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(54) Title: OXYGENATE REMOVAL FROM ORGANOMETALLIC COMPOUNDS

(57) Abstract: This invention provides a process for removing oxygenated impurities from an organometallic compound. The process is conducted in an inert environment, and comprises contacting the organometallic compound and at least one deoxygenating agent, to form a mixture comprising a deoxygenated organometallic compound; and separating at least a portion of the deoxygenated organometallic compound from any solids present in said mixture to form a purified organometallic compound. The deoxygenating agent is either a hydrated inorganic compound or a hydrated organic compound, and the organometallic compound is represented by the formula R_3M in which M is aluminum, gallium, or indium, and each R is, independently, a hydrogen atom, a C_1-C_{12} alkyl group, a C_6-C_{14} aryl group, or a C_7-C_{16} aryl-alkyl group, with the proviso that at least one of R is not a hydrogen atom.

OXYGENATE REMOVAL FROM ORGANOMETALLIC COMPOUNDS

TECHNICAL FIELD

[0001] This invention relates to removal of oxygenates from organometallic compounds, especially from trihydrocarbyl organometallic compounds.

BACKGROUND

[0002] Hydrocarbyl compounds of aluminum, gallium, and indium, especially the trialkyl compounds, are useful in electronics applications, in particular for chemical vapor deposition (CVD) of aluminum, indium, or gallium and for aluminum-containing, indium-containing, or gallium-containing films. For such electronics applications, the substances used must be relatively free of impurities. Such impurities include organosilicon, alkylated metal alkoxides, other alkylated metallic compounds such as hydrides or halides of Ti, Fe, Cu Na, etc., and hydrocarbon solvents. Of these the most difficult ones to remove are the alkylated metal alkoxides, which are often inevitably formed, even during a purification process.

[0003] One method for removing impurities from organometallic compounds is taught in U.S. 4,650,895, which describes addition of water to a solution of an organometallic compound, especially to less reactive higher alkylated organometallic compounds, to effect partial hydrolysis of the organometallic compound and thereby afford removal of metallic impurities from the organometallic compound. It should be noted that direct addition of water to trimethylaluminum (TMA), whether the TMA is neat or in solution, is inherently dangerous in terms of reactivity and often very explosive. GB 2432364 to Rohm and Haas describes the removal of oxygenates from R_3Al in the presence of a catalyst composition ($AlCl_3$, KF, etc.) and a higher alkylaluminum. Other sources of oxygenates in electronic materials application are ether adducts (solvent). In fact, R.W. Freer et al. (*Adv. Mater.*, 1995, 7, 478-481) showed that oxygen contamination in AlGaAs grown by CBE could be correlated directly with traces of diethyl ether in the R_3Ga precursor. Similarly, J.S. Roberts et al. (*J. Cryst. Growth*, 1998, 195, 668-675) identified ether as the main source of oxygen in AlInAs layers grown for metalorganic vapor phase epitaxy (MOVPE). These types of oxygenates are often removed by fractional distillation.

[0004] Oxygen, if present in any of the aluminum, gallium, or indium source compounds, becomes incorporated into the crystal lattice of the film being grown, where the oxygen interferes with the electronic behavior of the film. Accordingly, methods for providing organometallic compounds having very low oxygen content are desired.

SUMMARY OF THE INVENTION

[0005] This invention provides processes for removing oxygenated impurities from organometallic compounds. The process is straightforward, effective, and involves relatively inexpensive reagents. Advantageously, the oxygenated impurities can be removed without introducing substances that are difficult to separate from the organometallic compounds.

[0006] An embodiment of this invention is a process for removing oxygenated impurities from an organometallic compound. The process is conducted in an inert environment, and comprises contacting the organometallic compound and at least one deoxygenating agent, to form a mixture comprising a deoxygenated organometallic compound; and separating at least a portion of the deoxygenated organometallic compound from any solids present in said mixture to form a purified organometallic compound. The deoxygenating agent is either a hydrated inorganic compound or a hydrated organic compound, and the organometallic compound is represented by the formula

$$R_3M$$

in which M is aluminum, gallium, or indium, and each R is, independently, a hydrogen atom, a C_1-C_{12} alkyl group, a C_6-C_{14} aryl group, or a C_7-C_{16} aryl-alkyl group, with the proviso that at least one of R is not a hydrogen atom.

