

HYDROFORMYLATION PROCESS

FIELD OF THE INVENTION

This invention relates to a process for hydroformylating allyl alcohol to produce 4-hydroxybutyraldehyde.

BACKGROUND OF THE INVENTION

The hydroformylation of allyl alcohol is a well known and commercially practiced process. See, for example, U.S. Pat. Nos. 4,064,145, 4,215,077, 4,238,419, 4,678,857, and 5,290,743. In the hydroformylation reaction, allyl alcohol is reacted with a CO/H₂ gas mixture in the presence of a catalyst to form 4-hydroxybutyraldehyde (HBA). The HBA may then be separated from the catalyst, e.g., by water extraction, and hydrogenated to form 1,4-butanediol (BDO). See U.S. Pat. No. 5,504,261.

Various catalyst systems have been employed for the hydroformylation reaction, most notably a rhodium complex together with a phosphine ligand (see, e.g., U.S. Pat. Nos. 4,064,145, 4,238,419, and 4,567,305). Commonly employed phosphine ligands are trisubstituted phosphines such as triphenyl phosphine.

One disadvantage of the hydroformylation process is that other co-products or byproducts are also formed in addition to the desired HBA linear product. The hydroformylation of allyl alcohol typically produces some 3-hydroxy-2-methylpropionaldehyde (HMPA) branched co-product and C₃ byproducts such as n-propanol and propionaldehyde. Although HMPA may be hydrogenated to produce 2-methyl-1,3-propanediol (MPD), which is a useful material, the MPD co-product reduces the yield of BDO. Formation of the C₃ byproducts effectively represents another yield loss in the process which can have a severe adverse effect on the process economics.

To increase BDO yields, research continues to improve the hydroformylation process and reduce less desired co-product/byproducts. U.S. Pat. No. 6,127,584 discloses that the use of a trialkyl phosphine ligand having at least 2 methyl groups results in increased HBA:HMPA ratio. The use of diphosphine ligands has also been found to improve the HBA:HMPA ratio. The hydroformylation of allyl alcohol using rhodium complex catalysts and diphosphine ligands such as DIOP,

XANTPHOS, or trans-1,2-bis(diphenylphosphinomethyl)cyclobutane is shown in the art, notably in Japan Kokai Nos. 06-279345 and 06-279344 and U.S. Pat. No. 4,306,087. U.S. Pat. No. 6,225,509 discloses that maintaining the concentration of CO in the reaction liquid above about 4.5 mmols/liter reduces the make of undesirable C₃ co-products when using a catalyst comprised of a rhodium complex and a ligand such as DIOP. In addition, U.S. Pat. Nos. 7,271,295 and 7,279,606 disclose the use of a 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,5-di-n-alkylphenyl)phosphino]butane ligand or a trans-1,2-bis(bis(3,5-di-n-alkylphenyl)phosphinomethyl)cyclobutane ligand, respectively.

In sum, new processes for hydroformylating allyl alcohol to produce 4-hydroxybutyraldehyde are needed. Particularly valuable processes would result in high ratios of 4-hydroxybutyraldehyde to 3-hydroxy-2-methylpropionaldehyde.

