



(11) **EP 2 116 521 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**06.07.2016 Bulletin 2016/27**

(21) Application number: **07831598.3**

(22) Date of filing: **06.11.2007**

(51) Int Cl.:  
**C07C 41/30** <sup>(2006.01)</sup> **C01B 31/02** <sup>(2006.01)</sup>  
**B82Y 30/00** <sup>(2011.01)</sup> **C07C 1/32** <sup>(2006.01)</sup>  
**C07F 7/08** <sup>(2006.01)</sup> **C07F 7/18** <sup>(2006.01)</sup>  
**B82Y 40/00** <sup>(2011.01)</sup>

(86) International application number:  
**PCT/JP2007/071868**

(87) International publication number:  
**WO 2008/059771 (22.05.2008 Gazette 2008/21)**

(54) **PROCESS FOR PRODUCING FULLERENE DERIVATIVE**

VERFAHREN ZUR HERSTELLUNG EINES FULLERENDERIVATS

PROCÉDÉ DE PRODUCTION D'UN DÉRIVÉ DU FULLERÈNE

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR**

(30) Priority: **14.11.2006 JP 2006308357**

(43) Date of publication of application:  
**11.11.2009 Bulletin 2009/46**

(73) Proprietor: **Japan Science and Technology Agency**  
**Kawaguchi-shi**  
**Saitama 332-0012 (JP)**

(72) Inventors:  
• **NAKAMURA, Eiichi**  
**Tokyo 113-0021 (JP)**  
• **MATSUO, Yutaka**  
**Tokyo 104-0051 (JP)**  
• **IWASHITA, Akihiko**  
**Tokyo 154-0004 (JP)**

(74) Representative: **Gillard, Richard Edward et al**  
**Elkington and Fife LLP**  
**Thavies Inn House**  
**3-4 Holborn Circus**  
**London EC1N 2HA (GB)**

(56) References cited:  
**JP-A- 07 089 972 JP-A- 11 255 509**  
**JP-A- 2003 212 880 JP-A- 2003 212 881**  
**JP-A- 2005 232 165**

- **NAGASHIMA HIDEO ET AL: "Silylmethylations of C60 with Grignard Reagents: Selective Synthesis of HC60CH2SiMe2Y and C60(CH2SiMe2Y)2 with Selection of Solvents", JOURNAL OF ORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, EASTON.; US, vol. 59, no. 6, 25 March 1994 (1994-03-25), pages 1246-1248, XP002258205, ISSN: 0022-3263, DOI: 10.1021/JO00085A007**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 2 116 521 B1**

## Description

## TECHNICAL FIELD

5 **[0001]** The present invention relates to a method for producing a fullerene derivative. Specifically, the present invention relates to a method for producing a fullerene derivative comprising the step of adding an organic group to a fullerene or fullerene derivative.

## BACKGROUND ART

10 **[0002]** Since the method for synthesizing a carbon cluster (hereinafter also referred to as "fullerene"), in which carbon atoms are arranged to form a spherical shape or a rugby ball shape, was established, fullerene has been energetically studied. As a result, many fullerene derivatives have been synthesized.

15 **[0003]** With respect to specific examples of such fullerene derivatives, methods for synthesizing a fullerene derivative, in which 5 organic groups bind to a fullerene skeleton (hereinafter also just referred to as "penta(organo)fullerene derivative"), have been reported (e.g., Japanese Laid-Open Patent Publication No. Hei 10-167994 (Patent document 1); Japanese Laid-Open Patent Publication No. Hei 11-255509 (Patent document 2); J. Am. Chem. Soc., 118, 12850 (1996) (Non-patent document 1); Org. Lett., 2, 1919 (2000) (Non-patent document 2); and Chem. Lett., 1098 (2000) (Non-patent document 3)).

20 **[0004]** As a method for producing a penta(organo)fullerene derivative, for example, it is known that, by reacting an organocopper reagent prepared using a phenyl Grignard reagent and  $\text{CuBr}\cdot\text{S}(\text{CH}_3)_2$  with fullerene  $\text{C}_{60}$ , a phenylated fullerene derivative, in which phenyl groups constituting the phenyl Grignard reagent are regioselectively added to surround one 5-membered ring of fullerene  $\text{C}_{60}$  ( $\text{C}_{60}\text{Ph}_5\text{H}$ ), can be quantitatively obtained (e.g., Japanese Laid-Open Patent Publication No. 10-167994 (Patent document 1)).

25 **[0005]** The method for producing a fullerene derivative using the phenyl Grignard reagent and the organocopper reagent is extremely effective for production of a hexa(organo)fullerene derivative, a hepta(organo)fullerene derivative, a deca(organo)fullerene derivative or the like, realizing a high yield of a product of interest. However, there is a problem that, when synthesizing a fullerene derivative in which the number of substituents added is small (e.g., a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative, and a tetra(organo)fullerene derivative) using this method, the yield thereof is low.

30 **[0006]** Nagashima et al (J. Org. Chem. 1994, 59, 1246-1248) reports the preparation of a mono(organo)fullerene derivative in THF and of a di(organo)fullerene derivative in toluene. JP2005232165 discloses a method for preparing a fullerene derivative in which a fullerene is reacted with a Grignard reagent in the presence of an organo copper reagent and of pyridine. Pyridine is used in an amount of at least 10% of the total solvent amount which brings to a fullerene with 6 or 7 substituents.

## DISCLOSURE OF THE INVENTION

35 **[0007]** Under the above-described circumstances, for example, a method for producing a fullerene derivative in which the number of substituents added is small (e.g., a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative, and a tetra(organo)fullerene derivative) in good yield is desired.

40 **[0008]** The present inventors found a method for producing a fullerene derivative comprising the step of regioselectively adding an organic group to a fullerene or fullerene derivative by reacting at least a Grignard reagent and a polar substance with the fullerene (derivative) (organic group addition step A). Moreover, the present inventors found a method for producing a fullerene derivative comprising the step of further adding an organic group by reacting at least a basic compound and a halogen compound after the organic group addition step A (organic group addition step B). The present inventors achieved the present invention based on these findings.

45 **[0009]** The present invention provides a method for producing a fullerene derivative, etc. as follows.

50 [1] A method for producing a fullerene derivative which is a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative or a tetra(organo)fullerene derivative comprising the organic group addition step A for adding an organic group by reacting at least a Grignard reagent and a polar substance with a fullerene or fullerene derivative, in which the polar substance having the donor number of 25 or more is used in an amount of 3 to 60 equivalents of the fullerene or fullerene derivative to which the organic group is added.

55 [2] The method for producing a fullerene derivative according to item [1], in which the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A is a fullerene or fullerene derivative represented by the following formula (1): wherein organic groups have been each independently added to 0 to 4

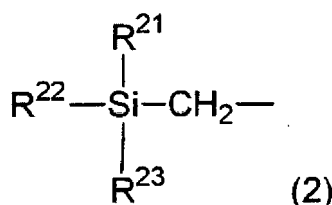
## EP 2 116 521 B1

carbons among 5 carbons positioned at A to E; and a hydrogen atom or C<sub>1</sub> - C<sub>30</sub> hydrocarbon group has been added to a carbon positioned at F, or nothing has been added thereto.

[3] The method for producing a fullerene derivative according to item [2], wherein in the organic group addition step A, the organic group is added to at least one of the carbons positioned at A to E in the fullerene or fullerene derivative represented by formula (1) to which the organic group has not been added.

[4] The method for producing a fullerene derivative according to any one of items [1] to [3], wherein the organic group for addition in the organic group addition step A is one or more substances selected from the group consisting of a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), and a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group).

[5] The method for producing a fullerene derivative according to any one of items [1] to [3], wherein the organic group for addition in the organic group addition step A is a group represented by the following formula (2):



wherein R<sup>21</sup> to R<sup>23</sup> are each independently a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group).

[6] The method for producing a fullerene derivative according to item [5], wherein R<sup>21</sup> to R<sup>23</sup> are each independently a C<sub>1</sub> - C<sub>20</sub> alkyl group.

[7] The method for producing a fullerene derivative according to any one of items [1] to [6], wherein the Grignard reagent is represented by the following formula (3):



wherein: R<sup>3</sup> represents an organic group; and X represents Cl, Br or I.

[8] The method for producing a fullerene derivative according to item [7], wherein R<sup>3</sup> in formula (3) is a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group).

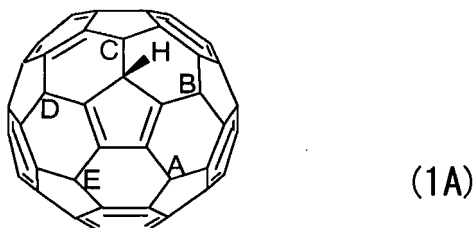
[9] The method for producing a fullerene derivative according to item [8], wherein R<sup>3</sup> is a C<sub>1</sub> - C<sub>20</sub> alkyl group.

## EP 2 116 521 B1

[10] The method for producing a fullerene derivative according to any one of items [1] to [9], wherein the Grignard reagent is used in an amount of 1 to 20 equivalents of the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A. That is, in the method in item [10], the Grignard reagent in an amount of 1 to 20 equivalents of the fullerene or fullerene derivative is put in the reaction system in which the reaction step for addition of the organic group is carried out.

[12] The method for producing a fullerene derivative according to any one of items [1] to [10], wherein the polar substance is N,N-dimethylformamide, dimethyl sulfoxide or pyridine.

[13] The method for producing a fullerene derivative according to item 3, wherein the fullerene derivative to which the organic group has been added in the organic group addition step A is a fullerene derivative represented by the following formula (1A):



wherein: organic groups have been each independently added to 1 to 5 carbons among 5 carbons positioned at A to E.

[14] The method for producing a fullerene derivative according to item [13], wherein in formula (1A), the organic groups added to the carbons positioned at A to E are each independently a hydrogen atom, a substituted or unsubstituted  $C_1 - C_{30}$  hydrocarbon group, a substituted or unsubstituted  $C_1 - C_{30}$  alkoxy group, a substituted or unsubstituted  $C_6 - C_{30}$  aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ( $-SY^1$ : in the formula,  $Y^1$  is a substituted or unsubstituted  $C_1 - C_{20}$  alkyl group), a substituted or unsubstituted arylthio group ( $-SY^2$ : in the formula,  $Y^2$  is a substituted or unsubstituted  $C_6 - C_{18}$  aryl group), a substituted or unsubstituted alkylsulfonyl group ( $-SO_2Y^3$ : in the formula,  $Y^3$  is a substituted or unsubstituted  $C_1 - C_{20}$  alkyl group), or a substituted or unsubstituted arylsulfonyl group ( $-SO_2Y^4$ : in the formula,  $Y^4$  is a substituted or unsubstituted  $C_6 - C_{18}$  aryl group).

[15] The method for producing a fullerene derivative according to any one of items [1] to [14], which comprises the organic group addition step B for further adding an organic group by reacting at least a basic compound and a halogen compound with the fullerene derivative obtained by addition of a hydrogen atom and an organic group in the organic group addition step A.

[16] The method for producing a fullerene derivative according to item [15], wherein the basic compound to be used in the organic group addition step B comprises one or more substances selected from the group consisting of a metal hydride, a metal alkoxide, an alkali metal reagent, an alkali metal and an organic alkali.

[17] The method for producing a fullerene derivative according to item [15], wherein the basic compound to be used in the organic group addition step B is alkoxide comprising K or Na.

[18] The method for producing a fullerene derivative according to item [15], wherein the basic compound to be used in the organic group addition step B is t-BuOK or t-BuONa.

[19] The method for producing a fullerene derivative according to any one of items [15] to [18], wherein the halogen compound to be used in the organic group addition step B is represented by the following formula (4):



wherein:  $R^4$  represents an organic group; and X represents a halogen atom.

[20] The method for producing a fullerene derivative according to item [19], wherein in formula (4):  $R^4$  is a hydrogen atom, a substituted or unsubstituted  $C_1 - C_{30}$  hydrocarbon group, a substituted or unsubstituted  $C_1 - C_{30}$  alkoxy

group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group); and X is Cl, Br or I.

**[0010]** As used herein, "fullerene" is a general term for carbon clusters which are formed by arranging carbon atoms in a spherical shape or a rugby ball shape (see Gendai-Kagaku, June 2000, page 46; and Chemical Reviews, 98, 2527 (1998)). Examples thereof include fullerene C<sub>60</sub> (so-called buckminsterfullerene), fullerene C<sub>70</sub>, fullerene C<sub>76</sub>, fullerene C<sub>78</sub>, fullerene C<sub>82</sub>, fullerene C<sub>84</sub>, fullerene C<sub>90</sub>, fullerene C<sub>94</sub>, and fullerene C<sub>96</sub>.

**[0011]** When the method for producing a fullerene derivative according to the preferred embodiment of the present invention is used, a fullerene derivative in which the number of groups added is small (e.g., a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative, and a tetra(organo)fullerene derivative) can be produced in good yield.

**[0012]** When the method for producing a fullerene derivative according to the preferred embodiment of the present invention is used, specific organic groups can be added to the fullerene or fullerene derivative in a stepwise manner, and moreover, the aforementioned organic groups can be regioselectively added thereto.

**[0013]** Furthermore, when the method for producing a fullerene derivative according to the preferred embodiment of the present invention is used, a fullerene derivative in which specific organic groups are added to specific positions of the fullerene derivative can be selectively produced.

## BEST MODE FOR CARRYING OUT THE INVENTION

### I. Organic group addition step A of the present invention

**[0014]** The organic group addition step A of the present invention is a step of adding an organic group by reacting at least a Grignard reagent and a polar substance with a fullerene or fullerene derivative.

