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(54) **Process for preparing optically active alcohols**

Verfahren zur Herstellung von optisch aktiven Alkoholen

Procédé pour la préparation d'alcools optiquement actifs

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Description

[0001] The present invention relates to a method for producing optically active alcohols according to the claims. More specifically, the present invention relates to a novel, highly practical method for producing optically active alcohols useful for various utilities such as intermediates for synthesizing pharmaceutical chemicals, liquid crystal materials and agents for optical resolution.

[0002] Various methods for producing optically active compounds have been known conventionally. As the method for asymmetrically synthesis of optically active alcohol compounds, for example, the following methods have been known;

(1) a method by using enzymes such as baker's yeast; and
(2) a method for asymmetric hydrogenation of carbonyl compounds by using metal complex catalysts. For the method (2), inparticular, a great number of examples of asymmetric catalytic reactions have been reported for example as follows; (1) an asymmetric hydrogenation of carbonyl compounds with functional groups, by means of optically active ruthenium catalysts, as described in detail in Asymmetric Catalysis in Organic Synthesis, Ed. R. Noyori. , pp.56-82 (1994); (2) a method through hydrogen transfer-type reduction by means of chiral complex catalysts of ruthenium, rhodium or iridium, as described in Chem. Rev. , Vol. 92, pp. 1051-1069 (1992);
(3) a process of asymmetric hydrogenation tartaric acid by means of a modified nickel catalyst with tartaric acid as described in Oil Chemistry, pp.882-831 (1980) and Advances in Catalysis, Vol.32, pp.215 (1983), Ed. Y. Izumi; (4) an asymmetric hydrosilylation method, as described in Asymmetric Synthesis, Vol.5, Chap.4 (1985), Ed. J. D. Morrison and J. Organomet. Chem. Vol.346, pp.413-424 (1988) ; and (5) a borane reduction process in the presence of chiral ligands, as described J. Chem. Soc., Perkin Trans.1, pp.2039-2044 (1985) and J. Am. Chem. Soc., Vol. 109, pp. 5551-5553 (1987).

[0003] By the conventional method by means of enzymes, however, alcohols can be recovered at a relatively high optical purity, but the reaction substrate therefor is limited and the absolute configuration in the resulting alcohols is limited to specific one. By the asymmetric hydrogenation method by means of transition metal complex catalysts, optically active alcohols can be produced at a high selectivity, but a pressure-resistant reactor is required therefor because hydrogen gas is used as the hydrogen source, which is disadvantageous in terms of operational difficulty and safety. Furthermore, the method through such asymmetric hydrogen transfer-type reduction by using conventional metal complex catalysts is limited in that the method requires reaction conditions under heating and the reaction selectivity is insufficient, disadvantageously in practical sense.

[0004] Accordingly, it has been desired conventionally that a new, very general method for synthesizing optically active alcohols by using a highly active and highly selective catalyst with no use of hydrogen gas be achieved.

[0005] But no highly efficient and highly selective method for producing such secondary alcohols through asymmetric synthetic reaction by using catalysts similar to those described above has been established yet.

[0006] As to the optically active secondary alcohols, a method for synthesizing optically active secondary alcohols via optical resolution of racemic secondary alcohols has been known for some reaction substrate which can hardly be reduced, although an excellent optical purity is hardly attained (Asymmetric Catalysis in Organic Synthesis, Ed. R. Noyori). Because hydrogen transfer-type reduction is a reversible reaction according to the method, dehydrogenation-type oxidation as its adverse reaction is used according to the method. Therefore, the method is called as kinetic optical resolution method. According to the method, however, no process of producing optically active secondary alcohols with catalysts at a high efficiency has been reported yet. Zassinovich and Mestroni, Chemical Reviews, vol. 92, no. 5, 1992, p. 1051-1069 describes asymmetric hydrogen transfer reactions promoted by homogenous transition metal catalysts. Ruthenium (II) catalysts are described.

[0007] Krasik and Alper, Tetrahedron, vol. 50, no. 15, 11 April 1994, p. 4347-4354 describes Schiff bases as added chiral ligands for the $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ catalysed hydrogen transfer reduction of ketones with 2-propanol.

[0008] Alternatively, a great number of transition metal complexes have been used conventionally as catalysts for organic metal reactions; particularly because rare metal complexes are highly active and stable with the resultant ready handleability despite of high cost, synthetic reactions using the complexes have been developed. The progress of such asymmetric synthetic reactions using chiral complex catalysts is innovative, and a great number of reports have been issued, reporting that highly efficient organic synthetic reactions have been realized.

[0009] Among them, a great number of asymmetric reactions using chiral complexes catalysts with optically active phosphine ligands as the catalysts have already been developed, and some of them have been applied industrially (Asymmetric catalysis in Organic Synthesis, Ed. R. Noyori).

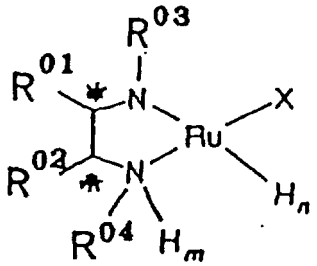
[0010] As complexes of optically active nitrogen compounds coordinated with transition metals such as ruthenium, rhodium and iridium, a great number of such complexes additionally having excellent properties as catalysts for asymmetric synthetic action have been known. So as to enhance the properties of these catalysts, a great number of propositions concerning the use of optically active nitrogen compounds of specific structures have been done (Chem. Rev. ,

Vol.92, pp.1051-1069 (1992)).

[0011] For example, reports have been issued about (1) optically active 1,2-diphenylethylenediamines and rhodium-diamine complexes with ligands of cyclohexanediamines, as described in Tetrahedron Asymmetry, Vol. 6, pp. 705-718 (1995) ; (2) ruthenium-imide complex with ligands of optically active bisaryliminocyclohexanes, as described in Tetrahedron, Vol.50, pp.4347-4354 (1994); (3) iridium-pyridine complex with ligands of pyridines, as described in Japanese Patent Laid-open Nos. 62-281861 and 63-119465; (4) optically active 1,2-diphenylethylenediamines or iridium-diamine complex with ligands of cyclohexanediamines, as described in Japanese Patent Laid-open No.62-273990; (5) ruthenium-diamine complex of RuCl[p-TsNCH(C_6H_5)CH(C_6H_5)NH_2] (arene) (chloro-(N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(arene) ruthenium) (arene represents benzene which may or may not have a substituent), which is produced by coordinating ruthenium with optically active N-p-toluenesulfonyl-1,2-diphenylethylenediamine [referred to as "p-TsNHCH(C_6H_5)CH(C_6H_5)NH_2" hereinabove and below], as described in J. Am. Chem. Soc. , Vol.117, pp.7562-7563(1995); J. Am. Chem. Soc., Vol.118, pp.2521-2522 (1996) and J. Am. Chem. Soc., Vol.118, pp.4916-4917 (1996).

[0012] Even if these complexes are used, however, problems currently remain to be overcome for practical use, including insufficient catalyst activities, sustainability and optical purities, depending on the subjective reactions and reaction substrates.

[0013] So as to overcome the aforementioned problems, the present invention provides a method for producing optically active secondary alcohols, comprising subjecting racemic secondary alcohols or meso-type diols to hydrogen transfer reaction in the presence of an optically active ruthenium-diamine complex catalyst represented by the following general formula (VII);



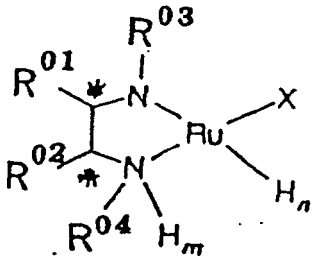
(VII)

wherein * represents an asymmetric carbon atom; R^{01} and R^{02} are the same or different, independently representing alkyl group, or phenyl group or cycloalkyl group which may or may not have an alkyl group; or R^{01} and R^{02} together form an alicyclic ring unsubstituted or substituted with an alkyl group; R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with an alkyl group, an alkoxyl group or halogen atom, or benzoyl group which may or may not be substituted with alkoxycarbonyl group or alkyl group; R^{04} represents hydrogen atom or alkyl group; X represents an aromatic compound which may or may not be substituted with an alkyl group; and m and n together represent 0 or 1.

[0014] In accordance with the present invention, the characteristic methods for producing optically active compounds as described above are provided. The detail is described below.

[0015] The catalyst system to be used for the hydrogen transfer-type asymmetric reduction in accordance with the present invention is very characteristic and has never been known up to now.

[0016] The optically active ruthenium-diamine complex represented by the following formula (VII) as described above as one metal complex composed of a transition metal and an optically active nitrogen-containing compound ligand is useful as a catalyst for producing optically active secondary alcohol compounds, comprising subjecting racemic secondary alcohol or meso-type diols to hydrogen transfer reaction, and therefore, the complex draws higher attention.



(VII)

In the formula, * represents an asymmetric carbon atom; R^{01} and R^{02} are the same or different, independently representing alkyl group, or phenyl group or cycloalkyl group which may or may not have an alkyl group; or R^{01} and R^{02} together form an alicyclic ring unsubstituted or substituted with an alkyl group; R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with an alkyl group, an alkoxyl group or halogen atom, alkoxycarbonyl group, or benzoyl group which may or may not be substituted with an alkyl group; R^{04} represents hydrogen atom or alkyl group; X represents an aromatic compound which may or may not be substituted with an alkyl group; and m and n simultaneously represent 0 or 1.

[0017] For more description of the optically active ruthenium-diamine complex of the formula (VII), the aromatic compound which may or may not have an alkyl group represented by X, for example alkyl groups with C1 to C4 , means for example benzene, toluene, xylene, mesitylene, hexamethylbenzene, ethylbenzene, tert-butylbenzene, p-cymene, and cumene and preferably includes benzene, mesitylene and p-cymene.

[0018] R^{01} and R^{02} may represent a linear or branched alkyl group, for example alkyl groups with C1 to C4. More specifically, the alkyl group may be methyl, ethyl, n-propyl, isopropyl, n-, iso-, sec- and tert-butyl. More preferably, the group is methyl, ethyl, n-propyl or iso-propyl.

[0019] If R^{01} and R^{02} are bonded together to form an alicyclic group, the group may satisfactorily be a C5 to C7-membered ring. The alkyl group which may or may not be a substituent thereof, for example alkyl substituent group with C1 to C4, includes methyl group, ethyl group, n-propyl group, isopropyl group, and n-, iso-, sec- and tert-butyl groups. Preferably, the alkyl group is methyl.

[0020] R^{01} and R^{02} as phenyl group wherein R^{01} and R^{02} may have an alkyl group, for example methyl group, specifically include phenyl, o-, m- and p-tolyl groups.

[0021] R^{01} and R^{02} representing cycloalkyl group contain carbon atoms in 5 to 6-membered rings, preferably including cyclopentyl or cyclohexyl.

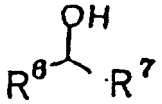
[0022] In more preferable examples, R^{01} and R^{02} are independently phenyl or R^{01} and R^{02} together mean tetramethylene ($-(CH_2)_4-$).

[0023] R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with alkyl group, for example alkyl group with C1 to C3, alkoxy group for example alkoxy group with C1 to C3, or halogen atom, or benzoyl group which may or may not be substituted with alkyl group, for example C1 to C4 alkoxycarbonyl groups, or alkyl group, for example C1 to C4 alkyl group.

