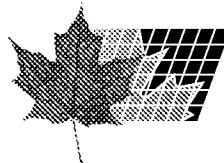


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(54) SYSTEMES DE CATALYSEURS A SUPPORTS
(54) SUPPORTED CATALYST SYSTEM

(57) Systèmes catalyseurs à supports, pouvant être obtenus par A) réaction d'un matériau support inorganique avec un composé métallique de formule générale (I): $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$, dans laquelle M^1 représente un métal alcalin ou alcalinoterreux ou un métal du groupe principal III ou IV de la classification périodique des éléments; R^1 représente hydrogène, alkyle C^1-C_{10} , aryle C_6-C_{15} , alkylaryle ou arylalkyle comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; R^2 à R^4 représentent hydrogène, halogène, alkyle C^1-C_{10} , aryle C_6-C_{15} , alkylaryle, arylalkyle, alcoxy ou dialkylamino comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; r est un nombre entier compris entre 1 et 4; et s , t et u sont des nombres entiers compris entre 0 et 3, la somme $r+s+t+u$ correspondant à la valence de M^1 ; B) par réaction du

(57) Supported catalyst obtainable by A) reacting an inorganic carrier material with a metal compound of the general formula (I): $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$ in which M^1 is an alkalyne or alkalyne earth metal or a metal of main group III or IV of the periodic system; R^1 is hydrogen, C^1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^2 to R^4 are hydrogen, C^1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl, alkoxy or dialkylamino with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; r is a whole number from 1 to 4; and s , t and u are whole numbers from 0 to 3, where the sum $r+s+t+u$ corresponds to the valency of M^1 ; B) reacting the material obtained from A) with a metallocene complex in its metal dihalogenide form and a metallocenium ion-forming compound; and C) subsequent reaction with a metal compound of the



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matériau obtenu selon A) avec un complexe métallocène sous sa forme dihalogénure métallique et un composé formant des ions métallocène; et C) réaction d'un composé métallique de formule générale (II): $M^2(R^5)_o(R^6)_p(R^7)_q$, dans laquelle M^2 représente un métal alcalin ou alcalinoterreux ou un métal du groupe principal III de la classification périodique des éléments; R^5 représente hydrogène, alkyle C^1-C_{10} , aryle C_6-C_{15} , alkylaryle ou arylalkyle comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; R^6 et R^7 représentent hydrogène, halogène, alkyle C^1-C_{10} , aryle C_6-C_{15} , alkylaryle, arylalkyle, ou alcoxy comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; o est un nombre entier compris entre 1 et 3; et p et q sont des nombres entiers compris entre 0 et 2, la somme $o+p+q$ correspondant à la valence de M^2 .

general formula (II): $M^2(R^5)_o(R^6)_p(R^7)_q$ in which M^2 is an alkalyne or alkalyne earth metal or a metal of main group III of the periodic system; R^5 is hydrogen, C^1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^6 to R^7 are hydrogen, C^1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl, aryl alkyl or alkoxy with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; o is a whole number from 1 to 3; and p and q are whole numbers from 0 to 2 where the sum $o+p+q$ corresponds to the valency of M^2 .



PCT

WELTORGANISATION FÜR GEISTIGES EIGENTUM

Internationales Büro

INTERNATIONALE ANMELDUNG VERÖFFENTLICH NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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(54) Title: SUPPORTED CATALYST SYSTEM

(54) Bezeichnung: GETRÄGERTE KATALYSATORSYSTEME

(57) Abstract

Supported catalyst obtainable by A) reacting an inorganic carrier material with a metal compound of the general formula (I): $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$ in which M^1 is an alkyne or alkynyl earth metal or a metal of main group III or IV of the periodic system; R^1 is hydrogen, C₁-C₁₀ alkyl, C₆-C₁₅ aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^2 to R^4 are hydrogen, C₁-C₁₀ alkyl, C₆-C₁₅ aryl, alkyl aryl or aryl alkyl, alkoxy or dialkylamino with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; r is a whole number from 1 to 4; and s , t and u are whole numbers from 0 to 3, where the sum $r+s+t+u$ corresponds to the valency of M^1 ; B) reacting the material obtained from A) with a metallocene complex in its metal dihalogenide form and a metallocenium ion-forming compound; and C) subsequent reaction with a metal compound of the general formula (II): $M^2(R^5)_o(R^6)_p(R^7)_q$ in which M^2 is an alkyne or alkynyl earth metal or a metal of main group III of the periodic system; R^5 is hydrogen, C₁-C₁₀ alkyl, C₆-C₁₅ aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^6 to R^7 are hydrogen, C₁-C₁₀ alkyl, C₆-C₁₅ aryl, alkyl aryl, aryl alkyl or alkoxy with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; o is a whole number from 1 to 3; and p and q are whole numbers from 0 to 2 where the sum $o+p+q$ corresponds to the valency of M^2 .

