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(54) Title: PROCESS TO MAKE METAL COMPLEXES WITH VOLATILE LIQUID METAL COMPOUNDS

(57) Abstract: Processes for making metal complexes that are useful in organic light emitting devices M (OLEDs) involve reacting a volatile liquid metal compound with a compound that has at least one hydroxyl (OH) group, such as 8-hydroxyquinoline. Exemplary volatile liquid metal compounds include trimethylaluminum, triethylaluminum, triisobutylaluminum, diisobutylaluminum hydride, dimethylaluminum chloride, and diethylaluminum chloride. One useful metal complex that can be produced is tris(8-hydroxyquinoline)aluminum (Alq3).

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PROCESS TO MAKE METAL COMPLEXES WITH VOLATILE LIQUID METAL COMPOUNDS

FIELD OF THE INVENTION

[0001] This invention relates to a process of producing metal complexes, such as 8-quinolinoline metal complexes, which can be useful as electroluminescent materials.

BACKGROUND OF THE INVENTION

[0002] An organic light emitting device (OLED) is generally constructed of layers of organic compounds between electrodes. A typical arrangement of such a device is anode/electroluminescent material/cathode. A standard electroluminescent material used in such devices is tris(8-hydroxyquinoline)aluminum ("Alq3"). See, *e.g.*, Appl. Phys Lett., 51, 913 (1987). Substituted 8-quinolinolaluminum and related complexes as well as other metal ligand complexes are also known for use in OLEDs.

[0003] As OLED technology has advanced, purity requirements for electroluminescent materials has increased. See, for example, U.S. Patent No. 6,583,583. Typically, electroluminescent materials are made by (i) reacting low volatility metal salts, such as aluminum carboxylates, alkoxides, and chlorides, with 8-hydroxyquinolinyl or similar compounds, and then (ii) purifying by sublimation.

[0004] Crude materials produced by such conventional processes usually require multiple sublimations to raise the purity to a suitable level. As the technology progresses, conventional sublimation processes alone may not be sufficient to increase the purity to meet future needs. Accordingly, a need exists to provide a process for the production of a crude electroluminescent material that is of sufficient purity that the need for sublimation is either reduced or eliminated.

SUMMARY OF THE INVENTION

[0005] The present invention provides a process for making metal complexes, which may be useful as electroluminescent materials. In particular, the present invention provides a process for making metal complexes by reacting a volatile liquid metal compound having a melting point of less than about 50°C and a vapor pressure of greater than about 50 mmHg at 150°C with a compound comprising at least one hydroxyl (OH) group. The reaction can occur in an organic solvent, such as toluene, or in the gas phase.

[0006] The volatile liquid metal compound may, for example, include metal compounds comprising at least one alkyl, halide, or hydride group, where the alkyl, halide, or hydride group(s) can be the same or different. Examples of volatile liquid metal compounds include: metal alkyl compounds, metal halide compounds, metal hydride compounds, metal alkyl-halide compounds, metal alkyl-hydride compounds, metal halo-hydride compounds, and metal alkyl-halo-hydride compounds. The metal alkyl compounds can, for example, include trimethylaluminum, triethylaluminum, and triisobutylaluminum. The metal alkyl-hydride compounds can, for example, include dimethylaluminum hydride, diethylaluminum hydride, and diisobutylaluminum hydride. The metal alkyl-halo compounds can, for example, include methylaluminum sesquichloride, dimethyaluminum chloride, and diethylaluminum chloride.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The use of Alq3 and other 8-quinolinoline metal complexes in OLED applications has created increased demand for such materials. Current industry practice is to purify the crude materials by multiple pass vacuum sublimations. However, multiple sublimations can be expensive, and are often difficult to scale up to satisfy the increased demands.

[0008] Existing processes to produce these compounds usually use, as starting materials, various low volatility metal salts, such as aluminum carboxylates, alkoxides, and chlorides to react with 8-hydroxyquinoline or similar compounds with hydroxyl moieties or other reactive sites. In contrast, this invention provides a novel process of reacting a volatile liquid metal compound with a compound comprising at least one hydroxyl (OH) group.

[0009] The volatile liquid metal compound preferably reacts quickly, and to the extent possible, completely, with the compound comprising at least one hydroxyl group, and produces light hydrocarbon byproducts that are generally removed easily from the crude reaction product, essentially leaving only the desired product and some unreacted ligand.

