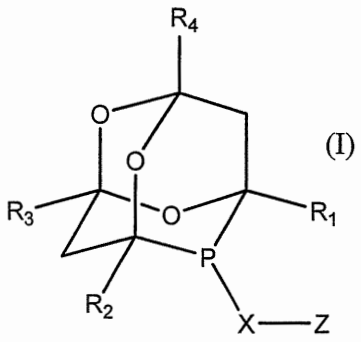
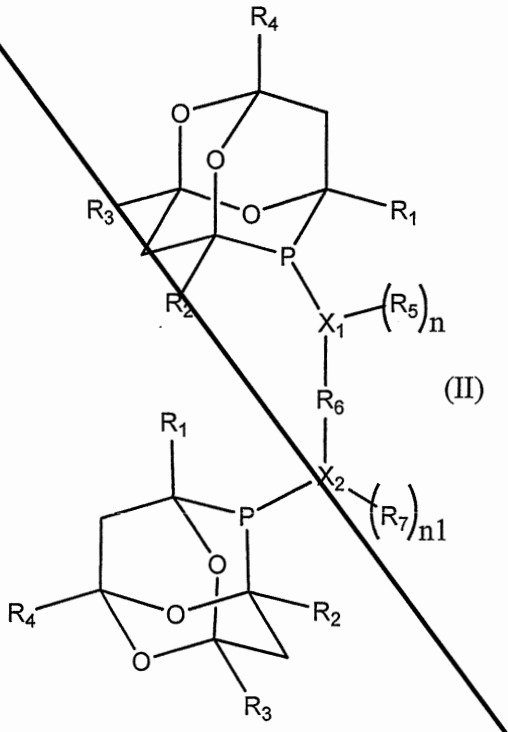
CLAIMS

1. Organophosphorus compounds, characterized in that they correspond to one of the general formulae (I) or (II):



(I)



(II)

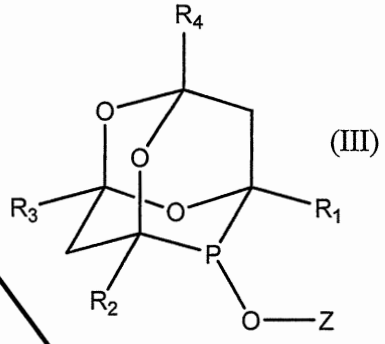
in which:

- R_1, R_2, R_3, R_4, R_5, R_7 and Z, which may be identical or different, represent a hydrogen atom, a linear or branched alkyl radical having from 1 to 12 carbons which can contain heteroatoms, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical, a halogen atom, a nitrile group or a haloalkyl group having 1 to 12 carbon atoms
- X, X1 and X2, which may be identical or different, represent an oxygen, nitrogen, sulphur, carbon or silicon atom
- R_6 represents a covalent bond, a linear or branched aliphatic radical, a radical comprising a

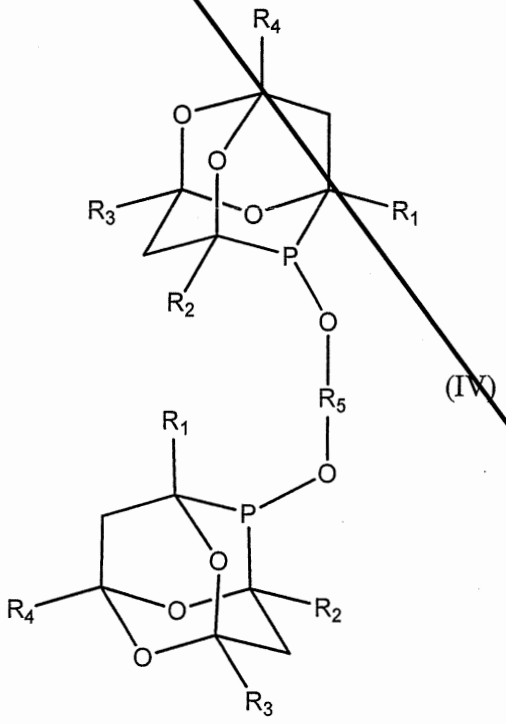
substituted or unsubstituted aromatic or cycloaliphatic ring or several aromatic rings, condensed or joined together by a bond

- n and n1, which may be identical or different, are integers respectively equal to the valency of elements X_1, X_2 reduced by 2.

2. Compounds according to Claim 1, characterized in that they belong to the family of the organophosphinites and that they correspond to one of the general formulae (III) or (IV):



(III)

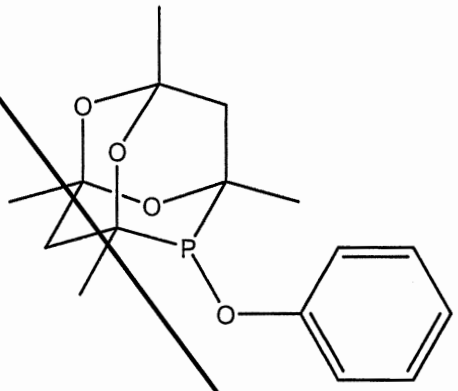


(IV)

