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(54) **PROCEDE POUR POLYMERISER LES OLEFINES**

(54) **A PROCESS FOR POLYMERIZING OLEFINS**

(57) Procédé pour polymériser les oléfines, selon lequel on met des oléfines en contact avec un catalyseur contenant un métal de transition et avec un cocatalyseur. Le procédé est caractérisé par le fait que le cocatalyseur est un composé de formule XR_4 , dans laquelle X est Si, Ge, Sn ou Pb, et R est hydrogène ou un groupe alkyle, aryle, arylalkyle ou alkylaryle, et au moins un groupe R n'est pas hydrogène et contient un ou plusieurs atomes d'halogène; ou bien le cocatalyseur est un composé de formule $[XR_5]^-[Y]^+$, dans laquelle X est Si, Ge, Sn ou Pb, R est hydrogène ou un groupe alkyle, aryle, arylalkyle ou alkylaryle, et au moins un groupe R n'est pas hydrogène et contient un ou plusieurs atomes d'halogène, et Y est un cation.

(57) A process for polymerizing olefins by bringing olefins into contact with a transition metal catalyst and a cocatalyst, characterized in that the cocatalyst is a compound in accordance with formula XR_4 , wherein X is Si, Ge, Sn or Pb, and R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms or the cocatalyst is a compound in accordance with formula $[XR_5]^-[Y]^+$, wherein X is Si, Ge, Sn or Pb, R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms, and Y is a cation.

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(54) Title: A PROCESS FOR POLYMERIZING OLEFINS

(57) Abstract

A process for polymerizing olefins by bringing olefins into contact with a transition metal catalyst and a cocatalyst, characterized in that the cocatalyst is a compound in accordance with formula XR_4 , wherein X is Si, Ge, Sn or Pb, and R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms or the cocatalyst is a compound in accordance with formula $[XR_5]^-[Y]^+$, wherein X is Si, Ge, Sn or Pb, R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms, and Y is a cation.

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A PROCESS FOR POLYMERIZING OLEFINS

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The invention relates to a process for polymerizing olefins by bringing olefins into contact with a transition metal catalyst and a cocatalyst.

10 The polymerization of olefins usually requires the use of not only a transition metal catalyst, but also the use of a cocatalyst to obtain an active catalyst system.

15 Since the Fifties, Ziegler-Natta catalysts have been used for the polymerization of olefins. If olefin polymerizations are to proceed satisfactory with these Ziegler-Natta catalysts, it is necessary to add cocatalysts. Aluminium-containing cocatalysts such as, for example, diethylaluminium chloride, are often used 20 in combination with Ziegler-Natta catalysts.

Recently, other types of transition metal catalysts such as, for example, metallocene catalysts have also been used for the polymerization of olefins. If olefin polymerizations using metallocene catalysts 25 are to proceed satisfactory it is likewise necessary to use a cocatalyst. Among cocatalysts often used in combination with metallocene catalysts are aluminoxanes. An example of an aluminoxane is methyl-aluminoxane (MAO).

30 The use of aluminoxanes as a cocatalyst in the polymerization of olefins with the aid of a metallocene catalyst has the drawback that a very large excess of the aluminoxane with respect to the metallocene catalyst has to be used in order to obtain 35 an active catalyst system. Consequently, the polyolefin produced contains a high aluminium concentration, and as a result it is often necessary for the aluminium to be washed out from the polyolefin.

It is an object of the invention to provide cocatalysts which can be used in conjunction with a transition metal catalyst for the polymerization of olefins, which do not have this drawback.

5 The invention relates to a cocatalyst in accordance with formula

XR_4 ,

wherein

X is Si, Ge, Sn or Pb,

10 R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms, or to a cocatalyst in accordance with the formula $[XR_5]^- [Y]^-$, wherein

15 X is Si, Ge, Sn or Pb,

R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms, and

Y is a cation.

20 In this way an active catalyst system consisting of a transition-metal catalyst with one of the compounds according to the invention as co-catalyst is obtained which is suitable for the polymerization of olefins. If the compounds according to the invention 25 are used as a cocatalyst for the polymerization of olefins, the amount of cocatalyst which has to be used with respect to the transition metal catalyst is much lower than when an aluminoxane is used as a cocatalyst.

Lewis acids or ion complexes are also used as 30 cocatalysts in combination with metallocene catalysts. Examples of Lewis acids are boranes such as, for example, tris(pentafluorophenyl)borane, and examples of ion complexes are borates such as, for example, dimethylanilinium tetrakis(pentafluorophenyl)borate, 35 triphenylcarbenium tetrakis(pentafluorophenyl)borate and trityl tetrakis(3,5-trifluoromethylphenyl)borate.