[00010] The volatile liquid metal compound may be distilled by conventional methods to high purity before reacting it with a compound comprising at least one hydroxyl group to produce a higher purity crude electroluminescent material. By comparison, compounds commonly used to synthesize metal complexes typically lack the volatility to be good candidates for purification by conventional distillation. For example, aluminum isopropoxide, which is commonly used to synthesize Alq3 (see Synth. and React. in Inorganic and Metal-Organic Chemistry (1999), 29(10), 1747-1767; Indian J. Chem., Section A (1976), 14A(6), 408-9), has a reported melting

point of 118°C and a vapor pressure of 5.25 mmHg at 145-150°C. Other alcoholates and carboxylates employed have similar volatilities.

[00011] In contrast, as illustrated in Table 1, examples of volatile liquid metal compounds that may be used in the present invention are substantially more volatile and, hence, can be more easily purified by conventional distillation.

Table 1

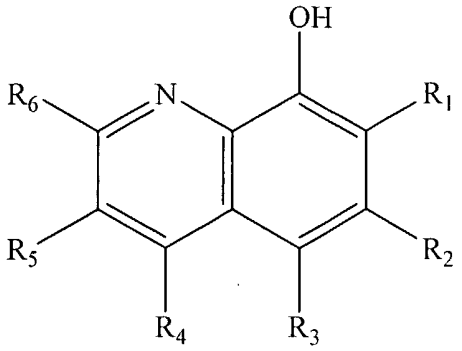
Compound	Melting Point °C	Vapor Pressure at 150°C, mm Hg
Trimethylaluminum	15	1490
Dimethylaluminum Chloride	-21	1444
Triethylaluminum	-46	168
Diethylaluminum Chloride	-74	130
Methylaluminum Sesquichloride	23	923
Ethylaluminum Dichloride	31	181
Ethylaluminum Sesquichloride	-21	149
Triisobutylaluminum	1	128

[00012] In addition, while the process of the invention can be carried out in a solvent, the use of a volatile liquid metal compound can allow for production of electroluminescent compounds in the gas phase, without the need for a solvent.

[00013] As used herein, the term "metal complex" defines compounds of the formula:

$$M(L)_x$$

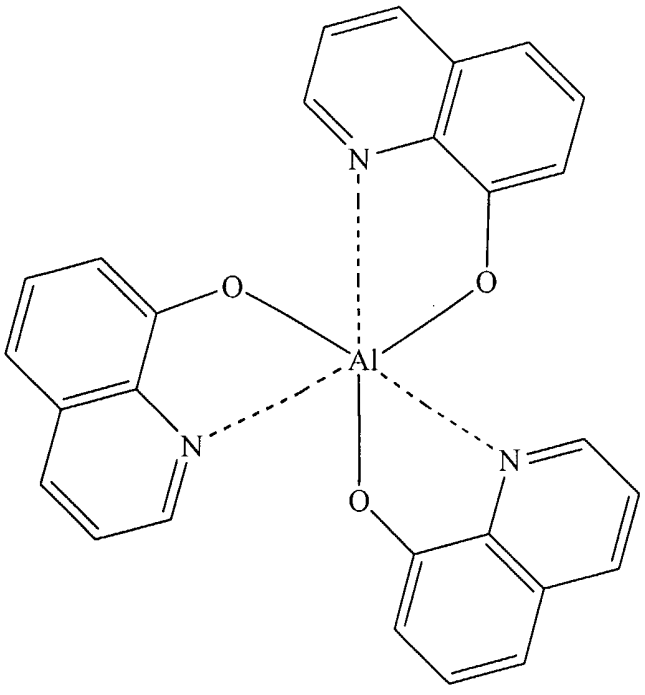
wherein M represents a metal, x represents an integer from 1 to the charge number of the metal cation, such as, for example, from 1 to 3, and L represents a ligand derived from a compound comprising at least one hydroxyl (OH) group, wherein L can be the same or different. An example of a compound comprising at least one hydroxyl (OH) group is a compound represented by Formula I:



I

wherein R_1-R_6 are selected from the group consisting of hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, amino, amido and cyano.