#### 1. Fullerene or fullerene derivative to which organic group is added in the organic group addition step A

##### 1.1. Fullerene to which organic group is added in the organic group addition step A

**[0015]** A fullerene to which the organic group is added in the organic group addition step A of the present invention is not particularly limited, and examples thereof include fullerene C<sub>60</sub> (so-called buckminsterfullerene), fullerene C<sub>70</sub>, fullerene C<sub>76</sub>, fullerene C<sub>78</sub>, fullerene C<sub>82</sub>, fullerene C<sub>84</sub>, fullerene C<sub>90</sub>, fullerene C<sub>94</sub>, and fullerene C<sub>96</sub>. Among them, a fullerene in which nothing has been added to the carbons at the positions A to F in the above-described formula (1) is particularly preferred.

**[0016]** There is no specific limitation on the method for producing a fullerene, and a fullerene produced according to a publicly-known method can be used as a starting material for the production method of the present invention. One type of fullerene or a mixture of two or more types of fullerenes can be suitably used.

##### 1.2. Fullerene derivative to which organic group is added in the organic group addition step A

**[0017]** A fullerene derivative to which the organic group is added in the organic group addition step A of the present invention is a fullerene derivative in which the organic group has been added to a fullerene. Further, a fullerene, which is the basic skeleton of the fullerene derivative, is the same as the fullerene as the starting material in the production method of the present invention.

**[0018]** The fullerene derivative to which the organic group is added in the organic group addition step A is preferably a mono(organo)fullerene derivative in which one organic group has been added or a di(organo)fullerene derivative in which two organic groups have been added, but is not limited thereto.

**[0019]** As the fullerene derivative to which the organic group is added in the organic group addition step A, a fullerene derivative in which a hydrogen atom or organic group has been added to one or more carbons among those positioned at A to F in the above-described formula (1) is preferred.

**[0020]** Regarding the fullerene derivative to which the organic group is added in the organic group addition step A of the present invention, the organic group to be added to the fullerene skeleton is not particularly limited, and examples thereof include a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>20</sub> aryloxy group, a substituted or unsubstituted amino group,

a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), and a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group).

**[0021]** In the present specification, the hydrocarbon group of the "C<sub>1</sub> - C<sub>30</sub> hydrocarbon group" may be a saturated or unsaturated acyclic group or a saturated or unsaturated cyclic group. When the C<sub>1</sub> - C<sub>30</sub> hydrocarbon group is acyclic, it may be linear or branched. The "C<sub>1</sub> - C<sub>30</sub> hydrocarbon group" includes C<sub>i</sub> - C<sub>30</sub> alkyl group, C<sub>2</sub> - C<sub>30</sub> alkenyl group, C<sub>2</sub> - C<sub>30</sub> alkynyl group, C<sub>4</sub> - C<sub>30</sub> alkyldienyl group, C<sub>6</sub> - C<sub>28</sub> aryl group, C<sub>7</sub> - C<sub>30</sub> alkylaryl group, C<sub>7</sub> - C<sub>30</sub> arylalkyl group, C<sub>4</sub> - C<sub>30</sub> cycloalkyl group, C<sub>4</sub> - C<sub>30</sub> cycloalkenyl group, and (C<sub>3</sub> - C<sub>15</sub> cycloalkyl) C<sub>1</sub> - C<sub>15</sub> alkyl group.

**[0022]** In the present specification, the "C<sub>1</sub> - C<sub>30</sub> alkyl group" is preferably C<sub>1</sub> - C<sub>20</sub> alkyl group, and more preferably C<sub>1</sub> - C<sub>10</sub> alkyl group. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, and dodecanyl.

**[0023]** In the present specification, the "C<sub>2</sub> - C<sub>30</sub> alkenyl group" is preferably C<sub>2</sub> - C<sub>20</sub> alkenyl group, and more preferably C<sub>2</sub> - C<sub>10</sub> alkenyl group. Examples of alkenyl groups include, but are not limited to, vinyl, allyl, propenyl, isopropenyl, 2-methyl-1-propenyl, 2-methylallyl, and 2-butenyl.

**[0024]** In the present specification, the "C<sub>2</sub> - C<sub>30</sub> alkynyl group" is preferably C<sub>2</sub> - C<sub>20</sub> alkynyl group, and more preferably C<sub>2</sub> - C<sub>10</sub> alkynyl group. Examples of alkynyl groups include, but are not limited to, ethynyl, propynyl, and butynyl.

**[0025]** In the present specification, the "C<sub>4</sub> - C<sub>30</sub> alkyldienyl group" is preferably C<sub>4</sub> - C<sub>20</sub> alkyldienyl group, and more preferably C<sub>4</sub> - C<sub>10</sub> alkyldienyl group. Examples of alkyldienyl groups include, but are not limited to, 1,3-butadienyl.

**[0026]** In the present specification, the "C<sub>6</sub> - C<sub>28</sub> aryl group" is preferably C<sub>6</sub> - C<sub>10</sub> aryl group. Examples of aryl groups include, but are not limited to, phenyl, 1-naphthyl, 2-naphthyl, indenyl, biphenyl, anthryl, and phenanthryl.

**[0027]** In the present specification, the "C<sub>7</sub> - C<sub>30</sub> alkylaryl group" is preferably C<sub>7</sub> - C<sub>12</sub> alkylaryl group. Examples of alkylaryl groups include, but are not limited to, o-tolyl, m-tolyl, p-tolyl, 2,3-xylyl, 2,4-xylyl, 2,5-xylyl, o-cumenyl, m-cumenyl, p-cumenyl, and mesityl.

**[0028]** In the present specification, the "C<sub>7</sub> - C<sub>30</sub> arylalkyl group" is preferably C<sub>7</sub> - C<sub>12</sub> arylalkyl group. Examples of arylalkyl groups include, but are not limited to, benzyl, phenethyl, diphenylmethyl, triphenylmethyl, 1-naphthylmethyl, 2-naphthylmethyl, 2,2-diphenylethyl, 3-phenylpropyl, 4-phenylbutyl, and 5-phenylpentyl.

**[0029]** In the present specification, the "C<sub>4</sub> - C<sub>30</sub> cycloalkyl group" is preferably C<sub>4</sub> - C<sub>10</sub> cycloalkyl group. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

**[0030]** In the present specification, the "C<sub>4</sub> - C<sub>30</sub> cycloalkenyl group" is preferably C<sub>4</sub> - C<sub>10</sub> cycloalkenyl group. Examples of cycloalkenyl groups include, but are not limited to, cyclopropenyl, cyclobutenyl, cyclopentenyl, and cyclohexenyl.

**[0031]** In the present specification, the "C<sub>1</sub> - C<sub>30</sub> alkoxy group" is preferably C<sub>1</sub> - C<sub>10</sub> alkoxy group, and more preferably C<sub>1</sub> - C<sub>6</sub> alkoxy group. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy, butoxy, and pentyloxy.

**[0032]** In the present specification, the "C<sub>6</sub> - C<sub>30</sub> aryloxy group" is preferably C<sub>6</sub> - C<sub>10</sub> aryloxy group. Examples of aryloxy groups include, but are not limited to, phenoxy, naphthoxy, and biphenyloxy.

**[0033]** In the present specification, in "alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group)" and "alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group)", Y<sup>1</sup> and Y<sup>3</sup> are preferably C<sub>1</sub> - C<sub>10</sub> alkyl group, and more preferably C<sub>1</sub> - C<sub>6</sub> alkyl group. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, and dodecanyl.

**[0034]** In the present specification, in "arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group)" and "arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group)", Y<sup>2</sup> and Y<sup>4</sup> are preferably C<sub>6</sub> - C<sub>10</sub> aryl group. Examples of aryl groups include, but are not limited to, phenyl, 1-naphthyl, 2-naphthyl, indenyl, biphenyl, anthryl, and phenanthryl.

**[0035]** "C<sub>1</sub> - C<sub>30</sub> hydrocarbon group," "C<sub>1</sub> - C<sub>30</sub> alkoxy group," "C<sub>6</sub> - C<sub>30</sub> aryloxy group," "amino group," "silyl group," "alkylthio group," "arylthio group," "alkylsulfonyl group," and "arylsulfonyl group" may be substituted. Examples of substituents in these cases include ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group. In these cases, one or more substituents (up to the maximum possible number) may be introduced into replaceable positions, and preferably, 1 to 4 substituents may be introduced. When the number of substituents is 2 or more, the substituents may be the same or different.

**[0036]** In the present specification, examples of "substituted or unsubstituted amino group" include, but are not limited to, amino, dimethylamino, methylamino, methylphenylamino, and phenylamino.

**[0037]** In the present specification, examples of "substituted or unsubstituted silyl group" include, but are not limited to, dimethylsilyl, diethylsilyl, trimethylsilyl, triethylsilyl, trimethoxysilyl, triethoxysilyl, diphenylmethylsilyl, triphenylsilyl, triphenoxysilyl, dimethylmethoxysilyl, dimethylphenoxysilyl, and methylmethoxyphenyl.

**[0038]** In the present specification, examples of "aromatic group" include phenyl group, biphenyl group, and terphenyl

group.

**[0039]** In the present specification, examples of "heterocyclic group" include thienyl group, pyrrolyl group, pyridyl group, bipyridyl group, oxazolyl group, oxadiazolyl group, thiazolyl group, thiadiazolyl group, and terthienyl group.

**[0040]** In the present specification, examples of "condensed polycyclic aromatic group" include fluorenyl group, naphthyl group, fluoranthenyl group, anthryl group, phenanthryl group, pyrenyl group, tetracenyl group, pentacenyl group, triphenylenyl group, and perirenyl group.

**[0041]** In the present specification, examples of "condensed polycyclic heterocyclic group" include carbazolyl group, acridinyl group and phenanthrolyl group.

**[0042]** Further, examples of substituents which can be had by these "aromatic group," "heterocyclic group," "condensed polycyclic aromatic group" and "condensed polycyclic heterocyclic group" include, but are not limited to, C<sub>1</sub> - C<sub>10</sub> hydrocarbon group (e.g., methyl, ethyl, propyl, butyl, phenyl, naphthyl, indenyl, tolyl, xylyl and benzyl), C<sub>1</sub> - C<sub>10</sub> alkoxy group (e.g., methoxy, ethoxy, propoxy and butoxy), C<sub>6</sub> - C<sub>10</sub> aryloxy group (e.g., phenoxy, naphthyloxy and biphenyloxy), amino group, hydroxyl group, halogen atom (e.g., fluorine, chlorine, bromine and iodine) and silyl group. In these cases, one or more substituents may be introduced into replaceable positions, and preferably, 1 to 4 substituents are introduced. When the number of substituents is 2 or more, the substituents may be the same or different.

## 2. Grignard reagent used in the organic group addition step A

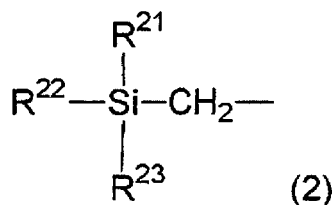
**[0043]** The Grignard reagent used in the organic group addition step A in the production method of the present invention is represented by the above-described formula (3).

**[0044]** In formula (3), R<sup>3</sup> is not particularly limited as long as it is an organic group having an inactive substituent by which the Grignard reagent can be adjusted.

**[0045]** In formula (3), R<sup>3</sup> is preferably a C<sub>1</sub> - C<sub>20</sub> alkyl group, an allyl group, a benzyl group, a 4-methoxybenzyl group, a phenyl group, a *p*-methoxyphenyl group, a carbazolylphenyl group, a biphenyl group, a 1-naphthyl group, a pyrenyl group, a di(alkyloxy)benzoyloxyphenyl group or the like.

**[0046]** Further, in formula (3), R<sup>3</sup> is preferably a naphthalene tetracarboxylic diimide derivative-containing group, an anthraquinone derivative-containing group, a tetrathiafulvalene derivative-containing group, a polythiophene derivative-containing group or the like.

**[0047]** In formula (3), R<sup>3</sup> is preferably a group represented by the following formula (2):



wherein R<sup>21</sup> to R<sup>23</sup> are each independently a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group). Among them, R<sup>3</sup> is preferably a trimethylsilylmethyl group, an (alkyl)dimethylsilylmethyl group (e.g., a (hexyl)dimethylsilylmethyl group, and a (dodeca)dimethylsilylmethyl group), a (isopropoxy)dimethylsilylmethyl group, a (phenyl)dimethylsilylmethyl group, a (4-methoxyphenyl)dimethylsilylmethyl group, a (4-biphenyl)dimethylsilylmethyl group, a (1-naphthyl)dimethylsilylmethyl group, a (pyrenoxyphenyl)dimethylsilylmethyl group, an ((alkyloxy)benzoyloxyphenyl)dimethylsilylmethyl group, a (di(alkyloxy)benzoyloxyphenyl)dimethylsilylmethyl group, a (terpyridinyl)dimethylsilylmethyl group, a (carbazolylphenyl)dimethylsilylmethyl group, or a (pyrenylphenyl)dimethylsilylmethyl group.

**[0048]** In the organic group addition step A, the Grignard reagent is used, preferably in an amount of 1 to 20 equivalents, and more preferably in an amount of 1 to 10 equivalents, of the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A.

**[0049]** According to the preferred embodiment of the present invention, R<sup>3</sup> in the above-described formula (3) is to be added to the fullerene or fullerene derivative as the starting material.

## 3. Polar substance used in the organic group addition step A

[0050] The polar substance used in the organic group addition step A in the production method of the present invention is not particularly limited as long as it has polar properties and the donor number (DN) of the polar substance is 25 or more.

[0051] As the polar substance used in the production method of the present invention, an aprotic solvent is preferred, and it is more preferred to use N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine or the like. Among them, N,N-dimethylformamide is particularly preferably used since the yield of a fullerene derivative obtained becomes higher.

[0052] In the organic group addition step A, the polar substance is used in an amount of 3 to 60 equivalents, more preferably in an amount of 5 to 60 equivalents, and particularly preferably in an amount of 10 to 50 equivalents, of the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A, since the yield of a fullerene derivative obtained becomes higher.

## 4. Production of fullerene derivative using the organic group addition step A

[0053] With the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A, at least the Grignard reagent and the polar substance are reacted to add the organic group, thereby producing a fullerene derivative.