[0024] More specifically, R^{03} representing benzenesulfonyl group which may or may not be substituted with C1 to C3 alkyl group, C1 to C3 alkoxyl group or halogen atom, includes benzenesulfonyl, o-, m- and p-toluenesulfonyl, o-, m-, and p-ethylbenzenesulfonyl, o-, m-, and p-methoxybenzenesulfonyl, o-, m-, and p-ethoxybenzenesulfonyl, o-, m-, and p-chlorobenzenesulfonyl, 2,4,6-trimethylbenzenesulfonyl, 2,4,6-triisopropylbenzenesulfonyl, p-fluorobenzenesulfonyl, and pentafluorobenzenesulfonyl, and more preferably includes benzenesulfonyl or p-toluenesulfonyl. Specifically, R^{03} representing C1 to C4 alkoxycarbonyl groups includes methoxycarbonyl, ethoxycarbonyl, isopropyloxycarbonyl, and tert-butoxycarbonyl, preferably including methoxycarbonyl or tert-butoxycarbonyl. R^{03} representing benzoyl group which may or may not be substituted with C1 to C4 alkyl groups specifically includes benzoyl, o-, m-, and p-methylbenzoyl, o-, m-, and p-ethylbenzoyl, o-, m-, and p-isopropylbenzoyl, and o-, m-, and p-tert-butylbenzoyl, preferably including benzoyl or p-methylbenzoyl.

[0025] In the most preferable example, R^{03} is methanesulfonyl, trifluoromethanesulfonyl, benzenesulfonyl or p-toluenesulfonyl.

[0026] R^{04} representing hydrogen atom or alkyl group, for example C1 to C4 alkyl groups, specifically includes for example hydrogen, methyl, ethyl, n-propyl, isopropyl, n-, iso-, sec- and tert-butyl, and more preferably includes hydrogen atom or methyl group. Preferably, the racemic secondary alcohols as the raw material compounds in accordance with the present invention are illustrated by the following formula (VIII). It is needless to say that the racemic alcohols are not limited to those represented by the formula.

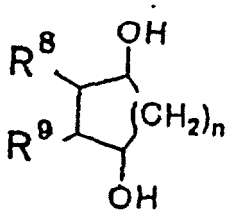


(VIII)

[0027] R^6 represents an aromatic monocyclic or polycyclic hydrocarbon group, unsubstituted or substituted or a hetero monocyclic or polycyclic group containing hetero atoms including nitrogen, oxygen, sulfur atoms and the like, specifically representing aromatic monocyclic or polycyclic groups such as phenyl group, 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl, 2-tert-butylphenyl, 2-methoxyphenyl, 2-chlorophenyl, 2-vinylphenyl, 3-methylphenyl, 3-ethylphenyl, 3-isopro-

pylphenyl, 3-methoxyphenyl, 3-chlorophenyl, 3-vinylphenyl, 4-methylphenyl, 4-ethylphenyl, 4-isopropylphenyl, 4-tert-butylphenyl, 4-vinylphenyl, cumenyl, mesityl, xylyl, 1-naphthyl, 2-naphthyl, anthryl, phenanthryl, and indenyl; hetero monocyclic or polycyclic groups such as thienyl, furyl, pyranyl, xanthenyl, pyridyl, pyrrolyl, imidazolyl, indolyl, carbazoyl, and phenthronylyl; and ferrocenyl group. Furthermore, R^7 represents hydrogen atom, a saturated or unsaturated hydrocarbon group, or a functional group containing hetero atoms, including for example alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyelohexyl; and unsaturated hydrocarbons such as benzyl, vinyl, and allyl. R^6 and R^7 may be bonded together to form a ring, and in this case, R^7 includes for example a saturated or unsaturated alicyclic group giving a cyclic ketone such as cyclopentanone, cyclohexanone, cycloheptane, cyclopentenone, cyclohexenone, and cycloheptenone; or a saturated and unsaturated alicyclic group with a substituent group having an alkyl group, an aryl group, a unsaturated alkyl group or a linear or cyclic hydrocarbon group on each of the individual carbons.

[0028] Additionally, the meso-type diols are represented for example by the following formula (IX).



(IX)

It is needless to say that the meso-diols are not limited to them.

[0029] In this case, R^8 and R^9 are the same and represent a saturated or unsaturated hydrocarbon group which may or may not have a substituent group, or R^8 and R^9 may be bonded together to form a saturated or unsaturated alicyclic group which may or may not have a substituent group.

[0030] More specifically, the ruthenium-diamine complex of the present invention is for example such that m and n are simultaneously zero in the formula (VII). Herein, η is used to represent the number of carbon atoms bonded to a metal in unsaturated ligands, and therefore, hexahapto (six carbon atoms bonded to metal) is represented by η^6; p-Ts represents p-toluenesulfonyl group; Ms represents methanesulfonyl group; and Tf represents trifluoromethanesulfonyl group.

Ru [(S, S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-benzene) (((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)

Ru[(R,R)-p-TsNCH(C_6H_5)CH(C_6H_5)NH](η^6-benzene) (((R,R)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)

Ru[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH](η^6-p-cymene)(((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium)

Ru[(R,R)-p-TsNCH(C_6H_5)CH(C_6H_5)NH](η^6-p-cymene)(((R, R)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium)

Ru[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH](η^6-mesitylene)(((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium)

Ru[(R, R) -p-TsNCH (C_6H_5) CH (C_6H_5) NH] (η^6-mesitylene) (((R, R) -N-p-toluenesulfonyl- 1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium)

Ru [(S,S)-MsNCH(C_6H_5)CH (C_6H_5)NH](η^6-benzene)(((S, S)-N-methanesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene) ruthenium)

Ru[(R,R)-MsNCH(C_6H_5)CH(C_6H_5)NH](η^6-benzene)(((R,R)-N-methanesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene) ruthenium)

Ru[(S,S)-MsNCH(C_6H_5)CH(C_6H_5)NH](η^6-p-cymene)(((S,S)-N-methanesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium)

Ru[(R,R)-MsNCH(C_6H_5)CH(C_6H_5)NH](η^6-p-cymene)(((R, R)-N-methanesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium)

Ru[(S, S)-MsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-mesitylene) (((S, S)-N-methanesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium)

Ru[(R, R)-MsNCH (C_6B_5)CH(C_6H_5) NH] (η^6-mesitylene)(((R, R)-N-methanesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium)

Ru[(S, S)-TfNCB(C_6H_5)CH(C_6H_5) NH] (η^6-benzene) (((S, S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)

Ru[(R,R) -TfNCH(C_6H_5)CH(C_6H_5) NH] (η^6-benzene) ((R, R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)

Ru[(S,S)-TfNCH(C_6H_5)CH(C_6H_5) NH] (η^6-p-cymene) (((S, S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium)

Ru[(R,R)-TfNCH(C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene)(((R, R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium)

Ru[(S,S)-TfNCH(C_6H_5)CH(C_6H_5)NH] (η^6-mesitylene)(((S, S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium)

Ru[(R,R)-TfNCH(C_6H_5)CH(C_6H_5)NH] (η^6-mesitylene)(((R, R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene)ruthenium)

Ru[(S,S)-$C_6H_5SO_2$NCH(C_6H_5)CH(C_6H_5)NH] (η^6-benzene)(((S,S)-N-benzenesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)

Ru[(R,R)-$C_6H_5SO_2$NCH(C_6H_5)CH(C_6H_5)NH] (η^6-benzene)(((R, R)-N-benzenesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)

Ru[(S,S)-$C_6H_5SO_2$NCH(C_6H_5)CH (C_6H_5)NH] (η^6-p-cymene) (((S,S)-N-benzenssulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium)

Ru[(R, R) -$C_6B_5SO_2$NCH (C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene) ((R,R)-N-benzenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium)

Ru[(S,S)-$C_6H_5SO_2$NCH(C_6H_5)CH (C_6H_5)NH] (η^6-mesitylene) (((S,S)-N-benzenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium)

Ru[(R, R)-$C_6H_5SO_2$NCE(C_6H_5)CH (C_6H_5)NH] (η^6-mesitylene) (((R, R)-N-benzenesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene) ruthenium)

Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine(η^6-benzene)(((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine(η^6-benzene)ruthenium)

Ru[(R,R)-N-p-Ts-1,2-cyclohexanediamine] (η^6-benzene)(((R,R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-benzene)ruthenium)

Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-p-cymene) (((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium)

Ru[(R,R)-N-p-Ts-1,2-cyclohexanediamine] (η^6-p-cymene) (((R,R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene) ruthenium)

Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-mesitylene) (((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

Ru[(R,R)-N-p-Ts-1,2-cyclohexanediamine] (η^6-mesitylene)(((R,R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

Ru[(S,S)-N-Ms-1,2-cyclohexanediamine] (η^6-benzene)(((S,S)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-benzene) ruthenium)

Ru [(R,R)-N-Ms-1,2-cyclohexanediamine] (η^6-benzene) (((R, R) -N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-benzene)ruthenium)

Ru[(S,S)-N-Ms-1,2-cyclohexanediamine] (η^6-p-cymene)(((S,S)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium)

Ru [(R,R)-N-Ms-1,2-cyclohexanediamine] (η^6-p-cymene)(((R,R)-N-methanesulfonyl-1, 2-cyclohexanediamine) (η^6-p-cymene)ruthenium)

Ru[(S,S)-N-Ms-1,2-cyclohexanediamine] (η^6-mesitylene) (((S,S)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6-mesitylene)ruthenium)

Ru[(R,R)-N-Ms-1,2-cyclohexanediamine] (η^6-mesitylene)(((R,R)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

Ru[(S,S)-N-Tf-1,2-cyclohexanediamine] (η^6-benzene) (((S,S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-benzene)ruthenium)

Ru[(R,R)-N-Tf-1,2-cyclohexanediamine] (η^6-benzene)(((R, R) -N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-benzene) ruthenium)

Ru[(S,S)-N-Tf-1,2-cyclohexanediamine] (η^6-p-cymene) (((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexarxediamine) (η^6-p-cymene) ruthenium)

Ru [(R,R)-N-Tf-1,2-cyclohexanediamine] (η^6-p-cymene) (((R,R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene) ruthenium)

Ru[(S,S)-N-Tf-1,2-cyclohexanediamine](η^6-mesitylene) (((S,S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

Ru[(R,R)-N-Tf-1,2-cyclohexanediamine] (η^6-mesitylene) (((R, R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

Ru[(S,S)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine] (η^6-benzene)(((S, S)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-benzene)ruthenium)
Ru[(R,R)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine] (η^6-benzene)(((R, R)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-benzene)ruthenium)
Ru [(S, S)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine] (η^6-p-cymene) (((S, S)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene) ruthenium)
Ru [(R,R)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine] (η^6-p-cymene) (((R, R)-N-benzeneesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium)
Ru[(S,S)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine] (η^6-mesitylene) (((S, S)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)
Ru [(R, R)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine](η^6-mesitylene)(((R, R)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

[0031] Those of the formula (VII) wherein m and n are simultaneously 1 are illustrated as follows. Herein, η is used to represent the number of carbon atoms bonded to a metal in unsaturated ligands, and therefore, hexahapto (six carbon atoms bonded to metal) is represented by η^6; p-Ts represents p-toluenesulfonyl group; Ms represents methanesulfonyl group; and Tf represents trifluoromethanesulfonyl group.

