Abstract: The present invention relates to the use of Ru complexes, having a cyclopentadienyl derivatives and a diene as ligands, together with some acidic additives for improving the selectivity in the 1,4-hydrogenation of conjugated dienes into the corresponding "cis"-alkene as major product, i.e. wherein the two substituents in position 2,3 of said diene are in a cis configuration in the corresponding alkene.
1,4-HYDROGENATION OF DIENES WITH RU COMPLEXES

Technical field

The present invention relates to the field of catalytic hydrogenation and, more particularly to the use of specific Ru complexes with cyclopentadienyl derivatives, as one of the ligands, in 1,4-hydrogenation processes for the reduction of dienes into the corresponding "cis"-alkene as major product, i.e. wherein the two substituents in position 2,3 of the diene are in a cis configuration in the corresponding alkene.

Prior Art

Selective 1,4-hydrogenation of conjugated dienes into their corresponding "cis"-alkene is a very interesting reaction in organic chemistry, since it renders accessible a number of compounds which are obtained in general with a poor selectivity.

One of the mandatory and characterizing elements of such processes is the catalyst or the catalytic system. The development of useful catalysts or catalytic systems for the 1,4-hydrogenation of diene into the corresponding "cis"-alkene is still an important, difficult and unpredictable task in chemistry, in particular because the chemical industry is always eager for higher selectivity, as well as to maintain a high conversion or yield.

From the prior art, it is known that sorbic acid can be hydrogenated into the corresponding "cis"-alkene in the presence of [(Cp*)RuCO(phosphine)](anion) or [(Cp*)RuCO(sorbic acid)](anion) complexes, (see Driessen et al, in Chem.Commun., 2000, 217 or in J.Organomet.Chem, 1998, 141), however the yields (conversions x selectivity) are quite low.

Furthermore, in EP 1394170, it is reported the cisoid hydrogenation of dienes using as catalytic systems the complex [(Dienyl)Ru(acyclic diene)](anion) (in particular [(Cp*)Ru(sorbic acid)](anion) or [(Cp*)Ru(sorbol)](anion). In this document it is expressively shown that the use of cyclic diene, instead of acyclic diene, is highly detrimental to the overall yield. The only conditions displayed as providing good yields require nitromethane as solvent, the latter being relatively toxic and hazardous for industrial applications. Finally, Table 4 of said document shows that the addition of Lewis acids is highly detrimental to the yields.

Therefore, there is a need for processes using alternative catalytic systems possibly providing high selectivity and/or conversions.
Description of the invention

In order to overcome the problems aforementioned, the present invention relates to processes for the catalytic reduction by 1,4-hydrogenation, using molecular H₂, of a conjugated diene (I) into the corresponding "cis"-alkene (II), characterized in that said process is carried out in the presence of at least an acidic additive of the type specified further below, the catalyst or pre-catalyst being a ruthenium complex comprising as ligand a cyclopentadienyl derivative.

The invention's process is shown in Scheme 1:

![Scheme 1](image)

wherein the R¹ to R⁶ are the substituents of the diene and of the alkene and wherein in compound (II) the R¹ and R² groups are in a cis configuration.

A particular embodiment of the invention is a process for the catalytic reduction by 1,4-hydrogenation, using molecular H₂, of a C₅-C₂₂ conjugated diene of formula

![Formula](image)

wherein R¹, R², R³, R⁴, R⁵ and R⁶ represent, simultaneously or independently from each other, a hydrogen atom or a C₁-C₁₂ alkyl or alkenyl group optionally substituted; one of R² or R⁶ may also represent a C₁-C₁₂ alkoxy or acyloxy group optionally substituted; and R¹ and R³, or R³ and R⁴, or R² and R⁶, or R⁶ and R⁵, or R⁴ and R⁵, taken together, may form a C₂-i₆ alkanediyl or de-conjugated alkenediyl group, optionally substituted; into the corresponding alkene, of formula
wherein R\textsuperscript{1} to R\textsuperscript{6} have the same meaning as for the compound of formula (I), and wherein the isomer having the R\textsuperscript{1} and R\textsuperscript{2} groups in a cis configuration is predominant (i.e. the "czV-alkene);
said process being characterized in that it is carried out in the presence of
- at least one ruthenium catalyst or pre-catalyst of formula

\[
[Ru(L)(Diene)(L')_n]X \quad \text{(III)}
\]

wherein L represents a C5-C25 derivative of cyclopentadienyl ligand (Cp), Diene represents a C4-C22 diene and X represents a non coordinated anion, n represent 2, 1 or 0 and L' represents a solvent; and
- at least an acidic additive of the type described further below, preferably in a total amount of about 0.1, or even 0.2, to 100 molar equivalents, relative to the compound (III).

Possible substituents of R\textsuperscript{1} to R\textsuperscript{6}, when taken alone or together, are one or two groups which do no stop the reduction of the substrate by the catalyst. Non-limiting typical examples of such substituents are OR\textsuperscript{7}, COR\textsuperscript{7}, OCOR\textsuperscript{7} or COOR\textsuperscript{8}, R\textsuperscript{7} representing a hydrogen atom or a C1-C12 alkyl or alkenyl group, if one of the R\textsuperscript{1} to R\textsuperscript{6} is substituted with two geminal OR\textsuperscript{7} groups, said two R\textsuperscript{7} can be bound together to form a C2-C4 alkanediyl group, R\textsuperscript{8} representing a C1-C12 alkyl or alkenyl group.

According to a particular embodiment of the invention, possible substituents of R\textsuperscript{1} to R\textsuperscript{6}, when taken alone or together, are OR\textsuperscript{7}, OCOR\textsuperscript{7} or COOR\textsuperscript{8}, R\textsuperscript{7} representing a hydrogen atom or a C1-C\textsubscript{6} alkyl or alkenyl group, if one of the R\textsuperscript{1} to R\textsuperscript{6} is substituted with two geminal OR\textsuperscript{7} groups, said two R\textsuperscript{7} can be bound together to form a C2-C4 alkanediyl group, R\textsuperscript{8} representing a C1-C\textsubscript{6} alkyl or alkenyl group. Said R\textsuperscript{7} or R\textsuperscript{8} can even be C1-C\textsubscript{6} alkyl group.

When any of R\textsuperscript{1}, R\textsuperscript{2}, R\textsuperscript{3}, R\textsuperscript{4}, R\textsuperscript{5} or R\textsuperscript{6} represent an alkenyl group, then said group can be a de-conjugated or conjugated alkenyl group. It is understood that by
"de-conjugated alkenyl" it is meant that the carbon carbon double bond of said group is not conjugated with the diene moiety, i.e. does not form a conjugated triene system.

It is understood that by "alkyl or de-conjugated alkenyl group" it is meant that said R<sub>1</sub> to R<sub>6</sub> can be in the form of, e.g., a linear, branched or (poly)cyclic group or can also be in the form of a mixture of said type of groups, e.g. a specific group may comprise a linear alkyl and a (poly)cyclic alkyl moiety, unless a specific limitation to only one type is mentioned.

Concerning compound (II), since it is an olefin, it can be obtained in the form of a mixture of two isomers, i.e. the one wherein the groups R<sub>1</sub> and R<sub>2</sub> are in a cis configuration ("czV-alkene (H)) or wherein the groups R<sub>1</sub> and R<sub>2</sub> are in a trans configuration ("trans"-alkene (IF))

It is understood that according to the invention the alkene obtained is in the form of a mixture "cis"-alkene and "trans"-alkene, wherein the ratio "cis"-alkene / "trans"-alkene (cis/trans) is above 1. According to a particular embodiment, said ratio is above 4 or even above 10. In another particular embodiment, said cis/trans ratio can be above 19 or even above 30, and in some cases ratio of above 45 or more can be obtained. In any case the presence of the acidic additive in the prescribed concentration range allows to improve said ratio.

The substrate (I), due to the fact that it is a diene, can be in the form of a mixture of its three configuration isomers, i.e. the (Z,Z), (E,Z) and (E,E) isomers.

