

DESCRIPTION

METHOD FOR SUPPRESSING PRECIPITATION OF METAL FROM
TRANSITION METAL COMPLEX

5

TECHNICAL FIELD

The present invention relates to a method for suppressing precipitation of a transition metal in a solution containing a transition metal complex having the transition metal and an organic ligand. Particularly, the present invention relates to a method for suppressing precipitation of a transition metal from a transition metal complex catalyst in a solution after a reaction such as a hydrogenation reaction or isomerization reaction using a transition metal/organic phosphorus-containing ligand complex catalyst.

BACKGROUND ART

A complex catalyst comprising a transition metal and an organic phosphorus-containing ligand such as a phosphite ligand, is used in many reaction processes, and as such reaction processes, a hydrogenation reaction of an unsaturated compound, an isomerization reaction, a hydroformylation reaction of an olefin, and a dimerization reaction of an olefin, are, for example, known. Further, it is also known to remove an acidic compound which is produced as a by-product, since in a

hydroformylation reaction, if a phosphite ligand constituting a rhodium-phosphite ligand complex catalyst is partially decomposed by the by-product acidic substance or by hydrolysis, the complex tends to be
5 unstable, and the metal of the complex catalyst will precipitate in the reaction solution (Patent Document 1). The transition metal such as rhodium (Group 8) or palladium (Group 10) in the complex catalyst used in such a reaction, is separated and recovered from the reaction
10 solution after the reaction.

However, in an actual reaction process, if precipitation of a metal from a complex catalyst takes place in a reaction process, not only the catalyst metal will be lost, but such will be a cause for contamination
15 within the apparatus, thus leading to a problem against smooth operation, such as a decrease in the thermal conductivity.

With respect to precipitation of a metal from a metal complex catalyst, it is one of causes for such
20 precipitation that the ligand is partially decomposed during the reaction or at the time of separation and recovery of the desired product, whereby the complex becomes unstable. Accordingly, it is desired to prevent decomposition or the like of the ligand in the complex
25 catalyst thereby to secure the stability and to suppress precipitation of the metal in the process step and to take out the metal complex catalyst-containing solution

out of the reaction system.

Patent Document 1: JP-A-2000-501712

DISCLOSURE OF THE INVENTION

5 OBJECT TO BE ACCOMPLISHED BY THE INVENTION

The present invention is to provide a method for suppressing precipitation of a transition metal in a reaction solution after a reaction using a transition metal complex catalyst containing an organic phosphorus
10 ligand, whereby the transition metal complex catalyst is efficiently taken out of the reaction system as a solution containing it.

MEANS TO ACCOMPLISH THE OBJECT

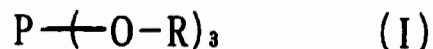
15 The present inventors have conducted an extensive study on the state of a transition metal complex in a reaction solution after a reaction, to prevent precipitation of a transition metal, in the solution for the reaction using a transition metal complex catalyst
20 containing a phosphite ligand, etc. to be used in various reactions, and as a result, have found that a ligand such as a phosphite ligand of such a transition metal complex catalyst is partially decomposed during the reaction or by e.g. oxidation during the separation and recovery, and
25 the complex thereby becomes unstable, thus causing precipitation of the metal of the complex. Further, it has been found possible to stabilize the transition metal

complex and prevent precipitation of the transition metal by contact treatment of the transition metal complex in the reaction solution with a phosphite as an antioxidant. The present invention has been accomplished on the basis
5 of such discoveries.

Namely, the present invention provides the following.

1. A method which comprises contacting a solution containing a transition metal complex of transition metal
10 selected from Groups 8 to 10 transition metals and having a ligand made of a trivalent organic phosphorus compound, with an aromatic phosphite different from said trivalent organic phosphorus compound, to suppress precipitation of metal from the transition metal complex in the solution.

15 2. The method according to the above 1, wherein the aromatic phosphite is represented by the following formula (I):



wherein each of three R which are independent of one
20 another, is a hydrocarbon group which may have a substituent, provided that at least one R is an aryl group.

3. The method according to the above 2, wherein at least one aryl group in the formula (I) of the aromatic
25 phosphite, has a substituent at its ortho-position.

4. The method according to the above 3, wherein the

substituent at the ortho-position of at least one aryl group in the formula (I) of the aromatic phosphite, is a substituent bonded by a tertiary or quaternary carbon atom.

5 5. The method according to the above 4, wherein the three R in the formula (I) of the aromatic phosphite, are the same and phenyl groups having, at their ortho-positions, a substituent bonded by a tertiary or quaternary carbon atom.

10 6. The method according to any one of the above 1 to 5, wherein the aromatic phosphite is a monodentate phosphite.

7. The method according to any one of the above 1 to 6, wherein the trivalent organic phosphorus compound is
15 at least one member selected from the group consisting of phosphines, phosphites and phosphoramidites.

8. The method according to any one of the above 1 to 7, wherein the trivalent organic phosphorus compound is
20 at least one member selected from the group consisting of polydentate phosphines, phosphites and phosphoramidites.

9. The method according to any one of the above 1 to 8, wherein the transition metal selected from Groups 8 to 10 transition metals, is palladium or platinum.

10. The method according to any one of the above 1 to
25 9, wherein the solution containing a transition metal complex containing transition metal selected from Groups 8 to 10 transition metals and a trivalent organic

phosphorus compound, is a solution after either an isomerization, hydrogenation, hydroformylation, dehydrogenation, oligomerization, metathesis, coupling or allyl-forming reaction, carried out by using such a transition metal complex as a catalyst.

11. The method according to the above 10, wherein the solution containing a transition metal complex containing transition metal selected from Groups 8 to 10 transition metals and a trivalent organic phosphorus compound, is a solution after an isomerization reaction of a starting material allyl compound derivative, which contains an allyl compound derivative different from the starting material.

12. The method according to the above 10 or 11, wherein the solution containing a transition metal complex containing transition metal selected from Groups 8 to 10 transition metals and a trivalent organic phosphorus compound, is a reaction solution after an isomerization reaction of an acetoxyallyl compound.

13. The method according to the above 12, wherein the acetoxyallyl compound is a solution containing 3,4-diacetoxy-1-butene as the main component, obtained from an oxidation diacetoxy-forming reaction product of butadiene.

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EFFECTS OF THE INVENTION

According to the method of the present invention, in

a reaction solution after a reaction using a transition metal complex catalyst containing an organic phosphorus ligand, precipitation of a transition metal is suppressed, whereby the complex is stabilized, and
5 accordingly, the transition metal complex catalyst can efficiently be taken out of the reaction system as a solution containing it, without causing a loss of metal in the reaction system, whereby it is possible to suppress e.g. contamination within the apparatus or a
10 decrease in the thermal conductivity.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing a change with time of dissolved residual ratio of Pd in Example 9 and
15 Comparative Example 7. The ordinate represents dissolved residual ratio of Pd (%), the abscissa represents time (hr), and DBPO represents tris(2,4-di-t-butylphenyl) phosphite.

20 BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will be described in detail.

The transition metal complex catalyst in the present invention is made of a transition metal complex
25 containing a ligand made of a trivalent organic phosphorus compound and transition metal selected from Groups 8 to 10 transition metals, wherein the ligand has

a P-C bond, a P-O bond or a P-N bond. Such a transition metal complex catalyst is a known transition metal complex catalyst to be used for many production processes such as isomerization of an allyl compound derivative,
 5 hydrogenation of an unsaturated compound, hydroformylation of an olefin, dehydrogenation, oligomerization of an olefin, metathesis, coupling reaction, hydrocyane-conversion of diene (adiponitrile-conversion of butadiene), etc.

10 The ligand made of a trivalent organic phosphorus compound contained in the transition metal complex catalyst in the present invention, is a compound having a P-C bond, a P-O bond or a P-N bond and includes monodentate and polydentate ligands selected from
 15 phosphines, phosphites and phosphoramidites.

The phosphines may, for example, be a trialkylphosphine, an alkyl diarylphosphine, a dialkylarylphosphine, a dicycloalkylarylphosphine, a cycloalkyl diarylphosphine, a trialkylphosphine, a
 20 tricycloalkylphosphine and a triarylphosphine and may, for example, be represented by the following formula (i):



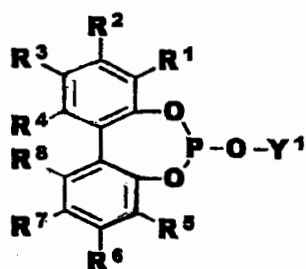
In the above formula (i), each of three R' which are independent of one another and may be the same or
 25 different, is a substituted or unsubstituted alkyl or aryl group.

The aryl group may, for example, be a phenyl group, a naphthyl group or a diphenyl group, and the alkyl group may, for example, be a C₁₋₁₀ alkyl group such as a methyl group, an ethyl group, a propyl group, a butyl group or a cyclohexyl group. The substituent which such groups may have, may, for example, be an alkyl group, an alkoxy group, a silyl group, an amino group, an acyl group, a carboxy group, a halogen atom, a sulfonyl group, a sulfonic acid group, a cyano group or a trifluoromethyl group. Among them, an aryl group such as a phenyl group or a naphthyl group is preferred.

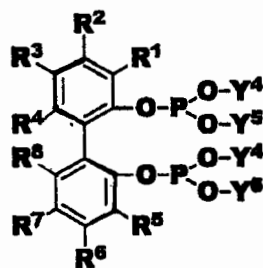
Specific examples of the above phosphines include triphenylphosphine, tris-p-tolylphosphine, tris-p-methoxyphenylphosphine, tris-p-fluorophenylphosphine, tris-p-chlorophenylphosphine, tris-dimethylaminophenylphosphine, propyldiphenylphosphine, t-butyldiphenylphosphine, n-butyldiphenylphosphine, n-hexyldiphenylphosphine, cyclohexyldiphenylphosphine, dicyclohexylphenylphosphine, tricyclohexylphosphine, trimethylphosphine, triethylphosphine, tributylphosphine and trioctylphosphine.

The above phosphites may, for example, be monodentate and bidentate ligands represented by the following formulae (1-1) and (2-1).

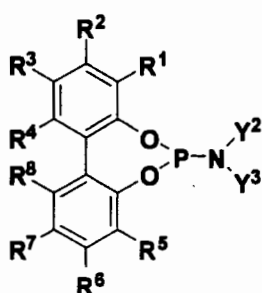
The above phosphoramidites may, for example, be monodentate and bidentate ligands represented by the following formulae (1-2), (2-2), (2-3), (2-4) and (2-5).



