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CATALYST COMPOSITION FOR ALKENE OLIGOMERISATION AND CO-OLIGOMERISATION
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- (56) Prior Art Documents
WO 91/09882
- (57) Claim

1. A catalyst composition when used for alkene oligomerisation, comprising a first component which is a substituted-bis(cyclopentadienyl) titanium, zirconium or hafnium compound, also containing a substituent which is attached to the metal and which is capable of reacting with a cation and a second component which is a compound having a bulky and labile anion which is substantially non-coordinating under the reaction conditions and a cation, characterized in that the substituted bis-cyclopentadienyl ligand pair is bis-tetramethylcyclopentadienyl.

12. A process for the preparation of linear alpha alkenes having 4 to 24 carbon atoms by oligomerisation or co-oligomerisation of ethene and/or an alpha ketone having 3 to 10 carbon atoms in the presence of a catalyst composition as claimed in any one of claims 1 to 11.

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II

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(21) International Application Number: PCT/EP94/01430 (22) International Filing Date: 26 April 1994 (26.04.94) (30) Priority Data: 93201229.7 28 April 1993 (28.04.93) EP <i>(34) Countries for which the regional or international application was filed:</i> GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: DOYLE, Michael, John; Badhuisweg 3, NL-1031 CM Amsterdam (NL). HEERES, Hero, Jan; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AU, BR, CA, CN, CZ, FI, JP, KR, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. 683060	
(54) Title: CATALYST COMPOSITION FOR ALKENE OLIGOMERISATION AND CO-OLIGOMERISATION			
(57) Abstract A catalyst composition comprising a first component which is a substituted bis(cyclopentadienyl)titanium, zirconium or hafnium compound, also containing a substituent which is attached to the metal and which is capable of reacting with a cation and a second component which is a compound having a bulky and labile anion which is substantially non-coordinating under the reaction conditions and a cation, wherein the substituted bis-cyclopentadienyl ligand pair is bis-tetramethylcyclopentadienyl.			

CATALYST COMPOSITION FOR ALKENE OLIGOMERISATION
AND CO-OLIGOMERISATION

This invention relates to a novel catalyst composition and to its use in the oligomerisation and co-oligomerisation of one or more alkenes, in particular alpha alkenes. More in particular, the invention relates to the oligomerisation of ethene.

5 Polymerisation processes of olefins, including alkenes, such as the production of polyethylene from ethene, whereby soluble catalyst systems of the Ziegler-Natta type are used, are well known. In particular, oligomerisation processes of lower olefins to higher olefins are also well known. For example, from GB-A-1353873
10 it is known that C_4 - C_{20} linear alpha olefins can be prepared from ethene by oligomerisation in the presence of a nickel containing catalyst. The product linear alpha olefins, in particular those having 6-10 carbon atoms, are in great demand as intermediates in the preparation of detergents, lubricant additives and polyolefins.

15 However, the oligomerisation reaction also produces less valuable products, such as internal olefins and branched olefins and olefins having a number of carbon atoms outside the range of 4-24. By further processing, these by-products can be converted to the desired linear alpha olefins.

20 EP-A-0277003 and EP-A-0277004 both disclose catalyst compositions for the polymerisation and copolymerisation of olefins, comprising a combination of a first component which is a bis(cyclopentadienyl)titanium, zirconium or hafnium compound containing a substituent which is attached to the metal and which
25 is capable of reacting with a cation, and a second component which is a compound having a bulky and labile anion which is substantially non-coordinating under the reaction conditions and a cation, capable of donating a proton. The two cyclopentadienyl groups may be substituted. The products according to these
30 documents are true polymers, having a molecular weight of above

100000 (when determined in the Examples). Consequently, no attention is paid to properties which are important to olefins having a number of carbon atoms of less than 30, such as linearity and the position of the double bond.

5 The present Applicant's EP-A-0443686 and EP-B-0526943 both disclose methods for the co-oligomerisation of ethene with at least one other alpha olefin in the presence of a catalyst composition as broadly described above, wherein one or both of the cyclopentadienyl groups may be substituted. The preferred and only
10 exemplified substituted ligand pair is bis-pentmethylcyclopentadienyl. The product oligomers still contain a substantial proportion of the less valuable branched olefins and internal olefins.

15 It has now been found that catalyst compositions as described above, wherein the ligand pair is bis-tetramethylcyclopentadienyl, are particularly useful in the oligomerisation or co-oligomerisation of ethene and other lower alkenes to higher alkenes, in that they effect a more preferential production of the linear alpha alkenes of the range having 4-24 carbon atoms and more in
20 particular 6-10 carbon atoms.