According to a further embodiment of the invention, the substrate is a diene comprising at least one ester or an alcohol functional group. Said diene can advantageously provide an unsaturated ester or alcohol useful in the pharmaceutical, agrochemical or perfumery industry as final product or as an intermediate. Particularly preferred substrate is a diene comprising at least one ester or an alcohol functional group, and said diene will provide an unsaturated ester or alcohol useful in the perfumery industry as final product or as an intermediate.
According to another embodiment of the invention, the substrate is a compound of formula (I) wherein

R¹, R², R³, R⁴, R⁵ and R⁶ represent, simultaneously or independently from each other, a hydrogen atom or a Ci-Cs alkyl or de-conjugated alkenyl group, optionally substituted; and

R¹ and R³, or R³ and R⁴, or R² and R⁶, or R⁶ and R⁵, or R⁴ and R⁵, taken together, may form a C₃-10 alkanediyl or de-conjugated alkenediyl group, optionally substituted.

According to another embodiment of the invention, the substrate is a compound of formula (I) wherein

R¹, R⁴ and R⁵ represent each a hydrogen atom; and

R², R³ and R⁶ represent, simultaneously or independently from each other, a hydrogen atom or a Ci-Cs alkyl or de-conjugated alkenyl group, optionally substituted.

Possible substituents of R¹ to R⁶, when taken alone or together, are as described above.

Particular examples of substrate (I) are those of formula

\[ R^a \underset{\text{R}}{\text{=}} \text{R}^b \]  

wherein R⁴ represents a linear, branched or cyclic Ci-Cs alkyl or alkenyl group, preferably a linear or branched alkyl one; and

R⁵ represents a (CH₂)ₘX group, m representing 0, 1, 2 or 3, X representing a CHO, OH, OCOR, OR or COOR group, R⁶ being a Ci-C₈ alkyl or alkenyl group.

More specific examples are the compounds of formula (F) wherein R⁴ represents a methyl, ethyl or propyl group, and R⁵ a (CH₂)ₘX group, m representing 0, 1, or 2, X being as defined above. According to a particular embodiment the substrate can be sorból, a Ci₅ alkyl sorbate, or a sorból esters of Ci₅ carboxylates.

Furthermore, said substrate (F) can be essentially in the form of its (Z,Z) isomer (e.g. comprising at least 99% w/w of the isomer (Z,Z)).

Other particular examples of substrate (I) are those of formula

\[ R^d \underset{\text{R}}{\text{=}} \text{R}^e \]
wherein \( R^d \) and \( R^e \) represent a hydrogen atom or a \( \text{Ci-Cs} \) alkyl or alkenyle group, optionally substituted by a \( \text{OH, OCOR}^f \), \( \text{OR}^f \) or \( \text{COOR}^f \) group, \( R^f \) being a \( \text{Ci-C}_8 \) alkyl or alkenyl group, provided that \( R^d \) and \( R^e \) do not represent each a hydrogen atom.

More specific examples of the compounds of formula (I”) can be the ocimene, myrcene, myrcenol or its \( \text{Ci}_8 \) carboxylates.

The process of the invention is characterized by the use, as catalyst or pre-catalyst (hereinafter referred to as complexes unless specified otherwise), of a ruthenium complex as described above.

According to a particular embodiment of the invention \( L' \) can be acyclic or cyclic non aromatic ketone or esters, such as acetone or methyl acetate. The ketone can be coordinated in its enolic form.

According to a particular embodiment of the invention, \( L \) can be a \( \text{C}_6^\text{a}-\text{C}_{25} \) compound of formula

![Diagram](image)

wherein each \( R^9 \) represents, simultaneously or independently from each other, a hydrogen atom, a phenyl group optionally substituted, or a \( \text{C}_1^\text{a}-\text{C}_{10} \) alkyl or alkenyl group optionally substituted; and

one or two of said groups \( R^9 \) can be a \( \text{CF}_3 \) group, a \( \text{OSiR} \) \( \text{\textsuperscript{11}} \), \( \text{OCOR} \) \( \text{\textsuperscript{10}} \), \( \text{COR} \) \( \text{\textsuperscript{10}} \) or \( \text{COOR} \) \( \text{\textsuperscript{10}} \) group, \( R^1 \) representing a \( \text{Ci-Cn} \), or preferably a \( \text{Ci-C}_6 \), alkyl group, \( R^9 \) representing a \( \text{R}^1 \) or \( \text{CF}_3 \) group or a phenyl group optionally substituted; and

at least one \( R^9 \) is an alkyl group; two adjacent \( R^9 \) can be bound together to form a \( \text{C}_2^\text{a}-\text{C}_{10} \) alkanediyl group.

Possible substituents of \( R^9 \), when representing a alkyl or alkenyl group, include one or two methyl, ethyl, methoxy or ethoxy groups. Possible substituents of \( R^9 \), when representing a phenyl group, or of \( R^9 \), include one or two methyl, ethyl, methoxy, ethoxy or nitro groups or \( \text{CF}_3 , \text{F}, \text{Cl}, \text{Br} \) groups.

According to an embodiment of the invention, \( L \) can be a \( \text{C}_6^\text{a}-\text{C}_{2} \) compound of formula (IV) wherein
each \( R^9 \) represents, simultaneously or independently from each other, a hydrogen atom, a Ci-Cio alkyl or alkenyl group; and

one or two of said groups \( R^9 \) can be a OSiR\(^{11}\), OCOR\(^{10}\), COR\(^{10}\) or COOR\(^{10}\) group, \( R^{11} \) representing a C\(_1\)-C\(_4\) alkyl group, \( R^{10} \) representing a \( R^{11} \) or CF\(_3\) group or a phenyl group optionally substituted, as described above; and

at least one \( R^9 \) is an alkyl group.

According to an embodiment of the invention, \( L \) can be a C\(_6\)-C\(_2\)Ocompound of formula (IV) wherein each \( R^9 \) represents, simultaneously or independently from each other, a hydrogen atom, a Ci-Cio alkyl or alkenyl group; and

one or two of said groups \( R^9 \) can be a OSiR\(^{11}\), \( R^{11} \) representing a C1-C4 alkyl group; and at least one \( R^9 \) is an alkyl group.

According to an embodiment of the invention, four \( R^9 \) represent, simultaneously or independently from each other, a hydrogen atom or a Ci-C4 alkyl group (such as methyl or ethyl) and one \( R^9 \) represents OSiR\(^{11}\), \( R^{11} \) representing a C1-C4 alkyl group (such as methyl or ethyl), and at least one \( R^9 \) is an alkyl group.

According to an embodiment of the invention, two \( R^9 \) represent, simultaneously or independently from each other, a hydrogen atom or a Ci-C4 alkyl group (such as methyl or ethyl) and the three other \( R^9 \) represent, simultaneously or independently, a Ci-C4 alkyl groups (such as methyl or ethyl).

According to another particular embodiment of the invention one \( R^9 \) represents a hydrogen atom or a methyl or ethyl group and the other \( R^9 \) represent a methyl or ethyl group. In particular compound (IV) can be 1,2,3,4,5-pentamethyl-cyclopentadienyl (i.e. Cp\(^*\) or C\(_5\)Me\(_5\)), 1-ethyl-2,3,4,5-tetramethyl-cyclopentadienyl (i.e. C\(_5\)EtMe4), 1,2-diethyl-3,4,5-trimethyl-cyclopentadienyl (i.e. C\(_5\)(1,2-Et\(_2\))Me\(_3\)) or 1,2,3,4,5-pentaethyl-cyclopentadienyl (C\(_5\)Et\(_5\)).

The cyclopentadiene precursor CpH of the cyclopentadienyl ligand Cp (L) mentioned above can be obtained by applying standard general methods which are well known in the state of the art and by the person skilled in the art (see for example WO 2006/051503). Some of said ligands are even commercially available.

The Diene can be a C\(_4\)-C\(_{22}\) non-aromatic hydrocarbon group comprising two carbon-carbon double bonds, said carbon-carbon double bonds can be conjugated or non-conjugated. Said Diene can be in particular a linear, branched or cyclic C\(_5\)-Ci\(_2\).
hydrocarbon diene optionally substituted by the same substituents as described for R₁ to R₆ herein above. Furthermore, it is also understood that said Diene can be the substrate itself or a different compound.

According to a particular embodiment the Diene is preferably a conjugated or non-conjugated cyclic C₆-Ci₂ alkadiene, and in particular one of the cyclooctadienes (COD).

