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(54) Title: METHOD FOR PREPARING AN ORGANO-FUNCTIONAL SILANE

(57) Abstract: A process includes reacting an organometallic cuprate and a silicon precursor in the presence of a solvent. The process produces a reaction product including an organo-functional silane.



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Method for Preparing an Organo-functional Silane

[0001] Silicon-carbon bonds are formed by reacting zero-valent silicon (Si^0) with alkyl halides to produce organo-functional silanes, such as organohalosilanes useful as raw materials in the silicones industry. Typically, organohalosilanes are produced commercially by the Mueller-Rochow Direct Process, which comprises passing an organohalide, such as methyl chloride, over Si^0 in the presence of a copper catalyst and various promoters to produce a mixture of organohalosilanes. Of the organohalosilanes produced in the Direct Process, dimethyldichlorosilane is the most valuable. Organohalosilanes are hydrolyzed to produce a wide range of silicones, such as polydiorganosiloxanes and silicone resins, which are sold into many different industries. Silicones can also be produced by hydrolysis and condensation of other organo-functional silanes, such as alkoxysilanes. Alkoxysilanes can be produced by alkoxylation of halosilanes with alcohols and thus stem from the same raw materials as described above.

[0002] Si^0 is expensive to produce due to high energy requirements for reducing SiO_2 by carbothermic reduction. There is a need in the silicones industry for reactions that produce organo-functional silanes without utilizing Si^0 and that offer an energy and/or cost advantage.

SUMMARY OF THE INVENTION

[0003] A process comprises reacting ingredients comprising (a) an organometallic cuprate and (b) a silicon precursor in the presence of a solvent. The process produces a reaction product comprising an organo-functional silane.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0004] All amounts, ratios, and percentages are by weight, unless otherwise indicated by the context of the specification. The articles 'a', 'an', and 'the' each refer to one or more, unless otherwise indicated by the context of the specification. The following abbreviations have these meanings herein: "Me" means methyl, "Et" means ethyl, "Pr" means propyl and includes n-propyl and isopropyl, "Bu" means butyl and includes n-butyl, iso-butyl, t-butyl and sec-butyl, and "THF" means tetrahydrofuran.

[0005] "Alkyl" means an acyclic, branched or unbranched, saturated monovalent hydrocarbon group. Alkyl is exemplified by, but not limited to, Me, Et, Pr (*e.g.*, iso-propyl and/or n-propyl), Bu (*e.g.*, isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (*e.g.*, isopentyl, neopentyl, and/or tert-pentyl), hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl as well as branched saturated monovalent hydrocarbon groups of 6 to 12 carbon atoms. Alkyl groups may have 1 to 30 carbon atoms, alternatively 1 to 24 carbon atoms, alternatively 1 to 20 carbon atoms, alternatively 1 to 12 carbon atoms, alternatively 1 to 10 carbon atoms, and alternatively 1 to 6 carbon atoms.

[0006] “Alkenyl” means an acyclic, branched or unbranched, monovalent hydrocarbon group having one or more carbon-carbon double bonds. Alkenyl is exemplified by, but not limited to, vinyl, allyl, propenyl, and hexenyl. Alkenyl groups may have 2 to 30 carbon atoms, alternatively 2 to 24 carbon atoms, alternatively 2 to 20 carbon atoms, alternatively 2 to 12 carbon atoms, alternatively 2 to 10 carbon atoms, and alternatively 2 to 6 carbon atoms.

[0007] “Alkynyl” means an acyclic, branched or unbranched, monovalent hydrocarbon group having one or more carbon-carbon triple bonds. Alkynyl is exemplified by, but not limited to, ethynyl, propynyl, and butynyl. Alkynyl groups may have 2 to 30 carbon atoms, alternatively 2 to 24 carbon atoms, alternatively 2 to 20 carbon atoms, alternatively 2 to 12 carbon atoms, alternatively 2 to 10 carbon atoms, and alternatively 2 to 6 carbon atoms.

[0008] “Organo-functional silane” means a compound containing an organic group covalently bonded to a silicon atom. Organo-functional silane includes organo-functional monosilanes in which one silicon atom is present per molecule. Organo-functional silane also includes organo-functional polysilanes in which an organic group is covalently bonded to a silicon atom and two or more silicon atoms are present per molecule, *i.e.*, the molecule has at least one Si-Si bond.