[00014] The metal complex may, for example, include metals (M), such as aluminum, zinc and boron. A particularly preferred metal is aluminum and a particularly preferred ligand is one in which R_1-R_6 in formula I are hydrogen, such that when x is 3, the metal complex is Alq3, as shown in Formula II:



II

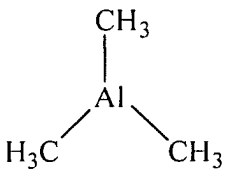
[00015] As used herein the term "compound comprising at least one hydroxyl (OH) group" defines compounds reactive with volatile liquid metal compounds used in the invention, wherein the hydrogen atom of the at least one hydroxyl group is active (i.e., can be removed), allowing for the formation of metal complexes produced by the invention. Examples of such compounds include 3-(2-benzothiazolyl)-4-hydroxy-2H-1-benzopyran-2-one and 4-hydroxyacridine. Preferred compounds include substituted and unsubstituted hydroxyquinolines, including the compound represented by Formula I. By "substituted" is meant compounds of a given structural class where at least one hydrogen atom is replaced by a different substituent, such as, for example, halogen, alkyl, aryl, alkoxy, aryloxy, amino, amido and cyano. A particularly preferred compound is 8-hydroxyquinoline.

[00016] As used herein, the term "volatile liquid metal compound" defines organometallic compounds with melting points less than about 50°C, and vapor pressures of greater than about 50 mmHg at 150°C, and having the general structure

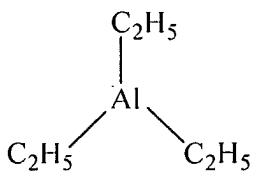
$$M(R)_x$$

wherein R is a group that is reactive with the hydrogen moiety of the at least one hydroxyl group, and x represents an integer from 1 to the charge number of the metal cation, such as, for example, from 1 to 3. Examples of R, which can be the same or different, include alkyl, halide and hydride groups.

[00017] As used herein, the term "metal alkyl compounds" describes, for example, volatile liquid metal compounds having hydrocarbon ligands, which may be the same or different, of the formula C_xH_y wherein x ranges from 1 to 8 and y ranges from 3 to 17. Examples of such compounds include triisobutylaluminum, as well as trimethylaluminum of Formula III and triethylaluminum of Formula IV:



III

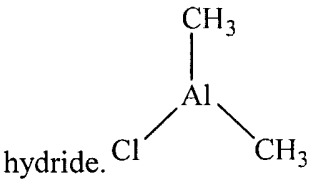


IV

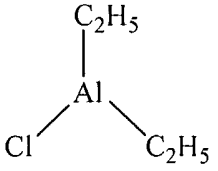
[00018] As used herein, the term "metal halide compounds" describes volatile liquid metal compounds having halogen ligands (F, Cl, Br, I) that may be the same or different.

[00019] As used herein, the term "metal hydride compounds" describes volatile liquid metal compounds having hydrogen (H) ligands.

[00020] As used herein, the term "metal alkyl-halide compounds" describes, for example, volatile liquid metal compounds having at least one hydrocarbon ligand of the formula C_xH_y, wherein x ranges from 1 to 8 and y ranges from 3 to 17, and at least one halogen ligand, wherein each of the hydrocarbon and halogen ligands can be the same or different. Examples of such compounds include methylaluminum sesquichloride and ethylaluminum sesquichloride, as well as dimethylaluminum chloride of Formula V and diethylaluminum chloride of Formula VI:



V



VI

hydride.

[00021] As used herein, the term "metal alkyl-hydride compounds" describes, for example, volatile liquid metal compounds having at least one hydrocarbon ligand of the formula C_xH_y, wherein x ranges from 1 to 8 and y ranges from 3 to 17, and at least one hydrogen ligand, wherein the hydrocarbon ligands can be the same or different. Examples of such compounds include dimethylaluminum hydride, diethylaluminum hydride and diisobutylaluminum

[00022] As used herein, the term "metal halo-hydride compounds" describes volatile liquid metal compounds having at least one halogen ligand, that may be the same or different, and at least one hydrogen ligand.

[00023] As used herein, the term "metal alkyl-halo-hydride compounds" describes volatile liquid metal compounds having at least one hydrocarbon ligand of the formula C_xH_y, wherein x ranges from 1 to 8 and y ranges from 3 to 17, at least one halogen ligand, and at least one hydrogen ligand.

