

Moreover, the anion or a derivative thereof remains behind in the reaction mixture. In the process according to US-A-5.198.401 this is N-N-dimethylaniline, a toxic substance, which ends up in the polymer formed and limits its applicability, for instance in food packagings. That is why there is a need for precursors that can be activated in situ without the above-mentioned adverse effects occurring.

It is the aim of the invention to provide a precursor that at least partly meets this demand.

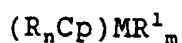
According to the invention this aim is achieved in that the precursor contains a non-coordinating A^- anion which can stabilize a catalyst obtained by activation of the precursor and which is bound to a cationic group of the Cp derivative or is bound to a cationic group forming part of or being bound to a bridge bound to the Cp derivative within the precursor, the cationic group containing a subgroup that is capable of reacting with a metal-bound alkyl, benzyl, or phenyl group.

The precursor according to the invention can simply be activated by contacting it with only an alkylating compound, upon which the anion stabilizes the metal that has become cationic on activation without affecting the capability of the cationic metal complex to act as catalyst. For this reason the anion must be labile enough to be replaced by a monomer to be polymerized. Although the inventor does not want to be bound by any theoretical explanation, the following seems to be a plausible description of the mechanism that occurs. The reaction with the alkylating compound causes two or more of the non-Cp ligands on the metal to be replaced by an alkyl group, of which at least one subsequently reacts in turn with the subgroup bound to the cationic group which is capable of reacting with a metal-bound alkyl, benzyl, or phenyl group. This causes the metal to become cationic, while also the non-

coordinating anion is liberated. The non-coordinating anion then stabilizes the cationic metal complex. Thus, a catalyst is formed which, apart from the presence of a neutral residue of the cationic group, corresponds to the known precursor described above after it has been activated with a non-coordinating anion, if necessary in the presence of an alkylating compound, to yield a catalyst.

The precursor according to the invention differs from the known precursors in that it already contains the non-coordinating anion, so that this anion is always available in the right amount, and in that the addition of an alkylating compound directly results in its conversion into the active catalyst, without the formation of undesirable byproducts.

As basis for the precursor according to the invention essentially any compound can be used in which a transition metal or lanthanide with a ligand system containing at least one Cp derivative is present and which can be activated to yield a catalyst by a non-coordination anion, if necessary in the presence of an alkylating agent. A great many of such compounds are known. The precursor according to the invention differs from these known compounds in that it contains a cationic group that is bound to the Cp derivative or a cationic group that forming part of or being bound to a bridge bound to the Cp derivative within the precursor, the cationic group containing a group that is capable of reacting with a metal-bound alkyl, benzyl or phenyl group. Thus, the precursor according to the invention also exists in a great many variants. Examples of basic forms of compounds, known per se, which can serve as precursor according to the invention if they contain a non-coordinating anion bound to a cationic group at one of the positions specified above are:



(I)

wherein:

R_nCp is a cyclopentadienyl derivative, in which Cp is a cyclopentadienyl group or a group derived from such a group, for example an indenyl group or a fluorenyl group, including the corresponding compounds which contain at least one hetero atom in the Cp ring, chosen from group 15 or 16 of the Periodic System of the Elements, as printed on the inside cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990; the R groups each separately are hydrogen, a hydrocarbon radical with 1-20 C-atoms, for example alkyl, aryl, aralkyl, or a corresponding group which instead of carbon or hydrogen contains one or more hetero atoms from group 15 or 16 of the Periodic System;

M is a transition metal chosen from group 4, 5 or 6 of the Periodic System of the Elements or a lanthanide, preferably titanium, zirconium or hafnium, which may be either in its highest valence state or in a reduced valence state;

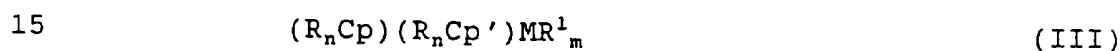
R^1 is a mono-anionic ligand, excluding a Cp derivative or a group from such a derivative and excluding an alkyl group. In connection with the choice of a component R^3 of the cationic group, to be specified below, R^1 may be subject to other limitations and preferences. These will be specified when the cationic group is discussed.

