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(54) Title: OLEFIN POLYMERISATION CATALYST CONTAINING A CYCLOALKANE DICARBOXYLATE AS ELECTRON DONOR

(57) Abstract: A catalyst system useful in polymerizing olefins comprising a solid, hydrocarbon-insoluble catalyst component containing magnesium, titanium and halogen and an internal or external electron donor comprising a substituted hydrocarbyl four to eight-membered cycloalkane dicarboxylate wherein the substituents are positioned on the cycloalkane to place the dicarboxylate groups into adjacent conformational positions and wherein the substitutes contain 1 to 20 carbon atoms and may be joined to the cycloalkane structure to form a bicyclo structure.



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Field of the Invention

This invention relates to components useful in propylene polymerization catalysts, and particularly relates to electron donor components used in combination
5 with magnesium-containing supported titanium-containing catalyst components.

Background of the Invention

Use of solid, transition metal-based, olefin polymerization catalyst components is well known in the art including such solid components supported on a metal oxide, halide or other salt such as widely-described magnesium-containing, titanium halide-
10 based catalyst components. Such catalyst components are referred to as "supported." Although many polymerization and copolymerization processes and catalyst systems have been described for polymerizing or copolymerizing alpha-olefins, it is advantageous to tailor a process and catalyst system to obtain a specific set of properties of a resulting polymer or copolymer product. For example, in certain
15 applications, a combination of high activity, stereospecificity are required together with polymer characteristics such as good morphology, desired particle size distribution, acceptable bulk density, molecular weight distribution, and the like.

Typically, supported catalyst components useful for polymerizing propylene and higher alpha-olefins as well as for polymerizing propylene and higher olefins with
20 a minor amounts of ethylene and other alpha-olefins contain an electron donor component as an internal modifier. Such internal modifier is an integral part of the solid supported component as is distinguished from an external electron donor component, which together with an aluminum alkyl component, comprises the catalyst system. Typically, the external modifier and aluminum alkyl are combined
25 with the solid supported component shortly before the combination is contacted with an olefin monomer.

Selection of the internal modifier can affect catalyst performance and the resulting polymer formed from a catalyst system. As stated above, it is advantageous and an advance in the art to discover internal modifiers including
30 combinations of modifiers which, when incorporated into a supported catalyst, produce desired effects on the polymerization process and the polymer produced.

Generally, organic electron donors have been described as useful in preparation of the stereospecific supported catalyst components including organic

compounds containing oxygen, nitrogen, sulfur, and/or phosphorus. Such compounds include organic acids, organic acid anhydrides, organic acid esters, alcohols, ethers, aldehydes, ketones, amines, amine oxides, amides, thiols, various phosphorus acid esters and amides, and the like. Mixtures of organic electron
5 donors have been described as useful in incorporating into supported catalyst components. Examples of organic electron donors include dicarboxy esters such as alkyl phthalate and succinate esters.

Examples of substituted succinate ester and cyclohexane dicarboxylate electron donors are described in U.S. Patents 4,442,276 and 4,952,649, European
10 Published Application 86,288, and PCT Published Application WO 00/63261, all incorporated by reference herein.

Numerous individual processes or process steps have been disclosed to produce improved supported, magnesium-containing, titanium-containing, electron donor-containing olefin polymerization or copolymerization catalysts. For example,
15 Arzoumanidis et al., U.S. Patent No. 4,866,022, incorporated by reference herein, discloses a method for forming an advantageous alpha-olefin polymerization or copolymerization catalyst or catalyst component which involves a specific sequence of specific individual process steps such that the resulting catalyst or catalyst component has exceptionally high activity and stereospecificity combined with very
20 good morphology. A solid hydrocarbon-insoluble, alpha-olefin polymerization or copolymerization catalyst or catalyst component with superior activity, stereospecificity and morphology characteristics is disclosed as comprising the product formed by 1) forming a solution of a magnesium-containing species from a magnesium hydrocarbyl carbonate or magnesium carboxylate; 2) precipitating solid
25 particles from such magnesium-containing solution by treatment with a transition metal halide and an organosilane; 3) reprecipitating such solid particles from a mixture containing a cyclic ether; and 4) treating the reprecipitated particles with a transition metal compound and an electron donor.

Arzoumanidis et al., U.S. Patent No. 4,540,679, incorporated by reference
30 herein, discloses a process for the preparation of a magnesium hydrocarbyl carbonate by reacting a suspension of a magnesium alcoholate in an alcohol with carbon dioxide and reacting the magnesium hydrocarbyl carbonate with a transition metal component.

Arzoumanidis et al., U.S. Patent No. 4,612,299, incorporated by reference herein, discloses a process for the preparation of a magnesium carboxylate by reacting a solution of a hydrocarbyl magnesium compound with carbon dioxide to precipitate a magnesium carboxylate and reacting the magnesium carboxylate with a transition metal component.

Particular uses of propylene polymers depend upon the physical properties of the polymer, such as molecular weight, viscosity, stiffness, flexural modulus, and polydispersity index (molecular weight distribution (M_w/M_n)). In addition, polymer or copolymer morphology often is critical and typically depends upon catalyst morphology. Good polymer morphology generally involves uniformity of particle size and shape, resistance to attrition and an acceptably high bulk density. Minimization of very small particles (fines) typically is important especially in gas-phase polymerizations or copolymerizations in order to avoid transfer or recycle line pluggage. A particularly advantageous polymer for certain uses would have a broadened polydispersity index, preferably above about 5, more preferably above about 6, and may be above 7, while maintaining an acceptable flexural modulus, preferably above about 1800, more preferably above about 2000 MPa, and may be above 2400 MPa.

Summary of the Invention

A solid, hydrocarbon-insoluble, catalyst component useful in polymerizing olefins containing magnesium, titanium, and halogen further contains an internal electron donor comprising a substituted hydrocarbyl 4-8 membered cycloalkane dicarboxylate wherein the substituents are positioned on the cycloalkane to place the dicarboxylate groups into conformational proximity positions and wherein the substitutes contain 1 to 20 carbon atoms and may be joined to the cycloalkane structure to form a bicyclo structure.

Description of the Preferred Embodiment(s)

Supported catalyst components of this invention contain at least one internal electron donor comprising a substituted hydrocarbyl 4-8 membered cycloalkane dicarboxylate wherein the substituents are positioned on the cycloalkane to place the dicarboxylate groups into conformational proximity positions and wherein the substitutes contain 1 to 20 carbon atoms and may be joined to the cycloalkane structure to form a bicyclo structure.

Typical electron donor compounds of this invention are alkyl esters of substituted cycloalkane dicarboxylic acids, in which the alkyls contain 1 to about 20 carbon atoms. Such alkyls typically contain at least two and preferably at least three carbon atoms. Suitable alkyls also may contain up to 12 and, typically, up to 8 carbon atoms. Other suitable alkyls contain from 4 to 6 carbon atoms. Typical examples of alkyl esters useful in this invention include ethyl, propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, n-pentyl, isopentyl, hexyl, 2-ethylhexyl, and octyl, esters. Especially suitable alkyls are isopropyl, n-butyl, and s-butyl.

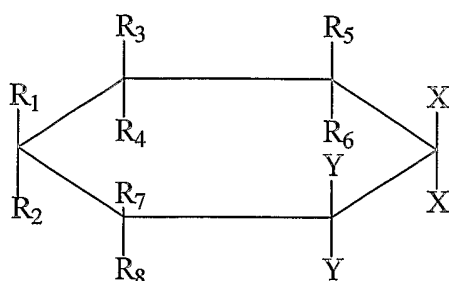
Although, typically, the alkyl groups forming alkyl dicarboxylic acid esters of this invention are the same, the invention includes alkyl dicarboxylic acid esters having different alkyl groups.

In alkyl dicarboxylic acid esters of this invention, the carboxylate groups are placed in conformational proximity positions. Preferably, such carboxylate groups are attached to adjacent carbon atoms forming an alkyl cycloalkane 1,2 dicarboxylate. In another aspect of the invention, such carboxylate groups may form a cycloalkane 1,3 dicarboxylate and the like where the carboxylate groups are not on adjacent carbon atoms. In any case, the conformational structure of the cycloalkane is constrained by substituent groups (or chemical bonds in the case of bicyclo structures) such that the carboxylate groups are placed in conformational proximity positions. A structure is constrained when bond rotation or ring conformation change is restricted such that a particular conformation is preferred.

Substituent groups that are sufficiently bulky to constrain a ring conformation change typically contain at least 3 carbon atoms, although groups containing compatible heteroatoms such as nitrogen, sulfur, silicon, and the like may contain at least one carbon atom. Typically, such bulky substituent groups contain up to 20 carbon atoms and may contain up to 12 carbon atoms. Typically suitable bulky substituent groups are isopropyl, isobutyl, t-butyl, s-butyl, isopentyl, isohexyl, 2-ethylhexyl, and the like. Compounds of this invention may contain one or more of such bulky substituent group. Multiple bulky groups may be substituents to produce a constrained conformational structure.

Alkyl groups used in this invention also may be substituted with compatible groups containing heteroatoms including silicon and halogens.

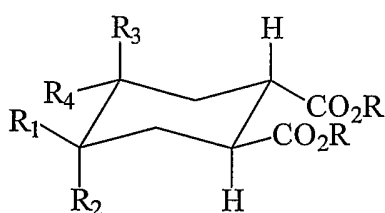
Typical examples of these compounds are represented by the substituted cyclohexane:



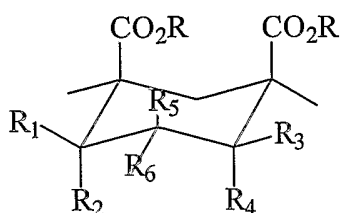
- 5 in which one X and one Y are carboxylate (CO_2R) groups, wherein R is selected from lower alkyl groups containing 1 to 20 carbon atoms; $\text{R}_1\text{-R}_8$ are selected from bulky and non-bulky alkyl or substituted alkyl groups to produce a ring conformation that places the carboxylate groups into proximity; and remaining the X and Y groups are selected from hydrogen and methyl, and provided two of the $\text{R}_1\text{-R}_8$
- 10 groups may be connected to form a bicyclo structure.