[00024] The volatile liquid metal compound preferably has a high degree of purity. Purification of the volatile liquid metal compound can be performed, for example, by conventional distillation. In this regard, typical purity of commercially available trimethylaluminum is illustrated in Table 2.

Table 2

98-99 wt% trimethylaluminum
1-2 wt% hydrocarbon
trace metals (>20 ppm): silicon, sodium, iron

[00025] When distilled to high-purity for electronic applications, trimethylaluminum purity can, for example, be at least about 99.99%, or even, for example, at least about 99.9999% based upon the total weight of the volatile liquid metal compound and trace metals (*i.e.*, 0.1 ppm total trace metals). Electroluminescent materials produced from this electronic grade trimethylaluminum and, for example, a purified 8-hydroxyquinoline compound can be expected to contain substantially lower trace metals, thereby reducing or avoiding time consuming purification by sublimation.

[00026] The processes of the invention can be generally conducted with an excess of the compound comprising at least one hydroxyl (OH) group, such as where the molar ratio of the compound comprising at least one hydroxyl (OH) group to the volatile liquid metal compound ranges from about the charge number of the metal cation (x) to 1 to about 1+x to 1, such as from about 3 to 1 to about 4 to 1 when the volatile liquid metal compound is a trialkyl aluminum compound. Following reaction, wash steps can be used to remove the excess of the compound comprising at least one reactive hydroxyl group (OH), as described in the examples below. Finally, product drying is performed to remove residual solvent.

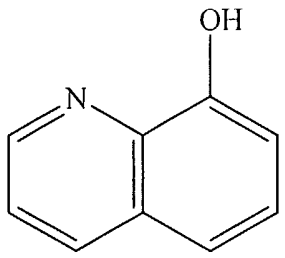
[00027] The compound comprising at least one hydroxyl (OH) group is reacted in excess in order to ensure that all of the substituents on the volatile liquid metal compound are completely reacted with the compound comprising at least one reactive hydroxyl (OH) group. Complete reaction on all of the substituents on the volatile liquid metal compound helps minimize the occurrence of reaction by-products, since many volatile liquid metal compounds are reactive to oxygen and/or water which could be present during the washing and product drying steps.

[00028] The rate at which the volatile liquid metal compound is preferably added to the compound comprising at least one reactive hydroxyl (OH) group is a function of the rate at which the energy of reaction and any gaseous by-products can be removed. If the volatile liquid metal compound is added too quickly, such that the energy of reaction is generated at a rate that is greater than it can be removed, the reaction temperature will increase, which can potentially lead to the formation of increased by-product impurities.

[00029] With proper control of the reaction, the processes of the invention can be conducted neat, with, for example, a solvent that is inert to alkyls such as toluene, or in the gas phase. Other solvents that may be used include any branched or straight-chain aliphatic hydrocarbons (e.g. hexane, heptane, isohexane), other aromatics (e.g. benzene), alkylated aromatics, or mixtures or any of these species (e.g. distillate cuts from a refinery). When conducted in the gas phase at temperatures below about 50°C, an inert carrier gas, such as nitrogen, can be used to volatilize both the volatile liquid metal compound and the compound comprising the at least one reactive hydroxyl (OH) group.

[00030] The processes of the invention can be conducted as a batch process or as a continuous process. These processes, whether batch or continuous, can, for example, be conducted at a temperature ranging from about 0°C to about 100°C, such as from about 0°C to about 50°C, and, for example, at pressures of up to about 1 atmosphere. Higher temperatures can generally be expected to result in increased formation of reaction by-product impurities whereas lower temperatures can result in the need for increased solvent in order to dissolve the compound comprising at least one hydroxyl (OH) group. However, when conducted in the gas phase, higher reaction temperatures, such as those in excess of 100°C, may result in suitably low quantities of by-product impurities due to the generally lower local concentrations of reactants in the gas phase. In addition when a batch process is used, lower reaction temperatures, such as those below 0°C, should not require additional solvent to dissolve the compound comprising at least one hydroxyl (OH) group, since said compound may be charged accurately as a solid in a batch process, as compared to a continuous process where continuous solid feed could lead to poor stoichiometry control.