In addition, n ranges from 0 up to and including the number of positions that are free for substitution on Cp and m is the valence state of M minus 1.

Such compounds are known, for example, from EP-A-420.134.



wherein R, R¹, Cp, n and M are as defined above, m is the valence of M minus 2 and Z forms a bridge between Cp and Y. Such compounds are known from US-A-5.272.236 and Z and Y here have the same meaning as in said patent specification.



wherein R, R¹, Cp, n and M are as defined above, Cp' may have been chosen independently of Cp from the same group as Cp and m is equal to the valence of M minus 2. Such compounds are known from EP-A-406.912.



where R, R¹, Cp, Cp' and n are as defined above, A' forms a bridge between Cp and Cp' and m is equal to the valence of M minus 2. Such compounds and bridges suitable for use therein and a process for the preparation thereof are known from EP-A-459.320.

The precursor according to the invention differs from said compounds in that a cationic group X⁺ is present in the precursor. Also, a non-coordinating anion A⁻ is bound to this cationic group X⁺. The precursor therefore contains a group of the form -X⁺A⁻, while in all complexes mentioned, (I)-(IV), X may take the place of a group R. In complexes having the form (II) X may also be bound to Y or Z or X may also form part of Z. In complexes having the form (IV) X may also form part of the bridge A' or be bound to it.

The cationic group X⁺ preferably has the form



5 wherein Q may be absent or be a hydrocarbon group with 1-20 C atoms, for example alkylidene, arylidene, arylalkylidene, optionally with a substituted side chain. Preferably, Q has the following structure:



wherein preferably p = 1-4, E is an atom from group 14 of the Periodic System and the R⁴ groups are each separately hydrogen, a hydrocarbon residue with 1-20 C
15 atoms, for example alkyl, aryl, aralkyl or a corresponding group which instead of carbon or hydrogen contains one or more hetero atoms from group 15-16 of the Periodic System. Examples of such Q-groups then are dialkylsililene, dialkylgermylene, tetraalkyl-
20 disilylene, tetraalkylsiliethylene. The alkyl groups in such a Q-group preferably have 1-4 C-atoms and are more preferably a methyl or ethyl group.

Further, D is a hetero atom chosen from group 15 or 16, R² is a hydrocarbon radical with 1-20 C-atoms,
25 for example alkyl, aryl, aralkyl, or a corresponding substituent which instead of carbon or hydrogen contains one or more hetero atoms from group 15-16 of the Periodic System, R³ is a group that is capable of reacting with a metal-bound alkyl, benzyl or phenyl
30 group and preferably H, and k is the valence of D minus 1 when X is bound to Cp, Cp' or to a bridge and equal to the valence of D minus 2, when X forms part of a bridge. The group R¹ described above must not be reactive with R³ and preferably R¹ is a halogen, more
35 preferably chlorine.

Examples of transition metal compounds with a Cp-derived ligand in which a cationic group is present

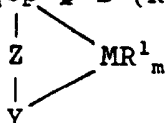
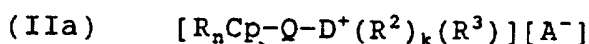
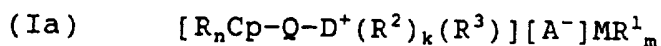
are known from the Journal of Organometallic Chemistry 486 (1995) 287-289. This publication teaches that the incorporation of N-functionality into Cp complexes affects the solubility and the association behaviour of these complexes. The insight that the advantages described in the foregoing can be attained by incorporating a non-coordinating anion into Cp-containing transition metal complexes is wholly absent in this reference.