Such boron-containing cocatalysts are described, for example, in EP-A-426,637, EP-A-277,003 and EP-A-277,004.

A further advantage of the use of the 5 compounds according to the invention as a cocatalyst in the polymerization of olefins is that using these compounds is cheaper, as a rule, than using aluminoxanes, boranes or borates.

Compounds suitable as a cocatalyst are 10 compounds in accordance with the formula XR_4 and compounds in accordance with the formula $[XR_5]^- [Y]^+$. X is an atom from group 14 of the Periodic Table of the Elements and can be selected from Si, Ge, Sn and Pb. Preferably, X is Si, because Si is not toxic. 15 Here and hereinafter, the Periodic Table of the Elements is to be understood as the periodic table shown on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990 (New IUPAC notation). 20 The R groups may be identical or different and can be selected from hydrogen and alkyl, aryl, arylalkyl or alkylaryl groups. At least one R group is not hydrogen and contains one or more halogen atoms. This implies that in a compound in accordance with the formula XR_4 or 25 in accordance with the formula $[XR_5]^- [Y]^+$ at least one halogen atom is present which does not form part of the cation Y. Preferably, the R group is a hydrocarbon group containing 1-20 carbon atoms. Examples of suitable R groups are methyl, ethyl, propyl, isopropyl, 30 hexyl, decyl and phenyl. Two R groups may together form a bridged R₂ group such as, for example, a biphenyl-2,2'-diyl group and a diphenyl-2,2'-diylmethane group. These R groups may contain one or more halogen atoms.

35 Halogen atoms are F, Cl, Br and I. Combinations of different halogen atoms may be present in one R group or distributed over various R groups. Examples

of R groups containing a halogen atom are chloromethyl, 1,2-dibromoethyl, pentafluorophenyl and octafluorobiphenyl-2,2'-diyl.

Preferably, at least 2 R groups together form a bridged 5 aryl group.

More preferably, the compound in accordance with the formula XR_4 or $[XR_5]^- [Y]^+$ contains octafluorobiphenyl-2,2'-diyl groups.

The cation Y is, for example, a Brönsted acid 10 which is able to donate a proton, a cation of an alkali metal or a carbene. Examples of cations are Li^+ , K^+ , Na^+ , H^+ , triphenylcarbenium, anilinium, guanidinium, 15 glycinium, ammonium or a substituted ammonium cation in which at most 3 hydrogen atoms have been replaced by a hydrocarbyl radical having 1-20 carbon atoms, or a substituted hydrocarbyl radical having 1-20 carbon atoms, in which 1 or more of the hydrogen atoms have 20 been replaced by a halogen atom, phosphonium radicals, substituted phosphonium radicals, in which at most 3 hydrogen atoms have been replaced by a hydrocarbyl radical having 1-20 carbon atoms or a substituted hydrocarbyl radical having 1-20 carbon atoms, in which 1 or more of the hydrogen atoms have been replaced by a halogen atom.

25 Preferably, the cation is dimethylanilinium, triphenylcarbenium or Li^+ .

Compounds in accordance with the formula XR_4 , 30 which contain at least one halogen atom are disclosed, for example, by 'Cohen and Massey, J. Organometal. Chem. 10(1967) 471-481', 'Tamborski et al., J. Organometal. Chem., 4(1965) 446-454' and 'Fearon and Gilman, J. Organometal. Chem., 10(1967) 409-419'. Compounds in accordance with the formula $[XR_5]^- [Y]^+$ are 35 disclosed in Angew. Chem. Int. Ed. Engl. 1996, 35, No. 10. This publication mentions lithium (2,2'-biphenyldiyltrimethylsilicate).4THF, lithium (2,2'-

biphenyldiyldimethylphenylsilicate).4THF, lithium (2,2'-biphenyldiyldimethyl-t-butylsilicate).4THF and lithium pentaphenylsilicate.4HMPA. (THF is tetrahydrofuran and HMPA is hexamethyl-
5 phosphortriamide.) These compounds however, do not contain any halogen atoms and nothing is suggested regarding the possible use of these compounds as a cocatalyst in the polymerization of olefins.

The abovementioned compounds can be
10 synthesized in accordance with synthesis methods known to the man skilled in the art.