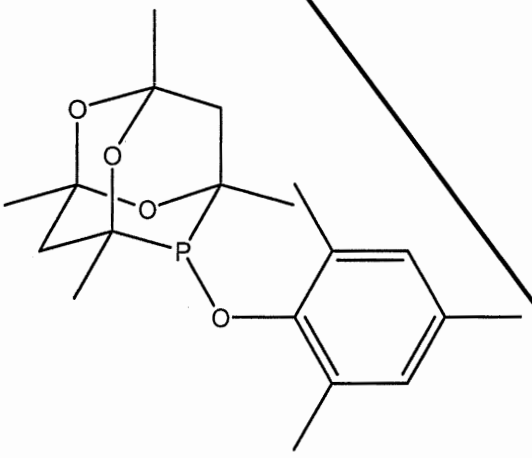
in which:

- R_1, R_2, R_3, R_4, which may be identical or different, represent a hydrogen atom, a linear or branched alkyl radical having from 1 to 12 carbon atoms which can contain heteroatoms,
- Z represents a substituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical, a halogen atom, a nitrile group or a haloalkyl group having 1 to 12 carbon atoms,
- R_5 represents a covalent bond, a linear or branched aliphatic radical, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic ring or several aromatic rings, condensed or joined together by a bond.

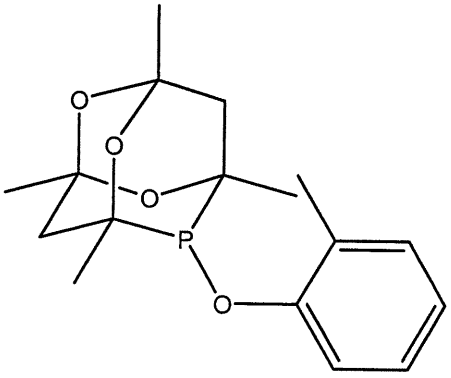
3. Compounds according to Claim 1 or 2, characterized in that they are selected from the group comprising the compounds with the following formulae:



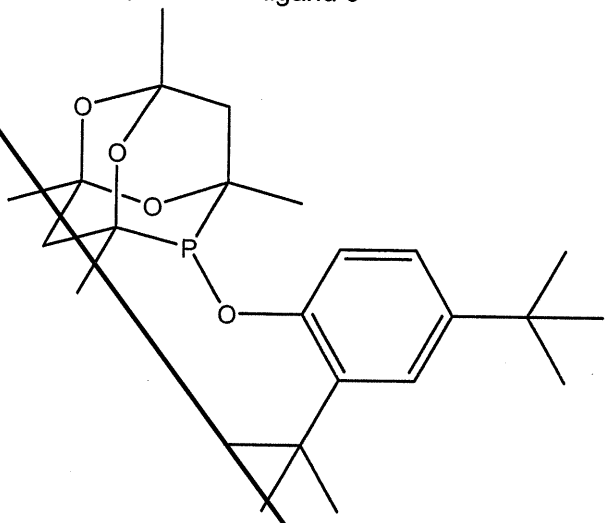
ligand 1



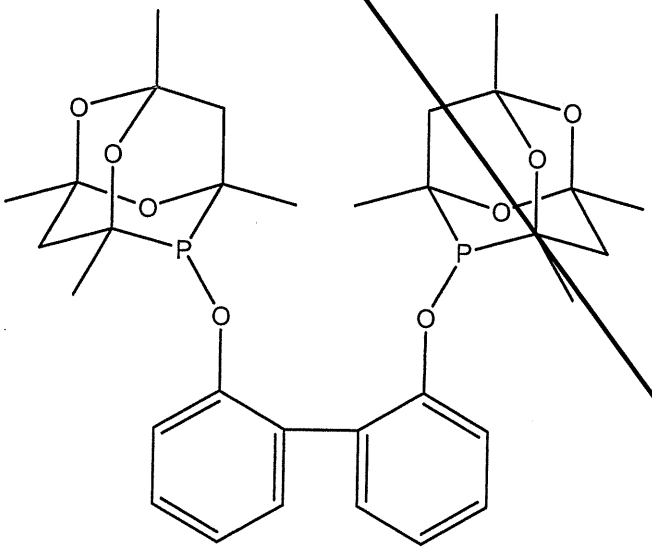
ligand 2



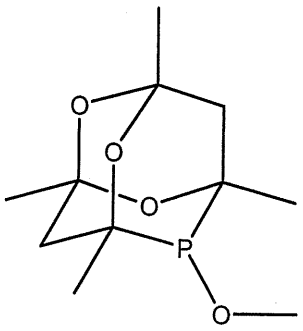
ligand 3



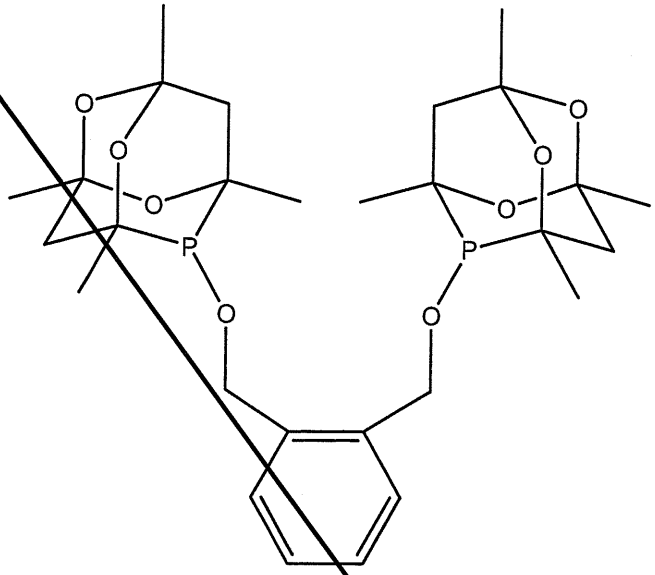
ligand 4



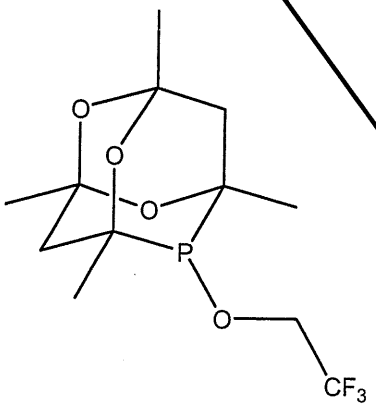
ligand 5



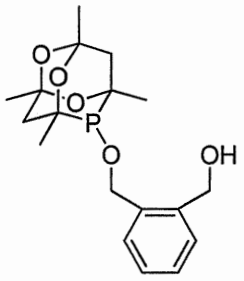
ligand 6



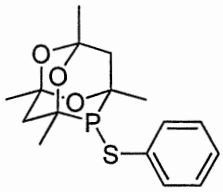
ligand 7



ligand 8



ligand 9



ligand 10

4. Catalytic system comprising a metallic element forming a complex with an organophosphorus compound according to one of Claims 1 to 3, characterized in that the complex corresponds to the following general formulae (V) or (VI):

$$M\,[L_f]_t \quad (V)$$

$$HM\,[L_f]_{t-n}CO_{4-n} \quad (VI)$$

in which:

M is a transition metal

L_f represents at least one organophosphorus ligand of formula (I), (II), (III) or (IV)

t represents a number between 1 and 10 (inclusive)

n represents a number between 1 and 4 (inclusive)

5. System according to Claim 4, characterized in that the metallic element M is selected from the group comprising nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium, mercury.

6. Method of hydrocyanation of a hydrocarbon compound comprising at least one ethylenic unsaturation by reaction in a liquid medium with hydrogen cyanide in the presence of a catalytic system according to Claim 4 or 5, characterized in that the metallic element is nickel.

7. Method according to Claim 6, characterized in that the organic compounds bearing at least one ethylenic unsaturation are selected from the diolefins such as butadiene, isoprene,

hexadiene-1,5, cyclooctadiene-1,5, ethylenically unsaturated aliphatic nitriles, particularly linear pentenenitriles such as pentene-3-nitrile, pentene-4-nitrile, monoolefins such as styrene, methylstyrene, vinylnaphthalene, cyclohexene, methylcyclohexene as well as mixtures of several of these compounds.

8. Method according to Claim 6 or 7, characterized in that the amount of nickel compound is selected in such a way that there is, per mol of organic compound that is to undergo hydrocyanation or isomerization, between 10^{-4} and 1 mol of nickel or of the other transition metal employed and in that the amount of organophosphorus compounds used is selected in such a way that the number of moles of these compounds relative to 1 mol of transition metal is from 0.5 to 100.

9. Method according to one of Claims 6 to 8, characterized in that the ethylenically unsaturated compounds are ethylenically unsaturated nitrile compounds and in that it is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one compound of formula (I), (II), (III) or (IV) and a cocatalyst consisting of at least one Lewis acid.

10. Method according to Claim 9, characterized in that the ethylenically unsaturated nitrile compounds are selected from the ethylenically unsaturated aliphatic nitriles comprising linear pentenenitriles such as pentene-3-nitrile, pentene-4-nitrile and mixtures thereof.

11. Method according to one of Claims 9 to 10, characterized in that the Lewis acid employed as cocatalyst is selected from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the periodic system.

12. Method according to one of Claims 9 to 11, characterized in that the Lewis acid is selected from zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, chlorides or bromides of rare earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium, cobalt chloride, ferrous chloride, yttrium chloride and mixtures thereof, organometallic compounds.

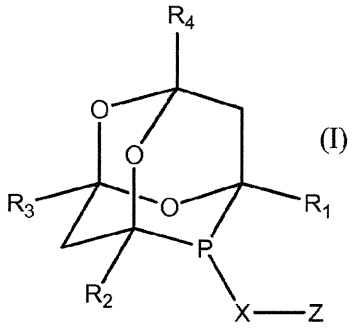
13. Method according to one of Claims 6 to 12, characterized in that the isomerization, to pentenenitriles, of the methyl-2-butene-3-nitrile present in the reaction mixture resulting from the hydrocyanation of butadiene, is carried out in the absence of hydrogen cyanide, working in the presence of a catalyst bearing at least one compound of formula (I), (II), (III) or (IV) and at

least one compound of a transition metal.

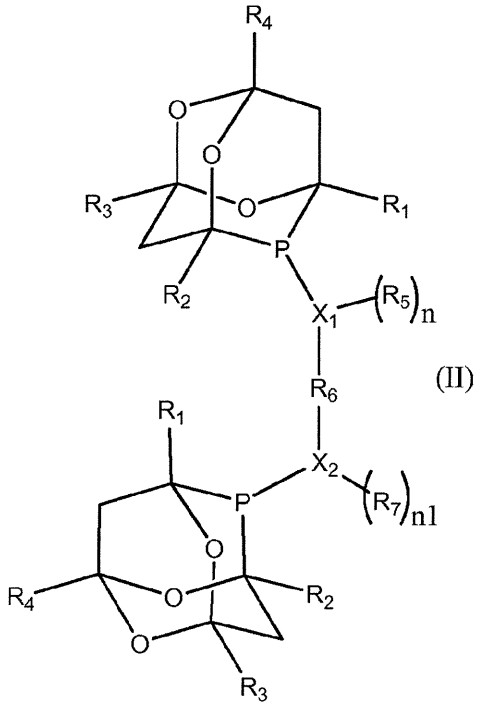
14. Method of hydroformylation of alkenes in the presence of a catalytic system according to Claim 4 or 5, characterized in that the metallic element is rhodium or cobalt.