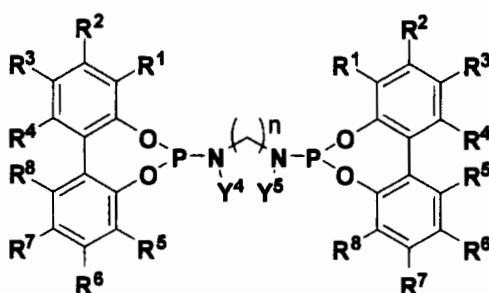
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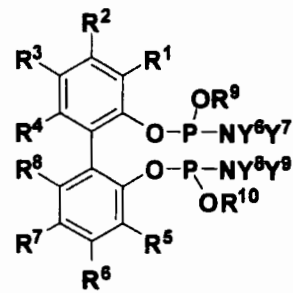
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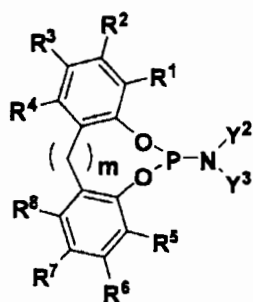
(1-2)



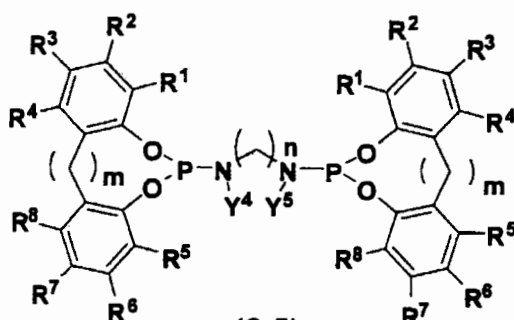
(2-2)



(2-3)



(2-4)



(2-5)

5 In the above formulae, each of Y^1 , Y^2 , Y^3 , Y^4 , Y^5 , Y^6 , Y^7 , Y^8 and Y^9 which are independent of one another, is a linear or cyclic alkyl group, an aryl group or a heterocyclic group, which may further have a substituent. Further, Y^2 and Y^3 , Y^4 and Y^5 , Y^6 and Y^7 , or Y^8 and Y^9 ,
 10 may be connected to each other to form a ring. n

represents the length of a methylene chain ($-\text{CH}_2-$), and n is from 1 to 10, preferably from 1 to 5, particularly preferably from 2 to 4. m represents the length of a methylene chain, and m is from 1 to 5, preferably from 1 to 3.

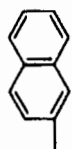
Each of R^1 and R^5 which are independent of each other, is a hydrogen atom or a C_{3-20} secondary or tertiary hydrocarbon group which may have a substituent, and each of R^2 , R^3 , R^6 , R^7 , R^9 and R^{10} which are independent of one another, is a C_{1-20} hydrocarbon group which may have a substituent, or a C_{1-10} alkoxy group which may have a substituent. Each of R^4 and R^5 which are independent of each other, is a hydrogen atom, a C_{1-4} hydrocarbon group, a halogen atom or a C_{1-4} alkoxy group.

The above linear or cyclic alkyl group, or the alkyl moiety of an alkoxy group, usually has from 1 to 20 carbon atoms, preferably from 1 to 14 carbon atoms. Its specific examples may, for example, be a methyl group, an ethyl group, a *n*-propyl group, an *i*-propyl group, a *n*-butyl group, an *i*-butyl group, a *sec*-butyl group, a *t*-butyl group, a pentyl group, a hexyl group, an octyl group, a decyl group, a cyclohexyl group and a cyclopentyl group. Further, the substituent which the alkyl group may have, may, for example, be a C_{1-10} alkoxy group, a C_{6-10} aryl group, an amino group, a cyano group, an ester group having from 2 to 10 carbon atoms, a hydroxyl group or a halogen atom.

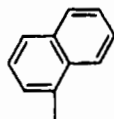
The above aryl group usually has from 6 to 20 carbon atoms, preferably from 6 to 14 carbon atoms. As a specific example of the aryl group, a phenyl group or a naphthyl group may be mentioned. The substituent which
 5 such a group may have, may, for example, be a hydrogen atom, a C₁₋₂₀ alkyl group, a C₁₋₁₀ alkoxy group, a C₃₋₂₀ cycloalkyl group, a C₆₋₂₀ aryl group, a C₆₋₂₀ aryloxy group, a C₆₋₂₀ alkylaryl group, a C₆₋₂₀ alkylaryloxy group, a C₆₋₂₀ arylalkyl group, a C₆₋₂₀ arylalkoxy group, a cyano
 10 group, an ester group, a hydroxyl group or a halogen atom such as chlorine or fluorine.

In a case where each of Y¹ to Y⁹ is an aryl group which may have a substituent, its specific example may be a phenyl group, a 2-methylphenyl group, a 3-methylphenyl
 15 group, a 4-methylphenyl group, a 2,3-dimethylphenyl group, a 2,4-dimethylphenyl group, a 2,5-dimethylphenyl group, a 2,6-dimethylphenyl group, a 2-ethylphenyl group, a 2-isopropylphenyl group, a 2-t-butylphenyl group, a 2,4-di-t-butylphenyl group, a 2-chlorophenyl group, a 3-
 20 chlorophenyl group, a 4-chlorophenyl group, a 2,3-dichlorophenyl group, a 2,4-dichlorophenyl group, a 2,5-dichlorophenyl group, a 3,4-dichlorophenyl group, a 3,5-dichlorophenyl group, a 4-trifluoromethylphenyl group, a 2-methoxyphenyl group, a 3-methoxyphenyl group, a 4-
 25 methoxyphenyl group, a 3,5-dimethoxyphenyl group, a 4-cyanophenyl group, a 4-nitrophenyl group, a trifluoromethylphenyl group, a pentafluorophenyl group

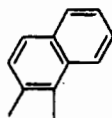
and the following (C-1) to (C-8) groups.



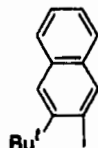
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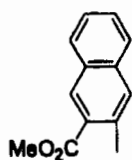
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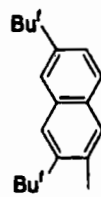
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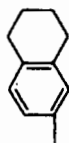
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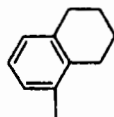
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(C-6)

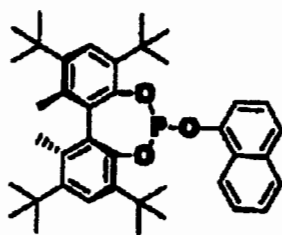


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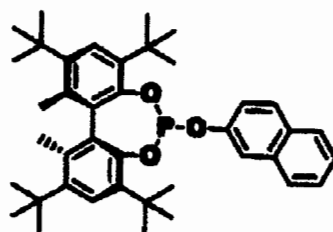


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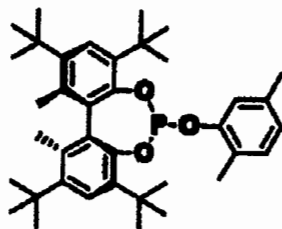
Specific examples of the ligands represented by the
 5 above formulae (1-1), (1-2), (2-1), (2-2), (2-3), (2-4)
 and (2-5), are shown below.



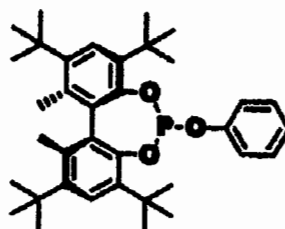
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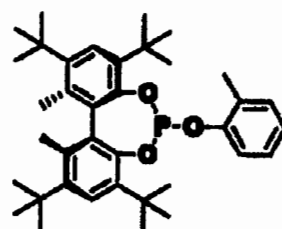
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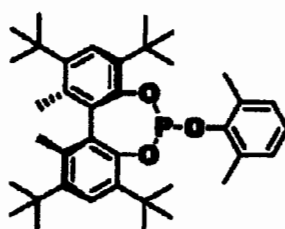
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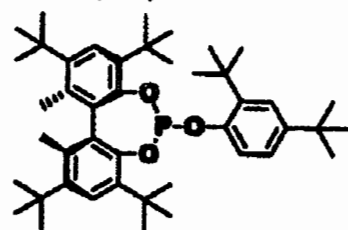
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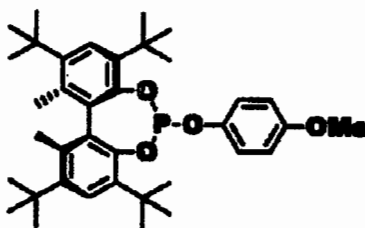
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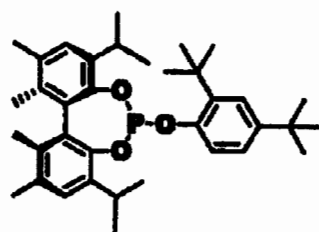
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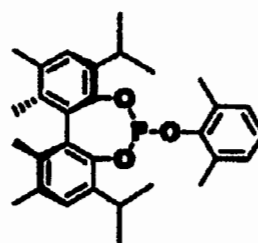
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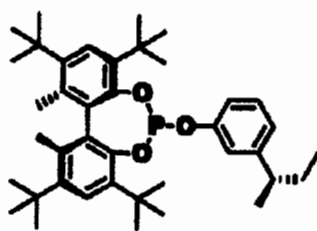
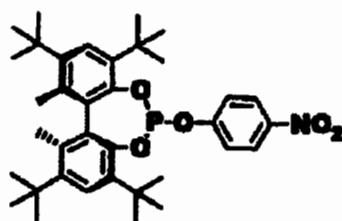
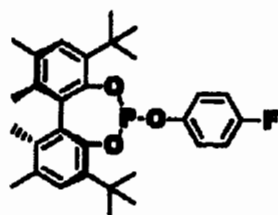
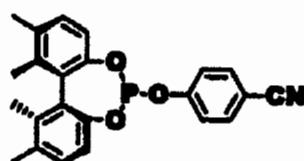
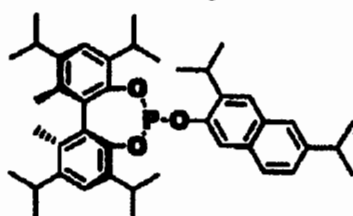
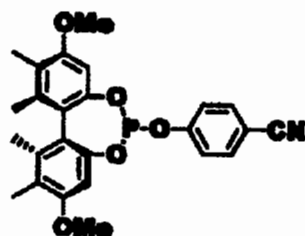
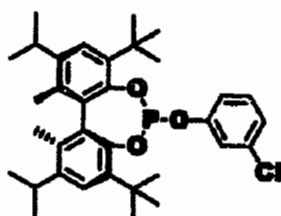
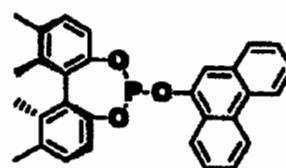
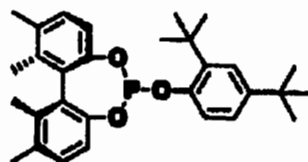
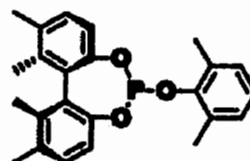
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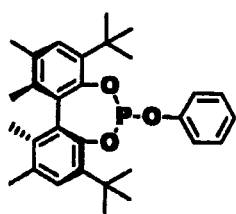
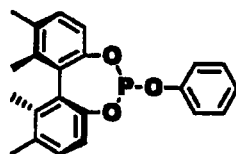
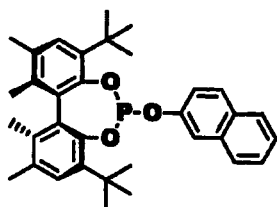
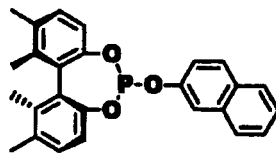


