OPIC
OFFICE DE LA PROPRIÉTÉ INTELLECTUELLE DU CANADA

CIPO
CANADIAN INTELLECTUAL PROPERTY OFFICE

(12) (19) (CA) **Demande-Application**

(21) (A1) **2,308,160**
(86) 1998/10/17
(87) 1999/04/29

(72) MITCHELL, JONATHAN PAUL, US
(72) VILLAFANE, MICHAEL E., US
(71) AKZO NOBEL N.V., NL

(51) Int.Cl.^{6} C07F 11/00, C08F 4/69, C08F 10/00
(30) 1997/10/20 (08/796,726) US

(54) PROCEDE DE PREPARATION D'UN CONSTITUANT DE CATALYSEUR DE POLYMERISATION D'OLEFINES A BASE DE METAL DU GROUPE VI

(54) PROCESS FOR PREPARING GROUP VI METAL-BASED OLEFIN POLYMERIZATION CATALYST COMPONENT

(57) Constituant de catalyseur de polymérisation d'oléfines contenant des ligands, à base de métal du groupe VIB, qui peut être préparé en utilisant du trihalogénure de métal du groupe VIB en tant que réactif de départ pour le métal du groupe VIB. Le procédé consiste à mettre en contact (par ex. dans du tétrahydrofuranne) le trihalogénure de métal du groupe VIB, tel que du trichlorure de chrome, avec le ou les réactif(s) des ligands, tels qu'un composé de lithium contenant du cyclopentadiényle et un composé de lithium contenant de l'alkyle inférieur, en présence d'un ligand de stabilisation donneur de sigma, tel que la pyridine.

(57) A Group VIB metal-based, ligand-containing olefin polymerization catalyst component can be made by using Group VIB metal trihalide as the starting reagent for the Group VIB metal which process comprises contacting (e.g., in tetrahydrofuran) the Group VIB metal trihalide, such as chromium trichloride, with the ligand reagent or reagents, such as a cyclopentadienyl-containing lithium compound and a lower alkyl-containing lithium compound, in the presence of a sigma donor stabilizing ligand, such as pyridine.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} :
C07F 11/00, C08F 4/69, 10/00

A1

(11) International Publication Number: **WO 99/20636**

(43) International Publication Date: 29 April 1999 (29.04.99)

(21) International Application Number: PCT/EP98/07005

(22) International Filing Date: 17 October 1998 (17.10.98)

(30) Priority Data:
08/796,726 20 October 1997 (20.10.97) US

(71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventors: MITCHELL, Jonathan, Paul; 123 Farragut Avenue, Hastings-on-Hudson, NY 10706 (US). VILLAFANE, Michael, E.; 5 Orchard Parkway, White Plains, NY 10606 (US).

(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).

(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS FOR PREPARING GROUP VI METAL-BASED OLEFIN POLYMERIZATION CATALYST COMPONENT

(57) Abstract

A Group VIB metal-based, ligand-containing olefin polymerization catalyst component can be made by using Group VIB metal trihalide as the starting reagent for the Group VIB metal which process comprises contacting (e.g., in tetrahydrofuran) the Group VIB metal trihalide, such as chromium trichloride, with the ligand reagent or reagents, such as a cyclopentadienyl-containing lithium compound and a lower alkyl-containing lithium compound, in the presence of a sigma donor stabilizing ligand, such as pyridine.