[0007] Other embodiments of this invention include purified organometallic compounds formed by the processes of this invention.

[0008] These and other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0009] Typically, the inert environment in which the processes of this invention are conducted is a moisture-free, oxygen free environment such as argon, nitrogen or helium. It is preferred that the components used in the processes of this invention as well as the resultant products of the processes be handled in an inert environment. The operations described herein are conducted under conventional inert atmospheres using suitably anhydrous materials.

[0010] As used throughout this document, the term "substantial absence" indicates that the substances or types of substances, except for adventitious impurities, are not present during, or introduced into, the processes of this invention.

[0011] Without wishing to be bound by theory, exposure of organometallic compounds to molecular oxygen (O_2) forms hydrocarbyl metal hydrocarbyloxides (*e.g.*, an alkyl aluminum alkoxide) from the at least some of the organometallic compounds. In terms of the formula R_3M, some of the R groups react with O_2 to form OR groups (oxygenates). To remove the hydrocarbyl metal hydrocarbyloxides, which are contaminants or impurities in electronic applications, from the organometallic compounds, the deoxygenating agent reacts directly with or complexes the hydrocarbyl metal hydrocarbyloxides and/or forms a small amount of aluminoxanes, galloxanes, or indinoxanes, which are believed to sequester hydrocarbyl metal hydrocarbyloxides.

[0012] This invention provides processes for removing oxygenated impurities from an organometallic compound. The process is conducted in an inert environment, and comprises contacting the organometallic compound and at least one deoxygenating agent, to form a mixture comprising a deoxygenated organometallic compound; and separating at least a portion of the deoxygenated organometallic compound from any solids present in said mixture to form a purified organometallic compound.

[0013] The deoxygenating agent is either a hydrated inorganic compound or a hydrated organic compound.

[0014] The deoxygenating agents used in the practice of this invention are at least one hydrated inorganic compound and/or at least one hydrated organic compound. These compounds generally lose their water of hydration relatively easily.

[0015] The hydrated inorganic compounds are hydrates of alkali metal hydroxides or alkaline earth metal hydroxides, hydrates of inorganic salts, and hydrated or partially hydrated inorganic oxides.

[0016] Suitable hydrated alkali metal hydroxides or alkaline earth metal hydroxides include lithium hydroxide monohydrate, sodium hydroxide monohydrate and dihydrate, potassium hydroxide dihydrate, barium hydroxide octahydrate, calcium hydroxide hydrates, magnesium hydroxide hydrates, and cesium hydroxide monohydrate, and the like. Preferred hydroxides are the alkali metal hydroxides, especially lithium hydroxide monohydrate.

[0017] Suitable hydrated inorganic salts include hydrated sulfate salts and hydrated chlorides, such as hydrated copper sulfate, hydrated aluminum sulfate, hydrated iron(III) sulfate, hydrated lithium chloride, hydrated aluminum chloride, and the like.

[0018] Suitable hydrated or partially hydrated inorganic oxides include hydrates of alumina, silica, aluminosilicates (zeolites or molecular sieves), and the like. Molecular sieves with

larger pore sizes (*e.g.*, 5 Å or 10Å) are preferred. A preferred inorganic oxide is alumina (wet alumina).

[0019] Hydrated organic compounds include gas hydrates and wet hydrocarbons. Gas hydrates suitable for use in this invention include hydrated carbon dioxide, hydrated methane, hydrated ethane, hydrated propane, hydrated isobutane, and the like. Wet hydrocarbons that can be used in the practice of this invention include hydrated pentane, hydrated cyclopentane, hydrated hexanes, hydrated octane, hydrated benzene, hydrated toluene, and the like. The use of gas hydrates and/or certain wet hydrocarbons may introduce impurities that are difficult to separate from the organometallic compound.