As typical, and non-limiting, examples of Diene, one may cite the following: cycloocta-1,5-diene, cycloocta-1,4-diene, cycloocta-1,3-diene, NBD (norbornadiene), hepta-1,4-diene, pentadiene, 2,4-dimethylpentadiene, 2,3-dimethylpentadiene, 2,3,4-trimethylpentadiene, 2,4-di(tert-butyl)-pentadiene or yet 2,4-dimethyl-1-oxapentadiene, butadiene, hexa-1,5-diene, or a compound of formula (F) or (I') as mentioned above.

Particular examples of the non-coordinating anion X are Cl(V, R²SO⁻), wherein R² is a chlorine of fluoride atom or an Ci-Cs fluoroalkyl or fluoroaryl group, BF₄⁻, PF₆⁻, SbCl₆⁻, SbF₆⁻, or BR₃Y⁻, wherein R³ is a phenyl group optionally substituted by one to five groups such as halide atoms or methyl or CF₃ groups.

According to a preferred embodiment of the invention, the anion is BF₄⁻, PF₆⁻, C₆F₅SO⁻, BPh₄⁻, CF₃SO₃⁻ or yet B[3,5-(CF₃)₂C₆H₄]₄⁻, even more preferably BF₄⁻.

As examples of the complex (III) one may cite the following:

[Ru(C₅Me₃)(1,3-COD)]BF₄⁻, [Ru(C₅Et₂)(1,3-COD)]BF₄⁻,
[Ru(C₅Me₄H)(1,3-COD)]BF₄⁻, [Ru(C₅P(C₃Me)₂)(1,3-COD)]BF₄⁻,
[Ru(C₅(1,2,4-Bu₃H)₂)(1,3-COD)]BF₄⁻, [Ru(C₅Me₄Bu)(1,3-COD)]BF₄⁻,
[Ru(C₅Me₃OSiMe₂)X](3-COD)]BF₄⁻, [Ru(C₅Me₃)(1,2-Et₂Me)](1,3-COD)]BF₄⁻,
[Ru(C₅Me₃)(1,3-COD)]PF₆⁻, [Ru(C₅Me₃)(1,3-COD)]SbF₆⁻,
[Ru(C₅Me₃)(1,3-COD)]ClO₄⁻, [Ru(C₅Me₃)(1,3-COD)]CF₃SO₃⁻,
[Ru(C₅Me₃)(NBD)(C₃H₆O)]BF₄⁻, [Ru(C₅Me₃)(1,5-hexadiene)(C₃H₆O)]BF₄⁻, or
[Ru(C₅Me₃)(dimethylbutadiene)(C₃H₆O)]BF₄⁻.

In a general way, the complexes of formula (III) can be prepared and isolated prior to their use in the process according to some methods described in the literature for example by P.J. Fagan et al. (Organometallics, 1990, 9, pg 1843-1852), F. Bouachir et al. (Organometallics, 1991, 10, pg 455-462) or P. Alvarez et al. (Organometallics, 1991, 20, pg 3762-3771), the one choosen depending on the nature of cyclopentadienyl and diene ligands and also of the non-coordinating anion.

It is also understood that the complex of formula (III) can also be obtained in situ
from complexes which have a similar formula and are cationic or anionic according to the
standard knowledge of a person skilled in the art. For example, reaction can be run using
[Ru(Cp*)(COD)Y] (Y being F, Cl, Br or I and method for preparation having been
described by P.J. Fagan et al. in Organometallics, 1990, 9, pg 1843-1852) as precursors in
the presence of the substrate and silver or tellurium salts).

From the present invention, it is preferably excluded the case wherein the substrate
is sorbol and the catalysts is [(Cp*)Ru(COD)]X.

Many of the above-mentioned complexes of formula (III) are new and therefore
represent also another aspect of the present invention.

In particular said new complexes (III) can be the ones wherein L is a C₆-C₂₅
compound of formula

\[
\text{(IV)}
\]

wherein each R⁹ represents, simultaneously or independently from each other, a hydrogen
atom, a phenyl group optionally substituted, or a C₁-C₁₀ alkyl or alkenyl group optionally
substituted; and

one or two of said groups R⁹ is a OSiR¹¹ or OCOR¹⁰ group, R¹¹ representing a C₁-C₆
alkyl group, R¹⁰ representing a R¹¹ or CF₃ group or a phenyl group optionally substituted;
and

at least one R⁹ is an alkyl group; two adjacent R⁹ can be bound together to form a C₂-C₁₀
alkanediyl group.

Possible substituents of R⁹, when representing a alkyl or alkenyl group, include
one or two methyl, ethyl, methoxy or ethoxy groups. Possible substituents of R⁹, when
representing a phenyl group, or of R¹⁰, include one or two methyl, ethyl, methoxy, ethoxy
or nitro groups or CF₃, F, Cl, Br groups.

According to an embodiment of the invention, four R⁹ represent, simultaneously or
independently from each other, a hydrogen atom or a C₁-C₄ alkyl group (such as methyl
or ethyl) and one R⁹ represents OSiR¹¹, R¹¹ representing a C₁-C₄ alkyl group (such as
methyl or ethyl), and at least one R⁹ is an alkyl group.
To carry out the processes of the invention, it is required also to use at least an acidic additive. By "acidic additive" it is meant a compound capable of providing at least one proton to the catalytic cycle. Said acidic additive is preferably an organic or inorganic compound having a pKa comprised between 0.8 and 7, but in the case of phenols or boron derivatives said pKa can range up to 10.

Furthermore, said acidic additive can be selected from the group consisting of:
- compound of formula \( R^{14}_{(3-x)} MO(OH)_x \) wherein \( R^{14} \) is a \( R^{14} \) or \( R^{14} \) group wherein \( R^{14} \) is a Ci-Cs alkyl, \( \text{P} \) or As and \( x \) is 1 or 2;
- a boron derivative of formula \( R^{14} B(OH)_2 \), wherein \( R^{14} \) is as defined above; and
- phenol or a phenol substituted by up to three C1-C4 alkyl, alkoxy or carboxylic groups, nitro groups or halogen atoms;
- a C1-C12 mono-carboxylic non-amino acid;
- a HOOCCH=CHCOOH di-acide, or the tetronic acid.

By "mono-carboxylic non-amino acid" it is meant here a mono-carboxylic acid which is not substituted by a primary, secondary or tertiary amino group or heteroaromatic nitrogen derivatives.

According to a particular embodiment, said \( R^{14}_{(3-x)} MO(OH)_x \) acids can be a derivative wherein \( R^{14} \) is a Ci-Cs alkyl or alkoxy group or a C6-Cs phenyl or phenoxyl group optionally substituted, M is P or As and \( x \) is 1 or 2.

Similarly said \( R^{14} B(OH)_2 \) acids can be those wherein \( R^{14} \) is a Ci-Cs alkyl or alkoxy group or a Ci-Cs phenyl or phenoxyl group optionally substituted.

According to another embodiment of the invention, said acid can be the phenol or a phenol substituted by one C1-C4 alkyl, alkoxy or carboxylic group, a nitro group or a halogen atom.

Furthermore, according to an other particular embodiment of the invention, said acidic additive can be a mono-carboxylic acid of formula \( R^{15} \text{COOH} \), wherein \( R^{15} \) represents a C1-C12 hydrocarbon group or a Ci-Ci halogenated or per-halogenated hydrocarbon group, optionally substituted by one alcohol group or one or two ether or ester groups. According to a further embodiment, said carboxylic acid is advantageously selected from the group consisting of:
- a carboxylic acid of formula \( R^{15} \text{COOH} \), wherein \( R^{15} \) represents a halogenated or per-halogenated Ci-Cs hydrocarbon group;
- a \( R^{16} \text{CH(OR}^{16} \) group, \( R^{16} \) being a hydrogen atom or a Ci-C6 hydrocarbon group;
a C₁⁻C₁₂ hydrocarbon group, optionally substituted by one or two ether or ester groups, the optional substituent being by one, two or three C₁⁻C₄ alkyl, alkoxy or carboxylic groups, or nitro groups or halogen atoms.