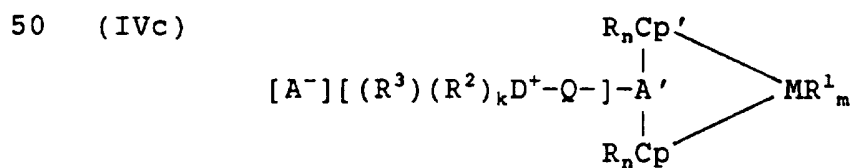
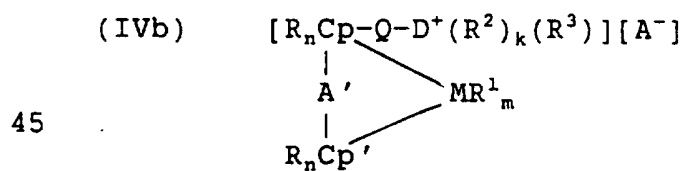
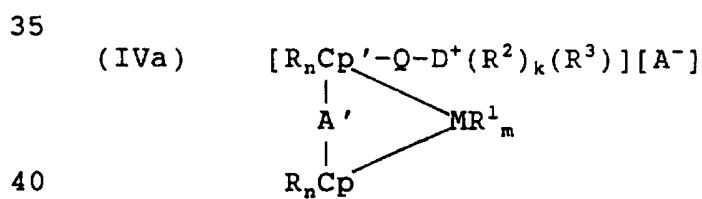
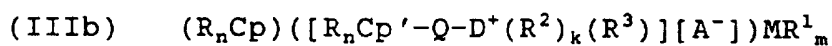
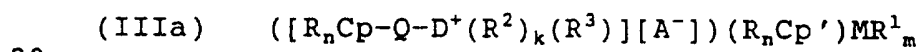
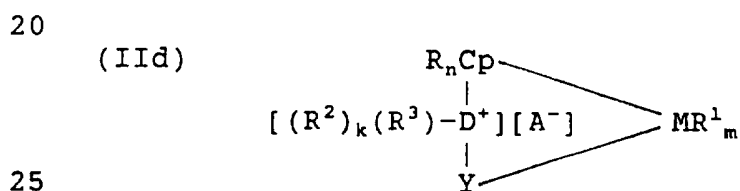
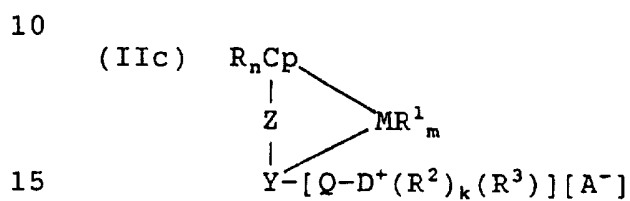
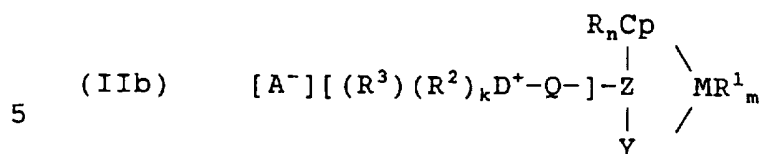
Particularly suitable compounds in which the actual valence state of the metal is not the highest possible valence state and which are not known from the state of the art are those according to the following formula VI:

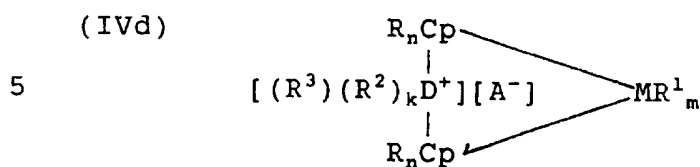


wherein m is equal to the actual valence of M minus 1. The cationic group X⁺ can be formed in these compounds by a compound of a group R³. Preferably, M is Ti(III) and m consequently 2. The presence of the -QD(R²)_k group is essential for the catalytic action of these compounds.

Examples of precursors according to the invention based on the known precursors according to formulas I-IV and differing therefrom by the presence of a cationic group according to formula V and a non-coordinating anion bound thereto are the following:



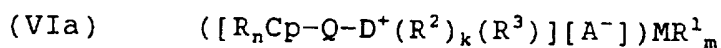




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An example of a precursor according to the invention based on a compound according to formula VI is the following:

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The anion A^- is a non-coordinating anion and can stabilize a catalyst obtained by activation of the precursor. A^- preferably contains at least an element from group 13. Particularly suitable are the non-coordinating anions that are known from US-A-5.198.401. These consist, for example, of a compound of a metal or

25 metalloids having a formal valence m' with more than m' radicals which independently may be a hydride radical, a bridged or unbridged dialkylamido radical, alkoxide and aryloxy radical, a hydrocarbyl or substituted hydrocarbyl radical, a halocarbyl or substituted

30 halocarbyl radical or a hydrocarbyl- or halocarbyl-substituted organometalloid radical, which each, but not more than one at a time, may be a halide radical. The charge of the anion equals the number of radicals minus the formal valence of the metal or metalloid.