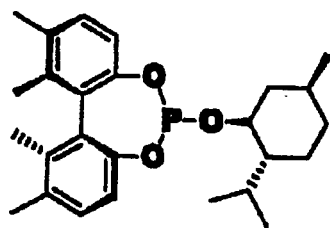
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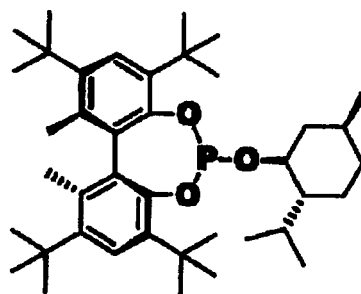
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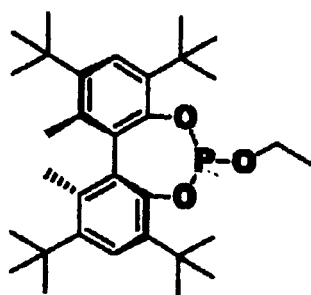
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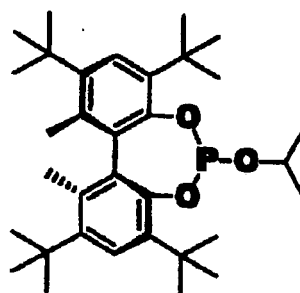
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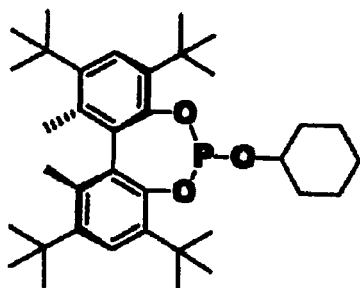
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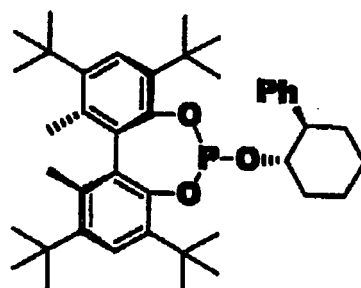
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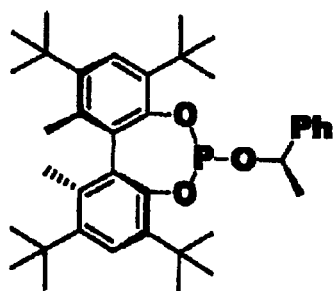
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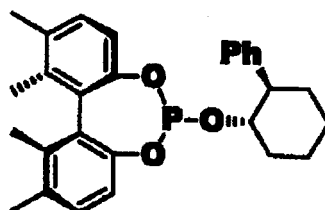
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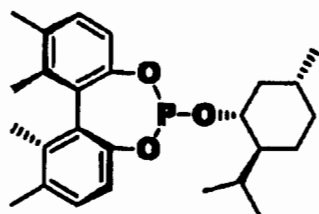
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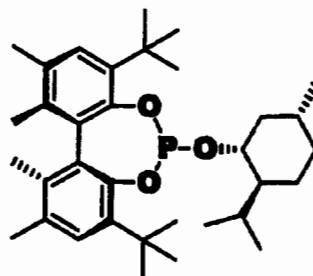
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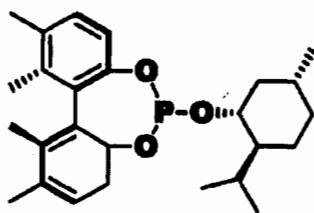
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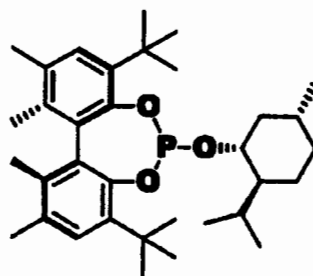
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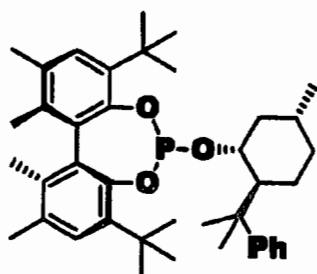
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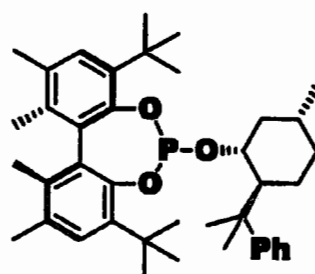
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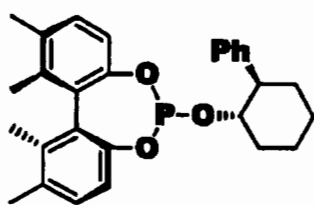
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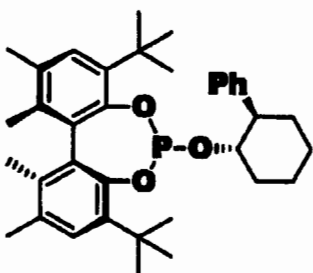
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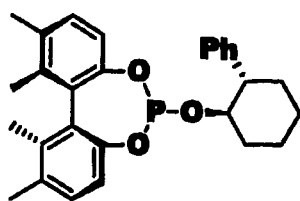
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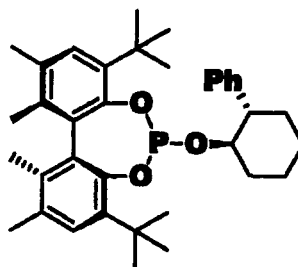
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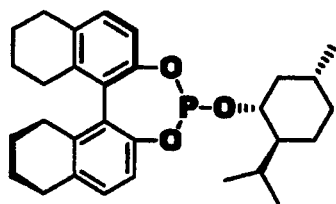
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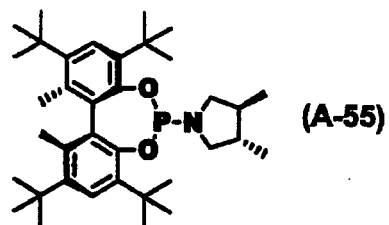
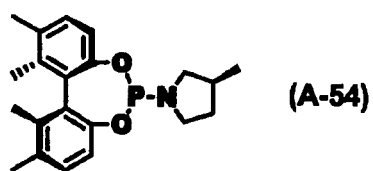
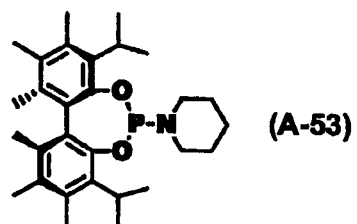
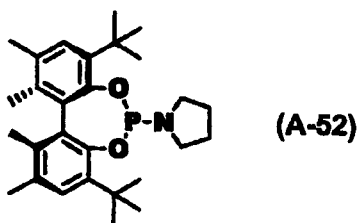
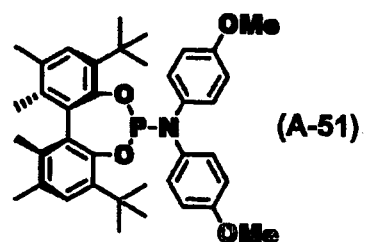
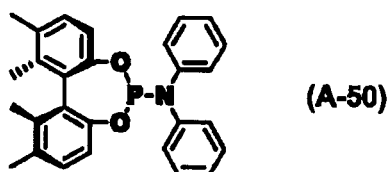
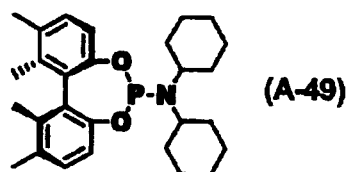
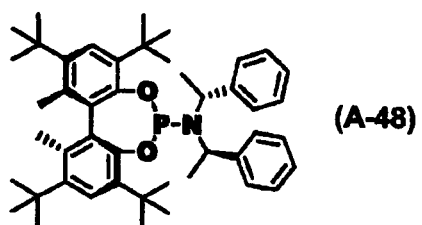
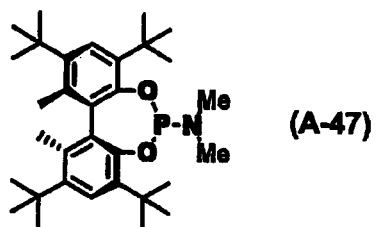
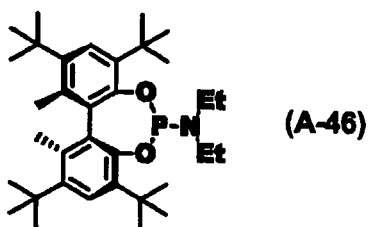
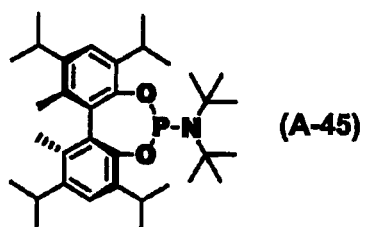
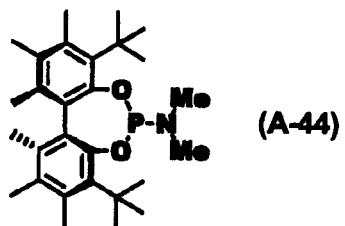
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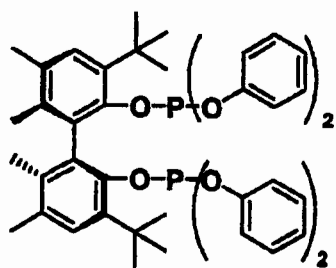


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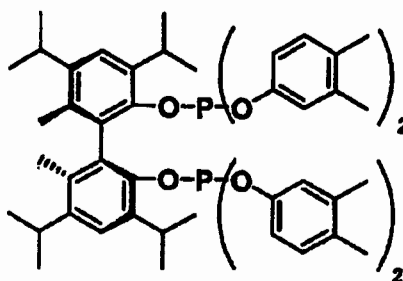


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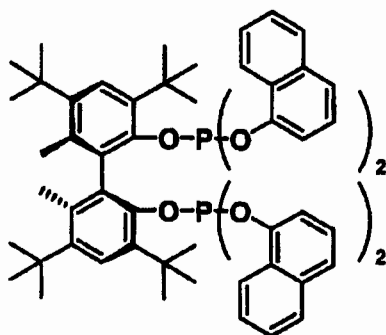