One can cite, as non-limiting examples, of said acidic additive the following:

- (BuO)₂PO(OH), (₃BuO)₂PO(OH), (PhO)₂PO(OH), (PhCH₂O)₂PO(OH), ₃BuPO(OH)₂,
- Ph₂PO(OH), PhPO(OH)₂, PhAsO(OH)₂, (Me)₂AsO(OH), CF₃COOH, HCF₂COOH,
- maleic or fumaric acid, glycolic acid, pyruvic acid, sorbic, acetic or oleic acid, tetronic acid, C₆H₃B(OH)₂, PhB(OH)₂, p-OMe-benzoic, benzoic or p-(COOMe)-benzoic acid,
- phenol, 3,5-dimethoxy-phenol or 2-methoxy-phenol. Of course, other suitable acidic additives responding to the above description can be used.

According to another embodiment of the invention, said acidic additives can be selected from the group consisting of:

- a compound of formula R¹⁴₂MO(OH) or R¹⁴MO(OH)₂, wherein R¹⁴ is a C₁⁻C₆ alkyl or alkoxy group or a C₆⁻C₈ phenyl or phenoxy and M is P or As; and
- maleic or glycolic acid and an halogenated or per-halogenated C₁⁻C₇ mono-carboxylic acid.

As previously mentioned, the processes of the invention consist in the hydrogenation of a substrate using a ruthenium complex and an acidic additive. A typical process implies the mixture of the substrate with the ruthenium complex, at least one acidic additive and optionally a solvent, and then treating such a mixture with molecular hydrogen at a chosen pressure and temperature.

The complexes of the invention, an essential parameter of the process, can be added to the reaction medium in a large range of concentrations. As non-limiting examples, one can cite as complex concentration values those ranging from 0.01 mol% to 5 mol%, the molar percentage being relative to the amount of substrate. Preferably, the complex concentration will be comprised between 0.03 mol% to 2 mol%. It goes without saying that the optimum concentration of complex will depend, as the person skilled in the art knows, on the nature of the latter, on the nature of the substrate, on the nature of the solvent and on the pressure of H₂ used during the process, as well as the desired time of reaction.

Useful quantities of acidic additive, added to the reaction mixture, may be comprised in a relatively large range. Apart from the one above cited, one can cite, as non-limiting examples, total amounts ranging between 0.5 to 50 molar equivalents,
relative to the complex, preferably 0.8 to 20, and even more preferably between about 2 and about 10 molar equivalents.

The hydrogenation reaction can be carried out in the presence or absence of a solvent. When a solvent is required or used for practical reasons, then any solvent current in hydrogenation reactions can be used for the purposes of the invention. Non-limiting examples include non-aromatic solvents such as C_{1-12} non aromatic ketones, esters, alkanes ethers, chlorinated alkanes and alcohols or mixtures thereof. According to an embodiment of the invention, the solvent is advantageously selected amongst the C_{12} alkyl ketones, esters, ethers or chlorinated alkanes. In particular and as non-limiting examples one may cite the following: acetone ethyl acetate, MTBE, THF, iso-propyl acetate, Et_2O, dichloromethane, 1,2-dichloethane, EtoH, MeOH, pentane, hexane. The choice of the solvent can be done as a function of the nature of the complex and the person skilled in the art is well able to select the solvent most convenient in each case to optimize the hydrogenation reaction.

In the hydrogenation process of the invention, the reaction can be carried out at a H_2 pressure comprised between 10^5 Pa and 80x10^5 Pa (1 to 80 bars) or even more if desired. Again, a person skilled in the art is well able to adjust the pressure as a function of the catalyst load and of the dilution of the substrate in the solvent. As examples, one can cite typical pressures of 1 to 30x10^5 Pa (1 to 30 bar).

The temperature at which the hydrogenation can be carried out is comprised between 0^0C and 120^0C, more preferably in the range of between 40^0C and 100^0C. Of course, a person skilled in the art is also able to select the preferred temperature as a function of the melting and boiling point of the starting and final products as well as the desired time of reaction or conversion.

**Examples**

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

All the procedures described hereafter have been carried out under an inert atmosphere unless stated otherwise. Hydrogenations were carried out in open glass tubes placed inside a stainless steel autoclave. H_2 gas (99.99990%) was used as received. All substrates and solvents were distilled from appropriate drying agents under Ar. NMR
spectra were recorded on a Bruker AM-400 (400 MHz) spectrometer and normally measured at 300 K, in CD$_2$Cl$_2$ unless indicated otherwise. Chemical shifts are listed in ppm and coupling constant J are in Hz.

Example 1

A) Synthesis of cyclopentadienes
Cyclopentadienes were synthesized starting from substituted cyclopentenones prepared according to procedure previously described in patent WO 2006051503.

R$_n$ is an alkyl or alkenyl group
A solution of cyclopentenone (1 equivalents) in THF (1.6 M) was added at 0°C under inert atmosphere to a solution of R·MgCl (1.2 equivalents). Reaction mixture was then allowed to warm to room temperature and stirred for 3 hours. Acetic acid 10% was then added to the reaction mixture and the organic phase was extracted with Et$_2$O. HCl (20% in water) was added to the organic phase and allowed to stir for 30 minutes. The organic phase was then neutralized with NaHCO$_3$ (5% in water). Washing with water, drying and evaporation of solvent gave a crude product, which was purified by distillation.

R$_n$= H
Cyclopentenones were reduced by NaBH$_4$ (0.5 equivalents) in EtOH under inert atmosphere. After work-up, the crude products were purified by fractionated distillation.

R$_n$= alkoxy or siloxy
A solution of Li(NiPr)$_2$ (1.2 equivalents) in THF (2M) was added to a solution of cyclopentanone (1 equivalent) in THF (0.1 M) at -78°C. After 1 hour stirring the alkyl
halide R^n-halide or the siloxy halide (R^π)3Si-halide (1.5 equivalents) was added to the reaction mixture.

Reaction mixture was then allowed to warm to room temperature and stirred for 5 hours. Reaction mixture was evaporated to dryness and n-hexane was added. The solid salts were eliminated by filtration and the solution was then evaporated to dryness. The crude product was purified by distillation.

Ligand Cs(1,2,4-BUs)H₂ was synthesized according to the literature (E. V. Dehmlow, C. Bollmann, Z.Naturforsch., 1993, 48b, 457-460).

B) Catalyst synthesis

Ruthenium catalysts were synthesized according to three different ways depending on the nature of cyclopentadienyle and diene ligands but also of the counter-ion. All the solvent used were dried and stored under inert atmosphere.

**Method 1:**

[Ru(L)(1,3-COD)]BF₄ complexes with L being a cyclopentadienyl ligand bearing no aromatic groups were obtained in two steps starting from [Ru(COD)(COT)], via [(CODyl)₂RuH][BF₄], both obtained according to a procedure previously described by F. Bouachir, B. Chaudret, F. Dahan, F. Agbossou, I. Tkatchenko, *Organometallics*, 1991, 10, 455-462.

To [Ru(CODyl)₂H]BF₄ in solution in CH₂Cl₂ (0.05 M) under inert atmosphere was added a stoichiometric amount of the desired substituted cyclopentadiene derivative L (1 equivalent / Ru) and reaction mixture was stirred at room temperature for 16 hours. It was then concentrated to dryness. [(L)Ru(1,3-COD)][BF₄] complexes were crystallized from a CH₂Cl₂/Et₂O mixture. It was obtained in more than 80% molar yield after filtration and drying under vacuum.

[Ru(C₅Me₅)(1,3-COD)]BF₄:

^1H NMR (233°K): 6.44 (t, J=6.8, 1H); 4.89 (m, 2H); 3.38 (m, 2H); 1.89 (m, 2H); 1.85 (s, 15H); 1.50 (m, 2H); 1.41 (m, 1H); 0.35 (q, J=13.6, 1H); -0.41 (s broad, 1H).

^13C NMR (233°K): 106.36, 98.30, 83.88, 40.94, 21.92, 18.89, 10.27.
[Ru(C₅Et₅)(1,3-COD)]BF₄:

¹H NMR(233K): 6.41 (t, J=6.8, IH); 4.87 (m, 2H); 3.36 (m, 2H); 2.20 (q, J=7.5, 10H); 1.91 (m, 2H); 1.47 (m, 2H); 1.40 (m, IH); 1.22(t, J=7.52, 15H); 0.37 (m, 1H); -10.48 (s broad, IH).

¹³C NMR (233K): 102.61, 91.20, 77.49, 48.92, 29.35, 21.98, 10.01.