RuH[(S, S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-benzene) (hydride-((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene)ruthenium)
RuH[(R, R)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-benzene) (hydride-((R, R)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene)ruthenium)
RuH[(S, S)-p-TsNCH(C_6H_5)CH (C_6H_5)NH_2] (η^6-p-cymene) (hydride-((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene) ruthenium)
RuH[(R,R)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-p-cymene)(hydride-((R, R)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene) ruthenium)
RuH[(S, S)-p-TsNCH(C_6H_5)CH (C_6H_5)NH_2] (η^6-mesitylene)(hydride- ((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene)ruthenium)
RuH[(R,R)-p-TsNCH(C_6H_5)CH(C_6R_5)NH_2] (η^6-mesitylene)(hydride-((R, R)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene)ruthenium)
RuH[(S,S)-MsNCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-benzene)(hydride- ((S,S)-N-methanesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene)ruthenium)
RuH[(R, R)-MsNCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-benzene)(hydride- ((R,R)-N-methanesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene)ruthenium)
RuH[(S,S)-MsNCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-p-cymene) (hydride-((S,S)-N-methanesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium)
RuH[(R, R) -MsNCH(C_6H_5)CH (C_6H_5)NH_2](η^6-p-cymene)(hydride-((R,R)-N-methanesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene) ruthenium)
RuH[(S,S)-MsNCH(C_6H_5)CH(C_6H_5)NH_2](η^6-mesitylene) (hydride- ((S, S)-N-methanesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene)ruthenium)
RuH[(R,R)-MsNCH(C_6H_5)CH(C_6H_5)-NH_2](η^6-mesitylene) (hydride- ((R, R)-N-methanesulfonyl-1,2-diphenylethylene-di-amine) (η^6-mesitylene) ruthenium)
RuH[(S, S)-TfNCH(C_6H_5)CH(C_6H_5)NH_2](η^6-benzene) (hydride- ((S,S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-benzene) ruthenium)
RuH[(R,R)-TfNCH (C_6H_5)CH(C_6H_5) NH_2] (η^6-benzene) (hydride- ((R,R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene) ruthenium)
RuH[(S, S)-TfNCH (C_6H_5)CH(C_6H_5) NH_2] (η^6-p-cymene) (hydride- ((S,S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium)
RuH[(R, R)-TfNCH (C_6H_5)CH(C_6H_5) NH_2] (η^6-p-cymene) (hydride- ((R, R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium)
RuH[(S, S)-TfNCH (C_6H_5)CH (C_6H_5)NH_2] (η^6-mesitylene) (hydride- ((S, S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene)ruthenium)
RuH[(R,R)-TfNCH(C_6H_5)CH(C_6H_5)NH_2] η^6-mesitylene)(hydride- ((R, R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene)ruthenium)
RuH[(S,S)-$C_6H_5SO_2$NCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-benzene) (hydride- ((S, S)-N-benzenesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene) ruthenium)
RuH[(R, R)-$C_6H_5SO_2$NCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-benzene) (hydride- ((R, R)-N-benzenesulfonyl-1,2-diphenylethylenediamine)(η^6-benzene) ruthenium)
RuH[(S, S)-$C_6H_5SO_2$NCH(C_6H_5)CH(C_6H_5)NH_2] (η^6-p-cymene)(hydride- ((S, S)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium)

RuH[(R, R)-$C_6H_5SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$] ($\eta^6$-p-cymene) (hydride- ((R, R)-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium)

RuH[(S, S)-$C_6H_5SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$] ($\eta^6$-mesitylene) (hydride-((S,S)-N-benzenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium)

RuH[(R,R)-$C_6H_5SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$] ($\eta^6$-mesitylene) (hydride-((R, R)-N-benzenesulfonyl-1,2-diphenylethylenediamine)(η^6-mesitylene) ruthenium)

RuH[(S,S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-benzene)(hydride-((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-benzene)ruthenium)

RuH[(R,R)-N-p-Ts-1,2-cyclohexanediamine] (η^6-benzene) (hydride-((R,R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6-benzene)ruthenium)

RuH[(S,S)-N-p-Ts-1,2-cyclohexanediamine] η^6-p-cymene) (hydride-((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium)

RuH[(R, R) -N-p-Ts- 1,2-cyclohexanediamine] (η^6- p-cymene) (hydride-((R, R) -N-p-toluenesulfonyl- 1,2-cyclohexanediamine) η^6-p-cymene)ruthenium)

RuH[(S,S)-N-p-Ts-1,2-cyclohexanediamine](η^6-mesitylene) (hydride-((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) η^6-mesitylene)ruthenium)

RuH[(R, R) -N-p-Ts- 1,2-cyclohexanediazmine] (η^6-mesitylene) (hydride-((R, R) -N-p-toluenesulfonyl- 1,2-cyclohexanediamine) η^6-mesitylene) ruthenium)

RuH[(S,S)-N-Ms-1,2-cyclohexanediamine] η^6-benzene(hydride-((S, S)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-benzene) ruthenium)

RuH[(R,R) -N-Ms-1,2-cyclohexanediamine] (η^6-benzene) (hydride- ((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6-benzene)ruthenium)

RuH[(S,S)-N-Ms-1,2-cyclohexanediamine] η^6-p-cymene) (hydride-((S,S)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium)

RuH[(R,R) -N-Ms-1,2-cyclohexanediamine] (η^6-p-cymene) (hydride-((R,R)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene) ruthenium)

RuH[(S,S)-N-Ms-1,2-cyclohexanediamine] (η^6-mesitylene) (hydride-((S,S)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene) ruthenium)

RuH[(R,R)-N-Ms-1,2-cyclohexanediamine] (η^6-mesitylene) (hydride-((R,R)-N-methanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene) ruthenium)

RuH[(S,S)-N-Tf-1,2-cyclohexanediamine] (η^6-benzene) (hydride- ((S, s)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-benzene) ruthenium)

RuH[(R,R)-N-Tf-1,2-cyclohexanediamine] (η^6-benzene) (hydride-((R,R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6-benzene) ruthenium)

RuH[(S,S)-N-Tf-1,2-cyclohexanediamine] (η^6-p-cymene) (hydride-((S,S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6-p-cymene) ruthenium)

RuH[(R,R)-N-Tf-1,2-cyclohexanediamine] (η^6-p-cymene)(hydride-((R,R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6-p-cymene) ruthenium)

RuH[(S,S)-N-Tf-1,2-cyclohexanediamine](η^6-mesitylene) (hydride-((S,S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

RuH[(R,R)-N-Tf-1,2-cyclohexanediamine](η^6-mesitylene) (hydride-((R,R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

RuH[(S,S)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine](η^6-benzene) (hydride-((S,S)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-benzene) ruthenium)

RuH[(R,R)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine](η^6-benzene) (hydride-((R,R)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-benzene) ruthenium)

RuH[(S,S)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine] (η^6-p-cymene) (hydride-((S,S)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium)

RuH [(R,R)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine](η^6-p-cymene) (hydride-((R,R)-N-benzeneesulfonyl-1,2-cyclohexanediamine)(η ^{6}-p-cymene)ruthenium)

RuH [(S,S)-N-$C_6H_5SO_2$-1,2-cyclohexanediamine) (η^6-mesitylene) (hydride-((S,S)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

RuH[(R,R)-N-$C_6H_5SO_2$-1,2-cyclohexanediaimine)(η^6-mesitylene) (hydride-((R,R)-N-benzenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium)

[0032] Among the compounds represented by the general formula (VII), the complex of the formula (VII) wherein m and n are simultaneously 0 can be produced as follows. More specifically,

Ru[(S,S)-, (R, R)-TsNCH(R^{01})CH(R^{02})NH] (η^6-p-cymene) (((S,S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine)(η^6-p-cymene)ruthenium

(wherein R^{01} and R^{02} are the same as described above and Ts is p-toluenesulfonyl group), is readily synthesized by reacting a raw material $[RuCl_2(\eta^6\text{-p-cymene})]_2$(tetrachlorobis($\eta^6$-p-cymene) diruthenium) prepared by the method described in a reference J. Chem. Soc., Dalton Trans., pp.233 - 241(1974) with (S,S)-, (R, R)-$TsNHCH(R^{01})CH(R^{02})NH_2$ ((S,S) and (R,R)-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine) in the presence of alkali metal hydroxide or alkali metal alcolate in a solvent.

[0033] The reaction is generally carried out quantitatively, by reacting a raw material $[RuCl_2(\eta^6\text{-p-cymene})]_2$(tetrachlorobis ($\eta^6$-p-cymene)diruthenium (1 mole) and (S, S)-, (R,R)-$TsNHCH(R^{01})CH(R^{02})NH_2$(((S, S) and (R, R)-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine)(2 moles) with alkali metal hydroxide or alkali metal alcolate in the stream of inactive gases such nitrogen, helium or argon in an inactive solvent at a temperature of -10 to 50 °C for 30 minutes to 3 hours, and leaving the reaction product to stand alone, prior to liquid separation procedure to remove the aqueous phase, and subsequently removing the solvent under reduced pressure.

[0034] The alkali metal hydroxide or alkali metal alcolate specifically includes NaOH, $NaOCH_3$, $NaOC_2H_5$, KOH, $KOCH_3$, ROC_2H_5, LiOH, $LiOCH_3$, and $LiOC_2H_5$, preferably including NaOR or KOH. The amount of the alkali metal hydroxide or alkali metal alcolate is 5 to 10 fold the amount of ruthenium. The inactive solvent appropriately includes for example hydrocarbons such as benzene, toluene, xylene, cyclohexane, and methylcyclohexane; ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyl-tert-butyl ether, tetrahydrofuran, 1,3-dioxolanee, and 1,4-dioxane; halogenated hydrocarbons such as chloroform, methylene chloride and chlorobenzene.

[0035] The complex can be produced by another method. Specifically, Ru[(S,S)-, (R,R)-$TsNCH(R^{01})CH(R^{02})NH$]($\eta^6$-p-cymene)(((S,S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine)(η^6-p-cymene)ruthenium (wherein R^{01} and R^{02} are the same as described above and Ts is p-toluenesulfonyl group) , is readily synthesized by reacting a raw material RuCl[(S,S)-, (R,R)- $TsNCH(R^{01})CH(R^{02})NH_2$]($\eta^6$-p-cymene)(chloro-((S,S) and (R,R)-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine)(η^6-p-cymene)ruthenium prepared through the reaction of $[RuCl_2(\mu^6\text{-p-cymene})]_2$(tetrachlorobis ($\eta^6$-p-cymene) diruthenium, (S, S)-, (R,R)-$TsNHCH(R^{01})CH(R^{02})NH_2$((S,S) and (R,R)-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine) with a tertiary amine (for example, triethylamine) for example by the method described in J. Am. Chem. Soc., Vol. 117, pp.7562-7563 (1995), J. Am. Chem. Soc., Vol.118, pp.2521-2522 (1996) and J. Am. Chem. Soc., Vol.118, pp.4916-4917 (1996), in the presence of alkali metal hydroxide or alkali metal alcolate in a solvent.

[0036] The reaction is generally carried out quantitatively, by reacting a raw material RuCl[(S,S)-, (R,R)-$TsNCH(R^{01})CH(R^{02})NH_2$] ($\eta^6$-p-cymene) (chloro-((S,S) and (R,R) -N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6-p-cymene) ruthenium) (1 mole) with alkali metal hydroxide or alkali metal alcolate in the stream of inactive gases such nitrogen, helium or argon in an inactive solvent at a temperature of -10 to 50 °C for 30 minutes to 3 hours, and leaving the reaction product to stand alone, prior to liquid separation procedure to remove the aqueous phase, and subsequently removing the solvent under reduced pressure.

[0037] The alkali metal hydroxide or alkali metal alcolate specifically includes NaOH, $NaOCK_3$, $NaOC_2H_5$, KOH, $KOCH_3$, KOC_2H_5, LiOH, $LiOCH_3$, and $LiOC_2H_5$, preferably including NaOH or KOH. The amount of the alkali metal hydroxide or alkali metal alcolate is 1 to 2-fold in mole the amount of ruthenium. The inactive solvent appropriately includes for example hydrocarbons such as benzene, toluene, xylene, cyclohexane, and methylcyclohexane; ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyltert-butyl ether, tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane; and halogenated hydrocarbons such as chloroform, methylene chloride and chlorobenzene.