Preferably, for non-bicyclo structures, the carboxylate groups are trans and R_1 and R_4 are selected from bulky groups. Preferably, the non-bulky groups are hydrogen.

- Other representations of these substituted cyclohexanes demonstrating
- 15 conformation of the carboxyl groups is:

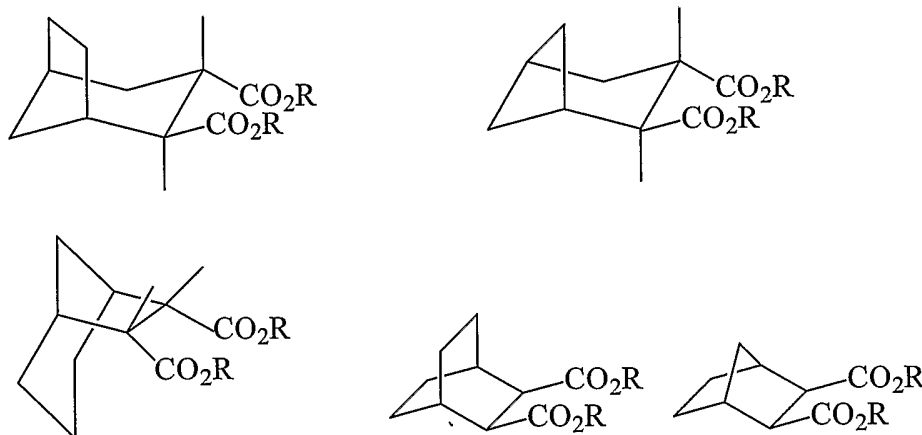


- in which R is selected from lower alkyl groups containing 1 to 20 carbon
- 20 atoms, at least one of R_1 and R_4 are selected from bulky groups sufficient to place the carboxyl groups into conformational proximity positions, and R_2 and R_4 are selected from hydrogen and methyl. The remaining substituents on such a ring structure usually are hydrogen, but may be other compatible groups that produce the desired ring conformation.

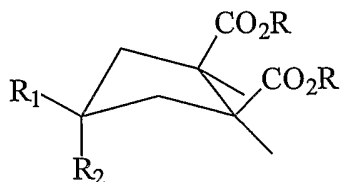


in which R is selected from lower alkyl groups containing 1 to 20 carbon atoms, at least one of R_1 , R_3 , and R_6 are selected from bulky groups sufficient to place the carboxyl groups into conformational proximity positions, and R_2 , R_4 , and R_5 are selected from hydrogen and methyl. The remaining substituents on such a ring structure usually are hydrogen, but may be other compatible groups that produce the desired ring conformation.

Representations of bicyclo compounds of this invention are:



A representation of a cyclopentane of this invention is:

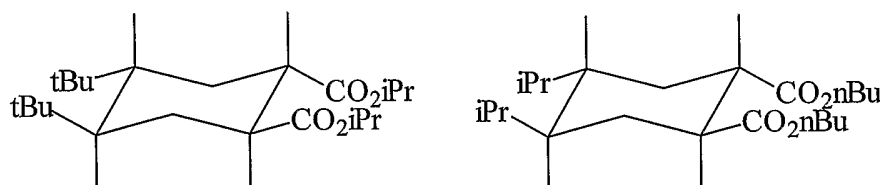


in which R_1 and R_2 are selected to place the carboxylate groups into conformational proximity.

In one aspect of this invention, carboxylate groups are positioned onto cycloalkyl structures such that at least two carboxylate groups are in conformational proximity, i.e. at the preferred confirmation of the cycloalkyl ring structure, the carboxylate groups will be spaced close enough to experience van der Waals repulsion between the groups. Such repulsion typically is sufficient that would place the ring into another preferred conformation if the ring conformation was not otherwise constrained.

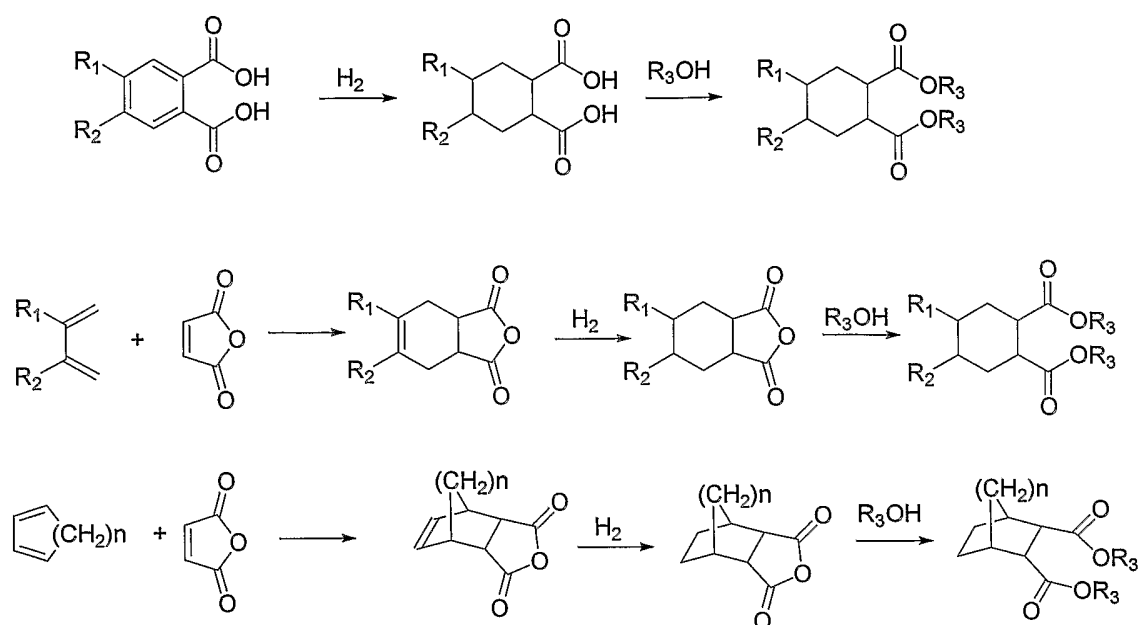
In another aspect of this invention, the carboxylate groups are spaced at least as proximate as corresponding phthalate carboxylate groups.

An example of conformational proximate carboxylate groups are trans-di-n-butyl-4,5-di-isopropylcyclohexane trans-dicarboxylate and trans-diisopropyl 4,5-di-tert-butylcyclohexane trans-dicarboxylate:



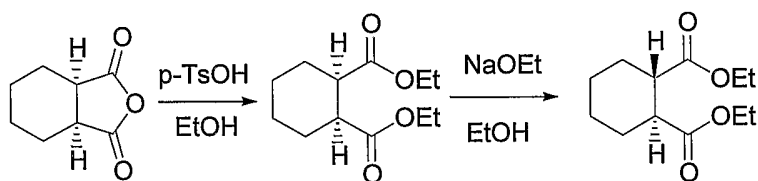
In these structures, spatially bulky tertiary-butyl and isopropyl groups are in a trans configuration on the cyclohexane ring, which inhibits ring reversal and produces a preferred confirmation in which the bulky groups are in the equatorial positions on the cyclohexane ring. The result is to place the carboxylate groups in equatorial positions, which are in conformational proximity.

Below are summarized general methods which can be used to prepare the donors which are described. The first method entails hydrogenation of an appropriately substituted aromatic diacid followed by esterification. The second method employs first a Diels-Alder reaction of a substituted diene and maleic anhydride to form the substituted cyclohexene structure. After hydrogenation and esterification the substituted cyclic diester is formed. The bicyclic compounds can be formed by the third route employing a Diels-Alder reaction of maleic anhydride and a cyclic diene to form the bicyclic structure. Hydrogenation and esterification would yield the bicyclic diester. These reactions are known in the art.

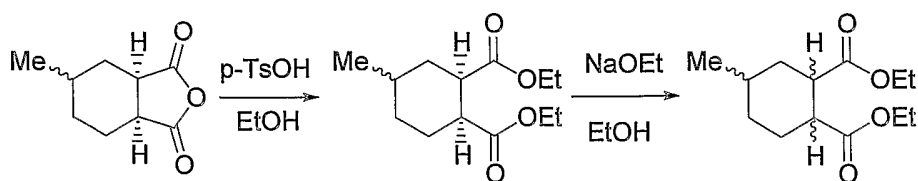


5 The routes we are employing to prepare examples of the above are as follows:

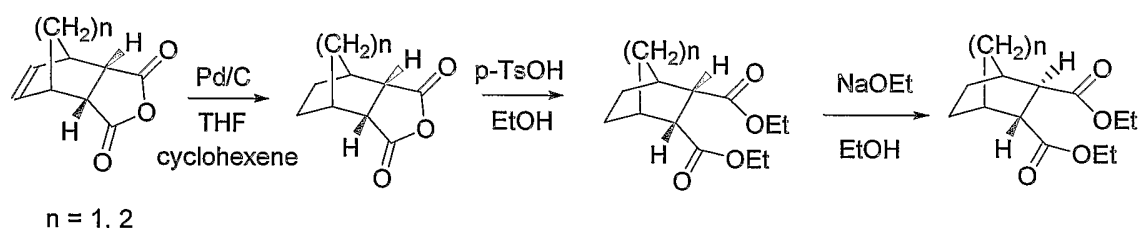
Cyclohexane anhydride was esterified with ethanol and a p-toluenesulfonic acid catalyst to yield the cis diester, which was used as an internal donor to prepare a catalyst according to the procedures outlined above. The cis diester may be
 10 epimerized to the more thermodynamically stable trans isomer with sodium ethoxide and ethanol and a catalyst may be prepared as described above.



15 In a similar route, the methyl-cyclohexane anhydride also was esterified as shown below. The product was a mixture of isomers, which is believed to be predominantly a combination of cis fused products. That material also was used directly in a catalyst preparation. Also this may be epimerized and subsequently used in a catalyst preparation.