[Ru(C₅Me₄HX1,3-COD)]BF₄:

¹H NMR (233K): 6.46 (t, J=6.8, IH); 5.37 (s, 2H); 4.97 (m, 2H); 3.43 (m, 2H); 1.87 (dt, J=4.12, 15.68, 2H); 1.77 (s, 6H); 1.74 (s, 6H); 1.50 (m, 2H); 1.37 (dt, J=3.4, 15.0, IH)

¹³C NMR (233K): 106.59, 100.01, 99.30, 83.79, 82.64, 40.76, 21.93, 18.88, 11.56, 9.76.

[Ru(C₅Me₄Me₂X1,3-COD)]BF₄:

¹H NMR (233K): 6.51 (t, J=6.8, IH); 4.93 (m, 2H); 3.41 (m, 2H); 1.96 (m, 2H); 1.91 (s, 6H); 1.66 (s, 6H); 1.55 (m, 2H); 1.51 (s, 9H); 1.44 (m, IH); 0.48 (m,lH); -10.35 (s broad, IH).

¹³C NMR (233K): 108.79, 106.83, 99.73, 99.21, 84.21, 41.77, 33.84, 32.47, 22.31, 18.91, 13.18, 9.97.

[Ru(C₅[1,2-Pr₃]Me₂X1,3-COD)]BF₄:

¹H NMR (233K): 6.54(t, J=6.8, IH); 4.97(m, 2H); 3.51 (m, 2H); 2.88 (m, 2H)1.96 (dt, J=3.4, 15.7, 2H); 1.83 (s, 6H); 1.54 (m, 2H); 1.51 (s, 3H); 1.45 (m, IH); 1.36(d, J=6.8, 6H); 1.32(d, J=7.5, 6H); 0.44 (qt, J=3.4, 14.3, IH); -10.36 (s broad, IH).

¹³C NMR (233K): 102.61, 91.20, 95.71, 77.49, 48.92, 29.35, 21.98, 10.01.

[Ru(C₅Me₄(Me₃SiO))(U-COD)]BF₄:

¹H NMR (233K): 6.23 (t, J=6.8, IH); 4.74 (m, 2H); 3.34 (m, 2H); 2.03 (s, 6H); 1.47 (s, 6H); 1.51 (m, 2H); 1.35 (m, IH); 0.38 (m,lH); 0.03 (s, 9H); 9.19 (s broad, IH).

¹³C NMR (233K): 138.96, 106.79, 92.85, 90.86, 86.49, 83.59, 39.76, 22.25, 19.35, 9.26, 9.18, 0.00.

[Ru(C₅(U₄-Bu₃)H₂)(1,3-COD)]BF₄:

¹H NMR (233K): 7.02 (t, J=6.8, IH); 5.51 (m, 2H); 5.22 (s, 2H); 3.97 (m, 2H); 2.01 (m, 2H); 1.54 (m, 2H); 1.49 (m, IH); 1.35 (s, 18H); 1.19 (s, 9H); 0.48 (m,lH); 10.89 (s broad, IH).
\(^{13}\)C NMR (233K): 114.06, 112.76, 106.98, 83.66, 81.94, 36.93, 33.31, 31.35, 31.21, 30.78, 21.58, 18.60.

Method 2:


[\([\text{Ru}(L)\text{Cl}_2]\)\] was first obtained reacting \([\text{RuCl}_3\text{X}_2]_\text{H}_2\text{O}\) in EtOH (0.25 M) with an excess of the desired substituted cyclopentadiene derivative \(L\) (2.5 equivalents/Ru). The reaction mixture was heated to reflux under inert atmosphere for 3 hours and then cooled down to room temperature. Desired product was recovered by filtration. It was obtained in more than 70% molar yield after washings with EtOH and drying under vacuum.

[\([\text{Ru}(L)\text{Cl}]_4\) was then obtained by reaction at room temperature under inert atmosphere of a [\([\text{Ru}(L)\text{Cy}_n\) suspension in THF (0.6 M) with 1 equivalent/Ru of a 1 M lithium triethylborohydride solution in THF. After stirring at room temperature for 1 hour, reaction mixture was filtered under inert atmosphere. Recovered product was obtained in more than 75% molar yield after washing with THF and drying under vacuum.

[\([\text{Ru}(L)(\text{diene})\text{Cl}]\) was obtained by reaction at room temperature under inert atmosphere of [\([\text{Ru}(L)\text{Cl}]_4\) in solution in THF (0.05 M) with a slight excess of the desired diene (1.5 equivalents / Ru). After stirring for 1 hour, reaction mixture was filtered under inert atmosphere and the retrieved solution was concentrated to dryness. The obtained residue was precipitated by trituration in pentane and solid product was retrieved by filtration under inert atmosphere. It was obtained in more than 75% molar yield after washing with pentane and drying under vacuum.

[\([\text{Ru}(L)(\text{diene})X]\) was obtained by reaction at room temperature under inert atmosphere of [\([\text{Ru}(L)(\text{diene})\text{Cl}]\) in solution in acetone (0.25 M) with stoechiometric amount (1 equivalents / Ru) of AgX. After stirring at room temperature for 1 hour, reaction mixture was filtered under inert atmosphere and the retrieved solution was concentrated.
to dryness. \([\text{Ru}(L)(\text{diene})\text{X}]\) was crystallized from a \(\text{CH}_2\text{Cl}_2\text{ZEt}_2\text{O}\) mixture. It was obtained in more than 75% molar yield after filtration drying under vacuum. It is worth noticing that product was sometimes obtained as the acetone adduct depending mainly on the nature of the diene, acetone being then coordinated to the ruthenium centre as the ketone or enol form (observed by IR spectroscopy).

\[\text{[Ru(C}_5\text{Me}_5)(\text{NBD})\text{]}\text{BF}_4:}\n
\(^1\text{H}\) NMR (298K): 4.61 (m, 2H); 4.52 (m, 2H); 4.26 (m, 2H); 3.86 (m, 2H); 1.55 (s, 15H).

\(^{13}\text{C}\) NMR (298K): 94.95, 78.43, 65.53, 64.54, 51.99, 9.48.

\[\text{[Ru(C}_5\text{Me}_5)(\text{dimethylbutadiene})\text{]}\text{BF}_4:}\n
\(^1\text{H}\) NMR (298K): 4.01 (s, 4H); 1.96 (s, 6H); 1.55 (s, 15H).


\[\text{[Ru(C}_5\text{Me}_5)(2,4\text{-hexadienylacetate})\text{]}\text{BF}_4:}\n
\(^1\text{H}\) NMR (298K): 6.32 (dq, \(J = 6.84, 15.17, 1\)H); 5.85 (m, 1H); 5.36 (m, 1H); 4.43 (d, \(J = 6.08, 1\)H); 4.29 (t, \(J = 10.6, 1\)H); 3.08 (d, \(J = 10.6, 1\)H), 1.94 (s, 3H), 1.63 (dd, \(J = 1.52, 6.84, 3\)H), 1.56 (s, 15H).


\[\text{[Ru(C}_5\text{Me}_5)(U-COD)}\text{]}\text{CF}_3\text{SO}_3:}\n
\(^1\text{H}\) NMR (233K): 6.45 (t, \(J = 6.8\)Hz, 1H); 4.91 (m, 2H); 3.39 (m, 2H); 1.90 (m, 2H); 1.85 (s, 15H);1.51 (m, 2H); 1.40 (m, 1H); 0.37 (qt, \(j=3.4, 13.64, 1\)H); 10.40 (s broad, 1H).

\(^{13}\text{C}\) NMR (233K): 106.59, 98.42, 84.29, 41.29, 22.01, 18.92, 10.08.

\[\text{[Ru(C}_5\text{Me}_5)(1,3\text{-COD})\text{]}\text{PF}_6:}\n
\(^1\text{H}\) NMR (233K): 6.39 (t, \(J=6.8\)Hz, 1H); 4.86 (m, 2H); 3.37 (m, 2H); 1.91(m, 2H); 1.84 (s, 15H);1.51 (m, 2H); 1.41 (m, 1H); 0.37 (qt, \(j=3.4, 14.4, 1\)H);-10.41 (s broad, 1H).