(57) Zusammenfassung

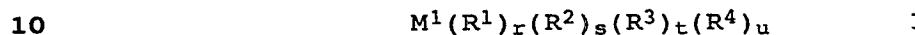
Geträgerte Katalysatorsysteme, erhältlich durch A) Umsetzung eines anorganischen Trägermaterials mit einer Metallverbindung der allgemeinen Formel (I) $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$ in der M^1 ein Alkali-, ein Erdalkalimetall oder ein Metall der III. oder IV. Hauptgruppe des Periodensystems bedeutet, R^1 Wasserstoff, C₁- bis C₁₀-Alkyl, C₆- bis C₁₅-Aryl, Alkylaryl oder Arylalkyl mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, R^2 bis R^4 Wasserstoff, Halogen, C₁- bis C₁₀-Alkyl, C₆- bis C₁₅-Aryl, Alkylaryl, Arylalkyl, Alkoxy oder Dialkylamino mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, r eine ganze Zahl von 1 bis 4 und s , t und u ganze Zahlen von 0 bis 3 bedeuten, wobei die Summe $r+s+t+u$ der Wertigkeit von M^1 entspricht, B) Umsetzung des nach A) erhaltenen Materials mit einem Metallocenkomplex in seiner Metalldihalogenid-Form und einer metalloceniumionenbildenden Verbindung und C) anschließender Umsetzung mit einer Metallverbindung der allgemeinen Formel (II) $M^2(R^5)_o(R^6)_p(R^7)_q$ in der M^2 ein Alkali-, ein Erdalkalimetall oder ein Metall der III. Hauptgruppe des Periodensystems bedeutet; R^5 Wasserstoff, C₁- bis C₁₀-Alkyl, C₆- bis C₁₅-Aryl, Alkylaryl oder Arylalkyl mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, R^6 und R^7 Wasserstoff, Halogen, C₁- bis C₁₀-Alkyl, C₆- bis C₁₅-Aryl, Alkylaryl, Arylalkyl oder Alkoxy mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, o eine ganze Zahl von 1 bis 3 und p und q ganze Zahlen von 0 bis 2 bedeuten, wobei die Summe $o+p+q$ der Wertigkeit von M^2 entspricht.

SC1

Supported catalyst systems

The present invention relates to supported catalyst systems obtainable by

A) reaction of an inorganic carrier with a metal compound of the general formula I



where

15 M^1 is an alkali metal, an alkaline earth metal or a metal of main group III or IV of the Periodic Table,

20 R^1 is hydrogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl or arylalkyl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

25 R^2 to R^4 are each hydrogen, halogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl, arylalkyl, alkoxy or dialkylamino, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

30 r is an integer from 1 to 4

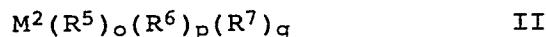
and

35 s , t and u are integers from 0 to 3, the sum $r+s+t+u$ corresponding to the valency of M^1 ,

B) reaction of the material obtained according to A) with a metallocene complex in its metal dihalide form and a compound 35 forming metallocenium ions

and

C) subsequent reaction with a metal compound of the general formula II



where

45

M² is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table,

5 R⁵ is hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl or aryl-alkyl each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

10 R⁶ and R⁷ are each hydrogen, halogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl or alkoxy, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

o is an integer from 1 to 3

15 and

p and q are integers from 0 to 2, the sum o+p+q corresponding to the valency of M².

20 The present invention furthermore relates to processes for the preparation of such supported catalyst systems and their use for the preparation of polyolefins.

In recent years, homogeneous metallocene catalysts have made it 25 possible to obtain well defined poly-1-olefins having a narrow molecular weight distribution and high chemical uniformity. However, industrial use necessitates the conversion of these catalysts to heterogeneous form so that simple handling of the catalyst and effective control of the morphology of the product are 30 ensured. Supported metallocene catalysts are known per se. Thus, EP-A 323 716 describes those systems in which moist SiO₂ is reacted with a trialkyl aluminum to give an alumoxane-laden carrier. The metallocene is applied to this carrier, an active catalyst being formed.

35 WO 91/09882 discloses the preparation of a supported, cationic metallocene catalyst by applying the reaction mixture of the dialkylmetallocene with an ionic compound, which has a Brönsted acid as the cation and a noncoordinating opposite ion, such as 40 tetrakis(pentafluorophenyl)borate, as the anion, to an inorganic carrier. Here too, an active catalyst is obtained.

Similar supported catalyst systems are also disclosed in WO 94/03506 and WO 95/14044.

EP-A 628 574 describes supported catalyst systems in which a metallocene dihalide is reacted with an alkyl aluminum in the presence of a hydridoborate and this solution, which is active with respect to polymerization, is applied to a carrier.

5

Such catalysts which are already active readily give rise to problems in the metering of the catalyst into the reactor.

What is therefore advantageous is a catalyst which is still inactive and cannot be activated until a later stage, for example 10 during metering or in the reactor itself.

EP-A 613 908 discloses supported metallocene catalyst systems, some of which are not activated until they are in the reactor. 15 Here, however, the polymers formed have a broad molecular weight distribution M_w/M_n .

WO 95/15815 describes catalysts which are obtained by supporting a metallocene dichloride and a borate on a crosslinked polymer. The 20 use of deactivated inorganic carriers gives catalysts which, after activation in the polymerization reactor, have either only slight activity or no activity at all.

It is an object of the present invention to provide supported 25 catalyst systems which do not have the stated disadvantages, in particular can be activated at any desired time, are air- and moisture-insensitive, can be stored for a long time and are not flammable, the polymers formed having a narrow molecular weight distribution.

