ORGANOPHOSPHORUS COMPOUNDS, CATALYTIC SYSTEMS COMPRISING SAID COMPOUNDS AND METHOD OF HYDROCYANATION USING SAID CATALYTIC SYSTEMS

[001] The present invention relates to organophosphorus compounds belonging to the phosphinite-phosphite family, their use in catalytic systems and methods of synthesis of organic compounds using said catalytic systems, notably the methods of hydrocyanation of ethylenically unsaturated organic compounds to compounds comprising at least one nitrile function.

[002] The reaction of hydrocyanation is, for example, described in French patent 1 599 761 which relates to a method of preparation of nitriles by addition of hydrocyanic acid to organic compounds having at least one ethylenic double bond, in the presence of a catalyst comprising nickel and an organophosphorus ligand, a triarylphosphite. This reaction can be carried out in the presence or absence of a solvent.

[003] When a solvent is used, it is preferably a hydrocarbon, such as benzene or xylenes or a nitrile such as acetonitrile.

[004] The catalyst employed is an organic nickel complex, containing ligands such as phosphines, arsines, stibines, phosphites, arsenites or antimonites.

[005] The presence of a promoter for activating the catalyst, such as a boron compound or a metal salt, generally a Lewis acid, is also recommended in said patent.

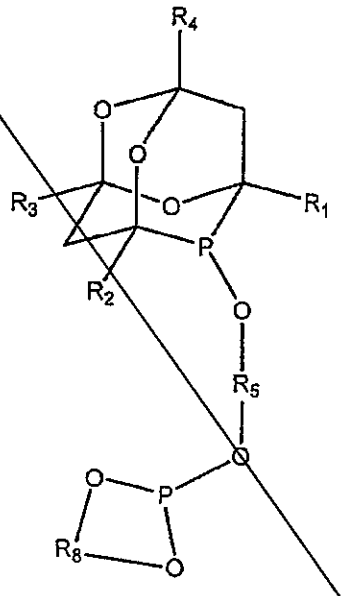
[006] Numerous other catalytic systems have been proposed, generally comprising organophosphorus compounds belonging to the family of the phosphites, phosphonites, phosphinites and phosphines. These organophosphorus compounds can comprise one phosphorus atom per molecule and are described as monodentate ligands, or several phosphorus atoms per molecule, which are then called multidentate ligands. More particularly, numerous ligands containing two phosphorus atoms per molecule (bidentate ligand) have been described in numerous patents.

[007] However, new catalytic systems with better performance both with respect to catalytic activity and with respect to stability are always being sought for improving the general economics of the method.

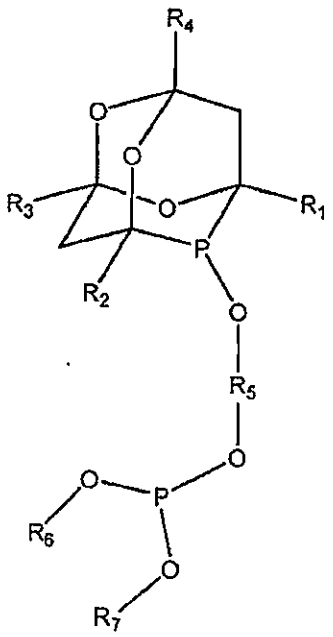
[008] One of the aims of the present invention is to propose a novel family of ligands which makes it possible to obtain, with transition metals, catalytic systems displaying good catalytic

CLAIMS

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



(I)

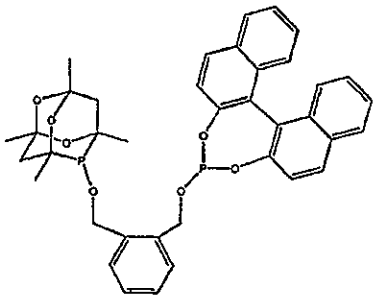


(II)