[0009] The process comprises: (1) reacting ingredients comprising (a) an organometallic cuprate and (b) a silicon precursor in the presence of a solvent. The organometallic cuprate may have formula (A): $M^+[CuR_2]^-$, where M is a metal atom selected from group 1 or group 2 of the periodic table and each R is independently a monovalent organic group. Alternatively, M may be selected from Li, Mg, and Na. Alternatively, M may be Li. Alternatively, R may be a monovalent hydrocarbon group, such as alkyl, alkenyl, or alkynyl, as defined above. Alternatively, R may be alkyl or alkenyl. Alternatively, R may be an alkyl group, such as Me, Et, Pr, or Bu; alternatively Me.

[0010] The organometallic cuprate for ingredient (a) may be prepared, for example, by reacting an organometallic compound of formula R_cM with a copper(I) precursor (“Cu(1) precursor”). R and M are as described above. Subscript c is an integer from 1 to a maximum valence of the metal atom selected for M; alternatively, subscript c may be 1 to 2.

[0011] The Cu(1) precursor has formula CuR^5 , where R^5 is a displaceable substituent, which is capable of reacting with the metal atom selected for M, for example, R^5 may be a halogen atom or an alkoxy group. Alternatively, the Cu(1) precursor may have formula CuX , where X is a halogen atom. The halogen atom for X may be Br, Cl, F, or I; alternatively Br, Cl, or I; alternatively Cl or I; and alternatively I. A conventional technique

for preparing the organometallic cuprate may be used, for example, a technique described in WO90/02718 which is hereby incorporated by reference for the purpose of disclosing how to prepare organometallic cuprates. The organometallic cuprate may be prepared *in situ*, where the organometallic cuprate is prepared in a solvent and the resulting solvent solution of organometallic cuprate is added to the silicon precursor, or where the silicon precursor is added to the solvent solution used to prepare the organometallic cuprate.

[0012] The silicon precursor for ingredient (b) may be silicon metal or a silane. As used herein, "silicon precursor" means any compound or composition capable of providing silicon in the present process to form the organo-functional silane. The silicon precursor used in the process may be free of copper halide, such as CuCl. Alternatively, the silicon precursor may be free of metal halides. As used herein, "free of" means containing none or an amount insufficient to prevent formation of the organo-functional silane, alternatively containing 0% to 5%, alternatively containing 0% to 1%, and alternatively containing 0% to 0.1%. Silicon metal is commercially available. For example, chemical grade silicon metal from Dow Corning Alabama of Mount Meigs, Alabama, U.S.A. When silicon metal is used as the silicon precursor, the silicon metal may have a purity of >95%, alternatively ≥99%, and alternatively ≥99.9%. Alternatively, the silicon metal may have a purity ranging from 95% to 100%, alternatively 99% to 100%, and alternatively 99.9% to 99.99999%.

[0013] Alternatively, the silicon precursor may be a silane. The silane may have formula (b1): $R^1_{(4-n)}SiR^2_n$. In formula (b1), subscript n is an integer from 0 to 3, alternatively 0 to 2, alternatively 0 to 1, and alternatively 0. Each R^1 is independently selected from a halogen atom and a group of formula QR^3 , where Q is selected from NH, O, and S, and R^3 is a monovalent hydrocarbon group. Each R^2 is independently selected from H and a monovalent hydrocarbon group.

[0014] Alternatively, the silane for ingredient (b) may be an alkoxysilane, *i.e.*, when R^1 is QR^3 , Q is an oxygen atom, and R^3 is an alkyl group. The alkoxysilane may be a tetraalkoxysilane of formula (b2): $Si(OR^4)_4$, where each R^4 is independently a monovalent hydrocarbon group, such as an alkyl group, an alkenyl group, an aryl group, an aralkyl group, or an alkaryl group. Alternatively, each R^4 may be an alkyl group of 1 to 4 carbon atoms. Alternatively, each R^4 may be Me or Et. Alternatively, each R^4 may be Me.

[0015] The amounts of organometallic cuprate and silicon precursor are sufficient to produce the organo-functional silane in the reaction product. The molar ratio of organometallic cuprate : silicon may range from 1:1 to 10:1, alternatively 1:1 to 2:1, and alternatively 1:1. Without wishing to be bound by theory, the amount of organometallic

cuprate may be used to influence selectivity of the organo-functional silane in the reaction product. For example, when 1 mole organometallic cuprate and 1 mole of silane are used, it is thought that the reaction product may comprise an organo-functional silane of formula $RR^1_{(3-n)}SiR^2_n$, where R, R^1 , R^2 , and subscript n are as described above, and when 2 mole organometallic cuprate and 1 mole of silane are used, the it is thought that the reaction product may comprise an organo-functional silane of formula $R_2R^1_{(2-n)}SiR^2_n$, where R, R^1 , R^2 , and subscript n are as described above.