35 Examples of suitable metals Al, Au, and Pt. Examples of suitable metalloids are B, P and Si.

Suitable B-containing compounds are, for example, tetra(phenyl)borate, tetra(p-tolyl)borate, tetra(o-tolyl)borate, tetra(pentafluorophenyl)borate, tetra(o,p-dimethylphenyl) borate, tetra(m,m-dimethylphenyl)borate

40

and tetra(p-trifluoromethylphenyl)borate. Preferably, tetra(pentafluorophenyl)borate is used.

The precursors according to the invention are prepared in a way that is analogous with the preparation of a compound according to any of the formulas I-IV or the other suitable starting compounds mentioned, use being made of the processes described for these. The difference with these processes is that at a suitable moment during the execution of the known process the cationic group is bound to the Cp derivative or to a bridge bound to the Cp derivative within the precursor or is incorporated into this bridge and that then a non-coordinating anion A^- , which can stabilize a catalyst obtained by activation of the precursor, is bound to the cationic group. For the preparation of a precursor according to the invention preferably first of all a compound having the form $-QD(R^2)_k$ is bound to one of the constituent parts, from which according to a process known for this a corresponding basic compound can be prepared. In conformity with the foregoing these constituent parts are a Cp derivative or a bridge. One skilled in the art will be able to join the $-QD(R^2)_k$ group to a Cp derivative or the bridges as described above by means of chemical reactions known per se for this purpose. Afterwards the analogous compound, provided with a bound $-QD(R^2)_k$ group, is prepared in conformity with the process known for the preparation of the basic compound. In the next step, the R^3 group is bound to the $-QD(R^2)_k$ group, the entire compound being neutralized by a counterion T^- , so that a group of the form $-QD^+(R^2)_k(R^3)T^-$, or denoted in another fashion X^+T^- , is formed. In a last step the compound thus obtained is then contacted with a compound of the form Z^+A^- , in which A^- is the non-coordinating anion and Z^+ a positively charged counterion. This must take place under conditions in which A^- and T^- change position,

yielding the precursor according to the invention. This may be effected, for example, by dissolving the compounds in a medium in which the compound Z^+T^- , as a rule a salt, is insoluble. As counterion T^- halides are preferably used, preferably chloride, and as counterion Z^+ preferably alkali metals, preferably lithium. If the compound HA is present, the last and the penultimate step can be combined and A^- can be combined with the $-QD(R^2)_k$ group in a single step, it being understood that in that case the R^3 group in the precursor is hydrogen.

The invention also relates to a process for the polymerization of α -olefines, diolefines and other ethylenically unsaturated monomers in the presence of a catalyst comprising a transition metal or lanthanide with a ligand system in which at least one Cp derivative is present and that is stabilized with a non-coordinating anion A^- .

Such a process is known from US-A-5.198.401. In this process a metallocene compound according to formula III or IV as defined above (which means it is a precursor known from the state of the art) and in which R^1 is an organic radical, as a rule methyl, is reacted in an organic solvent with a complex containing the non-coordinating anion, after which an olefinic monomer is passed through the solution. This leads to the formation of the corresponding olefinic polymer. In the complex at least a hydrogen atom is present, which in the reaction of the complex with the compound according to formula III or IV combines with the organic radical R^1 .

A drawback of this known process is that besides the desired catalyst byproducts may be formed, as described in US-A-5.198.401, that may have an adverse effect on the polymerization process or, if they display catalytic activity themselves, may give rise to the formation of undesired byproducts.

The aim of the invention is to provide a

process in which this drawback is eliminated or reduced.