30

We have found that this object is achieved by the supported catalyst systems defined at the outset.

We have furthermore found processes for the preparation of such 35 supported catalyst systems and their use for the preparation of polyolefins.

The novel supported catalyst systems are obtainable by reacting an inorganic carrier with a metal compound of the general formula 40 I in a first stage A).

Preferably used carriers are finely divided solids whose particle diameters are from 1 to 200 μm , in particular from 30 to 70 μm .

45 Examples of suitable carriers are silica gels, preferably those of the formula $\text{SiO}_2 \cdot a \text{Al}_2\text{O}_3$, where a is from 0 to 2, preferably from 0 to 0.5; these are therefore aluminosilicates or silica.

Such products are commercially available, for example Silica Gel 332 from Grace.

Other inorganic compounds, such as Al_2O_3 or $MgCl_2$, or mixtures 5 containing these compounds may also be used as carriers.

Preferred metal compounds of the general formula I are those in which M^1 is a metal of main group III of the Periodic Table, in particular aluminum, R^1 is C_1-C_{10} -alkyl and R^2 to R^4 are each 10 C_1-C_{10} -alkyl. For the particularly preferred case where M^1 is aluminum, u is zero and R^1 to R^3 have in particular the same meaning, preferably methyl, ethyl, isobutyl or hexyl, preferably isobutyl.

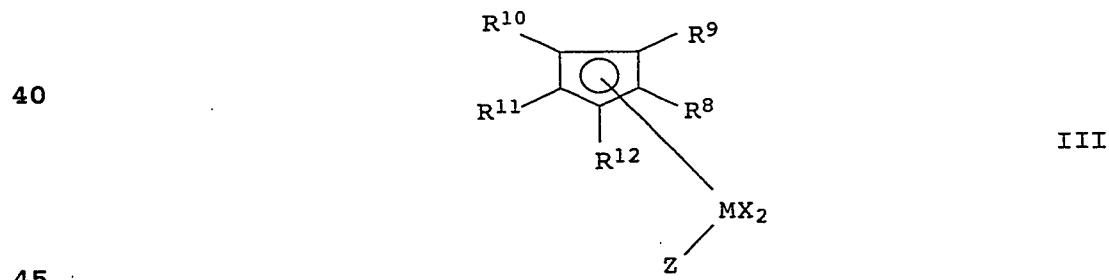
15 Preferably, the metal compound of the general formula I is added as a solution to a suspension of the carrier. Particularly suitable solvents or suspending agents are hydrocarbons, such as heptane. The amount of metal compound I may be varied within wide limits, the minimum amount depending on the number of hydroxyl 20 groups of the carrier. The temperatures, reaction times and pressures are not critical per se, temperatures of from 0 to 80°C and reaction times of from 0.1 to 48 hours being preferred.

It has proven suitable to remove the excess metal compound I by 25 thorough washing, for example with hydrocarbons, such as pentane or hexane, after the carrier pretreatment and to dry the carrier.

The material thus prepared can be stored for up to 6 months and is not pyrophoric.

30 This material is then reacted, in a further stage B), with a metallocene complex in its metal dihalide form and a compound forming metallocenium ions.

35 Examples of suitable metallocene complexes are the following compounds of the general formula III:



where

M is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

5

X is fluorine, chlorine, bromine or iodine,

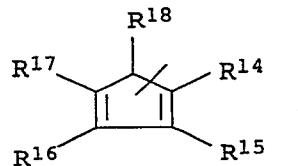
10 R⁸ to R¹² are each hydrogen, C₁-C₁₀-alkyl, 5- to 7-membered cycloalkyl which in turn may carry a C₁-C₁₀-alkyl as a substituent, C₆-C₁₅-aryl or arylalkyl, where two adjacent radicals together may furthermore form a cyclic group of 4 to 15 carbon atoms, or Si(R¹³)₃, where

15 R¹³ is C₁-C₁₀-alkyl, C₃-C₁₀-cycloalkyl or C₆-C₁₅-aryl,

15

and

20 Z is X or



25 where

R¹⁴ to R¹⁸ are each hydrogen, C₁-C₁₀-alkyl, 5- to 7-membered cycloalkyl which in turn may carry a C₁-C₁₀-alkyl as a substituent, C₆-C₁₅-aryl or arylalkyl, where two adjacent radicals together may furthermore form a cyclic group of 4 to 15 carbon atoms, or Si(R¹⁹)₃, where