The bicyclic materials may be prepared by first reducing the double bonds of the purchased anhydrides with $n = 1$ and 2. After esterification, cis fusion appears again to be preserved and a catalyst has been prepared from the bicyclo[2.2.1] system. and a catalyst may be prepared from the bicyclo[2.2.2] system. The bicyclo[2.2.2] system will need to be treated again with hydrogen to fully reduce the initial double bond before proceeding. Both materials will also may be epimerized to the predicted more stable trans isomers to be used in catalyst preparations.



High activity supported (HAC) titanium-containing components useful in this invention generally are supported on hydrocarbon-insoluble, magnesium-containing compounds in combination with an electron donor compound. Such supported titanium-containing olefin polymerization catalyst component typically is formed by reacting a titanium (IV) halide, an organic electron donor compound and a magnesium-containing compound. Optionally, such supported titanium-containing reaction product may be further treated or modified by further chemical treatment with additional electron donor or Lewis acid species.

Suitable magnesium-containing compounds include magnesium halides; a reaction product of a magnesium halide such as magnesium chloride or magnesium bromide with an organic compound, such as an alcohol or an organic acid ester, or with an organometallic compound of metals of Groups I-III; magnesium alcoholates; or magnesium alkyls.

Examples of supported catalysts are prepared by reacting a magnesium chloride, alkoxy magnesium chloride or aryloxy magnesium chloride with a titanium halide, such as titanium tetrachloride, and further incorporation of an electron donor compound. In a preferable preparation, the magnesium-containing compound is dissolved, or is in a slurry, in a compatible liquid medium, such as a hydrocarbon to produce suitable catalyst component particles.

The possible solid catalyst components listed above only are illustrative of many possible solid, magnesium-containing, titanium halide-based, hydrocarbon-insoluble catalyst components useful in this invention and known to the art. This invention is not limited to a specific supported catalyst component.

5 In a typical supported catalyst of this invention, the titanium to magnesium atom ratio is above about 0.5 to 1 and may range to about 20 to 1. Greater amounts of titanium may be employed without adversely affecting catalyst component performance, but typically there is no need to exceed a titanium to magnesium ratio of about 20:1. More preferably, the titanium to magnesium ratio ranges from about
10 2:1 to about 15:1. The internal electron donor components typically are incorporated into the solid, supported catalyst component in a total amount ranging up to about 1 mole per gram atom of titanium in the titanium compound, and preferably from about 0.001 to about 0.6 mole per gram atom of titanium in the titanium compound. Typical amounts of internal donor are at least 0.01 mole per gram atom of titanium,
15 preferably above about 0.05 and typically above about 0.1 mole per gram atom of titanium. Also, typically, the amount of internal donor is less than 1 mole per gram atom of titanium, and preferably below about 0.5, and more preferably below about 0.3 mole per gram atom of titanium.

The internal electron donor material of this invention is incorporated into a
20 solid, supported catalyst component during formation of such component. Typically, such electron donor material is added with, or in a separate step, during treatment of a solid magnesium-containing material with a titanium (IV) compound. Most typically, a solution of titanium tetrachloride and the internal electron donor modifier material is contacted with a magnesium-containing material. Such magnesium-containing
25 material typically is in the form of discrete particles and may contain other materials such as transition metals and organic compounds.

The preferred solid, hydrocarbon-insoluble catalyst or catalyst component of this invention for the stereoregular polymerization or copolymerization of alpha-olefins comprises the product formed by a process, which comprises a first step of
30 forming a solution of a magnesium-containing species in a liquid wherein the magnesium-containing species is formed by reacting a magnesium-containing compound with carbon dioxide or sulfur dioxide. The magnesium-containing compound from which the magnesium-containing species is formed is a magnesium

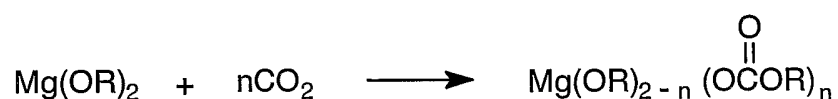
alcoholate, a magnesium hydrocarbyl alcoholate, or a hydrocarbyl magnesium compound. When carbon dioxide is used, the magnesium-containing species is a hydrocarbyl carbonate or a carboxylate. When sulfur dioxide is employed, the resulting magnesium-containing species is a hydrocarbyl sulfite (ROSO_2^-) or an

5 hydrocarbyl sulfinatate (RSO_2^-).

Generally, magnesium hydrocarbyl carbonate is prepared by reacting carbon dioxide with a magnesium alcoholate. For example, magnesium hydrocarbyl carbonate is formed by suspending magnesium ethoxide in ethanol and adding carbon dioxide until the magnesium ethoxide dissolves forming magnesium ethyl

10 carbonate. If, however, the magnesium ethoxide were suspended in 2-ethylhexanol, magnesium 2-ethylhexyl carbonate, magnesium ethyl carbonate and magnesium ethyl/2-ethylhexyl carbonate may be formed. If the magnesium ethoxide is suspended in a liquid hydrocarbon or halohydrocarbon which is free of alcohol, the addition of carbon dioxide results in the breaking apart of the magnesium ethoxide

15 particles and the magnesium hydrocarbyl carbonate reaction product does not dissolve. The reaction of a magnesium alcoholate with carbon dioxide can be represented as:



wherein n is a whole number or fraction up to 2, and wherein R is a hydrocarbyl

20 group of 1 to 20 carbon atoms. In addition, a magnesium alcoholate-containing two different aforesaid hydrocarbyl groups may be employed. From the standpoint of cost and availability, magnesium alcoholates which are preferred for use according to this invention are those of the formula $\text{Mg}(\text{OR})_2$ wherein R is as defined below. In terms of catalytic activity and stereospecificity, best results are achieved through the

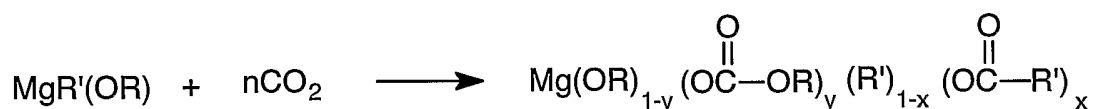
25 use of magnesium alcoholates of the formula $\text{Mg}(\text{OR}')_2$ wherein R' is an alkyl radical of 1 to about 8 carbon atoms, an aryl radical of 6 to about 12 carbon atoms or an alkaryl or aralkyl radical of 7 to about 12 carbon atoms. Magnesium ethoxide is most preferred.

Specific examples of magnesium alcoholates that are useful according to this

30 invention include: $\text{Mg}(\text{OCH}_3)_2$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, $\text{Mg}(\text{OC}_4\text{H}_9)_2$, $\text{Mg}(\text{OC}_6\text{H}_5)_2$,

Mg(OC₆H₁₃)₂, Mg(OC₉H₁₉)₂, Mg(OC₁₀H₇)₂, Mg(OC₁₂H₉)₂, Mg(OC₁₂H₂₅)₂,
 Mg(OC₁₆H₃₃)₂, Mg(OC₁₈H₃₇)₂, Mg(OC₂₀H₄₁)₂, Mg(OCH₃)(OC₂H₅),
 Mg(OCH₃)(OC₆H₁₃), Mg(OC₂H₅)(OC₈H₁₇), Mg(OC₆H₁₃)(OC₂₀H₄₁),
 Mg(OC₃H₇)(OC₁₀H₇), Mg(OC₂H₄Cl)₂ and Mg(OC₁₆H₃₃)(OC₁₈H₃₇). Mixtures of
 5 magnesium alcoholates also may be used if desired.

A suitable magnesium hydrocarbyl alcoholate has the formula MgR(OR') wherein R and R' are as defined hereinabove for the magnesium alcoholate. When alcohol is used as the suspending medium for the reaction between the magnesium hydrocarbyl alcoholate and carbon dioxide or sulfur dioxide, the magnesium hydrocarbyl alcoholate is a functional equivalent of the magnesium alcoholate because the magnesium hydrocarbyl alcoholate is converted to the magnesium alcoholate in alcohol. However, when the suspending medium does not contain alcohol, the magnesium hydrocarbyl alcoholate reacts with carbon dioxide as:



15 wherein $y+x = n \geq 2$ and $y = 0$ for $x = n \leq 1.0$.

In the case of $y+n=2$, $\text{RCO}-\text{Mg}-\text{O}-\text{C}-\text{OR}'$ is the resulting magnesium-containing species.

When the magnesium compound from which the magnesium-containing species is formed is a hydrocarbyl magnesium compound having the formula XMgR, where X is a halogen and R is a hydrocarbyl group of 1 to 20 carbon atoms, the reaction of the hydrocarbyl magnesium compound with carbon dioxide forms a magnesium carboxylate and can be represented as follows:



25 If the hydrocarbyl magnesium compound contains two hydrocarbyl groups, the reaction is represented as:



where R is as defined for X-MgR.