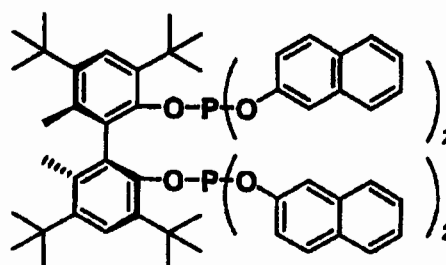
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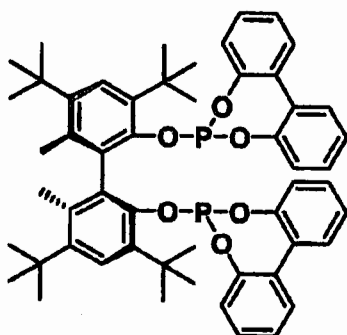
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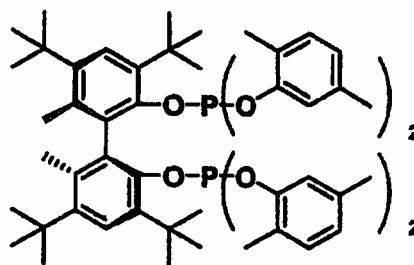
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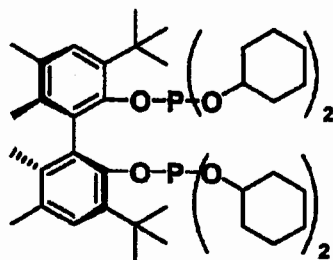
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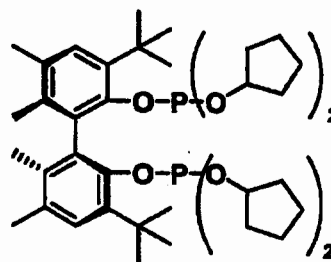
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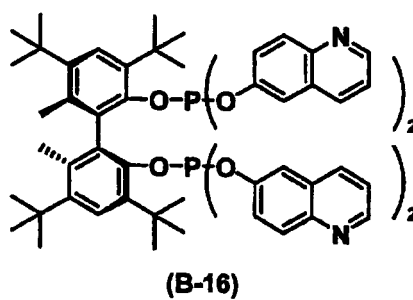
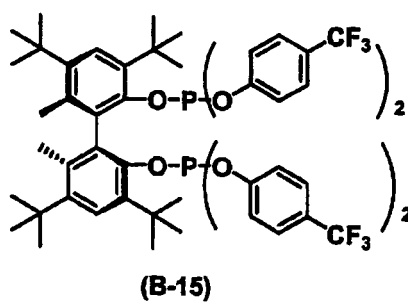
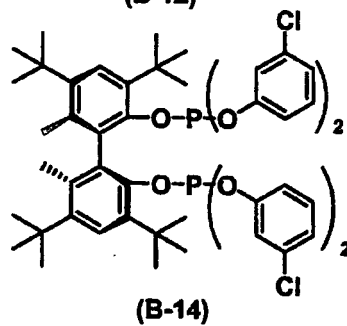
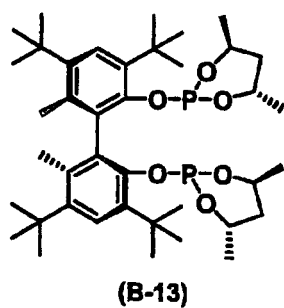
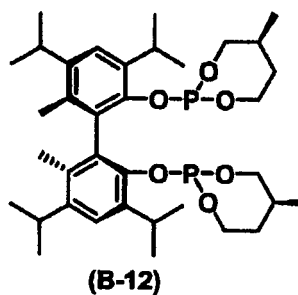
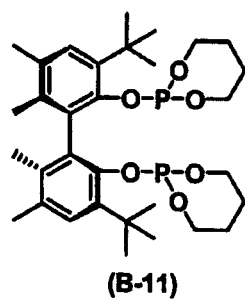
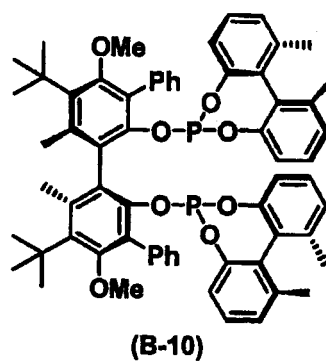
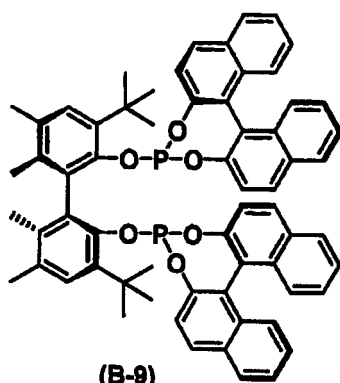
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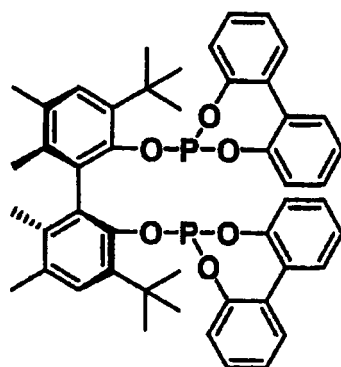


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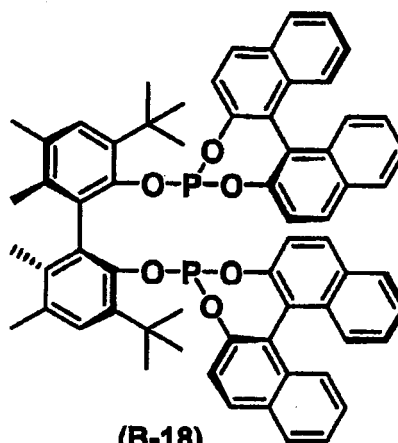


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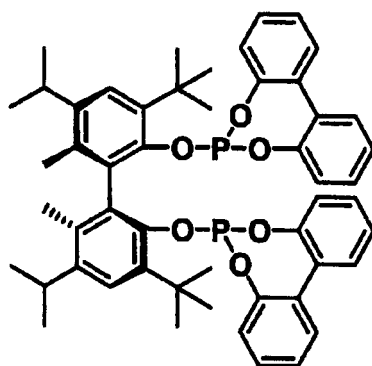




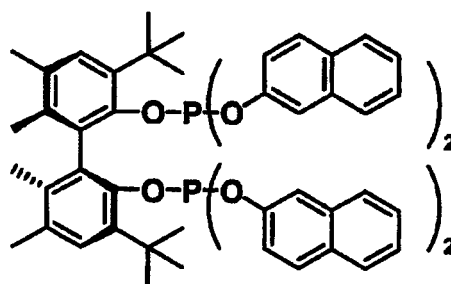
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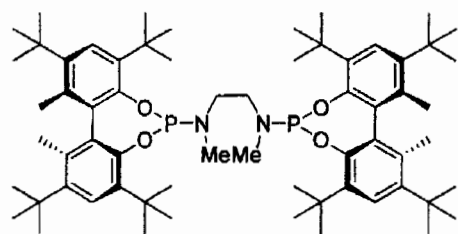
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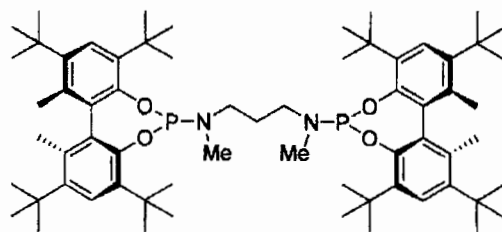
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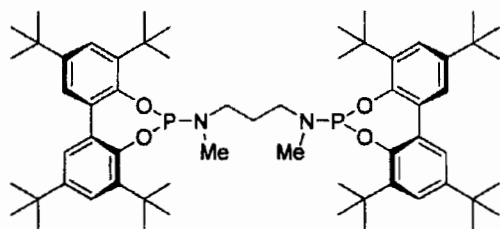
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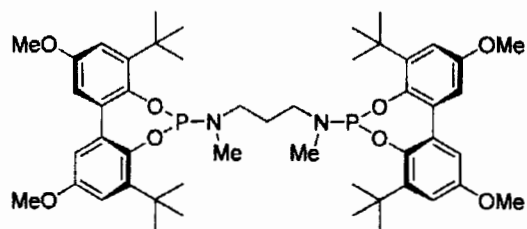
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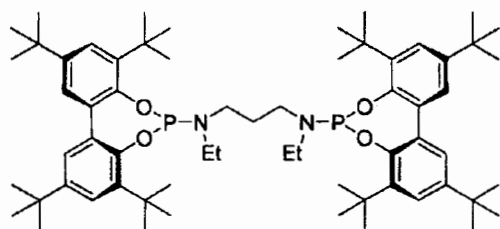
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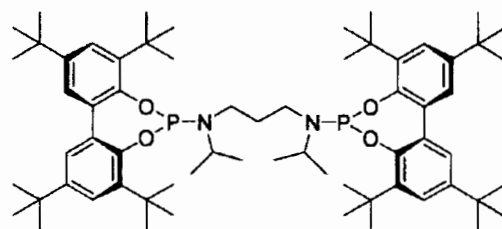
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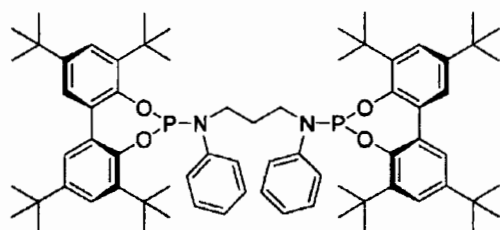
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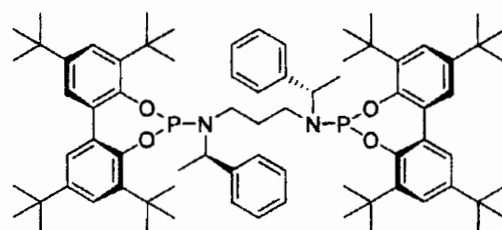
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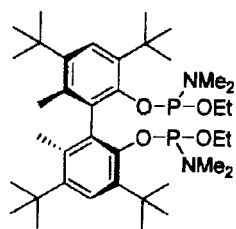
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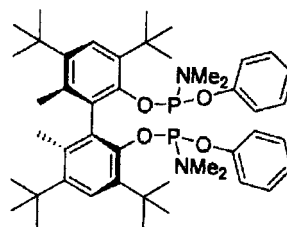
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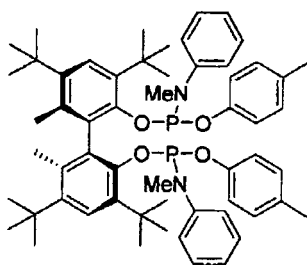
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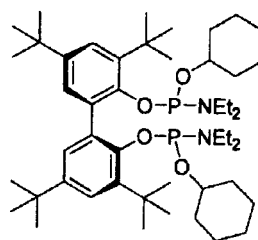
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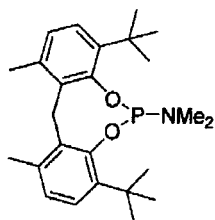
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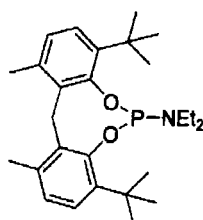
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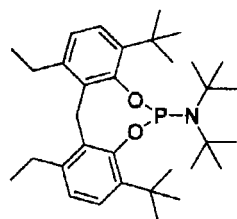
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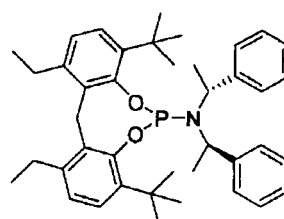
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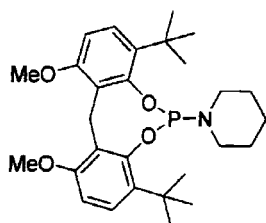
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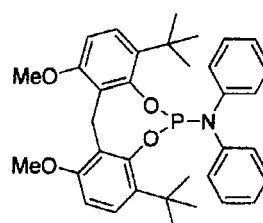
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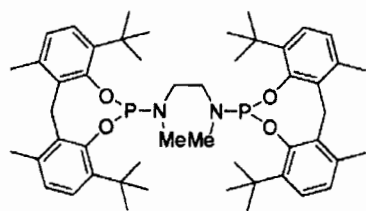
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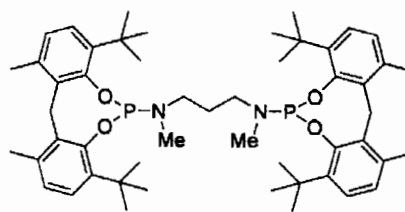
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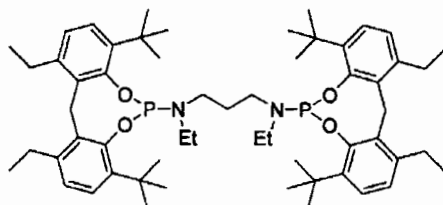
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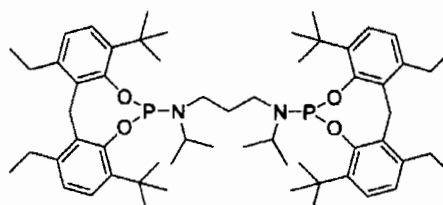
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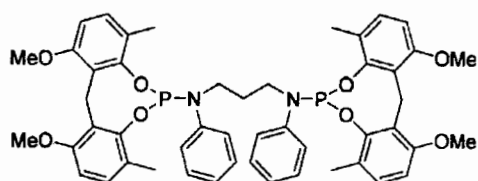
(B-39)



