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(54) Title: METAL COMPOUND AND PREPARATION METHOD THEREFOR

(57) Abstract: The invention concerns the preparation of a metal chelate, in particular a precious metal β -diketonate or a precious metal phosphine complex ML_aX_b , where M is a metal atom, L is a ligand, X is an anion which is preferably a halide, HCO_3^- , NO_3^- , CO_3^{2-} or carboxylate, a is a number equal to or less than the coordination number of the metal, b is 0, 1, 2 or 3, comprising reacting an ammine compound of metal M with a complexing compound, which is preferably a phosphine or a diketonate. Metal compounds which can be made by this process are also described.

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Metal compound and preparation method therefor

The present invention concerns the preparation of a metal compound, in particular a precious metal β -diketonate or a precious metal phosphine complex.

- 5 Precious metal β -diketonates such as palladium (II) acetylacetonate are used in many chemical processes as catalysts or as components of catalyst systems. Palladium (II) acetylacetonate is typically manufactured from palladium (II) chloride. For example, GB-A-1475834 describes a process comprising dissolving PdCl_2 or a complex tetrachloro-palladinate in hydrochloric acid, reacting the resulting solution with an at least stoichiometric
- 10 amount of acetylacetone, stirring the mixture to a clear solution, then adjusting the pH to from 7 to 8 by gradual addition of aqueous alkali metal hydroxide, separating off the precipitated Pd(II) acetylacetonate, and washing and drying it.

It is an object of the present invention to provide an alternative process for the preparation of

15 precious metal complexes such as precious metal β -diketonates and phosphines. It is a further object of the invention to provide novel precious metal compounds which may be made by the process of the invention.

According to the invention, a process for the preparation of a metal complex ML_aX_b , where M

20 is a metal atom, L is a ligand, X is an anion, a is a number equal to or less than the coordination number of the metal, and b is 0, 1, 2 or 3, , comprises reacting an ammine compound of metal M with a complexing compound.

According to a second aspect of the invention, we provide a metal complex ML_aX_b , where M is

25 a metal atom, L is a ligand, X is an anion, a is a number equal to or less than the coordination number of the metal, and b is 0, 1, 2 or 3. Such metal complexes are preferably made by the process of the invention. Certain of the metal complexes are believed to be novel materials particularly when X is selected from the group consisting of bicarbonate, carbonate, carboxylate, and nitrate, and b is 1, 2 or 3.

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The process of the invention provides a process for the preparation of a palladium complex which does not use palladium dichloride as a starting material. Since PdCl_2 is generally made from an ammine by calcining/ reduction to palladium sponge followed by reaction with chlorine and hydrochloric acid, the use of the process of the invention avoids these additional process

35 steps and has environmental benefits.

The metal M is preferably a precious metal selected from a Group VIII metal, especially ruthenium, rhodium, palladium, osmium, iridium and platinum. More preferably the metal is palladium or platinum, especially palladium.

- 5 X in an anion which is preferably selected from a halide (preferably chloride), bicarbonate, carbonate, carboxylate, or nitrate. By carboxylate, we mean an anion of general formula $R-COO^-$, where R is H or an organic group which is preferably an alkyl group such as methyl or a substituted hydrocarbyl moiety in which the substituents are preferably hydroxyl, or carboxyl. Suitable carboxylate anions include acetate, lactate and citrate. b is a number which satisfies
- 10 the valency of metal m and depends upon the anionic charge on the anion. For example, when M is palladium, it may be Pd(II) or Pd(0). b is therefore 2 or 0 in this case when the anion has a single negative charge.

- The metal ammine compound may be an ionic compound. In this case, the anion is preferably
- 15 selected from a halide (preferably chloride), bicarbonate, carbonate, carboxylate (e.g. acetate, lactate or citrate), or nitrate. Suitable palladium ammine compounds include, $Pd(NH_3)_2Cl_2$, $Pd(NH_3)_4(HCO_3)_2$, $Pd(NH_3)_4(CH_3CO_2)_2$, $Pd(NH_3)_4(NO_3)_2$. $Pd(NH_3)_2Cl_2$ is a particularly preferred metal ammine compound.