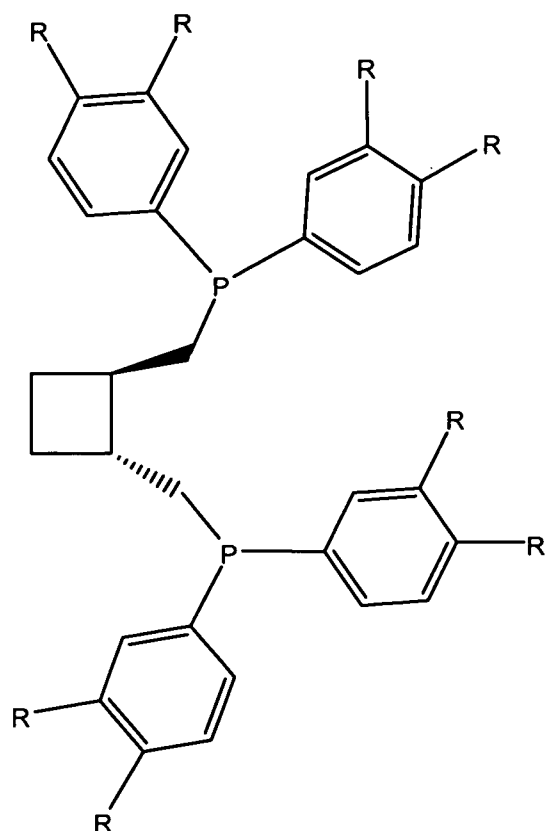
SUMMARY OF THE INVENTION

The invention is a process that comprises reacting allyl alcohol with carbon monoxide and hydrogen in the presence of a solvent and a catalyst to produce 4-hydroxybutyraldehyde. The catalyst comprises a rhodium complex and a trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane and/or a 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino]butane. The invention also includes the catalyst. The invention surprisingly results in high ratios of 4-hydroxybutyraldehyde product to 3-hydroxy-2-methylpropionaldehyde.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention comprises hydroformylating allyl alcohol in the presence of a solvent and a catalyst. The catalyst of the invention comprises a rhodium complex and a diphosphine ligand. The diphosphine is a trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane and/or a 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino]butane.

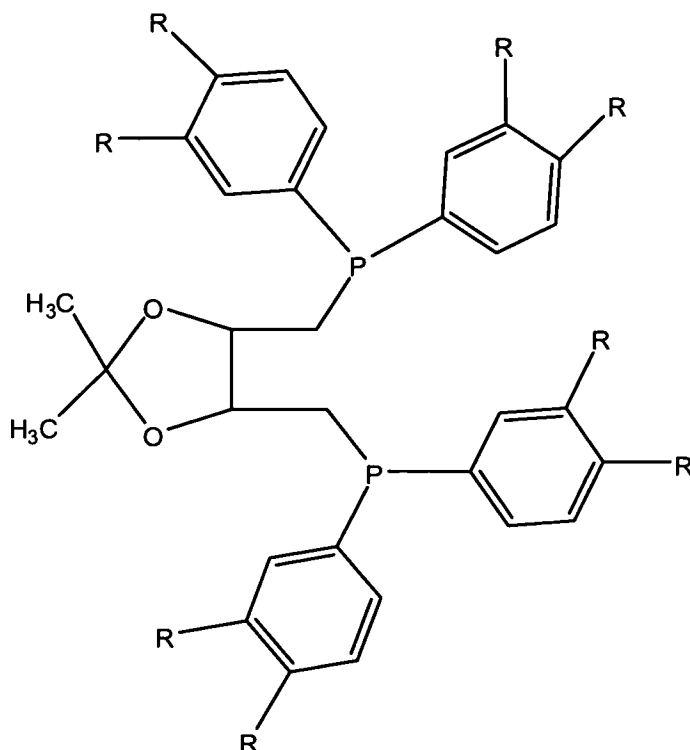
Trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl) cyclobutanes have the formula:



wherein each R is independently an n-alkyl group. Preferably, R is methyl, ethyl, or propyl.

The trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl) cyclobutane diphosphine ligand is most preferably trans-1,2-bis(bis(3,4-dimethylphenyl)phosphinomethyl)cyclobutane or trans-1,2-bis(bis(3,4-diethylphenyl)phosphinomethyl)cyclobutane.

2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino]butanes have the formula:



wherein each R is independently an n-alkyl group. Preferably, R is methyl, ethyl, or propyl.

The 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl) phosphino]butane diphosphine ligand is most preferably 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-dimethylphenyl) phosphino]butane or 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-diethylphenyl) phosphino]butane.

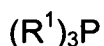
The diphosphine ligand may be prepared by any possible method. For instance, 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl) phosphino]butanes may be prepared by the reaction of 2,2-dimethyl-4,5-bis[(toluenesulfonyloxymethyl) methyl]-1,3-dioxolane with lithium di(3,4-di-n-alkylphenyl)phosphines. Trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl) cyclobutanes may be prepared by the reaction of trans-1,2-cyclobutanedimethanol, bis(toluenesulfonate) with lithium di(3,4-di-n-alkylphenyl)phosphines.

The catalyst of the invention also comprises a rhodium complex. Suitable rhodium complexes contain rhodium attached to ligand groups. The rhodium complex is preferably soluble in the solvent. There are no particular restrictions regarding the choice of ligands attached to the rhodium complex. For example, suitable ligands include hydrides, carbonyl, substituted and unsubstituted cyclopentadienyls, 2,4-alkanedionates, trialkyl phosphines, triaryl phosphines,

diphosphines, and mixtures thereof. Particularly preferred ligands include carbonyl, acetylacetonate (2,4-pentanedionate), triphenylphosphine, and mixtures thereof. Examples of preferred rhodium complexes include (acetylacetonato) dicarbonylrhodium and tris(triphenylphosphine)rhodium carbonyl hydride.