[0016] The solvent may comprise an ether, such as diethyl ether, dimethyl ether, ethylmethyl ether, n-butylmethyl ether, n-butylethyl ether, di-n-butyl ether, di-isobutyl ether, isobutylmethyl ether, isobutylethyl ether, or THF. In addition, the solvent may further comprise a hydrocarbon solvent such as an aliphatic, cycloaliphatic or aromatic hydrocarbon exemplified by heptane, cyclohexane, or toluene. The amount of solvent is not critical; the amount of solvent is sufficient to solubilize the organometallic cuprate and the silane. The exact amount of solvent will vary depending on factors including the type of solvent selected and the silicon precursor selected.

[0017] The reaction product prepared by the process comprises the organo-functional silane. When the silicon precursor is silicon metal, the organo-functional silane produced may have formula (I) R_ySi_z , where R is as described above, subscript y is an integer of 4 or more, subscript z is an integer of 1 or more, and $y = (2z + 2)$. Alternatively, subscript z may be 1 to 4. Examples of organo-functional silanes of formula (I) may comprise one or more of R_4Si , $(R_3Si)_2SiR_2$, $(R_3Si)_2(SiR_2)_2$, or a combination thereof; where each R is as described above. Alternatively, when each R is Me, and $Li^+CuMe_2^-$ is reacted with chemical grade silicon powder, organo-functional silanes comprising: Me_4Si , $(Me_3Si)_2SiMe_2$, and $(Me_3Si)_2(SiMe_2)_2$ are generated. The organo-functional silanes of formula (I) may be used, for example, as raw materials in the silicon carbide industry, *e.g.*, the organo-functional silane of formula (I) may be used as raw materials in chemical vapor deposition processes for preparing silicon carbide.

[0018] Alternatively, when the silicon precursor is a silane, the reaction product may comprise an organo-functional silane of formula (II) $R_aR^1_{(4-a-b)}SiR^2_b$, where R, R^1 , and R^2 are as described above, subscript a is an integer from 1 to 4, and subscript b is an integer from 0 to 3. Alternatively, subscript a may be 1 to 3, alternatively 1 to 2, and alternatively 1. For example, when the silicon precursor is an alkoxysilane, such as a tetraalkoxysilane, the reaction product may comprise an organo-functional silane of formula (III) $R_xSi(OR)_{(4-x)}$, where each R is as described above, and subscript x is an integer of 1

to 4; alternatively 1 to 3; alternatively 1 to 2; and alternatively 1. Examples of organo-functional silanes of formula (III) include organoalkoxysilanes such as $\text{Me}_2\text{Si}(\text{OMe})_2$ and $\text{MeSi}(\text{OMe})_3$. Organoalkoxysilanes are useful as intermediates in the silicones industry. Organoalkoxysilanes may be hydrolyzed to make silicones, such as polydiorganosiloxanes and/or silicone resins.

[0019] Alternatively, when the silicon precursor is a halosilane, then the reaction product may comprise an organo-functional silane of formula (IV) $\text{R}_j\text{X}_{(4-j-k)}\text{SiR}^2_k$, where R, X, and R^2 are as described above, subscript j is an integer from 1 to 4, and subscript k is an integer from 0 to 3. Alternatively, subscript j may be 1 to 3, alternatively 1 to 2, and alternatively 1. Alternatively, subscript k may be an integer from 0 to 2, and alternatively 0 to 1. Examples of organo-functional silanes of formula (IV) include organohalosilanes such as MeHSiCl_2 , Me_2HSiCl , MeSiCl_3 , Me_2SiCl_2 , or a combination thereof. Organohalosilanes are useful as intermediates in the silicones industry. Organohalosilanes may be hydrolyzed to make silicones, such as polydiorganosiloxanes and/or silicone resins.