Claims

1. An organophosphorus compound, wherein the compound has the formula (I) or (II):



(I)



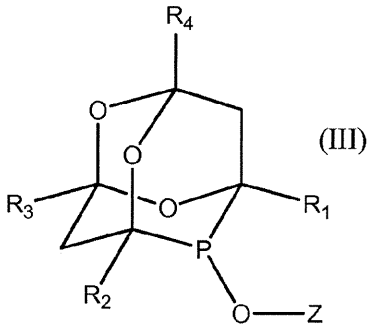
(II)

in which:

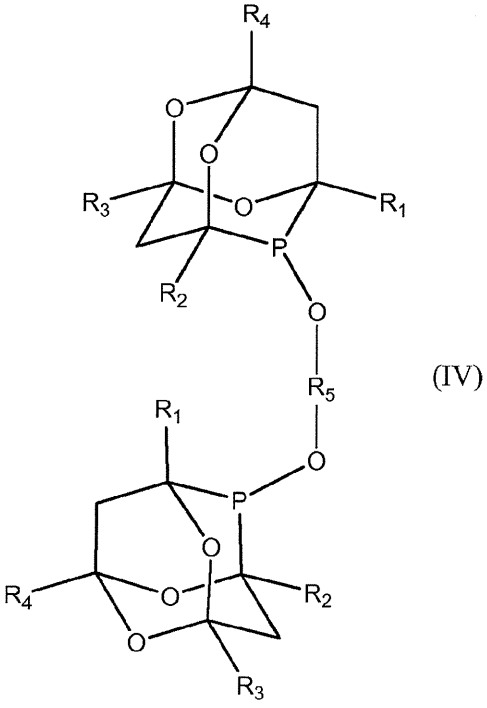
- R_1, R_2, R_3, R_4, R_5, R_7 and Z, which can be identical or different, represent a hydrogen atom; a linear orbranched alkyl radical having from 1 to 12 carbons which can comprise heteroatoms; a radical comprising asubstituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl grouphaving 1 to 12 carbon atoms;
- X, X1 and X2, which can be identical or different, represent an oxygen, nitrogen, sulphur, or silicon atom;

- R_6 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond; and
- n and n1, which can be identical or different, are integers respectively equal to the valency of elements X_1 and X_2 reduced by 2.

2. The compound according to Claim 1, wherein the compound has formula (III) or (IV):



(III)



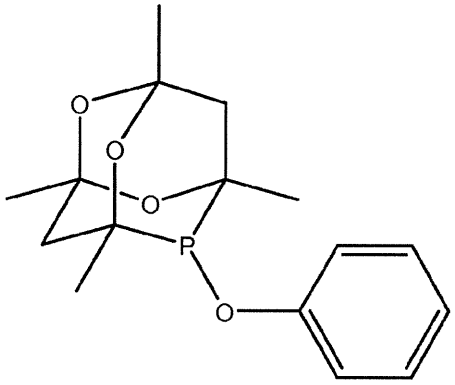
(IV)

in which:

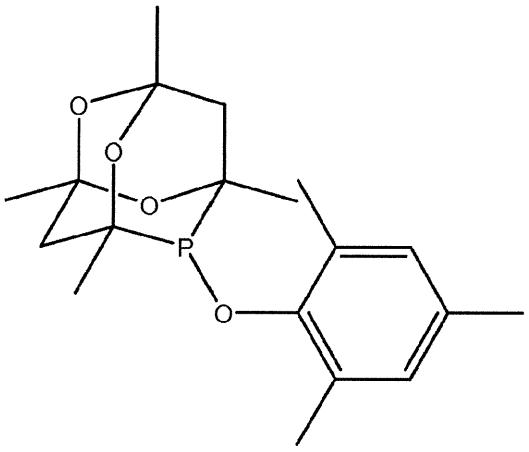
- R_1, R_2, R_3, and R_4, which can be identical or different, represent a hydrogen atom; or a linear or branched alkylradical having from 1 to 12 carbon atoms which can comprise heteroatoms;

- Z represents a substituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms,a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl group having 1 to 12 carbon atoms;
- R_5 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond.

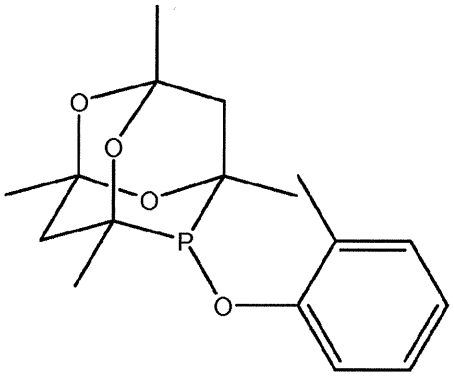
3. The compound according to Claim 1, wherein the compound is selected from the group consisting of compounds having the following formulae:



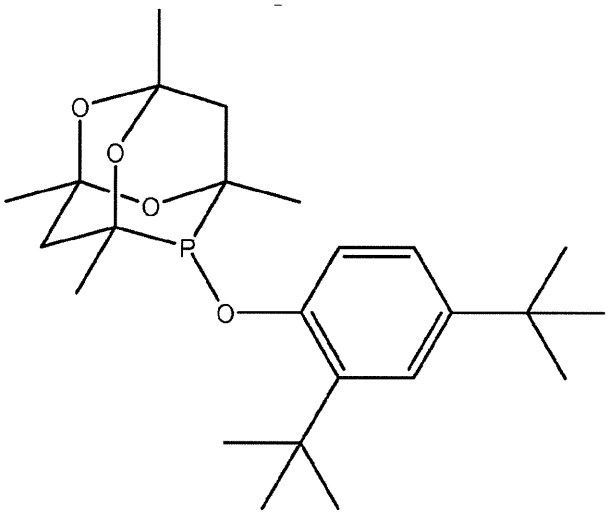
ligand 1



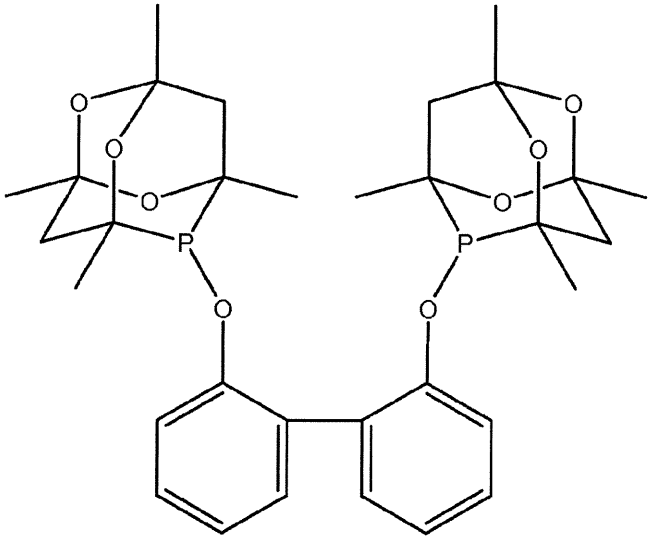
ligand 2



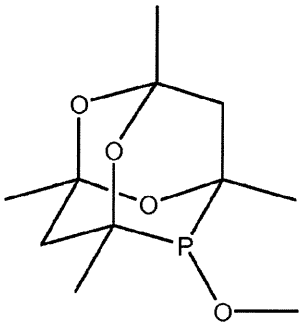
ligand 3



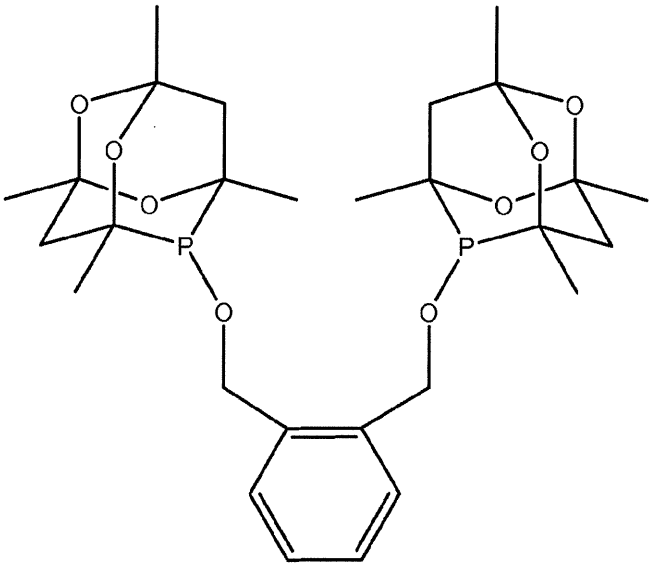
ligand 4



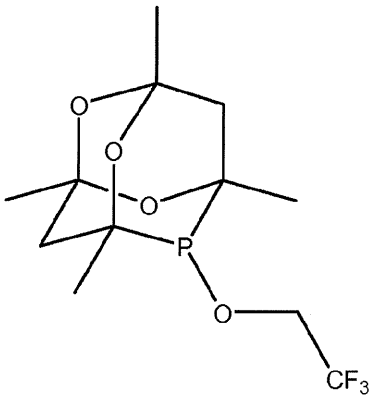
ligand 5



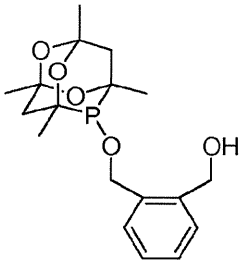
ligand 6



ligand 7

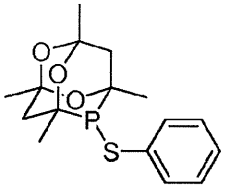


ligand 8



ligand 9

and



ligand 10

4. A catalytic system comprising a metallic element (M) forming a complex with an organophosphorus compound wherein the complex has the following formula (V) or (VI):

$$M\,[L_f]_t \quad (V) \text{ or}$$

$$HM\,[L_f]_{t+n2}CO_{4-n2} \quad (VI)$$

in which:

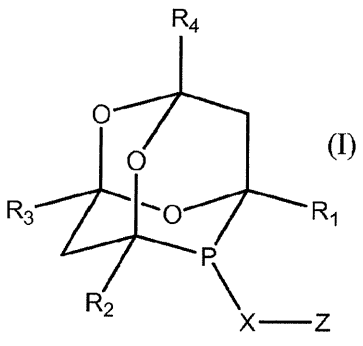
M is a transition metal;