- 20 The ligand L is preferably a β -diketonate or a phosphine so that the complexing compound is a β -diketone or a phosphine. The β -diketone is preferably acetyl acetone or an ester of acetoacetic acid. The phosphine may be a monodentate or a bidentate phosphine. Tertiary phosphines are preferred and examples include triphenylphosphine, tricyclohexylphosphine, tri(tert-butyl)phosphine, tris(p-tolyl)phosphine, tris(o-tolyl)phosphine, 1,2-bis(di-
- 25 tertbutylphosphinomethyl)benzene, 1,3-bis(di-tertbutylphosphinomethyl)propane, 1,2-bis(di-phenylphosphinomethyl)benzene, 1,2-bis(di-phenylphosphino)ethane, 1,2-bis(di-phenylphosphino)propane, 1,2-bis(di-phenylphosphino)butane, 1,1'-bis(di-phenylphosphino)ferrocene.
- 30 The reaction is preferably carried out at a temperature in the range from 20°C to 120°C, more preferably from 20°C to 90°C, especially from 50°C to 80°C. It is preferred that the reaction temperature is maintained below the decomposition temperature and so when the metal β -diketonate is known to decompose within the temperature ranges given above, the reaction temperature should be maintained at least 10°C (and preferably at least 20°C) below the
- 35 decomposition temperature.

Preferably the complexing compound is present in the reaction mixture in stoichiometric excess. Preferably the amount of complexing compound in the reaction mixture is calculated to provide a molar excess of at least 10% over the amount required for the stoichiometric

- reaction, more preferably an excess of at least 50%, especially at least 90%. When the ligand L is a phosphine, we prefer to use an excess of phosphine of 10 – 25%. When the metal is reduced in the formation of the product complex (e.g. when the starting ammine compound contains Pd(II) and the resulting complex contains Pd(0)), the reduction may be effected by
- 5 the complexing compound and some excess complexing compound is preferably available in the reaction mixture to accomplish this. When no reduction of the oxidation state of the metal is desired then the phosphine should be used in smaller excess (for example up to about 10% excess).
- 10 The reaction may be carried out in the presence of a solvent. The concentration of the metal ammine compound in the solvent is preferably equivalent to from 5 – 25g of Pd per litre of solution. When water is used as a solvent (especially when a β -diketone is used as the complexing compound) the pH of the solution may be controlled. Acetylacetone is a weak acid and the solution should therefore be kept acidic. The pH of the reaction mixture is
- 15 preferably adjusted and maintained to within a range from 2 to 7. A buffer solution may be added to the reaction mixture. Alternative solvents include alcohols (e.g. methanol, ethanol, propanol, methylated spirits) acetonitrile, tetrahydrofuran, toluene, aliphatic esters such as ethyl acetate and ketones such as methylethyl ketone. Organic solvents are required when the complexing compound is a phosphine. When no reduction of the metal is desired then it
- 20 may be preferable to avoid using reducing solvents such as alcohols.

The reactants may be added in any suitable order, but in a preferred process of the invention the metal ammine compound is placed in a reaction vessel, together with a solvent (if used), an alkali (if used) and a buffer solution (if used), heated if necessary and then the complexing

25 compound is added. The reaction mixture is stirred as appropriate. The reaction may be continued for a period of from 30 minutes to several hours, but is normally complete within about four hours. On completion, the product palladium complex is separated from the reaction mixture by any appropriate method which is dependent upon the physical form of the product. When the product is palladium (II) acetylacetonate, for example, it may be filtered

30 from the supernatant, optionally washed, and dried.

The invention will be further described in the following examples.

Example 1 - 4

- 35 Palladium diammine dichloride (4.35 g Pd, 40.9 mmoles), water (192 ml) and buffer solution (2.79 ml where added) were combined in a jacketed vessel with overhead stirrer. The buffer comprised 2.5 ml, 4.2350 g 87.32% phosphoric acid and 3.4369 g 45.94% sodium hydroxide made up to 25 ml. Acetylacetone, as shown in Table 1, was added and the mixture heated to

the desired temperature. It was maintained at temperature for an hour, then cooled to room temperature and filtered.

Table 1

Example	Moles acac : moles Pd	Temp (°C)	Buffer	IR peak difference 1515-1598 (cm ⁻¹)	Final pH	Product wt (g)	Pd assay	Cl % (w/w)
1	2.2	60	Yes	0.2158	3.79	7.51	45.92	22.03
2	2.2	80	No	0.4477	2.90	8.97	36.58	6.83
3	4	60	No	0.3972	3.14	11.13	45.54	22.73
4	4	80	Yes	0.5676	2.56	12.83	36.05	3.5

- 5 The product was analysed for palladium content and chloride by standard wet chemical analysis. The identity of the product as palladium acetylacetonate was confirmed by infra-red spectroscopy. In the IR spectrum, palladium acetylacetonate gives a strong peak at 1515 cm⁻¹ and palladium diammine dichloride has a strong peak at 1598 cm⁻¹. The difference in peak height was therefore taken as the extent of reaction.