[0020] The organometallic compound is represented by the formula

$$R_3M$$

in which M is aluminum, gallium, or indium, and each R is, independently, a hydrogen atom, a C_1-C_{12} alkyl group, a C_6-C_{14} aryl group, or a C_7-C_{16} aryl-alkyl group, with the proviso that at least one of R is not a hydrogen atom.

[0021] In the practice of this invention, the organometallic compound is represented by the formula R_3M in which M is aluminum, gallium, or indium, preferably aluminum; and each R is, independently, a hydrogen atom, a C_1-C_{12} alkyl group, a C_6-C_{14} aryl group with or without one or more alkyl substituents, or a C_7-C_{16} aryl-alkyl group with or without one or more alkyl substituents, with the proviso that at least one of R is not a hydrogen atom. The alkyl groups may be straight-chain, branched, or cyclic, preferably a straight-chain. R is preferably a C_1-C_{12} alkyl group, especially a C_1-C_6 alkyl group, more preferably a methyl or ethyl group, especially a methyl group.

[0022] Suitable organometallic compounds when M is aluminum include trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, tripentylaluminum, tricyclopentylaluminum, trihexylaluminum, tricyclohexylaluminum, tri(methylcyclohexyl)aluminum, triheptylaluminum, trioctylaluminum, trinonylaluminum, tridecylaluminum, tri(undecyl)aluminum, tri(dodecyl)aluminum, triphenylaluminum, tritolylaluminum, trixylylaluminum, tri(ethylphenyl)aluminum, trinaphthylaluminum, tribenzylaluminum, dimethylaluminum hydride, diethylaluminum hydride, methylaluminum dihydride, ethylaluminum dihydride, dipropylaluminum hydride, diisobutylaluminum hydride, isobutylaluminum dihydride, dicyclohexylaluminum hydride, diphenylaluminum hydride, phenylaluminum dihydride, ditolylaluminum hydride, tolylaluminum dihydride, dinaphthylaluminum hydride, naphthylaluminum dihydride, dibenzylaluminum hydride,

benzylaluminum dihydride, and the like, including mixtures of any two or more of the foregoing. Preferred are the trialkylaluminum compounds, especially those having one to six carbon atoms. More preferred are trimethylaluminum and triethylaluminum, particularly trimethylaluminum.

[0023] Suitable organometallic compounds when M is gallium include trimethylgallium, triethylgallium, tripropylgallium, triisobutylgallium, tripentylgallium, tricyclopentylgallium, trihexylgallium, tricyclohexylgallium, tri(methylcyclohexyl)gallium, triheptylgallium, trioctylgallium, trinonylgallium, tridecylgallium, tri(undecyl)gallium, tri(dodecyl)gallium, triphenylgallium, tritolylgallium, trixylylgallium, tri(ethylphenyl)gallium, trinaphthylgallium, tribenzylgallium, dimethylgallium hydride, diethylgalllium hydride, methylgallium dihydride, ethylgallium dihydride, dipropylgallium hydride, diisobutylgallium hydride, isobutylgallium dihydride, dicyclohexylgallium hydride, diphenylgallium hydride, phenylgallium dihydride, ditolylaluminum hydride, tolylgallium dihydride, dinaphthylgallium hydride, naphthylgallium dihydride, dibenzylgallium hydride, benzylgallium dihydride, and the like, including mixtures of any two or more of the foregoing. Preferred are the trialkylgallium compounds, especially those having one to six carbon atoms. More preferred are trimethylgallium and triethylgallium, particularly triethylgallium.