According to the invention this is achieved in that the catalyst is formed by contacting a precursor according to the invention as described above with an alkylating compound.

With the process according to the invention the non-coordinating anion is already present, being bound one to one to the precursor, and there is no need to add it in complex form, so that the formation of foreign components in the polymerization mixture is avoided.

In the process according to the invention the precursors described above can be used. One skilled in the art will choose the suitable precursor on the basis of his knowledge of the suitability of the catalyst formed in the activation with the alkylating compound for the intended polymerization. These possible applications are usually known per se from the publications which describe the relevant catalysts and their properties. It should be noted that a plurality of methods are known per se for solution, suspension or gas-phase polymerization of olefinic monomers by the action of transition metals with a Cp derivative as ligand. Since after activation the precursor according to the invention is essentially the same as the catalysts prepared according to the known process or differs from these only because of the presence of the residual $-Q-D(R^2)_k$ group, it can in principle be used in any of these known processes.

Suitable alkylating compounds are compounds meeting the general formula $M'R^5_{k-m}X'_m$, wherein M' is an element from group 1, 2, 12 or 13 of the Periodic System of the Elements, k is the oxidation state of M' , R^5 is a hydrocarbon radical with 1-20 carbon atoms, X' is a halogen atom or an alkoxy group with 1-20 carbon atoms, m has a value of 0, 1 or 2, and $(k-m) \geq 1$. If $k > 1$,

X' may also be a hydrogen atom. If $m=1$ the alkyl and/or alkoxy groups may be the same or different. Mixtures of these compounds can also be used. Oligomeric organo-aluminium compounds with linear and cyclic structures, such as for example MAO (methylaluminoxane), are also suitable. Examples of suitable alkylating compounds are methylolithium, butyllithium, phenyllithium, ethylbutylmagnesium, butyloctylmagnesium, methylmagnesiumchloride, ethylmagnesiummethoxide, ethylmagnesiumchloride, ethylmagnesiumbromide, phenylmagnesiumbromide, ethylmagnesiumhydride, benzylmagnesiumchloride, trimethylaluminium, triethylaluminium, triisobutylaluminium, trioctylaluminium, ethylaluminiumsesquichloride, ethylaluminiumdichloride, diethylaluminiummethoxide, dioctylaluminiumiodide, diethylaluminiumhydride, methylaluminoxane, ethylaluminoxane, triethylboron and dimethylboronbromide. Preferably, butyllithium, triethylaluminium, triisobutylaluminium, trioctylaluminium or methylaluminoxane are used as alkylating compound.

The invention will be explained with reference to the following examples.

25 Example I

Synthesis of $[(\text{CpEtNMe}_2\text{H})[\text{B}(\text{C}_6\text{F}_5)_4])\text{TiCl}_3$.

I.1. Synthesis of dimethylaminoethylcyclopentadienyltitaniumtrichloride.

30 After cooling to -60°C , a solution of 1.0 ml (9.12 mmol) of titaniumtetrachloride in 30 ml of dichloromethane was added to a solution of 1.96 g (9.37 mmol) of trimethylsilyldimethylaminoethylcyclopentadiene in 30 ml of dichloromethane which had been
35 cooled to -60°C . An orange/brown solution formed practically immediately. The reaction mixture was stirred for about 10 hours at room temperature and then

it was filtered and the filtrate was evaporated down to a few millilitres. Subsequently, 50 ml of special boiling point solvent (SBPS) was added, so that a slurry was formed, from which a yellow/orange precipitate separated out. This precipitate was washed with special boiling point solvent and evaporated. 2.4 g (η:91%) of $\text{NMe}_2\text{EtCpTiCl}_3$ was obtained in the form of an orange/yellow solid.

^1H -NMR (CD_2Cl_2) analysis showed the composition to be: 6.9 ppm (dd, 2H ar); 6.8 ppm (dd, 2H ar); 3.2 ppm (t, 2H CH_2N); 3.0 ppm (t, 2H CH_2); 2.6 ppm (s, 6H NMe_2).

