

AS ORIGINALLY FILED

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Preparation of ruthenium complexes

- 10 The present invention relates to processes for preparing ruthenium complexes which can be used, for example, as catalysts in metathesis reactions.

In its simplest form, olefin metathesis (disproportionation) is a reversible, metal-catalyzed transalkylidenation of olefins by rupture and re-formation of carbon-carbon
15 double bonds. In the metathesis of acyclic olefins, a distinction is made, for example, between self-metathesis, in which an olefin is converted into a mixture of two olefins of different molar masses (for example conversion of propene into ethene and 2-butene), and cross- or co-metathesis, which describes the reaction of two different olefins (for example of propene with 1-butene to give ethene and 2-pentene). Further
20 application areas of olefin metathesis are syntheses of unsaturated polymers by ring-opening metathesis polymerization (ROMP) of cyclic olefins and the acyclic diene metathesis polymerization (ADMET) of α , ω -dienes. More recent applications are the selective ring opening of cyclic olefins using acyclic olefins, and also ring closure reactions (RCM) by means of which unsaturated rings of different ring sizes can be
25 produced, preferably from α , ω -dienes.

Suitable catalysts for metathesis reactions are in principle homogeneous and heterogeneous transition metal compounds, in particular ruthenium compounds.

- 30 Heterogeneous catalysts, for example molybdenum oxide, tungsten oxide or rhenium oxide on inorganic oxidic supports, have a high activity and regenerability in reactions of non-functionalized olefins but often have to be pretreated with an alkylating agent to increase the activity when functionalized olefins such as methyl oleate are used. Olefins having protic functional groups (such as hydroxyl groups,
35 carboxyl groups or amino groups) lead to spontaneous deactivation of the heterogeneous catalyst.

In recent years, increasing efforts have been made to prepare homogeneous catalysts which are stable in a protic medium and in the presence of atmospheric oxygen. Catalysts which have been found to be of particular interest are specific ruthenium-alkylidene compounds. Such complexes and processes of preparing them are known.

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WO 93/20111 describes ruthenium- and osmium-carbene complexes for olefin metathesis polymerization. The complexes have the structure $\text{RuX}_2(\text{=CH-CH=CR}_2)\text{L}_2$. Ligands L used are triphenylphosphine and substituted triphenylphosphine. The preparation is carried out, for example, by reacting $\text{RuCl}_2(\text{PPh}_3)_3$ with suitable disubstituted cyclopropenes as carbene precursors. However, the synthesis of cyclopropene derivatives consists of a number of stages and is of little interest from an economic point of view.

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Similar reactions are described in WO 96/04289. In addition, processes for olefin metathesis polymerization are indicated.

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The use of such catalysts for peroxide-crosslinking of ROMP polymers is described in WO 97/03096.

WO 97/06185 likewise describes metathesis catalysts based on ruthenium-carbene complexes. Apart from the above-described process, they can also be prepared by reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with diazoalkanes. However, handling diazoalkanes poses a safety risk, particularly when the process is carried out on an industrial scale.

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In addition, the organometallic starting materials of the formula $\text{RuCl}_2(\text{PPh}_3)_3$ have to be prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ using a large excess of triphenylphosphine. Subsequently, PPh_3 ligands are again lost by ligand exchange in the catalyst synthesis itself. The carbene precursors used require multistage syntheses and do not have an unlimited shelf life.

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Organometallics 1996, 15, 1960-1962 describes a process for preparing ruthenium complexes in which polymeric $[\text{RuCl}_2(\text{cyclooctadiene})]_x$ in i-propanol is reacted with hydrogen and then with 1-alkynes in the presence of phosphine. This eliminates the necessity of phosphine exchange. An undefined mixture of products is obtained. In addition, long reaction times are required when starting from a polymeric starting material. The cyclooctadiene present in the organometallic starting material does not contribute to the reaction and is lost.

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J. Chem. Soc. Commun. 1997, 1733-1734 describes the synthesis of a methylene complex $\text{RuCl}_2(=\text{CH}_2)(\text{PCy}_3)_2$ starting from dichloromethane and the ruthenium polyhydride $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$. However, the ruthenium-polyhydride complex is difficult to obtain. Furthermore, long reaction times are required.

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The known synthetic routes for preparing metathesis catalysts of the type $\text{RuX}_2(=\text{CH}-\text{CH}_2\text{R})(\text{PR}'_3)_2$ are uneconomical for the reasons mentioned.