[0024] Suitable organometallic compounds when M is indium include trimethylindium, triethylindium, tripropylindium, triisobutylindium, tripentylindium, tricyclopentylindium, trihexylindium, tricyclohexylindium, tri(methylcyclohexyl)indium, triheptylindium, trioctylindium, trinonylindium, tridecylindium, tri(undecyl)indium, tri(dodecyl)indium, triphenylindium, tritolylindium, trixylylindium, tri(ethylphenyl)indium, trinaphthylindium, tribenzylindium, dimethylindium hydride, diethylindium hydride, methylindium dihydride, ethylindium dihydride, dipropylindium hydride, diisobutylindium hydride, isobutylindium dihydride, dicyclohexylindium hydride, diphenylindium hydride, phenylindium dihydride, ditolylindium hydride, tolylindium dihydride, dinaphthylindium hydride, naphthylindium dihydride, dibenzylindium hydride, benzylindium dihydride, and the like, including mixtures of any two or more of the foregoing. Preferred are the trialkylindium compounds, especially those having one to six carbon atoms. More preferred are trimethylindium and triethylindium, particularly trimethylindium.

[0025] Regarding the formulae for the organometallic compounds, especially the aluminum compounds, it is known that the empirical formulae are often not an accurate representation of the actual structure. The scope of this invention includes organometallic compounds of

various structures that are represented by the empirical formula and names set forth in this disclosure.

[0026] The organometallic compounds in the process of this invention typically have less than about 5 wt%, preferably less than 2.5 wt%, more preferably less than 1 wt%, still more preferably less than about 0.5 wt% of metallic impurities, and most preferably less than about 0.25 wt% of metallic impurities, which metallic impurities generally include titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and the like.

[0027] In the processes of this invention, the amount of deoxygenating agent depends on the amount of oxygen-containing impurities in the organometallic compound, and the amount of water in the deoxygenating agent. The deoxygenating agent is generally used in an amount of about 30 wt% or less, *e.g.*, about 0.1 wt% to about 30 wt%, preferably about 5 wt% or less, *e.g.*, 0.1 wt% to about 5 wt%, and more preferably about 3 wt% or less, *e.g.*, about 0.1 wt% to about 3 wt%, relative to the organometallic compound. The deoxygenating agent is still more preferably about 0.25 wt% to about 1.5 wt% relative to the organometallic compound. When two or more deoxygenating agents are used, the amount refers to the total amount of deoxygenating agent(s) used. As more deoxygenating agent is used, more of the organometallic compound may be lost. Thus it is advantageous to use as little deoxygenating agent as possible. While larger amounts of deoxygenating agent are more likely to remove all of the oxygen-containing impurities, as more deoxygenating agent is used, more of the organometallic compound is consumed.

[0028] For the processes of this invention, the temperature is generally in the range of about −20°C to about 140°C. Preferably, the temperature is in the range of about −5°C to about 40°C, more preferably in the range of about 5°C to about 30°C. Ambient temperatures (about 18°C to about 25°C) are often preferred.

[0029] Normally and preferably, the processes of this invention are conducted in the absence of solvent, because any solvent introduced will need to be separated from the organometallic compound. Preferably, there is less than about 0.5 mole of solvent per mole of organometallic compound; more preferably, less than about 0.25 mole, still more preferably, less than about 0.10 mole, even more preferably less than about 0.05 mole, especially preferably less than about 0.01 mole of solvent per mole of organometallic compound. Most preferably, the processes of this invention are conducted in the substantial absence of solvent.

[0030] For the contacting of the components of the process, it is recommended and preferred that the deoxygenating agent is added to the organometallic compound. Other methods can be used, such as co-feeding the organometallic compound and the deoxygenating agent. In at least some instances, the contacting should be gradual, to minimize heat evolution due to the exothermicity of the reaction.

[0031] The processes of this invention are preferably conducted at atmospheric pressure, although subatmospheric or superatmospheric pressure can be employed if needed or desired.

[0032] In the processes of this invention, mixtures are formed, which typically contain a deoxygenated organometallic compound and solids. Often, a small amount of aluminoxane, galloxane, or indinoxane will be present. The deoxygenated organometallic compound can be separated from the solids by conventional methods such as decantation, filtration, and/or distillation. Preferred methods include a separation step such as decantation followed by distillation of the organometallic compound. After separating the deoxygenated organometallic compound from any solids present in said mixture, a purified organometallic compound is obtained.

[0033] The purified organometallic compound preferably has an oxygenate content of about 5 ppm or less, more preferably about 2.5 ppm or less, still more preferably about 1 ppm or less, as measured spectroscopically.