(B-40)



(B-41)



(B-42)

In the present invention, the transition metal of Groups 8 to 10 in the transition metal complex catalyst is preferably ruthenium, rhodium, nickel, palladium, platinum or the like, particularly preferably palladium. Such a transition metal is supplied in the form of a compound, and as a specific compound, an acetate, a sulfate, a nitrate, a halide, an organic salt, an inorganic salt, an acetylacetonate compound, an alkene-coordinated compound, an amine-coordinated compound, a pyridine-coordinated compound, a carbon monoxide-coordinated compound, a phosphine-coordinated compound or a phosphite-coordinated compound, may, for example, be

mentioned.

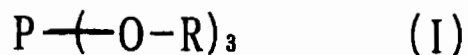
A specific palladium compound may, for example, palladium metal, palladium acetate, palladium trifluoroacetate, palladium sulfate, palladium nitrate, 5 palladium chloride, palladium bromide, palladium iodide, bis(acetylacetonate) palladium, dichlorocyclooctadiene palladium, dichlorobis(triphenylphosphine) palladium, tetrakis(triphenylphosphine) palladium, bis(dibenzylacetone) palladium, potassium 10 tetrachloropalladate, sodium tetrachloropalladate, dichlorobis(benzonitrile) palladium, dichlorobis(acetonitrile) palladium, as well as other carboxylate compounds, olefin-containing compounds, organic phosphine-containing compounds, allyl palladium 15 chloride dimer, etc. Particularly from the viewpoint of the cost, handling efficiency, etc., palladium acetate, palladium trifluoroacetate, bis(acetylacetonate) palladium or tetrakis(triphenylphosphine) palladium is, for example, preferably employed.

20 With respect to the amount of the above ligand in the transition metal complex of the present invention, the molar ratio of phosphorus atom in the ligand is preferably from 0.1 to 1,000, more preferably from 1 to 100, particularly preferably from 1 to 10, to 1 mol of 25 the transition metal in the transition metal complex. Further, as the ligand, one type or plural types of ligands may be contained. The method for preparation of

the transition metal complex is not particularly limited, and for example, at the time of the reaction to convert the complex to a catalyst, a transition metal compound and a ligand compound are heated and reacted in a desired
 5 ratio to obtain a catalyst-containing solution.

In the present invention, an aromatic phosphite is brought in contact with a solution containing a transition metal complex containing the above-mentioned ligand made of a trivalent organic phosphorus compound
 10 and the transition metal of Groups 8 to 10. Here, the aromatic phosphite is different from the trivalent organic phosphorus compound as the ligand.

A cause for precipitation of the metal of the transition metal complex catalyst is such that the
 15 phosphite ligand of the metal complex catalyst is oxidized during the reaction or during the separation and recovery, whereby the complex becomes unstable. Accordingly, the aromatic phosphite to be contacted may be one to prevent oxidation of the ligand made of the
 20 trivalent organic phosphorus compound, which the above metal complex catalyst has, and to function by itself as a component to be oxidized, and an aromatic phosphite represented by the following formula (I) may be mentioned.



In the above formula (I), each of three R which are

independent of one another, is a hydrocarbon group which may have a substituent, provided that at least one R is an aryl group.

The hydrocarbon group in the formula (I) is selected
5 from an alkyl group or an aryl group.

The alkyl group may be a linear or branched alkyl group having usually from 1 to 20 carbon atoms, preferably from 1 to 14 carbon atoms, or a cyclic alkyl group. As a specific alkyl group, a methyl group, an
10 ethyl group, a n-propyl group, an i-propyl group, a n-butyl group, an i-butyl group, a sec-butyl group, a t-butyl group, a pentyl group, a hexyl group, an octyl group, a decyl group, a cyclohexyl group or a cyclopentyl group may, for example, be mentioned. Further, as the
15 substituent which the alkyl group may have, a C₁₋₁₀ alkoxy group, a C₆₋₁₀ aryl group, an amino group, a cyano group, a C₂₋₁₀ ester group, a hydroxy group or a halogen atom, may, for example, be mentioned.

The aryl group usually has from 6 to 20 carbon
20 atoms, preferably from 6 to 14 carbon atoms. As a specific example of the aryl group, a phenyl group or a naphthyl group may be mentioned. As the substituent which such a group may have, a hydrogen atom, a C₁₋₂₀ alkyl group, a C₁₋₁₀ alkoxy group, a C₃₋₂₀ cycloalkyl
25 group, a C₆₋₁₀ aryl group, a C₆₋₂₀ aryloxy group, a C₆₋₂₀ alkylaryl group, a C₆₋₂₀ alkylaryloxy group, a C₆₋₂₀ arylalkyl group, a C₆₋₂₀ arylalkoxy group, a cyano group,

an ester group, a hydroxyl group or a halogen atom such as chlorine or fluorine, may, for example, be mentioned. As the substituent, preferred is an i-propyl group, an i-butyl group, a sec-butyl group, a t-butyl group or a cyclohexyl group, and a t-butyl group is particularly preferred.

The aromatic phosphite is preferably such that at least one aryl group in the formula (I) has a substituent at its ortho-position (2-position or 6-position), and the substituent at the ortho-position is preferably a substituent bonded to the aryl group by a tertiary or quaternary carbon atom. A particularly preferred aromatic phosphite is such that the three R in the formula (I) are the same and phenyl groups, having at their ortho-positions, a substituent bonded by a tertiary or quaternary carbon atom. Further, the aromatic phosphite is preferably a monodentate phosphite.

Specifically, the aromatic phosphite may, for example, be triphenyl phosphite, tris-o-tolyl phosphite, tris-o-i-propylphenyl phosphite, tris-2-t-butylphenyl phosphite, tris-i-butylphenyl phosphite, tris-i-propylphenyl phosphite, tris-2,4-di-t-butylphenyl phosphite, tris-2,5-di-t-butylphenyl phosphite, tris-2,6-di-t-butylphenyl phosphite, tris-2,3-di-t-butylphenyl phosphite, tris-2,4-di-i-propylphenyl phosphite, tris-2,5-di-i-propylphenyl phosphite, tris-2,6-di-i-propylphenyl phosphite, tris-2,3-di-i-propylphenyl

phosphite, propyldi(2-t-butylphenyl) phosphite, t-butyldi(2-t-butylphenyl) phosphite, n-butyldi(2-t-butylphenyl) phosphite, n-hexyldiphenyl phosphite, t-butyldi(2,4-t-butylphenyl) phosphite, n-butyldi(2,4-t-butylphenyl) phosphite, di(2,4-t-butylphenyl)cyclohexyl phosphite, tris-2-t-butylcyclohexyl phosphite or di(2-t-butylcyclohexyl)phenyl phosphite. Among them, preferred is tris-2-t-butylphenyl phosphite, tris-i-butylphenyl phosphite, tris-i-propylphenyl phosphite, tris-2,4-di-t-butylphenyl phosphite or tris-2,4-di-t-butylphenyl phosphite, and particularly preferred is tris-2,4-di-t-butylphenyl phosphite.

In the present invention, the solution containing a transition metal complex containing transition metal of Groups 8 to 10 and a ligand made of a trivalent organic phosphorus compound, is specifically a reaction solution obtained by a reaction using the transition metal complex catalyst. The reaction using the transition metal complex catalyst may, for example, be isomerization of an allyl compound derivative, hydrogenation of an unsaturated compound, hydroformylation of an olefin, dehydrogenation, oligomerization of an olefin, metathesis, coupling reaction or hydrocyane-conversion of a diene (adiponitrile-conversion of butadiene). Particularly, in the present invention, a reaction solution after an isomerization reaction of an allyl compound derivative using the transition metal complex as

a catalyst is preferred, and a reaction solution of an isomerization reaction of an acetoxyallyl compound obtained by an oxidation acetoxy-conversion reaction of butadiene i.e. 3,4-diacetoxy-1-butene to 1,4-diacetoxy-2-butene, is particularly preferred.

In the method of the present invention, the reaction solution obtained by the reaction using the above transition metal catalyst is contacted with an aromatic phosphite, and the reaction solution may be the reaction solution after the reaction itself, or the residual liquid having the product removed from the reaction solution or a reaction solution containing the catalyst. It is particularly preferred to contact the reaction solution after the reaction. The contact of the reaction solution with the aromatic phosphite may specifically be carried out by adding and contacting an aromatic phosphite-containing solution to the reaction solution after the reaction. The aromatic phosphite may be solid itself or may be in its solution. However, from the contact efficiency with the reaction solution at the time of the addition, it is preferably preliminarily uniformly dissolved.

Thus, after the reaction step, in the reaction solution, the transition metal complex catalyst and the aromatic phosphite are transported in the form of a uniform solution in the piping and in the apparatus such as a distillation column within the process step, whereby

a loss of metal due to precipitation of the catalyst metal in the piping and in the apparatus such as a distillation column, or contamination within the process system will be suppressed. Further, the catalyst metal
5 can be taken out of the system in the form of a solution containing it as dissolved, and the taken out solution is subjected to catalyst treatment (recovery of catalyst or disposal). In the catalyst treatment step, the taken out solution may be subjected to incineration as it is, or
10 transported to another place for recovery of the metal, or subjected to e.g. recovery as a metal ash by e.g. an in-water combustion apparatus installed in the plant.

The mixture of the reaction solution and the aromatic phosphite is heat-treated, if necessary. The
15 heat treatment temperature is usually from 20°C to 200°C, preferably from 80°C to 180°C. If the treatment is carried out at a high temperature beyond this range, the thermal decomposition of the aromatic phosphite itself will proceed. On the other hand, if the temperature is
20 too low, the solubility of the aromatic phosphite in the reaction solution tends to be low, whereby the effect to suppress precipitation of metal tends to be low.

As a standard for selection of the aromatic phosphite, it is necessary to avoid decomposition due to
25 a factor other than oxygen in order to maximize the oxidation-preventing function of the phosphite, and specifically, it is not desirable to use a phosphite

which is thermally or chemically easily decomposable. Accordingly, a thermally stable aromatic phosphite is preferred, and further, in order to increase the chemical stability, or in order to prevent cleavage of the P-O bond by a reaction with another chemical component, it is preferred to employ a phosphite wherein the aromatic ring has a bulky substituent at the ortho-position to the P-O bond. Further, a monodentate aromatic phosphite is preferred, since a monodentate phosphite is usually inexpensive as compared with a polydentate phosphite and in view of the function and costs.