[0054] The reaction in the organic group addition step A is preferably performed using a solvent. As the solvent, for example, toluene, tetrahydrofuran, dichlorobenzene, a mixed solvent thereof or the like is used. Among them, dichlorobenzene is preferably used as the solvent.

[0055] In order to accelerate the reaction in the organic group addition step A, various additives may be used depending on various purposes. Types of catalysts and additives are not particularly limited, and may be suitably selected depending on the type of the starting material or a fullerene derivative to be produced (type of group to be added).

[0056] The reaction system for reacting the Grignard reagent and the polar substance with the fullerene or fullerene derivative may be any reaction system, and any of a closed-type system, open-type system and gas-flow-type system may be employed. Further, the reaction method is not particularly limited, and may be appropriately selected in view of types, amounts, etc. of fullerene, fullerene derivative, Grignard reagent and polar substance to be used.

[0057] The addition order of the fullerene or fullerene derivative, the Grignard reagent and the polar substance to a reaction tank and the method for the addition thereof may be optionally selected. However, it is preferred that the polar substance is added to a solvent in which the fullerene or fullerene derivative has been dissolved, and thereafter adding the Grignard reagent thereto.

[0058] The reaction temperature is generally in the range of -70 to 70°C, and preferably in the range of -50 to 50°C. There is a tendency that, when the reaction temperature is too low, the reaction rate is insufficient, and when the reaction temperature is too high, a side reaction preferentially occurs. The reaction pressure is not particularly limited, and may be ordinary pressure or high pressure. However, ordinary pressure is preferred. The reaction time may be suitably selected depending on the types of the fullerene and organometallic compound to be used, the type of the solvent, the type of the oxidant, the reaction method, etc. In general, the reaction is performed for 2 minutes to 2 hours, and preferably for 5 minutes to 1 hour.

[0059] The termination of the reaction is performed, for example, by adding aqueous ammonium chloride solution or the like to the reaction system.

[0060] In the organic group addition step A of the present invention, by reacting the Grignard reagent and the polar substance with the fullerene or fullerene derivative, an adduct of fullerene (e.g., a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative, and a tetra(organo)fullerene derivative) can be selectively produced.

[0061] The fullerene derivative produced by the reaction is not required to be purified if the selective production rate thereof is high. However, there is a case where the fullerene derivative is obtained as a crude product in which by-products such as the raw material fullerene, a slight amount of hydroalkylated body and oxide are mixed therewith. Therefore, it is preferred that a fullerene derivative to which a predetermined organic group has been added is isolated/purified from the crude product. Examples of techniques for isolating/purifying a fullerene derivative produced include a technique utilizing chromatography such as HPLC and column chromatography, and a technique of solvent extraction using an organic solvent or the like.

[0062] When a fullerene derivative to which an organic group has been added is used as the fullerene derivative to which the organic group is added in the organic group addition step A, according to the preferred embodiment of the organic group addition step A of the present invention, the organic group to be added can be added to a specific position. Specifically, when a fullerene derivative represented by the above-described formula (1) in which an organic group has been added to 1 to 4 carbons among 5 carbons positioned at A to E is used as the starting material, an organic group is newly added to carbons positioned at A to E, to which no organic group has been added, in the organic group addition



step A of the present invention.

#### 5. Fullerene derivative produced by the organic group addition step A

5 **[0063]** The fullerene derivative produced in the organic group addition step A is not particularly limited as long as the organic group is added to carbons constituting a fullerene. However, according to the preferred embodiment of the present invention, a fullerene derivative represented by the above-described formula (1A) is produced.

10 **[0064]** In the fullerene derivative represented by the above-described formula (1A) produced in the organic group addition step A, it is preferred that organic groups, which are added to 1 to 5 carbons among 5 carbons positioned at A to E, are each independently a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group). Among them, a C<sub>1</sub> - C<sub>20</sub> alkyl group, an allyl group, a benzyl group, a 4-methoxybenzyl group, a phenyl group, a *p*-methoxyphenyl group, a carbazolyphenyl group, a biphenyl group, a 1-naphthyl group, a pyrenyl group, or a di(alkyloxy)benzoyloxyphenyl group is preferred.

20 **[0065]** In the fullerene derivative represented by the above-described formula (1A) produced in the organic group addition step A, it is preferred that organic groups, which are added to 1 to 5 carbons among 5 carbons positioned at A to E, are each independently a naphthalene tetracarboxylic diimide derivative-containing group, an anthraquinone derivative-containing group, a tetrathiafulvalene derivative-containing group, or a polythiophene derivative-containing group.

25 **[0066]** Further, in the fullerene derivative represented by the above-described formula (1A) produced in the organic group addition step A, it is preferred that organic groups, which are added to 1 to 5 carbons among 5 carbons positioned at A to E, are each independently a group represented by the following formula (2):



wherein R<sup>21</sup> to R<sup>23</sup> are each independently a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group). Among them, a trimethylsilylmethyl group, an (alkyl)dimethylsilylmethyl group (e.g., a (hexyl)dimethylsilylmethyl group, and a (dodeca)dimethylsilylmethyl group), a (isopropoxy)dimethylsilylmethyl group, a (phenyl)dimethylsilyl group, a (4-methoxyphenyl)dimethylsilylmethyl group, a (4-biphenyl)dimethylsilylmethyl group, a (1-naphthyl)dimethylsilylmethyl group, a (pyrenoxyphenyl)dimethylsilylmethyl group, an ((alkyloxy)benzoyloxyphenyl)dimethylsilylmethyl group, a (di(alkyloxy)benzoyloxyphenyl)dimethylsilylmethyl group, a (terpyridinyl)dimethylsilylmethyl group, a (carbazolyphenyl)dimethylsilylmethyl group, or a (pyrenylphenyl)dimethylsilylmethyl group is preferred.

#### 50 II. Organic group addition step B

**[0067]** The organic group addition step B of the present invention is a step of reacting at least a basic compound and a halogen compound with a fullerene derivative to which a hydrogen atom has been added to dehydrogenate the fullerene derivative and to add an organic group to the fullerene derivative.

55

## 1. Fullerene derivative to which organic group is added in the organic group addition step B

**[0068]** The fullerene derivative to which the organic group is added in the organic group addition step B is a fullerene derivative to which a hydrogen atom and an organic group have been added in the organic group addition step A.

## 2. Basic compound used in the organic group addition step B

**[0069]** The basic compound to be used in the organic group addition step B in the production method of the present invention is not particularly limited as long as it is a compound having basicity.

**[0070]** As the basic compound to be used in the organic group addition step B, a metal hydride (e.g., KH, NaH, CaH<sub>2</sub>), a metal alkoxide (t-BuOK (potassium t-butoxide), t-BuONa (sodium t-butoxide)), an alkali metal reagent (e.g., BuLi), an alkali metal (e.g., K, Na, Li) or an organic alkali (e.g., tetrabutylammonium hydroxide) is preferably used. Among them, a metal alkoxide including Na or K is preferred, and t-BuOK or t-BuONa is particularly preferred.

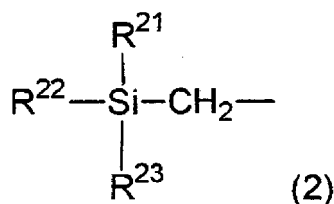
**[0071]** In the organic group addition step B, the basic compound is used preferably in an amount of 1 to 3 equivalents, and more preferably in an amount of 1 to 2 equivalents of the fullerene derivative to which the organic group is added in the organic group addition step B, since the yield of a fullerene derivative obtained becomes higher.

## 3. Halogen compound used in the organic group addition step B

**[0072]** The halogen compound to be used in the organic group addition step B in the production method of the present invention is preferably a compound represented by the above-described formula (4). In formula (4), R<sup>4</sup> is preferably a C<sub>1</sub> - C<sub>30</sub> alkyl group, an allyl group, a benzyl group, a 4-methoxybenzyl group, a phenyl group, a *p*-methoxyphenyl group, a carbazolylphenyl group, a biphenyl group, a 1-naphthyl group, a pyrenyl group, or a di(alkyloxy)benzoyloxyphenyl group.

**[0073]** Further, in formula (4), R<sup>4</sup> is preferably a naphthalene tetracarboxylic diimide derivative-containing group, an anthraquinone derivative-containing group, a tetrathiafulvalene derivative-containing group, a polythiophene derivative-containing group or the like.

**[0074]** In formula (4), R<sup>4</sup> is preferably a group represented by the following formula (2):



wherein R<sup>21</sup> to R<sup>23</sup> are each independently a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group

(-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group). Among them, R<sup>4</sup> is preferably a trimethylsilylmethyl group, an (alkyl)dimethylsilylmethyl group (e.g., a (hexyl)dimethylsilylmethyl group, and a (dodeca)dimethylsilylmethyl group), a (isopropoxy)dimethylsilylmethyl group, a (phenyl)dimethylsilylmethyl group, a (4-methoxyphenyl)dimethylsilylmethyl group, a (4-biphenyl)dimethylsilylmethyl group, a (1-naphthyl)dimethylsilylmethyl group, a (pyrenoxyphenyl)dimethylsilylmethyl group, an ((alkyloxy)benzoyloxyphenyl)dimethylsilylmethyl group, a (di(alkyloxy)benzoyloxyphenyl)dimethylsilylmethyl group, a (terpyridinyl)dimethylsilylmethyl group, a (carbazolylphenyl)dimethylsilylmethyl group, a (pyrenylphenyl)dimethylsilylmethyl group or the like.

**[0075]** According to the preferred embodiment of the present invention, R<sup>4</sup> in the above-described formula (4) is to be added to the fullerene derivative to which the organic group is added in the organic group addition step B.

**[0076]** In the organic group addition step B, the halogen compound is used preferably in an amount of 5 to 100 equivalents, and more preferably in an amount of 10 to 50 equivalents of the fullerene derivative to which the organic group is added in the organic group addition step B, since the yield of a fullerene derivative obtained becomes higher.

## 4. Production of fullerene derivative using the organic group addition step B

**[0077]** With a fullerene derivative to which a hydrogen atom has been added (starting material), at least the basic

compound and the halogen compound are reacted, thereby adding an organic group to the fullerene derivative (organic group addition step B).

[0078] The reaction in the organic group addition step B is preferably performed under inert gas atmosphere using a solvent. As the solvent, a solvent which can dissolve the fullerene derivative as the starting material is preferred, and examples thereof include benzonitrile.

[0079] In order to accelerate the reaction in the organic group addition step B, various additives may be used depending on various purposes. Types of catalysts and additives are not particularly limited, and may be suitably selected depending on the type of the starting material or a fullerene derivative to be produced (type of group to be added).

[0080] The reaction system for reacting the basic compound and the halogen compound with the fullerene or fullerene derivative may be any reaction system, and any of a closed-type system, open-type system and gas-flow-type system may be employed. Further, the reaction method is not particularly limited, and may be appropriately selected in view of types, amounts, etc. of fullerene derivative, basic compound and halogen compound to be used.

[0081] The addition order of the fullerene derivative (starting material), basic compound and halogen compound to a reaction tank and the method for the addition thereof may be optionally selected. However, it is preferred that the basic compound is added to a solvent in which the fullerene derivative has been dissolved, and thereafter adding the halogen compound thereto. According to the preferred embodiment of the organic group addition step B of the present invention, the basic compound is added dropwise to the solvent in which the fullerene derivative has been dissolved and the mixture is stirred for 5 to 20 minutes, and after that, the halogen compound is added thereto to cause a reaction in the temperature range of generally 20 to 180°C, and preferably 50 to 150°C, for 2 to 12 hours, and preferably 4 to 10 hours. The reaction pressure is not particularly limited, and may be near ordinary pressure or high pressure. However, near ordinary pressure is preferred.

[0082] In the organic group addition step B of the present invention, by reacting the Grignard reagent and the polar substance with the fullerene or fullerene derivative, a multiple adduct of fullerene (e.g., a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative, and a tetra(organo)fullerene derivative) can be selectively produced.

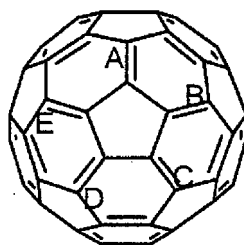
[0083] Further, it is preferred that a fullerene derivative produced is isolated/purified, and the technique thereof is the same as that in the organic group addition step A.

[0084] According to the preferred embodiment of the organic group addition step B of the present invention, the organic group to be added can be added to a specific position. Specifically, when a fullerene derivative represented by the above-described formula (1A) is used as the starting material, according to the organic group addition step B of the present invention, an organic group is newly added to carbons positioned at A to E, to which no organic group has been added. That is, a new organic group is added to 5 carbon atoms located around carbon atoms constituting a pentagon shape including those to which a hydrogen atom has been added.

[0085] The fullerene derivative produced by the reaction is not required to be purified if the selective production rate thereof is high. However, purification thereof may be carried out using a technique utilizing chromatography such as HPLC and column chromatography, a technique of solvent extraction using an organic solvent or the like, etc.

#### 5. Fullerene derivative produced in the organic group addition step B

[0086] The fullerene derivative produced in the organic group addition step B is not particularly limited as long as the organic group has been added to carbon(s) constituting the fullerene, but according to the preferred embodiment of the present invention, a fullerene derivative represented by the following formula (1B) is produced:



(1B)

[0087] Regarding the fullerene derivative represented by the above-described formula (1B) produced in the organic group addition step B, examples of organic groups added to 1 to 5 carbons among 5 carbons positioned at A to E are the same as the examples of the organic groups added to the carbons positioned at A to E in formula (1A).