\(^{13}\text{C}\) NMR (233K): 106.49, 98.46, 84.20, 41.32, 21.99, 18.90, 10.04.

\[\text{[Ru(C}_5\text{Me}_5)(1,3\text{-COD})\text{]}\text{ClO}_4:}\n
\(^1\text{H}\) NMR (233K): 6.45 (t, \(j=6.8\), 1H); 4.91 (m, 2H); 3.39 (m, 2H); 1.90 (m, 2H); 1.86 (s, 15H);1.53 (m, 2H); 1.41 (m, 1H); 0.38 (qt, \(j=3.4, 14.4, 1\)H);-10.38 (s broad, 1H).

\(^{13}\text{C}\) NMR (233K): 106.58, 98.43, 84.28, 41.31, 22.01, 18.94, 10.11
[Ru(C₅Me₅)(1,3-COD)]SbF₆:

$^1$H NMR (233K): 6.38 (t, J=6.8, 1H); 4.85 (m, 2H); 3.37 (m, 2H); 1.91 (m, 2H); 1.84 (s, 15H); 1.51 (m, 2H); 1.42 (m, 1H); 0.38 (qt, J=3.4, 14.4, 1H); -10.39 (s broad, 1H).

$^{13}$C NMR (233K): 106.49, 98.49, 84.22, 41.37, 22.01, 18.91, 10.04.

**Method 3:**

[Ru(L)(COD)]BF₄ complexes with cyclopentadienyl ligands L bearing aromatic groups were obtained according to a multi-step procedure previously described by P. Alvarez, J. Gimeno, E. Lastra, S. Garcia-Granda, J. F. Van der Maelen, M. Bassetti, *Organometallics* 2001, 20, 3762-3771.

[Ru(L)(diene)Cl] was obtained by reaction at room temperature under inert atmosphere of [Ru(diene)Cl₂] in suspension in THF (0.05) with a stoechiometric amount (1 equivalents/Ru) of a freshly prepared solution of L sodium salt in THF. After stirring for 1 hour at room temperature, a slight excess (1.2 equivalents / Ru) of HCl in solution in Et₂O (2 M) was added to reaction mixture that was stirred at this temperature for an additional hour. It was then filtered under inert atmosphere and the retrieved solution was concentrated to dryness. The obtained residue was precipitated by trituration in pentane and solid product was retrieved by filtration under inert atmosphere. It was obtained in more than 70% molar yield after washing with pentane and drying under vacuum.

[Ru(L)(diene)]] was obtained by reaction at room temperature under inert atmosphere of [Ru(L)(diene)Cl] in solution in acetone (0.25 M) with stoechiometric amount (1 equivalent/Ru) of AgX. After stirring at room temperature for 1 hour, reaction mixture was filtered under inert atmosphere and the retrieved solution was concentrated to dryness. [Ru(L)(diene)]X was crystallized from a CH₂Cl₂:ZEt₂O mixture. It was obtained in more than 75% molar yield after filtration drying under vacuum. It is worth noticing that product was sometimes obtained as the acetone adduct depending mainly on the nature of the diene, acetone being then coordinated to the ruthenium centre as the ketone or enol form.

**Example 2**

Hydrogenation processes according to the invention
Typical hydrogenation reaction procedure

Substrate, solvent, [Ru(L)(Diene)]X and the acidic additive according to the invention were loaded altogether under inert atmosphere an autoclave and the mixture was purged at room temperature with nitrogen (2 bars, 3 times) and then hydrogen (2 bars, 3 times) under stirring. The autoclave was then pressurized to the desired hydrogen pressure and heated at the desired temperature. The reaction was followed by hydrogen absorption monitoring and/or GC analysis sampling. The ruthenium catalyst was easily removed by distillation on residues and product isomers mixture was usually recovered in more than 90% molar yield.

The results obtained are summarized in the following tables.

Table 1: influence of the acidic additive and of its presence on hydrogenation selectivity

<table>
<thead>
<tr>
<th>Acidic additive</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene /“trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>&gt; 98%</td>
<td>52 / 48</td>
</tr>
<tr>
<td>(Ph)₂P(O)(OH)</td>
<td>&gt; 98%</td>
<td>82 / 18</td>
</tr>
<tr>
<td>maleic acid</td>
<td>&gt; 98%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>(BuO)₂P(O)OH</td>
<td>&gt; 98%</td>
<td>87 / 13</td>
</tr>
<tr>
<td>Me₂As(O)OH</td>
<td>&gt; 98%</td>
<td>74 / 26</td>
</tr>
<tr>
<td>2-methoxyphenol</td>
<td>&gt; 98%</td>
<td>65 / 35</td>
</tr>
<tr>
<td>Sorbic acid</td>
<td>&gt; 98%</td>
<td>60 / 40</td>
</tr>
<tr>
<td>Trifluoroacetic acid</td>
<td>&gt; 95%</td>
<td>80 / 20</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>&gt; 98%</td>
<td>85 / 15</td>
</tr>
</tbody>
</table>
Table 2: influence of the acidic additive and of its presence on hydrogenation selectivity

- reaction type:

\[
\text{[Ru(C₅Me₆)(1,3-COD)]BF₄ (0.1 mol.%)}
\]

\[
\text{acidic additive (0.5 mol.%)}
\]

\[
\text{H₂ (5 bars), 70°C, acetone (50 wt.%)}
\]

<table>
<thead>
<tr>
<th>Acidsic additive</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>&gt; 98%</td>
<td>45 / 55</td>
</tr>
<tr>
<td>(C₆H₄)B(OH)₂</td>
<td>&gt; 98%</td>
<td>52 / 48</td>
</tr>
<tr>
<td>sorbic acid</td>
<td>&gt; 98%</td>
<td>55 / 45</td>
</tr>
<tr>
<td>(Ph)₂P(O)(OH)</td>
<td>&gt; 98%</td>
<td>82 / 18</td>
</tr>
<tr>
<td>maleic acid</td>
<td>&gt; 98%</td>
<td>96 / 4</td>
</tr>
<tr>
<td>(BuO)₂P(O)OH</td>
<td>&gt; 98%</td>
<td>85 / 15</td>
</tr>
<tr>
<td>2-methoxyphenol</td>
<td>&gt; 98%</td>
<td>60 / 40</td>
</tr>
<tr>
<td>Trifluoroacetic acid</td>
<td>&gt; 95%</td>
<td>75 / 25</td>
</tr>
<tr>
<td>Me₂As(O)OH</td>
<td>&gt; 98%</td>
<td>70 / 30</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>&gt; 98%</td>
<td>80 / 20</td>
</tr>
</tbody>
</table>

Table 3: influence of the acidic additive and of its presence on hydrogenation selectivity

- reaction type:

\[
\text{[Ru(C₅Me₆)(U-COD)]BF₄ (0.1 mol.%)}
\]

\[
\text{acidic additive (0.5 mol.%)}
\]

\[
\text{H₂ (5 bars), 70°C, acetone (50 wt.%)}
\]

<table>
<thead>
<tr>
<th>Acidsic additive</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>&gt; 98%</td>
<td>3 / 97</td>
</tr>
<tr>
<td>(Ph)₂P(O)(OH)</td>
<td>&gt; 98%</td>
<td>83 / 17</td>
</tr>
<tr>
<td>(BuO)₂P(O)OH</td>
<td>&gt; 98%</td>
<td>88 / 12</td>
</tr>
</tbody>
</table>
Table 4: Influence of the acidic additive and of its presence on hydrogenation selectivity

- Reaction type:

\[ [\text{Ru(C}_5\text{Me}_5)(\text{1,3-COD})\text{BF}_4 (0.1 \text{ mol.\%}) ] \text{ acidic additive (0.5 mol.\%)} \]

\[ \text{H}_2 (5 \text{ bars}), 700^\circ\text{C}, \text{ acetone (50 wt.\%)} \]

<table>
<thead>
<tr>
<th>Acidic additive</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>&gt; 98%</td>
<td>83 / 17</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>&gt; 98%</td>
<td>93 / 7</td>
</tr>
<tr>
<td>Trifluoroacetic</td>
<td>&gt; 90%</td>
<td>80 / 20</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>&gt; 98%</td>
<td>85 / 15</td>
</tr>
</tbody>
</table>

Table 5: Influence of the acidic additive and of its presence on hydrogenation selectivity