The hydrocarbyl magnesium compounds useful in this invention have the structure R-Mg-Q wherein Q is hydrogen, halogen or R' (each R' is independently a hydrocarbyl group of 1 to 20 carbon atoms.) Specific examples of hydrocarbyl magnesium compounds useful in this invention include: $\text{Mg}(\text{CH}_3)_2$, $\text{Mg}(\text{C}_2\text{H}_5)_2$, $\text{Mg}(\text{C}_4\text{H}_9)_2$, $\text{Mg}(\text{C}_6\text{H}_5)_2$, $\text{Mg}(\text{C}_6\text{H}_{13})_2$, $\text{Mg}(\text{C}_9\text{H}_{19})_2$, $\text{Mg}(\text{C}_{10}\text{H}_7)_2$, $\text{Mg}(\text{C}_{12}\text{H}_9)_2$, $\text{Mg}(\text{C}_{12}\text{H}_{25})_2$, $\text{Mg}(\text{C}_{16}\text{H}_{33})_2$, $\text{Mg}(\text{C}_{20}\text{H}_{41})_2$, $\text{Mg}(\text{CH}_3)(\text{C}_2\text{H}_5)$, $\text{Mg}(\text{CH}_3)(\text{C}_6\text{H}_{13})$, $\text{Mg}(\text{C}_2\text{H}_5)(\text{C}_8\text{H}_{17})$, $\text{Mg}(\text{C}_6\text{H}_{13})(\text{C}_{20}\text{H}_{41})$, $\text{Mg}(\text{C}_3\text{H}_7)(\text{C}_{10}\text{H}_7)$, $\text{Mg}(\text{C}_2\text{H}_4\text{Cl})_2$ and $\text{Mg}(\text{C}_{16}\text{H}_{33})(\text{C}_{18}\text{H}_{37})$, $\text{Mg}(\text{C}_2\text{H}_5)(\text{H})$, $\text{Mg}(\text{C}_2\text{H}_5)(\text{Cl})$, $\text{Mg}(\text{C}_2\text{H}_5)(\text{Br})$, etc. Mixtures of hydrocarbyl magnesium compounds also can be employed if desired. From the standpoint of cost and availability, dihydrocarbyl magnesium compounds preferred for use in this invention are those of the formula MgR_2 wherein R is as defined above. In terms of catalytic activity and stereospecificity, best results are achieved through the use of hydrocarbyl magnesium halide compounds of the formula $\text{MgR}'\text{Q}'$ wherein R' is an alkyl radical of 1 to about 18 carbon atoms, an aryl radical of 6 to about 12 carbon atoms or an alkaryl or aralkyl radical of 7 to about 12 carbon atoms and Q' is chloride or bromide.

Most preferably, the magnesium-containing compound is a magnesium alcoholate, and the resulting magnesium-containing species is a magnesium hydrocarbyl carbonate.

For example, a magnesium alcoholate may be used which is prepared by reacting magnesium metal turnings to completion with a lower molecular weight alcohol, such as methanol, ethanol, or 1-propanol, with or without a catalyst such as iodine or carbon tetrachloride, to form a solid magnesium alcoholate. Any excess alcohol is removed by filtration, evaporation or decantation. Use as the magnesium-containing compound of a magnesium alcoholate produced in this manner affords a solution of the magnesium-containing species which has a substantially reduced viscosity.

Diluents or solvents suitable for use in the carbonation of the magnesium compounds to form the magnesium-containing species include alcohols containing from 1 to 12 carbon atoms, non-polar hydrocarbons and halogenated derivatives thereof, ethers and mixtures thereof that are substantially inert to the reactants employed and, preferably, are liquid at the temperatures of use. It also is contemplated to conduct the reaction at elevated pressure so that lower-boiling solvents and diluents can be used even at higher temperatures. Examples of useful solvents and diluents include alcohols such as methanol, ethanol, 1- or 2-propanol, t-butyl alcohol, benzyl alcohol, the amyl alcohols, 2-ethylhexanol and branched alcohols containing 9 or 10 carbon atoms; alkanes such as hexane, cyclohexane, ethylcyclohexane, heptane, octane, nonane, decane, undecane, and the like; haloalkanes such as 1,1,2-trichloroethane, carbon tetrachloride, and the like; aromatics such as xylenes and ethylbenzene; and halogenated and hydrogenated aromatics such as chlorobenzene, o-dichlorobenzene, tetrahydronaphthalene and decahydronaphthalene.

The solution of the magnesium-containing species typically comprises at least one monohydroxy alcohol containing from 2 to about 18 carbon atoms, preferably at a ratio of the total number of moles of the at least one alcohol to the number of moles of the aforesaid magnesium-containing compound in the range of from about 1.45:1, more preferably from about 1.6:1, to about 2.3:1, more preferably to about 2.1:1. Alcohols that are suitable for use in the present invention include those having the structure HOR wherein R is an alkyl radical of 1 to about 18 carbon atoms, an aryl radical of 6 to about 12 carbon atoms or an alkaryl or aralkyl radical of 7 to about 12 carbon atoms. Typically, one or more alcohols containing from 1 to 12 carbon atoms can be used, such as ethanol, 1- or 2-propanol, t-butyl alcohol, cyclohexanol, 2-ethylhexanol, amyl alcohols including isoamyl alcohol, and branched alcohols having 9 to 12 carbon atoms. Preferably, 2-ethylhexanol or ethanol is employed.

In somewhat greater detail, the magnesium-containing species is prepared by dissolving or suspending the magnesium-containing compound in a liquid. Approximately 10 to 80 parts by weight of the magnesium-containing compound is employed per 100 parts by weight liquid. A sufficient amount of carbon dioxide is bubbled into the liquid suspension to provide from about 0.1 to 4 moles of carbon dioxide per mole of the magnesium compound with mild stirring. Typically,

approximately 0.3 to 4 moles of CO₂ are added to the solution or suspension of the magnesium-containing compound with stirring at a temperature of about 0 to 100°C over a period of approximately 10 minutes to 24 hours.

Irrespective of which of the aforesaid magnesium-containing compounds is used to form the magnesium-containing species, solid particles are precipitated from the aforesaid solution of the magnesium-containing species by treatment with a transition metal or Group IV halide and preferably additionally with a morphology controlling agent. The transition metal or Group IV halide preferably is a titanium (IV) or silicon halide and more preferably is titanium tetrachloride. While any convenient conventional morphology controlling agent can be employed, organosilanes are particularly suitable for use as the morphology controlling agent. Suitable organosilanes for this purpose include those having a formula: $R_nSiR'_{4-n}$, wherein $n = 0$ to 4 and wherein R is hydrogen or an alkyl, alkoxy, haloalkyl or aryl radical containing one to about ten carbon atoms, or a halosilyl radical or haloalkylsilyl radical containing one to about eight carbon atoms, and R' is OR or a halogen. Typically, R is an alkyl or chloroalkyl radical containing one to about eight carbon atoms and one to about four chlorine atoms, and R' is chlorine or an -OR radical containing one to four carbon atoms. A suitable organosilane may contain different R' groups. Mixtures of organosilanes may be used. Preferable organosilanes include tri-methylchlorosilane, trimethylethoxysilane, dimethyldichlorosilane, tetraethoxy-silane, and hexamethyldisiloxane.

Broadly, in accordance with this invention, the precipitated particles are treated with a transition metal compound and an electron donor. Suitable transition metal compounds which can be used for this purpose include compounds represented by the formula $T_aY_bX_{c-b}$ wherein T_a is a transition metal selected from Groups IV-B, V-B and VI-B of the Periodic Table of Elements, Y is oxygen, OR' or NR'₂; wherein each R' is independently hydrogen or hydrocarbyl group of 1 to 20 carbon atoms; X is halogen, preferably chlorine or bromine; c has a value corresponding to the valence of the transition metal, T_a ; b has a value of from 0 to 5 with a value of c-b being from at least 1 up to the value of the valence state of the transition metal T_a . Suitable transition metal compounds include halide compounds of titanium, zirconium, vanadium and chromium, such as chromyl chloride, vanadium oxytrichloride, zirconium tetrachloride, vanadium tetrachloride, and the like.

In addition to supported catalyst components formed from magnesium alcoholates or magnesium hydrocarbyl carbonates as described above, other magnesium-containing supported components may be produced by reacting titanium halide-containing compounds with magnesium halides, such as magnesium chloride, magnesium oxyhalides, magnesium alkoxides, and the like. In preparation of suitable supported catalysts useful for olefin polymerization, an electron donor material is added during formation of such component in which a magnesium compound is reacted with a titanium halide-containing compound as described in the art. Irrespective of the method of formation, the supported catalyst components of this invention include the internal electron donor material described in this invention.

Titanium (IV) compounds useful in preparation of the catalyst or catalyst component of this invention are titanium halides and haloalcoholates having 1 to about 20 carbon atoms per alcoholate group such as methoxy, ethoxy, butoxy, hexoxy, phenoxy, decoxy, naphthoxy, dodecoxy and eicosoxy. Mixtures of titanium compounds can be employed if desired. Preferred titanium compounds are the halides and haloalcoholates having 1 to 8 carbon atoms per alcoholate group. Examples of such compounds include TiCl_4 , TiBr_4 , $\text{Ti}(\text{OCH}_3)\text{Cl}_3$, $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{OC}_4\text{H}_9)\text{Cl}_3$, $\text{Ti}(\text{OC}_6\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{OC}_6\text{H}_{13})\text{Br}_3$, $\text{Ti}(\text{OC}_8\text{H}_{17})\text{Cl}_3$, $\text{Ti}(\text{OCH}_3)_2\text{Br}_2$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_6\text{H}_{13})_2\text{Cl}_2$, $\text{Ti}(\text{OC}_8\text{H}_{17})_2\text{Br}_2$, $\text{Ti}(\text{OCH}_3)_3\text{Br}$, $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_6\text{H}_{13})_3\text{Br}$, and $\text{Ti}(\text{OC}_8\text{H}_{17})_3\text{Cl}$. Titanium tetrahalides and particularly TiCl_4 are most preferred from the standpoint of attaining maximum activity and stereospecificity.

The particles formed as described above, the titanium halide component, and the electron donor components described in this invention are reacted at temperatures ranging from about -10°C to about 170°C , generally over a period of several minutes to several hours, and are contacted in amounts such that the atomic ratio of titanium to magnesium components in the reaction mixture (calculated as magnesium in magnesium compound from which the magnesium-containing species is formed) is at least about 0.5:1. Preferably, this ratio ranges from about 0.5:1 to about 20:1. Greater amounts of titanium may be employed without adversely affecting catalyst component performance, but typically there is no need to exceed a titanium to magnesium ratio of about 20:1. More preferably, the titanium to magnesium ratio ranges from about 2:1 to about 15:1 to ensure that the catalyst

components contain sufficient titanium to exhibit good activities without being wasteful of the titanium compound employed in preparation. The internal electron donor components are employed in a total amount ranging up to about 1.0 mole per gram atom of titanium in the titanium compound, and preferably from about 0.001 to about 0.6 mole per gram atom of titanium in the titanium compound. Best results are achieved when this ratio ranges from about 0.01 to about 0.3 mole per gram atom of titanium.

