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(54) Title: PROCESS FOR THE PREPARATION OF RUTHENIUM COMPOUNDS

(57) Abstract: We describe a process for the preparation of a ruthenium compound of formula (I): [Ru(dienyl)$_2$], wherein "dienyl" represents a subsituted pentadienyl or cycloheptadienyl group, which process comprises reacting dichloro(2,7-dimethylocta-2,6-dien-1,8-diyl)-ruthenium with an appropriate diene in the presence of: 1) a primary or secondary alcohol capable of reducing Ru(IV) to Ru(II); and 2) a carbonate of an alkaline metal. The title compounds are useful as precursors of Ru catalysts.

Process for the preparation of ruthenium compounds

Technical Field

The present invention relates to the preparation of ruthenium compounds useful as precursors of ruthenium catalysts. It concerns more particularly a process for the preparation of a ruthenium compound of formula

$$[Ru(dienyl)_2] \qquad (I)$$

wherein "dienyl" represents a substituted pentadienyl or cycloheptadienyl group.

Prior Art

A compound of the invention, bis(2,4-dimethyl-2,4-pentadienyl)-ruthenium or $[Ru(DMPD)_2]$, is a known product useful for the preparation of a great number of ruthenium catalysts, in particular compounds useful in asymmetric catalysis. Although a prior synthesis of this compound has been described by L. Stahl et al. In Organometallics 1983, 2, 1229-1234, practical working of this known process showed that it is not useful for industrial exploitation as it provides the desired compound in low yields, below 40%

Description of the invention

In order to overcome the limitation of the prior art process, the invention relates more particularly to a new process for the preparation of a ruthenium compound of formula

$$[Ru(dienyl)_2] \qquad (I)$$

wherein "dienyl" represents a substituted pentadienyl or cycloheptadienyl group, which process comprises reacting dichloro(2,7-dimethylocta-2,6-dien-1,8-diyl)-ruthenium with an appropriate diene in the presence of :

1) a primary or secondary alcohol capable of reducing Ru(IV) to Ru(II) ; and
2) a carbonate of an alkaline metal.

By "an appropriate diene" it is meant here the diene which, for a particular compound (I), provides the corresponding dienyl group.

According to a preferred embodiment of the invention the reaction is carried out in the presence of a catalytic amount of acetonitrile.

The process of the invention is particularly useful for preparing compounds (I) wherein "dienyl" stands for a 2,4-dimethyl-2,4-pentadienyl, 2,3,4-trimethyl-2,4-pentadienyl, 2,4-dimethyl-1-oxa-2,4-pentadienyl or 2,4-cycloheptadienyl group.

Dichloro(2,7-dimethylocta-2,6-dien-1,8-diyl)-ruthenium, used as the starting compound in the process of the invention, is a known compound. Several synthesis of this compound have in fact been described, e.g. by L. Porri et al., Tetrahedron Lett. **1965**, 4187-4189, D. N. Cox et al., Inorg. Chem. **1990**, 29, 1360-1365 and J. G. Toerien et al., J. Chem Soc. Dalton Trans. **1991**, 1563-1568. However, to our knowledge, there has never been any report or suggestion of the use of this known compound for the preparation of compounds of formula (I).

Primary or secondary alcohols suitable for use in the process of the invention include ethanol, methanol and isopropanol, amongst other. Preferably, ethanol will be used.

Carbonates of alkaline metals appropriate for the process of the invention include lithium, sodium, and potassium carbonates in particular. Preferably lithium carbonate will be used.

According to an advantageous embodiment of the invention, dichloro(2,7-dimethylocta-2,6-dien-1,8-diyl)-ruthenium is reacted with 2,4-dimethyl-1,3-pentadiene, in the presence of ethanol, acetonitrile and lithium carbonate to provide bis(2,4-dimethyl-2,4-pentadienyl)-ruthenium or $[Ru(DMPD)_2]$.

Unlike the prior art process, the process of the instant invention makes it possible to prepare compounds (I) in high yields, in many cases above 90%. It can be carried out in simple equipment and it does not require particular temperature or pressure conditions.

The invention will now be described in further detail by way of the following examples, in which the temperatures are indicated in degrees centigrade and the abbreviations have the meaning usual in the art.

Example 1

Preparation of [Ru(2,4-dimethyl-2,4-pentadienyl)$_2$]

{$RuCl_2$(2,7-dimethyl-2,6-octadien-1,8-diyl}$_2$ (3.8 g, 6.16 mmol) and Li_2CO_3 (8.8 g, 119 mmol) were suspended in a mixture of EtOH (150 ml), MeCN (0.33 ml), and 2,4-dimethyl-1,3-pentadiene (4.6 g, 48 mmol), and the resulting mixture was stirred at reflux for 5 h. The low-boiling volatiles were removed on a rotary evaporator, the residue was extracted with CH_2Cl_2, the extract filtered and concentrated, and the resulting residue purified by sublimation (10^{-3} bar, 80°C).