Accordingly, the present invention provides a catalyst composition comprising

- a first component which is a substituted bis(cyclopentadienyl)titanium, zirconium or hafnium compound, also
25 containing a substituent which is attached to the metal and which is capable of reacting with a cation and
- a second component which is a compound having a bulky and labile anion which is substantially non-coordinating under the reaction conditions and a cation,
30 characterized in that the substituted bis-cyclopentadienyl ligand pair is bis-tetramethylcyclopentadienyl.

The first component of the catalyst composition according to the invention is preferably a compound of the general formula $(Cp^*)_2MR_1R_2$, wherein $(Cp^*)_2$ is the bis-tetramethylcyclopentadienyl

ligand pair, M is a metal chosen from the group of titanium, zirconium or hafnium and R_1 and R_2 are identical or different and selected from unsubstituted or substituted hydrocarbyl groups, ^{alkoxy groups,} \wedge hydrogen and halogen.

5 Preferably, R_1 and R_2 are alkyl groups, typically of from 1 to 5 carbon atoms, such as methyl.

Preferred metals are zirconium or hafnium.

The most preferred first component of the catalyst composition according to the present invention is bis-tetramethylcyclopenta-
10 dienyl zirconium dimethyl.

Complexes such as the first component according to the invention can be prepared for example by the routes described in "Chemistry of Organo-Zirconium and Hafnium Compounds", by Lappert et al., 1986, published by John Wiley & Sons, Chichester, England.

15 The second component of the catalyst composition according to the invention is preferably an ionic combination of a bulky anion containing a plurality of boron atoms and a proton-donating cation, the anion being such that it is substantially non-coordinating under the reaction conditions employed. Thus, it is intended that
20 the anion should not coordinate, or at least coordinate only weakly, to the bis(cyclopentadienyl) metal entity of the first component. The boron-containing non-coordinating anion is preferably a carborate anion, suitably a carborate anion of the formula $B_{11}CH_{12}^-$. Such carborates are known and can be prepared by
25 methods such as that of Shelly et al, J. Am. Chem. Soc. 107 (1985) 5955-5959. Other bulky boron containing anions may also be used, such as a tetrakis(rfluorophenyl) boron anion. The proton-donating cation is preferably a quaternary ammonium cation such as a trialkylammonium cation, for example tri-n-butylammonium cation.

30 Alternatively a cation may be used which is not proton-donating, such as a metal cation e.g. a silver ion, or a triphenylcarbenium ion.

The catalyst composition may be formed by mixing together the two components, preferably in solution in a suitable solvent such



as toluene, chlorobenzene, an alkane or an alkene, to form a liquid catalyst system. The two components are generally employed in substantially equimolar amounts, although the molar ratio of the first component to the second component may vary within the range of from 0.1 to 5.0. Such a quantity of the catalyst system is usually employed in the
 5 reaction mixture as to contain from 10^{-1} to 10^{-7} gram atoms, in particular from 10^{-3} to 10^{-5} gram atoms, of the metal per mole of olefine to be reacted.

The catalyst composition may be formed prior to its introduction to the reaction vessel, or it may be formed in situ.

The invention also provides the use of this catalyst composition in oligomerisation
 10 or co-oligomerisation, in particular for the preparation of linear alpha alkenes having 4-24 carbon atoms by oligomerisation or co-oligomerisation of ethene and/or an alpha alkene having 3-10 carbon atoms. The oligomerisation reaction according to the invention can be carried out in batch or continuous operation.

The oligomerisation reaction is generally, although not necessarily, carried out in an
 15 inert liquid which is suitably also the solvent for the catalyst components. The reaction is suitably carried out at an elevated temperature, preferably in the range of from 20 to 175°C, more preferably at 50 to 150°C. The reaction is suitably carried out under conditions of moderately elevated pressure, preferably in the range of from 100 to 10000 kPa, more preferably from 500 to 6000 kPa. The optimum conditions of temperature and
 20 pressure used in a particular reaction system in order to maximise the yield of the desired linear alpha alkenes can be readily established by those skilled in the art, but it has been found that conditions of between 70-120°C and between 1000-3000 kPa are particularly advantageous in this respect with the catalyst systems of the present invention.

The starting reactants may be supplied to the reactor together with an inert diluent,
 25 such as nitrogen or helium when the reactant is gaseous, and a liquid solvent, e.g. the same solvent as that of the catalyst components, when the reactant is in the liquid form.