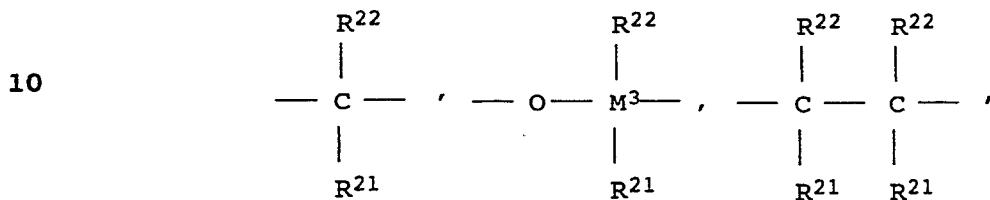
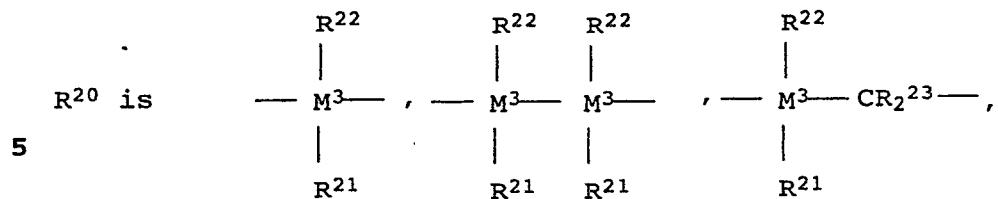
30 R¹⁹ is C₁-C₁₀-alkyl, C₆-C₁₅-aryl or C₃-C₁₀-cycloalkyl,

35 or where R¹¹ and Z together form a group -R²⁰-A-, where

40

45

6



15 $= BR^{22}$, $= AlR^{22}$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $= SO$, $= SO_2$,
 $= NR^{22}$, $= CO$, $= PR^{22}$ or $= P(O)R^{22}$,

where R^{21} , R^{22} and R^{23}

20 are identical or different and are each hydrogen,
 C_1-C_{10} -alkyl, C_1-C_{10} -fluoroalkyl, C_6-C_{10} -fluoro-
aryl, C_6-C_{10} -aryl, C_1-C_{10} -alkoxy, C_2-C_{10} -alkenyl,
 C_7-C_{40} -arylalkyl, C_8-C_{40} -arylalkenyl or C_7-C_{40} -alkylaryl
or where two adjacent radicals together with the atoms
linking them may form a ring, and

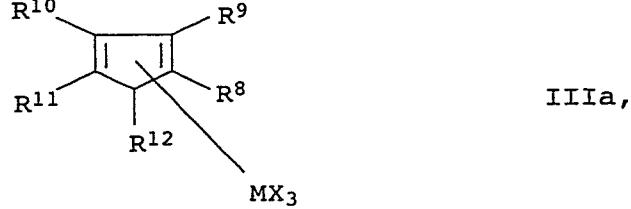
25 M^3 is silicon, germanium or tin,

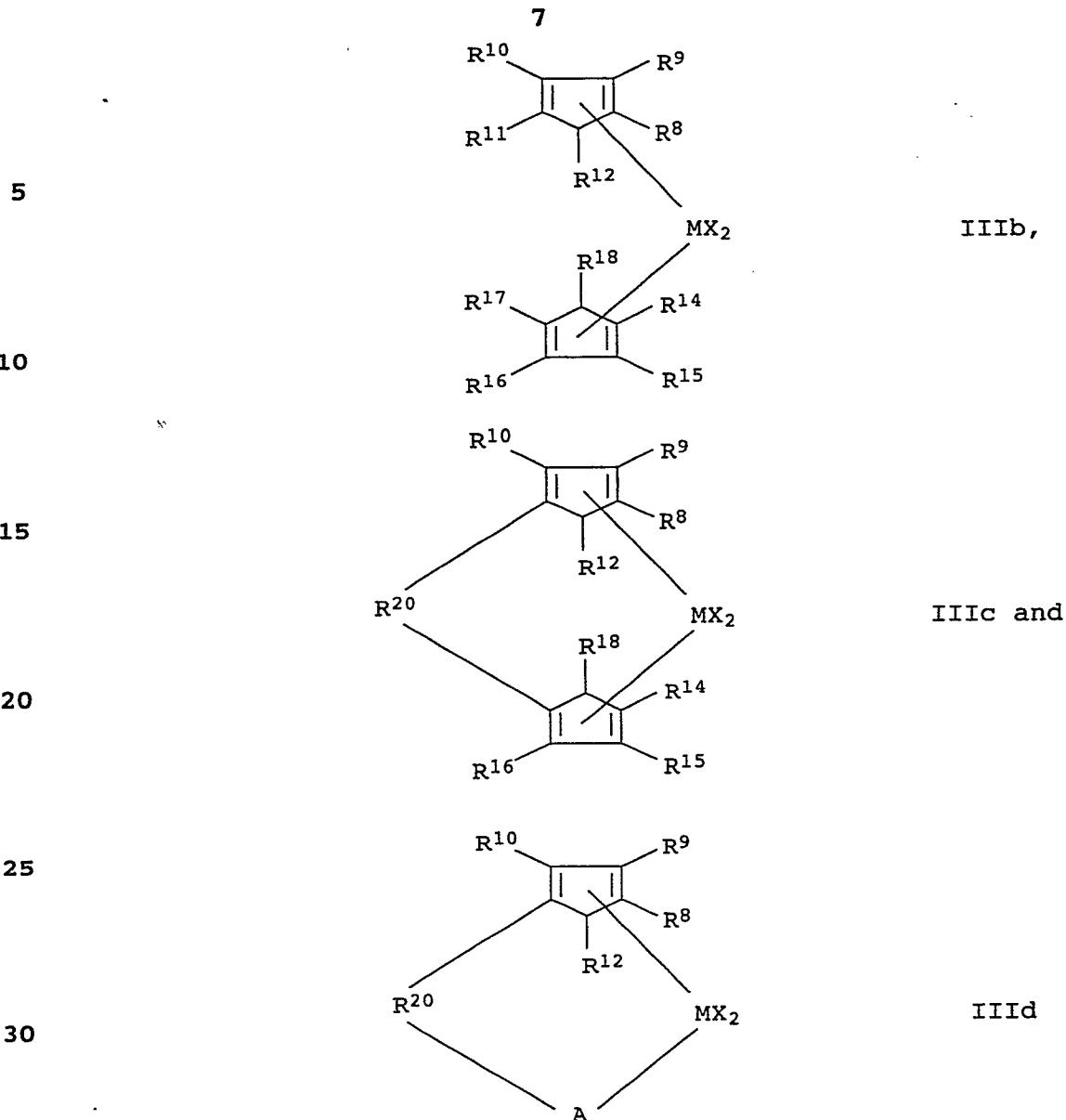
30 A is $\text{---} O \text{---}$, $\text{---} S \text{---}$, $\text{---} NR^{24} \text{---}$ or $\text{---} PR^{24} \text{---}$, where