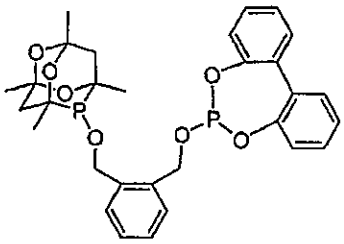
in which:

- R_1, R_2, R_3, R_4, R_6 and R_7, 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, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic ring 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 and R_8, which may be identical or different, represent a linear or branched aliphatic radical having from 1 to 12 carbon atoms which can contain heteroatoms, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic ring which can contain heteroatoms or several aromatic rings, condensed or joined together.

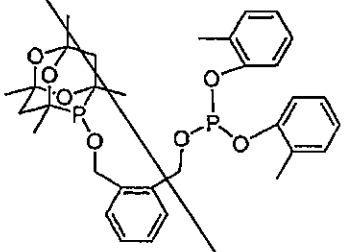
2. Compounds according to Claim 1, characterized in that they are selected from the group comprising the compounds with the following formulae:



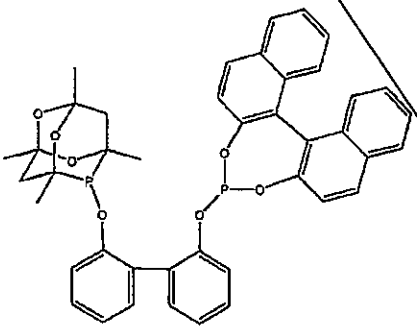
Ligand A



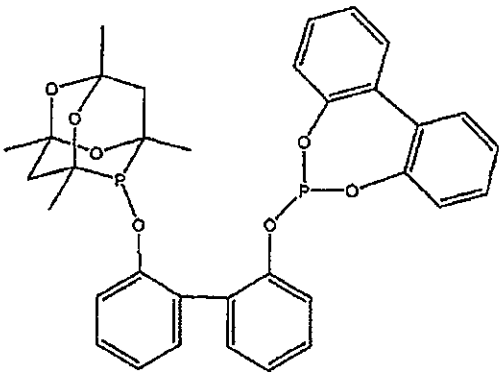
Ligand B



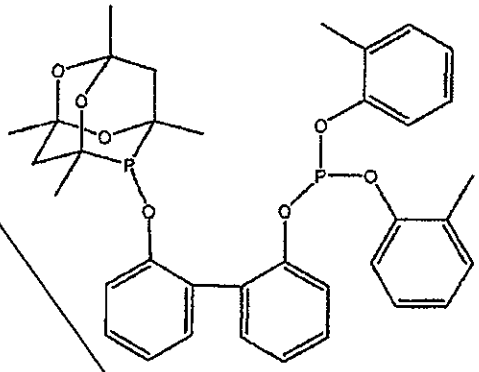
Ligand C



Ligand D

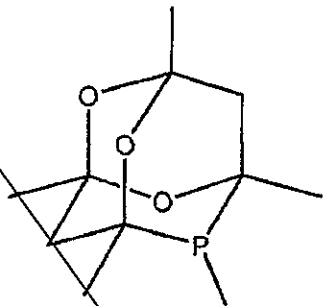


Ligand E

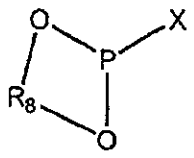


Ligand F

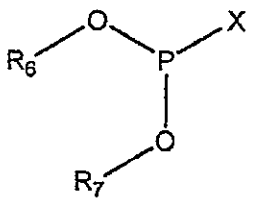
3. Method for preparing compounds according to Claim 1 or 2, characterized in that a compound obtained by reaction of the compound of formula OH-R_5-OH with an organo-alkali metal compound is reacted, on the one hand, with a CgPX compound of formula (1) below where X represents a halogen atom and, on the other hand, with a halogenated organophosphite corresponding to the phosphite residue linked to R5 in general formulae I and II, of formula (2) or (3)



(1)



(2)



(3)

4. Method according to Claim 3, characterized in that the compound obtained by reaction of the compound of formula OH-R_5-OH with an organoalkali metal compound is reacted with a CgPX compound of formula (1) in a first stage, and then the product of reaction with the halogenated organophosphite corresponding to the phosphite residue linked to R5 in general formulae I and II, of formula (2) or (3), is reacted in a second stage.