5 The rhodium complex can be pre-associated with the trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane or 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino] butane diphosphine ligand prior to use in the hydroformylation reaction such that the bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane or 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino] butane forms part of the rhodium complex, or it can be added separately. However, it is preferable to add the rhodium complex separate from the trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane or 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino]butane. The molar ratio of the diphosphine ligand:rhodium complex is preferably in the range of 0.5:1 to 5:1.

15 Although not necessary, the catalyst may additionally comprise a monophosphine compound. The monophosphine compound is in addition to any phosphine ligand that may be associated with the rhodium complex. The monophosphine compound is a trisubstituted phosphine that is represented by the formula:



wherein R^1 is an aryl or alkyl group. Suitable aliphatic R^1 groups include methyl, ethyl, n-butyl, sec-butyl, octyl, and decyl. Suitable aromatic R^1 groups include phenyl, tolyl, and naphthyl. The R^1 groups may be the same or are different, but preferably are the same. Preferably, the monophosphine is a trisubstituted aryl phosphine. More preferably, the monophosphine is triphenylphosphine or tritolylphosphine. Triphenyl phosphine is particularly preferred.

25 A reaction solvent is also required for the process of the invention. Typical solvents are those that are capable of solubilizing the rhodium complex and are not reactive to the hydroxyaldehydes that are produced in the hydroformylation step. Suitable solvents include any organic solvent having very low or minimal solubility in water. Preferred solvents include C_5 - C_{20} aliphatic hydrocarbons, C_6 - C_{20} aromatic

hydrocarbons, alcohols, ethers, and mixtures thereof. Particularly preferred solvents include toluene, cyclohexane, methyl t-butyl ether, and mixtures thereof.

Typical reaction conditions for the hydroformylation step are mild to favor the formation of the linear 4-hydroxybutyraldehyde (HBA) rather than branched 3-hydroxy-2-methylpropionaldehyde (HMPA) reaction product. Reaction conditions are preferably in the range of from 20 to 120°C and pressures of from 20 to 600 psig, more preferably from 45 to 85°C and 30 to 400 psig, and most preferably from 50 to 80°C and 40 to 300 psig. The molar ratio of CO:H₂ is typically about 1:1, although the ratio can vary considerably. The partial pressure of CO is typically within the range of 5 to 100 psig. The partial pressure of hydrogen is typically within the range of 40 to 200 psig. The reaction is conducted at these conditions until a predominance of the allyl alcohol has reacted, e.g. 60 to 99.9%, the products being largely 4-hydroxybutyraldehyde with some branched reaction products. The amount of reaction time is not critical, but usually a reaction time of 0.5 to 4 hours is adequate.

Preferably, the allyl alcohol starting concentration on a reaction solvent to feed basis is in the range of 5 to 40 percent by weight in the solvent; more preferably, lower concentration in the range of 5 to 10 percent by weight may be used.

Preferably, the hydroformylation of allyl alcohol is carried out such that the concentration of CO in the liquid phase ([CO]_{liq}) is maintained above 4 mmols/liter (0.004 M) during the hydroformylation. The value of [CO]_{liq} is defined in U.S. Pat. No. 6,225,509, the teachings of which are incorporated herein by reference. Preferably, the liquid phase hydrogen:carbon monoxide molar ratio is in the range of from 10:1 to 1:2, more preferably from 5:1 to 1:2.

Following the hydroformylation step, the HBA product is preferably separated from the solvent and catalyst by water extraction in an extraction vessel. Water extraction methods are well known in the art and can be affected by any suitable means, such as mixer-settlers, packed or trayed extraction columns, rotating disk contactors, or passed to a settling tank for resolution of the mixture into aqueous and organic phases. HBA, and any HMPA, remains soluble in the water (aqueous) phase and is separated from the solvent (organic) phase.

The 4-hydroxybutyraldehyde (and any 3-hydroxy-2-methylpropionaldehyde) reaction product is preferably subjected to an additional step of hydrogenating the 4-hydroxybutyraldehyde in the presence of a hydrogenation catalyst to produce 1,4-butanediol (BDO). Hydrogen is added to the reaction vessel for the hydrogenation.