In a case where an aromatic phosphite is added and contacted to a reaction solution obtained by a reaction using a transition metal catalyst, the proportion of the aromatic phosphite to the reaction solution is usually from 1 mol equivalent to 1,000 mol equivalent, preferably from 2 mol equivalent to 50 mol equivalent, to one mol of metal of the transition metal catalyst, although it may vary depending upon the type, amount, etc. of the transition metal catalyst contained in the reaction solution. If the amount is less than this proportion, no adequate effect to suppress precipitation of metal will be obtained. On the other hand, if the amount is too large, no further effect by such an additional amount will be obtainable, and such being undesirable from the viewpoint of the cost.

The concentration in the aromatic phosphite solution

to be added varies depending upon the type of the aromatic phosphite, but it is usually from 50 wt ppm to 1 wt%, preferably from 100 wt ppm to 5,000 wt ppm.

Now, a method of contacting a reaction solution
5 after an isomerization reaction of an acetoxyallyl compound using a transition metal complex catalyst, with an aromatic phosphite, will be described.

A method for producing a 3,4-diacetoxy-1-butene and/or a 1,4-diacetoxy-2-butene as an acetoxyallyl
10 compound by a diacetoxy oxide-conversion reaction of a conjugated diene such as butadiene, is known. Most commonly, butadiene, acetic acid and oxygen are reacted in the presence of a palladium type catalyst to produce 1,4-diacetoxy-2-butene and 3,4-diacetoxy-1-butene. The
15 reaction solution usually also contains 1-acetoxy-4-hydroxy-2-butene, 3-hydroxy-4-acetoxy-1-butene, 4-hydroxy-3-acetoxy-1-butene, etc. as hydrolyzates of such diacetoxybutenes.

3,4-diacetoxy-1-butene to be supplied as a starting
20 material for the isomerization reaction may be not only a pure product but also the reaction solution itself after the diacetoxy-forming reaction of the above butadiene, or one having at least a part of by-products having boiling points lower than 3,4-diacetoxy-1-butene such as acetic
25 acid, water, etc. removed by e.g. distillation, or one having part or all of by-products having boiling points higher than 3,4-diacetoxy-1-butene removed by

distillation, or further one having part or all of both of low boiling point by-products and high boiling point by-products removed. In the method of the present invention, such a material is used as "a solution
5 containing 3,4-diacetoxy-1-butene as the main component". Usually, "a solution containing 3,4-diacetoxy-1-butene as the main component" to be used in the present invention contains 1,4-diacetoxy-2-butene, but may further contain 3-hydroxy-4-acetoxy-1-butene, 4-hydroxy-3-acetoxy-1-
10 butene and/or 3,4-dihydroxy-1-butene as a hydrolyzate of 3,4-diacetoxy-1-butene, and further 1-acetoxy-4-hydroxy-2-butene and/or 1,4-dihydroxy-2-butene as a hydrolyzate of 1,4-diacetoxy-2-butene.

A transition metal complex to be used as a catalyst
15 in the above isomerization reaction of an acetoxyallyl compound or the like, is a complex catalyst of palladium with a ligand, preferably a phosphite or phosphoramidite, particularly preferably a phosphoramidite. The amount of the transition metal complex is from 0.001 wt ppm to
20 1,000 wt ppm, preferably from 0.001 to 100 wt ppm, particularly preferably from 0.01 to 100 wt ppm, to the acetoxyallyl compound as the starting material for the reaction.

The temperature for the isomerization reaction is
25 usually from 20 to 200°C, preferably from 80 to 180°C, particularly preferably from 100 to 160°C. If the reaction temperature is too high, deterioration by metal-

conversion of the transition metal complex catalyst proceeds, thereby leading to disappearance of the activity. On the other hand, if the reaction temperature is too low, the reaction rate tends to be low, and a
5 large size reactor will be required.

The pressure for the isomerization reaction is usually 1 atm, and it is preferably from 1 to 10 atm, particularly preferably from 1 to 3 atm, although the reaction may be carried out under reduced pressure or
10 elevated pressure. If the reaction pressure is too low, the catalytic activity tends to be low as the reaction temperature lowers, and on the other hand, if the reaction pressure is too high, the cost of the reactor will increase.

15 The isomerization reaction is carried out usually in a liquid phase, and the isomerization reaction may be carried out in the presence or absence of a solvent. In a case where a solvent is used, a preferred solvent is not particularly limited so long as it is capable of
20 dissolving the catalyst and the raw material compounds. Specific examples of such a solvent include an ether such as diglyme, diphenyl ether, dibenzyl ether, diallyl ether, tetrahydrofuran (THF) or dioxane; an amide such as N-methyl-2-pyrrolidone, N,N-dimethylformamide or N,N-
25 dimethylacetamide; a ketone such as cyclohexanone; an ester such as n-butyl acetate, γ -butyrolactone or di(n-octyl)phthalate; an aromatic hydrocarbon such as toluene,

xylene or dodecylbenzene; an aliphatic hydrocarbon such as n-pentane, n-hexane, n-heptane or n-octane; a by-product formed by the isomerization reaction itself; the allyl compound derivative as the starting material
5 itself; the allyl compound as the product itself; and a compound derived from a leaving group of the starting material allyl compound. A particularly preferred solvent may be an allyl compound as the starting material itself, or an allyl compound as the product itself.

10 The amount of the solvent to be used is not particularly limited. However, the isomerization reaction proceeds mainly as an intramolecular reaction and is therefore preferably carried out by using a solvent in an amount smaller than in a conventional
15 method. It is usually from 0 to 10 times by weight, preferably from 0 to 5 times by weight, most preferably from 0 to 1 time by weight, to the total weight of the allyl compound derivative as the starting material. If the amount of the solvent is too much, the reaction rate
20 decreases.

As a reaction system, the isomerization reaction may be carried out by a continuous system, a semicontinuous system or a batch system by using a stirring type complete mixing reactor or a plug flow type reactor. The
25 gas phase portion in the reactor is preferably formed by an inert gas such as argon or nitrogen, in addition to a vapor derived from the solvent, the starting material

compound, the reaction product, the reaction by-products, the catalyst-decomposed products, etc. Especially, inclusion of oxygen due to e.g. leaking in of air, causes deterioration of the catalyst i.e. disappearance of
5 oxidation of the phosphorus compound, and accordingly, it is desired to minimize such an inclusion.

To the reaction solution flowing out continuously from the isomerization reactor, a solution of an aromatic phosphite is injected from a supply port provided in the
10 piping in the vicinity of the outlet of the reactor. The injection of the aromatic phosphite solution may be carried out continuously or intermittently, preferably continuously. The reaction solution to which the aromatic phosphite has been supplied, is transported to a
15 separation step (distillation column) to separate the product (1,4-diacetoxy-2-butene) obtained by the isomerization reaction of 3,4-diacetoxy-1-butene, from the isomerization reaction solution and separated by distillation. For the separation of the product, a
20 common separation operation may be adopted.

Specifically, not only a distillation operation such as, simple distillation, distillation under reduced pressure, thin film distillation or steam distillation, but also a separation operation such as gas-liquid separation,
25 evaporation, gas stripping, gas absorption or extraction, may be mentioned. Each separation operation may be carried out in an independent step, or separation of two

or more components may be carried out simultaneously. Further, the product, as well as the residual liquid after separating the starting material allyl compound, etc. may be subjected to the above-mentioned catalyst
5 treatment.

As an example of a reaction other than the above-mentioned isomerization reaction, a hydroformylation reaction of an olefin may be mentioned. A hydroformylation reaction of an olefin is carried out
10 usually by reacting an olefin with an oxogas (a mixed gas of carbon monoxide and hydrogen) in the presence or absence of a solvent by means of a metal complex catalyst containing a transition metal (such as Rh or Pd) and a ligand made of an organic phosphorus compound. the
15 amount of the catalyst is usually at least 0.1 ppm mol, preferably at least 1 ppm mol, to 1 mol of the reaction substrate and usually at most 0.2 mol%, preferably at most 0.1 mol%. The reaction temperature is usually from -20°C to 150°C, preferably from 0°C to 100°C. The
20 reaction pressure is usually from 0.01 MPa to 30 MPa, preferably from 0.05 MPa to 20 MPa.

Further, as another reaction example, a hydrogenation reaction of e.g. an olefin, a carbonyl compound or an imine compound by means of the above
25 transition metal complex catalyst, may be mentioned. The amount of the catalyst in the hydrogenation reaction is usually at least 0.1 ppm mol, preferably at least 1 ppm

mol, to 1 mol of the reaction substrate and usually at most 0.2 mol%, preferably at most 0.1 mol%. The reaction temperature is usually from -20°C to 150°C, preferably from 0°C to 100°C, and the hydrogen partial pressure is
5 usually from 0.001 MPa to 30 MPa, preferably from 0.05 MPa to 20 MPa.

The method of the present invention may be applied to the reaction solutions obtained by the above-described reaction examples, whereby transition metal-containing
10 solutions may be taken out from the reaction solutions without any trouble.

EXAMPLES

Now, the method of the present invention will be
15 described in further detail with reference to Examples and Comparative Examples. However, it should be understood that the present invention is by no means restricted to such Examples.

REFERENCE EXAMPLE 1

20 In the presence of 1 kg of a Pd-Te catalyst, 0.21 kg/hr of butadiene, 2.94 kg/hr of acetic acid and 0.34 kg/hr of a mixed gas of 6 vol% of oxygen/94 vol% of nitrogen, were permitted to flow and subjected to an acetoxylation reaction under conditions of 80°C and 6 MPa
25 to obtain a mixed liquid containing 81 wt% of 1,4-diacetoxy-2-butene, 9 wt% of 3,4-diacetoxy-1-butene, 2 wt% of 3-hydroxy-4-acetoxy-1-butene, 3 wt% of acetic

acid, 3 wt% of other components having boiling points lower than 3,4-diacetoxy-1-butene and 2 wt% of other components having boiling points higher than 3,4-diacetoxy-1-butene.

5 REFERENCE EXAMPLE 2

11 L of the mixed liquid obtained in Reference Example 1 was separated into a 3,4-diacetoxy-1-butene-containing liquid and a 1,4-diacetoxy-2-butene-containing liquid by continuous distillation. Here, for the
10 distillation, an Oldershow distillation column with 40-trays was used. The continuous distillation was carried out by maintaining the column top temperature to be 20 mmHg, the reflux ratio to be 3, the column top temperature to be 95°C and the column bottom temperature
15 to be 151°C, by continuously introducing the mixed liquid at a position of the 20th tray from the column bottom, at a flow rate of 150 cc/hr, by carrying out continuous distillation at a rate of 27 cc/hr from the column top and by carrying out continuous withdrawal at a rate of
20 123 cc/hr from the column bottom. By this continuous distillation, a 1,4-diacetoxy-2-butene-containing liquid was obtained as the bottoms from the column bottom, and a 3,4-diacetoxy-1-butene-containing liquid was obtained as a distillate from the column top. The obtained 3,4-
25 diacetoxy-1-butene-containing liquid was a mixed liquid containing 45 wt% of 3,4-diacetoxy-1-butene, 11 wt% of 3-hydroxy-4-acetoxy-1-butene, 22 wt% of acetic acid, 20 wt%

of other components having boiling points lower than 3,4-diacetoxy-1-butene and 2 wt% of other components having boiling points higher than 3,4-diacetoxy-1-butene.