PROCESS FOR PREPARING GROUP VI METAL-BASED OLEFIN POLYMERIZATION CATALYST COMPONENT

Background of the Invention

Chromium-based catalysts are used in the commercial polymerization of small alpha olefins such as ethylene and propylene. U. S. Patent No. 5,418,200 to Carney et. al. describes a series of Group VIB metal-based, ligand-containing olefin polymerization catalyst components which when in combination with a suitable cocatalyst and supported on an inorganic metal oxide or inorganic metal phosphate produce high productivity alpha-olefin polymerization catalysts. The present invention relates to an improved process for preparing such Group VIB metal-based, ligand-containing olefin polymerization catalyst components. For example, the half-sandwich chromium-based olefin polymerization catalyst component, $Cp^*Cr(CH_3)_2(pyr)$, where Cp* designates the radical C_5Me_5 and pyr designates pyridine, can be produced in high yield and in a pure form. This represents a significant advantage of the current invention over the type of synthetic procedure known to persons in the art. Previously published syntheses of $Cp^*Cr(Me_2)(pyr)$, for example as described in Example 15 of U. S. Patent No. 5,418,200 to Carney et al. and in S.K. Noh et al., *J. Am. Chem. Soc.* 1989, 111, 9127, require the use of the starting material $CrCl_3(THF)_3$, where THF designates tetrahydrofuran. This starting material must be synthesized, typically by a Soxhlet extraction of $CrCl_3$ with Zn metal in refluxing THF. This is both tedious to perform and difficult to scale up for commercial synthesis in order to produce $CrCl_3(THF)_3$ of sufficient purity for subsequent catalyst component synthesis. The current invention (as typified by Example 1) removes this synthetic stage and uses commercially available $CrCl_3$ as the starting material for the catalyst synthesis.

Summary of the Invention

A process for preparing a Group VIB metal-based, ligand-containing complex component using a Group VIB metal trihalide as the starting reagent for the Group VIB metal which comprises contacting the Group VIB metal trihalide with the ligand reagent or reagents in the presence of a sigma donor stabilizing ligand.

Description of the Preferred Embodiments

In the process of the present invention, a Group VIB metal trihalide is an essential reagent. It is preferred that trichlorides be utilized, although other trihalides, such as tribromides and triiodides, can also be selected for use. Preferably, the Group VIB metal is chromium.

The starting material is contacted with reagents for the other desired ligands on the final catalyst component in the presence of a sigma donor stabilizing ligand. The reagents that are used to provide some of the other hydrocarbyl ligands include hydrocarbyl lithium compounds, hydrocarbyl potassium compounds, hydrocarbyl magnesium compounds, and hydrocarbyl silyl compounds, of which hydrocarbyl lithium compounds are preferred. Representative reagents include cyclopentadienyl-containing lithium compounds, of the type described in U. S. Patent No. 5,418,200 to Carney at Col. 4, lines 19 to 31, wherein the preferred species is pentamethylcyclopentadienyl lithium, and cyclopentadienyl amide-containing lithium compounds, of the type described in Y. Liang et. al. *Organometallics*, 1996, 15, 5284, wherein the preferred species is $Li_2(THF)[Me_4C_5SiMe_2N^tBu]_n$, and also the lower hydrocarbyl lithium compounds of the type described in U. S. Patent No. 5,418,200 to Carney at Col. 4, lines 46 to 59. Also used in the present process is a sigma donor stabilizing ligand of the type described in U. S. Patent No. 5,418,200 to Carney at Col. 4, line 60 to Col. 5, line 2, wherein the preferred species include the ether, tetrahydrofuran, and the amine, pyridine.

Examples of such Group VIB catalyst components that can be made by the present invention are described in U. S. Patent No. 5,418,200 to Carney at Col. 5, lines 3 to 39, in PCT International Patent Publication No. WO 96/23006 in Examples 2 and 4, and in PCT International Patent Publication No. WO 96/27621 at Col. 14, lines 17 to 21.

The process of the present invention can be advantageously conducted by first contacting the Group VIB metal trihalide with an ether solvent, such as tetrahydrofuran, followed by reaction of about an equimolar amount of the cyclopentadienyl-containing reagent, either as a solid or in an ether solvent, preferably at temperatures of from about -80°C to about ambient (20°C to 25°C), more preferably from about -20°C to about ambient temperature, most preferably from about 0°C to about ambient temperature. The resulting product may then be reacted, for example, at ambient temperature, with a suitable sigma donor ligand in a molar ratio, of from about 1 chromium complex:1.3 sigma donor ligand, for example pyridine, preferably 1:1.1, most preferably 1:1.05, and then, preferably, at temperatures of from about -80°C to about ambient (20°C to 25°C), more preferably from about -20°C to about ambient, most preferably from about 0°C to about ambient, with the lower hydrocarbyl-containing reagent in a molar ratio of about 1 chromium complex:2 lower hydrocarbyl-containing reagent to produce the end product.