Preferably, the aforesaid electron donor compounds and titanium compound is contacted with the precipitated solid particles in the presence of an inert hydrocarbon or halogenated diluent, although other suitable techniques can be employed. Suitable diluents are substantially inert to the components employed and are liquid at the temperature and pressure employed.

Preferably, although optional, the precipitated particles are reprecipitated from a solution containing, typically, a cyclic ether, and then the reprecipitated particles are treated with a transition metal compound and an electron donor as described above

In a typical reprecipitation procedure, the precipitated particles are entirely solubilized in a cyclic ether solvent and then particles are allowed to reprecipitate to form particles of uniform size. The preferable ether is tetrahydrofuran, although other suitable cyclic ethers, such as tetrahydropyran and 2-methyltetrahydrofuran, may be used, which can solubilize the particles. Also, thioethers such as tetrahydrothiophene can be used. In some instances, such as the use of 2,2,5,5-tetrahydrofuran and tetrahydropyran-2-methanol, reprecipitation occurs upon heating to about 55°-85°C. Other compounds may be used which act in an equivalent manner, i.e., materials which can solubilize the particles formed in Step B and from which solid uniform particles can be reprecipitated, such as cyclohexene oxide, cyclohexanone, ethyl acetate and phenyl acetate. Mixtures of such suitable materials may also be used.

A suitable diluent that can be used in any of the aforesaid steps should be substantially inert to the reactants employed and preferably is liquid at the temperatures and pressures used. A particular step may be conducted at an elevated pressure so that lower boiling diluents can be used at higher temperatures. Typical suitable diluents are aromatic or substituted aromatic liquids, although other hydrocarbon-based liquids may be used. Aromatic hydrocarbons, such as toluene,

and substituted aromatics are useful. An especially suitable diluent is a halogenated aromatic such as chlorobenzene or a mixture of a halogenated aromatic such as chlorobenzene and a halogenated aliphatic such as dichloroethane. Also useful are higher boiling aliphatic liquids such as kerosene. Mixtures of diluents may be used.

5 One useful diluent component is Isopar G[®] which is a C₁₀-average isoparaffinic hydrocarbon boiling at 156-176°C. Other examples of useful diluents include alkanes such as hexane, cyclohexane, methylcyclohexane, heptane, octane, nonane, decane, undecane, and the like; haloalkanes such as 1,2-dichloroethane, 1,1,2-trichloroethane, carbon tetrachloride and the like; aromatics such as benzene,
10 toluene, xylenes and ethylbenzene; and halogenated and hydrogenated aromatics such as chlorobenzene and o-di-chlorobenzene.

Each of the aforesaid preparative steps is conducted in the substantial absence of water, oxygen, carbon monoxide, and other extraneous materials capable of adversely affecting the performance of the catalyst or catalyst component of this
15 invention. Such materials are conveniently excluded by carrying out the procedures in the presence of an inert gas such as nitrogen or argon, or by other suitable means. Optionally, all or part of the process can be conducted in the presence of one or more alpha-olefins which, when introduced into the preparative system in gaseous form, can serve to exclude catalyst poisons. The presence of one or more alpha-
20 olefins also can result in improved stereospecificity. Useful alpha-olefins include ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, and mixtures thereof. Of course, any alpha-olefin employed should be of relatively high purity, for example, polymerization grade or higher. Other precautions which aid in excluding extraneous poisons include purification of any diluent to be employed, such
25 as by percolation through molecular sieves and/or silica gel prior to use, and drying and/or purifying other reagents.

As a result of the above-described preparation steps, there is obtained a solid reaction product suitable for use as a catalyst or catalyst component. Prior to such use, it is desirable to remove incompletely-reacted starting materials from the solid
30 reaction product. This is conveniently accomplished by washing the solid, after separation from any preparative diluent, with a suitable solvent, such as a liquid hydrocarbon or chlorocarbon, preferably within a short time after completion of the

preparative reaction because prolonged contact between the catalyst component and unreacted starting materials may adversely affect catalyst component performance.

Although not required, the final solid reaction product prepared may be contacted with at least one Lewis acid prior to polymerization. Such Lewis acids
5 useful according to this invention are materials which are liquid or soluble in a liquid diluent at treatment temperatures and have a Lewis acidity high enough to remove impurities such as unreacted starting materials and poorly affixed compounds from the surface of the solid reaction product. Preferred Lewis acids include halides of Group III-V metals which are in the liquid state at temperatures up to about 170°C.
10 Specific examples of such materials include BCl₃, AlBr₃, TiCl₄, TiBr₄, SiCl₄, GeCl₄, SnCl₄, PCl₃ and SbCl₅. Preferable Lewis acids are TiCl₄ and SiCl₄. Mixtures of Lewis acids can be employed if desired. Such Lewis acid may be used in a compatible diluent.

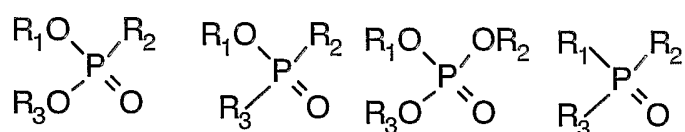
Although not required, the final solid reaction product may be washed with an
15 inert liquid hydrocarbon or halogenated hydrocarbon before contact with a Lewis acid. If such a wash is conducted, it is preferred to substantially remove the inert liquid prior to contacting the washed solid with Lewis acid.

In an advantageous procedure, the precipitated particles are treated with titanium tetrachloride and then with titanium tetrachloride in the presence of the
20 mixture of electron donors. More preferably, the product is treated one or more times with a liquid aromatic hydrocarbon such as toluene and finally with titanium tetrachloride again.

In an embodiment of this invention, a mixture of electron donors is incorporated into the supported catalyst component comprising a first electron donor
25 and an additional electron donor. The first electron donor is selected from the group of electron donors described above as representing the class of electron donors of this invention. The second electron donor is a dialkylphthalate wherein each alkyl group may be the same or different and contains from 3 to 5 carbon atoms. The additional electron donor is preferably a dibutylphthalate and more preferably is di-n-
30 butylphthalate or di-i-butylphthalate. The mole ratio of the additional electron donor to the first electron donor may range from about 0.1:1 to about 20:1, preferably from about 0.3:1 to about 1:1.

Also, the internal electron donor material useful in this invention may be combined with additional electron donors such as a polyhydrocarbyl phosphonate, phosphinate, phosphate or phosphine oxide or an alkyl aralkylphthalate, wherein the alkyl moiety contains from 2 to 10, preferably 3 to 6, carbon atoms and the aralkyl moiety contains from 7 to 10, preferably to 8, carbon atoms, or an alkyl ester of an aromatic monocarboxylic acid wherein the monocarboxylic acid moiety contains from 6 to 8 carbon atoms and the alkyl moiety contains from 1 to 3 carbon atoms.

Useful polyhydrocarbyl phosphonates, phosphinates, phosphates, or phosphine oxides include:



wherein each hydrocarbyl group (R_1 , R_2 , and R_3) may be the same or different and may be alkyl or aryl, and each contains from 1 to 12 carbon atoms

Preferably each hydrocarbyl group (R_1 , R_2 and R_3) is an alkyl group. Preferably a phosphonate is employed. Particular phosphonates that are suitable for use as an aforesaid preferable component include dimethyl methylphosphonate, diethyl ethylphosphonate, diisopropyl methylphosphonate, dibutylbutylphosphonate, and di(2-ethylhexyl) 2-ethylhexyl phosphonate.

The additional component also may be a dialkylphthalate wherein each alkyl moiety may be the same or different and each contains at least 6 carbon atoms, preferably up to 10 atoms. Particular dialkylphthalates which are suitable for use as an additional electron donor include dihexylphthalate and dioctylphthalate.

Also, the additional component may be an alkyl ester of an aliphatic monocarboxylic acid wherein carboxylic acid moiety contains 2 to 20, preferably 3 to 6, carbon atoms and the alkyl moiety contains from 1 to 3 carbon atoms. Particular alkyl esters that are suitable for use as the aforesaid first electron donor include methyl valerate, ethyl pivalate, methyl pivalate, methyl butyrate, and ethyl propionate.

In another alternative, the additional component may be a dicycloaliphatic ester of an aromatic dicarboxylic acid wherein each cycloaliphatic moiety may be the same or different and each contains from 5 to 7 carbon atoms, and preferably contains 6 carbon atoms. Preferably the ester is a dicycloaliphatic diester of an ortho aromatic dicarboxylic acid. Particular dicycloaliphatic esters that are suitable for use

as the aforesaid first electron donor include dicyclopentylphthalate, dicyclohexylphthalate, and di-(methylcyclopentyl)-phthalate.

The additional component may be an alkyl aralkyl phthalate wherein the alkyl moiety contains 2 to 10, preferably 3 to 6, carbon atoms, and the aralkyl moiety
5 contains from 7 carbon atoms up to 10, preferably up to 8, carbon atoms. Particularly, alkyl aralkyl phthalates suitable for use as an additional component include benzyl n-butyl phthalate and benzyl i-butyl phthalate. In another alternative, such additional component also may be an alkyl ester of an aromatic monocarboxylic acid wherein the monocarboxylic acid moiety contains from 6 to 8 carbon atoms and
10 the alkyl moiety contains from 1 to 3 carbon atoms. Particular alkyl esters that are suitable for use as an additional component include methyl toluate, ethyl toluate, methyl benzoate, ethyl benzoate and propyl benzoate.

The mole ratio of first electron donor component described in this invention to the additional component is in the range of from about 0.5:1, preferably from about
15 1:1, to about 3:1, preferably to about 2.5:1. The mole ratio of the aforesaid second electron donor to the combination of the first electron donor and the additional electron donor ranges from about 4:1, preferably from about 7:1, to about 15:1, preferably to about 9:1.

Although the chemical structure of the catalyst or catalyst components of this
20 invention is not known precisely, the components generally comprise from about 1 to about 6 weight percent titanium, from about 10 to about 25 weight percent magnesium, and from about 45 to about 65 weight percent halogen. Preferably, the catalyst component of this invention comprise from about 2.0 to about 4 weight percent titanium, from about 15 to about 21 weight percent magnesium and from
25 about 55 to about 65 weight percent chlorine.