The reaction is preferably carried out in the absence of air or moisture.

Reaction times of from 1 minute to 5 hours have been found to be suitable, depending on the activity of the catalyst system and on the reaction conditions. After a suitable reaction time, a conventional catalyst deactivating agent such as water, methanol, or another alcohol, may be added if desired to the reaction mixture in order to terminate the reaction. Alternatively, the reaction can simply be terminated by the introduction of air.

The product mixed alkenes are preferentially linear alpha alkenes having a chain length within the range of 5 to 24 carbon atoms, of which those having between 6 and 10 carbon atoms in the chain are particularly preferred. They may be suitably recovered by distillation and separation techniques known in the art.

If desired, unconverted starting material and oligomeric products having a molecular weight outside the desired molecular weight may be recovered, processed if necessary and recycled to be used as starting material in a subsequent oligomerisation reaction.

The invention will be further illustrated by the following examples.

Examples 1 to 4: oligomerisation of ethene

The procedures were carried out with rigorous exclusion of oxygen and moisture.

Catalyst liquors were prepared by dissolving in toluene, as First Component, in 30 ml, 0.25 mmol of $(Cp^*)_2MR_2$, wherein M is zirconium, R_2 is dimethyl and $(Cp^*)_2$ is:
in comparative Example 1: bis-pentamethylcyclopentadienyl;
in comparative Example 2: bis-methylcyclopentadienyl;
in comparative Example 3: bis-cyclopentadienyl;
in Example 4: bis-tetramethylcyclopentadienyl;
and as Second Component, in 70 ml, in all cases 0.05 mmol of $Bu_3NHB_{11}CH_{12}$ (tri-n-butylammonium 1-carbadodecaborate).

The Second Component of the catalytic composition was first added to an autoclave of 500 ml, followed by pressurising the autoclave with ethene to 1000 kPa, and heating to 90 °C.

Subsequently, the reaction was started by adding the First Component of the catalytic composition. Pressure was maintained at 1000 kPa during the reaction by continuously recharging of consumed ethene.

5 At the end of the (predetermined) reaction time, the reaction was terminated by water injection. The product distribution was determined by gas-liquid chromatography.

10 The amount of ethene consumed during the reaction, the amounts of C_4 , C_6 - C_{10} and C_{12+} olefins produced, and the wt% distribution of alpha-, beta- and branched hexenes are given in Table 1.

TABLE 1

Example	1	2	3	4
Reaction time (min)	3	103	102	23
Ethene consumed (g)	25	25	25	25
Product C_4 olefin (g)	0.9	2.0	1.6	1.2
Product C_{6-10} olefins (g)	3.8	7.0	5.2	4.9
hexene (g)	1.1	2.3	1.7	1.4
Product C_{12+} olefins (g)	20.3	16.0	18.2	18.9
Distribution of hexenes (wt%)				
1-hexene	81.8	57.9	43.5	98.8
2-hexene	17.6	39.4	53.2	1.1
2-ethyl- 1-butene	0.7	2.7	3.3	0.1

Examples 5 to 8: co-oligomerisation of ethene with pentene

The procedure in comparative Examples 5-7 and in Example 8 was the same as that of comparative Examples 1 to 3 and Example 4, respectively, except that the First and Second Components of the catalyst composition were dissolved in 15 and 60 ml of toluene respectively and that, together with the Second Component, 210 mmol of 1-pentene (co-monomer for reacting with the ethene) was injected into the autoclave. Comparative Example 7 differed in that the amounts of toluene and 1-pentene used were 300 ml and 91 mmol, respectively.

The amount of ethene consumed during the reaction, the amounts of C_4 , C_{6+8+10} , C_{7+9+11} and C_{12+} olefins produced, and the wt% distribution of alpha-, beta- and branched hexenes and heptenes are given in Table 2.