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DE-A 198 00 934, which has earlier priority but is not a prior publication, describes a process for preparing ruthenium complexes of the type $\text{RuX}_2(=\text{CH}-\text{CH}_2\text{R})\text{L}^1\text{L}^2$, in which RuX_3 is reacted [lacuna] in an inert solvent in the presence of a reducing agent and of hydrogen and subsequently with alkyne compounds.

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It is an object of the present invention to provide a process for preparing ruthenium alkylidene complexes of the type $\text{RuX}_2(=\text{CH}-\text{CH}_2\text{R})\text{L}^1\text{L}^2$, which process leads, in a rapid and atom-economical reaction starting from readily available starting materials, to the desired products in high yield without ligand exchange and without ligand excess. The process should also have no complex work-up steps, be able to be carried out under mild reaction conditions and also be inexpensive.

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We have found that this object is achieved by a process for preparing ruthenium complexes of the formula I



25 where

X is an anionic ligand,

R is hydrogen or a substituted or unsubstituted C_1 - C_{20} -alkyl radical or C_6 - C_{20} -aryl radical and

30 L^1 and L^2 are, independently of one another, uncharged electron donor ligands,

by

35 (a) reaction of RuX_3 with a diene in a solvent based on one or more aliphatic secondary alcohols in the presence or absence of a reduction aid, and then with L^1 and L^2 in the presence of at least one coordinating weak base and hydrogen and, without isolation of intermediates,

(b) subsequent reaction with compounds of the formula II



where R is as defined above, in the presence of a soluble chloride source.

5 It has been found that the abovementioned ruthenium complexes can be obtained in very good yields directly from RuX_3 , preferably $\text{RuCl}_3 \cdot 3(\text{H}_2\text{O})$, by simple reaction with dienes and then with ligands L^1 and L^2 , hydrogen and terminal alkynes of the formula II, preferably in the presence of reduction aids, without isolation of intermediates. The ruthenium complexes have no vinylic substituents on the carbene
10 carbon atom. The starting materials can be prepared inexpensively and are readily available.

RuX_3 is first reacted with the diene and then with the ligands L^1 and L^2 in a solvent based on one or more aliphatic secondary alcohols, preferably in the presence of a
15 reduction aid, at least one coordinating weak base and of hydrogen. The solvent is based on one or more aliphatic secondary alcohols. These alcohols preferably have from 3 to 10, particularly preferably from 3 to 6, carbon atoms. Particular preference is given to isopropanol, 2-butanol, cyclohexanol or a mixture thereof. Very particular preference is given to using isopropanol.

20 The coordinating weak base is a secondary or preferably tertiary amine. An example of a secondary amine is dicyclohexylamine. Particular preference is given to tertiary aliphatic amines, in particular trialkylamines in which the alkyl radicals have from 1 to 12, preferably from 2 to 6, carbon atoms. Particular preference is given to using
25 triethylamine. The coordinating weak base, in particular the triethylamine, is preferably used in at least the stoichiometric amount, based on RuX . The reaction mixture is preferably pretreated with the coordinating weak base prior to the addition of the ligand L.

30 Prior to the addition of the ligand L, the reaction mixture is reacted with a diene, preferably a C_4 - C_{10} -diene, in particular isoprene, preferably in the presence of a reduction aid, in particular an alkali metal carbonate or alkaline earth metal carbonate. As alkali metal carbonate or alkaline earth metal carbonate, particular preference is given to using sodium carbonate and/or calcium carbonate. The molar
35 ratio of diene to RuX_3 is preferably at least 5:1 and the molar ratio of alkali metal carbonate and/or alkaline earth metal carbonate to RuX_3 is from 0.1 to 1, particularly preferably about 0.5.

The reduction with hydrogen is carried out in the presence of a coordinating weak base, preferably a secondary or tertiary amine. Particular preference is given to using triethylamine.

- 5 The reaction of the reaction mixture with a 1-alkyne is carried out in the presence of a soluble chloride source, in particular an alkaline earth metal chloride. Particular preference is given to using magnesium chloride.

- 10 The temperature in this reaction step (a) is preferably from 0 to 100°C, particularly preferably from 20 to 80°C, in particular from 40 to 60°C. The pressure is preferably from 0.1 to 100 bar, particularly preferably from 0.5 to 5 bar, in particular from 0.8 to 1.5 bar. The reaction is carried out for a period of preferably from 10 minutes to 100 hours, particularly preferably from one hour to 10 hours. The molar ratio of ligands L^1 and L^2 together to the ruthenium salt used is preferably 2-20:1, particularly
15 preferably 2-5:1. After the reaction step (a), the reaction mixture is, preferably at from -80 to 100°C, particularly preferably from -40 to 50°C, in particular from -30 to 20°C, reacted with a 1-alkyne. Here, the molar ratio of ruthenium salt originally used to 1-alkyne is preferably from 1:1 to 1:10. The reaction is preferably carried out at a pressure of from 0.1 to 10 bar, particularly preferably from 0.8 to 1.5 bar, in
20 particular from 1 to 1.4 bar, for a period of preferably from 30 seconds to 10 hours, particularly preferably for from one minute to one hour.