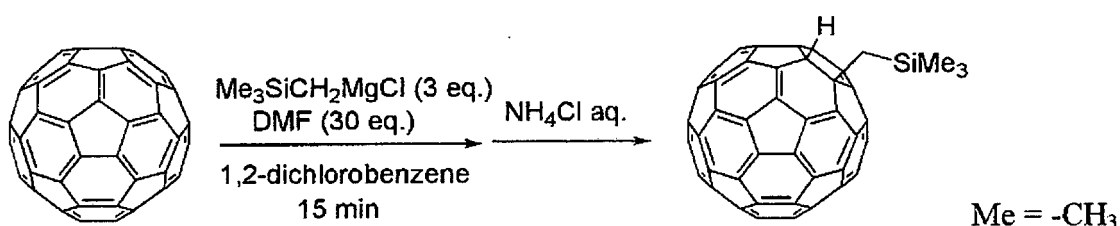
## EXAMPLES

[0088] Hereinafter, the present invention will be specifically described by way of examples, but the present invention is not limited thereby.

[Example 1] Production of  $C_{60}(CH_2Si(CH_3)_3)H$

[0089]

Scheme 1



[0090] As indicated in Scheme 1 above, fullerene  $C_{60}$  (400 mg, 0.555 mmol) was dissolved in *o*-dichlorobenzene (100 mL) under nitrogen atmosphere at room temperature, and *N,N*-dimethylformamide (DMF) was added thereto in an amount of 30 equivalents of the fullerene (1.29 mL, 16.7 mmol).  $Me_3SiCH_2MgCl$  in tetrahydrofuran (THF) solution was added dropwise to the obtained purple solution using a syringe in an amount of 3 equivalents of the fullerene (2.81 mL, 0.592 M, 1.67 mmol). The mixture was stirred for 10 minutes, and to the obtained brown-black solution, saturated ammonium chloride solution (0.2 mL) was added to terminate the reaction. The obtained reaction mixture was passed through a short-pass silica gel column using toluene as a developing solvent to remove by-products such as magnesium salt, and after that, purification was carried out by high-performance liquid chromatography (HPLC) (column: Buckyprep manufactured by Nakalai Tesque, 20 mm x 250 mm, eluting solution: toluene/2-propanol = 7/3). Fractions of  $C_{60}(CH_2Si(CH_3)_3)H$  were collected and concentrated, and thereafter methanol was added thereto to precipitate fullerene derivative  $C_{60}(CH_2Si(CH_3)_3)H$ . By filtration and drying,  $C_{60}(CH_2Si(CH_3)_3)H$  was obtained (isolated yield: 93%).

[0091] Regarding the obtained fullerene derivative  $C_{60}(CH_2Si(CH_3)_3)H$ , the measurement of APCI-HRMS utilizing  $^1H$  NMR,  $^{13}C$  NMR and TOF method was carried out. Results are shown below:

$^1H$  NMR (400 MHz,  $CDCl_3/CS_2$ ):  $\delta$  0.604 (s, 9H, SiMe), 2.96 (s, 2H,  $CH_2$ ), 6.46 (s, 1H,  $C_{60}H$ );  
 $^{13}C$  NMR (100 MHz,  $CDCl_3/CS_2$ ):  $\delta$  0.819 (3C, Si $CH_3$ ), 38.96 (1C,  $CH_2$ ), 61.72 (1C,  $C_{60}H$ ), 62.28 (1C,  $C_{60}CH_2$ ), 134.76 (2C,  $C_{60}$ ), 136.57 (2C,  $C_{60}$ ), 140.07 (2C,  $C_{60}$ ), 140.30 (2C,  $C_{60}$ ), 141.61 (2C,  $C_{60}$ ), 141.62 (2C,  $C_{60}$ ), 141.92 (2C,  $C_{60}$ ), 141.99 (2C,  $C_{60}$ ), 142.01 (2C,  $C_{60}$ ), 142.07 (2C,  $C_{60}$ ), 142.51 (2C,  $C_{60}$ ), 142.52 (2C,  $C_{60}$ ), 143.25 (2C,  $C_{60}$ ), 144.63 (2C,  $C_{60}$ ), 144.67 (2C,  $C_{60}$ ), 145.25 (2C,  $C_{60}$ ), 145.31 (2C,  $C_{60}$ ), 145.36 (2C,  $C_{60}$ ), 145.41 (2C,  $C_{60}$ ), 145.59 (2C,  $C_{60}$ ), 145.81 (2C,  $C_{60}$ ), 146.14 (2C,  $C_{60}$ ), 146.17 (2C,  $C_{60}$ ), 146.24 (2C,  $C_{60}$ ), 146.36 (2C,  $C_{60}$ ), 149.90 (2C,  $C_{60}$ ), 147.30 (1C,  $C_{60}$ ), 147.42 (1C,  $C_{60}$ ), 153.99 (2C,  $C_{60}$ ), 158.07 (2C,  $C_{60}$ );  
 APCI-HRMS (-): calcd for  $C_{64}H_{11}Si$  (M-H $^+$ ), 807.06300; found, 807.05929.

[Examples 2 to 3 Comparative Example 1]

[0092]  $C_{60}(CH_2Si(CH_3)_3)H$  was synthesized under the same conditions as those of Example 1, except that DMF was used in an amount of 3 equivalents of the fullerene as the starting material (Example 2).

[0093]  $C_{60}(CH_2Si(CH_3)_3)H$  was synthesized under the same conditions as those of Example 1, except that DMF was used in an amount of 10 equivalents of the fullerene as the starting material (Example 3).

[0094]  $C_{60}(CH_2Si(CH_3)_3)H$  was synthesized under the same conditions as those of Example 1, except that no DMF was used (Comparative Example 1).

[0095] In Examples 1 to 3 and Comparative Example 1, as the standard sample,  $C_{60}(Ph)_5H$  (4.98 mM/*o*-dichlorobenzene solution) was used. Analysis was carried out utilizing high-performance liquid chromatography: HPLC (column: Buckyprep manufactured by Nakalai Tesque, eluting solution: toluene/2-propanol = 7/3), and yields of  $C_{60}$  and  $C_{60}(CH_2Si(CH_3)_3)H$  were measured. Results are shown below:

Table 1

	DMF equivalent	Yield of product (HPLC)	Collection rate of fullerene (HPLC)
Comparative Example 1	0 eq.	10 %	63 %
Example 2	3 eq.	47 %	49 %
Example 3	10 eq.	82 %	17 %
Example 1	30 eq.	91 %	7 %

**[0096]** Next, the relationship between the donor number (DN) of the polar substance and the ratio of adduct added to fullerene C<sub>60</sub> (yield of product) was examined. Specifically, in addition to the aforementioned test example in which DMF was used as the polar substance, a test example using dimethyl sulfoxide (DMSO), a test example using pyridine, and a test example using ethanol were carried out. In these 4 test examples, C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)H was synthesized from C<sub>60</sub>, and analysis thereof was carried out using HPLC as in the case described above, thereby examining the yield of product and the collection rate of fullerene. The method for synthesizing C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)H was the same as that in the aforementioned step. Results are shown in Table 2.

Table 2

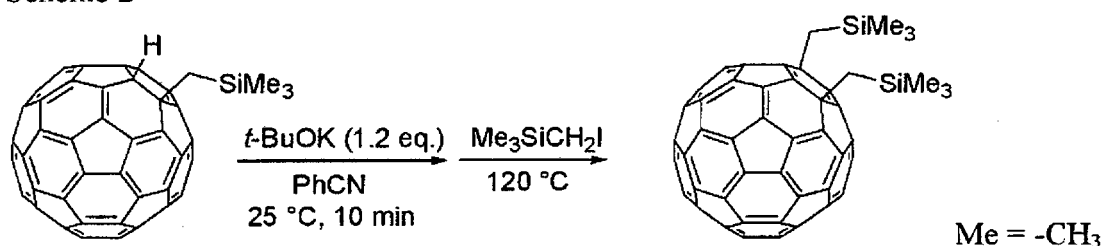
Polar substance used	Donor number	Additive amount (equivalent)	Yield of product (HPLC)	Collection rate of fullerene (HPLC)
DMF	26.6	30 eq.	91%	7%
DMSO	29.8	30 eq.	83%	14%
Pyridine	33.1	30 eq.	40%	47%
Ethanol	20.0	30 eq.	2%	88%

**[0097]** Based on the results, it was found that there is a tendency that the yield of a product becomes higher when a polar substance which is aprotic and has a higher donor number is used in the organic group addition step A.

[Example 5] Production of C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>

**[0098]**

Scheme 2



**[0099]** The fullerene derivative C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)H (300 mg, 0.371 mmol) produced in Example 1 was dissolved in benzonitrile (60 mL) and potassium t-butoxide (t-BuOK) in THF solution (0.445 mL, 0.445 mmol) was added dropwise thereto, and the mixture was stirred for 10 minutes. To the obtained brown-black solution, Me<sub>3</sub>SiCH<sub>2</sub>I (1.10 mL, 7.42 mmol) was added, and the mixture was heated to 120°C and stirred for 8 hours. After the solvent was distilled away under reduced pressure, purification was carried out using silica gel column chromatography (eluting solution: carbon disulfide/hexane = 1/2). Fractions of fullerene derivative C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> were collected and concentrated, and thereafter methanol was added thereto to precipitate C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>. By filtration and drying, C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> was obtained (isolated yield: 93%).

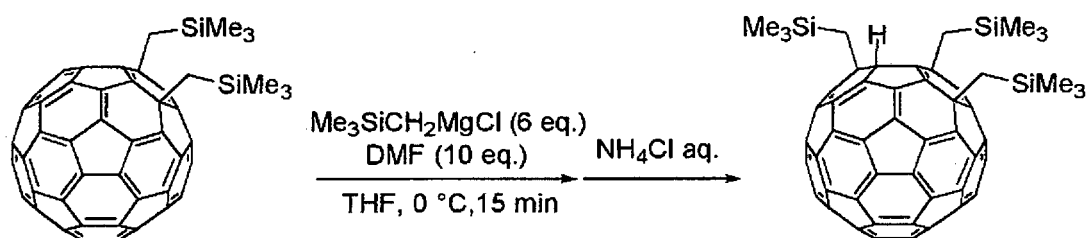
**[0100]** Regarding the obtained fullerene derivative C<sub>60</sub>(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, the measurement of APCI-HRMS utilizing <sup>1</sup>H NMR, <sup>13</sup>C NMR and TOF method was carried out. Results are shown below:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.40 (s, 18H, SiMe), 2.47 (d, 2H,  $^2J = 15$  Hz,  $\text{CH}_2$ ), 2.61 (d, 2H,  $^2J = 15$  Hz,  $\text{CH}_2$ );  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.704 (6C, SiMe), 33.94 (2C,  $\text{CH}_2$ ), 56.28 (2C,  $\text{CCH}_2$ ), 138.42 (2C,  $\text{C}_{60}$ ), 138.79 (2C,  $\text{C}_{60}$ ), 140.85 (1C,  $\text{C}_{60}$ ), 141.91 (2C,  $\text{C}_{60}$ ), 141.95 (1C,  $\text{C}_{60}$ ), 142.63 (2C,  $\text{C}_{60}$ ), 142.68 (1C,  $\text{C}_{60}$ ), 142.70 (2C,  $\text{C}_{60}$ ), 142.92 (2C,  $\text{C}_{60}$ ), 143.12 (2C,  $\text{C}_{60}$ ), 143.28 (2C,  $\text{C}_{60}$ ), 143.58 (2C,  $\text{C}_{60}$ ), 143.79 (2C,  $\text{C}_{60}$ ), 144.12 (2C,  $\text{C}_{60}$ ), 144.25 (2C,  $\text{C}_{60}$ ), 144.28 (2C,  $\text{C}_{60}$ ), 144.50 (2C,  $\text{C}_{60}$ ), 144.58 (1C,  $\text{C}_{60}$ ), 144.74 (2C,  $\text{C}_{60}$ ), 145.01 (2C,  $\text{C}_{60}$ ), 145.10 (2C,  $\text{C}_{60}$ ), 145.45 (2C,  $\text{C}_{60}$ ), 146.83 (2C,  $\text{C}_{60}$ ), 146.98 (2C,  $\text{C}_{60}$ ), 147.13 (2C,  $\text{C}_{60}$ ), 147.45 (2C,  $\text{C}_{60}$ ), 147.54 (2C,  $\text{C}_{60}$ ), 148.03 (2C,  $\text{C}_{60}$ ), 148.59 (2C,  $\text{C}_{60}$ ), 153.80 (2C,  $\text{C}_{60}$ ), 158.06 (2C,  $\text{C}_{60}$ );  
 APCI-HRMS (-): calcd for  $\text{C}_{68}\text{H}_{22}\text{Si}_2$  ( $\text{M}-\text{H}^+$ ), 894.12600; found, 894.12492.

[Example 6] Production of  $\text{C}_{60}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_3\text{H}$

[0101]

Scheme 3



[0102] As indicated in Scheme 3 above,  $\text{C}_{60}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_2$  (100 mg, 0.112 mmol) produced in Example 5 was dissolved in THF (100 mL) under nitrogen atmosphere at  $0^\circ\text{C}$ , and DMF (86.7  $\mu\text{L}$ , 1.12 mmol) was added thereto. To the obtained brownish solution,  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  in THF solution (1.13 mL, 0.592 M, 0.670 mmol) was slowly added dropwise using a syringe. After stirring for 15 minutes, to the obtained brown-black solution, saturated ammonium chloride solution (0.1 mL) was added to terminate the reaction. The obtained reaction mixture was passed through a short-pass silica gel column using toluene as a developing solvent to remove by-products such as magnesium salt. After the solvent was distilled away under reduced pressure, purification was carried out by silica gel column chromatography (eluting solution: carbon disulfide/hexane = 1/1). Fractions of the title compound were collected and concentrated, and thereafter methanol was added thereto to precipitate the product of interest. By filtration and drying, the title compound was obtained (isolated yield: 64%).