TABLE 2

Example	5	6	7	8
Reaction time (min)	4	150	30	38
Ethene consumed (g)	25	25	34	25
Product C_4 olefin (g)	0.2	0.8	5.0	1.2
Product C_{6+8+10} olefins (g)	0.8	2.9	9.8	5.2
hexene (g)	0.2	1.0	4.3	1.6
Product C_{7+9+11} olefins (g)	4.5	2.7	1.6	2.5
heptene (g)	1.4	1.0	0.8	0.8
Product C_{12+} olefins (g)	24.5	21.6	18.0	18.3
Distribution of hexenes (wt%)				
1-hexene	89.8	60.3	36.0	98.8
2-hexene	10.2	38.9	62.4	1.1
2-ethyl-1-butene	0.0	0.8	1.6	0.1
Distribution of heptenes (wt%)				
1-heptene	86.3	57.6	36.2	97.6
2-heptene	13.4	31.6	55.7	1.1
2-ethyl-1-pentene	0.3	10.8	8.1	1.3

From these Examples it is apparent, that catalyst compositions according to the invention, when used in the oligomerisation of ethene (Example 4) and in the co-oligomerisation of ethene and pentene (Example 8), have the advantage above comparative catalyst compositions of promoting the selectivity of the reaction towards linear alpha-olefin reaction products and of suppressing the formation of branched and internal olefins.

The claims defining the invention are as follows:

1. A catalyst composition when used for alkene oligomerisation, comprising a first component which is a substituted-bis(cyclopentadienyl) titanium, zirconium or hafnium compound, also containing a substituent which is attached to the metal and which
5 is capable of reacting with a cation and a second component which is a compound having a bulky and labile anion which is substantially non-coordinating under the reaction conditions and a cation, characterized in that the substituted bis-cyclopentadienyl ligand pair is bis-tetramethylcyclopentadienyl.
2. A catalyst composition according to claim 1, characterized in that the first
10 component of the catalyst is a compound of the general formula $(Cp^*)_2MR_1R_2$, wherein $(Cp^*)_2$ is the bis-tetramethyl-cyclopentadienyl ligand pair, M is a metal chosen from the group of titanium, zirconium or hafnium and R_1 and R_2 are two identical or different groups selected from unsubstituted or substituted hydrocarbyl groups, alkyloxy groups, hydrogen or halogen.
- 15 3. A catalyst composition according to claim 2, characterized in that R_1 and R_2 are unsubstituted alkyl groups of from 1 to 5 carbon atoms.
4. A catalyst composition according to claim 3, characterized in that the first component of the catalyst is bis(tetramethylcyclopentadienyl)zirconium dimethyl.
5. A catalyst composition according to any one of claims 1 to 4, characterized in
20 that the second component of the catalyst is a ionic combination of a bulky anion containing a plurality of boron atoms which is substantially non-coordinating under the reaction conditions employed, with a cation.
6. A catalyst composition according to claim 5, characterized in that the boron-containing non-coordinating anion is a carborate anion.
- 25 7. A catalyst composition according to claim 6, characterized in that the carborate anion is of the formula $B_{11}CH_{12}^-$.
8. A catalyst composition according to any one of claims 5 to 7, characterized in that the cation is a proton-donating cation.
9. A catalyst composition according to claim 8, characterized in that the proton-
30 donating cation is a quaternary ammonium cation.
10. A catalyst according to any one of claims 5 to 7, characterized in that the cation is a silver ion.
11. A catalyst composition, substantially as hereinbefore described with reference to any one of the Examples.
- 35 12. A process for the preparation of linear alpha alkenes having 4 to 24 carbon atoms by oligomerisation or co-oligomerisation of ethene and/or an alpha ketone having 3 to 10 carbon atoms in the presence of a catalyst composition as claimed in any one of claims 1 to 11.

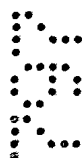
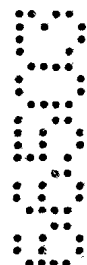


13. A linear alpha alkene produced by the process of claim 12.

Dated 28 July, 1997
Shell International B.V.

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

5



INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/EP 94/01430

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07C2/34 B01J31/22

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 5 C07C B01J C08F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 09882 (EXXON CHEMICAL PATENT) 11 July 1991 see page 10, line 6 see page 15, line 16 - line 35 see claim 1	1-5,8,9
Y	---	6,7,11
Y	EP,A,0 443 686 (SHELL) 18 September 1991 see claims 1,13	6,7,11
A	---	
	EP,A,0 447 880 (TOSOH CORPORATION) 25 September 1991 -----	

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

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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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.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Appl. No.

PCT/EP 94/01430

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9109882	11-07-91	AU-B- 643255	11-11-93
		AU-A- 7181191	24-07-91
		CA-A- 2072752	03-07-91
		EP-A- 0507876	14-10-92

EP-A-0443686	28-08-91	CN-A- 1054987	02-10-91
		JP-A- 4211616	03-08-92

EP-A-0447880	25-09-91	JP-A- 3258812	19-11-91
		US-A- 5100983	31-03-92