Further, the 1,4-diacetoxy-2-butene content in the 3,4-diacetoxy-1-butene-containing liquid was not higher than 1 wt%.

REFERENCE EXAMPLE 3

300 kg of the 3,4-diacetoxy-1-butene-containing liquid obtained in Reference Example 2 was subjected to continuous distillation to separate the majority of components having boiling points higher than 3,4-diacetoxy-1-butene. Here, for the distillation, a packed column having ordered packing material TM-700M (MC pack) packed in 5 m was used (HETP 140 mm/NTP). The continuous distillation was carried out by maintaining the column top pressure to be 100 mmHg, the reflux ratio to be 3, the column top temperature to be 77°C and the column bottom temperature to be 144°C, by continuously introducing 300 kg of said liquid at a position of 2,610 mm from the column bottom at a flow rate of 20 kg/hr, by carrying out continuous distillation at a rate of 7.6 kg/hr from the column top and by carrying out continuous withdrawal at a rate of 11.4 kg/hr as a side stream from a position of 580 mm from the column bottom and at a rate of 1 kg/hr from the column bottom. By this continuous distillation, components having boiling points lower than 3,4-diacetoxy-1-butene were obtained as a distillate from

the column top. The distillate contained 71 wt% of acetic acid, 0.18 wt% of 3,4-diacetoxy-1-butene (corresponding to 0.17 wt% of the amount of the 3,4-diacetoxy allyl compound introduced to the distillation column) and 21 wt% of other components having boiling points lower than 3,4-diacetoxy-1-butene. Further, the liquid withdrawn from the column bottom contained 70 wt% of 3,4-diacetoxy-1-butene, 9 wt% of 3-hydroxy-4-acetoxy-1-butene and 3 wt% of other components having boiling points lower than 3,4-diacetoxy-1-butene, and 18 wt% of other components having boiling points higher than 3,4-diacetoxy-1-butene. Further, the liquid withdrawn from the side stream was purified 3,4-diacetoxy-1-butene containing 69 wt% of 3,4-diacetoxy-1-butene, 15 wt% of 3-hydroxy-4-acetoxy-1-butene and 4 wt% of other components having boiling points lower than 3,4-diacetoxy-1-butene and 12 wt% of other components having boiling points higher than 3,4-diacetoxy-1-butene.

EXAMPLE 1

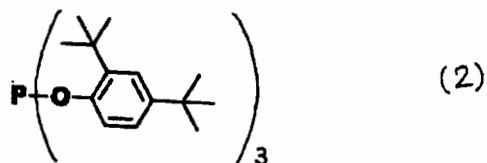
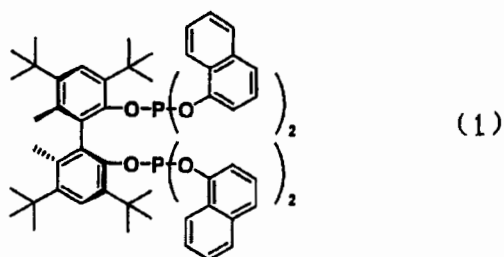
In a nitrogen gas atmosphere, into a glass flask, palladium acetate (3.2 mg), a ligand represented by the following formula (1) (31.2 mg of a ligand represented by the above-mentioned formula (B-3), 2 mol equivalent to the palladium metal) and 75 g of the 3,4-diacetoxy-1-butene-containing liquid obtained from the side stream in Reference Example 3, were added, and heated and stirred at 80°C for one hour for dissolution to prepare a

palladium catalyst solution. The dissolved palladium metal concentration in this palladium catalyst solution was measured by ICP-MS (Inductively Coupled Plasma Mass Spectrometry), whereby the metal palladium concentration was 20 wt ppm. To 2 cc of this palladium catalyst solution, DBPO (tris(2,4-di-t-butylphenyl) phosphite) represented by the following formula (2) was added (5.0 mg, 20 mol equivalent to the palladium metal), followed by heating at 175°C for 27 hours under atmospheric pressure. The catalyst solution after the heating was filtered by means of a filter having a mesh size of 8 μ m, and the concentration of palladium remaining as dissolved in the filtrate was measured by ICP-MS. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 20 wt ppm. From the initial concentration before the heating and the residual dissolved concentration, the dissolved residual ratio of palladium metal was calculated. As a result, the dissolved residual ratio of palladium metal was 100%, and the Pd metal precipitation ratio was 0%.

Dissolved residual ratio (%) = residual dissolved concentration/initial concentration

Pd metalized amount (wt ppm) = initial concentration - residual dissolved concentration

Pd metal precipitation rate (%) = [Pd metalized amount]/[initial concentration]



COMPARATIVE EXAMPLE 1

5 BLANK TEST

A test was carried out in the same manner as in Example 1 except that in Example 1, the palladium catalyst solution was heated at 175°C under atmospheric pressure without adding DBPO thereto. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 6 wt ppm, and the Pd metal precipitation ratio was 70%.

COMPARATIVE EXAMPLE 2

COMPARISON IN EFFECTS OF DBPO AND TRIPHENYLPHOSPHINE

15 A test was carried out in the same manner as in Example 1 except that in Example 1, the palladium catalyst solution was heated at 175°C under atmospheric pressure without adding DBPO thereto and instead by adding triphenylphosphine (0.4 mg, 4 mol equivalent to the palladium metal). As a result, the residual dissolved palladium metal concentration after the thermal

20

filtration was 2 wt ppm, and the Pd metal precipitation ratio was 90%.

EXAMPLE 2

IN THE PRESENCE OF 1,000 wt ppm OF TRIPHENYLPHOSPHINE

5 In a nitrogen gas atmosphere, into a glass flask, palladium acetate (7.9 mg), a ligand represented by the formula (1) (78.8 mg, 2 mol equivalent to the palladium metal), triphenylphosphine (76.5 mg, triphenylphosphine concentration in the catalyst solution: 1,000 wt ppm) and
10 75 g of the 3,4-diacetoxy-1-butene-containing liquid obtained from the side stream in Reference Example 3, were added, and heated and stirred at 80°C for one hour for dissolution to prepare a palladium catalyst solution. The dissolved palladium metal concentration in this
15 palladium catalyst solution was measured by ICP-MS, whereby the metal palladium concentration was 54 wt ppm. To 2 cc of this palladium catalyst solution, DBPO (tris(2,4-di-t-butylphenyl) phosphite) represented by the above formula (2) was added (12.6 mg, 20 mol equivalent
20 to the palladium metal), followed by heating at 175°C for 10 hours under atmospheric pressure. The catalyst solution after the heating was filtered by means of a filter having a mesh size of 8 μ m, and the concentration of palladium remaining as dissolved in the filtrate was
25 measured by ICP-MS. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 52 wt ppm. From the initial concentration

before the heating and the residual concentration, the dissolved residual ratio of palladium metal was calculated. As a result, the dissolved residual ratio of palladium metal was 96%, and the Pd metal precipitation
5 ratio was 4%.

EXAMPLE 3

A test was carried out in the same manner as in Example 2 except that in Example 2, the amount of DBPO was changed to 6.3 mg (10 mol equivalent to the palladium
10 metal). As a result, the residual dissolved palladium metal concentration after the thermal filtration was 50 wt ppm, and the Pd metal precipitation ratio was 7%.

EXAMPLE 4

A test was carried out in the same manner as in
15 Example 2 except that in Example 2, to the palladium catalyst solution, triphenylphosphite ($P(OPh)_3$) was added (5 μ L, 4 mol equivalent to the palladium metal) instead of DBPO, and heated at 175°C under atmospheric pressure. As a result, the residual dissolved palladium metal
20 concentration after the thermal filtration was 23 wt ppm, and the Pd metal precipitation ratio was 57%.

EXAMPLE 5

In a nitrogen gas atmosphere, into a glass flask, palladium acetate (5.0 mg), the ligand represented by the
25 formula (1) (48.4 mg, 2 mol equivalent to the palladium metal), triphenylphosphine (12.4 mg, triphenylphosphine concentration in the catalyst solution: 500 wt ppm) and

24 g of the 3,4-diacetoxy-1-butene-containing liquid obtained from the side stream in Reference Example 3, were added, and heated and stirred at 80°C for one hour for dissolution to prepare a palladium catalyst solution.

5 To 3 cc of this palladium catalyst solution, 1.8 g of a 3,4-diacetoxy-1-butene-containing liquid containing DBPO (tris(2,4-di-t-butylphenyl) phosphite) represented by the above formula (2) was added (20 mol equivalent to the palladium metal). The dissolved palladium metal

10 concentration in this palladium catalyst solution was measured by ICP-MS, whereby the metal palladium concentration was 59 wt ppm. This palladium catalyst solution was heated at 175°C for 10 hours under atmospheric pressure. The catalyst solution after the

15 heating was filtered by means of a filter having a mesh size of 8 μ m, and the residual dissolved palladium concentration in the filtrate was measured by ICP-MS. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 55 wt ppm.

20 From the initial concentration before the heating and the residual concentration, the dissolved residual ratio of palladium metal was calculated. As a result, the dissolved residual ratio of palladium metal was 93%, and the Pd metal precipitation ratio was 7%.

25 COMPARATIVE EXAMPLE 3

A test was carried out in the same manner as in Example 2 except that in Example 2, no DBPO was added to

the palladium catalyst solution. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 4 wt ppm, and the Pd metal precipitation ratio was 93%.

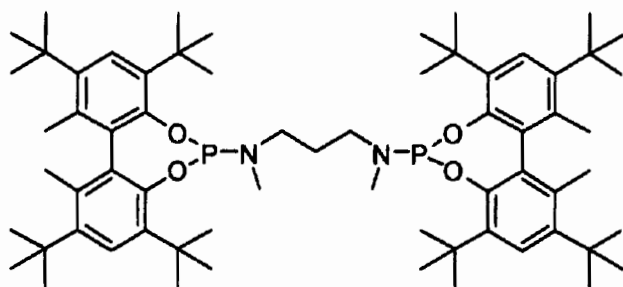
5 COMPARATIVE EXAMPLE 4

A test was carried out in the same manner as in Example 2 except that in Example 2, to the palladium catalyst solution, tri-n-butyl phosphite ($P(On-Bu)_3$) was added (5 μ L, 4 mol equivalent to the palladium metal)
10 instead of DBPO. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 2 wt ppm, and the Pd metal precipitation ratio was 96%.

The results of the above Examples 1 to 5 and
15 Comparative Examples 1 to 4 are summarized and shown in Table 1.

