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(54) [Title of Invention] **Preparation Method for Tris(acetylacetonato)ruthenium (III)**

(57) [Summary]

[Objective] A preparative method is offered for obtaining tris(acetylacetonato)ruthenium (III) with an improved yield and purity.

[Constitution] Ruthenium (III) chloride is dissolved in a solvent, acetylacetone is added to the solution and allowed to react, potassium hydrogen carbonate is then added to the reaction solution and allowed to react, after which it is extracted with benzene, the benzene solution is concentrated and the product is filtered off, washed and dried, while the ruthenium is prevented from precipitating, and the minimum amount of acetylacetone is added.

[Claims]

[Claim 1] the method of preparing tris (acetylacetonato)ruthenium (III) wherein ruthenium (III) chloride is dissolved in a solvent, acetylacetone is added to this solution and they are allowed to react, potassium hydrogen carbonate is added to this reaction solution and it is allowed to react, followed by extraction with benzene, and the benzene solution is concentrated and the product is filtered off, washed and dried.

[Claim 2] the method of preparing tris (acetylacetonato)ruthenium (III) wherein ruthenium (III) chloride is dissolved in a solvent, acetylacetone is added to this solution and they are allowed to react, then the reaction solution is neutralized by the addition of alkali and this operation is repeated 2~5 times more, and after extracting with benzene, the benzene layer is concentrated and the product is filtered off, washed and dried.

[Claim 3] The method of preparing tris (acetylacetonato)ruthenium (III) described in Claim 2 wherein the above-mentioned alkali is potassium hydroxide solution or sodium hydroxide solution.

[Claim 4] The method of preparing tris (acetylacetonato)ruthenium (III) described in Claim 2 wherein the above-mentioned alkali is potassium hydrogen carbonate solution or sodium hydrogen carbonate solution.

[Claim 5] The method of preparing tris (acetylacetonato)ruthenium (III) described in Claims 1, 2, 3 or 4 wherein each of the above-mentioned reactions are refluxed at a temperature of 60~100 °C.

[Claim 6] The method of preparing tris (acetylacetonato)ruthenium (III) described in Claims 1, 2, 3 or 4 wherein each of the above-mentioned reactions are refluxed at a temperature of 100 °C.

[Description of Invention]

[0001]

[Field of Industrial Utility] the present invention concerns a method of preparing tris (acetylacetonato)ruthenium (III).

[0002]

[Prior Art] tris (acetylacetonato)ruthenium (III), $[\text{Ru}(\text{acac})_3]$; $[\text{Ru}(\text{C}_5\text{H}_7\text{O}_3)_3] = 398.40$, has been employed in asymmetric synthesis as a homogeneous catalyst or as a raw material in MOCVD (Metal Organic Chemical Vapor Deposition), and heretofore the following method has been used to prepare it. First, ruthenium (III) chloride (RuCl_3) is dissolved in a solvent, then potassium hydrogen carbonate (KHCO_3) is added to the solution and allowed to react, and then potassium hydrogen carbonate is added again and allowed to react. Next, after the above-mentioned reaction solution is concentrated, extracted with benzene and filtered, and after the benzene solution is concentrated the product is filtered off, washed and dried.

[0003]

[Problem to be Solved by the Invention] However, in the previous method of preparing tris (acetylacetonato)ruthenium (III), many portions of potassium hydrogen carbonate are added to the ruthenium chloride solution, part of which ends up precipitating as ruthenium black, and the consequent lower yield is detrimental. However, in order to increase the yield, a ten-fold amount of acetylacetone relative to the ruthenium must be added, and the excess acetylacetone remains behind, and is extracted by the benzene along with the desired compound, and the decreased purity is also detrimental. In this regard, the aim of the present invention is to offer a method of preparing tris (acetylacetonato)ruthenium (III) in which the yields and purity are improved.

[0004]

[Means to Solve the Problem] in order to solve the above-mentioned problem, in the first method of the present invention for preparing tris (acetylacetonato)ruthenium (III), ruthenium (III) chloride is dissolved in a solvent, acetylacetone is added to this solution and they are allowed to react, then potassium hydrogen carbonate is added to this reaction solution and it is allowed to react, followed by extraction with benzene, after which the benzene solution is concentrated and the product is filtered off, washed and dried. Furthermore, in the second method of the present invention for preparing tris (acetylacetonato)ruthenium (III), ruthenium (III) chloride is dissolved in a solvent, acetylacetone is added to this solution and they are allowed to react, after which this reaction solution is neutralized by the addition of alkali, and this operation is repeated 2~5 times more, then after extracting with benzene, the benzene layer is concentrated and the product is filtered off, washed and dried. For the above-mentioned alkali, potassium hydroxide solution or sodium hydroxide solution are desirable. Furthermore, the above-mentioned alkali is optionally potassium hydrogen carbonate solution or sodium hydrogen carbonate solution. For each of the above-mentioned reactions, refluxing at a temperature of 60~100 °C is desirable. Furthermore, for each of the above-mentioned reactions, refluxing at a temperature of 100 °C is more desirable.