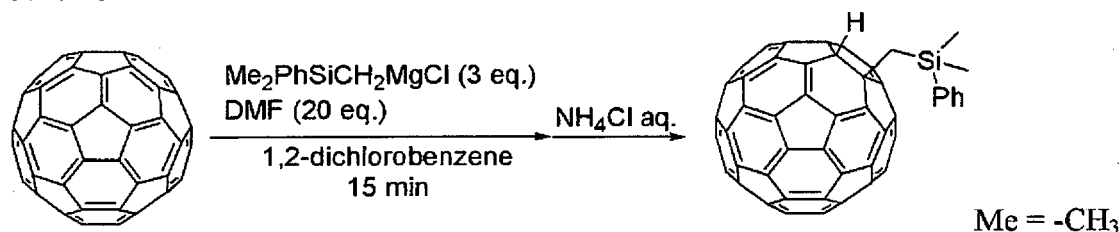
[0103] Regarding the obtained fullerene derivative  $\text{C}_{60}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_3\text{H}$ , the measurement of APCI-HRMS utilizing  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and TOF method was carried out. Results are shown below:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.222 (s, 9H, SiMe<sub>3</sub>), 0.285 (s, 9H, SiMe<sub>3</sub>), 0.288 (s, 9H, SiMe<sub>3</sub>), 2.05 (d, 1H,  $^2J = 14.2$  Hz,  $\text{CH}_2$ ), 2.23 (d,  $^2J = 14.6$  Hz, 1H,  $\text{CH}_2$ ), 2.29 (d,  $^2J = 14.2$  Hz, 1H,  $\text{CH}_2$ ), 2.28 (d,  $^2J = 14.6$  Hz, 1H,  $\text{CH}_2$ ), 2.37 (d,  $^2J = 14.6$  Hz, 1H,  $\text{CH}_2$ ), 2.40 (d,  $^2J = 14.6$  Hz, 1H,  $\text{CH}_2$ ), 5.29 (s, 1H,  $\text{C}_{60}\text{H}$ );  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.492 (3C, SiMe<sub>3</sub>), 0.540 (3C, SiMe<sub>3</sub>), 0.788 (3C, SiMe<sub>3</sub>), 31.92 (1C,  $\text{CH}_2$ ), 32.53 (1C,  $\text{CH}_2$ ), 37.97 (1C,  $\text{CH}_2$ ), 52.86 (1C,  $\text{C}_{60}$ ), 54.91 (1C,  $\text{C}_{60}$ ), 56.79 (1C,  $\text{C}_{60}$ ), 61.88 (1C,  $\text{C}_{60}$ ), 133.81 (1C,  $\text{C}_{60}$ ), 134.80 (1C,  $\text{C}_{60}$ ), 136.56 (1C,  $\text{C}_{60}$ ), 137.84 (1C,  $\text{C}_{60}$ ), 140.31 (1C,  $\text{C}_{60}$ ), 140.66 (1C,  $\text{C}_{60}$ ), 141.35 (1C,  $\text{C}_{60}$ ), 141.78 (1C,  $\text{C}_{60}$ ), 142.50 (1C,  $\text{C}_{60}$ ), 142.59 (1C,  $\text{C}_{60}$ ), 142.71 (1C,  $\text{C}_{60}$ ), 142.87 (1C,  $\text{C}_{60}$ ), 143.32 (1C,  $\text{C}_{60}$ ), 143.66 (1C,  $\text{C}_{60}$ ), 143.75 (1C,  $\text{C}_{60}$ ), 143.91 (1C,  $\text{C}_{60}$ ), 144.35 (1C,  $\text{C}_{60}$ ), 144.37 (1C,  $\text{C}_{60}$ ), 144.45 (1C,  $\text{C}_{60}$ ), 144.50 (1C,  $\text{C}_{60}$ ), 144.54 (1C,  $\text{C}_{60}$ ), 144.69 (1C,  $\text{C}_{60}$ ), 144.76 (1C,  $\text{C}_{60}$ ), 144.78 (1C,  $\text{C}_{60}$ ), 145.06 (1C,  $\text{C}_{60}$ ), 145.23 (1C,  $\text{C}_{60}$ ), 145.26 (1C,  $\text{C}_{60}$ ), 145.37 (1C,  $\text{C}_{60}$ ), 145.60 (1C,  $\text{C}_{60}$ ), 145.75 (1C,  $\text{C}_{60}$ ), 145.77 (1C,  $\text{C}_{60}$ ), 146.41 (1C,  $\text{C}_{60}$ ), 146.48 (1C,  $\text{C}_{60}$ ), 146.52 (1C,  $\text{C}_{60}$ ), 146.55 (1C,  $\text{C}_{60}$ ), 146.69 (1C+1C,  $\text{C}_{60}$ ), 146.79 (1C,  $\text{C}_{60}$ ), 146.87 (1C,  $\text{C}_{60}$ ), 147.40 (1C,  $\text{C}_{60}$ ), 147.41 (1C,  $\text{C}_{60}$ ), 147.62 (1C,  $\text{C}_{60}$ ), 147.63 (1C,  $\text{C}_{60}$ ), 147.78 (1C,  $\text{C}_{60}$ ), 148.65 (1C,  $\text{C}_{60}$ ), 149.01 (1C,  $\text{C}_{60}$ ), 149.18 (1C,  $\text{C}_{60}$ ), 149.45 (1C,  $\text{C}_{60}$ ), 150.03 (1C,  $\text{C}_{60}$ ), 152.35 (1C,  $\text{C}_{60}$ ), 155.03 (1C,  $\text{C}_{60}$ ), 156.27 (1C,  $\text{C}_{60}$ ), 157.00 (1C,  $\text{C}_{60}$ ), 158.41 (1C,  $\text{C}_{60}$ ), 159.94 (1C,  $\text{C}_{60}$ ), 162.94 (1C,  $\text{C}_{60}$ );  
 APCI-HRMS (-): calcd for  $\text{C}_{72}\text{H}_{33}\text{Si}_3$  ( $\text{M}-\text{H}^+$ ), 981.18900; found, 981.18524.

[Example 7] Production of  $\text{C}_{60}(\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)\text{H}$

[0104]

Scheme 4



[0105] As indicated in Scheme 4, the fullerene derivative C<sub>60</sub>(Si(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>)H was synthesized in a manner similar to that in Example 1 except that Me<sub>2</sub>PhSiCH<sub>2</sub>MgCl (3.04 mL, 0.550 M, 1.67 mmol) was used in an amount of 3 equivalents of the fullerene instead of Me<sub>3</sub>SiCH<sub>2</sub>MgCl and N,N-dimethylformamide (DMF) was used in an amount of 20 equivalents of the fullerene (415 mg, isolated yield: 86%).

15 [0106] Regarding the fullerene derivative, the measurement of APCI-HRMS utilizing <sup>1</sup>H NMR, <sup>13</sup>C NMR and TOF method was carried out. Results are shown below:

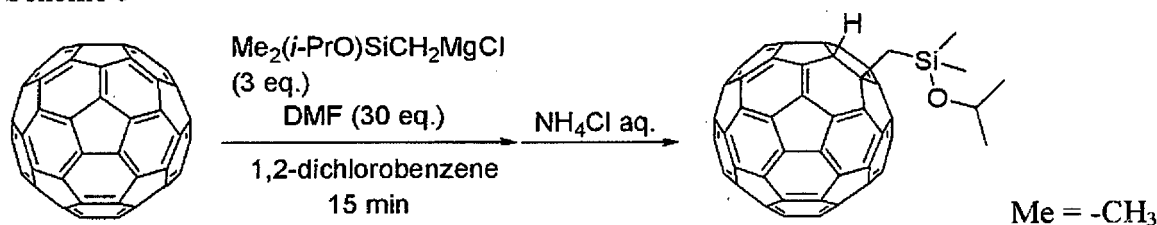
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.892 (s, 6H, SiMe), 3.16 (s, 2H, CH<sub>2</sub>), 6.39 (s, 1H, C<sub>60</sub>H), 7.44-7.46 (m, 3H, Ph), 7.88-7.90 (m, 2H, Ph);

20 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ -0.752 (2C, SiCH<sub>3</sub>), 38.03 (1C, CH<sub>2</sub>), 61.57 (1C, C<sub>60</sub>H), 62.23 (1C, C<sub>60</sub>CH<sub>2</sub>), 128.19 (2C, Ph), 129.68 (1C, Ph), 134.16 (2C, Ph), 134.89 (2C, C<sub>60</sub>), 136.57 (2C, C<sub>60</sub>), 138.22 (1C, Ph), 140.05 (2C, C<sub>60</sub>), 140.20 (2C, C<sub>60</sub>), 141.63 (2C, C<sub>60</sub>), 141.64 (2C, C<sub>60</sub>), 141.94 (2C, C<sub>60</sub>), 141.97 (2C, C<sub>60</sub>), 142.03 (2C, C<sub>60</sub>), 142.06 (2C, C<sub>60</sub>), 142.54 (2C+2C, C<sub>60</sub>), 143.27 (2C, C<sub>60</sub>), 144.66 (2C, C<sub>60</sub>), 144.71 (2C, C<sub>60</sub>), 145.28 (2C, C<sub>60</sub>), 145.36 (2C, C<sub>60</sub>), 145.39 (2C+2C, C<sub>60</sub>), 145.64 (2C, C<sub>60</sub>), 145.88 (2C, C<sub>60</sub>), 146.18 (2C, C<sub>60</sub>), 146.22 (2C, C<sub>60</sub>), 146.30 (2C, C<sub>60</sub>), 146.41 (2C, C<sub>60</sub>), 149.92 (2C, C<sub>60</sub>), 147.35 (1C, C<sub>60</sub>), 147.49 (1C, C<sub>60</sub>), 154.05 (2C, C<sub>60</sub>), 157.86 (2C, C<sub>60</sub>); APCI-HRMS (-): calcd for C<sub>60</sub>H<sub>13</sub>Si (M-H<sup>+</sup>), 869.07865; found, 869.07425.

[Example 8] Production of C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>(*i*-PrO))H

30 [0107]

Scheme 5



[0108] As indicated in Scheme 5, the fullerene derivative C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>(*i*-PrO))H was synthesized in a manner similar to that in Example 1 except that Me<sub>2</sub>(*i*-PrO)SiCH<sub>2</sub>MgCl (2.69 mL, 0.620 M, 1.67 mmol) was used in an amount of 3 equivalents of the fullerene instead of Me<sub>3</sub>SiCH<sub>2</sub>MgCl. The obtained fullerene derivative was purified using silica gel column chromatography (eluting solution: carbon disulfide/hexane = 5/3) (422mg, isolated yield: 89%).

45 [0109] Regarding the obtained fullerene derivative C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>(*i*-PrO))H, the measurement of APCI-HRMS utilizing <sup>1</sup>H NMR, <sup>13</sup>C NMR and TOF method was carried out. Results are shown below:

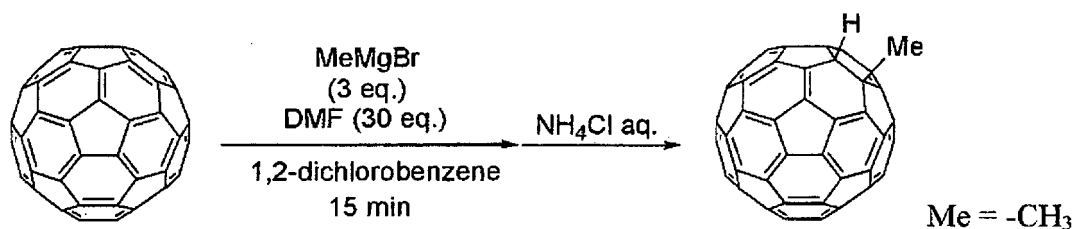
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.664 (s, 6H, CH<sub>2</sub>SiCH<sub>3</sub>), 1.36 (d, *J* = 6.10 Hz, 6H, CHCH<sub>3</sub>), 2.95 (s, 2H, CH<sub>2</sub>), 4.38 (m, *J* = 6.10, 1H, CHCH<sub>3</sub>), 6.82 (s, 1H, C<sub>60</sub>H);

50 <sup>13</sup>C NMR (125 MHz, THF-*d*<sub>8</sub>): δ 1.023 (2C, SiMe<sub>2</sub>), 26.38 (2C, CHCH<sub>3</sub>), 38.49 (1C, CH<sub>2</sub>), 62.36 (1C, C<sub>60</sub>H), 63.04 (1C, CCH<sub>2</sub>), 66.72 (1C, CHCH<sub>3</sub>), 136.10 (2C, C<sub>60</sub>), 137.55 (2C, C<sub>60</sub>), 140.88 (2C, C<sub>60</sub>), 141.03 (2C, C<sub>60</sub>), 142.45 (2C, C<sub>60</sub>), 142.48 (2C, C<sub>60</sub>), 142.83 (2C, C<sub>60</sub>), 142.91 (2C, C<sub>60</sub>), 142.99 (2C, C<sub>60</sub>), 143.14 (2C, C<sub>60</sub>), 143.38 (2C+2C, C<sub>60</sub>), 144.14 (2C, C<sub>60</sub>), 145.58 (2C, C<sub>60</sub>), 145.67 (2C, C<sub>60</sub>), 146.12 (2C, C<sub>60</sub>), 146.17 (2C, C<sub>60</sub>), 146.22 (2C, C<sub>60</sub>), 146.23 (2C, C<sub>60</sub>), 146.90 (2C, C<sub>60</sub>), 147.03 (2C+2C, C<sub>60</sub>), 147.04 (2C, C<sub>60</sub>), 147.07 (1C, C<sub>60</sub>), 147.16 (2C, C<sub>60</sub>), 147.24 (2C, C<sub>60</sub>), 148.20 (2C, C<sub>60</sub>), 148.39 (1C, C<sub>60</sub>), 156.49 (2C, C<sub>60</sub>), 159.93 (2C, C<sub>60</sub>); APCI-HRMS (-): calcd for C<sub>66</sub>H<sub>15</sub>O<sub>2</sub>Si (M-H<sup>+</sup>), 851.08922; found, 851.08765.