- Reaction type:

\[ [\text{Ru(C}_5\text{Me}_5)(\text{1,3-COD})\text{BF}_4 (0.1 \text{ mol.\%}) ] \text{ acidic additive (0.5 mol.\%)} \]

\[ \text{H}_2 (5 \text{ bars}), 700^\circ\text{C}, \text{ acetone (50 wt.\%)} \]

<table>
<thead>
<tr>
<th>Acidic additive</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>&gt; 98%</td>
<td>88 / 12</td>
</tr>
<tr>
<td>(Ph)_2P(O)(OH)</td>
<td>&gt; 98%</td>
<td>96 / 4</td>
</tr>
<tr>
<td>(BuO)_2P(O)OH</td>
<td>&gt; 98%</td>
<td>95 / 5</td>
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<tr>
<td>Maleic acid</td>
<td>&gt; 98%</td>
<td>98 / 2</td>
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</table>
Table 6: influence of the acidic additive and of its presence on hydrogenation selectivity
influence of the Diene

<table>
<thead>
<tr>
<th>Diene</th>
<th>Presence of Maleic Acid</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
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</thead>
<tbody>
<tr>
<td>1,3-COD</td>
<td>no</td>
<td>&gt; 98%</td>
<td>52 / 48</td>
</tr>
<tr>
<td>1,3-COD</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>NBD</td>
<td>no</td>
<td>&gt; 97%</td>
<td>53 / 47</td>
</tr>
<tr>
<td>NBD</td>
<td>yes</td>
<td>&gt; 97%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>1,5-hexadiene</td>
<td>no</td>
<td>&gt; 96%</td>
<td>54 / 46</td>
</tr>
<tr>
<td>1,5-hexadiene</td>
<td>yes</td>
<td>&gt; 96%</td>
<td>96 / 4</td>
</tr>
</tbody>
</table>

Table 7: influence of the acidic additive and of its presence on hydrogenation selectivity
influence of the ligand L

<table>
<thead>
<tr>
<th>L</th>
<th>Presence of Maleic Acid</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅Me₅</td>
<td>no</td>
<td>&gt; 98%</td>
<td>52 / 48</td>
</tr>
<tr>
<td>C₅Me₅</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>1,2-(iPr)₂C₅Me₃</td>
<td>no</td>
<td>&gt; 99%</td>
<td>65 / 35</td>
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</table>
Table 8: influence of the acidic additive and of its presence on hydrogenation selectivity

<table>
<thead>
<tr>
<th>Reaction type:</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 98%</td>
<td>52 / 48</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 98%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 95%</td>
<td>88 / 12</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 96%</td>
<td>92 / 8</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 92%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 94%</td>
<td>92 / 8</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 94%</td>
<td>92 / 8</td>
</tr>
<tr>
<td>Maleic acid (none or 0.5 mol.%)</td>
<td>&gt; 98%</td>
<td>96 / 4</td>
</tr>
</tbody>
</table>

Table 9: influence of the acidic additive and of its presence on hydrogenation selectivity

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<tr>
<th>Reaction type:</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myrcene</td>
<td>&gt; 99%</td>
<td>97.5 / 2.5</td>
</tr>
<tr>
<td>Myrcene</td>
<td>&gt; 99%</td>
<td>85 / 15</td>
</tr>
<tr>
<td>Myrcene</td>
<td>&gt; 99%</td>
<td>98.5 / 1.5</td>
</tr>
<tr>
<td>Myrcene</td>
<td>&gt; 99%</td>
<td>58 / 42</td>
</tr>
<tr>
<td>Myrcene</td>
<td>&gt; 99%</td>
<td>90 / 10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction type:</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene / “trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 98%</td>
<td>52 / 48</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 98%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 95%</td>
<td>88 / 12</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 96%</td>
<td>92 / 8</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 92%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 94%</td>
<td>92 / 8</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 94%</td>
<td>92 / 8</td>
</tr>
<tr>
<td>2,4-hexad ιenol</td>
<td>&gt; 98%</td>
<td>96 / 4</td>
</tr>
</tbody>
</table>
### Table 10: Influence of the Acidic Additive and of its Presence on Hydrogenation Selectivity

<table>
<thead>
<tr>
<th>L</th>
<th>Presence of (C₅H₅)₂P(O)(OH) acid</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene/“trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅Me₄H</td>
<td>no</td>
<td>&gt; 98%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>C₅Me₄H</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>97.5 / 2.5</td>
</tr>
<tr>
<td>C₅Et₅</td>
<td>no</td>
<td>&gt; 98%</td>
<td>88 / 12</td>
</tr>
<tr>
<td>C₅Et₅</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>98 / 2</td>
</tr>
<tr>
<td>1,2-(iPr)₂C₅Me₃</td>
<td>no</td>
<td>&gt; 99%</td>
<td>80 / 20</td>
</tr>
<tr>
<td>1,2-(iPr)₂C₅Me₃</td>
<td>yes</td>
<td>&gt; 99%</td>
<td>95 / 5</td>
</tr>
<tr>
<td>1,2,4-(tBu)₂C₅H₂</td>
<td>no</td>
<td>&gt; 99%</td>
<td>50 / 50</td>
</tr>
<tr>
<td>1,2,4-(tBu)₂C₅H₂</td>
<td>yes</td>
<td>&gt; 99%</td>
<td>70 / 30</td>
</tr>
<tr>
<td>(Me₃SiO)C₅Me₄</td>
<td>no</td>
<td>&gt; 99%</td>
<td>85 / 15</td>
</tr>
<tr>
<td>(Me₃SiO)C₅Me₄</td>
<td>yes</td>
<td>&gt; 99%</td>
<td>95 / 5</td>
</tr>
</tbody>
</table>

- Reaction type:

\[
\text{[Ru(C₅Me₅, XDiene)(L')ₙBF₄ (0.05 mol %)](C₅H₅)₂P(O)(OH) (none or 0.25 mol %)}
\]

\[\text{H₂ (5 bars), 70°C, acetone (50 wt %)}\]

2,4-hexadiene complete conversion

L' being acetone in its ketone or enol form (n 0 or 1)

### Table 5: Influence of the Diene

<table>
<thead>
<tr>
<th>L</th>
<th>Presence of (C₅H₅)₂P(O)(OH) acid</th>
<th>1,4-Selectivity</th>
<th>Ratio “cis”-alkene/“trans”-alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBD</td>
<td>no</td>
<td>&gt; 98%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>NBD</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>98 / 2</td>
</tr>
<tr>
<td>dimethylbutadiene</td>
<td>no</td>
<td>&gt; 98%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>dimethylbutadiene</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>98 / 2</td>
</tr>
<tr>
<td>1,5-hexadiene</td>
<td>no</td>
<td>&gt; 99%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>1,5-hexadiene</td>
<td>yes</td>
<td>&gt; 99%</td>
<td>98 / 2</td>
</tr>
<tr>
<td>2,4-hexadienylacetate</td>
<td>no</td>
<td>&gt; 98%</td>
<td>90 / 10</td>
</tr>
<tr>
<td>2,4-hexadienylacetate</td>
<td>yes</td>
<td>&gt; 98%</td>
<td>98 / 2</td>
</tr>
</tbody>
</table>
Claims