[0005]

[Utility] In the first method of the present invention for preparing tris (acetylacetonato)ruthenium (III), a ruthenium chloride solution and acetylacetone are allowed to react and then made alkaline and allowed to react further, while the precipitation of ruthenium is prevented, and the minimum necessary amount of acetylacetone will be added. Furthermore, in the second method of the present invention for preparing tris (acetylacetonato)ruthenium (III), a ruthenium chloride solution and acetylacetone are reacted together and alkali is added in small portions until the reaction has been brought to neutrality, so that the decomposition of the ruthenium (III) chloride is prevented, and so that the precipitation of ruthenium can be much better prevented, and the neutralization and the repetition of the reaction make it possible to decrease the amount of acetylacetone added together and for the reaction to proceed steadily. If the reaction temperature is less than 60 °C, the reaction proceeds slowly, and the yield is decreased. Moreover, it is sufficient for the reaction temperature to be between 60~100 °C, and it is desirable for the temperature to be as high as 100 °C.

[0006]

[Working Example] Below the working examples of the present invention are explained together with related prior art examples.

[0007]

[Working Example 1] First, 5 g of ruthenium(III) chloride is dissolved in 250 mL of water, 7.5 mL of acetonylacetone is added to this solution, and this is allowed to react at reflux at a temperature of 100 °C for a period of 2 h. Next, 8.8 g of potassium hydrogen carbonate is added to the above reaction mixture, and after being allowed to react at reflux at a temperature of 100 °C for a period of 2 h, it is extracted with benzene. Following this, the benzene solution is filtered through No. 5C quantitative filter paper, is concentrated by evaporation and the product is filtered off and washed, then dried under vacuum to yield 7 g (80% yield) of tris (acetylacetonato)ruthenium (III) as red monoclinic crystals.

[0008]

[Working Example 2] First, 5 g of ruthenium(III) chloride is dissolved in 250 mL of water, 7.5 mL of acetonylacetone is added to this solution, and this is allowed to react at reflux at a temperature of 100 °C for a period of 2 h. Next, the above reaction mixture is neutralized with a 10% solution of aqueous potassium hydroxide (KOH) and allowed to react at reflux at a temperature of 100 °C for a period of 2 h. The reaction mixture, which becomes acidic during the course of the reflux, is subjected twice more to the procedure of neutralizing with 10% KOH solution and heating to reflux at 100 °C for a period of 2 h, and afterwards is extracted with benzene. Following this, after the benzene solution is filtered through No. 5C quantitative filter paper, it is concentrated by evaporation and the product is filtered off and washed, then dried under vacuum to yield 7.7 g (88% yield) of tris (acetylacetonato)ruthenium (III) as red monoclinic crystals.

[0009]

[Working Example 3] The process of Working Example 2 is employed with the substitution of 10% sodium hydroxide solution for the 10% potassium hydroxide solution, otherwise the process is carried out in the same manner.

[0010]

[Previous Example] First, 5 g of ruthenium(III) chloride is dissolved in 250 mL of water, and after this solution is made alkaline by the addition of 15 g of potassium hydrogen carbonate in small portions, 30 mL of acetylacetone is added to this solution, and this is allowed to react at reflux. Next, to the above reaction mixture is added 10 g of potassium hydrogen carbonate, and after it is allowed to react at reflux, it is concentrated to 150 mL by evaporation, and then extracted with benzene. Following this, the benzene solution is filtered through No. 5C quantitative filter paper, then concentrated by evaporation and the product is filtered off and washed, then dried under vacuum to yield 4.3 g (49% yield) of tris (acetylacetonato)ruthenium (III) as red monoclinic crystals.

[0011]

[Previous Example 2] First, 5 g of ruthenium(III) chloride is dissolved in 250 mL of water, and after this solution is made alkaline by the addition of 8.8 g of potassium hydrogen carbonate in small portions, 7.5 mL of acetylacetone is added to this solution, then it is allowed to react at reflux and extracted with benzene. Next, the benzene solution is passed through No. 5C quantitative filter paper, then it is concentrated by evaporation, and the product is filtered off and

washed, then dried under vacuum to yield 2.8 g (32% yield) of tris (acetylacetonato)ruthenium (III) as red monoclinic crystals.

[0012] Table 1 shows the results of carbon and hydrogen content and the purity from CHN analysis for samples from the Working Examples 1-3 and the Previous Examples 1-2.

[0013]
[Table 1]

	C (%)	H (%)	Purity (%)
Theoretical values	45.22	5.31	—
Working Example 1	45.48	5.38	99.4
Working Example 2	45.50	5.40	99.4
Working Example 3	45.43	5.35	99.5
Previous Example 1	46.57	5.58	97.1
Previous Example 2	45.63	5.4	99.1

[0014] It can be recognized that the method based upon the invention which includes each of the examples and Table 1 mentioned above produces a broad improvement in yield and purity when compared with the previous examples. Furthermore, while each Working Example is described for the case of using ruthenium(III) chloride in water as a solvent, a solvent which is a mixture of water and an alcohol would work as well.

[0015]
[Effect of the Invention] As explained above, in the first method of producing tris (acetylacetonato)ruthenium (III), the ability to prevent the precipitation of ruthenium, and the possibility of adding an equivalent amount of acetylacetone, produces a broad improvement in yield and purity when compared with the previous methods. Furthermore, in the second method of producing tris (acetylacetonato)ruthenium (III), with the possibility of avoiding the decomposition of the ruthenium (III) chloride, and being much more able to prevent the precipitation of ruthenium, and being able to decrease the amount of acetylacetone added, together with the reaction proceeding steadily, it is possible to achieve a much broader improvement in the yield and purity.

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