[00031] For instance, in one embodiment, the present invention provides a process of making Alq3 by reacting triethylaluminum of Formula IV with 8-hydroxyquinoline of formula VII:



VII

in toluene at a temperature ranging from about 0°C to about 40°C.

[00032] In practice, this invention is not limited to 8-hydroxyquinolinyl or aluminum compounds. This invention could also be applied to producing other metal complexes useful for OLED applications such as reacting a zinc dialkyl, such as diethylzinc, with ligands like 3-(2-benzothiazolyl)-4-hydroxy-2H-1-benzopyran-2-one or 4-hydroxyacridine. A wide range of combinations can be produced in which a volatile liquid metal compound is reacted with a ligand having an active hydrogen.

[00033] The processes of the invention can, for example, result in products having a purity, based on the total weight of the metal complex product, of at least about 99.7%, such as at least about 99.9%, when measured by ^{1}H-NMR. When such purity is achieved, the need for sublimation to further purify the reaction product to provide for suitable electroluminescent materials is either reduced or eliminated.

[00034] The following examples further illustrate the present invention. In each of the examples, a Bruker Avance 400 mHz NMR, having an estimated average limit of detection of about 50 ppm, was used for the analysis. The ^{1}H-NMR results reported in the examples, unless otherwise stated, report impurities as "wt% of organic impurities formed during the reaction" and has reference to by-product organic impurities detected in the reaction product. The only other organic impurities detected in the reaction product besides "organic impurities formed during the reaction" were incidental amounts of toluene (solvent) and 8-hydroxyquinoline (reactant). The amounts of such solvent and reactant impurities may generally be expected to constitute less than 0.1% by weight of the total metal complex product, when the washing and product drying steps following the reaction are conducted carefully. In addition, potential non-organic impurities, such as trace metals, can be expected to be relatively negligible (less than 1 ppm or 0.01wt%), provided that the starting volatile liquid metal compound is sufficiently pure.

Example 1

[00035] 50 grams (0.344 mole) of 8-hydroxyquinoline and 26 grams of anhydrous toluene were added to a 250 mL round-bottom flask. The contents of the flask were heated to 70°C. Once the temperature stabilized at 70°C, 8.66 grams (0.0759 mole) of triethylaluminum was added slowly to the round-bottom flask. Temperature was maintained between 80 and 150°C during the addition period. The product slurry was diluted with an additional 40 grams of anhydrous toluene and filtered under ambient conditions. The filtered solids were first washed with 70.8 grams of anhydrous toluene. A second wash was performed with 148.6 grams of anhydrous toluene and the wet cake was dried under vacuum at room temperature.

[00036] ^{1}H-NMR results indicate that about 0.3 to about 0.4wt% of organic impurities formed during the reaction were present in the reaction product

Example 2

[00037] 50 grams (0.344 mole) of 8-hydroxyquinoline and 50 grams of anhydrous toluene were added to a 250 mL round-bottom flask. Once the temperature of the flask contents were stabilized at 25°C, 9.85 grams (0.0863 mole) of triethylaluminum dissolved in 50 grams of anhydrous toluene was added over a 60 minute period to the round-bottom flask. Temperature was maintained between 22 and 80°C during the addition period. The product slurry was filtered under ambient conditions. The filtered solids were first washed with 50.9 grams of anhydrous toluene. A second wash was performed with 96.1 grams of anhydrous toluene and the wet cake was dried under vacuum at room temperature.

[00038] ^{1}H-NMR results indicate that about 0.3 to about 0.4wt% of organic impurities formed during the reaction were present in the reaction product.

Example 3

[00039] 25 grams (0.172 mole) of 8-hydroxyquinoline and 75 grams of anhydrous toluene were added to a 250 mL round-bottom flask. Once the temperature of the contents stabilized at 25°C, 4.93 grams (0.0432 mole) of triethylaluminum dissolved in 25 grams of anhydrous toluene was added over a 55 minute period to the round-bottom flask. Temperature was maintained between 16 and 53°C during the addition period. The product slurry was filtered under ambient conditions. The filtered solids were first washed with 38.6 grams of anhydrous toluene. A second wash was performed with 51 grams of anhydrous toluene and the wet cake was dried under vacuum at room temperature.

[00040] ^{1}H-NMR results indicate that less than about 0.1wt% of organic impurities formed during the reaction were present in the reaction product.