35 R^{24} is C_1-C_{10} -alkyl, C_6-C_{15} -aryl, C_3-C_{10} -cycloalkyl, alkyl-
aryl or $Si(R^{25})_3$ and

40 R^{25} is hydrogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, which in turn
may be substituted by C_1-C_4 -alkyl, or C_3-C_{10} -cycloalkyl
or where R^{11} and R^{17} together form a group $-R^{20}-$.

45 Among the metallocene complexes of the general formula III,





35 are preferred.

The radicals X may be identical or different but are preferably identical.

40 Particularly preferred compounds of the formula IIIa are those in which

M is titanium, zirconium or hafnium,

X is chlorine and

45 R⁸ to R¹² are each hydrogen or C₁-C₄-alkyl.

Preferred compounds of the formula IIIb are those in which

M is titanium, zirconium or hafnium,
 X is chlorine,
 R⁸ to R¹² are each hydrogen, C₁-C₄-alkyl or Si(R¹³)₃ and
 R¹⁴ to R¹⁸ are each hydrogen, C₁-C₄-alkyl or Si(R¹⁹)₃.

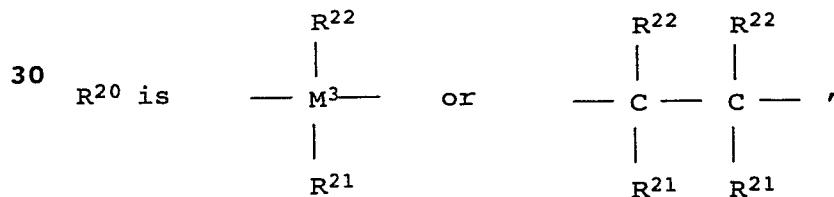
5

Particularly suitable compounds of the formula IIIb are those in which the cyclopentadienyl radicals are identical.

Examples of particularly suitable compounds include
 10 bis(cyclopentadienyl)zirconium dichloride,
 bis(pentamethylcyclopentadienyl)zirconium dichloride,
 bis(methylcyclopentadienyl)zirconium dichloride,
 bis(ethylcyclopentadienyl)zirconium dichloride,
 bis(n-butylcyclopentadienyl)zirconium dichloride and
 15 bis(trimethylsilylcyclopentadienyl)zirconium dichloride.

Particularly suitable compounds of the formula IIIc are those in which

20 R⁸ and R¹⁴ are identical and are each hydrogen or C₁-C₁₀-alkyl,
 R¹² and R¹⁸ are identical and are each hydrogen, methyl, ethyl,
 isopropyl or tert-butyl,
 R¹⁰ and R¹⁶ are C₁-C₄-alkyl
 R⁹ and R¹⁵ are each hydrogen
 25 or two adjacent radicals R⁹ and R¹⁰ on the one hand and
 R¹⁵ and R¹⁶ on the other hand together form a cyclic
 group of 4 to 12 carbon atoms,



35

M is titanium, zirconium or hafnium and
 X is chlorine.

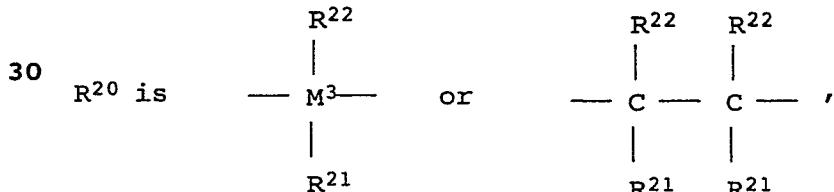
Examples of particularly suitable complex compounds include
 40 dimethylsilanediylbis(cyclopentadienyl)zirconium dichloride,
 dimethylsilanediylbis(indenyl)zirconium dichloride,
 dimethylsilanediylbis(tetrahydroindenyl)zirconium dichloride,
 ethylenebis(cyclopentadienyl)zirconium dichloride,
 ethylenebis(indenyl)zirconium dichloride,
 45 ethylenebis(tetrahydroindenyl)zirconium dichloride,
 tetramethylethylene-9-fluorenylcyclopentadienylzirconium dichloride,

dimethylsilanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)-
 zirconium [sic] dichloride,
 dimethylsilanediylbis(-3-tert-butyl-5-ethylcyclopentadienyl)-
 zirconium [sic] dichloride,
 5 dimethylsilanediylbis(-2-methylindenyl)zirconium [sic]
 dichloride,
 dimethylsilanediylbis(-2-isopropylindenyl)zirconium [sic]
 dichloride,
 dimethylsilanediylbis(-2-tert-butylindenyl)zirconium [sic]
 10 dichloride,
 diethylsilanediylbis(-2-methylindenyl)zirconium [sic]
 dibromide,
 dimethylsilanediylbis(-3-methyl-5-methylcyclopentadienyl)-
 zirconium [sic] dichloride,
 15 dimethylsilanediylbis(-3-ethyl-5-isopropylcyclopentadienyl)-
 zirconium [sic] dichloride,
 dimethylsilanediylbis(-2-methylindenyl)zirconium [sic]
 dichloride,
 dimethylsilanediylbis(-2-methylbenzindenyl)zirconium [sic]
 20 dichloride and dimethylsilanediylbis(-2-methylindenyl)hafnium
 [sic] dichloride.

Particularly suitable compounds of the general formula IIId are
 those in which

25

M is titanium or zirconium,
 X is chlorine,



35

A is $— O —$, $— S —$, $\begin{array}{c} \diagup \\ NR^{24} \end{array}$

40 and

45 R⁸ to R¹⁰ and R¹² are each hydrogen, C₁-C₁₀-alkyl, C₃-C₁₀-cyclo-alkyl, C₆-C₁₅-aryl or Si(R¹⁴)₃, or where two adjacent radicals form a cyclic group of 4 to 12 carbon atoms.

10

The synthesis of such complex compounds can be carried out by methods known per se, the reaction of the appropriately substituted, cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum being preferred.

5

Examples of appropriate preparation processes are described, inter alia, in J. Organometal. Chem., 369 (1989), 359-370.

Mixtures of different metallocene complexes may also be used.

10

Particularly suitable compounds forming metallocenium ions are strong, neutral Lewis acids, ionic compounds having Lewis acid cations and ionic compounds having Brönsted acids as cations.

15 Preferred strong, neutral Lewis acids are compounds of the general formula IV



20 where

M^4 is an element of main group III of the Periodic Table, in particular B, Al or Ga, preferably B, and

25 X^1 , X^2 and X^3

are each hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl, aryl-alkyl, haloalkyl or haloaryl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical, or fluorine, chlorine, bromine or iodine, in particular haloaryl, preferably pentafluorophenyl.

Particularly preferred compounds of the general formula IV are those in which X^1 , X^2 and X^3 are identical, preferably tris(pentafluorophenyl)borane.

35

Suitable ionic compounds having Lewis acid cations are compounds of the general formula V



40

in which

Y is an element of main group I to VI or subgroup I to VIII of the Periodic Table,

45

11

Q₁ to Q_z are radicals having a single negative charge, such as C₁-C₂₈-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl, haloalkyl, haloaryl each having 6 to 20 carbon atoms in the aryl radical and 1 to 28 carbon atoms in the alkyl radical, C₁-C₁₀-cycloalkyl, which may be substituted by C₁-C₁₀-alkyl, or halogen, C₁-C₂₈-alkoxy, C₆-C₁₅-aryloxy, silyl or mercaptyl,

5 a is an integer from 1 to 6,
10 z is an integer from 0 to 5 and
d corresponds to the difference a-z, but d is greater
than or equal to 1.

Carbonium cations, oxonium cations and sulfonium cations and
15 cationic transition metal complexes are particularly suitable. Particular examples are the triphenylmethyl cation, the silver cation and the 1,1'-dimethylferrocenyl cation. They preferably have noncoordinating opposite ions, in particular borane compounds, as also stated in WO 91/09882, preferably tetrakis(penta-
20 fluorophenyl)borate.

Ionic compounds having Brönsted acids as cations and preferably also noncoordinating opposite ions are stated in WO 91/09882, a preferred cation being N,N-dimethylanilinium.

25 The amount of compounds forming metallocenium ions is preferably from 0.1 to 10 equivalents, based on the metallocene complex III.

The conditions for the reaction with the metallocene complex with
30 the compound forming metallocenium ions are not critical per se; the reaction is preferably carried out in solution, particularly suitable solvents being hydrocarbons, preferably aromatic hydrocarbons, such as toluene.

35 The material prepared according to A) is then added to this. An amount of from 0.1 to 10% by weight, based on the inorganic carrier, of metallocene complex is particularly suitable. The conditions for this reaction are likewise not critical, temperatures of from 20 to 80°C and reaction times of from 0.1 to 20
40 hours having proven particularly suitable.

The material obtained according to B) can then be isolated and can be stored for up to at least 6 months.

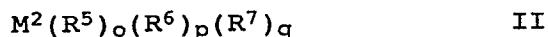
45 In a further stage C), the activation stage, the material obtained according to B) is reacted with a metal compound of the general formula II. This activation can be carried out at any

12

desired time, ie. before, during or after the metering of the material obtained according to B) in the reactor. The activation is preferably carried out after the metering of the material obtained according to B) into the reactor.