I.2. Synthesis of dimethylaminohydrochloride-ethylcyclopentadienyltitanium-trichloride.

To a solution of 1.0 g (3.4 mmol) of dimethylaminoethylcyclopentadienyl-titaniumtrichloride in 30 ml of dichloromethane (DCM) were subsequently added at room temperature 0.5 ml (3.9 mmol) of trimethylchlorosilane and 0.3 ml (7.4 mmol) of methanol. A red/orange slurry is formed practically immediately.

After stirring for 2 hours the slurry was washed twice with 50 ml of SBPS and evaporated. 1.1 g of dimethylaminohydrochloride-ethylcyclopentadienyl-titaniumtrichloride was obtained in the form of an orange powder (quantitative).

^1H -NMR (D_2O) analysis showed the composition to be: 6.4 ppm (m, 4H ar); 3.3 ppm (m, 2H CH_2); 3.0 ppm (m, 2H CH_2); 2.8 ppm (d, 6H NMe_2).

I.3. Synthesis of dimethylammoniumtetrakis(pentafluorophenyl) borate-ethyl-cyclopentadienyl-titaniumtrichloride

To a slurry of 1.07 g (3.28 mmol) of the dimethylamino-hydrochloride-ethylcyclopentadienyl-titaniumtrichloride obtained in I.2 in 30 ml of DCM,

which slurry had been cooled to $-60\text{ }^{\circ}\text{C}$, a solution, cooled to $-60\text{ }^{\circ}\text{C}$, of 2.64 g (3.2 mmol) of $\text{LiB}(\text{C}_6\text{F}_5)_4 \cdot 2\text{Et}_2\text{O}$ in 30 ml of DCM was added. After a few minutes cooling was stopped, upon which a yellow slurry formed. After 3.5 hours the slurry was filtered and the filtrate was evaporated. A yellow foam was obtained. After addition to SBPS a yellow slurry was obtained, which was washed twice with SBPS and evaporated. This yielded 2.8 g (η :93%) of diethyletherate of dimethylammoniumtetra-kis(pentafluorophenyl)borate-ethylcyclopentadienyl-titaniumtrichloride in the form of a yellow powder (Precursor A).

^1H NMR (CD_2Cl_2) analysis showed the composition to be: 7.1 ppm (dd, 2H ar); 6.8 ppm (dd, 2H ar); 3.4 ppm (m, 2H CH_2N); 3.3 ppm (m, 2H CH_2); 3.0 ppm (d, 6H NMe_2); 1.1 ppm (t, $\text{CH}_3\text{CH}_2\text{O}$).

Neutron activation analysis (NAA) showed that the ratio $\text{Ti} : \text{Cl} : \text{F} = 1 : 3.1 : 24.7$ (mol/mol).

Example II

Synthesis of $([\text{Cp}^*\text{EtNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4])\text{TiCl}_3$

II.1 Synthesis of dimethylaminoethyltetramethylcyclopentadienyltitanium-trichloride.

A slurry, cooled to $-65\text{ }^{\circ}\text{C}$, of 12.3 g (61.7 mmol) of dimethylaminoethyltetramethylcyclopentadienyllithium in 150 ml of SBPS was added to a slurry of 22.9 g (61.8 mmol) of $\text{TiCl}_3 \cdot 3\text{THF}$ in 250 ml of THF, which slurry had been cooled to $-65\text{ }^{\circ}\text{C}$. A pale green slurry formed. After 2 hours at $-65\text{ }^{\circ}\text{C}$ the reaction medium was heated to room temperature, yielding a dark green slurry. After stirring for 2 days at room temperature 30 ml was taken from the reaction mixture. After evaporation 1.65 g of $\text{Cp}^*\text{EtNMe}_2\text{TiCl}_2 \cdot \text{LiCl}$ was obtained. Subsequently, this compound (4.66 mmol) was dissolved in 30 ml of THF and 1.14 g (7.95 mmol) of

AgCl was added at room temperature. After some minutes a red/brown solution formed. After stirring for 2 hours the reaction mixture was evaporated. 40 ml of DCM was added and the resulting slurry was filtered. The
5 filtrate was evaporated and subsequently 50 ml of special boiling point solvent was added, so that a slurry formed, from which a precipitate separated out. The red/brown precipitate was washed with SBPS and evaporated. 1.1 g (η :70%) of $\text{NMe}_2\text{EtCp}^*\text{TiCl}_3$ was obtained
10 as a red/brown solid.