Example 4

[00041] 20.64 grams (0.142 mole) of 8-hydroxyquinoline and 75 grams of anhydrous toluene were added to a 250 mL round-bottom flask. Once the temperature of the contents stabilized at 25°C, 4.93 grams (0.0432 mole) of triethylaluminum, dissolved in 25 grams of anhydrous toluene, was added over a 68 minute period to the round-bottom flask.

Temperature was maintained between 14 and 80°C during the addition period. Above 55°C, the viscosity of the reaction mass substantially increased thus reducing the ability to remove the heat of reaction and causing the temperature to spike to 80°C. The product slurry was filtered under

ambient conditions. The filtered solids were first washed with 49.5 grams of anhydrous toluene. A second wash was performed with 78 grams of anhydrous toluene and the wet cake was dried under vacuum at room temperature.

[00042] ^{1}H-NMR results indicate that about 0.1wt% of organic impurities formed during the reaction were present in the reaction product.

Example 5

[00043] 20.64 grams (0.142 mole) of 8-hydroxyquinoline and 75 grams of anhydrous toluene were added to a 250 mL round-bottom flask. Once the temperature of the flask contents were stabilized at 25°C, 4.93 grams (0.0432 mole) of triethylaluminum, dissolved in 25 grams of anhydrous toluene, was added over a 68 minute period to the round-bottom flask. Temperature was maintained between 20 and 49°C during the addition period. The product slurry was filtered under ambient conditions. The filtered solids were first washed with 50 grams of anhydrous toluene. A second wash was performed with 78 grams of anhydrous toluene and the wet cake was dried under vacuum at 70°C.

[00044] ^{1}H-NMR detected no organic impurities formed during the reaction.

Example 6

[00045] 400 grams (2.76 mole) of 8-hydroxyquinoline and 1400 mL of anhydrous toluene were added to a 3-liter round-bottom flask. Once the temperature of the contents stabilized at 15°C, 79 grams (0.69 mole) of triethylaluminum, dissolved in 465 mL of anhydrous toluene, was added over a 50 minute period to the round-bottom flask. Temperature was maintained between 15 and 40°C during the addition period. The product slurry was filtered under ambient conditions. The filtered solids were first washed with 1200 grams of anhydrous toluene. A second wash was performed with 1200 grams of anhydrous toluene and the wet cake was dried under vacuum at 70°C.

[00046] ^{1}H-NMR detected no organic impurities formed during the reaction.

CLAIMS

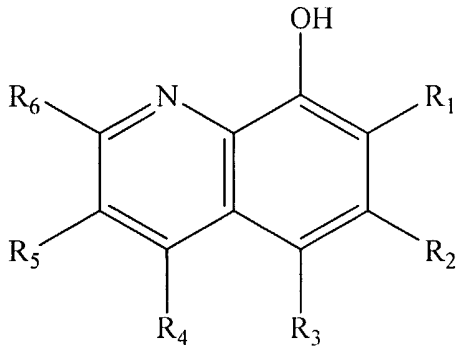
What is claimed is:

1. A reaction product of a volatile liquid metal compound and a compound comprising at least one hydroxyl (OH) group, wherein the purity of the volatile liquid metal compound is at least about 99.99%, based upon the total weight of the volatile liquid metal compound and trace metals.

2. The reaction product of Claim 1, having a purity of at least about 99.7% as measured by ^{1}H-NMR, based on the total weight of the reaction product.

3. The reaction product of Claim 1, wherein the compound comprising at least one hydroxyl (OH) group is selected from substituted and unsubstituted hydroxyquinolines and the volatile liquid metal compound is selected from the group consisting of metal alkyl compounds, metal alkyl-halide compounds, metal alkyl-hydride compounds, metal-halo-hydride compounds, and metal-alkyl-halo-hydride compounds.

4. The reaction product of Claim 3, wherein the compound comprising at least one hydroxyl (OH) group is an 8-hydroxyquinoline compound of Formula I:



I

wherein R_1-R_6 are each selected independently from the group consisting of hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, amino, amido and cyano; and the volatile liquid metal compound is an aluminum compound.