TABLE 1

	Ex. 1	Comp. Ex. 1	Comp. Ex. 2	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 3	Comp. Ex. 4	Ex. 5
Dissolved Pd concentration in initial solution (wt ppm)	20	20	20	54	54	54	54	54	59
Molar ratio of additive ① to Pd metal	DBPO/ Pd=20	-	PPh ₃ / Pd=4	DBPO/ Pd=20	DBPO/ Pd=10	P(OPh) ₃ / Pd=10	-	P(OnBu) ₃ / Pd=4	DBPO/ Pd=20
Additive ② (wt ppm)	-	-	-	PPh ₃ : 1,000 wt ppm	PPh ₃ : 1,000 wt ppm	PPh ₃ : 1,000 wt ppm	PPh ₃ : 1,000 wt ppm	PPh ₃ : 1,000 wt ppm	PPh ₃ : 500 wt ppm
Temperature (°C)	175	175	175	175	175	175	175	175	175
Time (hr)	27	27	27	10	10	10	10	10	10
Dissolved Pd concentration after thermal filtration (wt ppm)	20	6	2	52	50	23	4	2	55
Dissolved Pd residual ratio (%)	100	30	10	96	93	43	7	4	93
Pd metal precipitation ratio (%)	0	70	90	4	7	57	93	96	7



(3)

EXAMPLE 6

In a nitrogen gas atmosphere, into a glass flask, palladium acetate (2.2 mg), a ligand represented by the

5 formula (3) (19.5 mg, 2 mol equivalent to the palladium metal) and 20 g of the 3,4-diacetoxy-1-butene-containing liquid obtained from the side stream in Reference Example 3, were added, and heated and stirred at 80°C for one hour for dissolution to prepare a palladium catalyst

10 solution. The dissolved palladium metal concentration in this palladium catalyst solution was measured by ICP-MS, whereby the metal palladium concentration was 42 wt ppm. To 3 cc of this palladium catalyst solution, DBPO

(tris(2,4-di-*t*-butylphenyl) phosphite) represented by the

15 above formula (2) was added (19 mg, 20 mol equivalent to the palladium metal), followed by heating at 175°C for 10 hours under atmospheric pressure. The catalyst solution after the heating was filtered by means of a filter

having a mesh size of 8 μ m, and the residual dissolved

20 palladium concentration in the filtrate was measured by ICP-MS. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 41

wt ppm. From the initial concentration before the heating and the residual concentration, the dissolved residual ratio of palladium metal was calculated. As a result, the dissolved residual ratio of palladium metal was 98%, and the Pd metal precipitation ratio was 2%.

COMPARATIVE EXAMPLE 5

A test was carried out in the same manner as Example 6, except that in Example 6, no DBPO was added to the palladium catalyst solution. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 0 wt ppm, and the Pd metal precipitation ratio was 100%.

EXAMPLE 7

In a nitrogen gas atmosphere, into a glass flask, palladium acetate (2.2 mg), the ligand represented by the formula (3) (19.5 mg, 2 mol equivalent to the palladium metal), triphenylphosphine (20 mg, triphenylphosphine concentration in the catalyst solution: 1,000 wt ppm) and 20 g of the 3,4-diacetoxy-1-butene-containing liquid obtained from the side stream in Reference Example 3, were added, and heated and stirred at 80°C for one hour for dissolution to prepare a palladium catalyst solution. The dissolved palladium metal concentration in this palladium catalyst solution was measured by ICP-MS, whereby the metal palladium concentration was 42 wt ppm. To 2 cc of this palladium catalyst solution, DBPO (tris(2,4-di-*t*-butylphenyl) phosphite) represented by the

above formula (2) was added (19 mg, 20 mol equivalent to the palladium metal), followed by heating at 175°C for 10 hours under atmospheric pressure. The catalyst solution after the heating was filtered by means of a filter
5 having a mesh size of 8 μ m, and the residual dissolved palladium concentration in the filtrate was measured by ICP-MS. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 40 wt ppm. From the initial concentration before the
10 heating and the residual concentration, the dissolved residual ratio of palladium metal was calculated. As a result, the dissolved residual ratio of palladium metal was 96%, and the Pd metal precipitation ratio was 4%.

COMPARATIVE EXAMPLE 6

15 A test was carried out in the same manner as Example 7, except that in Example 7, no DBPO was added to the palladium catalyst solution. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 0 wt ppm, and the Pd metal precipitation
20 ratio was 100%.

EXAMPLE 8

In a nitrogen gas atmosphere, into a glass flask, palladium acetate (5.1 mg), the ligand represented by the formula (3) (46.2 mg, 2 mol equivalent to the palladium
25 metal), triphenylphosphine (12.7 mg, triphenylphosphine concentration in the catalyst solution: 500 wt ppm) and 24 g of the 3,4-diacetoxy-1-butene-containing liquid

obtained from the side stream in Reference Example 3, were added, and heated and stirred at 80°C for one hour for dissolution to prepare a palladium catalyst solution. To 3 cc of this palladium catalyst solution, 1.8 g of a
5 3,4-diacetoxy-1-butene-containing liquid containing 1 wt% of DBPO (tris(2,4-di-t-butylphenyl) phosphite) represented by the above formula (2) was added (20 mol equivalent to the palladium metal). The dissolved palladium metal concentration in this palladium catalyst
10 solution was measured by ICP-MS, whereby the metal palladium concentration was 58 wt ppm. This palladium catalyst solution was heated at 175°C for 10 hours under atmospheric pressure. The catalyst solution after the heating was filtered by means of a filter having a mesh
15 size of 8 μ m, and the residual dissolved palladium concentration in the filtrate was measured by ICP-MS. As a result, the residual dissolved palladium metal concentration after the thermal filtration was 56 wt ppm. From the initial concentration before the heating and the
20 residual concentration, the dissolved residual ratio of palladium metal was calculated. As a result, the dissolved residual ratio of palladium metal was 97%, and the Pd metal precipitation ratio was 3%.

The results of the above Examples 6 to 8 and
25 Comparative Examples 5 and 6 are summarized and shown in Table 2.

TABLE 2

	Ex. 6	Comp. Ex. 5	Ex. 7	Comp. Ex. 6	Ex. 8
Dissolved Pd concentration in initial solution (wt ppm)	42	42	42	42	58
Molar ratio of additive ① to Pd metal	DBPO/ Pd=20	-	DBPO/ Pd=20	-	DBPO/ Pd=20
Additive ② (wt ppm)	-	-	PPh ₃ : 1,000 wt ppm	PPh ₃ : 1,000 wt ppm	PPh ₃ : 500 wt ppm
Temperature (°C)	175	175	175	175	175
Time (hr)	10	10	10	10	10
Dissolved Pd concentration after thermal filtration (wt ppm)	41	0	40	0	56
Dissolved Pd residual ratio (%)	98	0	96	0	97
Pd metal precipitation ratio (%)	2	100	4	100	3

EXAMPLE 9

SUPPRESSION OF METAL PRECIPITATION OF PALLADIUM METAL BY

5 DBPO UNDER REDUCED PRESSURE CONDITION

In a nitrogen gas atmosphere, into a glass flask, palladium acetate (21 mg), the ligand represented by the formula (1) (200 mg, 2 mol equivalent to the palladium metal), triphenylphosphine (49 mg, triphenylphosphine
 10 concentration in the catalyst solution: 10 wt ppm) and 400 cc of the 3,4-diacetoxy-1-butene-containing liquid

obtained from the side stream in Reference Example 3,
were added, and heated and stirred at 80°C for one hour
to prepare a catalyst solution to obtain a reaction
solution having a metal palladium concentration of 50 wt
5 ppm. The reaction solution and DBPO represented by the
formula (2) (1.22 g, 20 mol equivalent to the palladium
metal) were introduced into a container having a cover,
and after being sealed with the cover, the container was
heated under reduced pressure (from 300 to 280 torr) to
10 165°C. While maintaining the same temperature, the
palladium concentration in the reaction solution was
measured every predetermined time from the point of time
(time=0) when the temperature reached 165°C, and the
change with time was observed. The results are shown in
15 Fig. 1.

Here, the palladium concentration was measured by
IPC-MS. Further, the dissolved residual ratio of
palladium (%) is the ratio to the initial concentration
in the reaction solution.

20 COMPARATIVE EXAMPLE 7

The change with time of the palladium concentration
was observed in the same manner as in Example 9 except
that in Example 7, no DBPO was added, and the results are
shown in Fig. 1.

25

INDUSTRIAL APPLICABILITY

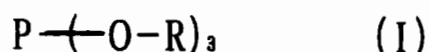
The method of the present invention is a method

whereby in an industrial reaction such as an isomerization reaction or hydrogenation reaction carried out by using a transition metal complex as a catalyst, it is possible to suppress a loss of metal due to precipitation of a catalyst in the piping or in the apparatus such as a distillation column and to suppress formation of a contamination by a catalyst metal in the process system, and further, it is possible to efficiently take out the catalyst metal out of the system in the form of a solution having such a metal dissolved therein.

The entire disclosure of Japanese Patent Application No. 2007-288508 filed on November 6, 2007 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

CLAIMS

1. A method which comprises contacting a solution containing a transition metal complex of transition metal selected from Groups 8 to 10 transition metals and having
5 a ligand made of a trivalent organic phosphorus compound, with an aromatic phosphite different from said trivalent organic phosphorus compound, to suppress precipitation of metal from the transition metal complex in the solution.
2. The method according to Claim 1, wherein the aromatic
10 phosphite is represented by the following formula (I):



wherein each of three R which are independent of one another, is a hydrocarbon group which may have a substituent, provided that at least one R is an aryl
15 group.

3. The method according to Claim 2, wherein at least one aryl group in the formula (I) of the aromatic phosphite, has a substituent at its ortho-position.
4. The method according to Claim 3, wherein the
20 substituent at the ortho-position of at least one aryl group in the formula (I) of the aromatic phosphite, is a substituent bonded by a tertiary or quaternary carbon atom.
5. The method according to Claim 4, wherein the three R
25 in the formula (I) of the aromatic phosphite, are the same and phenyl groups having, at their ortho-positions,

a substituent bonded by a tertiary or quaternary carbon atom.

6. The method according to any one of Claims 1 to 5, wherein the aromatic phosphite is a monodentate phosphite.

5 7. The method according to any one of Claims 1 to 6, wherein the trivalent organic phosphorus compound is at least one member selected from the group consisting of phosphines, phosphites and phosphoramidites.

8. The method according to any one of Claims 1 to 7,
10 wherein the trivalent organic phosphorus compound is at least one member selected from the group consisting of polydentate phosphines, phosphites and phosphoramidites.

9. The method according to any one of Claims 1 to 8, wherein the transition metal selected from Groups 8 to 10
15 transition metals, is palladium or platinum.

10. The method according to any one of Claims 1 to 9, wherein the solution containing a transition metal complex containing transition metal selected from Groups 8 to 10 transition metals and a trivalent organic
20 phosphorus compound, is a solution after either an isomerization, hydrogenation, hydroformylation, dehydrogenation, oligomerization, metathesis, coupling or allyl-forming reaction, carried out by using such a transition metal complex as a catalyst.

25 11. The method according to Claim 10, wherein the solution containing a transition metal complex containing transition metal selected from Groups 8 to 10 transition

metals and a trivalent organic phosphorus compound, is a solution after an isomerization reaction of a raw material allyl compound derivative, which contains an allyl compound derivative different from the raw material.

5 12. The method according to Claim 10 or 11, wherein the solution containing a transition metal complex containing transition metal selected from Groups 8 to 10 transition metals and a trivalent organic phosphorus compound, is a reaction solution after an isomerization reaction of an
10 acetoxyallyl compound.

13. The method according to Claim 12, wherein the acetoxyallyl compound is a solution containing 3,4-diacetoxy-1-butene as the main component, obtained from an oxidation diacetoxy-forming reaction product of
15 butadiene.