[0038] The complex represented by the general formula (V) wherein m and n are simultaneously 1 can be produced as follows. More specifically, RuH[(S,)-, (R,R)-$TsNCH(R^{01})CH(R^{02})NH_2$]($\eta^6$-p-cymene)(hydride- ((S, S) and (R,R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6-p-cymene) ruthenium) (wherein R^{01} and R^{02} are the same as described above and Ts is p-toluenesulfonyl group) , is readily synthesized, by reacting a raw material Ru [(S,S)-, (R, R) -$TsNCH(R^{01})CH(R^{02})NH$]($\eta^6$-p-cymene) (((S, S) and (R,R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6-p-cymene) ruthenium) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) in an alcohol solvent.

[0039] The reaction is generally carried out quantitatively, by reacting a raw material Ru[(S,S)-, (R,R)-$TsNCH(R^{01})CH(R^{02})NH$] ($\eta^6$-p-cymene)(((S,S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6-p-cymene)ruthenium) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) in an inactive gas stream in an alcohol solvent at a temperature of 0 to 100 °C for 3 minutes to 1 hour for hydrogen transfer reaction, and subsequently removing the solvent under reduced pressure. Appropriate alcohol solvents include for example methanol, ethanol, n-propanol, isopropanol, n-butanol, iso-butanol, and sec-butanol.

[0040] The complex can be produced by another method. Specifically, RuH[(S,S)-, (R,R) -$TsNCH(R^{01})CH(R^{02})NH_2$] ($\eta^6$-p-cymene)(hydride- ((S, S) and (R,R)-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine)(η^6-p-cymene)ruthenium) (wherein R^{01} and R^{02} are the same as described above and Ts is p-toluenesulfonyl group) , is readily synthesized, by reacting for example a raw material Ru[(S,S)-, (R,R)-$TsNCH(R^{01})CH(R^{02})NH$] ($\eta^6$-p-cymene)(((S,S) and (R,R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6-p-cymene) ruthenium) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group), in a solvent in pressurized hydrogen.

[0041] The reaction is generally carried out quantitatively, by hydrogenating a raw material RuH[(S,S)-, (R,R)-TsNCH (R^{01}) CH(R^{02})NH_2] (η^6-p-cymene) (hydride-((S, S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6-p-cymene) ruthenium) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) , in an inactive solvent at a temperature of 0 to 50 °C for 30 minutes to 24 hours (preferably 1 to 10 hours) in pressurized hydrogen and subsequently removing the solvent under reduced pressure. The hydrogen pressure is within a range of 1 to 150 atm, preferably 20 to 100 atm.

[0042] Appropriate inactive solvents include for example hydrocarbons such as benzene, toluene, xylene, hexane, heptane, cyclohexane, and methylcyclohexane; and ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyl-tert-butyl ether, tetrahydrofuran, 1,3-dioxolane and 1,4-dioxane.

[0043] An optically active diamine of the formula
(S,S)-, (R, R) -R^{03}NHCH(R^{01})CH(R^{02})NH_2((S, S) and (R, R) -N-substituted-1,2-disubstituted ethylenediamines) (wherein R^{01} R^{02} and R^{03} are the same as described above) is synthesized, by using raw materials (S,S)-, (R,R)-NH_2CH(R^{01}) CH(R^{02})NH_2((S,S) and (R, R)-1,2-disubstituted ethylenediamines in a conventional manner [Protective Groups in Organic Synthesis, Vol.2, pp.309-405 (1991)]. More specifically,
(S,S)-, (R, R) -TsNHCH(R^{01}) CH (R^{02}) NH_2 ((S,S) and (R,R) -N-P-toluenesulfonyl-1,2-disubstituted ethylenediamines) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) are readily synthesized, by reacting for example (S,S)-, (R,R)-NH_2CH(R^{01})CH(R^{02})NH_2((S,S) and (R,R)-1,2-disubstituted ethylenediamines) as raw materials with TsCl (p-toluenesulfonyl chloride) in the presence of an alkali (for example, tertiary amine, alkali metal salts and the like) in a solvent.

[0044] The reaction is generally carried out quantitatively, by reacting together
(S,S)-, (R,R)-NH_2CH(R^{01})CH(R^{02})NH_2((S,S) and (R,R)-1,2-disubstituted ethylenediamines) (1 mole) and TsCl (p-toluenesulfonyl chloride) (1 mole) with an alkali (for example, triethylamine) in an inactive solvent (for example, toluene, tetrahydrofuran, and methylene chloride) in an inactive gas stream such as nitrogen, helium or argon or the like at a temperature of O to 50 °C for 30 minutes to 3 hours, subsequently adding water to the resulting mixture to gently leave the reaction product to stand, prior to liquid separation procedure, to remove the aqueous phase, and evaporating the solvent under reduced pressure.

[0045] The optically active diamine (S,S)-, (R,R)-NH_2CH(R^{01})CH(R^{02})NH_2((S,S) and (R,R)-1,2-disubstituted ethylenediamines) (wherein R^{01} and R^{02} are the same as defined above) , is known and is sometimes commercially available or can be produced in a conventional manner or by conventional resolution process of racemates [Tetrahedron Lett., Vol.32, pp.999-1002) (1991), Tetrahedron Lett., Vol.34, pp.1905-1908 (1993)].

[0046] (S,S) and (R,R)-1,2-diphenylethylenediamines and (S,S) and (R, R)- 1,2-cyclohexanediamines are commercially available.

[0047] For example, the optically active diamine of the general formula (e) can be produced by the following method [Tetrahedron Lett., Vol.32, pp.999-1002 (1991)].

[0048] The optically active diamine of the general formula (e) ((S, S) and (R, R) -1, 2-disubstituted ethylenediamines) can be produced readily at a high yield, by preparing cyclophosphate from raw materials optically active 1,2-disubstituted ethylene diols, which is then reacted with amidine to recover imidazoline, and ring opening the imidazoline by using an acid catalyst.

[0049] The ruthenium-diamine complex may be isolated and used, but while generating the complex in a reaction solution, the resulting complex is used as a catalyst for asymmetric synthesis and the like.

[0050] The method for producing optically active secondary alcohols by utilizing a hydrogen transfer-type oxidation catalyst will now be described below.

[0051] The racemic secondary alcohols or meso-type diols to be used as the reaction substrates for producing optically active secondary alcohols are represented by the aforementioned formulas (VIII) and (IX). In the formula (VIII), the racemic secondary alcohols in this case specifically include
1-phenylethanol, 1- (2-methylphenyl)ethanol, 1-(2-ethylphenyl) ethanol, 1-(2-isopropylphenyl)ethanol, 1-(2-tert-butylphenyl)ethanol, 1-(2-methoxyphenyl)ethanol, 1-(2-ethoxyphenyl)ethanol, 1-(2-isopropoxyphenyl)ethanol, 1-(2-tert-butoxyphenyl)ethanol, 1-(2-dimethylaminophenyl)ethanol, 1-(3-methylphenyl)ethanol, 1-(3-ethylphenyl)ethanol, 1-(3-isopropylphenyl)ethanol, 1-(3-tert-butylphenyl)ethanol, 1-(3-methoxyphenyl)ethanol, 1-(3-ethoxyphenyl)ethanol, 1-(3-isopropoxyphenyl) ethanol, 1- (3-tert-butoxyphenyl) ethanol, 1- (3-dimethylaminophenyl)ethanol, 1-(4-methylphenyl)ethanol, 1-(4-ethylphenyl) ethanol, 1-(4-isopropylphenyl)ethanol, 1-(4-tert-butylphenyl)ethanol, 1-(4-methoxyphenyl)ethanol, 1-(4-ethoxyphenyl)ethanol, 1-(4-isopropoxyphenyl)ethanol, 1-(4-tert-butoxyphenyl)ethanol, 1-(4-dimethylaminophenyl) ethanol, 1-cumenylethanol, 1-mesitylethanol, 1-xylylethanol, 1-(1-naphthyl) ethanol, 1-(2-naphthyl)ethanol, 1-phenanthrylethanol, 1-indenylethanol, 1-(3,4-dimethoxyphenyl)ethanol, 1-(3,4-diethoxyphenyl) ethanol, 1-(3,4-methylenedioxyphenyl)ethanol, 1-ferrocenylethanol,
1-phenylpropanol, 1-(2-methylphenyl)propanol, 1-(2-ethylphenyl)propanol, 1-(2-isopropylphenyl)propanol, 1-(2-tert-butylphenyl)propanol, 1-(2-methoxyphenyl)propanol, 1-(2-ethoxyphenyl)propanol, 1-(2-isopropoxyphenyl)propanol, 1-(2-tert-butoxyphenyl)propanol, 1-(2-dimethylaminophenyl)propanol, 1-(3-methylphenyl)propanol, 1-(3-ethyl-