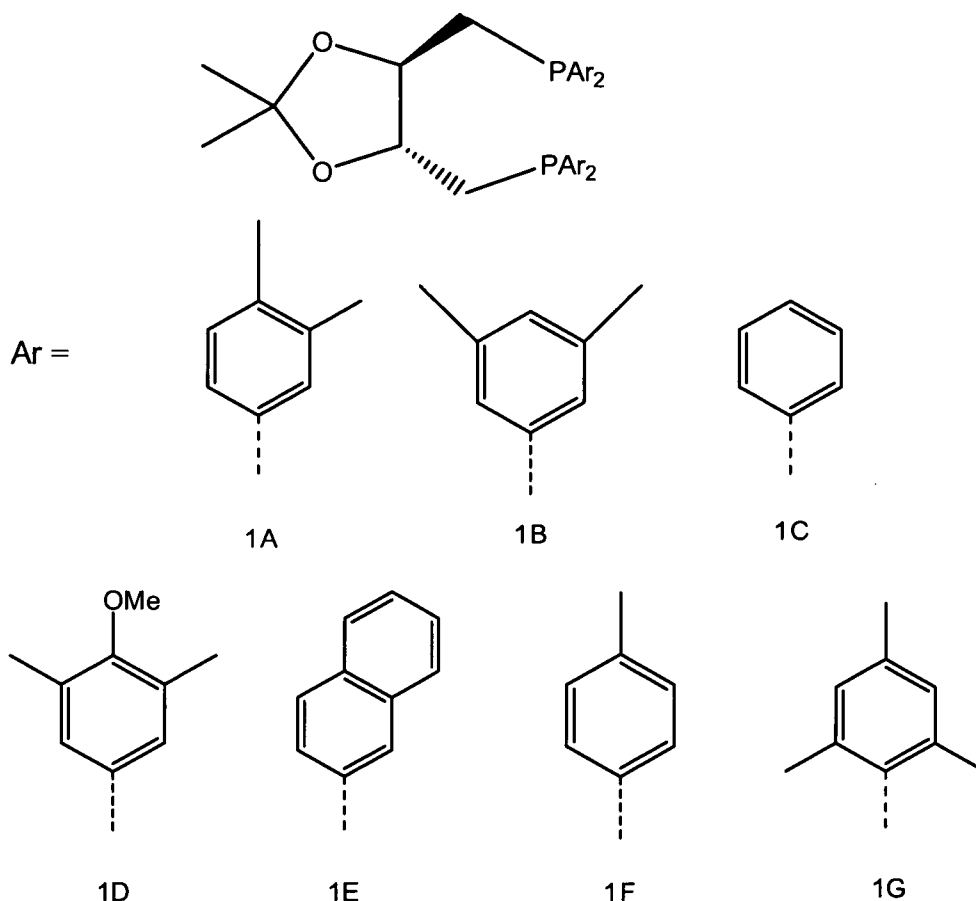
5 Suitable hydrogenation catalysts include any Group VIII metal, such as nickel, cobalt, ruthenium, platinum, and palladium, as well as copper, zinc and chromium and mixtures and alloys thereof. Especially preferred are nickel catalysts. Most preferred are Raney® nickel-type and fixed bed nickel catalysts.

10 The hydrogenation reaction conditions are preferably in the range of from 60 to 200°C and pressures of from 200 to 1000 psig, more preferably from 80 to 140°C and 300 to 1000 psig. Generally reaction times of 1 to 10 hours are appropriate. During the hydrogenation reaction, BDO and MPD formed while the high ratio of linear to branched products is substantially retained, along with other low co-product/byproducts.

15 The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLE 1: PREPARATION OF DIPHOSPHINES

1A, 1B, 1C, 1D, and 1E: Diphosphines 1A, 1B, 1C, 1D, and 1E of the following general formula are prepared as described below.



A solution of 2,2-dimethyl-4,5-bis[(toluenesulfonyloxymethyl) methyl]-1,3-dioxolane in dry/degassed THF (1 equivalent, 1.73 g, 3.7×10^{-3} moles of the dioxolane in 50 mL THF) is added drop-wise under argon to a solution of the appropriate lithium diarylphosphine (see formula above) in dry/degassed THF (2.3 equivalents in 100 mL THF). The mixture is heated at reflux for 2 hours, then cooled, and the solvent is removed under reduced pressure. The remaining solids are re-dissolved in dichloromethane, filtered through a silica bed, and the solvent is removed under reduced pressure to yield the 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diarylphosphino)butane.

Diphosphine 1A: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-dimethylphenyl)phosphino]butane.

Comparative Diphosphine 1B: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,5-dimethylphenyl)phosphino]butane.

Comparative Diphosphine 1C: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(phenyl)phosphino], known as DIOP.

5 Comparative Diphosphine 1D: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,5-dimethyl-4-methoxyphenyl)phosphino]butane.