5. The reaction product of Claim 4, wherein R_1-R_6 are hydrogen and the volatile liquid metal compound is selected from the group consisting of trimethylaluminum, triethylaluminum, triisobutylaluminum, dimethylaluminum hydride, diethylaluminum hydride, diisobutylaluminum

hydride, dimethylaluminum chloride, diethylaluminum chloride, methylaluminum sesquichloride and ethylaluminum sesquichloride.

6. The reaction product of Claim 5, wherein the volatile liquid metal compound is triethylaluminum.

7. A process for making metal complexes comprising: reacting a volatile liquid metal compound with a compound comprising at least one hydroxyl (OH) group, wherein the purity of the volatile liquid metal compound is at least about 99.99%, based upon the total weight of the volatile liquid metal compound and trace metals.

8. The process of Claim 7, wherein the purity of the metal complexes is at least about 99.7% as measured by ^{1}H-NMR, based on the total weight of the metal complexes.

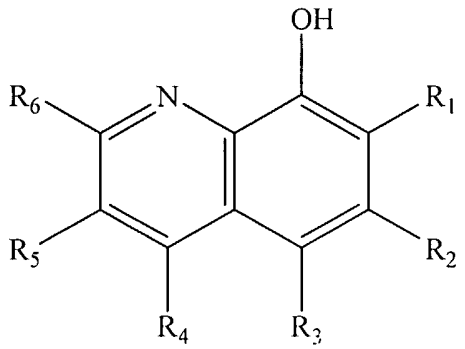
9. The process of Claim 7, wherein the reaction takes place in an organic solvent.

10. The process of Claim 7, wherein the reaction takes place in a gas phase.

11. The process of Claim 7, wherein the compound comprising at least one hydroxyl (OH) group is selected from the group consisting of substituted hydroxyquinolines, unsubstituted hydroxyquinolines, 3-(2-benzothiazolyl)-4-hydroxy-2H-1-benzopyran-2-one and 4-hydroxyacridine.

12. The process of Claim 11, wherein the compound comprising at least one hydroxyl (OH) group is selected from substituted and unsubstituted hydroxyquinolines and the volatile liquid metal compound is selected from the group consisting of metal alkyl compounds, metal alkyl-halide compounds, metal alkyl-hydride compounds, metal-halo-hydride compounds, and metal-alkyl-halo-hydride compounds.

13. The process of Claim 12, wherein the compound comprising at least one hydroxyl (OH) group is an 8-hydroxyquinoline compound of Formula I:



I

wherein R_1-R_6 are each selected independently from the group consisting of hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, amino, amido and cyano; and the volatile liquid metal compound is an aluminum compound.

14. The process of Claim 13, wherein R_1-R_6 are hydrogen and the volatile liquid metal compound is selected from the group consisting of trimethylaluminum, triethylaluminum, triisobutylaluminum, dimethylaluminum hydride, diethylaluminum hydride, diisobutylaluminum hydride, dimethylaluminum chloride, diethylaluminum chloride, methylaluminum sesquichloride and ethylaluminum sesquichloride.

15. The process of Claim 14, wherein the volatile liquid metal compound is triethylaluminum, the reaction takes place in toluene, and the reaction temperature ranges from about 0°C to about 100°C.

16. The process of Claim 11, wherein the compound comprising at least one hydroxyl (OH) group is selected from the group consisting of 3-(2-benzothiazolyl)-4-hydroxy-2H-1-benzopyran-2-one and 4-hydroxyacridinemetal, and the volatile liquid metal compound is a zinc compound.

17. The process of Claim 16, wherein the volatile liquid metal compound is diethylzinc.

18. A process for making metal complexes comprising: reacting a volatile liquid metal compound with a compound comprising at least one hydroxyl (OH) group.

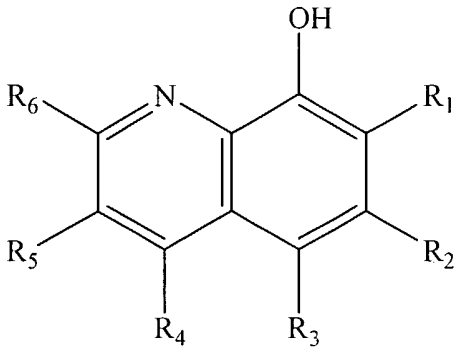
19. The process of Claim 18, wherein the purity of the metal complexes is at least about 99.7% as measured by ^{1}H-NMR, based on the total weight of the metal complexes.