^1H -NMR (CD_2Cl_2) analysis showed the composition to be: 2.9 ppm (t, 2H CH_2N); 2.6 ppm (t, 2H CH_2); 2.4 ppm (d, 6H NMe_2); 2.2 ppm (s, 12H CpCH_3).

15

II.2 Synthesis of dimethylaminohydrochloride-ethyltetramethylcyclopentadienyltitaniumtrichloride

At room temperature 0.5 ml (3.9 mmol) of trimethylchlorosilane and 0.25 ml (6.4 mmol) of
20 methanol were subsequently added to a solution of 1.1 g (3.2 mmol) of dimethylaminoethyltetramethylcyclopentadienyltitaniumtrichloride in 30 ml of DCM. A red/orange slurry was formed practically immediately. After 2 hours' stirring the slurry was washed with two
25 portions of 50 ml of SBPS and evaporated. 1.2 g of dimethylaminohydrochloride-ethyltetramethylcyclopentadienyltitaniumtrichloride was obtained in the form of an orange powder (quantitative).

30 ^1H -NMR (D_2O) analysis showed the composition to be: 3.1 ppm (m, 2H CH_2); 2.9 ppm (m, 2H CH_2); 2.9 ppm (d, 6H NMe_2); 2.0 ppm (d, 12H CpMe).

II.3 Synthesis of dimethylammoniumtetrakis
(pentafluorophenyl) borate-ethyl-
tetramethylcyclopentadienyltitaniumtrichloride.

After cooling to -60°C , a solution of 1.6 g
5 (1.92 mmol) of $\text{LiB}(\text{C}_6\text{F}_5)_4 \cdot 2\text{Et}_2\text{O}$ in 30 ml of DCM was added
to a slurry, cooled to -60°C , of 0.75 g (1.96 mmol) of
dimethylamino-hydrochloride-ethyltetramethyl-
cyclopentadienyltitaniumtrichloride in 30 ml of DCM.
After a few minutes cooling was stopped. After 10
10 hours' stirring the orange/yellow slurry formed was
filtered and the filtrate was evaporated. An orange/red
foam was obtained. After addition to SBPS an orange/red
slurry was obtained, which was washed twice with SBPS
and evaporated. This yielded 1.75 g (η :90%) of
15 diethyletherate of dimethylammoniumtetrakis
(pentafluorophenyl) borate-ethyltetramethyl-
cyclopentadienyltitaniumtrichloride (precursor B) in
the form of an orange powder.

20 ^1H NMR (CD_2Cl_2) analysis showed the composition to be:
3.4 ppm (q, 2H $\text{CH}_3\text{CH}_2\text{O}$); 3.2 ppm (m, 2H CH_2N); 3.1 ppm
(m, 2H CH_2); 3.0 ppm (d, 6H NMe_2); 2.3 ppm (12H CpMe_4);
1.1 ppm (t, $\text{CH}_3\text{CH}_2\text{O}$).

NAA showed that the ratio Ti: Cl: F = 1: 3.1:
25 21.0 (mol/mol).

Examples III-V and comparative example A
Solution polymerization of ethylene

The compounds synthesized in Examples I and
30 II hereinafter to be referred to as precursors A
(Example I) and B (Example II), were tested in a batch
process for solution polymerization of ethylene under
isothermal conditions.

A 1.3 litre reactor was charged with 400 ml
35 of pentamethylheptane and ethylene and heating took
place up to the polymerization temperature of 160°C ;
the pressure eventually was 2 MPa. Subsequently, an

amount of a solution of an alkylating agent and a precursor slurry in toluene were successively pre-mixed at room temperature for 1 minute, after which the mixture was fed to the reactor. The catalyst metering vessel was flushed with 100 ml pentamethylheptane. The reactor pressure was kept constant by supplying ethylene. The reactor temperature was kept at 160 ± 5 °C by cooling. After a certain time the polymerization was stopped and the polymer formed was recovered from the reaction mixture by draining the latter from the reactor and drying it under vacuum at 50 °C. The precursors and alkylating agents used and the data recorded for the polymers obtained are presented in Table 1.