It is also possible to use the compounds according to the invention supported on a carrier material as a cocatalyst for the polymerization of
15 olefins. Suitable carrier materials to be mentioned are SiO_2 , Al_2O_3 , MgCl_2 and polymer particles such as polystyrene beads. These carrier materials may also be modified with, for example, silanes and/or aluminoxanes and/or aluminiumalkyls. The supported cocatalysts can
20 be synthesized prior to the polymerization but can also be formed in situ.

Various types of transition metal catalysts can be used as a catalyst for the polymerization of olefins. Examples of such catalysts are described, for
25 example, in US-A-5,096,867, WO-A-92/00333, EP-A-347,129, EP-A-344,887, EP-A-129,368, EP-A-476,671, EP-A-468,651, EP-A-416,815, EP-A-351,391, EP-A-351,392, EP-A-423,101, EP-A-503,422, EP-A-516,018, EP-A-490,256, EP-A-485,820, EP-A-376,154, DE-A-4,015,254, WO-A-96/13529, EP-A-530,908, WO-A-94/11406, EP-A-672,676 and WO-A-96/23010. Transition metal catalysts containing metals from group 3 of the Periodic Table of the Elements and the lanthanides can likewise be used. Supported transition metal catalysts can also be used.
30 Suitable carrier materials to be mentioned are SiO_2 , Al_2O_3 , MgCl_2 and polymer particles such as polystyrene

beads. These carrier materials may also be modified with, for example, silanes and/or aluminoxanes and/or aluminiumalkyls.

The supported transition metal catalysts may 5 be synthesized prior to the polymerization but may also be formed in situ.

Preference is given to the use of metallocene catalysts for the polymerization of olefins in combination with a cocatalyst according to the 10 invention. Metallocene catalysts are characterized by the presence of one or more π -bound ligands such as, for example, cyclopentadiene (Cp) ligands or ligands related to cyclopentadiene, such as, for example, indene and fluorene, in the transition metal catalyst. 15 More preference is given to the use of a transition metal catalyst in which the transition metal is in a reduced oxidation state, as described in WO-A-96/13529.

The polymerization of olefins, for example ethylene, propylene, butene, hexene, octene and 20 mixtures thereof and combinations with dienes can be carried out in the presence of a transition metal catalyst and the cocatalyst according to the invention. The above-described catalyst system can equally be used for the polymerization of vinylaromatic monomers such 25 as, for example, styrene and p-methylstyrene, for the polymerization of polar vinyl monomers such as, for example, monomers containing alcohol, amine, alkyl halide, ether, amide, imine or anhydride groups, and for the polymerization of cyclic olefins such as, for 30 example, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, norbornene, dimethano-octahydronaphthalene and substituted norbornenes.

The amount of cocatalyst used, based on the amount of transition metal catalyst (mol:mol), is 35 normally 1:100-1000:1, preferably 1:5-250:1.

The polymerizations can be carried out in the

manner known for this purpose, and the use of the cocatalyst according to the invention does not require any significant adaptation of these methods. The polymerizations can be carried out in suspension,
5 solution, emulsion, gas phase or as a bulk polymerization.

If the cocatalyst is to be used in a suspension polymerization or gas phase polymerization, it is preferable for the transition metal catalyst or
10 the cocatalyst according to the invention to be used on a carrier material. Likewise, both the catalyst and the cocatalyst can be used on a carrier material. The polymerizations are carried out at temperatures of between -50°C and +350°C, preferably between 50°C and
15 250°C. Pressures employed generally are between atmospheric pressure and 250 MPa, for bulk polymerizations more particularly between 50 and 250 MPa, for the other polymerization processes between 0.5 and 25 MPa. Dispersing agents and solvents which
20 can be employed include, for example, substituted and unsubstituted hydrocarbons such as pentane, heptane and mixtures thereof. Aromatic, possibly perfluorinated hydrocarbons, may also be used. Equally, a monomer to be used in the polymerization can be employed as a
25 dispersing agent.

The invention will be elucidated by means of the following not-restrictive examples.

Examples

30

MWD is molecular weight distribution, defined as M_w/M_n . Unless stated otherwise M_z , M_w and M_n are molecular weights determined using universal calibration procedure in SEC-DV measurements.

35

Example Ia) Synthesis of tetra(pentafluorophenyl)silane

25 ml n-butyllithium (40.1 mmol) were added to pentafluorobromobenzene (9.9 g, 40.1 mmol) in 50 ml dry diethylether at -78°C, resulting in a solution with a light red colour.