[Example 9] Production of  $C_{60}(CH_3)H$ 

[0110]

Scheme 6



[0111]  $C_{60}(CH_3)H$  was synthesized in a manner similar to that in Example 1 except that: 40.0 mg of  $C_{60}$ , 10 mL of 1,2-dichlorobenzene and 0.129 mL of DMF were used; and MeMgBr (0.167 mL, 1.0 M, 0.167 mmol) was used instead of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (18.7 mg, isolated yield: 46%).

[0112] Regarding the obtained  $C_{60}(CH_3)H$ , the measurement of APCI-HRMS utilizing  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and TOF method was carried out. Results are shown below:

$^1\text{H}$ NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ ):  $\delta$  3.26 (s, 3H,  $\text{CH}_3$ ), 6.40 (s, 1H,  $\text{C}_{60}\text{H}$ );

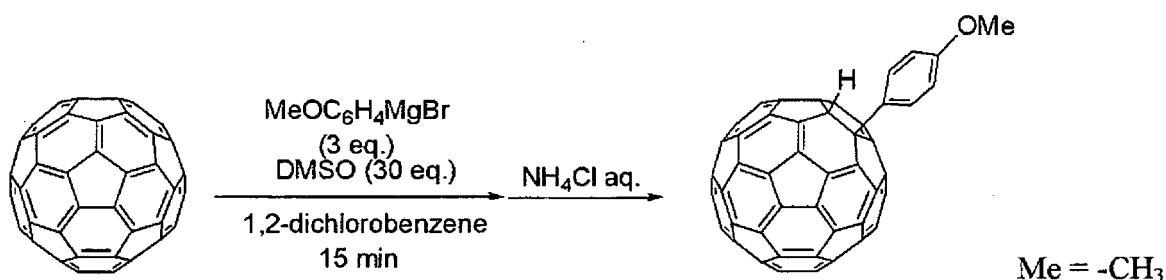
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ ):  $\delta$  35.05 (1C,  $\text{CH}_3$ ), 60.12 (1C,  $\text{C}_{60}\text{CH}_3$ ), 61.30 (1C,  $\text{C}_{60}\text{H}$ ), 135.20 (2C,  $\text{C}_{60}$ ), 136.33 (2C,  $\text{C}_{60}$ ), 140.07 (2C,  $\text{C}_{60}$ ), 140.32 (2C,  $\text{C}_{60}$ ), 141.55 (2C,  $\text{C}_{60}$ ), 141.56 (2C,  $\text{C}_{60}$ ), 141.85 (2C,  $\text{C}_{60}$ ), 141.90 (2C,  $\text{C}_{60}$ ), 141.92 (2C,  $\text{C}_{60}$ ), 142.06 (2C,  $\text{C}_{60}$ ), 142.44 (2C+2C,  $\text{C}_{60}$ ), 143.14 (2C,  $\text{C}_{60}$ ), 144.51 (2C,  $\text{C}_{60}$ ), 144.57 (2C,  $\text{C}_{60}$ ), 145.26 (2C,  $\text{C}_{60}$ ), 145.27 (2C,  $\text{C}_{60}$ ), 145.33 (2C,  $\text{C}_{60}$ ), 145.39 (2C,  $\text{C}_{60}$ ), 145.71 (2C,  $\text{C}_{60}$ ), 145.77 (2C,  $\text{C}_{60}$ ), 146.06 (2C,  $\text{C}_{60}$ ), 146.11 (2C,  $\text{C}_{60}$ ), 146.22 (2C,  $\text{C}_{60}$ ), 146.29 (2C,  $\text{C}_{60}$ ), 146.82 (2C,  $\text{C}_{60}$ ), 147.20 (1C,  $\text{C}_{60}$ ), 147.32 (1C,  $\text{C}_{60}$ ), 153.46 (2C,  $\text{C}_{60}$ ), 156.84 (2C,  $\text{C}_{60}$ );

APCI-HRMS (-): calcd for  $\text{C}_{61}\text{H}_3$  ( $\text{M}-\text{H}^+$ ), 735.02348; found, 735.02325.

[Example 10] Production of  $C_{60}(\text{C}_6\text{H}_4\text{OCH}_3)H$ 

[0113]

Scheme 7



[0114] Synthesis was carried out in a manner similar to that in Example 1 except that: 40.0 mg of  $C_{60}$  and 10 mL of 1,2-dichlorobenzene were used;  $\text{MeOC}_6\text{H}_4\text{MgBr}$  (0.211 mL, 0.790 M, 0.167 mmol) was used instead of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ ; and dimethyl sulfoxide (DMSO) (118  $\mu\text{L}$ , 1.67 mmol) was used instead of DMF. Purification was carried out using silica gel column chromatography (eluting solution: carbon disulfide/hexane = 2/1) to obtain  $C_{60}(\text{C}_6\text{H}_4\text{OCH}_3)H$  (24.5 mg, isolated yield: 53%)

[0115] Regarding the obtained fullerene derivative  $C_{60}(\text{C}_6\text{H}_4\text{OCH}_3)H$ , the measurement of APCI-HRMS utilizing  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and TOF method was carried out. Results are shown below:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{CS}_2$ ):  $\delta$  3.97 (s, 3H,  $\text{CH}_3$ ), 6.71 (s, 1H,  $\text{C}_{60}\text{H}$ ), 7.26 (m, 2H,  $\text{C}_6\text{H}_4$ ), 8.34 (m, 2H,  $\text{C}_6\text{H}_4$ );  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3/\text{CS}_2$ ):  $\delta$  55.21 (1C,  $\text{CH}_3$ ), 63.77 (1C,  $\text{C}_{60}\text{H}$ ), 67.21 (1C,  $\text{C}_{60}\text{O}$ ), 115.13 (2C,  $\text{C}_6\text{H}_4$ ), 128.62 (2C,  $\text{C}_6\text{H}_4$ ), 135.59 (2C,  $\text{C}_{60}$ ), 136.21 (2C,  $\text{C}_{60}$ ), 140.13 (2C,  $\text{C}_{60}$ ), 140.20 (2C,  $\text{C}_{60}$ ), 140.40 (1C,  $\text{C}_6\text{H}_4$ ), 141.48 (2C,



## EP 2 116 521 B1

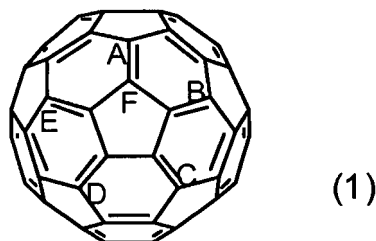
C<sub>60</sub>), 141.55 (2C, C<sub>60</sub>), 141.86 (2C, C<sub>60</sub>), 141.92 (2C, C<sub>60</sub>), 141.94 (2C, C<sub>60</sub>), 142.21 (2C, C<sub>60</sub>), 142.46 (2C, C<sub>60</sub>), 142.47 (2C, C<sub>60</sub>), 143.17 (2C, C<sub>60</sub>), 144.46 (2C, C<sub>60</sub>), 144.55 (2C, C<sub>60</sub>), 145.28 (2C, C<sub>60</sub>), 145.31 (2C, C<sub>60</sub>), 145.39 (2C, C<sub>60</sub>), 145.42 (2C, C<sub>60</sub>), 145.71 (2C, C<sub>60</sub>), 145.82 (2C, C<sub>60</sub>), 146.08 (2C, C<sub>60</sub>), 146.10 (2C, C<sub>60</sub>), 146.25 (2C, C<sub>60</sub>), 146.30 (2C, C<sub>60</sub>), 146.75 (2C, C<sub>60</sub>), 147.17 (1C, C<sub>60</sub>), 147.40 (1C, C<sub>60</sub>), 152.53 (2C, C<sub>60</sub>), 154.02 (2C, C<sub>60</sub>), 159.20 (1C, C<sub>6</sub>H<sub>4</sub>);  
APCI-HRMS (-): calcd for C<sub>67</sub>H<sub>7</sub>O (M-H<sup>+</sup>), 827.05096; found, 827.04969.

### INDUSTRIAL APPLICABILITY

**[0116]** The present invention can be utilized, for example, for an electron-conductive material, a semiconductor material, an optical functional material.

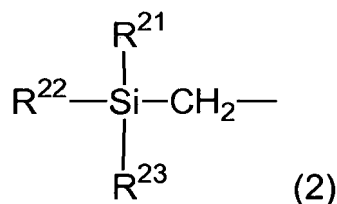
### Claims

1. A method for producing a fullerene derivative which is a mono(organo)fullerene derivative, a di(organo)fullerene derivative, a tri(organo)fullerene derivative or a tetra(organo)fullerene derivative comprising the organic group addition step A for adding an organic group by reacting at least a Grignard reagent and a polar substance with a fullerene or fullerene derivative, in which the polar substance having the donor number of 25 or more is used in an amount of 3 to 60 equivalents of the fullerene or fullerene derivative to which the organic group is added.
2. The method for producing a fullerene derivative according to claim 1, in which the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A is a fullerene or fullerene derivative represented by the following formula (1):



wherein: organic groups have been each independently added to 0 to 4 carbons among 5 carbons positioned at A to E; and a hydrogen atom or C<sub>1</sub> - C<sub>30</sub> hydrocarbon group has been added to a carbon positioned at F, or nothing has been added thereto.

3. The method for producing a fullerene derivative according to claim 2, wherein in the organic group addition step A, the organic group is added to at least one of the carbons positioned at A to E in the fullerene or fullerene derivative represented by formula (1) to which the organic group has not been added.
4. The method for producing a fullerene derivative according to any one of claims 1 to 3, wherein the organic group for addition in the organic group addition step A is one or more substances selected from the group consisting of a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), and a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group).
5. The method for producing a fullerene derivative according to any one of claims 1 to 3, wherein the organic group for addition in the organic group addition step A is a group represented by the following formula (2):



wherein  $\text{R}^{21}$  to  $\text{R}^{23}$  are each independently a hydrogen atom, a substituted or unsubstituted  $\text{C}_1 - \text{C}_{30}$  hydrocarbon group, a substituted or unsubstituted  $\text{C}_1 - \text{C}_{30}$  alkoxy group, a substituted or unsubstituted  $\text{C}_6 - \text{C}_{30}$  aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ( $-\text{SY}^1$ : in the formula,  $\text{Y}^1$  is a substituted or unsubstituted  $\text{C}_1 - \text{C}_{20}$  alkyl group), a substituted or unsubstituted arylthio group ( $-\text{SY}^2$ : in the formula,  $\text{Y}^2$  is a substituted or unsubstituted  $\text{C}_6 - \text{C}_{18}$  aryl group), a substituted or unsubstituted alkylsulfonyl group ( $-\text{SO}_2\text{Y}^3$ : in the formula,  $\text{Y}^3$  is a substituted or unsubstituted  $\text{C}_1 - \text{C}_{20}$  alkyl group), or a substituted or unsubstituted arylsulfonyl group ( $-\text{SO}_2\text{Y}^4$ : in the formula,  $\text{Y}^4$  is a substituted or unsubstituted  $\text{C}_6 - \text{C}_{18}$  aryl group).

6. The method for producing a fullerene derivative according to claim 5, wherein  $\text{R}^{21}$  to  $\text{R}^{23}$  are each independently a  $\text{C}_1 - \text{C}_{20}$  alkyl group.

7. The method for producing a fullerene derivative according to any one of claims 1 to 6, wherein the Grignard reagent is represented by the following formula (3):



wherein:  $\text{R}^3$  represents an organic group; and X represents Cl, Br or I.

8. The method for producing a fullerene derivative according to claim 7, wherein  $\text{R}^3$  in formula (3) is a substituted or unsubstituted  $\text{C}_1 - \text{C}_{30}$  hydrocarbon group, a substituted or unsubstituted  $\text{C}_1 - \text{C}_{30}$  alkoxy group, a substituted or unsubstituted  $\text{C}_6 - \text{C}_{30}$  aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ( $-\text{SY}^1$ : in the formula,  $\text{Y}^1$  is a substituted or unsubstituted  $\text{C}_1 - \text{C}_{20}$  alkyl group), a substituted or unsubstituted arylthio group ( $-\text{SY}^2$ : in the formula,  $\text{Y}^2$  is a substituted or unsubstituted  $\text{C}_6 - \text{C}_{18}$  aryl group), a substituted or unsubstituted alkylsulfonyl group ( $-\text{SO}_2\text{Y}^3$ : in the formula,  $\text{Y}^3$  is a substituted or unsubstituted  $\text{C}_1 - \text{C}_{20}$  alkyl group), or a substituted or unsubstituted arylsulfonyl group ( $-\text{SO}_2\text{Y}^4$ : in the formula,  $\text{Y}^4$  is a substituted or unsubstituted  $\text{C}_6 - \text{C}_{18}$  aryl group).

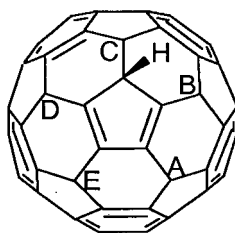
9. The method for producing a fullerene derivative according to claim 8, wherein  $\text{R}^3$  is a  $\text{C}_1 - \text{C}_{20}$  alkyl group.

10. The method for producing a fullerene derivative according to any one of claims 1 to 9, wherein the Grignard reagent is used in an amount of 1 to 20 equivalents of the fullerene or fullerene derivative to which the organic group is added in the organic group addition step A.

11. The method for producing a fullerene derivative according to any one of claims 1 to 10, wherein the donor number of the polar substance is 26.6 to 33.1 at an additive amount of 30 equivalents.

12. The method for producing a fullerene derivative according to any one of claims 1 to 10, wherein the polar substance is N,N-dimethylformamide, dimethyl sulfoxide or pyridine.

13. The method for producing a fullerene derivative according to claim 3, wherein the fullerene derivative to which the organic group has been added in the organic group addition step A is a fullerene derivative represented by the following formula (1A):



(1A)

wherein: organic groups have been each independently added to 1 to 5 carbons among 5 carbons positioned at A to E.