[0020] The process described above provides the advantage that it may be performed in existing production equipment. For example, the process may be performed in a continuously stirred tank reactor (CSTR) with continuous addition of the solvent, organometallic cuprate, and silicon precursor described above into the reactor and continuous flow of a solution comprising the reaction product out of the reactor. Some residence time inside the reactor is provided. The exact residence time depends on various factors including temperature and concentrations of silicon precursor and organometallic cuprate, however, residence time may range from 30 seconds to 60 minutes, alternatively 30 seconds to 5 minutes, alternatively 10 minutes to 30 minutes, alternatively 30 minutes to 60 minutes. The solution containing the reaction product taken out of the reactor can be treated to recover the organo-functional silane, e.g., by conventional techniques such as filtration to remove solids from the reaction product, and/or stripping and/or distillation to separate the organo-functional silane, from the solvent, from unreacted silicon precursor and/or organometallic cuprate (if present), and to separate different organo-functional silane from one another. The solvent and any unreacted silicon precursor and/or organometallic cuprate may be recycled back into the CSTR with make-up organometallic cuprate and/or silicon precursor.

[0021] When the silicon precursor is a silane, then the process may be performed in a solution phase reaction. The temperature may range from -78°C to room temperature of 25°C , alternatively to 0°C to 25°C , and alternatively -78°C to 0°C . When the silicon

precursor comprises silicon metal, then the process may be performed in a slurry reaction. The temperature may range from -78°C to 100°C, alternatively -78°C to 50°C, alternatively -78°C to 25°C, alternatively 0°C to 100°C, alternatively 25°C to 100°C, and alternatively 25°C to 50°C.

[0022] The pressure at which the process is performed is not critical and may be sub-atmospheric to atmospheric. The organometallic cuprate, silicon precursor, and solvent may be mixed to facilitate reaction. The order of addition is also not critical. The organometallic cuprate may be prepared, as described above, and the silicon precursor may be added to the organometallic cuprate. Alternatively, the organometallic cuprate may be prepared, and the organometallic cuprate may be added to the silicon precursor.

[0023] The process may further comprise recovering the organo-functional silane from the reaction product. The reaction product may comprise a solid and/or other side product in addition to the organo-functional silane. Recovering may include removal of all or a portion of the solvent and/or purifying the organo-functional silane and/or separating different organo-functional silanes from one another. Recovering may be performed using conventional techniques such as evaporation, stripping, distillation, condensation, filtration, and/or a combination thereof.

EXAMPLES

[0024] These examples are intended to illustrate certain embodiments of the invention, and should not be interpreted as limiting the scope of the invention set forth in the claims.

[0025] Example 1 - A Schlenk tube (50mL) was charged with CuI (0.5 gm, 2.62 mmol) and Et₂O (10 mL) followed by drop-wise addition of 1.6M MeLi in Et₂O (3.4 mL, 5.51 mmol) at 0°C for 10 min. The reaction mixture was stirred at 0°C for 1h, resulting in a colorless solution of Li⁺[CuMe₂]⁻. To this solution was added Si(OMe)₄ (0.4 gm, 2.62 mmol) in Et₂O (5 mL) over 10 min at 0°C, and the reaction mixture was stirred for additional 2 h at 23°C. The solid by-product was filtered out and the volatile Et₂O was evaporated-off. The colorless liquid obtained was used for quantification (GC) as well as characterization (GC-MS) that showed the selective formation of both Me₂Si(OMe)₂ and MeSi(OMe)₃, as the organo-functional silane. Quantitative analysis showed Si(OMe)₄ conversion of 55% with selectivity for Me₂Si(OMe)₂ (67%) and MeSi(OMe)₃ (32%) as well as trace amounts of Me₂-siloxanes.

[0026] Example 2 - A Schlenk tube (50mL) was charged with CuI (0.5 gm, 2.62 mmol) and Et₂O (10 mL) followed by drop-wise addition of 1.6M MeLi in Et₂O (3.4 mL, 5.51 mmol) at 0°C for 10 min. The reaction mixture was stirred at 0°C for 1h, resulting in a

colorless solution of $\text{Li}^+[\text{CuMe}_2]^-$. To this solution was added MeSiCl_3 (0.39 gm, 2.61 mmol) in Et_2O (5 mL) over 10 min at 0°C , and the reaction mixture was stirred for additional 2 h at 23°C . The solid by-product was filtered out from the solution mixture. The colorless liquid obtained was used for quantification (GC) and the product identity was confirmed by GC-MS. Quantitative analysis showed MeSiCl_3 conversion of 89% with selectivity for Me_4Si (0.7%), Me_3SiCl (13%), Me_2SiCl_2 (84%) and SiCl_4 (2.8%).