L_f represents at least one organophosphorus compound having formula (I), (II), (III) or (IV);

t represents a number between1 and 10 (inclusive); and

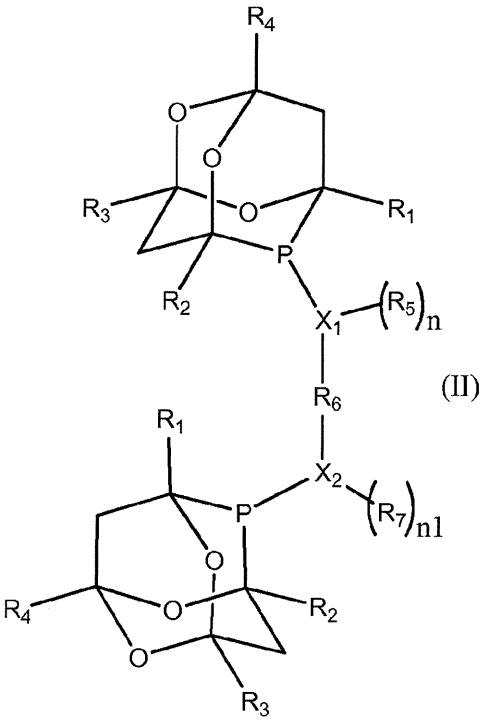
n2 represents a number between 1 and 4 (inclusive);

wherein formula (I) or (II) is:



(I)

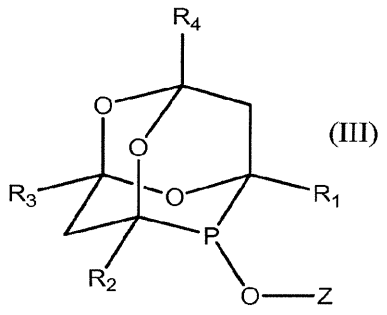
or



in which:

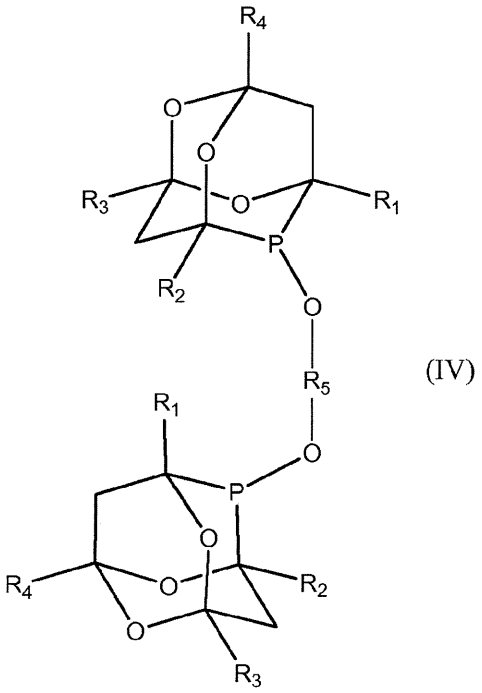
- R_1, R_2, R_3, R_4, R_5, R_7 and Z, which can be identical or different, represent a hydrogen atom; a linear orbranched alkyl radical having from 1 to 12 carbons which can comprise heteroatoms; a radical comprising asubstituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl grouphaving 1 to 12 carbon atoms;
- X, X1 and X2, which can be identical or different, represent an oxygen, nitrogen, sulphur, or silicon atom;
- R_6 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond; and
- n and n1, which can be identical or different, are integers respectively equal to the valency of elements X_1 and X_2reduced by 2; and

wherein formula (III) or (IV) is:



(III)

or



(IV)

in which:

- R_1, R_2, R_3, and R_4, which can be identical or different, represent a hydrogen atom; or a linear or branched alkylradical having from 1 to 12 carbon atoms which can comprise heteroatoms;
- Z represents a substituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms,a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl group having 1 to 12 carbon atoms;
- R_5 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond.

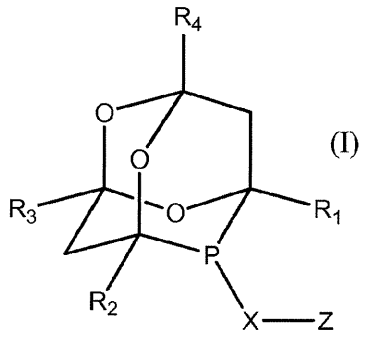
5. The system according to Claim 4, wherein the metallic element (M) is selected from the group consisting of nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium, and mercury.

6. A method of hydrocyanation of a hydrocarbon compound, the method comprising reacting a hydrocarbon compound comprising at least one ethylenic unsaturation, in a liquid medium with hydrogen cyanide in the presence of the catalytic system according to Claim 4, wherein the metallic element (M) is nickel.

7. The method according to Claim 6, wherein the hydrocarbon compound comprising at least one ethylenic unsaturation is selected from the group consisting of a diolefin, an ethylenicallyunsaturated aliphatic nitrile, a monoolefin, and a mixture ofthese compounds.