Comparative Diphosphine 1E: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(2-napthenyl)phosphino]butane.

10 Comparative Diphosphine 1F: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(4-methylphenyl)phosphino]butane.

Comparative Diphosphine 1G: 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(2,4,6-trimethylphenyl)phosphino]butane.

15 **EXAMPLE 2: Hydroformylation Reaction using Diphosphines**

Allyl alcohol is hydroformylated using diphosphines 1A-1E according to the following procedure:

A solution of the desired diphosphine (2 equivalents or 8.6×10^{-5} moles) in dry degassed toluene (15 g) is added to $[\text{Rh}(\text{CO})_2(\text{acac})]$ (1 equivalent or 4.3×10^{-5} moles) in a 100 mL Parr autoclave. The solution is flushed three times with a 1:1 CO/H_2 mixture and then pressurized to 180 psig with the CO/H_2 mixture. The autoclave is then heated to 65°C with stirring, allyl alcohol (3.5 mL) is injected, and the autoclave is pressurized to 200 psig with the CO/H_2 mixture. The autoclave is kept at a constant pressure of 200 psig, and the gas uptake of the reaction is monitored. When there is no further gas uptake, the autoclave is cooled and depressurized. The resulting solution is analyzed by gas chromatography to determine the products of the reaction. The reaction produces HBA, HMPA, and C_3 products (n-propanol and propionaldehyde).

TABLE 1: Diphosphine Comparisons

Diphosphine	Conversion (%)	HBA (%)	HMPA (%)	C ₃ (%)	HBA:HMPA ratio
1A	99.8	89.7	9.5	0.2	9.5
1B *	99.7	89.8	9.4	0.2	9.5
1C *	99.8	86.2	11.7	0.2	7.4
1D *	99.9	82.2	14.7	0.3	5.6
1E *	99.8	86.0	13.2	0.3	6.5
1F *	99.98	86.51	11.27	0.19	7.7
1G *	6.33	2.15	0.53	3.43	4.1

* Comparative Example

I claim:

1. A process to produce 4-hydroxybutyraldehyde comprising reacting allyl alcohol with carbon monoxide and hydrogen in the presence of a solvent and a catalyst comprising a rhodium complex and a diphosphine selected from the group consisting of a trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane, a 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino]butane, and mixtures thereof.
2. The process of claim 1 wherein the diphosphine is trans-1,2-bis(bis(3,4-di-methylphenyl)phosphinomethyl)cyclobutane.
3. The process of claim 1 wherein the diphosphine is trans-1,2-bis(bis(3,4-di-ethylphenyl)phosphinomethyl)cyclobutane.
4. The process of claim 1 wherein the diphosphine is 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-dimethylphenyl)phosphino]butane.
5. The process of claim 1 wherein the diphosphine is 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-diethylphenyl)phosphino]butane.
6. The process of claim 1 wherein the solvent is selected from the group consisting of C₅-C₂₀ aliphatic hydrocarbons, C₆-C₁₂ aromatic hydrocarbons, ethers, alcohols, and mixtures thereof.
7. The process of claim 1 wherein the solvent is selected from the group consisting of toluene, cyclohexane, methyl t-butyl ether, and mixtures thereof.
8. The process of claim 1 wherein the rhodium complex comprises rhodium and ligands selected from the group consisting of hydride, carbonyl, trialkyl phosphines, triaryl phosphines, diphosphines, cyclopentadienyls, 2,4-alkanedionates, and mixtures thereof.
9. The process of claim 1 wherein the catalyst further comprises a monophosphine compound.

10. The process of claim 1 further comprising hydrogenating the 4-hydroxybutyraldehyde in the presence of a hydrogenation catalyst to form 1,4-butanediol.

11. A catalyst comprising a rhodium complex and a diphosphine selected from the group consisting of a trans-1,2-bis(bis(3,4-di-n-alkylphenyl)phosphinomethyl)cyclobutane, a 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-di-n-alkylphenyl)phosphino]butane, and mixtures thereof.

12. The catalyst of claim 11 which comprises the rhodium complex and trans-1,2-bis(bis(3,4-dimethylphenyl)phosphinomethyl)cyclobutane.

13. The catalyst of claim 11 which comprises the rhodium complex and trans-1,2-bis(bis(3,4-diethylphenyl)phosphinomethyl)cyclobutane.

14. The catalyst of claim 11 which comprises the rhodium complex and 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-dimethylphenyl)phosphino]butane.

15. The catalyst of claim 11 which comprises the rhodium complex and 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(3,4-diethylphenyl)phosphino]butane.