[0027] Example 3 - A Schlenck tube (50mL) was charged with CuI (0.5 gm, 2.62 mmol) and Et_2O (10 mL) followed by drop-wise addition of 1.6M MeLi in Et_2O (3.4 mL, 5.51 mmol) at 0°C for 10 min. The reaction mixture was stirred at 0°C for 1h, resulting in a colorless solution of $\text{Li}^+[\text{CuMe}_2]^-$. To this solution was added MeHSiCl_2 (0.30 gm, 2.61 mmol) in Et_2O (5 mL) over 10 min at 0°C , and the reaction mixture was stirred for additional 2 h at 23°C . The solid by-product was filtered out from the reaction mixture. The colorless liquid obtained was used for quantification (GC) and the product identity was confirmed by GC-MS. Quantitative analysis showed MeHSiCl_2 conversion of 45% with selectivity for Me_3SiH (88%), Me_2HSiCl (2%) and Me_2SiCl_2 (10%).

[0028] Example 4 – As described above, a solution of $\text{Li}^+[\text{CuMe}_2]^-$ in Et_2O was prepared and then transferred into a head-space vial containing chemical grade silicon (50.0 mg, <100 micron size) from Dow Corning Alabama under an inert atmosphere. The reaction mixture was stirred at 23°C for 2 h, resulting into a slurry mixture. The vial containing the reaction mixture was heated at 50°C for 5 min and using a gas-tight syringe, the volatiles were injected into a GC-MS. The data showed production of organo-functional silanes identified as Me_4Si , $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3$ and $\text{Me}_3\text{Si}(\text{SiMe}_2)_2\text{SiMe}_3$.

[0029] Comparative Example 5 – A sample of direct process mass containing chemical grade silicon and [5% CuCl + promoters (Sn, Zn, P in ppm concentration)] was made independently. As described above, a solution of $\text{Li}^+[\text{CuMe}_2]^-$ in Et_2O was prepared and then transferred into a head-space vial containing direct process catalyst package mass (silicon + catalyst package (50.0 mg, <100 micron size)) under an inert atmosphere. The reaction mixture was stirred at 23°C for 2 h, resulting into a slurry mixture. The vial containing the reaction mixture was heated at 50°C for 5 min and using a gas-tight syringe, the volatiles were injected into a GC-MS. The data showed no production of an organo-functional silane.

[0030] Comparative Example 6 – A sample of direct process mass was obtained. The direct process mass contained 95% chemical grade silicon and 5% of a combination of

CuCl and promoters (Sn, Zn, and P, each in ppm concentrations) was activated by heating the direct process mass under nitrogen at 300 °C for 2 h. As described above, a solution of Gilman reagent, $\text{Li}^+[\text{CuMe}_2]^-$ in Et_2O , was prepared and then transferred into a head-space vial containing the activated direct process silicon mass (50.0 mg, <100 micron size) under an inert atmosphere. The reaction mixture was stirred at 23 °C for 2 h, resulting into a slurry mixture. The vial containing the reaction mixture was heated at 50 °C for 5 min. Using a gas-tight syringe, the volatiles were injected into a GC-MS. The data showed no production of an organo-functional silane.

[0031] A process for preparing a reaction product comprising an organo-functional silane, is described herein. The process comprises:

- (1) forming an organometallic cuprate of formula $\text{M}^+[\text{CuR}_2]^-$, where M represents a metal atom selected from metals of group 1 and group 2 of the periodic table, and each R is independently a monovalent organic group; and
- (2) reacting the organometallic cuprate and a silicon precursor. Without wishing to be bound by theory, it is thought that in comparative examples 5 and 6, the Cl (halide) present in the direct process mass formed MeCl with the Me₂ from the Gilman reagent of formula $\text{Li}^+[\text{CuMe}_2]^-$, rather than the desired reaction in step (2) to react the Me group onto the silicon atom. Direct process mass is the starting material for the Mueller-Rochow direct process to make organohalosilanes and hydrohalosilanes. Without wishing to be bound by theory, it is thought that direct process mass is not suitable for use as the silicon precursor in the process described herein. Alternatively, the ingredients used in step (2) of the process may be free of copper halide, such as CuCl. Alternatively, the ingredients used in step (2) may be free of metal halides.