- To prepare the complexes of the formula I, no isolation of the intermediate from step (a) is necessary, but it is possible.

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The reaction mixture obtained is preferably worked up by filtering off the precipitated solid, washing and drying.

- 30 In the ruthenium complexes of the formula I, X is a monodentate anionic ligand, for example halogen, pseudohalogen, carboxylate, diketonate. X is particularly preferably halogen, in particular bromine or chlorine, especially chlorine. Particular preference is given to using $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in the reaction.

- 35 L^1 and L^2 are neutral electron donor ligands. Examples of such ligands are amines, phosphines, arsines and stilbines, preferably phosphines. L^1 and L^2 are particularly preferably selected from among phosphines of the formula III



(III)

where R^1 and R^2 are independently phenyl radicals or organic, sterically hindered radicals and R^3 is hydrogen, a substituted or unsubstituted C_1 - C_{20} -alkyl radical or C_6 - C_{20} -aryl radical or is as defined for R^1 . For the purposes of the present invention, a "sterically hindered radical" is a radical which has a bulky structure. Examples of such radicals are i-propyl, tert-butyl, cyclopentyl, cyclohexyl, phenyl or menthyl. Preference is given to using a cyclohexyl radical as sterically hindered radical. Particularly preferably, all three radicals R^1 , R^2 and R^3 are sterically hindered radicals or phenyl radicals, in particular cyclohexyl radicals. The radicals R^1 , R^2 and R^3 can each bear suitable substituents. Examples of such substituents are C_1 - C_6 -alkyl radicals, preferably C_1 - C_3 -alkyl radicals, C_1 - C_3 -fluoroalkyl radicals, halogen atoms, nitro groups, amino groups, ester functions and acid functions, -OH, C_1 - C_6 -alkoxy groups or sulfonate groups. The radicals are preferably not substituted. L^1 and L^2 are preferably employed in a molar ratio of from 1.5 to 4, particularly preferably about 2, based on RuX_3 .

The radical R is hydrogen or a substituted or unsubstituted C_1 - C_{20} -, preferably C_1 - C_6 -alkyl radical or C_6 - C_{20} -, preferably C_6 - C_8 -aryl radical. As regards the substituents, what has been said above applies. Particularly preferred ruthenium complexes of the formula I are $RuCl_2(=CH-CH_3)(PCy_3)_2$ and $RuCl_2(=CH-CH_2-Ph)(PCy_3)_2$ where Cy is a cyclohexyl radical and Ph is a phenyl radical.

A preferred embodiment comprises a single-vessel reaction in which $RuCl_3 \times H_2O$ together with Na_2CO_3 or $CaCO_3$ and isopropanol, 2-butanol or cyclohexanol are, under an inert gas atmosphere, placed in the reaction vessel and, after addition of isoprene, the mixture is heated. After removal of excess isoprene under reduced pressure, triethylamine and stoichiometric amounts of phosphine, in a preferred embodiment two equivalents of tricyclohexylphosphine, are added to the reaction mixture. In a hydrogen atmosphere of from 0.1 bar to 100 bar, preferably from 0.5 to 5 bar, particularly preferably from 0.8 to 1.5 bar, the mixture is subsequently stirred for from 10 minutes to 100 hours at from $0^\circ C$ to $100^\circ C$ and $MgCl_2 \times 6H_2O$ is then added. The reaction mixture obtained in this way is subsequently reacted continuously at from $-80^\circ C$ to $100^\circ C$, preferably from $-40^\circ C$ to $50^\circ C$, and pressures of from 0.1 to 10 bar, preferably from 0.8 to 1.5 bar, in a molar ratio of from 1:1 to 1:10, based on the ruthenium chloride used, with a 1-alkyne of the formula $HC \equiv CR$ for a period of from 30 to 180 minutes. The solid which precipitates almost quantitatively from the solution is the desired alkylidene complex which, after drying, can be used directly as a highly active metathesis catalyst for all the metathesis reactions described in the introduction.

In general, the entire reaction and work-up sequence is complete after from 2 to 100 hours, preferably after from 3 hours to 8 hours, and gives metathesis catalysts of the type $\text{RuCl}_2(=\text{CHCH}_2\text{R})(\text{PR}'_3)_2$ ($\text{R}=\text{H}$, alkyl, aryl) in yields of from at least 60 to 98% based on RuCl_3 and the phosphine used.