1. A process for the catalytic reduction by 1,4-hydrogenation, using molecular H₂, of a C₅-C₂₂ conjugated diene of formula

\[ R^1 \quad R^2 \quad R^3 \quad R^4 \quad R^5 \quad R^6 \quad (I) \]

wherein R¹, R², R³, R⁴, R⁵ and R⁶ represent, simultaneously or independently from each other, a hydrogen atom or a C₁⁻C₁₂ alkyl or alkenyl group optionally substituted; one of R² or R⁶ may also represent a C₁⁻C₁₂ alkoxy or acyloxy group optionally substituted; and R¹ and R³, or R³ and R⁴, or R² and R⁶, or R⁶ and R⁵, or R⁴ and R⁵, taken together, may form a C₂⁻₁₆ alkanediyl or de-conjugated alkenediyl group, optionally substituted; into the corresponding alkene, of formula

\[ R^1 \quad R^2 \quad R^3 \quad R^4 \quad R^5 \quad R^6 \quad (II) \]

wherein R¹ to R⁶ have the same meaning as for the compound of formula (I), and wherein the isomer having the R¹ and R² groups in a cis configuration is predominant;

said process being characterized in that it is carried out in the presence of at least one ruthenium catalyst or pre-catalyst of formula

\[ [Ru(L)(Diene)(L')]_n X \quad (III) \]

wherein L represents a C₅-C₂₅ substituted cyclopentadienyl ligand, Diene represents a C₄-C₂₂ diene and X represents a non coordinated anion, n represent 2, 1 or 0 and L'
represents a solvent; and
- at least an acidic additive selected from the group consisting of:
a compound of formula R$_{14}^{14}$MO(OH)$_x$ wherein R$_{14}^{14}$ is a R$_{14}^{14}$ or R$_{14}^{14}$O group wherein
R$_{14}^{14}$ is a C$_{1-10}$ group, M is P or As and x is 1 or 2; and
a boron derivative of formula R$_{14}^{14}$B(OH)$_2$, wherein R$_{14}^{14}$ is as defined above; and
phenol or a phenol substituted by up to three C$_{1-4}$ alkyl, alkoxy or carboxylic groups, nitro groups or halogen atoms; and
a C$_{1-12}$ mono-carboxylic non-amino acid; and
a HOOCCH=CHCOOH di-acide, and the tetronic acid;
provided that the processes wherein compound (I) is sorbol and compound (III) is of formula [Ru(Cp*)(COD)]X are excluded.

2. A process according to claim 1, characterised in that L is a C$_6$-C$_{25}$ compound of formula

![Diagram](IV)

wherein each R$^9$ represents, simultaneously or independently from each other, a hydrogen atom, a phenyl group optionally substituted, or a C$_{1-10}$ alkyl or alkenyl group optionally substituted; and
one or two of said groups R$^9$ can be a CF$_3$ group, a OSiR$_{11}^{11}$, OCOR$_{10}^{10}$, COR$_{10}^{10}$ or COOR$_{10}^{10}$ group, R$_{11}^{11}$ representing a C$_{1-10}$ alkyl group, R$_{10}^{10}$ representing a R$_{11}^{11}$ or CF$_3$ group or a phenyl group optionally substituted; and
at least one R$^9$ is an alkyl group; two adjacent R$^9$ can be bound together to form a C$_2$-C$_{10}$ alkanediyl group.

3. A process according to claim 2, characterised in that two R$^9$ represent, simultaneously or independently from each other, a hydrogen atom or a C$_{1-4}$ alkyl group and the three other R$^9$ represent, simultaneously or independently, a C$_{1-4}$ alkyl groups.
4. A process according to claim 2, characterised in that four \( R^9 \) represent, simultaneously or independently from each other, a hydrogen atom or a \( \text{Ci-C}_4 \) alkyl group and one \( R^9 \) represents \( \text{OSiR}^{11}_3 \), \( R^{11} \) representing a \( \text{Ci-C}_4 \) alkyl group, and at least one \( R^9 \) is an alkyl group.

5. A process according to any one of claims 1 to 4, characterised in that Diene is a conjugated or non conjugated cyclic \( \text{C}_6-\text{C}_2 \) alkadiene.

6. A process according to any one of claims 1 to 5, characterised in that \( X \) is \( \text{ClO}_4^- \), \( R^{12} \text{SO}_3^- \) wherein \( R^{12} \) is a chlorine of fluoride atom or an \( \text{Ci-Cs} \) fluoroalkyl or fluoroaryl group, \( \text{BF}_4^- \), \( \text{PF}_6^- \), \( \text{SbCl}_6^- \), \( \text{SbF}_6^- \), or \( \text{BR}^{13} \text{Y} \), wherein \( R^{13} \) is a phenyl group optionally substituted by one to five halide atoms or methyl or \( \text{CF}_3 \) groups.

7. A process according to any one of claims 1 to 6, said mono-carboxylic acid is selected from the group consisting of a carboxylic acid of formula \( \text{R}^{15} \text{COOH} \), wherein \( \text{R}^{15} \) represents:
   - a halogenated or per-halogenated \( \text{Ci-Cs} \) hydrocarbon group;
   - a \( \text{R}^{16} \text{CH(OR)}^{16} \) group, \( \text{R}^{16} \) being a hydrogen atom or a \( \text{Ci-C}_6 \) hydrocarbon group;
   - a \( \text{C}_1-\text{C}_{12} \) hydrocarbon group, optionally substituted by one or two ether or ester groups;
   - the optional substituent being by one, two or three \( \text{Ci-C}_4 \) alkyl, alkoxy or carboxylic groups, or nitro groups or halogen atoms.

8. A process according to claim 7, characterised in that said acidic additive is selected from the group consisting of
   - a compound of formula \( \text{R}^{14}_2\text{MO(OH)} \) or \( \text{R}^{14}\text{MO(OH)}_2 \), wherein \( \text{R}^{14} \) is a \( \text{Ci-C}_6 \) alkyl or alkoxy group or a \( \text{C}_6-\text{Cs} \) phenyl or phenoxy and \( M \) is \( \text{P} \) or \( \text{As} \); and
   - maleic or glycolic acid and an halogenated or per-halogenated \( \text{Ci}^-\text{C}_7 \) mono-carboxylic acid.

9. A process according to any one of claims 1 to 8, characterised in that the conjugated diene of formula (I) is a compound of formula (F).
wherein \( R^a \) represents a linear, branched or cyclic \( Ci-Cs \) alkyl or alkenyle group; and
\( R^b \) represents a \((CH_2)_nX\) group, \( n \) representing 0, 1, 2 or 3, \( X \) representing a \( CHO \), \( OH \), \( OCOR \), \( OR \) or \( COOR \) group, \( R^c \) being a \( Ci-C_8 \) alkyl or alkenyl group;
or of formula (I'):

\[
\begin{align*}
R^d & \quad \text{and} \quad R^e \\
\end{align*}
\]

wherein \( R^d \) and \( R^e \) represent a hydrogen atom or a \( Ci-C_8 \) alkyl or alkenyle group, optionally substituted by a \( OH \), \( OCOR \), \( OR \) or \( COOR \) group, \( R^f \) being a \( Ci-C_8 \) alkyl or alkenyl group, provided that \( R^d \) and \( R^e \) do not represent each a hydrogen atom.

10. A ruthenium complex of formula

\[
[Ru(L)(Diene)(L')n]X \quad \text{(III)}
\]

wherein Diene represents a \( C_4-C_{22} \) diene and \( X \) represents a non coordinated anion, \( n \) represents 2, 1 or 0 and \( L' \) represents a solvent; and
\( L \) represents a \( C_6-C_{25} \) compound of formula

\[
\begin{align*}
\end{align*}
\]

wherein each \( R^9 \) represents, simultaneously or independently from each other, a hydrogen atom, a phenyl group optionally substituted, or a \( Ci-C_{10} \) alkyl or alkenyl group optionally substituted; and
one or two of said groups \( R^9 \) is a \( OSiR^{11}_3 \) or \( OCOR^{10} \) group, \( R^{11} \) representing a \( Ci-C_6 \) alkyl group, \( R^{10} \) representing a \( R^{11} \) or \( CF_3 \) group or a phenyl group optionally substituted; and at least one \( R^9 \) is an alkyl group; two adjacent \( R^9 \) can be bound together to form a \( C_2 \)-ː\( Cio \) alkanediyl group.
A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C5/05 B01J31/22

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):
C07C BOIJ 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, CHEMABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>A</td>
<td>XUE ET AL: &quot;Reaction of [CpRu(H2O)(NBD)]+ with dihydrogen, silanes, olefins, alkynes and allenes&quot; ORGANOMETALLICS, vol. 25, no. 9, 2006, pages 2344-2354, XP002451877 USACS, COLUMBUS, OH. * page 2348, compound 1 *</td>
<td>10</td>
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</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search
20 August 2008

Date of mailing of the international search report
28/08/2008

Name and mailing address of the ISA/
European Patent Office, P.B. 5816 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epos nl,
Fax: (+31-70) 340-3016

Authorized officer
O'Sullivan, Paul
<table>
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<td>A</td>
<td>EP 1 394 170 A (DEGUSSA [DE]) 3 March 2004 (2004-03-03) cited in the application the whole document</td>
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<td>EP 1394170</td>
<td>03-03-2004</td>
<td>DE 10240255 A1</td>
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Form PCT/ISA/210 (patent family annex) (April 2005)