Table 1: Results of polymerization experiments

* Ti concentration in reactor: 0.02 mmol/l.

TABLE 1

Example	Precursor	Alkylating agent (1)	Al/Ti mol/mol	Activity gram PE/5 min
III	B	MAO	80	1.6
IV	B	TEA	80	1.6
V	A	MAO	80	0.6
A	(2)	(2)	(2)	1.2

(1)

MAO: Witco (1.6 M in toluene);

TEA: triethyl aluminium.

(2) Comparative example:

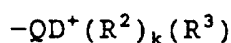
Cp*EtNMe₂Ti(III)Me₂/dimethylaniliniumtetra-
kis(pentafluorophenyl)borate ([DMAH][B(C₆F₅)₄])/
triethylaluminium (molar ratio 1:2:80).

5

The examples show that active catalysts can
be prepared from the precursors according to the
invention by addition of a relatively small amount of
alkylating agent, in other words, at a very favourable
10 (low) Al/transition metal ratio. In the comparative
example a certain amount of N,N-dimethylaniline remains
behind in the polymer formed, as a consequence of which
this polymer is in principle unsuitable for food
packaging applications.

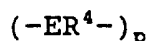
C L A I M S

1. Precursor for a catalyst, comprising a transition metal or lanthanide with a ligand system in which at least one Cp derivative is present, characterized in that the precursor contains a non-coordinating anion A^- , which can stabilize a catalyst obtained by activation of the precursor and which is bound to a cationic group of the Cp derivative or is bound to a cationic group forming part of or being bound to a bridge bound to the Cp derivative within the precursor, the cationic group containing a subgroup that is capable of reacting with a metal-bound alkyl, benzyl or phenyl group.
2. Precursor according to claim 1, characterized in that the cationic group has the form:



wherein Q, D, R^2 , R^3 and k have the meanings defined in the specification.

3. Precursor according to either of claims 1 and 2, wherein Q has the structure



where $p = 1-4$, E is an atom from group 14 of the Periodic System and the R^4 groups are each separately hydrogen, a hydrocarbon radical with 1-20 C-atoms or a corresponding group which instead of carbon or hydrogen contains one or more hetero atoms from group 15-16 of the Periodic System.

4. Precursor according to claim 2, characterized in that the group R^3 is a hydrogen atom.
5. Precursor according to either of the claims 1-2, characterized in that the hetero atom D is

nitrogen.

6. Precursor according to any one of claims 1-5, characterized in that the transition metal is titanium.
- 5 7. Precursor according to claim 6, characterized in that titanium has an oxidation state of 3⁺.
8. Precursor according to any one of claims 1-7, in which the non-coordinating anion is tetra(pentafluorophenyl)borate.
- 10 9. Process for the polymerization of α -olefines, diolefines and other ethylenically unsaturated monomers in the presence of a catalyst comprising a transition metal or lanthanide with a ligand system which contains at least one Cp derivative and which is stabilized with a non-coordinating anion A⁻, characterized in that the catalyst is
15 prepared by contacting a precursor according to any one of claims 1-8 with an alkylating compound.

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/NL 97/00231

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/603

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.
P,X	DE 195 06 557 A (BASF) 29 August 1996 see example 2 see page 3, line 7 - line 42 see claims 1,6 ---	1,5,8,9
X	US 5 198 401 A (EXXON) 30 March 1993 cited in the application see column 6, line 37 - line 44 see column 12, line 44 - line 48 see column 12, line 23 - line 24 see column 10, line 35 - column 11, line 37 ---	1
A	WO 91 14713 A (EXXON) 3 October 1991 see page 24, line 12 - line 13 ---	1
A	WO 95 29940 A (EXXON) 9 November 1995 see claim 34 ---	1
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Internal Application No
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