14. The method for producing a fullerene derivative according to claim 13, wherein in formula (1A), the organic groups added to the carbons positioned at A to E are each independently a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group).
15. The method for producing a fullerene derivative according to any one of claims 1 to 14, which comprises the organic group addition step B for further adding an organic group by reacting at least a basic compound and a halogen compound with the fullerene derivative obtained by addition of a hydrogen atom and an organic group in the organic group addition step A.
16. The method for producing a fullerene derivative according to claim 15, wherein the basic compound to be used in the organic group addition step B comprises one or more substances selected from the group consisting of a metal hydride, a metal alkoxide, an alkali metal reagent, an alkali metal and an organic alkali.
17. The method for producing a fullerene derivative according to claim 15, wherein the basic compound to be used in the organic group addition step B is alkoxide comprising K or Na.
18. The method for producing a fullerene derivative according to claim 15, wherein the basic compound to be used in the organic group addition step B is t-BuOK or t-BuONa.
19. The method for producing a fullerene derivative according to any one of claims 15 to 18, wherein the halogen compound to be used in the organic group addition step B is represented by the following formula (4):



wherein: R<sup>4</sup> represents an organic group; and X represents a halogen atom.

20. The method for producing a fullerene derivative according to claim 19, wherein in formula (4): R<sup>4</sup> is a hydrogen atom, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> hydrocarbon group, a substituted or unsubstituted C<sub>1</sub> - C<sub>30</sub> alkoxy group, a substituted or unsubstituted C<sub>6</sub> - C<sub>30</sub> aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (-SY<sup>1</sup>: in the formula, Y<sup>1</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), a substituted or unsubstituted arylthio group (-SY<sup>2</sup>: in the formula, Y<sup>2</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group), a substituted or unsubstituted alkylsulfonyl group (-SO<sub>2</sub>Y<sup>3</sup>: in the formula, Y<sup>3</sup> is a substituted or unsubstituted C<sub>1</sub> - C<sub>20</sub> alkyl group), or a substituted or unsubstituted arylsulfonyl group (-SO<sub>2</sub>Y<sup>4</sup>: in the formula, Y<sup>4</sup> is a substituted or unsubstituted C<sub>6</sub> - C<sub>18</sub> aryl group); and X is Cl, Br or I.

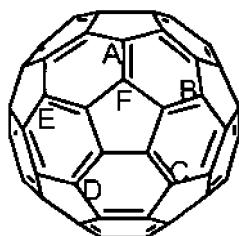
## Patentansprüche

1. Verfahren zum Herstellen eines Fullerenderivats, das ein mono-(organo-)Fullerenderivat, ein di-(organo-)Fullerenderivat, ein tri-(organo-)Fullerenderivat oder ein tetra-(organo-)Fullerenderivat ist, welches den Organische-Gruppe-Hinzufügungs-Schritt A zum Hinzufügen einer organischen Gruppe, indem wenigstens ein Grignard-Reagens und

eine polare Substanz mit einem Fulleren oder Fullerenderivat reagieren, umfasst, bei welchem die polare Substanz mit der Donatorenzahl 25 oder mehr in einer Menge von 3 bis 60 Äquivalenten des Fulleren oder des Fullerenderivats, zu welchem die organische Gruppe hinzugefügt wird, verwendet wird.

- 5 2. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 1, in welchem das Fulleren oder Fullerenderivat, zu welchem die organische Gruppe im Organische-Gruppe-Hinzufügungs-Schritt A hinzugefügt wird, ein Fulleren oder Fullerenderivat ist, das dargestellt wird durch die folgende Formel (1):

10



(1)

15

20

wobei: organische Gruppen jeweils unabhängig zu 0 bis 4 Kohlenstoffen von 5 an A bis E positionierten Kohlenstoffen hinzugefügt wurden; und ein Wasserstoffatom oder eine C<sub>1</sub> - C<sub>30</sub>-Kohlenwasserstoffgruppe zu einem an F positionierten Kohlenstoff hinzugefügt wurde, oder nichts dazu hinzugefügt wurde.

25

3. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 2, wobei die organische Gruppe in dem Organische-Gruppe-Hinzufügungs-Schritt A zu wenigstens einem der Kohlenstoffe hinzugefügt wird, die an A bis E in dem Fulleren oder Fullerenderivat positioniert sind, das von der Formel (1) dargestellt wird, zu welchem die organische Gruppe nicht hinzugefügt wurde.

30

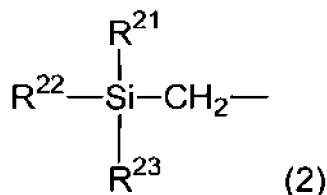
4. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 3, wobei die organische Gruppe zum Hinzufügen in dem Organische-Gruppe-Hinzufügungs-Schritt A eine oder mehrere Substanzen ist, die ausgewählt sind aus der Gruppe bestehend aus einem Wasserstoffatom, einer substituierten oder nicht substituierten C<sub>1</sub> - C<sub>30</sub>-Kohlenwasserstoffgruppe, einer substituierten oder nicht substituierten C<sub>1</sub> - C<sub>30</sub>-Alkoxygruppe, einer substituierten oder nicht substituierten C<sub>6</sub> - C<sub>30</sub>-Aryloxygruppe, einer substituierten oder nicht substituierten Aminogruppe, einer substituierten oder nicht substituierten Silylgruppe, einer substituierten oder nicht substituierten Alkylthiogruppe (-SY<sup>1</sup>: in der Formel steht Y<sup>1</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe), einer substituierten oder nicht substituierten Arylthiogruppe (-SY<sup>2</sup>: in der Formel steht Y<sup>2</sup> für eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe), einer substituierten oder nicht substituierten Alkylsulfonylgruppe (-SO<sub>2</sub>Y<sup>3</sup>: in der Formel steht Y<sup>3</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe) und einer substituierten oder nicht substituierten Arylsulfonylgruppe (-SO<sub>2</sub>Y<sup>4</sup>: in der Formel steht Y<sup>4</sup> für eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe).

35

40

5. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 3, wobei die organische Gruppe zum Hinzufügen im Organische-Gruppe-Hinzufügungs-Schritt A eine Gruppe ist, die dargestellt wird von der folgenden Formel (2):

45



50

55

wobei R<sup>21</sup> bis R<sup>23</sup> jeweils unabhängig für ein Wasserstoffatom, eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>30</sub>-Kohlenwasserstoffgruppe, eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>30</sub>-Alkoxygruppe, eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>30</sub>-Aryloxygruppe, eine substituierte oder nicht substituierte Aminogruppe, eine substituierte oder nicht substituierte Silylgruppe, eine substituierte oder nicht substituierte Alkylthiogruppe (-SY<sup>1</sup>: in der Formel steht Y<sup>1</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe), eine substituierte oder nicht substituierte Arylthiogruppe (-SY<sup>2</sup>: in der Formel steht Y<sup>2</sup> für eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe), eine substituierte oder nicht substituierte Alkylsulfonylgruppe (-SO<sub>2</sub>Y<sup>3</sup>: in der Formel steht Y<sup>3</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe) oder eine substituierte oder nicht substituierte Arylsulfonylgruppe (-SO<sub>2</sub>Y<sup>4</sup>:

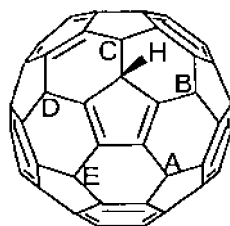
in der Formel steht  $Y^4$  für eine substituierte oder nicht substituierte  $C_6 - C_{18}$ -Arylgruppe) stehen.

6. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 5, wobei  $R^{21}$  bis  $R^{23}$  je unabhängig für eine  $C_1 - C_{20}$ -Alkylgruppe stehen.
7. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 6, wobei das Grignard-Reagens dargestellt wird von der folgenden Formel (3):



wobei:  $R^3$  für eine organische Gruppe steht; und X für Cl, Br oder I steht.

8. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 7, wobei  $R^3$  in der Formel (3) für eine substituierte oder nicht substituierte  $C_1 - C_{30}$ -Kohlenwasserstoffgruppe, eine substituierte oder nicht substituierte  $C_1 - C_{30}$ -Alkoxygruppe, eine substituierte oder nicht substituierte  $C_6 - C_{30}$ -Aryloxygruppe, eine substituierte oder nicht substituierte Aminogruppe, eine substituierte oder nicht substituierte Silylgruppe, eine substituierte oder nicht substituierte Alkylthiogruppe ( $-SY^1$ : in der Formel steht  $Y^1$  für eine substituierte oder nicht substituierte  $C_1 - C_{20}$ -Alkylgruppe), eine substituierte oder nicht substituierte Arylthiogruppe ( $-SY^2$ : in der Formel steht  $Y^2$  für eine substituierte oder nicht substituierte  $C_6 - C_{18}$ -Arylgruppe), eine substituierte oder nicht substituierte Alkylsulfonylgruppe ( $-SO_2Y^3$ : in der Formel steht  $Y^3$  für eine substituierte oder nicht substituierte  $C_1 - C_{20}$ -Alkylgruppe) oder eine substituierte oder nicht substituierte Arylsulfonylgruppe ( $-SO_2Y^4$ : in der Formel steht  $Y^4$  für eine substituierte oder nicht substituierte  $C_6 - C_{18}$ -Arylgruppe) steht.
9. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 8, wobei  $R^3$  für eine  $C_1 - C_{20}$ -Alkylgruppe steht.
10. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 9, wobei das Grignard-Reagens in einer Menge von 1 bis 20 Äquivalenten des Fulleren oder Fullerenderivats verwendet wird, zu dem die organische Gruppe in dem Organische-Gruppe-Hinzufügungs-Schritt A hinzugefügt wird.
11. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 10, wobei die Donatorenzahl der polaren Substanz bei einer Zusatzmenge von 30 Äquivalenten 26,6 bis 33,1 beträgt.
12. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 10, wobei die polare Substanz N,N-Dimethylformamid, Dimethylsulfoxid oder Pyridin ist.
13. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 3, wobei das Fullerenderivat, zu welchem die organische Gruppe in dem Organische-Gruppe-Hinzufügungs-Schritt A hinzugefügt wurde, ein Fullerenderivat ist, das dargestellt wird von der folgenden Formel (1A):



(1A)

wobei: organische Gruppen jeweils unabhängig zu 1 bis 5 Kohlenstoffen von 5 an A bis E positionierten Kohlenstoffen hinzugefügt wurden.

14. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 13, wobei die zu den an A bis E positionierten Kohlenstoffen hinzugefügten organischen Gruppen in der Formel (1A) jeweils unabhängig für ein Wasserstoffatom, eine substituierte oder nicht substituierte  $C_1 - C_{30}$ -Kohlenwasserstoffgruppe, eine substituierte oder nicht substituierte  $C_1 - C_{30}$ -Alkoxygruppe, eine substituierte oder nicht substituierte  $C_6 - C_{30}$ -Aryloxygruppe, eine substituierte oder nicht substituierte Aminogruppe, eine substituierte oder nicht substituierte Silylgruppe, eine substituierte oder nicht substituierte Alkylthiogruppe ( $-SY^1$ : in der Formel steht  $Y^1$  für eine substituierte oder nicht substituierte  $C_1 - C_{20}$ -Alkylgruppe), eine substituierte oder nicht substituierte Arylthiogruppe ( $-SY^2$ : in der Formel steht  $Y^2$  für eine

substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe), eine substituierte oder nicht substituierte Alkylsulfonylgruppe (-SO<sub>2</sub>Y<sup>3</sup>: in der Formel steht Y<sup>3</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe) oder eine substituierte oder nicht substituierte Arylsulfonylgruppe (-SO<sub>2</sub>Y<sup>4</sup>: in der Formel steht Y<sup>4</sup> für eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe) stehen.

5

15. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 1 bis 14, welches den Organische-Gruppe-Hinzufügungs-Schritt B umfasst, um weiter eine organische Gruppe hinzuzufügen, indem wenigstens eine basische Verbindung und eine Halogenverbindung mit dem im Organische-Gruppe-Hinzufügungs-Schritt A durch Hinzufügung eines Wasserstoffatoms und einer organischen Gruppe gewonnenen Fullerenderivat reagieren.

10

16. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 15, wobei die in dem Organische-Gruppe-Hinzufügungs-Schritt B zu verwendende basische Verbindung eine oder mehrere Substanzen umfasst, die ausgewählt sind aus der Gruppe bestehend aus einem Metallhydrid, einem Metallalkoxid, einem Alkalimetallreagens, einem Alkalimetall und einem organischen Alkali.

15

17. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 15, wobei die in dem Organische-Gruppe-Hinzufügungs-Schritt B zu verwendende basische Verbindung K oder Na umfassendes Alkoxid ist.

20

18. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 15, wobei die in dem Organische-Gruppe-Hinzufügungs-Schritt B zu verwendende basische Verbindung t-BuOK oder t-BuONa ist.

19. Verfahren zum Herstellen eines Fullerenderivats nach einem der Ansprüche 15 bis 18, wobei die in dem Organische-Gruppe-Hinzufügungs-Schritt B zu verwendende Halogenverbindung dargestellt wird von der folgenden Formel (4):

25



wobei: R<sup>4</sup> für eine organische Gruppe steht; und X ein Halogenatom steht.

20. Verfahren zum Herstellen eines Fullerenderivats nach Anspruch 19, wobei in der Formel (4): R<sup>4</sup> für ein Wasserstoffatom, eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>30</sub>-Kohlenwasserstoffgruppe, eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>30</sub>-Alkoxygruppe, eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>30</sub>-Aryloxygruppe, eine substituierte oder nicht substituierte Aminogruppe, eine substituierte oder nicht substituierte Silylgruppe, eine substituierte oder nicht substituierte Alkylthiogruppe (-SY<sup>1</sup>: in der Formel steht Y<sup>1</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe), eine substituierte oder nicht substituierte Arylthiogruppe (-SY<sup>2</sup>: in der Formel steht Y<sup>2</sup> für eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe), eine substituierte oder nicht substituierte Alkylsulfonylgruppe (-SO<sub>2</sub>Y<sup>3</sup>: in der Formel steht Y<sup>3</sup> für eine substituierte oder nicht substituierte C<sub>1</sub> - C<sub>20</sub>-Alkylgruppe) oder eine substituierte oder nicht substituierte Arylsulfonylgruppe (-SO<sub>2</sub>Y<sup>4</sup>: in der Formel steht Y<sup>4</sup> für eine substituierte oder nicht substituierte C<sub>6</sub> - C<sub>18</sub>-Arylgruppe) steht; und X für Cl, Br oder I steht.