In the solid catalyst component of this invention produced by the method of this invention, the atomic ratio of magnesium to titanium is at least about 0.3:1 and preferably, is from about 0.4:1 to about 20:1 and more preferably, from about 3:1 to about 9:1.

30 Prepolymerization or encapsulation of the catalyst or catalyst component of this invention also may be carried out prior to being used in the polymerization or copolymerization of alpha olefins. A particularly useful prepolymerization procedure is described in U.S. Patent 4,579,836, which is incorporated herein by reference.

Typically, the catalyst or catalyst component of this invention is used in conjunction with a cocatalyst component including a Group II or III metal alkyl and, typically, one or more modifier compounds. Useful Group II and IIIA metal alkyls are compounds of the formula MR_m wherein M is a Group II or IIIA metal, each R is independently an alkyl radical of 1 to about 20 carbon atoms, and m corresponds to the valence of M. Examples of useful metals, M, include magnesium, calcium, zinc, cadmium, aluminum, and gallium. Examples of suitable alkyl radicals, R, include methyl, ethyl, butyl, hexyl, decyl, tetradecyl, and eicosyl. From the standpoint of catalyst component performance, preferred Group II and IIIA metal alkyls are those of magnesium, zinc, and aluminum wherein the alkyl radicals contain 1 to about 12 carbon atoms. Specific examples of such compounds include $Mg(CH_3)_2$, $Mg(C_2H_5)_2$, $Mg(C_2H_5)(C_4H_9)$, $Mg(C_4H_9)_2$, $Mg(C_6H_{13})_2$, $Mg(C_{12}H_{25})_2$, $Zn(CH_3)_2$, $Zn(C_2H_5)_2$, $Zn(C_4H_9)_2$, $Zn(C_4H_9)(C_8H_{17})$, $Zn(C_6H_{13})_2$, $Zn(C_6H_{13})_3$, and $Al(C_{12}H_{25})_3$. A magnesium, zinc, or aluminum alkyl containing 1 to about 6 carbon atoms per alkyl radical may be used. Aluminum alkyls are preferred and most preferably trialkylaluminums containing 1 to about 6 carbon atoms per alkyl radical, and particularly triethylaluminum and triisobutylaluminum or a combination thereof are used.

If desired, metal alkyls having one or more halogen or hydride groups can be employed, such as ethylaluminum dichloride, diethylaluminum chloride, diethylaluminum hydride, diisobutylaluminum hydride, and the like.

A typical catalyst system for the polymerization or copolymerization of alpha olefins is formed by combining the supported titanium-containing catalyst or catalyst component of this invention and an alkyl aluminum compound as a co-catalyst, together with at least one external modifier which typically is an electron donor and, preferably, is a silane. Typically, useful aluminum-to-titanium atomic ratios in such catalyst systems are about 10 to about 500 and preferably about 30 to about 300. Typical aluminum-to-electron donor molar ratios in such catalyst systems are about 2 to about 60. Typical aluminum-to-silane compound molar ratios in such catalyst systems are about 3 to about 50.

To optimize the activity and stereospecificity of this cocatalyst system, it is preferred to employ one or more external modifiers, typically electron donors, and including compounds such as silanes, mineral acids, organometallic chalcogenide

derivatives of hydrogen sulfide, organic acids, organic acid esters and mixtures thereof.

Organic electron donors useful as external modifiers for the aforesaid cocatalyst system are organic compounds containing oxygen, silicon, nitrogen, sulfur, and/or phosphorus. Such compounds include organic acids, organic acid anhydrides, organic acid esters, alcohols, ethers, aldehydes, ketones, silanes, amines, amine oxides, amides, thiols, various phosphorus acid esters and amides, and the like. Mixtures of organic electron donors also may be used.

Particular organic acids and esters are benzoic acid, halobenzoic acids, phthalic acid, isophthalic acid, terephthalic acid, and the alkyl esters wherein the alkyl group contains 1 to 6 carbon atoms such as methyl chlorobenzoates, butyl benzoate, isobutyl benzoate, methyl anisate, ethyl anisate, methyl p-toluate, hexylbenzoate, and cyclohexyl benzoate, and diisobutyl phthalate as these give good results in terms of activity and stereospecificity and are convenient to use.

The aforesaid cocatalyst system advantageously and preferably contains an aliphatic or aromatic silane external modifier. Preferable silanes useful in the aforesaid cocatalyst system include alkyl-, aryl-, and/or alkoxy-substituted silanes containing hydrocarbon moieties with 1 to about 20 carbon atoms. Especially preferred are silanes having a formula: SiY_4 , wherein each Y group is the same or different and is an alkyl or alkoxy group containing 1 to about 20 carbon atoms. Preferred silanes include isobutyltrimethoxysilane, diisobutyldimethoxysilane, diisopropyldimethoxysilane, n-propyltriethoxysilane, isobutylmethyldimethoxysilane, isobutylisopropyldimethoxysilane, dicyclopentyldimethoxysilane, tetraethylorthosilicate, dicyclohexyldimethoxysilane, diphenyldimethoxysilane, di-t-butyltrimethoxysilane, and t-butyltrimethoxysilane.

In one aspect of this invention the substituted cycloalkane dicarboxylates identified above as catalyst component internal donors may be used as external donors alone or in combination with other suitable external donors including the above-identified silane compounds.

The catalyst or catalyst component of this invention is useful in the stereospecific polymerization or copolymerization of alpha-olefins containing 3 or more carbon atoms such as propylene, butene-1, pentene-1, 4-methylpentene-1, and hexene-1, as well as mixtures thereof and mixtures thereof with ethylene. The

catalyst or catalyst component of this invention is particularly effective in the stereospecific polymerization or copolymerization of propylene or mixtures thereof with up to about 30 mole percent ethylene or a higher alpha-olefin. According to the invention, highly crystalline polyalpha-olefin homopolymers or copolymers are prepared by contacting at least one alpha-olefin with the above-described catalyst or catalyst component of this invention under polymerization or copolymerization conditions. Such conditions include polymerization or copolymerization temperature and time, pressure(s) of the monomer(s), avoidance of contamination of catalyst, choice of polymerization or copolymerization medium in slurry processes, the use of additives to control homopolymer or copolymer molecular weights, and other conditions well known to persons skilled in the art. Slurry-, bulk-, and vapor-phase polymerization or copolymerization processes are contemplated herein.

The amount of the catalyst or catalyst component of this invention to be used varies depending on choice of polymerization or copolymerization technique, reactor size, monomer to be polymerized or copolymerized, and other factors known to persons of skill in the art, and can be determined on the basis of the examples appearing hereinafter. Typically, a catalyst or catalyst component of this invention is used in amounts ranging from about 0.2 to 0.02 milligrams of catalyst to gram of polymer or copolymer produced.

Irrespective of the polymerization or copolymerization process employed, polymerization or copolymerization should be carried out at temperatures sufficiently high to ensure reasonable polymerization or copolymerization rates and avoid unduly long reactor residence times, but not so high as to result in the production of unreasonably high levels of stereorandom products due to excessively rapid polymerization or copolymerization rates. Generally, temperatures range from about 0° to about 120°C with a range of from about 20°C to about 95°C being preferred from the standpoint of attaining good catalyst performance and high production rates. More preferably, polymerization according to this invention is carried out at temperatures ranging from about 50°C to about 80°C.

Olefin polymerization or copolymerization according to this invention is carried out at monomer pressures of about atmospheric or above. Generally, monomer pressures range from about 20 to about 600 psi (140 to 4100 kPa), although in vapor phase polymerizations or copolymerizations, monomer pressures should not be

below the vapor pressure at the polymerization or copolymerization temperature of the alpha-olefin to be polymerized or copolymerized.

The polymerization or copolymerization time will generally range from about 1/2 to several hours in batch processes with corresponding average residence times in continuous processes. Polymerization or copolymerization times ranging from about 1 to about 4 hours are typical in autoclave-type reactions. In slurry processes, the polymerization or copolymerization time can be regulated as desired. Polymerization or copolymerization times ranging from about 1/2 to several hours are generally sufficient in continuous slurry processes.

Diluents suitable for use in slurry polymerization or copolymerization processes include alkanes and cycloalkanes such as pentane, hexane, heptane, n-octane, isooctane, cyclohexane, and methylcyclohexane; alkylaromatics such as toluene, xylene, ethylbenzene, isopropylbenzene, ethyl toluene, n-propylbenzene, diethylbenzenes, and mono- and dialkylnaphthalenes; halogenated and hydrogenated aromatics such as chlorobenzene. Chloronaphthalene, ortho-dichlorobenzene, tetrahydro-naphthalene, decahydronaphthalene; high molecular weight liquid paraffins or mixtures thereof, and other well-known diluents. It often is desirable to purify the polymerization or copolymerization medium prior to use, such as by distillation, percolation through molecular sieves, contacting with a compound such as an alkylaluminum compound capable of removing trace impurities, or by other suitable means.

Examples of gas-phase polymerization or copolymerization processes in which the catalyst or catalyst component of this invention is useful include both stirred bed reactors and fluidized bed reactor systems and are described in U.S. Patents 3,957,448; 3,965,083; 3,971,786; 3,970,611; 4,129,701; 4,101,289; 3,652,527; and 4,003,712, all incorporated by reference herein. Typical gas phase olefin polymerization or copolymerization reactor systems comprise at least one reactor vessel to which olefin monomer and catalyst components can be added and which contain an agitated bed of forming polymer particles. Typically, catalyst components are added together or separately through one or more valve-controlled ports in the single or first reactor vessel. Olefin monomer, typically, is provided to the reactor through a recycle gas system in which unreacted monomer removed as off-gas and fresh feed monomer are mixed and injected into the reactor vessel. For production

of impact copolymers, homopolymer formed from the first monomer in the first reactor is reacted with the second monomer in the second reactor. A quench liquid, which can be liquid monomer, can be added to polymerizing or copolymerizing olefin through the recycle gas system in order to control temperature.