phenyl)propanol, 1-(3-isopropylphenyl)propanol, 1-(3-tert-butylphenyl)propanol, 1-(3-methoxyphenyl)propanol, 1-(3-ethoxyphenyl)propanol, 1-(3-isopropoxyphenyl)propanol, 1-(3-tert-butoxyphenyl)propanol, 1-(3-dimethylaminophenyl)propanol, 1-(4-methylphenyl)propanol, 1-(4-ethylphenyl)propanol, 1-(4-isopropylphenyl)propanol, 1-(4-tert-butylphenyl)propanol, 1-(4-methoxyphenyl)propanol, 1-(4-ethoxyphenyl)propanol, 1-(4-isopropoxyphenyl)propanol, 1-(4-tert-butoxyphenyl)propanol, 1-(4-dimethylaminophenyl)propanol,
1-cumenylpropanol, 1-mesitylpropanol, 1-xylylpropanol, 1-(1-naphthyl) propanol, 1-(2-naphthyl)propanol, 1-phenanthrylpropanol,
1-indenylpropanol, 1-(3,4-dimethoxyphenyl) propanol, 1-(3,4-diethoxyphenyl) propanol, 1-(3,4-methylenedioxyphenyl) propanol, 1-ferrocenylpropanol, 1-phenylbutanol, 1-(2-methylphenyl)butanol, 1-(2-ethylphenyl)butanol, 1-(2-isopropylphenyl)butanol, 1-(2-tert-butylphenyl)butanol, 1-(2-methoxyphenyl)butanol, 1-(2-ethoxyphenyl)butanol, 1-(2-isopropoxyphenyl)butanol, 1-(2-tert-butoxyphenyl)butanol, 1-(2-dimethylaminophenyl)butanol, 1-(3-methylphenyl)butanol, 1-(3-ethylphenyl)butanol, 1-(3-isopropylphenyl)butanol, 1-(3-tert-butylphenyl)butanol, 1-(3-methoxyphenyl)butanol, 1-(3-ethoxyphenyl)butanol, 1-(3-isopropoxyphenyl)butanol, 1-(3-tert-butoxyphenyl)butanol, 1-(3-dimethylaminophenyl) butanol, 1-(4-methylphenyl)butanol, 1-(4-ethylphenyl)butanol, 1-(4-isopropylphenyl)butanol, 1-(4-tert-butylphenyl)butanol, 1-(4-methoxyphenyl)butanol, 1-(4-ethoxyphenyl)butanol, 1-(4-isopropoxyphenyl)butanol, 1-(4-tert-butoxyphenyl) butanol, 1-(4-dimethylaminophenyl)butanol, 1-cumenylbutanol, 1-mesitylbutanol, 1-xylylbutanol, 1-(1-naphthyl)butanol, 1-(2-naphthyl)butanol, 1-phenanthrylbutanol, 1-indenylbutanol, 1-(3,4-dimethoxyphenyl)butanol, 1-(3,4-diethoxyphenyl) butanol, 1-(3,4-methylenedioxyphenyl)butanol, 1-ferrocenylbutanol,
1-phenylisobutanol, 1-(2-methylphenyl)isobutanol, 1-(2-ethylphenyl)isobutanol, 1-(2-isopropylphenyl)isobutanol, 1-(2-tert-butylphenyl)isobutanol, 1-(2-methoxyphenyl)isobutanol, 1-(2-ethoxyphenyl)isobutanol, 1-(2-isopropoxyphenyl) isobutanol, 1-(2-tert-butoxyphenyl)isobutanol, 1-(2-dimethylaminophenyl)isobutanol, 1-(3-methylphenyl)isobutanol, 1-(3-ethylphenyl)isobutanol, 1-(3-isopropylphenyl)isobutanol, 1-(3-tert-butylphenyl)isobutanol, 1-(3-ethoxyphenyl)isobutanol, 1-(3-ethoxyphenyl)isobutanol, 1-(3-isopropoxyphenyl)isobutanol, 1-(3-tert-butoxyphenyl)isobutanol, 1-(3-dimethylaminophenyl)isobutanol, 1-(4-methylphenyl)isobutanol, 1-(4-ethylphenyl)isobutanol, 1-(4-isopropylphenyl) isobutanol, 1-(4-tert-butylphenyl)isobutanol, 1-(4-methoxyphenyl)isobutanol, 1-(4-ethoxyphenyl)isobutanol, 1-(4-isopropoxyphenyl)isobutanol, 1-(4-tert-butoxyphenyl)isobutanol,1-(4-dimethylaminophenyl)isobutanol, 1-cumenylisobutanol, 1-mesitylisobutanol, 1-xylylisobutanol, 1-(1-naphthyl)isobutanol, 1-(2-naphthyl)isobutanol, 1-phenanthrylisobutanol, 1-indenylisobutanol, 1-(3,4-dimethoxyphenyl)isobutanol, 1-(3,4-diethoxyphenyl)isobutanol, 1-(3,4-methylenedioxyphenyl)isobutanol, 1-ferrocenylisobutanol, 1-phenylpentanol, 1-(2-methylphenyl)pentanol, 1-(2-ethylphenyl)pentanol, 1-(2-isopropylphenyl)pentanol, 1-(2-tert-butylphenyl)pentanol, 1-(2-methoxyphenyl)pentanol, 1-(2-ethoxyphenyl)pentanol, 1-(2-isopropoxyphenyl)pentanol, 1-(2-tert-butoxyphenyl)pentanol, 1-(2-dimethylaminophenyl)pentanol, 1-(3-methylphenyl)pentanol, 1-(3-ethylphenyl)pentanol, 1-(3-isopropylphenyl)pentanol, 1-(3-tert-butylphenyl)pentanol, 1-(3-methoxyphenyl)pentanol, 1-(3-ethoxyphenyl)pentanol, 1-(3-isopropoxyphenyl)pentanol, 1-(3-tert-butoxyphenyl)pentanol, 1-(3-dimethylaminophenyl)pentanol, 1-(4-methylphenyl)pentanol, 1-(4-ethylphenyl)pentanol, 1-(4-isopropylphenyl)pentanol, 1-(4-tert-butylphenyl)pentanol, 1-(4-methoxyphenyl)pentanol, 1-(4-ethoxyphenyl)pentanol, 1-(4-isopropoxyphenyl)pentanol, 1-(4-tert-butoxyphenyl)pentanol, 1-(4-dimethylaminophenyl)pentanol, 1-cumenylpentanol, 1-mesitylpentanol, 1-xylylpentanol, 1-(1-naphthyl)pentanol,1-(2-naphthyl)pentanol,1-phenanthrylpentanol, 1-indenylpentanol, 1-(3,4-dimethoxyphenyl)pentanol, 1-(3,4-diethoxyphenyl)pentanol, 1-(3,4-methylenedioxyphenyl)pentanol, 1-ferrocenylpentanol, 1-indanol, 1,2,3,4-tetrahydro-1-naphthol, 2-cyclopenten-1-ol, 3-methyl-2-cyclopenten-1-ol, 2-cyclohexen-1-ol, 3-methyl-2-cyclohexen-1-ol, 2-cycloheptan-1-ol, 3-methyl-2-cycloheptan-1-ol, 2-cyclooctan-1-ol, 3-methyl-2-cyclooctan-1-ol, and 4-hydroxy-2-cyclopenten-1-one. Additionally, the meso-type diol represented by the formula (IX) specifically represents meso-2-cyclopenten-1,4-diol, meso-2-cyclohexane-1,4-diol, meso-2-cycloheptane-1,4-diol, meso-2-cyclooctan-1,4-diol, 5,8-dihyroxy-1,4,4a, 5, 8, 8a-hexahydro-endo-1,4-methanonaphtharene and the like.

[0052] As the ruthenium-diamine complex to be used for the hydrogen transfer-type oxidation of the present invention, the optically active ligand diamine of the general formula (VII), namely (R, R) form or (S, S) form, may satisfactorily be used. Depending on the selection, an objective compound of the desired absolute configuration can be produced. Such ruthenium-diamine complex can be used at 1/10,000 to 1/10 fold in mole, preferably 1/2,000 to 1/200 fold in mole to the substrate compound.

[0053] For carrying out the reaction, the substrate compound and the ruthenium-diamine complex are added to ketone alone or an appropriate mixture of ketone with an inactive solvent, to prepare a homogenous solution, for reaction at a reaction temperature of 0 to 100 °C, preferably 10 to 50 °C, for 1 to 100 hours, preferably 3 to 50 hours.

[0054] Ketones including for example acetone, methyl ethyl ketone, diethyl ketone, diisopropyl ketone, methyltert-butyl ketone, cyclopentanone, and cyclohexanone are used. More preferably, acetone is better. These ketones may satisfactorily be used singly or in a mixture with an inactive solvent. Ketones can be used at an amount of 0.1 to 30 fold (volume/weight), depending on the type of the substrate, but preferably at an amount of 2 to 5 fold (volume/weight).

[0055] Appropriate inactive solvents include for example hydrocarbons such as benzene, toluene, xylene, hexane, heptane, cyclohexane, and methylcyclohexane; and ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyltert-butyl ether, tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane.

[0056] In accordance with the present invention, the reaction may be carried out in a batchwise manner or a continuous manner.

[0057] The resulting product can be purified by known processes such as silica gel column chromatography.

Examples

Example A

<Production of optically active alcohols>

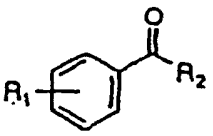
[0058] Production examples of optically active alcohols are shown below, and the inventive method will further be described in detail. Tables 1, 2 and 3 collectively show reaction substrates, transition metal complexes and optically active amine compounds as chiral ligands, which are to be used as typical examples.

[0059] The instrumental analysis was done by using the following individual systems.

NMR: JEOL GSX-400/Varian Gemini-200 (^{1}H-NMR sample: TMS, ^{31}P-NMR standard sample: phosphoric acid)
GLC: SHIMADZU GC-17A(column: chiral CP-Cyclodextrin-b-236-M19) HPLC: JASCO GULLIVER (column: CHIRALCEL OJ, OB-H, OB, OD)

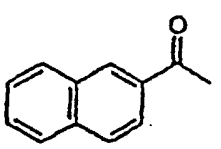
Table 1

Carbonyl compounds



1

a $R_1 = H$, $R_2 = CH_3$
b $R_1 = H$, $R_2 = C_2H_5$
c $R_1 = H$, $R_2 = CH(CH_3)_2$
d $R_1 = H$, $R_2 = C(CH_3)_3$
e $R_1 = CH_3$, $R_2 = CH_3$
f $R_1 = Cl$, $R_2 = CH_3$
g $R_1 = OCH_3$, $R_2 = CH_3$
h $R_1 = -CN$, $R_2 = -CH_3$
i $R_1 = H$, $R_2 = (CH_2)_3CO_2C_2H_5$



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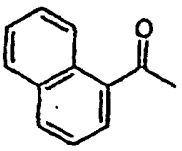

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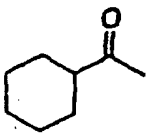

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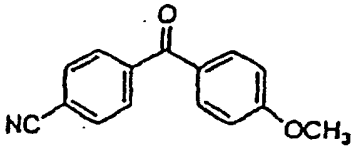

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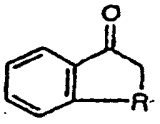
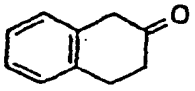


6 R = CH_2
7 R = $(CH_2)_2$



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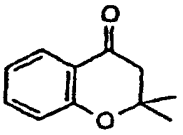

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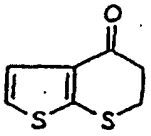

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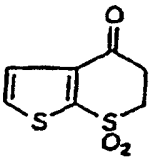

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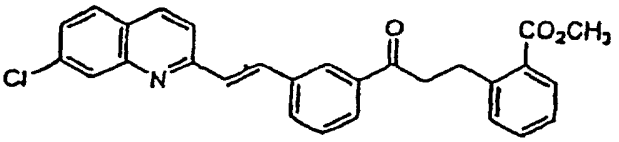


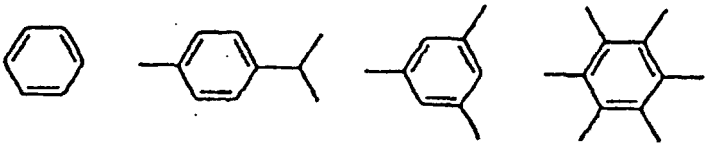
12

Table 2

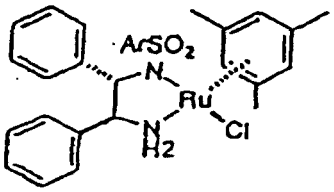
Asymmetric metal complexes

$[RuCl(arene)]_2$ - Reference

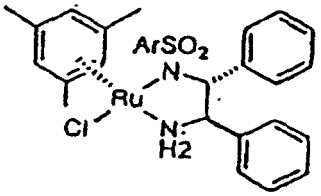
arene =



13 14 15 16

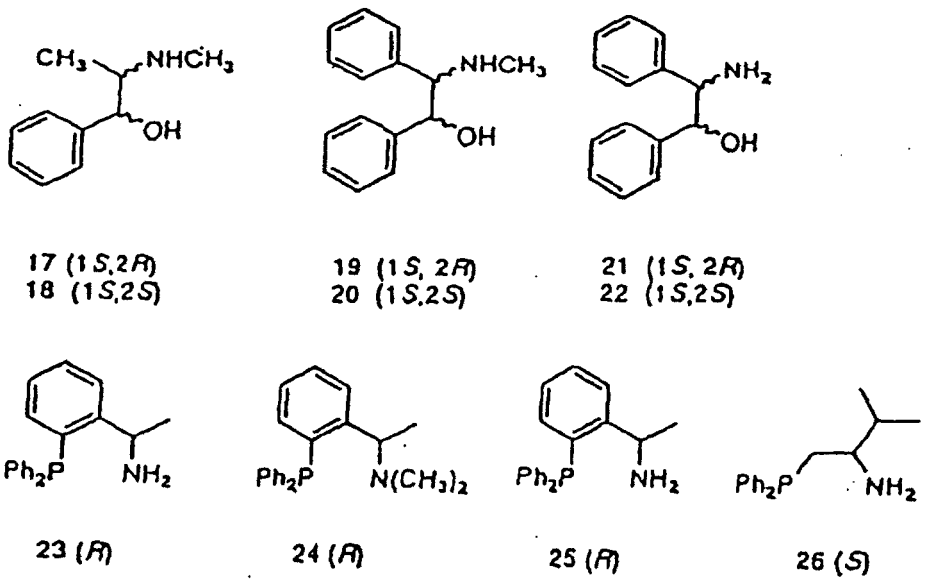


27 (*S,S*)



28 (*R,R*)

Table 3



17 (1S,2R)
18 (1S,2S)

19 (1S, 2R)
20 (1S,2S)

21 (1S, 2R)
22 (1S,2S)

23 (R)

24 (R)

25 (R)

26 (S)

Examples 1 through 19 - Reference

[0060] To dry 2-propanol (5.0 ml) were added various amino alcohol compounds (0.05 mmol) as chiral ligands of optically active amine compounds as shown in Table 3 and the ruthenium arene complex (0.0125 mmol) shown in Table 2, for agitation in argon or nitrogen gas atmosphere at 80 °C for 20 minutes, and the resulting mixture was cooled to room temperature, to which were then added frozen and degassed dry 2-propanol (45.0 ml), various carbonyl compounds (5 mmol) deaerated and distilled as shown in Table 1, and a solution of 0.05M KOH in 2-propanol (2.5 ml; 0.125 mmol) in this order, for subsequent agitation at room temperature. After completion of the reaction, dilute hydrochloric acid was added to adjust the resulting mixture to acidity, from which most of 2-propanol was evaporated off under reduced pressure, followed by addition of saturated sodium chloride solution. The resulting product was extracted into ethyl acetate, rinsed with saturated sodium chloride solution several times and dried over anhydrous sodium sulfate. The solvent was distilled off from the product. The final product was analyzed by ^{1}H-NMR ($CDCl_3$), to calculate the conversion. Then, the product was purified by thin-layer silica gel chromatography, and the isolated alcohol fraction was used to determine the optical purity and absolute configuration by HPLC or GLC. The results are collectively shown in Table 4. Furthermore, the conversion and optical purity of the sampled reaction solution can be calculated simultaneously by GLC.