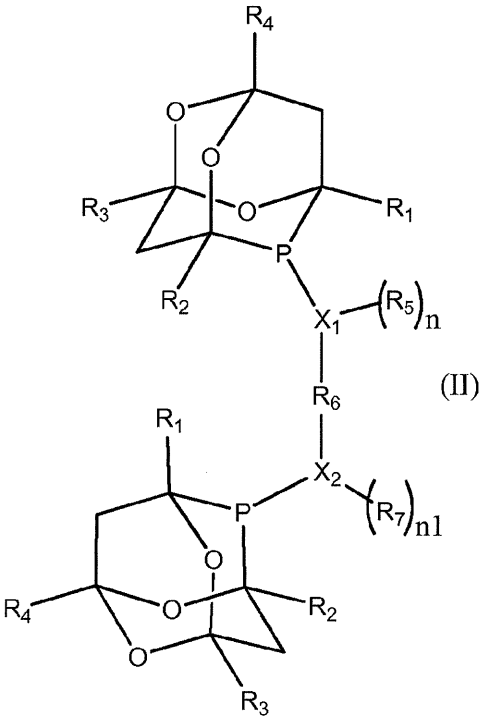
8. The method according to Claim 6,wherein the amount of nickel compound is between 10^{-4} and 1mol per mol of the hydrocarbon compound comprising at least one ethylenic unsaturation and the amount of organophosphorus compounds used is from 0.5 to 100 mol to 1 mol of nickel.

9. The method according to Claim 6, wherein the hydrocarbon compound is an ethylenic unsaturatednitrile compound and wherein the hydrocyanation is carried out in the presence of the catalytic system comprising nickel, and at least one organophosphorus compound of formula (I), (II), (III) or (IV) and further comprising at least one Lewis acid as a cocatalyst;
wherein formula (I) or (II) is:



(I)

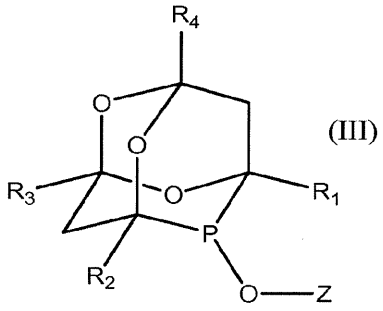
or



in which:

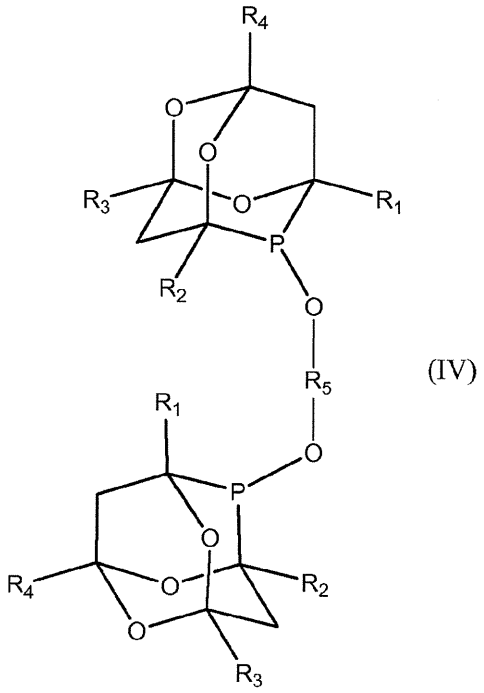
- R_1, R_2, R_3, R_4, R_5, R_7 and Z, which can be identical or different, represent a hydrogen atom; a linear orbranched alkyl radical having from 1 to 12 carbons which can comprise heteroatoms; a radical comprising asubstituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl grouphaving 1 to 12 carbon atoms;
- X, X1 and X2, which can be identical or different, represent an oxygen, nitrogen, sulphur, or silicon atom;
- R_6 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond; and
- n and n1, which can be identical or different, are integers respectively equal to the valency of elements X_1 and X_2reduced by 2; and

wherein formula (III) or (IV) is:



(III)

or



(IV)

in which:

- R_1, R_2, R_3, and R_4, which can be identical or different, represent a hydrogen atom; or a linear or branched alkylradical having from 1 to 12 carbon atoms which can comprise heteroatoms;
- Z represents a substituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms,a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl group having 1 to 12 carbon atoms;
- R_5 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond.

10. The method according to Claim 9, wherein the ethylenically unsaturated nitrile compound is an ethylenically unsaturated aliphatic nitrile.

11. The method according to Claim 9, wherein theLewis acidis a compound comprising an element selected from the group consisting ofgroupIb, groupIIb, groupIIIa, groupIIIb, groupIVa, groupIVb, groupVa, groupVb, groupVIb, groupVIIbandgroup VIII of the periodic table.

12. The method according to Claim 9, wherein the Lewis acid is selected from the group consisting of zinc chloride, zincbromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannouschloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, rare earth element of chloride or bromide, cobalt chloride, ferrous chloride,yttrium chloride, organometallic compounds, and mixtures thereof.

13. A method of hydroformylation of alkenes, wherein the method comprises reacting alkenes with a mixture of carbon monoxide (CO) and hydrogen (H_2) in the presence of the catalytic system according to Claim 4,wherein the metallic element (M) is rhodium or cobalt.

14. The method according to Claim7, wherein the diolefin is selected from the group consisting of butadiene, isoprene, hexadiene-1,5, and cyclooctadiene-1,5.

15. The method according to Claim7, wherein theethylenically unsaturated aliphatic nitrile is a linear pentenenitrile.

16. The method according to Claim15, wherein thelinear pentenenitrile is pentene-3-nitrile or pentene-4-nitrile.

17. The method according to Claim7, wherein the monoolefin is selected from the group consisting ofstyrene, methylstyrene, vinylnaphthalene, and cyclohexene.

18. The method according to Claim10, wherein theethylenically unsaturated aliphatic nitrile is a linear pentenenitrile.

19. The method according to Claim18, wherein thelinear pentenenitrile is pentene-3-nitrile or pentene-4-nitrile or a mixture thereof.