Yield 93% (3.36 g, 11.5 mmol, yellow crystals).

^{1}H-NMR(250MHz, C_6D_6) : δ = 4.63(s, 2H, H-3) ; 2.71(s, 4H, H-1_{exo}) ; 1.73(s, 12H, H-4) ; 0.86(s, 4H, H-1_{endo}).

^{13}C-NMR(62.9MHz, C_6D_6) : δ = 100.3(C-2), 97.8(C-3), 46.8(C-1), 26.3(C-4).

Example 2

Preparation of [Ru(2,4-cycloheptadienyl)$_2$]

{$RuCl_2$(2,7-dimethyl-2,6-octadien-1,8-diyl}$_2$ (0.31 g, 0.5 mmol) and Li_2CO_3 (0.15 g, 2.0 mmol) were suspended in a mixture of EtOH (10 ml), MeCN (26 µl, 0.5 mml), and 1,3-cycloheptadiene (0.94 g, 10 mmol), and the resulting mixture then processed as described in Example 1.

Yield 80% (0.23 g, 0.80 mmol).

^{1}H-NMR(250MHz, C_6D_6) : δ (ppm) = 5.01(t, 2H, H-1) ; 4.37(dd, 4H, H-2) ; 3.88(m, 4H, H-3) ; 2.15, 1.66(m, 8H, H-4).

^{13}C-NMR(62.9MHz, C_6D_6) : δ (ppm) = 94.56(C-1), 88.21(C-2), 64.88(C-3), 34.95(C-4).

Example 3

Preparation of [Ru(2,3,4-trimethyl-2,4-pentadienyl)$_2$]

2,3,4-Trimethylpenta-1,3-dien (0.33 g, 3.0 mmol) was used instead of 1,3-cycloheptadiene and the reaction carried out in a manner similar to that described in the preceding examples.

Yield 62% (0.20 g, 63%).

^{1}H-NMR(250MHz, C_6D_6) : δ = 2.73(s, 4H, H-1_{exo}) ; 1.53(s, 12H, H-4) ; 1.46(s, 6H, H-5) ; 0.86(s, 4H, H-1_{endo}).

^{13}C-NMR(62.9MHz, C_6D_6) : δ = 105.9(C-3) ; 96.26(C-2) ; 49.0(C-1) ; 25.2(C-4) ; 16.4(C-5).

Claims

1. Process for the preparation of a ruthenium compound of formula

$$[Ru(dienyl)_2] \qquad (I)$$

wherein "dienyl" represents a substituted pentadienyl or cycloheptadienyl group, which process comprises reacting dichloro(2,7-dimethylocta-2,6-dien-1,8-diyl)-ruthenium with an appropriate diene in the presence of :

1) a primary or secondary alcohol capable of reducing Ru(IV) to Ru(II) ; and

2) a carbonate of an alkaline metal.

2. Process according to claim 1, wherein the reaction takes place in the presence of a catalytic amount of acetonitrile.

3. Process according to claim 1 or 2, wherein the compound of formula (I) comprises 2,4-dimethyl-2,4-pentadienyl, 2,3,4-trimethyl-2,4-pentadienyl, 2,4-dimethyl-1-oxa-2,4-pentadienyl or 2,4-cycloheptadienyl group.

4. A process according to any one of claims 1 to 3, wherein said alcohol is ethanol or methanol.

5. A process according to claim 1 or 4, wherein there is used lithium carbonate.

6. A process according to claim 1, wherein dichloro(2,7-dimethylocta-2,6-dien-1,8-diyl)-ruthenium is reacted with 2,4-dimethyl-1,3-pentadiene, in the presence of ethanol, acetonitrile and lithium carbonate, to provide bis(2,4-dimethyl-2,4-pentadienyl)-ruthenium.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 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)
IPC 7 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)
CHEM ABS Data, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	STAHL, LOTHAR ET AL: "Synthesis and characterization of bis(pentadienyl) ruthenium compounds" ORGANOMETALLICS, vol. 2, no. 9, 1983, pages 1229-1234, XP000946340 cited in the application page 1229 ---	1
A	COX, DAVID N. ET AL: "Octadienediyl dichlorides of ruthenium(IV) as synthetic reagents in organoruthenium chemistry;isolation of a protonated open metallocene, 'Ru(.eta.5-C7H11)2H!'BF4!" J. CHEM. SOC., CHEM. COMMUN., no. 14, 1988, pages 951-953, XP002147842 page 952 -----	1

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

☐ 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

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