Examples 20 to 23 - Reference

[0061] Using the same method as in Example 1, aminophosphine compound was used as an optically active amine compound for the reaction. The results are collectively shown in Table 4.

Table 4

Examples	$[RuCl_2(arene)]_2$	Ligands	Carbonyl compounds	Time	% conv	% ee	config.
1	13	19	1a	1	64	52	S
2	13	20	1a	1	91	17	S
3	14	20	1a	1	97	59	S
4	14	21	1a	1	97	56	S
5	15	20	1a	1	97	56	S
6	15	21	1a	1	62	52	S
7	16	17	1a	1	95	91	S

Table continued

Examples	$[RuCl_2(arene)]_2$	Ligands	Carbonyl compounds	Time	% conv	% ee	config.
8	16	20	1a	1	94	92	S
9	16	21	1a	1	59	55	S
10	16	22	1a	1	96	75	S
11	16	20	1b	2	95	82	S
12	16	20	1c	15	93	5	S
13	16	20	1d	20	22	40	R
14	16	20	o-le	6	96	83	S
15	16	18	o-1f	1	99	89	S
16	16	20	p-1g	4	73	79	S
17	16	20	3	2	99	93	S
18	16	18	4	3	93	75	S
19	16	16	7	4	62	94	S
20	13	23	1a	1	65	0.4	S
21	13	24	1a	1	61	61	R
22	13	25	1a	1	70		
23	13	26	1a	1	73	4	S

Examples 24 to 41

[0062] By using the same method as described in Example 1 and using optically active amine compounds, the chiral Ru complexes shown in Table 2 were synthesized. The complex catalysts and carbonyl compounds were added to a mixture of formic acid and triethylamine (5:2), for reaction at room temperature for a given period. After completion of the reaction, the reaction mixture was diluted with water, to extract the product in ethyl acetate. After drying the organic phase over anhydrous sodium sulfate and evaporating the solvent off, ^{1}H-NMR ($CDCl_3$) was analyzed to calculate the conversion. The optical purity and absolute configuration were determined by HPLC or GLC. The results are collectively shown in Table 5. The conversion and optical purity of each sampled reaction solution can be calculated simultaneously by GLC.

[0063] In accordance with the present invention, optically active alcohols can be produced at a high optical purity and a high synthetic yield.

Table 5

Examples	Ru complex	Carbonyl compounds	Time	% conv	% ee	config.
24	27(S, S)	1a	24	>99	98	S
25	27(S, S)	1b	60	>99	97	S
26	27(S, S)	m-1f	21	>99	97	S
27	27(S, S)	p-1f	24	>99	95	S
28	27(S, S)	m-1g	20	>99	98	S
29	27(S, S)	p-1g	50	>99	97	S
30	27(S, S)	p-1h	14	>99	90	S
31	27(S, S)	1i	60	>99	95	S
32	27(S, S)	2	60	93	83	S
33	27(S, S)	3	22	>99	96	S
34	27(S, S)	5	60	>54	66	S
35	27(S, S)	6	48	>99	99	S
36	27(S, S)	7	48	>99	99	S
37	27(S, S)	8	60	70	82	S
38	27(S, S)	9	40	47	97	S
39	28(R, R)	10	40	95	99	R
40	28(R, R)	11	65	95	98	R
41	28(R, R)	12	72	68	92	R

Example C

<Production of optically active secondary alcohols by kinetic resolution method of alcohols>

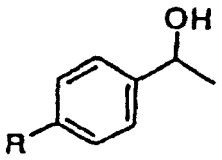
[0064] Production examples of optically active secondary alcohols are shown below, and the inventive method will further be described in detail. However, the invention is not limited to these examples. Collectively, Table 9 shows racemic secondary alcohols or meso-type diols to be used as typical examples and Table 10 shows ruthenium-diamine complexes.

[0065] Abbreviations used in the present Example are as follows. η : representing the number of carbon atoms bonded to the metal of unsaturated ligand; and hexahapto (6 carbon atoms bonded to metal) is expressed as η^6.

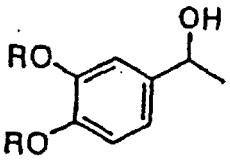
[0066] The instrumental analysis was done by using the following individual systems.

NMR: JEOL GSX-400/Varian Gemini-200 (^{1}H-NMR internal standard: TMS) GLC: SHIMADZU GC-17A(column: chiral CP-Cyclodextrin-b-236-M19) HPLC: JASCO GULLIVER (column: CHIRALCEL OJ, OB-H, OB, OD-H, OD)

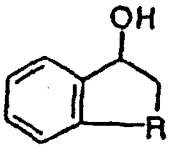
Table 9



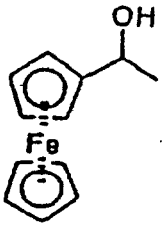
1a : R=H
1b : R=CH_3O
1c : R=$(CH_3)_2N$



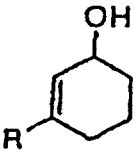
2a : R=CH_3
2b : R-R=CH_2



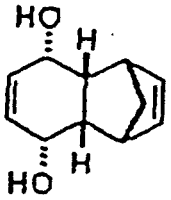
3a : R=CH_2
3b : R=$(CH_2)_2$



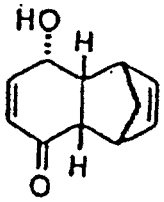
4



5a : R=H
5b : R=CH_3



6

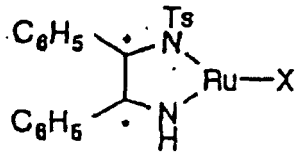


7

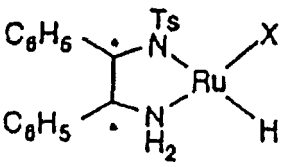
8

9

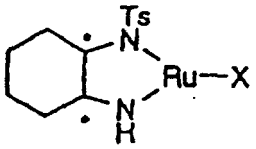
Table 10



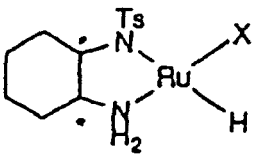
10 : X = *p*-cymene
11 : X = mesitylene



12 : X = *p*-cymene
13 : X = mesitylene



14 : X = *p*-cymene
15 : X = mesitylene



16 : X = *p*-cymene
17: X = mesitylene.

Reference Example 1

Synthesis of RuCl[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2](η^6-p-cymene) (chloro((S,S)-N-p-toluenesulfonyl-1, 2-diphenylethylenediamaine) (η^6-p-cymene)ruthenium

[0067] [$RuCl_2$ (η^6-p-cymene)]$_2$ (tetrachlorobis (η^6-p-cymene)diruthenium) (1.53 g; 2.5 mmol) and (S, S-p-TsNCE (C_6H_5)CH(C_6H_5)NH_2((S,S) -N-p-toluenesulfonyl-1, 2-diphenylethylenediamine) (1.83 g; 5.0 mmol) and triethylamine (1.4 ml; 10 mmol) are dissolved in 2-propanol (50 ml) in a Schlenk's reactor which is preliminarily dried in vacuum and of which the inside is then substituted with argon. The reaction solution was agitated at 80 °C for 1 hour and is then condensed, to recover crystal , which was then filtered and rinsed with a small amount of water, followed by drying under reduced pressure to recover orange crystal (2.99 g). The yield is 94 %. m.p.> 100 °C (decomposed)

IR(KBr)[cm^{-1}] : 3272, 3219, 3142, 3063 3030, 2963, 2874
^{1}H-NMR (400 MHz, ^{2}H-chloroform, δ): ppm

1.32 (d, 3H), 1.34 (d, 3H), 2.19 (s, 3H), 2. 28 (s, 3H), 3.07 (m, 1H), 3.26 (m, 1H), 3.54 (m, 1H), 3.66 (d, 1H), 5.68 (d, 1H), 5.70 (d, 1H), 5.72 (d, 1H), 5.86 (d, 1H), 6.61 (m, 1H), 6.29-7.20 (m, 14H)

Elemental analysis ($C_{31}H_{35}ClN_2O_2Rus$)	C	H	N	Cl	Ru
Theoretical values (%)	58.53	5.54	4.40	5.57	15.89
Elemental values (%)	58.37	5.44	4.36	5.75	18.83

[0068] The present catalyst was tested by X-ray crystallography. It was indicated that the complex was of a structure satisfying the analysis results.

Reference Example 2

Synthesis of RuCl[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2](η^6 -mesitylene)(chloro((S,S)-N-p-toluenesulfonyl-1,2 -diphenylethylenediamine) (η^6-mesitylene)ruthenium Instead of [$RuCl_2$(η^6-p-cymene)]$_2$(tetrachlorobis (η^6-p-cymene) diruthenium),

[0069] [$RuCl_2$(η^6-mesitylene)] $_2$ (tetrachlorobis (η^6-mesitylene) diruthenium) was used, and by the same procedures as in the Reference Example 1, the aforementioned catalyst was recovered as orange crystal. The yield was 64 %. m.p. 218.6-222.5 (decomposed),

^{1}H-NMR (400 MHz, ^{2}H-chloroform, δ): ppm

2.24(3H), 2.38(s.9H), 3.69(dd,1H), 3.7 9(d,1H), 3.99(dd,1H), 4.19(brd,1H), 5.3 0(s,3H), 6.65-6.93(m,9H), 7.06-7.15(m, 3H), 7.35(d,2H)

Reference Example 3

Synthesis of RuCl[(S,S)-N-p-Ts-cyclohexane-1,2-diamine](η^6-p-cymene)(chloro-((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene) ruthenium)

[0070] Instead of (S,S)-p-TsNCH(C_6B_5)CH(C_6B_5)NH_2((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine), (S, S)-N-p-Ts-cyclohexane-1,2-diamine)((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) was used, and by the same procedures as in the Reference Example 1, the aforementioned catalyst was recovered as orange crystal. The yield is 60 %.

Reference Example 4

Synthesis of RuCl[(S,S)-N-p-Ts-cyclohexane-1,2-diamine](η^6-mesitylene)(chloro-((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium

[0071] Instead of (S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine), (S, S)-N-p-Ts-cyclohexane-1,2-diamine)((1S,2S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) was used, and by the same procedures as in the Reference Example 2, the aforementioned catalyst was recovered as orange crystal. The yield is 58 %.