After 2 hours 1.12 ml SiCl_4 (9.9 mmol) was added at -78°C, the solution turning light yellow in colour followed by the formation of a white slurry. The reaction was allowed to warm slowly to room temperature. The white precipitate was separated from the solvent and dried under vacuum. The yield was 80%.

15 b) Addition of methyllithium to tetra(pentafluorophenyl)silane

Equimolar amounts of methyllithium and tetra(pentafluorophenyl)silane were mixed in tetrahydrofuran at -78°C. The temperature was allowed to increase to room temperature, resulting in a red-orange solution.

20 c) addition of triphenylchloromethyl to $(\text{C}_6\text{F}_5)_4\text{SiCH}_3^-$ $[\text{Li}(\text{THF})_4]^+$

A solution of triphenylchloromethyl in THF (6.60 ml, 4.29 mmol) was added to $[(\text{C}_6\text{F}_5)_4\text{SiCH}_3^-]^-$ $[\text{Li}(\text{THF})_4]^+$ (3.04 g, 4.29 mmol) at -78°C, the reaction mixture became an orange colour; the ice bath was removed after 15 minutes of Ph_3CCl addition. At room temperature the reaction mixture became a red-orange colour.

Evaporation of the tetrahydrofuran solvent yielded a light orange coloured solid.

Dry petrol (40 ml) was then added to the solid to yield a pink slurry; letting the slurry settle yielded an orange coloured petrol layer and a pink coloured precipitate the petrol was then evaporated to yield a

yellow solid with a small amount of white solid present.

Dry petrol (50 ml) was again added to yield a light orange pink coloured slurry; letting slurry settle 5 yielded a light orange coloured petrol and a light yellow precipitate.

The petrol was evaporated to yield a light orange coloured solid.

A toluene extraction was done 2 times to separate the 10 cation anion complex from LiCl; the evaporation of toluene yielded a light pink solid.

Petrol extraction was done 2 times to extract any unreacted triphenylchloromethane.

15 d) Polymerisation of ethylene

0.01 mmol of the metallocene catalyst bis(cyclopentadienyl)zirconiummonohydridemonochloride (obtained from Aldrich) was mixed in 100 ml pentamethylheptane at room temperature with 0.02 mmol 20 of the compound prepared under Ib) during 1 minute.

In a stainless steel bench rig of 1 l, 750 ml pentamethylheptane was introduced, followed by 0.4 mmol trioctylaluminium (Witco GmbH). The reactor was heated to 148°C and the ethylene pressure was equilibrated at 25 20 bar overpressure (21 bar).

In the next step the catalyst/cocatalyst mixture was introduced. The ethylene pressure was kept constant at 20 bars during the polymerisation. After 10 minutes the polymerization, which showed a rather constant activity 30 prophile in time, was stopped, the polymer was removed from the reactor and the yield was determined to be 10.51 g.

The polymer was analyzed by GPC. $M_w = 51.10^3$ g/mol, $M_n = 21.10^3$ g/mol, $M_z = 87.10^3$ g/mol.

Example II

The polymerisation described under example Id was repeated but now at 51°C. The yield was 4,0 g.

Example III

5 The polymerisation described under example Id was repeated but the polymerisation time was elongated to 60 minutes. The system remained active all the time and the polymer yield appeared to be 37.1 g.

10 Example IV

The polymerisation described under example Id was repeated but now at 160°C and at a polymerisation time of 30 minutes. The polymer yield was 27.3 g. The polymer was studied by GPC. $M_n = 18 \cdot 10^3$ g/mol.

15

Example V

The polymerisation described under example Id was repeated but now with a polymerisation time of 10 minutes at 159°C. The polymer yield was 16.4 g. The 20 polymer was studied by GPC. $M_n = 18 \cdot 10^3$ g/mol.

Example VI

The example Id was repeated at a temperature of 160°C during 10 minutes with a different transition 25 metal compound: $(Cp^*)C_2H_4(N(CH_3)_2)TiCl_2$, where Cp^* stands for a cyclopentadienyl ring with four methyl groups, C_2H_4 is an ethylene bridge, bridging the Cp^* to a $N(CH_3)_2$ -group.

The synthesis of this organometallic compound is 30 described in WO-A-96/13529, Example I.

The polymer yield was 7.4 g. The polymer was studied using GPC. $M_w = 150 \cdot 10^3$ g/mol.

Example VII

35 The polymerisation described under example Id was repeated but now with the catalyst bis(2-

methylindenyl) dimethyl zirconium and cocatalyst of example Ic) at a temperature of 100°C for 15 minutes. The polymer yield was 0.5 g.