Example 3 represents a preferred embodiment of the present invention which results in the elimination of a synthetic step, making the resulting process more amenable for scale up. If only tetrahydrofuran (THF) is used as a solvent, significant amounts of the byproduct salt (LiCl) are dissolved therein. This necessitates the removal of THF under vacuum before the product can be separated from the byproduct salt, e.g. by use of a solvent having a much lower solubility for that byproduct salt. This Example shows the use of less coordinating solvent systems than pure THF in the process. The reaction solvent containing the product can then simply be freed from the byproduct salt by simple filtration, without the need for a solvent removal stage prior to that step. In this way, the catalyst compound can be isolated while it still contains low levels of metal halide impurities. The use of less THF in the reaction also assists in reducing the level of byproduct formation, for example, of Cp*Cr(Me_2)(THF). The less coordinating solvent system is a solvent which, under equal conditions, dissolves less LiCl than THF. Examples of such solvents are acyclic ethers, aliphatic solvents and/or aromatic solvents. Particularly suitable solvents are diethylether, pentane, hexane, isohexane, cyclohexane, heptane, toluene and xylene. Depending on the process conditions and the solvents which are used it can be preferred to use a mixture of THF and further solvent(s) containing less than four, preferably less than three mole equivalents of THF per mole chromium compound starting material.

Combination of the thus produced Group VIB metal-based, ligand-containing complex component with one or more other cocatalytic compounds (such as an aluminoxane or a Group II or III alkyl compound) will produce a final catalyst that may be supported on, for example, silica, alumina, aluminum phosphate, or alumina aluminum phosphate. Such a catalyst is well suited for catalyzing polymerization reactions of α-olefins, such as propylene and ethylene.

The present invention is further illustrated by the Examples that follow. In the following Examples, all manipulations were conducted under nitrogen using standard glove box or Schlenk line techniques. All solvents were thoroughly dried and degassed prior to use.

Example 1 - Synthesis of Cp*$CrMe_2$(pyr) from $CrCl_3$

In a 5 liter flask, $CrCl_3$ (136.6 g, 0.86 mol) and 750 ml of THF were combined to give a purple slurry, which was subsequently cooled to 0°C using ice. In a separate 2 liter flask, Cp*Li (122.6 g, 0.86 mol) and 1.25 liters of chilled THF were combined at 0°C. The chilled Cp*Li slurry was then added dropwise over a period of one hour to the chilled $CrCl_3$ slurry. The resulting composition was allowed to warm to room temperature, and the resulting blue solution was stirred for sixteen hours.

At room temperature, pyridine (71.6 g, 1.00 mol, 1.05 equiv.) was then added dropwise over thirty minutes to the previously formed composition, resulting in the deposition of blue crystals. This mixture was stirred at room temperature for a further three hours before being cooled again to 0°C. To this mix was then added an ethereal methyllithium solution (902.1 g, 1.4 M, 1.72 mol, 2.00 equiv.) over a period of one hour. The resulting dark brown mixture was allowed to warm to room temperature and was stirred for sixteen hours. Volatiles were then removed *in vacuo* to give a dark brown solid.

The crude product was extracted from the LiCl byproduct using diethyl ether. Recrystallization gave dark brown crystals that were isolated and dried *in vacuo*. The total yield of $Cp^*Cr(Me)_2(pyr)$ was 193.1 g, 0.65 mol, 76%.

Comparative Example 2 - Synthesis of $Cp^*Cr(Me)_2(pyr)$ from $CrCl_3(THF)_3$

(I) Synthesis of $CrCl_3(THF)_3$

$CrCl_3(THF)_3$ was synthesized according to the Soxhlet extraction procedure given by J. P. Collman et al., *Inorganic Syntheses*, 1966, Vol. 8, 150. The use of 26.34 g of $CrCl_3$ and 2.6 g of Zn in 300 ml of tetrahydrofuran yielded 34.85 g of $CrCl_3(THF)_3$ (56% based on $CrCl_3$).