Example 71-a Reference

Synthesis of Ru [(S,S) -p-TsNCH (C_6H_5)CH (C_6H_5)NH](η^6-p-cymene) (S, S)-N-p-toluenesulfonyl-1,2-diamine)(η^6-p-cymene)ruthenium)

[0072] [$RuCl_2$(η^6-p-cymene)] $_2$ (tetrachlorobis (η^6-p-cymene)diruthenium) (306.2 mg; 0.5 mmol) and (S,S)-p-TsNCH (C_6H_5)CH (C_6H_5)NH_2((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (366.4 mg; 1.0 mmol) and potassium hydroxide (400 mg; 7.1 mmol) are dissolved in methylene chloride (7 ml) in a Schlenk's reactor which is preliminarily dried in vacuum and of which the inside is then substituted with argon. The reaction solution was agitated at room temperature for 5 minutes, and by adding water (7 ml) to the reaction solution, the color of the reaction solution turned from orange to deep purple. The organic phase was separated and rinsed in water (7 ml). The organic phase was dried over calcium hydroxide, from which the solvent was distilled off. Then, the resulting product was dried under reduced pressure, to recover catalyst No. 10 of deep purple crystal (522 mg) in Table 10. The yield is 87 %.

m.p.> 80 °C (decomposed)

IR(KBr)[cm^{-1}] : 3289, 3070, 3017, 2968 2920, 2859
^{1}H-NMR (400 MHz, ^{2}H-toluene, δ): ppm

1.20(d.3H), 1.25(d,3H), 2.05(s,3H),2. 22(s,3H), 2.53(m.1H), 4.08(d,1H), 4.89 (s,1H), 5.11(d,1H), 5.27(d,1H), 5.28(d, 1H), 5.39(d,1H), 6.64(brd,1H), 6.87(d,2 H), 7.67(d,2H), 7.2-7.7(m,10H)

Elemental analysis ($C_{31}H_{34}N_2O_2RuS$)					
	C	H	N	Ru	
Theoretical values	(%)	62.09	5.71	4.67	16.85
Elemental values	(%)	62.06	5.77	4.66	16.47

[0073] The present catalyst was tested by X-ray crystallography. It was indicated that the complex was of a structure satisfying the analysis results.

Example 71-b Reference

Alternative synthesis of Ru[(S, S) -p-TsNCH (C_6H_5) CH (C_6H_5) NH] (η^6-p-cymene)((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium)

[0074] RuCl [(1S,2S) -p-TsNCH (C_6H_5) CH(C_6H_5)NH_2] (η^6-p-cymene)(chloro-(1S,2S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium) (318.6 mg; 0.5 mmol) and potassium hydroxide (200 mg; 3.5 mmol) are dissolved in methylene chloride (7 ml) in a Shlenk's reactor which is preliminarily vacuum dried and of which the inside is substituted with argon. The reaction solution was agitated at room temperature for 5 minutes, and by adding water (7 ml) to the reaction solution, the color of the reaction solution turned from orange to deep purple. The organic phase was separated and rinsed in water (7 ml). The organic phase was dried over calcium hydroxide, from which the solvent was distilled off. Then, the resulting product was dried under reduced pressure, to recover crystal in deep purple crystal (522 mg). The yield is 87 %.

Example 72-a Reference

Synthesis of Ru[(S, S) -p-TsNCH (C_6H_5)CH (C_6H_5)NH](η^6-mesitylene)(((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium)

[0075] Instead of [$RuCl_2(\eta^6$-p-cymene)]$_2$(tetrachlorobis(η^6-p-cymene) diruthenium), [$RuCl_2(\eta^6$-mesitylene)]$_2$ (tetrachlorobis (η^6-mesitylene) diruthenium) was used, and by the same procedures as in the Example 71-a, the catalyst in purple crystal as No.11 in Table 10 was recovered. The yield is 80 %.
^{1}H-NMR (400 MHz, ^{2}H-chloroform, δ): ppm
1.91(s,9H), 1.99(s,3H), 3.83(d,1H),4. 51(s,1H), 4.95(s,3H), 5.92(brd,1H), 6.3 8~7.71(m,14H)

Example 72-b Reference

Alternative synthesis of Ru[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH](η^6-mesitylane)(((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium)

[0076] Instead of RuCl[(S, S)-p-TsNCH (C_6H_5)CH (C_6H_5)NH_2] (η^6-p-cymene)(chloro-((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium), RuCl [(S, S)-p-TsNCH (C_6H_5)CH(C_6H_5) NH_2] (η^6-mesitylene) (chloro- ((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium) synthesized as in the Reference Example 2 was used, and by the same procedures as in the Example 71-b, the catalyst in purple crystal was recovered. The yield is 90 %.

Example 73-a Reference

Synthesis of Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine](η ^{6}-p-cymene)(((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η ^{6}-p-cymene)ruthenium)

[0077] Instead of (S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2](((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine), (S,S)-N-p-Ts-1,2-cyclohexanediamine((l1,2S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) was used, and by the same procedures as in the Example 71-a, the catalyst in purple crystal as No.14 in Table 10 was recovered. The yield is 58 %.

Example 73-b Reference

[0078] Alternative synthesis of Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-p-cymene)(((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6-p-cymene) ruthenium)

[0079] Instead of RuCl[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2]) (η^6-p-cymene) (chloro-((S,S) -N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium), RuCl[(S, S)-N-p-Ts-cyclohexane-1,2-diamine synthesized in the Reference Example 3 was used, and by the same procedures as in the Example 71-b, the catalyst in purple crystal was recovered. The yield is 62 %.

Example 74-a Reference

Synthesis of Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine](η^6-mesitylene)((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η ^{6}-mesitylene) ruthenium)

[0080] Instead of (S, S) -p-TsNCH (C_6H_5) CH (C_6H_5) NH_2 ((S, S) -N-p-toluenesulfonyl-1,2-diphenylethylenediamine), (S,S)-N-p-Ts-cyclohexane-1,2-diamine ((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) was used, and by the same procedures as in the Example 71-a, the catalyst as No.15 shown in Table 10 was recovered as purple crystal. The yield is 60 %.

Example 74-b Reference

Alternative synthesis of Ru[(S,S)-N-p-Ts-1,2-cyclohexanediamine](η^6-mesitylene)((S,S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6-mesitylene)ruthenium)

[0081] Instead of RuCl[(S,S)-p-TsNCE(C_6H_5)CH(C_6H_5)NH_2] (η^6-p-cymene) (chloro-(S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium), RuCl[(S,S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-mesitylene) (chloro-(1S,2S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene)ruthenium) synthesized in the Reference Example 4 was used, and by the same procedures as in the Example 71-b, the aforementioned catalyst was recovered as purple crystal. The yield is 62 %.

Example 75-a Reference

Synthesis of RuH[(S, S)-p-TsNCH(C_6H_5)CH (C_6H_5)NH_2](η^6-p-cymene)(hydride-(S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium)

[0082] Ru [(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene) ((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene) ruthenium) (600 mg; 1.0 mmol) is dissolved in 2-propanol (10 ml) in a Shlenk's reactor which is preliminarily vacuum dried and of which the inside is substituted with argon. The reaction solution was agitated at room temperature for 15 minutes. The solvent was recovered under reduced pressure at room temperature, to recover a compound in brown yellow. After rinsing the compound in cool pentane and recrystallizing the compound in methanol, the catalyst No.12 in Table 10 was recovered as orange crystal. The yield is 85 %.
m.p. >. 60 °C (decomposed)

IR(KBr)[cm^{-1}] : 3335, 3317, 3228, 3153, 3060, 3025, 2960, 2917, 2867
^{1}H-NMR (400 MHz, ^{2}H-chloroform, δ) : ppm

-5.47(s,1H), 1.53(d,3H), 1.59(d,3H), 2. 29(d,3H), 2.45(s,3H), 2.79(m,1H), 2.93 (m.1H),3 .80(d,1H), 4.02(m,1H), 5.15(d, 1H), 5.19(d,1H), 5.29(m,1H), 5.43(d,1H), 5.58(d,1H), 6.49(d,2H), 6.9-7.3(m,10H), 7.59(d,2H)

Elemental analysis ($C_{31}H_{36}N_2O_2RuS$)		C	H	N	Ru	
Theoretical values	(%)	61.88	6.02	4.66	16.80	
Experimental values	(%)	61.79	5.94	4.70	16.56	

[0083] The X-ray crystallography shows that the complex was of a structure satisfying the analytical results.

Example 75-b Reference

Alternative synthesis of RuH[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2](η ^{6}-p-cymene)(hydride-((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium)

[0084] Toluene (7 ml) was added into the Ru[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene)((S,S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium) (306.2 mg; 0.5 mmol) synthesized in the Example 72 in an autoclave which was preliminarily vacuum dried and of which the inside was substituted with argon, for reaction at room temperature and a hydrogen pressure of 80 atm. After elimination of the solvent and rinsing in cool pentane and subsequent recrystallization in methanol, crystal in orange (420 mg) was recovered. The yield is 70 %.

Example 76-a Reference

Synthesis of RuH[(S,S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2](η^6-mesitylene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium)

[0085] Instead of Ru [(S, S) -p-TsNCH (C_6H_5) CH (C_6H_5)NH] (η^6-p-cymene)(((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene) ruthenium), Ru[(S, S)-p-TsNCH (C_6H_5)CH(C_6H_5)NH](η ^{6}-mesitylene) (((S, S) -N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene) ruthenium) synthesized in the Example 72 was used, and by the same procedures as in the Example 75-a, the aforementioned catalyst No.13 in Table 10 was recovered. The yield was 60 %.

Example 76-b Reference

Alternative synthesis of RuH[(S, S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH_2](η ^{6}-mesitylene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium)

[0086] Instead of Ru [(S, S)-p-TsNCH(C_6H_5)CH (C_6H_5)NH](η^6-p-cymene)(((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium), Ru [(S, S) -p-TsNCH (C_6H_5) CH(C_6B_5)NE] (η^6-mesitylene) (((S, S) -N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-mesitylene)ruthenium) synthesized in the Example 72 was used, and by the same procedures as in the Example 75-b, the aforementioned catalyst was recovered. The yield is 60 %.

Example 77-a Reference

Synthesis of RuH[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6-p-cymene)(hydride-(S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6-p-cymene) ruthenium)

[0087] Instead of Ru[(S, S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium), Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6-p-cymene) ruthenium) synthesized in the Example 73 was used, and by the same procedures as in the Example 75-a, the catalyst No.16 in Table 10 was recovered. The yield is 54 %.

Example 77-b Reference

Alternative synthesis of RuH[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6-p-cymene)(hydride-(S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η ^{6}-p-cymene) ruthenium)

[0088] Instead of Ru [(S, S) -p-TsHCH (C_6H_5) CH (C_6H_5)NH] (η^6-p-cymene)(chloro-(S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium), Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-p-cymene)((S,

S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-p-cymene)ruthenium) synthesized in the Example 73 was used, and by the same procedures as in the Example 75-b, the catalyst was recovered. The yield is 55 %.

Example 78-a Reference

Synthesis of RuH[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6-mesitylene)(hydride(S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η -mesitylene)ruthenium)

[0089] Instead of Ru[(S, S) -p-TsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene)((s, s)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6-p-cymene)ruthenium), Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-mesitylene) ((s, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene) ruthenium) synthesized in the Example 74 was used, and by the same procedures as in the Example 75-a, the catalyst No.17 in Table 10 was recovered. The yield is 52 %.

Example 78-b Reference

Alternative synthesis of RuH[(S, S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-mesitylene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6-mesitylene)ruthenium)

[0090] Instead of Ru[(S, S)-p-TsNCH(C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6-p-cymene)ruthenium), Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine] (η^6-mesitylene) ((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) (η^6-mesitylene) ruthenium) synthesized in the Example 74 was used, and by the same procedures as in the Example 75-b, the aforementioned catalyst was recovered. The yield is 48 %.