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Example 5 - 8

- Buffer solution (2.5 ml, 4.2350 g 87.32% phosphoric acid and 3.4369 g 45.94% sodium hydroxide made up to 25 ml) and palladium diammine dichloride (11.49 g, 33.86% Pd, 36.6 mmol) were combined in a 250 ml flask fitted with a condenser. Water (163.5 ml) was added. Acetylacetone (4 ml or 7.5 ml, 38.8 or 72.9 mmol) was added either at the start of the reaction or through a peristaltic pump at the desired reaction temperature over 30 minutes. The mixture was stirred and heated to the desired reaction temperature and held at this temperature for an hour. The mixture was cooled to room temperature and filtered. The filter cake was dried overnight in an oven at 60 °C. The pH of the filtrate was measured and the IR spectrum of the product recorded.

Table 2

Example	Acac: Pd mole ratio	Temperature (°C)	Acac Addition rate	IR: 1515-1598 cm ⁻¹
5	1.1	25	Fast	-0.1228
6	1.1	100	Slow	0.4166
7	2.0	25	Slow	-0.0991
8	2.0	100	Fast	0.3521

- It can be seen that when the reaction is performed at 25 °C, there is little or no product formed after one hour. The reaction proceeds faster at 100 °C, however, a dark colouration was noted in samples 6 & 8 and this was attributed to reduction of the palladium compound to palladium metal. Palladium acetylacetonate solutions in organic solvents have been reported to decompose at temperatures in the range 110 – 116 °C, so the observed reduction is likely to have been accelerated by the high temperature used.

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Example 9

Palladium diammine dichloride (4.35 g Pd, 40.9 mmoles) was slurried in water (190 ml) in a jacketed vessel with condenser. Acetylacetone (17 ml, 165 mmoles) was added and the slurry was heated to 70 °C and maintained at this temperature for 7 hours. The slurry was cooled to
5 room temperature and filtered. The solids were washed with water (2 x 200 ml) and dried in an oven at 60°C overnight. Yield was 95%, chloride 0.2% and Pd assay 35%. The solubility of the product was tested by heating 0.125g of product to 48 °C in 10 ml toluene and a clear solution resulted.

10 Example 10

Palladium diammine dichloride was suspended in acetonitrile at reflux for 4 hrs. 1 mole equivalent of triphenylphosphine was added and the mixture refluxed for several hours after which a clear solution was observed. A basic gas (believed to be ammonia) was evolved during the reaction. A further mole equivalent of triphenylphosphine was added and a yellow
15 precipitate formed immediately. This was filtered and dried. The bright yellow crystals were air stable and were identified as $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ by NMR and infra-red spectroscopy.

Example 11

Palladium tetrammine dihydrogencarbonate ($\text{Pd}(\text{NH}_3)_4(\text{HCO}_3)_2$) was reacted with 5 mole
20 equivalents of triphenylphosphine under N_2 in methanol at reflux. A bright yellow precipitate formed after 30 minutes and this was filtered off after a total reaction time of 90 minutes and then dried in a vacuum oven overnight. A basic gas (believed to be ammonia) was evolved during the reaction. It should be noted that some of the triphenylphosphine is used to reduce the Pd(II) starting compound to Pd(0). The yield was 98%, and was identified as $\text{Pd}(\text{PPh}_3)_4$ by
25 NMR and infra-red spectroscopy.

Example 12

Palladium tetrammine dihydrogencarbonate was reacted with 3 mole equivalents of tris(*ortho*-tolyl)phosphine (Po-tol_3) in methanol at reflux under N_2 for 3 hours. The reaction mixture was
30 cooled to 0°C and filtered to give product as bright yellow crystal. The filtrate was evaporated to 10ml, and filtered to give more yellow precipitate. Total yield = 98%. NMR and IR indicate pure product as $\text{Pd}(\text{Po-tol}_3)_2$ (Pd(0)).

Example 13

35 Example 12 was repeated using tricyclohexylphosphine (PCy_3) instead of the tris(*ortho*-tolyl)phosphine. The solvent was removed, a small amount of THF was added to dissolve the product and then hexane was added to form a cream precipitate. This was filtered in air and dried in vacuum at 30°C overnight. Some brown product indicates that the product is not stable in air. NMR shows the presence of $\text{Pd}(\text{PCy}_3)_2$ (Pd(0)).

Example 14

Palladium diammine dichloride and 1 mole equivalent of 1,2bis(diphenylphosphino)ferrocene (dppf) were suspended in acetonitrile at reflux for 4 hrs. A basic gas (believed to be ammonia) 5 was evolved during the reaction. The product was filtered off at room temperature and dried. The product contained 7.29% Fe and 14.44% Pd by standard wet chemical analysis and was identified as Pd(dppf)Cl₂ by infra-red spectroscopy.