20. The process of Claim 19, wherein the reaction takes place in an organic solvent.

21. The process of Claim 19, wherein the reaction takes place in a gas phase.

22. The process of Claim 18, wherein the compound comprising at least one hydroxyl (OH) group is selected from substituted and unsubstituted hydroxyquinolines and the volatile liquid metal compound is selected from the group consisting of metal alkyl compounds, metal alkyl-halide compounds, metal alkyl-hydride compounds, metal-halo-hydride compounds, and metal-alkyl-halo-hydride compounds.

23. The process of Claim 22, wherein the compound comprising at least one hydroxyl (OH) group is an 8-hydroxyquinoline compound of Formula I:



I

wherein R_1-R_6 are each selected independently from the group consisting of hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, amino, amido and cyano; and the volatile liquid metal compound is an aluminum compound.

24. The process of Claim 23, wherein R_1-R_6 are hydrogen and the volatile liquid metal compound is selected from the group consisting of trimethylaluminum, triethylaluminum, triisobutylaluminum, dimethylaluminum hydride, diethylaluminum hydride, diisobutylaluminum hydride, dimethylaluminum chloride, diethylaluminum chloride, methylaluminum sesquichloride and ethylaluminum sesquichloride.

25. The process of Claim 24, wherein the volatile liquid metal compound is triethylaluminum, the reaction takes place in toluene, and the reaction temperature ranges from about 0°C to about 100°C.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/010505

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D215/40 C09K11/06 C07F5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D C09K

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, 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.
E	WO 2004/073030 A (GEORGIA TECH RES INST ; WECK MARCUS (US); MEYERS AMY (US)) 26 August 2004 (2004-08-26) examples 1,5,7,8,13	1,3,4,7, 9,11-13, 18,20, 22,23
P,Y	ANONYMOUS: "Trimethylaluminum, Product No. 59,77-5, CAS Rn 75-24-1" INTERNET ARTICLE, [Online] XP002309618 Retrieved from the Internet: URL:http://www.sigmaaldrich.com/Brands/Fine_Chemicals/Product_Focus/Organics/Trimethylalu...> [retrieved on 2004-12-03] the whole document	1,3,4,7, 9,11-13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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	Date of mailing of the international search report
10 December 2004	26. 04. 2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Richter, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/010505

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/32717 A1 (SOUTH BANK UNIVERSITY ENTERPRISES LTD., UK) 8 June 2000 (2000-06-08) claims 1-6; examples 1,2	18
X	HOPKINS, T. A. ET AL: "Substituted aluminum and zinc quinolates with blue-shifted absorbance/luminescence bands: synthesis and spectroscopic, photoluminescence, and electroluminescence characterization" CHEMISTRY OF MATERIALS , 8(2), 344-51 CODEN: CMATEX; ISSN: 0897-4756, 1996, XP002309620	1-7,9, 11-15
X	page 350, right hand column: preparation of (2) and (3)	18,22
X	page 351, left hand column : preparation of AlQ3 and ZnQ2	18,22-25
X	page 346, column 1, paragraph 4 - column 2, paragraph 2	1,3,7,9, 12,18,22
X	US 2003/030193 A1 (ISHII KAZUO ET AL) 13 February 2003 (2003-02-13) examples 1,2	1-6,19
Y	"Katalog Handbuch Feinchemikalien und Laborgeräte 2003-2004" 2003, ALDRICH , XP002309934 page 175	1,3,4,7, 9,11-13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2004/010505

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

4-6, 13-15, 23-25; partly: 1-3, 7-12, 18-22

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 4-6,13-15,23-25; partly: 1-3,7-12 18-22

   Reaction of a volatile liquid aluminum compound and a hydroxyquinoline, and a metal complex prepared by this process

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2. claims: partly:1,2, 7-11,18-21

   Reaction of a volatile liquid aluminum compound and a compound comprising at least one hydroxy group other than hydroxyquinoline, and a metal complex prepared by this process

   ---

3. claims: 16,17, partly 1-3,7-12, 18-22

   Preparation process using a volatile liquid metal compound different from aluminium compounds, and a metal complex prepared by this process

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INTERNATIONAL SEARCH REPORT

nation on patent family members

Internal Application No
PCT/US2004/010505

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