[0034] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention.

[0035] All experiments of these Examples were carried out under inert atmosphere conditions, using Schlenk glassware and vacuum line, in conjunction with a N_2 drybox. Solvents were dried using standard methods with extra care to ensure the absence of dissolved oxygen. Filtration and vacuum distillation were performed inside a N_2 drybox, and volatiles were collected in a trap at –78°C. Reduction of oxygenate levels (as R_2AlOR, especially Me_2AlOMe) were determined by NMR methods by calculating their presence as oxygen content in parts per million (ppm). The oxygen content is reported as a ppm value for oxygen atoms, sometimes indicated by the notation [TMA-OMe (O)]. The water content of the wet alumina was determined by oven Karl Fischer (OKF) titration.

EXAMPLE 1

Partially Purified TMA (6 ppm oxygen) and LHM

[0036] Lithium hydroxide monohydrate (LHM, 0.24 g) was added to trimethylaluminum (TMA, 15.6 g) at room temperature (RT) during 2 hours. The mixture obtained was heated at 80°C with stirring for 3 hours. After cooling, the mixture was filtered, and the product (14.4 g, 92 % recovery) was analyzed and determined by ^{1}H NMR to contain <0.2 ppm oxygenates as oxygen atoms.

EXAMPLE 2

Crude TMA (70 ppm oxygen) and LHM

[0037] LHM (12 g) was added to TMA (240 g) at RT during about 2 hours. The mixture was heated at 80°C for 4 hours and allowed to cool to RT. The mixture was then filtered to obtain a clear colorless product (210 g, 87.5 % recovery). ^{1}H NMR showed that the product contained <0.2 ppm oxygen.

EXAMPLE 3

Crude TMA (44 ppm oxygen) and wet alumina

[0038] Wet alumina (1.6 g; 32 wt% H_2O) was added to TMA (52 g) at RT during 30 minutes, and allowed to stir at RT overnight. The mixture was then filtered to obtain a clear colorless product (49 g, 94 % recovery). The product was analyzed by ^{1}H NMR and found to contain <0.2-ppm oxygen.

EXAMPLE 4

Crude TMA (143 ppm oxygen) and wet alumina

[0039] Wet alumina (20 g) was added in batches during about 1 hour to TMA (200 g). The mixture was then stirred at RT for 2 hours, after which it was heated at 80°C with stirring for 5 hours. After cooling to RT, the mixture was filtered to obtain a clear colorless product (188 g, 94 % recovery). ^{1}H NMR analysis showed the product has less than 0.2 ppm oxygen.

EXAMPLE 5

TMA (5 ppm oxygen) and wet molecular sieves (aluminosilicate)

[0040] Molecular sieves (13X (10Å pore size), 2.0 g, 24.4 wt% H_2O, pellets) were added all at once to TMA (40 g) at room temperature. Next, the mixture was heated at 35°C for 4

hours with stirring, cooled to room temperature, and then filtered to obtain a clear, colorless product (38 g, 95% recovery). The product was analyzed by ^{1}H NMR and found to contain less than 0.2 ppm oxygen.

COMPARATIVE EXAMPLE

Direct water addition to TMA

[0041] An attempt to repeat Example 1 was made by replacing LHM with water. An addition of water directly to the TMA at –25°C was aborted, because even at such a low temperature, the reaction was dangerously violent.

[0042] To minimize the violence of the reaction, the TMA was diluted with toluene (16 g). Ordinarily it is counterintuitive to add an hydrocarbon since this will have to be removed prior to use in electronic applications. Water (0.2 g) was added during about 4 hours. Lots of solid was produced. ^{1}H NMR of the supernatant of this mixture showed about the same oxygen content as the starting material.

[0043] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

[0044] The invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[0045] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[0046] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0047] Each and every patent or other publication or published document referred to in any portion of this specification is incorporated *in toto* into this disclosure by reference, as if fully set forth herein.