5

Among the metal compounds of the general formula II



10 where

M^2 is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table, ie. boron, aluminum, gallium, indium or thallium,

15

R^5 is hydrogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl or arylalkyl each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

20 R^6 and R^7 are each hydrogen, halogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl, arylalkyl or alkoxy each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

25 o is an integer from 1 to 3

and

30 p and q are integers from 0 to 2 the sum $o+p+q$ corresponding to the valency of M^2 ,

preferred compounds are those in which

M^2 is lithium, magnesium or aluminum and

35

R^5 to R^7 are each C_1-C_{10} -alkyl.

Particularly preferred metal compounds of the general formula II are n-butyl lithium, n-butyl-n-octyl magnesium, n-butyl-n-heptyl magnesium and tri-n-hexyl aluminum.

The conditions for the reaction in stage C) are not critical per se. Temperatures, reaction times and pressures depend on the time when the reaction, ie. activation, is carried out.

45

13

With the aid of these novel supported catalyst systems, it is possible to prepare polyolefins, in particular polymers of alk-1-enes. These are understood as meaning homo- and copolymers of C_2 - C_{10} -alk-1-enes, preferably used monomers being ethylene, 5 propylene, but-1-ene, pent-1-ene and hex-1-ene.

However, cycloolefins or higher alk-1-enes and alkenes generally may also be used as monomers for the homo- or copolymerization.

10 The novel supported catalyst systems are distinguished in particular by high activity, can be activated at any desired time, can be stored for a long time, are not pyrophoric and can therefore be easily handled and lead to polymers having a narrow molecular weight distribution.

15

Examples

Examples 1 and 2: Reaction of SiO_2 with tri-isobutyl aluminum (stage A))

20

Example 1

100 g of SiO_2 (SG 332 from Grace; dried for 12 hours at 200°C) were suspended in 1 l of dry heptane. At room temperature, 140 ml 25 of a 2 molar solution of tri-isobutyl aluminum in heptane were added dropwise in the course of 30 minutes, the temperature increasing to 35°C. Thereafter, stirring was carried out overnight and the solid was filtered off and was washed twice with pentane. Drying was then carried out under reduced pressure from an oil 30 pump until the weight remained constant (carrier 1).

Example 2

50 g of SiO_2 (ES 70F from Crosfield; dried for 7 hours at 110°C 35 under reduced pressure) were suspended in 500 ml of dry heptane. At room temperature, 70 ml of a 2 molar solution of tri-isobutyl aluminum in heptane were added dropwise in the course of 30 minutes, the temperature increasing to 35°C. Thereafter, stirring was carried out overnight and the solid was filtered off and was 40 washed with heptane. Drying was then carried out under reduced pressure from an oil pump until the weight remained constant (carrier 2).

Example 3 Reaction with metallocene complex and N,N-dimethyl-anilinium tetrakis(pentafluorophenyl)borate 45 (stage B))

0.5 mmol of the respective metallocene complex and in each case 0.5 mmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)-borate were dissolved in 50 ml of absolute toluene at 80°C. In each case 5 g of the material obtained according to Example 1 or 2 were added to this, and the dispersion thus obtained was stirred for 30 minutes at 80°C. Thereafter, the solvent was stripped off at 10 mbar and the solid residue was dried under reduced pressure from an oil pump until a free-flowing powder remained.

10 Metallocene complexes used:

- III 1: Bis(cyclopentadienyl)zirconium dichloride
- III 2: Bis(n-butylcyclopentadienyl)zirconium dichloride
- III 3: Bis(trimethylsilylcyclopentadienyl)zirconium dichloride
- 15 III 4: Dimethylsilanediylbis(indenyl)zirconium dichloride
- III 5: Ethylenebis(indenyl)zirconium dichloride
- III 6: Dimethylsilanediylbis(-2-methylbenzindenyl)zirconium [sic] dichloride
- 20 III 7: Dimethylsilanediyl(N-tert-butylamido)(η^5 -2,3,4,5-tetramethylcyclopentadienyl)titanium dichloride

Examples 4 to 17: Preparation of polyethylene in suspension

A 1 l steel autoclave was heated to 70°C, then the corresponding metal compound II was injected through a lock using 20 ml of isobutane. Thereafter ethylene was introduced into the autoclave up to a pressure of 40 bar and a corresponding amount of the material prepared in Example 3 was blown in with ethylene. The polymerization was carried out at 70°C until 200 g of ethylene had 30 been absorbed and was stopped by letting down the pressure.

Metal compounds II used:

- II 1: Tri-n-hexyl aluminum
- 35 II 2: n-Butyl-n-heptyl magnesium
- II 3: n-Butyl lithium

Table 1 below provides information about the compounds used in each case and the properties of the polyethylenes.

40

The limiting viscosity η was determined according to ISO 1628/3.