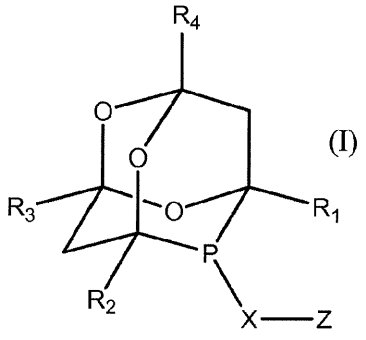
20. The method according to Claim12, wherein the rare earth element is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium,gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium, and lutetium.

21. A method of isomerization of an unsaturated nitrile to a linear unsaturated nitrile, the method comprises isomerizing an unsaturated nitrile in the absence of hydrogen cyanide and in the presence of the catalytic system according to claim 4.

22. The method of isomerization according to Claim 21, wherein the unsaturated nitrile is methyl-2-butene-3-nitrile and wherein the linear nitrile is pentenenitrile.

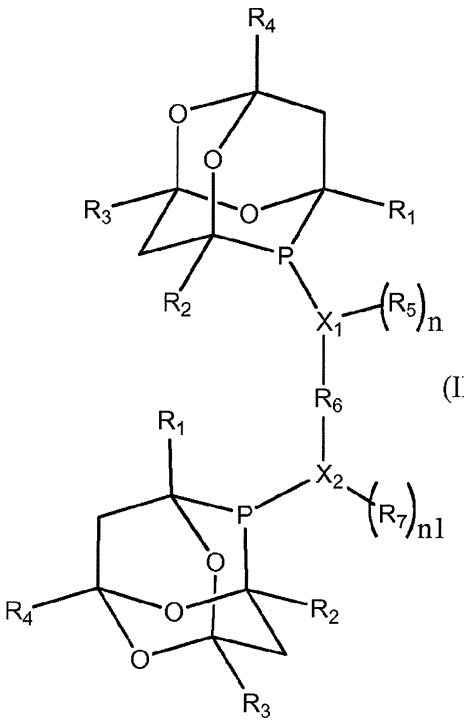
23. A method of hydrocyanation of a hydrocarbon compound, the method comprising reacting a hydrocarbon compound comprising at least one ethylenic unsaturation, in a liquid medium with hydrogen cyanide in the presence of the catalytic system according to Claim 4to form methyl-2-butene-3-nitrile, wherein the metallic element (M) is nickel and inthe absence of hydrogen cyanide and in the presence of a catalyst bearing atleast one compound of formula(I), (II), (III) or (IV) and at least one compound of a transition metal

wherein formula (I) or (II) is:



(I)

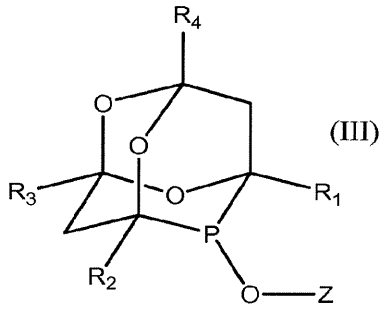
or



in which:

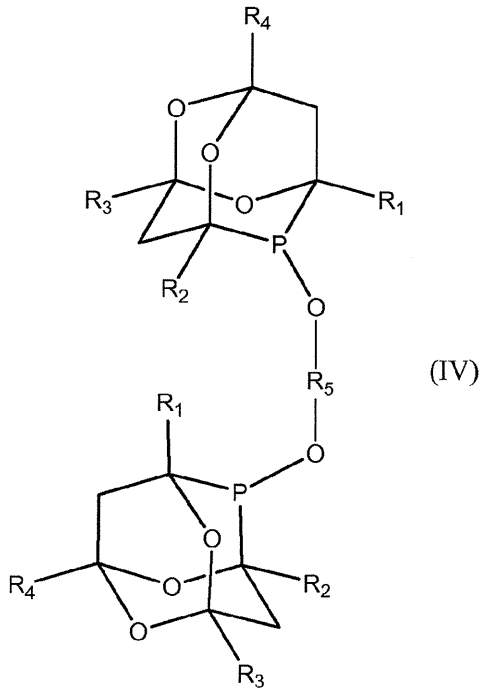
- R_1, R_2, R_3, R_4, R_5, R_7 and Z, which can be identical or different, represent a hydrogen atom; a linear orbranched alkyl radical having from 1 to 12 carbons which can comprise heteroatoms; a radical comprising asubstituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms, a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl grouphaving 1 to 12 carbon atoms;
- X, X1 and X2, which can be identical or different, represent an oxygen, nitrogen, sulphur, or silicon atom;
- R_6 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond; and
- n and n1, which can be identical or different, are integers respectively equal to the valency of elements X_1 and X_2reduced by 2; and

wherein formula (III) or (IV) is:



(III)

or



(IV)

in which:

- R_1, R_2, R_3, and R_4, which can be identical or different, represent a hydrogen atom; or a linear or branched alkylradical having from 1 to 12 carbon atoms which can comprise heteroatoms;
- Z represents a substituted or unsubstituted aromatic or cycloaliphatic radical which can comprise heteroatoms,a carbonyl, alkoxycarbonyl or alkoxy radical; a halogen atom; a nitrile group; or a haloalkyl group having 1 to 12 carbon atoms;
- R_5 represents a covalent bond; a linear or branched aliphatic radical; a radical comprising a substituted orunsubstituted aromatic or cycloaliphatic ring; or several aromatic rings, condensed or joined together by a bond.