[0048] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

CLAIMS:

1. A process for removing oxygenated impurities from an organometallic compound, which process is conducted in an inert environment, and comprises

a) contacting said organometallic compound and at least one deoxygenating agent, wherein said deoxygenating agent is either a hydrated inorganic compound or a hydrated organic compound, and wherein said organometallic compound is represented by the formula

$$R_3M$$

in which M is aluminum, gallium, or indium, and each R is, independently, a hydrogen atom, a C_1-C_{12} alkyl group, a C_6-C_{14} aryl group, or a C_7-C_{16} aryl-alkyl group, with the proviso that at least one of R is not a hydrogen atom,

to form a mixture comprising a deoxygenated organometallic compound; and

b) separating at least a portion of the deoxygenated organometallic compound from any solids present in said mixture, to form a purified organometallic compound.

2. A process as in Claim 1 wherein when said deoxygenating agent is a hydrated inorganic compound, the hydrated inorganic compound is a hydrated alkali metal hydroxide, a hydrated alkaline earth metal hydroxide, a hydrated inorganic salt, or a hydrated inorganic oxide; and when the deoxygenating agent is a hydrated organic compound, the hydrated organic compound is a gas hydrate or a wet hydrocarbon.

3. A process as in Claim 1 wherein said deoxygenating agent is a hydrated alkali metal hydroxide or a hydrated inorganic oxide.

4. A process as in Claim 1 wherein said deoxygenating agent is lithium hydroxide monohydrate, wet alumina, or an aluminosilicate.

5. A process as in Claim 1 wherein in said organometallic compound, M is aluminum.

6. A process as in Claim 1 or 5 wherein in said organometallic compound, R is a C_1-C_{12} alkyl group.

7. A process as in Claim 1 or 5 wherein in said organometallic compound, R is a C_1-C_6 alkyl group.

8. A process as in Claim 1 or 5 wherein in said organometallic compound, R is a methyl group or an ethyl group.

9. A process as in any of Claims 1-4 wherein said organometallic compound is trimethylaluminum, trimethylgallium, triethylgallium, or trimethylindium.

10. A process as in any of Claims 1-4 wherein said organometallic compound is trimethylaluminum.

11. A process as in Claim 1 wherein said deoxygenating agent is used in an amount of about 30 wt% or less relative to the organometallic compound.

12. A process as in any of Claims 1-11 wherein at least a portion of said deoxygenated organometallic compound is distilled.

13. A process as in any of Claims 1-12 wherein the purified organometallic compound is for use in electronic materials applications.

14. A process as in any of Claims 1-13 wherein said process is conducted in the substantial absence of solvent.

15. A purified organometallic compound formed by the process of Claim 1.

16. A compound as in Claim 15 wherein in said organometallic compound, M is aluminum.

17. A compound as in Claim 15 or 16 wherein in said organometallic compound, R is a C_1-C_{12} alkyl group.

18. A compound as in Claim 15 or 16 wherein in said organometallic compound, R is a C_1-C_6 alkyl group.

19. A compound as in Claim 15 or 16 wherein in said organometallic compound, R is a methyl group or an ethyl group.

20. A compound as in Claim 15 wherein said organometallic compound is trimethylaluminum.

21. A compound as in any of Claims 15-20 which has an oxygenate content, measured as oxygen atoms, of about 5 ppm or less.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/069110

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F5/06
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

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, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 041 583 A (SANGOKOYA SAMUEL A [US]) 20 August 1991 (1991-08-20) examples 1-5 claims 1-12	1-21
X	EP 0 116 319 A2 (SUMITOMO CHEMICAL CO [JP]) 22 August 1984 (1984-08-22) examples 1,2,5,6 (The preliminary reaction) page 7, line 3 - page 9, line 3	1,5-21
X	EP 0 523 525 A1 (JAPAN PIONICS [JP]) 20 January 1993 (1993-01-20) examples 2,3,5,6,8,9,11,12	15-21
X	JP 2006 342101 A (SHINETSU CHEMICAL CO) 21 December 2006 (2006-12-21) examples 1-4	15-21

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

☒ See patent family annex.

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22 January 2014	29/01/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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