5 Example VIII

a) Synthesis of tetra(pentafluorophenyl)germanium

14.9 ml n-butyllithium (23.9 mmol) was added to pentafluorobromobenzene (5.9 g, 23.9 mmol) in 100 ml dry diethylether at -78°C. The colour of the reaction 10 mixture became light purple. After two hours of stirring the reaction mixture had lost its purple colour. At that point 5.98 mmol germaniumtetrachloride were added at -78°C. After about 5 minutes a white precipitate was starting to form. The solvent was 15 separated from the white precipitate and evaporated to yield a light yellow solid which was washed two times with dry petrol (hexane mixture) followed by drying under vacuum. The yield of the product was 94%. The 13C- and 19F-NMR data showed that the 20 tetra(pentafluorophenyl)germanium was of excellent purity.

b) Addition of methyllithium to tetra(pentafluorophenyl)germanium

25 Methyllithium (369 μ l, 0.59 mmol) was added to $(C_6F_5)_4Ge$ (535.7 mg, 0.59 mmol) in dry tetrahydrofuran (50 ml), the reaction mixture became a red colour. The reaction mixture was warmed slowly to room 30 temperature, the reaction mixture became yellow.

c) Addition of triphenylchloromethane to $[C_6F_5)_4GeCH_3]^- [Li(THF)_4]^+$

A solution of triphenylchloromethane (0.156 M, 59 mmol)) was added to $[(C_6F_5)_4GeCH_3]^- [Li(THF)_4]^+$ at - 35 78°C, the reaction mixture remained yellow also at room temperature; the ice bath was removed after 15 minutes

of Ph₃CCl addition.

The tetrahydrofuran solvent was evaporated to yield a light yellow-white solid.

The solid was washed 3 times with dry petrol and dried 5 under vacuum to yield an off-white solid.

Dry petrol was used to extract any unreacted Ph₃CCl, extraction was done 3 times; evaporation of petrol yielded a white solid.

10 Example IX

Polymerization of ethylene

The example Id was repeated at a temperature of 100°C for 15 minutes, but now with the transition metal complex bis(2-methylindenyl) dimethyl zirconium, 15 and tetra(pentafluorophenyl)germanium ((C₆F₅)₄Ge) (Example VIIa) as the cocatalyst. The polymer yield was 1.9 g.

Example X

20 The example IX was repeated, but now with the transition metal complex bis(pentamethylcyclopentadienyl) dimethylzirconium. The polymer yield was 3.3 g.

Example XI

25 Synthesis of the 2H,2'H-Octafluorobiphenyl

Activated copper bronze (3.3 g, 51.9 mmol) dimethylformamide (25 ml), and 1-bromo-2,3,4,5-tetrafluorobenzene (5.0 g, 22.3 mmol) were refluxed overnight (16 hrs).

30 The copper was filtered off. In a next step, water was added to the filtrate and then the product was extracted with ether. The ether extract was separated using a separation funnel and dried with MgSO₄. The ether extract was filtered and evaporated under 35 vacuum to yield a brown solid (yield=40%)

The solid was sublimated to yield pure white crystals

(yield=34%) ^1H NMR (C_6D_6) multiplet due to H-F coupling at 6.1 ppm.

Example XII

5 Synthesis of bis(octafluorobiphenyl)germanium

3.6 mmol (1.0775 g) 2H,2'H-octafluorobiphenyl was dissolved in a schlenk in 50 ml dry ether. The schlenk was cooled to -65°C and 7.2 mmol (4.5 ml, 1.5 M) BuLi was added to the reaction mixture. This 10 resulted in a light yellow solution. After three hours stirring at this low temperature, the reaction mixture became colourless. Now, 1.8 mmol (205 μl) GeCl_4 was added at -65°C. After 5 minutes stirring, the reaction mixture became cloudy. The mixture was allowed to warm- 15 up to room temperature and after stirring overnight, the reaction mixture was a yellow-white slurry. Ether was evaporated and the resulting light yellow oil was washed two times with dry petrol to remove the ether. The result after evaporating the petrol was a 20 white oil.

Example XIII

a) Synthesis of bis(octafluorobiphenyl)silane via 2H,2'H-Octafluorobiphenyl

25 n-BuLi (4.5 ml, 7.2 mmol) was added to 2H,2'H-octafluorobiphenyl (1.07 g, 3.6 mmol) in dry ether (20 ml) at -78°C. The reaction mixture became a light orange colour.