(ii) Synthesis of $Cp^*Cr(Me)_2(pyr)$

$CrCl_3(THF)_3$ (30.00 g, 80.1 mmol) and 250 ml THF were combined to give a purple slurry. In a separate flask, Cp*Li (11.38 g, 80.0 mmol) and 150 ml THF were combined. The Cp*Li slurry was then added dropwise to the $CrCl_3(THF)_3$ slurry. The Cp*Li was washed with a further 150 ml of THF, and this was added to the reaction mixture. The resulting composition was then stirred at room temperature for one and one half hours.

Pyridine (6.65 g, 84.1 mmol, 1.05 equivalents) was added dropwise to the previous product, resulting in the deposition of blue crystals. This mixture was stirred at room temperature for a further hour before addition of an ethereal MeLi solution (83.81 g, 1.4 M, 160.3 mmol, 2.00 equivalents). The resulting dark brown mixture was allowed to stir at room temperature for thirty minutes before volatiles were removed *in vacuo*.

The crude product was extracted from the LiCl byproduct using heptane. Recrystallization gave dark brown crystals that were isolated and dried *in vacuo*. A second batch of crystals was isolated by exhaustive extraction using pentane and subsequent recrystallization. The total yield of $Cp^*Cr(Me)_2(pyr)$ was 10.13 g, 34.1 mmol, 43% based on $CrCl_3(THF)_3$.

EXAMPLE 3

This Example illustrates a particularly preferred process in accordance with the present invention.

In this Example, $CrCl_3$ (0.960 g, 6.06 mmol) and Cp*Li (0.861 g, 6.06 mmol) were combined in 30 ml of Et_2O and 1.5 ml of THF with stirring at room temperature for about twenty hours, resulting in a dark blue reaction mixture. At room temperature, pyridine (0.603 g, 7.62 mmol) was added and the reaction mixture was stirred for a further hour. The reaction mixture was then chilled in ice and a MeLi solution (6.583 g, 1.4 M in Et_2O, 12.59 mmol) was added dropwise. The resulting dark brown mixture was stirred at room temperature for approximately four hours. Filtration, followed by washing the LiCl salt with Et_2O (3 x 20 ml) and the removal of volatiles *in vacuo* gave $Cp^*Cr(Me)_2(pyr)$ as a brown solid. Analysis of this solid revealed 0.094 wt. % Cl.

The foregoing Examples merely illustrates a particular embodiment of the present invention in comparison with a prior art technique and, for that reason, should not be construed in a limiting sense. The scope of protection desired is set forth in the Claims that follow.

Claims

1. A process for preparing a Group VIB metal-based, ligand-containing complex component using a Group VIB metal trihalide as the starting reagent for the Group VIB metal which comprises contacting the Group VIB metal trihalide with the ligand reagent or reagents in the presence of a sigma donor stabilizing ligand.

2. A process as claimed in Claim 1 wherein the Group VIB metal trihalide is chromium trichloride.

3. A process as claimed in Claim 2 wherein the ligand reagents are a cyclopentadienyl-containing lithium compound and a lower alkyl-containing lithium compound.

4. A process as claimed in Claim 3 wherein the ligand reagents are C_5Me_5Li and methyl lithium.

5. A process as claimed in any one of the preceding claims wherein the sigma donor stabilizing ligand is pyridine.

6. A process according to any one of the preceding claims wherein the reaction is conducted in tetrahydrofuran solvent.

7. A process as claimed in Claim 6 wherein a solvent system is used containing tetrahydrofuran and at least one solvent that is less coordinating than tetrahydrofuran.

8. A process according to claim 7 wherein the further solvent is selected from the group of acyclic ethers, aliphatic solvents and aromatic solvents.

9. A process according to claim 8 wherein the solvent is selected from diethylether, pentane, hexane, isohexane, heptane, toluene and xylene.

10. Use of the Group VIB metal-based, ligand-containing complex component obtained in the process according to any one of claims 1-9, as a catalyst component for the polymerization of α-olefins.