Claims

1. A process for the preparation of a metal complex ML_aX_b , where M is a metal atom, L is a ligand, X is an anion, a is a number equal to or less than the coordination number of the metal, and b is 0, 1, 2 or 3, comprises reacting an ammine compound of metal M with a complexing compound.
2. A process as claimed in claim 1, wherein said metal M comprises a precious metal selected from ruthenium, rhodium, palladium, osmium, iridium and platinum.
3. A process as claimed in claim 2, wherein said metal M comprises palladium.
4. A process as claimed in any preceding claim, wherein said ligand L is a β -diketonate and the complexing compound is a β -diketone.
5. A process as claimed in claim 4, wherein said β -diketonate is selected from acetylacetonate or an alkylacetoacetate.
6. A process as claimed in any preceding claim, wherein said ligand L is a phosphine.
7. A process as claimed in claim 6, wherein said phosphine is a tertiary phosphine.
8. A process as claimed in claim 7, wherein said phosphine is selected from the group consisting of triphenylphosphine, tricyclohexylphosphine, tri(tert-butyl)phosphine, tris(p-tolyl)phosphine, tris(o-tolyl)phosphine, 1,2-bis(di-tertbutylphosphinomethyl)benzene, 1,3-bis(di-tertbutylphosphinomethyl)propane, 1,2-bis(di-phenylphosphinomethyl)benzene, 1,2-bis(di-phenylphosphino)ethane, 1,2-bis(di-phenylphosphino)propane, 1,2-bis(di-phenylphosphino)butane and 1,1'-bis(di-phenylphosphino)ferrocene.
9. A process as claimed in any one of the preceding claims, wherein X is a halide, bicarbonate, carbonate, carboxylate, or nitrate.
10. A process as claimed in any preceding claim, wherein the amount of complexing compound in the reaction mixture is calculated to provide a molar excess over the amount required for the stoichiometric reaction.
11. A process as claimed in any preceding claim, wherein the reaction is carried out in the presence of a solvent.

12. A process as claimed in any one of the preceding claims, wherein the ammine compound of metal M is an ionic compound.
13. A process as claimed in claim 12, wherein the anion is selected from a halide, bicarbonate, carbonate, carboxylate, or nitrate.
14. A process as claimed in any one of the preceding claims, wherein the ammine compound of metal M is selected from $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, $\text{Pd}(\text{NH}_3)_4(\text{HCO}_3)_2$, $\text{Pd}(\text{NH}_3)_4(\text{CO}_3)$, $\text{Pd}(\text{NH}_3)_4(\text{CH}_3\text{CO}_2)_2$, $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$.
15. A metal complex ML_aX_b , where M is a metal atom, L is a ligand, X is selected from the group consisting of bicarbonate, carbonate, carboxylate, and nitrate, a is a number equal to or less than the coordination number of the metal and b is 1, 2 or 3.
16. A metal complex as claimed in claim 15, wherein said metal M comprises a precious metal selected from ruthenium, rhodium, palladium, osmium, iridium and platinum.
17. A metal complex as claimed in claim 16, wherein said metal M comprises palladium.
18. A metal complex as claimed in any one of claims 15 - 17, wherein said ligand L is a β -diketonate.
19. A metal complex as claimed in claim 18, wherein said β -diketonate is selected from acetyl acetonate or an alkylacetoacetate.
20. A metal complex as claimed in any one of claims 15 - 17, wherein said ligand L is a phosphine.
21. A metal complex as claimed in claim 20, wherein said phosphine is a tertiary phosphine.
22. A metal complex as claimed in claim 21, wherein said phosphine is selected from the group consisting of triphenylphosphine, tricyclohexylphosphine, tri(tert-butyl)phosphine, tris(p-tolyl)phosphine, tris(o-tolyl)phosphine, 1,2-bis(di-tertbutylphosphinomethyl)benzene, 1,3-bis(di-tertbutylphosphinomethyl)propane, 1,2-bis(di-phenylphosphinomethyl)benzene, 1,2-bis(di-phenylphosphino)ethane, 1,2-bis(di-phenylphosphino)propane, 1,2-bis(di-phenylphosphino)butane and 1,1'-bis(di-phenylphosphino)ferrocene.
23. A metal complex made by the process of any one of claims 1 – 14.

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F15/00

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 practical, search terms used)

EPO-Internal, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 6 806 289 B1 (LIPPARD STEPHEN J [US] ET AL) 19 October 2004 (2004-10-19) columns 77,78; example 626	1,23
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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