After 2 hours SiCl_4 (203 μl , 1.79 mmol) was added. The 30 reaction mixture became a red-purple colour. The reaction was warmed to room temperature slowly. A white precipitate (LiCl) was formed. The reaction mixture was filtered off and then the ether was evaporated to yield a white oil.

35

b) Synthesis of bis(octafluorobiphenyl)silane via the

Grignard

Ethylmagnesiumbromide (6.8 ml, 6.8 mmol) was added to 2H,2'H-Octafluorobiphenyl (1.0 g, 3.4 mmol) in dry tetrahydrofuran (50 ml) at -78°C.

5 The reaction was warmed to room temperature slowly. The reaction mixture became a clear yellow solution. The reaction was cooled to -78°C. The reaction mixture obtained a non-clear yellow colour.

SiCl₄ (192 µl, 1.7 mmol) was added.

10 The reaction was warmed to reach room temperature slowly. The reaction mixture became a clear yellow colour.

The reaction was warmed to room temperature slowly. Letting the reaction mixture stir for five days yielded

15 a clear light yellow solution. Evaporation of tetrahydrofuran solvent yielded a white solid. The white solid was washed one time with petrol and dried under vacuum.

ClMgBr salt was separated from the white solid using

20 dichloromethane.

c) Addition of methyllithium to bis(octafluorobiphenyl) silane

Methyllithium (553 µl, 0.819 mmol) was added

25 to bis(octafluorobiphenyl)silane (507.7 mg, 0.819 mmol) in dry tetrahydrofuran (40 ml) at -78°C. The reaction mixture was warmed slowly to room temperature, no colour change was observed.

30 d) Addition of triphenylchloromethane to [Si(C₁₂F₈)₂CH₃]⁻ [Li.THF₄]⁺

A solution of triphenylchloromethane (1.28 ml, 0.619 mmol) was added to Si(C₁₂F₈)₂CH₃⁻ [LiTHF₄]⁺ (393.1 mg, 0.619 mmol) in dry tetrahydrofuran (30 ml) at -78°C. The ice bath was removed 15 minutes after Ph₃CCl addition. At room temperature the reaction

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mixture became a brown-yellow colour.
Evaporation of the tetrahydrofuran solvent yielded a
light brown which was washed 2 times with dry petrol
and dried under vacuum to yield a red-pink solid
5 (yield=97%).

C L A I M S

1. Process for polymerizing olefins by bringing olefins into contact with a transition metal catalyst and a cocatalyst, characterized in that the cocatalyst is a compound in accordance with formula
$$XR_4,$$
wherein
10 X is Si, Ge, Sn or Pb, and R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is not hydrogen and contains one or more halogen atoms.
- 15 2. Process for polymerizing olefins by bringing olefins into contact, under polymerization conditions, with a transition metal catalyst and a cocatalyst, characterized in that the cocatalyst is a compound in accordance with formula
20 $[XR_5]^- [Y]^+,$ wherein X is Si, Ge, Sn or Pb, R is hydrogen or an alkyl, aryl, arylalkyl or alkylaryl group and wherein at least one R group is hydrogen and contains one or more halogen atoms, and
25 Y is a cation.
3. Process according to either Claim 1 or 2, characterized in that the transition metal catalyst is a metallocene catalyst.
- 30 4. Process according to Claim 3, characterized in that the transition metal catalyst contains a transition metal which is in a reduced oxidation state.
5. Process according to any one of Claims 1-4,
35 characterized in that at least 2 R groups together form a bridged aryl group.

6. The use of a compound in accordance with formula XR_4 ,
wherein
X is Si, Ge, Sn or Pb,
5 R is hydrogen or an alkyl, aryl, arylalkyl or
alkylaryl group and wherein at least one R group
is not hydrogen and contains one or more halogen
atoms,
as a cocatalyst in the polymerization of olefins.

10 7. The use of a compound in accordance with the
formula $[XR_5]^- [Y]^+$,
wherein X is Si, Ge, Sn or Pb,
R is hydrogen or an alkyl, aryl, arylalkyl or
15 alkylaryl group and wherein at least one R group
is not hydrogen and contains one or more halogen
atoms,
and
Y is a cation, as a cocatalyst in the
polymerization of olefins.

20 8. Compound in accordance with formula
 $[XR_5]^- [Y]^+$,
wherein
X is Si, Ge, Sn or Pb,
R is hydrogen or an alkyl, aryl, arylalkyl or
25 alkylaryl group and wherein at least one R group
is not hydrogen and contains one or more halogen
atoms, and
Y is a cation.