5 Irrespective of polymerization or copolymerization technique, polymerization or copolymerization is carried out under conditions that exclude oxygen, water, and other materials that act as catalyst poisons. Also, according to this invention, polymerization or copolymerization can be carried out in the presence of additives to control polymer or copolymer molecular weights. Hydrogen is typically employed for
10 this purpose in a manner well known to persons of skill in the art. Although not usually required, upon completion of polymerization or copolymerization, or when it is desired to terminate polymerization or copolymerization or at least temporarily deactivate the catalyst or catalyst component of this invention, the catalyst can be contacted with water, alcohols, acetone, or other suitable catalyst deactivators in a
15 manner known to persons of skill in the art.

The products produced in accordance with the process of this invention are normally solid, predominantly isotactic polyalpha-olefins. Homopolymer or copolymer yields are sufficiently high relative to the amount of catalyst employed so that useful products can be obtained without separation of catalyst residues. Further, levels of
20 stereorandom by-products are sufficiently low so that useful products can be obtained without separation thereof. The polymeric or copolymeric products produced in the presence of the invented catalyst can be fabricated into useful articles by extrusion, injection molding, and other common techniques.

The polymer component of the composition of this invention primarily contains
25 a high crystalline polymer of propylene. Polymers of propylene having substantial polypropylene crystallinity content now are well-known in the art. It has long been recognized that crystalline propylene polymers, described as "isotactic" polypropylene, contain crystalline domains interspersed with some non-crystalline domains. Noncrystallinity can be due to defects in the regular isotactic polymer chain
30 which prevent perfect polymer crystal formation. The extent of polypropylene stereoregularity in a polymer can be measured by well-known techniques such as isotactic index, crystalline melting temperature, flexural modulus, and, recently by

determining the relative percent of meso pentads (%m₄) by carbon-13 nuclear magnetic resonance (¹³C NMR).

The propylene polymer especially useful in this invention has both a high nmr tacticity and a broadened molecular weight distribution ("MWD") as measured by the
 5 ration of the weight average to number average molecular weights (M_w/M_n). Such molecular weights typically are measured by gel permeation chromatography (GPC) techniques known in the art. In addition, preferable polymers of this invention have flexural moduli above about 1800 MPa and typically above about 2100 MPa. In addition the nmr pentad tacticity typically is above 90% and preferably is above about
 10 95% and may be above about 97%. Typical polymer melt flow rates are 1 to 20 g/10 min.

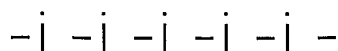
A method to determine stereoregularity of a propylene polymer uses ¹³C NMR and is based on the ability to identify relative positions of adjacent methyl groups on a polypropylene polymer backbone. If the methyl groups of two adjacent propylene
 15 monomer units (-CH(CH₃)-CH₂-) are on the same side of the polymer chain, such two methyl groups form a meso ("m") dyad. The relative percentage of these meso dyads is expressed as %m. If the two methyl groups of adjacent monomer units are on opposite sides of the polymer chain, such two methyl groups form a racemic ("r") dyad, and the relative percentage of these racemic dyads is expressed as %r.
 20 Advances in ¹³C NMR techniques permit measurement of the relative positioning of three, four, and five successive methyl groups, which are referred to as triads, tetrads and pentads, respectively.

Current NMR instruments can quantify the specific distribution of pentads in a polymer sample. There are ten unique pentads which are possible in a propylene
 25 polymer:

m m m m	r r r r
m m m r	m m r m
m m r r	m r r m
r m m r	r m r m
r m r r	m r r r

A ball and stick representation of the mmmm pentad is:

m m m m



Two of the possible pentads cannot be separated by NMR (mmrm and rmmr) and are reported together. Two of the ten pentads (mmrr and mrrm) result from the displacement of a single methyl group on the opposite side of the polymer chain in an isotactic sequence. Since the mmmm (m4) pentad represents a perfect isotactic stereoregular structure, measurement of this pentad (as %m4) reflects isotacticity and potential crystallinity. As used herein, the term NMR tacticity index is the percent of m4 (%m4) pentads as measured by ¹³C NMR. Thus, if 96% of pentads measured by ¹³C NMR in a propylene polymer are m4, the NMR tacticity index is 96.

The invention described herein is illustrated, but not limited, by the following examples.

Examples

A series of supported catalyst components are prepared using various mixtures of internal electron donors. Examples using electron donors of this invention are described below, together with Comparative Runs not using such internal electron donors.

Step A - Formation of Magnesium Alkyl Carbonate Solution

Into a two-liter reactor, equipped with a mechanical stirrer and flushed with dry nitrogen, is transferred a mixture of 153 grams of magnesium ethoxide, 276 milliliters of 2-ethyl-1-hexanol and 1100 milliliters of toluene. This mixture is agitated at 450 rpm under 30 psig of carbon dioxide and heated at 93°C for three hours. The resulting solution (1530 milliliters) is transferred to a two-liter bottle. The solution contains 0.10 gram-equivalents of magnesium ethoxide per milliliter.

Step B - Formation of Solid Particles

Into a 1.0-liter reactor is charged 150 milliliters of toluene, 20.5 milliliters of tetraethoxysilane, and 14 milliliters of titanium tetrachloride under a blanket of dry nitrogen. After the mixture is stirred at 300 rpm at 22-27°C for 15 minutes, 114 milliliters of the Step A magnesium hydrocarbyl carbonate solution is added to the reactor through a bomb and thereafter solid particles precipitate.

Step C - Reprecipitation

After the mixture containing the precipitate is stirred for five additional minutes, 27 milliliters of tetrahydrofuran (THF) were added rapidly through a syringe. The temperature in the reactor rises from 26°C to 38°C. Whereupon, the stirring is maintained at 300 rpm and the temperature is increased to 60°C within 15 minutes. The first formed solid dissolves in the THF solution. Within about 5 minutes after the THF addition, a solid begins to reprecipitate from solution. Stirring is continued for 1 hour at 60°C after which agitation is stopped and the resulting solid is allowed to settle. Supernatant is decanted and the solid washed two times with 50-milliliter portions of toluene.

Step D - Titanium (IV) Compound Treatment

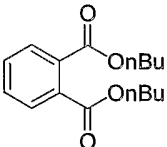
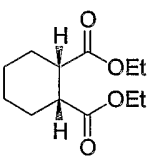
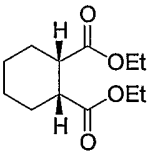
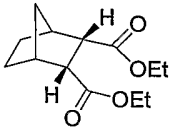
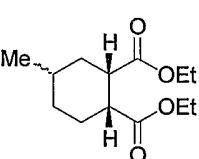
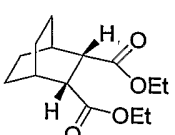
To the solid from Step C in the one-liter reactor are added 125 milliliters of toluene and 50 milliliters of titanium tetrachloride. The resulting mixture is heated to 116°C within 30 minutes and stirred at 300 rpm for one hour. After stirring is stopped, the resulting solid is allowed to settle and the supernatant is decanted. After 150 milliliters of toluene, 50 milliliters of titanium tetrachloride, the electron donor compounds of this invention are added to the resulting solid, the mixture is stirred at 300 rpm at 117°C for 90 minutes, the solid is allowed to settle and supernatant liquid is decanted. After 95 milliliters of toluene are added, the mixture is heated to 91°C for 30 minutes. After the agitation is stopped, the solid is allowed to settle and the supernatant decanted. An additional 125 milliliters of titanium tetrachloride are added, the mixture is heated at 91°C under agitation for 30 minutes, after which the agitation is stopped, and the supernatant liquid is decanted. The residue is washed four times with 50-milliliter portions of hexane and the solids are recovered. The mole ratio of magnesium/titanium/electron donor components in the reactants for the examples is 1/5/0.45.

Batch slurry phase propylene polymerization evaluation is performed in a two liter reactor at 71°C at a total reactor pressure of 150 pounds per square inch gauge with 7 millimoles of hydrogen, while stirring at 500 revolutions per minute with a reaction time of 2 hours. Triethylaluminum (TEA) is used as a co-catalyst together with diisobutyldimethoxysilane as an external modifier. The reactor is charged with TEA/modifier, titanium component, hydrogen, and propylene in that order.

In a typical procedure, a dry, nitrogen-purged, two-liter stainless steel autoclave reactor was charged with catalyst (~20 mg), triethylaluminum (3.6 mL of a 0.75 M solution in heptane), and diisobutyldimethoxysilane (1.0 mL of a 0.15 M solution in heptane), and 850 mL of heptane at 40 C. Hydrogen was introduced at 12.5 psig. Agitation and heating was started and a 15 psig pressure drop from a 75 mL vessel containing hydrogen was introduced to the reactor followed by an approximately 30 gram portion of propylene. When the temperature reaches 70 C, the propylene reservoir to the reactor was opened and a constant propylene pressure of 150 psig is maintained for one hour. The reactor was then vented and the resulting polymer slurry dumped from the reactor, filtered and dried. Analysis was performed after oven drying and weighing of the polymer powder.

Catalyst components were prepared in a manner consistent with the above-described procedure using various internal donors. Test runs using various internal modifiers are shown in Table 1.

Table 1

		Yield	MFR	Bulk	XS	Mn	Mw	Mz	Mz+1	M _w /M _n	M _z /M _w
Run	Modifier Structure	(g/g PP)	(g/10 min)	Density (g/cc)	(wt.%)	(X 10 ⁻³)	(X 10 ⁻³)	(X 10 ⁻³)	(x10 ⁻³)		
1		8160	8.40	0.425	2.7	50.2	272	894	2053	5.42	3.29
2		6080	11.68	0.397	4.78	44.6	259	917	2128	5.81	3.54
3*		5390	10.60	0.405	5.35	46.2	264	943	2173	5.71	3.57
4		3370	11.76	0.337	5.9	49.6	258	984	2505	5.20	3.81
5		5330	11.55	0.39	6.47	44.4	261	1009	2465	5.88	3.87
6											

"Yield" (grams of polymer produced per gram of solid catalyst component) is based on the weight of solid catalyst used to produce polymer. "Solubles" are determined by evaporating the solvent from an aliquot of filtrate to recover the amount of soluble polymer produced and are reported as the weight percent (% Sol.) of such soluble polymer based on the sum of the weights of the solid polymer isolated by filtration and of the soluble polymer. "Xylene Solubles" ("XS") are Solubles using boiling xylenes as the solvent. "Extractables" are determined by

measuring the loss in weight of a dry sample of ground polymer after being extracted in boiling n-hexane for three to six hours and are reported as the weight percent (% Ext.) of the solid polymer removed by the extraction. The bulk density (BD) is reported in units of pounds per cubic foot ($1 \text{ lbs/ft}^3 = 0.0149 \text{ g/ml}$). The viscosity of the solid polymer was measured according to ASTM D1238 Condition L (2.16 kg@230°C) and reported as the melt flow rate (MFR) in grams of polymer per 10 minutes.