Example 79

Synthesis of (R)-1-indanol

[0091] Ru[(S, S) -p-TsNCH (C_6H_5)CH(C_6H_5)NH] (η^6-p-cymene)((S, S) -N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(ruthenium-η^6-p-cymene mesitylene (6.0 mg; 10 μmmol) synthesized in the Example 71 and 1-indanol (671 mg; 5 mmol) were weighed in a shlenk's reactor which was preliminarily vacuum dried and of which the inside was substituted with argon, and acetone (2.5 ml) was then added to the resulting mixture for agitation at 28 °C for 6 hours. The solvent was distilled off under reduced pressure, prior to separation by silica gel chromatography (eluent; ethyl acetate : hexane = 1 : 3) , to recover (R)-indinol (286 mg) in colorless crystal. The yield is 84 %.
m.p. 71 - 72 °C
$[\alpha]^{24}_D$ = -30.1 ° (c = 1.96, chloroform)
[0092] The resulting (R)-1-indanol was analyzed by HPLC (high-performance liquid chromatography), and the objective (R)-1-indanol was at an optical purity of 97 % ee.

<HPLC analytical conditions>

[0093]

Column:	Chiralcel OB (manufactured by Daicell Chemical Industry, Co.)
Developing solution: isopropanol :	hexane = 10 : 90
Flow rate:	0.5 ml/min
Retention time:	(S)-1-indanol 18.6 minutes (R)-1-indanol 12.9 minutes.

Examples 80 to 93

[0094] According to the method described in Example 79, the optically active ruthenium-diamine complexes for racemic secondary alcohols and meso-type diols as reaction substrates as shown in Table 9 were used for reaction under reaction conditions of reaction time, to recover the individually corresponding optically active secondary alcohols at high yields. The results are collectively shown in Table 11.

Table 11

Examples	Substrates	Catalysts	Reaction time s/c	Reaction time (hr)	%(yield)	%ee	Products
80	1 a	(S, S)-10	500	36	50	92	1a(R)
81	1 a	(S, S)-11	500	30	51	94	1a(R)
82	1 a	(S, S)-10	500	22	47	92	1b(R)
83	1 b	(S, S)-11	500	30	44	98	1c(R)
84	1 c	(S, S)-11	500	36	47	97	2a (R)
85	2 a	(S, S)-11	500	24	47	97	2b(R)
79	2 b	(S, S)-10	500	6	46	97	3a(R)
86	3 a	(S, S)-10	500	6	49	99	3b(R)
87	3 b	(S, S)-11	500	36	51	98	4(R)
88	4	(S, S)-10	500	4. 5	43	93	5a (R)
89	5 a	(S, S)-10	500	5	46	95	5b (R)
90	5 b	(S, S)-11	200	3	70	96	7
91	5	(S, S)-10	200	3	56	87	9
92	1 a	(S, S)-14	500	36	48	82	1a(R)
93	1 a	(S, S)-15	500	36	48	86	1a(R)

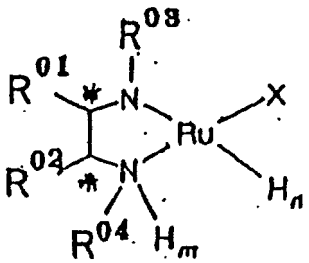
(In the table, s/c means the molar ratio of substrate/ruthenium-optically active diamine complex.)

[0095] In accordance with the present invention, optically active alcohols are provided, which are useful in various fields of pharmaceutical products, synthetic intermediates thereof, food, flavor, cosmetics and liquid crystal materials.

[0096] The ruthenium-diamine complex employed in the present invention is industrially useful as a chiral catalyst providing higher selectivity and activity in that the complex can be used for organic synthesis such as asymmetric synthetic reactions. If the complex is used as a hydrogen transfer-type asymmetric reduction catalyst of racemic secondary alcohols or meso-type diols, optically active secondary alcohols useful as production intermediates of drugs can be produced highly efficiently.

Claims

1. A method for producing optically active secondary alcohols, comprising subjecting racemic secondary alcohols or meso-type diols to hydrogen transfer reaction in the presence of an optically active ruthenium-diamine complex catalyst represented by the following general formula (VII) ;



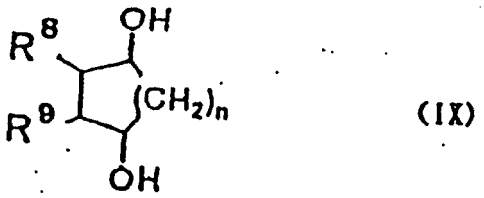
(VII)

wherein * represents an asymmetric carbon atom; R^{01} and R^{02} are the same or different, independently representing alkyl group, or phenyl group or cycloalkyl group which may or may not have an alkyl group; or R^{01} and R^{02} together form an alicyclic ring unsubstituted or substituted with an alkyl group; R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with an alkyl group, an alkoxyl group or halogen atom, or benzoyl group which may or

may not be substituted with alkoxycarbonyl group or alkyl group; R^{04} represents hydrogen atom or alkyl group; X represents an aromatic compound which may or may not be substituted with an alkyl group; and m and n together represent 0 or 1.

2. A method as claimed in claim 1, comprising the reaction of racemic secondary alcohols or meso-type diols represented by the following formulas (VIII) and (IX) ;

(VIII)

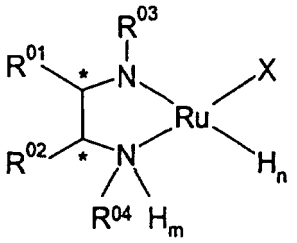


(IX)

wherein R^6 represents an aromatic monocyclic or polycyclic hydrocarbon group, unsubstituted or substituted or a hetero monocyclic or polycyclic group containing hetero atoms, or ferrocenyl group; R^7 represents hydrogen atom, a saturated or unsaturated hydrocarbon group, or a functional group containing hetero atoms; or R^6 and R^7 may be bonded together to form a saturated or unsaturated alicyclic group giving a cyclic ketone and the alicyclic group may or may not be substituted;
R^8 and R^9 furthermore independently represent a saturated or unsaturated hydrocarbon group which may or may not have a substituent, or R^8 and R^9 may be bonded together to form a saturated or unsaturated alicyclic group which may or may not have a substituent; and n is 1 or 2.

Patentansprüche

1. Verfahren zur Herstellung von optisch aktiven sekundären Alkoholen, umfassend die Umsetzung von racemischen sekundären Alkoholen oder von meso-Diolen in einer Wasserstoff-Transferreaktion in Gegenwart eines optisch aktiven Ruthenium-Diamin-Komplexkatalysators der folgenden allgemeinen Formel (VII)



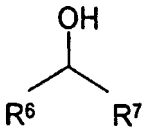
(VII)

worin

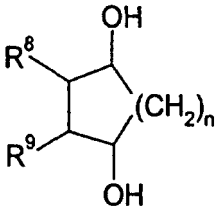
* für ein asymmetrisches Kohlenstoffatom steht;
R^{01} und R^{02} gleich oder verschieden sind und unabhängig voneinander für eine Alkylgruppe oder für eine Phenylgruppe oder eine Cycloalkylgruppe, die gegebenenfalls durch eine Alkylgruppe substituiert sind, stehen;

oder
R^{01} und R^{02} gemeinsam einen gegebenenfalls durch eine Alkylgruppe substituierten alicyclischen Ring bilden;
R^{03} für eine Methansulfonylgruppe, eine Trifluormethansulfonylgruppe, eine Naphthylsulfonylgruppe, eine Camphersulfonylgruppe, eine gegebenenfalls durch eine Alkylgruppe, eine Alkoxygruppe oder ein Halogenatom substituierte Benzolsulfonylgruppe oder eine gegebenenfalls durch eine Alkoxycarbonylgruppe oder Alkylgruppe substituierte Benzoylgruppe steht;
R^{04} für ein Wasserstoffatom oder eine Alkylgruppe steht;
X für eine gegebenenfalls durch eine Alkylgruppe substituierte aromatische Verbindung steht; und
m und n zusammen für 0 oder 1 stehen.

2. Verfahren nach Anspruch 1, umfassend die Umsetzung von racemischen sekundären Alkoholen oder von meso-Diolen der folgenden Formeln (VIII) und (IX)



(VIII)



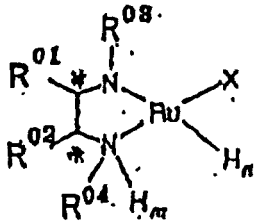
(IX)

worin

R^6 für eine gegebenenfalls substituierte aromatische monocyclische oder polycyclische Kohlenwasserstoffgruppe, eine monocyclische oder polycyclische Heteroatom-haltige Gruppe oder eine Ferrocenylgruppe steht;
R^7 für ein Wasserstoffatom, eine gesättigte oder ungesättigte Kohlenwasserstoffgruppe oder eine Heteroatom-haltige funktionelle Gruppe steht; oder
R^6 und R^7 gemeinsam eine gesättigte oder ungesättigte, ein cyclisches Keton bildende, gegebenenfalls substituierte alicyclische Gruppe bilden;
R^8 und R^9 des Weiteren unabhängig voneinander für eine gesättigte oder ungesättigte Kohlenwasserstoffgruppe, die gegebenenfalls einen Substituenten trägt, stehen; oder
R^8 und R^9 gemeinsam eine gesättigte oder ungesättigte alicyclische Gruppe, die gegebenenfalls einen Substituenten trägt, bilden; und
n für 1 oder 2 steht.

Revendications

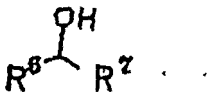
1. Procédé de production d'alcools secondaires optiquement actifs, comprenant le fait de soumettre des alcools secondaires racémiques ou des diols de type méso à une réaction de transfert d'hydrogène en présence d'un catalyseur de type complexe ruthénium-diammine optiquement actif représenté par la formule générale (VII) suivante :



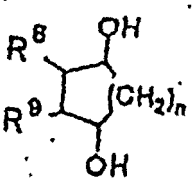
(VII)

dans laquelle * représente un atome de carbone asymétrique ; R^{01} et R^{02} sont identiques ou différents, et représentent indépendamment un groupe alkyle, ou un groupe phényle ou un groupe cycloalkyle qui peut éventuellement porter un groupe alkyle ; ou R^{01} et R^{02} forment ensemble un noyau alicyclique non substitué ou substitué avec un groupe alkyle ; R^{03} représente un groupe méthanesulfonyle, un groupe trifluorométhanesulfonyle, un groupe naphtylsulfonyle, un groupe camphosulfonyle ou un groupe benzènesulfonyle qui peut être éventuellement substitué par un groupe alkyle, un groupe alcoxyle ou un atome d'halogène, ou un groupe benzoyle qui peut être éventuellement substitué par un groupe alcoxy-carbonyle ou un groupe alkyle ; R^{04} représente un atome d'hydrogène ou un groupe alkyle ; X représente un composé aromatique qui peut être éventuellement substitué par un groupe alkyle ; et m et n ensemble ont une valeur de 0 ou 1.

2. Procédé selon la revendication 1, comprenant la réaction d'alcools racémiques secondaires ou de diols de type méso représentés par les formules (VIII) et (IX) suivantes :



(VIII)



(IX)

dans lesquelles R^6 représente un groupe hydrocarboné aromatique monocyclique ou polycyclique, non substitué ou substitué, ou un groupe monohétérocyclique ou polyhétérocyclique contenant des hétéroatomes, ou un groupe ferrocényle ; R^7 représente un atome d'hydrogène, un groupe hydrocarboné saturé ou insaturé, ou un groupe fonctionnel contenant des bétéroatomes ; ou bien R^6 et R^7 peuvent être reliés l'un à l'autre pour former un groupe alicyclique saturé ou insaturé donnant une cétone cyclique et le groupe alicyclique peut être éventuellement substitué ;

R^8 et R^9 représentent en outre indépendamment un groupe hydrocarboné saturé ou insaturé qui peut éventuellement porter un substituant, ou bien R^8 et R^9 peuvent être reliés l'un à l'autre pour former un groupe alicyclique saturé ou insaturé qui peut éventuellement porter un substituant ; et n est égal à 1 ou 2.