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Suitable reactors are generally glass or steel vessels which should be pressure-resistant if necessary.

The invention is illustrated by the example.

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Example:

Synthesis of the ethylidene complex $\text{RuCl}_2(=\text{CHMe})(\text{PCy}_3)_2$:

- 15 Under protective gas, 1.09 g (3.95 mmol) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 198 mg of CaCO_3 (1.98 mmol) in 150 ml of isopropanol are admixed with 4 ml of isoprene (40.0 mmol) and the reaction mixture is heated at 85°C for from 1 to 2 hours in the closed flask, with a color change from red through brownish black to orange-red being observed. Heating is removed, the volume of the solution is reduced to about
- 20 20-30 ml and 2 ml of triethylamine (14.4 mmol) are added to the mixture which is then stirred for 5 minutes. 2.24 g of tricyclohexylphosphine (7.99 mmol) are subsequently added. After stirring for 10 minutes, the protective gas is replaced by hydrogen at a gauge pressure of from 0.6 to 0.8 bar and the reaction solution is heated at 65°C for 45 minutes. An orange-yellow suspension is formed after only
- 25 15 minutes. After cooling the suspension to room temperature, hydrogen is replaced by protective gas, 1.60 g (7.87 mmol) of $\text{MgCl}_2 \times 6\text{H}_2\text{O}$ are added and 220 ml of acetylene (about 4.6 mmol) are then metered in continuously over a period of 90 minutes. After this addition is complete, the suspension is stirred for another 10 minutes and vacuum is applied briefly to remove residual acetylene. The violet
- 30 solid which has precipitated from the solution is filtered off, washed with water and methanol and dried under reduced pressure.
- Yield: 2.85 g (93%)

We claim:

- 5 1. A process for preparing ruthenium complexes of the formula I



where

- 10 X is an anionic ligand,
 R is hydrogen or a substituted or unsubstituted C_1 - C_{20} -alkyl radical or C_6 - C_{20} -aryl radical and
 L^1 and L^2 are, independently of one another, uncharged electron donor ligands,

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by

- (a) reaction of RuX_3 with a diene in a solvent based on one or more aliphatic secondary alcohols in the presence or absence of a reduction aid, and
 20 then with L^1 and L^2 in the presence of at least one coordinating weak base and hydrogen and, without isolation of intermediates,
 (b) subsequent reaction with compounds of the formula II



- 25 where R is as defined above, in the presence of a soluble chloride source.

2. A process as claimed in claim 1, wherein, before the addition of ligands L^1 and L^2 , a diene is added to the reaction mixture in a molar ratio of at least 5:1,
 30 based on RuX_3 .

3. A process as claimed in claim 1 or 2, wherein L^1 and L^2 are selected from among phosphines of the formula III



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where R^1 and R^2 are independently of one another, phenyl radicals or organic, sterically hindered radicals and R^3 is hydrogen, a substituted or unsubstituted C_1 - C_{12} -alkyl radical or C_6 - C_{20} -aryl radical and/or is as defined for R^1 .

- 5 4. A process as claimed in claim 3, wherein R^1 and R^2 are selected from among i-propyl, tert-butyl, cyclopentyl, cyclohexyl, phenyl or menthyl.
5. A process as claimed in any of claims 1 to 4, wherein X is halogen.
- 10 6. A process as claimed in any of claims 1 to 5, wherein the reaction of RuX_3 with a diene is carried out in the presence of Na_2CO_3 and/or $CaCO_3$, with the molar ratio of Na_2CO_3 and/or $CaCO_3$ to RuX_3 being 0.1 to 1.
- 15 7. A process as claimed in any of claims 1 to 6, wherein the reaction with hydrogen is carried out in the presence of a secondary and/or tertiary amine as coordinating weak base.
- 20 8. A process as claimed in any of claims 1 to 7, wherein the reaction with 1-alkynes is carried out in the presence of an alkaline earth metal chloride.
- 25 9. A process as claimed in any of claims 1 to 8, wherein the reaction in step (a) is carried out at a pressure in the range from 0.1 to 100 bar and that in step (b) is carried out at a pressure in the range from 0.1 to 10 bar.
- 30 10. A process as claimed in any of claims 1 to 9, wherein the reaction in step (a) is carried out at from 0 to 100°C and that in step (b) is carried out at from -80 to 100°C.
11. A process as claimed in any of claims 1 to 10, wherein the solvent is selected from among isopropanol, 2-butanol, cyclohexanol and mixtures thereof.



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