CLAIMS

1. A process for preparing a reaction product comprising an organo-functional silane, where the process comprises:
 - (1) forming an organometallic cuprate of formula $M^+[CuR_2]^-$, where M represents a metal atom selected from metals of group 1 and group 2 of the periodic table, and each R is independently a monovalent organic group; and
 - (2) reacting the organometallic cuprate and a silicon precursor.
2. The process of claim 1, where step (1) and/or step (2) is performed in the presence of a solvent.
3. The process of claim 2, where the solvent comprises an ether.
4. The process of any one of claims 1-3, where M is selected from Li, Mg, and Na, and each R is a monovalent hydrocarbon group.
5. The process of any one of claims 1-4, where the organometallic cuprate is formed by a method comprising reacting ingredient (i) and ingredient (ii) in the presence of the solvent, where ingredient (i) is an organometallic compound of formula R_cM , where subscript c is an integer from 1 to maximum valence of M, and ingredient (ii) is a copper (I) precursor of formula CuR^5 , where R^5 is a displaceable substituent, which is capable of reacting with the metal atom selected for M, thereby preparing the organometallic cuprate *in situ*.
6. The process of any one of the preceding claims, where the silicon precursor is a silane of formula: $R^1_{(4-n)}SiR^2_n$, where subscript n is an integer from 0 to 3, each R^1 is independently selected from a halogen atom and a group of formula QR^3 , where Q is selected from NH, O, and S, and R^3 is a monovalent hydrocarbon group, and each R^2 is independently selected from H and a monovalent hydrocarbon group.
7. The process of claim 6, where n is 0, and R^1 is OR^3 .
8. The process of claim 7, where the organo-functional silane has formula $R_xSi(OR)_{(4-x)}$, where subscript x is an integer from 1 to 3.
9. The process of claim 6, where the organo-functional silane has formula

$R_mSiR^1_nR^2_{(4-m-n)}$, where subscript m is an integer from 1 to 3, and $(m + n) \leq 4$.

10. The process of any one of claims 1-5, where the silicon precursor is silicon metal.

11. The process of claim 10, where the organo-functional silane has formula R_ySi_z , where subscript y is an integer of 4 or more, subscript z is an integer of 1 or more, and $y = (2z + 2)$.

12. The process of any one of the preceding claims, where the reaction product further comprises a solid side product.

13. The process of any one of claims 6-9, further comprising (3) recovering the organo-functional silane from the reaction product.

14. The process of claim 13, further comprising (4) hydrolyzing, and optionally condensing, the organo-functional silane.

15. A silicone product prepared by the process of claim 14.

16. The process of claim 10 or claim 11, further comprising chemical vapor deposition of the organo-functional silane.

17. A silicon carbide product prepared by the process of claim 16.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/060821

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C07F1/08 C23C16/32	C07F7/08 C08L83/00
	C07F7/12	C07F7/18
		C23C16/24
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C07F C23C C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	A. ALEXAKIS ET AL: "Vinyl-Copper Derivatives; X 1 . Alkylation of (Z)-Dialkenylcuprates", SYNTHESIS, vol. 1979, no. 10, 1 January 1979 (1979-01-01), pages 826-830, XP055093502, ISSN: 0039-7881, DOI: 10.1055/s-1979-28851	1-6,8,9, 12-14
A	compound 1 column 1, line equation 1 table 2 entry 17 (18) table 3 entry 20 (21) ----- -/-	7,10,11, 15-17
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 8 January 2014		Date of mailing of the international search report 15/01/2014
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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/060821

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	BRATOVANOV S ET AL: "A chiral (alkoxy)methyl-substituted silicon group as an auxiliary for the stereoselective cuprate addition to alpha,beta-unsaturated ketones: synthesis of (R)-phenyl 2-phenylpropyl ketone", TETRAHEDRON ASYMMETRY, PERGAMON PRESS LTD, OXFORD, GB, vol. 8, no. 10, 22 May 1997 (1997-05-22), pages 1587-1603, XP004064069, ISSN: 0957-4166, DOI: 10.1016/S0957-4166(97)00134-1	1-5, 12-14
A	* scheme 2 * page 1594, paragraph 2.1 - paragraph 2.2 page 1594, paragraph 3.1	6-11, 15-17
X	----- WO 2008/152666 A1 (GALILEO AVIONICA SPA [IT]; TAGLIONI GIOVANNI [IT]; NOVELLA LUCA [IT]) 18 December 2008 (2008-12-18) abstract -----	15-17

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Information on patent family members

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WO 2008152666	A1	18-12-2008	NONE