Decalin Solubles ("DS") is a measure of hydrocarbon soluble and extractable materials, such as atactic, non-crystalline, and oligomeric components, contained in a propylene polymer and is useful in correlating a particular resin to desirable resin properties such as processing window. DS is determined by completely dissolving a 2.0-gram sample of polymer in 100 milliliters of Irganox 1076-stabilized (0.020 grams/liter) decalin (decahydronaphthalene) by warming the slurry to 165°C and stirring the slurry for two hours. Once the polymer is dissolved, the solution is allowed to cool overnight (at least 16 hours). After the cooling period, the solution is filtered from the precipitated polymer. A measured portion of the solution is withdrawn and, after removing the decalin solvent, the resulting samples are completely dried in a 120°C vacuum oven. The final dried samples are weighed to determine the amount of decalin-soluble polymer. Results are reported as a weight percent polymer remaining soluble in decalin.

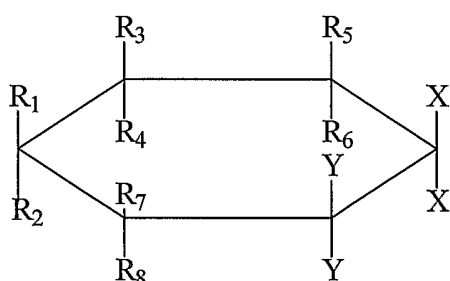
In order to demonstrate this invention further, propylene polymerizations are conducted in a laboratory gas-phase reactor using a magnesium halide supported HAC catalyst component produced in accordance with U.S. Patent 4,886,022. The catalyst component contains 17.32 wt. % magnesium and 2.29 wt % titanium. Triethylaluminum is used as the co-catalyst. The amount of silane modifier is controlled in the polymerizations such that the Al/Si ratio was in the range 6 to 24 and the target melt flow rate (MFR) of the polymer is 1 to 50. These propylene polymerizations are performed in a one-gallon (3.8-liter) continuous, horizontal, cylindrical gas-phase reactor measuring 10 cm in diameter and 30 cm in length based on that described in U. S. Patent 3,965,083. The reactor is equipped with an off-gas port for recycling reactor gas through a condenser and back through a recycle line to the recycle nozzles in the reactor. Propylene liquid is used as the quench

liquid to help remove the heat generated in the reactor during the polymerization. During operation, polypropylene powder produced in the reactor bed, passes over a weir, and was discharged through a powder discharge system into a secondary closed vessel blanketed with nitrogen. The polymer bed is agitated by paddles
5 attached to a longitudinal shaft within the reactor that was rotated at about 75 rpm. The reactor pressure is maintained 300 psig (2100 kPa). The titanium/magnesium-containing catalyst was introduced into the reactor as a 1.5 wt% slurry in heptane through a liquid propylene-flushed catalyst addition nozzle. A mixture of the silane
10 modifier and triethylaluminum in heptane at Al/Mg and Al/Si molar ratios indicated in Table I are fed separately to the reactor through a liquid propylene-flushed co-catalyst addition nozzle. Hydrogen was fed to the reactor. Production rate is about 200 g/hr.

That which is claimed is:

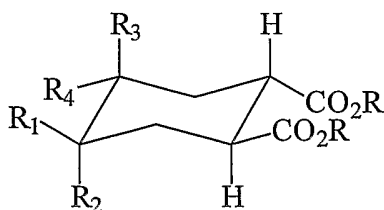
1. A solid, hydrocarbon-insoluble, catalyst component useful in polymerizing olefins containing magnesium, titanium, and halogen further containing an internal electron donor comprising a substituted hydrocarbyl 4-8 membered cycloalkane dicarboxylate wherein the substituents are positioned on the cycloalkane to place the dicarboxylate groups into conformational proximity positions and wherein the substituents contain 1 to 20 carbon atoms and may be joined to the cycloalkane structure to form a bicyclo structure.

2. The catalyst component of claim 1 wherein the internal electron donor is



in which one X and one Y are carboxylate (CO_2R) groups, wherein R is selected from lower alkyl groups containing 1 to 20 carbon atoms; $\text{R}_1\text{-R}_8$ are selected from bulky and non-bulky alkyl or substituted alkyl groups to produce a ring conformation that places the carboxylate groups into proximity; and remaining the X and Y groups are selected from hydrogen and methyl, and provided two of the $\text{R}_1\text{-R}_8$ groups may be connected to form a bicyclo structure.

3. The catalyst component of claim 1 wherein the internal electron donor is

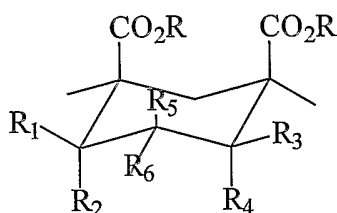


wherein R is selected from lower alkyl groups containing 1 to 20 carbon atoms, R_1 and R_4 are selected from bulky groups sufficient to place the carboxyl

groups into conformational proximity positions, and R_2 and R_4 are selected from hydrogen and methyl.

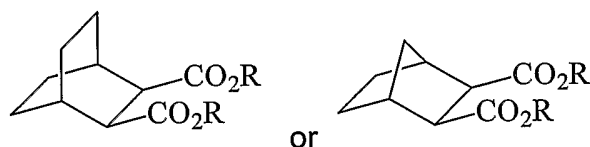
4. The catalyst component of claim 1 wherein the internal electron donor is trans-di-n-butyl-4,5-di-isopropylcyclohexane trans-dicarboxylate or trans-diisopropyl 4,5-di-t-butylcyclohexane trans-dicarboxylate.

5. The catalyst component of claim 1 wherein the internal electron donor is



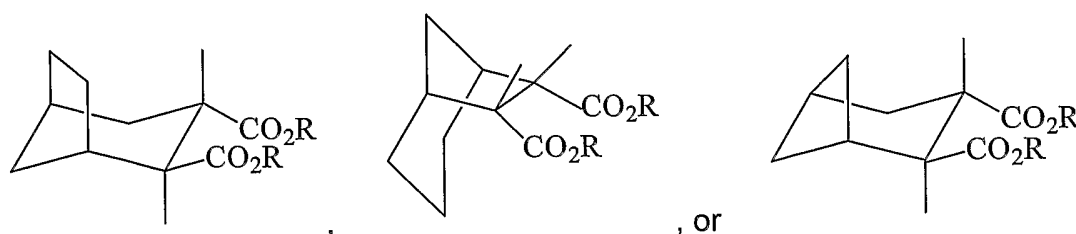
wherein R is selected from lower alkyl groups containing 1 to 20 carbon atoms, R_1 , R_3 , and R_6 are selected from bulky groups sufficient to place the carboxyl groups into conformational proximity positions, and R_2 , R_4 , and R_5 are selected from hydrogen and methyl.

6. The catalyst component of claim 1 wherein the internal electron donor is



wherein R is selected from lower alkyl groups containing 1 to 20 carbon atoms.

7. The catalyst component of claim 1 wherein the internal electron donor is



wherein R is selected from lower alkyl groups containing 1 to 20 carbon atoms.

8. The catalyst component of claim 1 wherein R is ethyl, propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, n-pentyl, isopentyl, hexyl, 2-ethylhexyl, or octyl.

5 9. The catalyst component of claim 1 wherein R contains 3 to 8 carbon atoms.

10. The catalyst component of claim 1 wherein R is ethyl, propyl, isopropyl, n-butyl, isobutyl, or s-butyl.

11. The catalyst component of claim 1 at least one bulky substituent group contains 3 to 20 carbon atoms.

10 12. The catalyst component of claim 1 at least one of isopropyl, isobutyl, t-butyl, s-butyl, isopentyl, isohexyl, or 2-ethylhexyl.

13. The catalyst component of claim 1 at least one of isopropyl, isobutyl, t-butyl, or s-butyl.

15 14. The catalyst component of claim 1 at least one bulky substituent group contains a hetero atom.

15 15. A olefin polymerization catalyst system comprising a solid, hydrocarbon insoluble component containing magnesium, titanium, and halogen and an internal electron donor compound, an aluminum alkyl compound, and an external electron donor compound comprising a substituted hydrocarbyl 4-8 membered cycloalkane dicarboxylate wherein the substituents are positioned on the cycloalkane to place the dicarboxylate groups into conformational proximity positions and wherein the substituents contain 1 to 20 carbon atoms and may be joined to the cycloalkane structure to form a bicyclo structure.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/008888

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/00 C08F4/651 C08F4/649

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

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

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

EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 21, 3 August 2001 (2001-08-03) & JP 2001 114811 A (IDEMITSU PETROCHEM CO LTD), 24 April 2001 (2001-04-24) abstract	1,15
X	& DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 2001, SADASHIMA, TAKANORI ET AL: "Aromatic group-free polymerization catalysts and manufacture of olefin polymers with high stereoregularity" XP002285935 retrieved from STN Database accession no. 2001:288858 abstract ----- -/--	1,8-10

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

☒ Patent family members are listed in annex.

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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

Date of the actual completion of the international search

30 June 2004

Date of mailing of the international search report

20/08/2004

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/008888

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 427 060 A (BASF AG) 15 May 1991 (1991-05-15) claims 1,2 -----	1,8,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/008888

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			AT 99334 T	15-01-1994
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