45

Table 1:

| Ex. | Carrier | Metallocene complex | Amount used of material prepared according to Ex. 3 [mg] | Metal compound | Productivity [g of polymer/g of catalyst ^{*)}] | η [dl/g] |
|-----|---------|---------------------|--|----------------|--|---------------|
| 4 | 1 | III 1 | 107 | 180 mg II 1 | 1495 | 3.75 |
| 5 | 2 | III 1 | 68 | 168 mg II 1 | 3970 | 4.04 |
| 6 | 2 | III 1 | 88 | 80 mg II 2 | 3460 | 4.06 |
| 7 | 1 | III 2 | 66 | 40 mg II 3 | 2560 | 3.97 |
| 8 | 2 | III 2 | 98 | 80 mg II 2 | 3010 | 4.24 |
| 9 | 2 | III 2 | 54 | 40 mg II 3 | 4900 | 4.05 |
| 10 | 1 | III 3 | 83 | 80 mg II 3 | 228 | 6.34 |
| 11 | 1 | III 4 | 116 | 20 mg II 3 | 1422 | 2.43 |
| 12 | 2 | III 4 | 41 | 60 mg II 2 | 4580 | 2.89 |
| 13 | 2 | III 6 | 94 | 80 mg II 2 | 2660 | 2.11 |
| 14 | 1 | III 7 | 140 | 60 mg II 2 | 2210 | 24.8 |
| 15 | 1 | III 7 | 81 | 20 mg II 3 | 2690 | 22.89 |
| 16 | 1 | III 7 | 250 | 40 mg II 3 | 506 | 21.2 |
| 17 | 1 | III 7 | 197 | 80 mg II 2 | 535 | 20.22 |

^{*)} Catalyst means the product obtained according to stage B)

Examples 18 to 21: Preparation of polyethylene in the gas phase

30

A 1 l steel autoclave was filled with 80 g of polyethylene granules, heated to 70°C and flushed with argon for 1 hour. 3 ml of a 0.2 molar solution of tri-n-hexyl aluminum in heptane were then injected. Thereafter, 50 mg of the material prepared in

35 Example 3 were blown in with ethylene, and the ethylene pressure was increased to 40 bar. The polymerization was carried out at 70°C until 150 g of ethylene had been absorbed and was stopped by letting down the pressure.

40 Table 2 below provides information about the compounds used and the properties of the polyethylenes.

The limiting viscosity η was likewise determined according to ISO 1628/3.

45

Table 2:

| Ex. | Carrier | Metallocene complex | Productivity [g of polymer/g of catalyst]*) | η [dl/g] |
|-----|---------|---------------------|---|---------------|
| 5 | 18 | III 2 | 1604 | 4.52 |
| | 19 | III 4 | 3290 | 2.23 |
| | 20 | III 5 | 2256 | 1.54 |
| | 21 | III 7 | 1306 | 13.9 |

*) Catalyst means the product obtained according to B)

15 Example 22: Preparation of polypropylene (bulk polymerization)

0.3 l of liquid propene was initially taken at room temperature in a 1 l steel autoclave flushed with nitrogen. 1 mmol of tri-isobutyl aluminum (as a 2 molar solution in heptane) was added 20 via a lock. After stirring had been carried out for 5 minutes, 72 mg of the material prepared in Example 3 (carrier 1, metallocene complex III6) were added, likewise via the lock, and the autoclave was heated to 60°C. The polymerization was carried out at 70°C over a period of 10 minutes. 90 g of isotactic polypropylene having a melting point of 144.9°C were obtained.

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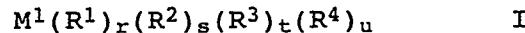
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We claim:-

1. A supported catalyst system obtainable by

5

A) reaction of an inorganic carrier with a metal compound of the formula I



10

where

M^1 is an alkali metal, an alkaline earth metal or a metal of main group III or IV of the Periodic Table,

15

R^1 is hydrogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl or arylalkyl each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

20

R^2 to R^4 are each hydrogen, halogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl, arylalkyl, alkoxy or dialkyl-amino each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

25

r is an integer from 1 to 4

and

30

s , t and u are integers from 0 to 3 the sum $r+s+t+u$ corresponding to the valency of M^1 ,

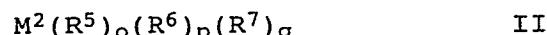
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B) reaction of the material obtained according to A) with a metallocene complex in its metal dihalide form and a compound forming metallocenium ions

and

40

C) subsequent reaction with a metal compound of the formula II



where

45

M² is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table,

5 R⁵ is hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl or arylalkyl each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

10 R⁶ and R⁷ are each hydrogen, halogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl or alkoxy each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

15 o is an integer from 1 to 3

and

p and q are integers from 0 to 2 the sum o+p+q corresponding to the valency of M².

20 2. A supported catalyst system as claimed in claim 1, wherein the material obtained according to A) is isolated and dried.

25 3. A supported catalyst system as claimed in claims 1 and 2, wherein, in the formula I, M¹ is aluminum, R¹ to R³ are each C₁-C₁₀-alkyl and u is zero.

30 4. A supported catalyst system as claimed in any of claims 1 to 3, wherein a coordination complex compound selected from the group consisting of the strong, neutral Lewis acids, the ionic compounds having Lewis acid cations and the ionic compounds having Brönsted acids as cation is used as the compound forming metallocenium ions.

35 5. A supported catalyst system as claimed in any of claims 1 to 4, wherein, in the formula II, R⁵ to R⁷ are each C₁-C₁₀-alkyl.

6. A process for the preparation of supported catalyst systems under the process conditions of claim 1.

40 7. The use of supported catalyst systems as claimed in any of claims 1 to 5 for the preparation of polyolefins.