40

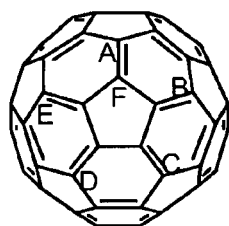
## Revendications

1. Procédé de production d'un dérivé de fullerène qui est un dérivé de mono(organo)fullerène, un dérivé de di(organo)fullerène, un dérivé de tri(organo)fullerène ou un dérivé de tétra(organo)fullerène comprenant l'étape A d'addition d'un groupe organique permettant l'addition d'un groupe organique en mettant à réagir au moins un réactif de Grignard et une substance polaire avec un fullerène ou un dérivé de fullerène, dans lequel la substance polaire ayant le nombre donneur de 25 ou plus est utilisée en une quantité de 3 à 60 équivalents du fullerène ou du dérivé de fullerène auquel le groupe organique est ajouté.

45

2. Procédé de production d'un dérivé de fullerène selon la revendication 1, dans lequel le fullerène ou le dérivé de fullerène auquel le groupe organique est ajouté dans l'étape A d'addition d'un groupe organique est un fullerène ou un dérivé de fullerène représenté par la formule (1) suivante :

55



(1)

5

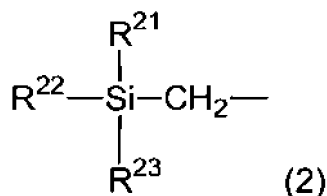
10 dans laquelle : des groupes organiques ont été chacun indépendamment ajoutés à 0 à 4 atomes de carbone parmi les 5 atomes de carbone positionnés en A à E ; et un atome d'hydrogène ou un groupe en C<sub>1</sub> à C<sub>30</sub> a été ajouté à un atome de carbone positionné en F, ou rien n'a été ajouté à celui-ci.

15 3. Procédé de production d'un dérivé de fullerène selon la revendication 2, dans lequel dans l'étape A d'addition d'un groupe organique, le groupe organique est ajouté à au moins l'un des atomes de carbone positionnés en A à E dans le fullerène ou le dérivé de fullerène représenté par la formule (1) auquel le groupe organique n'a pas été ajouté.

20 4. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 3, ledit groupe organique destiné à l'addition dans l'étape A d'addition d'un groupe organique étant une ou plusieurs substances choisies dans le groupe constitué par un atome d'hydrogène ou un groupe hydrocarboné en C<sub>1</sub> à C<sub>30</sub> substitué ou non substitué, un groupe alcoxy en C<sub>1</sub> à C<sub>30</sub> substitué ou non substitué, un groupe aryloxy en C<sub>6</sub> à C<sub>30</sub> substitué ou non substitué, un groupe amino substitué ou non substitué, un groupe silyle substitué ou non substitué, un groupe alkylthio substitué ou non substitué (-SY<sup>1</sup> : dans la formule, Y<sup>1</sup> représente un groupe alkyle en C<sub>1</sub> à C<sub>20</sub> substitué ou non substitué), un groupe arylthio substitué ou non substitué (-SY<sup>2</sup> : dans la formule, Y<sup>2</sup> représente un groupe aryle en C<sub>6</sub> à C<sub>18</sub> substitué ou non substitué), un groupe alkylsulfonyl substitué ou non substitué (-SO<sub>2</sub>Y<sup>3</sup> : dans la formule, Y<sup>3</sup> représente un groupe alkyle en C<sub>1</sub> à C<sub>20</sub> substitué ou non substitué), et un groupe arylsulfonyl substitué ou non substitué (-SO<sub>2</sub>Y<sup>4</sup> : dans la formule, Y<sup>4</sup> représente un groupe aryle en C<sub>6</sub> à C<sub>18</sub> substitué ou non substitué).

25 30 5. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 3, ledit groupe organique destiné à l'addition dans l'étape A d'addition d'un groupe organique étant un groupe représenté par la formule (2) suivante :

35



40

45 dans laquelle R<sup>21</sup> à R<sup>23</sup> représentent chacun indépendamment un atome d'hydrogène, un groupe hydrocarboné en C<sub>1</sub> à C<sub>30</sub> substitué ou non substitué, un groupe alcoxy en C<sub>1</sub> à C<sub>30</sub> substitué ou non substitué, un groupe aryloxy en C<sub>6</sub> à C<sub>30</sub> substitué ou non substitué, un groupe amino substitué ou non substitué, un groupe silyle substitué ou non substitué, un groupe alkylthio substitué ou non substitué (-SY<sup>1</sup> : dans la formule, Y<sup>1</sup> représente un groupe alkyle en C<sub>1</sub> à C<sub>20</sub> substitué ou non substitué), un groupe arylthio substitué ou non substitué (-SY<sup>2</sup> : dans la formule, Y<sup>2</sup> représente un groupe aryle en C<sub>6</sub> à C<sub>18</sub> substitué ou non substitué), un groupe alkylsulfonyl substitué ou non substitué (-SO<sub>2</sub>Y<sup>3</sup> : dans la formule, Y<sup>3</sup> représente un groupe alkyle en C<sub>1</sub> à C<sub>20</sub> substitué ou non substitué), ou un groupe arylsulfonyl substitué ou non substitué (-SO<sub>2</sub>Y<sup>4</sup> : dans la formule, Y<sup>4</sup> représente un groupe aryle en C<sub>6</sub> à C<sub>18</sub> substitué ou non substitué).

50

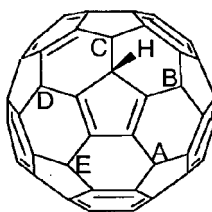
6. Procédé de production d'un dérivé de fullerène selon la revendication 5, lesdits groupes R<sup>21</sup> à R<sup>23</sup> représentant chacun indépendamment un groupe alkyle en C<sub>1</sub> à C<sub>20</sub>.

55 7. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 6, ledit réactif de Grignard étant représenté par la formule (3) suivante :



dans laquelle :  $R_3$  représente un groupe organique et X représente un atome Cl, Br ou I.

- 5 8. Procédé de production d'un dérivé de fullerène selon la revendication 7, ledit groupe  $R^3$  dans la formule (3) représentant un groupe hydrocarboné en  $C_1$  à  $C_{30}$  substitué ou non substitué, un groupe alcoxy en  $C_1$  à  $C_{30}$  substitué ou non substitué, un groupe aryloxy en  $C_6$  à  $C_{30}$  substitué ou non substitué, un groupe amino substitué ou non substitué, un groupe silyle substitué ou non substitué, un groupe alkylthio substitué ou non substitué ( $-SY^1$  : dans la formule,  $Y^1$  représente un groupe alkyle en  $C_1$  à  $C_{20}$  substitué ou non substitué), un groupe arylthio substitué ou non substitué ( $-SY^2$  : dans la formule,  $Y^2$  représente un groupe aryle en  $C_6$  à  $C_{18}$  substitué ou non substitué), un groupe alkylsulfonyl substitué ou non substitué ( $-SO_2Y^3$  : dans la formule,  $Y^3$  représente un groupe alkyle en  $C_1$  à  $C_{20}$  substitué ou non substitué), ou un groupe arylsulfonyl substitué ou non substitué ( $-SO_2Y^4$  : dans la formule,  $Y^4$  représente un groupe aryle en  $C_6$  à  $C_{18}$  substitué ou non substitué).
- 10
- 15 9. Procédé de production d'un dérivé de fullerène selon la revendication 8, ledit groupe  $R^3$  représentant un groupe alkyle en  $C_1$  à  $C_{20}$ .
- 20 10. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 9, ledit réactif de Grignard étant utilisé en une quantité de 1 à 20 équivalents du fullerène ou du dérivé de fullerène auquel le groupe organique est ajouté dans l'étape A d'addition d'un groupe organique.
- 25 11. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 10, ledit nombre donneur de la substance polaire valant 26,6 à 33,1 à une quantité additive de 30 équivalents.
- 30 12. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 10, ladite substance polaire étant le N,N-diméthylformamide, le diméthylsulfoxyde ou la pyridine.
- 35 13. Procédé de production d'un dérivé de fullerène selon la revendication 3, ledit dérivé de fullerène auquel le groupe organique a été ajouté dans l'étape A d'addition d'un groupe organique étant un dérivé de fullerène représenté par la formule (1A) suivante :



(1A)

40 dans laquelle : des groupes organiques ont été chacun indépendamment ajoutés à 1 à 5 atomes de carbone parmi les 5 atomes de carbone positionnés en A à E.

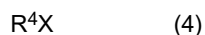
- 45 14. Procédé de production d'un dérivé de fullerène selon la revendication 13, dans lequel dans la formule (1A) les groupes organiques ajoutés aux atomes de carbone positionnés en A à E représentent chacun indépendamment un atome d'hydrogène, un groupe hydrocarboné en  $C_1$  à  $C_{30}$  substitué ou non substitué, un groupe alcoxy en  $C_1$  à  $C_{30}$  substitué ou non substitué, un groupe aryloxy en  $C_6$  à  $C_{30}$  substitué ou non substitué, un groupe amino substitué ou non substitué, un groupe silyle substitué ou non substitué, un groupe alkylthio substitué ou non substitué ( $-SY^1$  : dans la formule,  $Y^1$  représente un groupe alkyle en  $C_1$  à  $C_{20}$  substitué ou non substitué), un groupe arylthio substitué ou non substitué ( $-SY^2$  : dans la formule,  $Y^2$  représente un groupe aryle en  $C_6$  à  $C_{18}$  substitué ou non substitué), un groupe alkylsulfonyl substitué ou non substitué ( $-SO_2Y^3$  : dans la formule,  $Y^3$  représente un groupe alkyle en  $C_1$  à  $C_{20}$  substitué ou non substitué), ou un groupe arylsulfonyl substitué ou non substitué ( $-SO_2Y^4$  : dans la formule,  $Y^4$  représente un groupe aryle en  $C_6$  à  $C_{18}$  substitué ou non substitué).
- 50
- 55 15. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 1 à 14, qui comprend l'étape B d'addition d'un groupe organique permettant d'ajouter en outre un groupe organique en mettant à réagir au moins un composé basique et un composé halogéné avec le dérivé de fullerène obtenu par addition d'un atome d'hydrogène et d'un groupe organique dans l'étape A d'addition d'un groupe organique.
16. Procédé de production d'un dérivé de fullerène selon la revendication 15, ledit composé basique à utiliser dans



## EP 2 116 521 B1

l'étape B d'addition d'un groupe organique comprenant une ou plusieurs substances choisies dans le groupe constitué par un hydrure métallique, un alcoxyde métallique, un réactif de métal alcalin, un métal alcalin et un alcali organique.

- 5 17. Procédé de production d'un dérivé de fullerène selon la revendication 15, ledit composé basique à utiliser dans l'étape B d'addition d'un groupe organique étant un alcoxyde comprenant K ou Na.
- 10 18. Procédé de production d'un dérivé de fullerène selon la revendication 15, ledit composé basique à utiliser dans l'étape B d'addition d'un groupe organique étant t-BuOK ou t-BuONa.
- 15 19. Procédé de production d'un dérivé de fullerène selon l'une quelconque des revendications 15 à 18, ledit composé halogéné à utiliser dans l'étape B d'addition d'un groupe organique étant représenté par la formule (4) suivante :



15 dans laquelle :  $R^4$  représente un groupe organique et X représente un atome d'halogène.

- 20 20. Procédé de production d'un dérivé de fullerène selon la revendication 19, dans lequel dans la formule (4) :  $R^4$  représente un un atome d'hydrogène, un groupe hydrocarboné en  $C_1$  à  $C_{30}$  substitué ou non substitué, un groupe alcoxy en  $C_1$  à  $C_{30}$  substitué ou non substitué, un groupe aryloxy en  $C_6$  à  $C_{30}$  substitué ou non substitué, un groupe amino substitué ou non substitué, un groupe silyle substitué ou non substitué, un groupe alkylthio substitué ou non substitué ( $-SY^1$  : dans la formule,  $Y^1$  représente un groupe alkyle en  $C_1$  à  $C_{20}$  substitué ou non substitué), un groupe arylthio substitué ou non substitué, ( $-SY^2$  : dans la formule,  $Y^2$  représente un groupe aryle en  $C_6$  à  $C_{18}$  substitué ou non substitué), un groupe alkylsulfonyl substitué ou non substitué ( $-SO_2Y^3$  : dans la formule,  $Y^3$  représente un groupe alkyle en  $C_1$  à  $C_{20}$  substitué ou non substitué), ou un groupe arylsulfonyl substitué ou non substitué ( $-SO_2Y^4$  : dans la formule,  $Y^4$  représente un groupe aryle en  $C_6$  à  $C_{18}$  substitué ou non substitué) ; et X représente un atome Cl, Br ou I.
- 25
- 30
- 35
- 40
- 45
- 50
- 55

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- JP HEI10167994 B [0003]
- JP HEI11255509 B [0003]
- US 10167994 B [0004]
- JP 2005232165 B [0006]

**Non-patent literature cited in the description**

- *J. Am. Chem. Soc.*, 1996, vol. 118, 12850 [0003]
- *Org. Lett.*, 2000, vol. 2, 1919 [0003]
- *Chem. Lett.*, 2000, 1098 [0003]
- **NAGASHIMA et al.** *J. Org. Chem.*, 1994, vol. 59, 1246-1248 [0006]
- *Gendai-Kagaku*, June 2000, 46 [0010]
- *Chemical Reviews*, 1998, vol. 98, 2527 [0010]