5. Catalytic system comprising a metallic element forming a complex with an organophosphorus compound according to Claim 1 or 2, characterized in that the complex corresponds to the following general formula (III):

$$M\,[L_f]_t \qquad (III)$$

in which:

M is a transition metal

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

t represents a number between 1 and 10 (inclusive).

6. Catalytic system according to Claim 5, 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.

7. 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 5 or 6, characterized in that the metallic element is nickel.

8. Method according to Claim 7, 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.

9. Method according to Claim 7 or 8, 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.

10. Method according to one of Claims 7 to 9, 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 phosphinite-phosphite of formula (I) or (II) and a cocatalyst consisting of at least one Lewis acid.

11. Method according to Claim 10, 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.

12. Method according to either of Claims 10 and 11, 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.

13. Method according to one of Claims 10 to 12, 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.

14. Method according to one of Claims 7 to 13, 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) or (II) and at least one compound of a transition metal.

ORGANOPHOSPHORUS COMPOUNDS, CATALYTIC SYSTEMS INCLUDING SAID COMPOUNDS, AND HYDROCYANATION METHOD USING SAID CATALYTIC SYSTEMS

[001] The present invention relates to organophosphorus compounds belonging to the phosphinite-phosphite family, their use in catalytic systems and methods of synthesis of organic compounds using said catalytic systems, notably the methods of hydrocyanation of ethylenically unsaturated organic compounds to compounds comprising at least one nitrile function.

[002] The reaction of hydrocyanation is, for example, described in French patent 1 599 761 which relates to a method of preparation of nitriles by addition of hydrocyanic acid to organic compounds having at least one ethylenic double bond, in the presence of a catalyst comprising nickel and an organophosphorus ligand, a triarylphosphite. This reaction can be carried out in the presence or absence of a solvent.

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[006] Numerous other catalytic systems have been proposed, generally comprising organophosphorus compounds belonging to the family of the phosphites, phosphonites, phosphinites and phosphines. These organophosphorus compounds can comprise one phosphorus atom per molecule and are described as monodentate ligands, or several phosphorus atoms per molecule, which are then called multidentate ligands. More particularly, numerous ligands containing two phosphorus atoms per molecule (bidentate ligand) have been described in numerous patents.

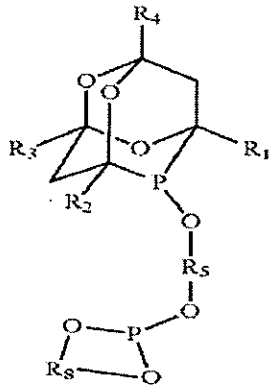
[007] However, new catalytic systems with better performance both with respect to catalytic activity and with respect to stability are always being sought for improving the general economics of the method.

[008] One of the aims of the present invention is to propose a novel family of ligands which makes it possible to obtain, with transition metals, catalytic systems displaying good catalytic

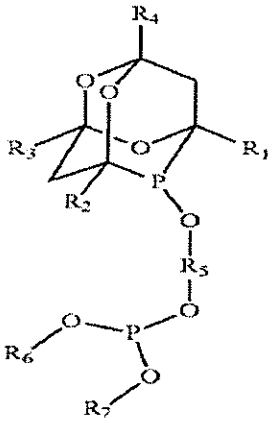
The invention claimed is:

1. An organophosphorus compound belonging to the phosphinite-phosphite family, wherein the compound corresponds to formulae (I) or (II):

(I)



(II)



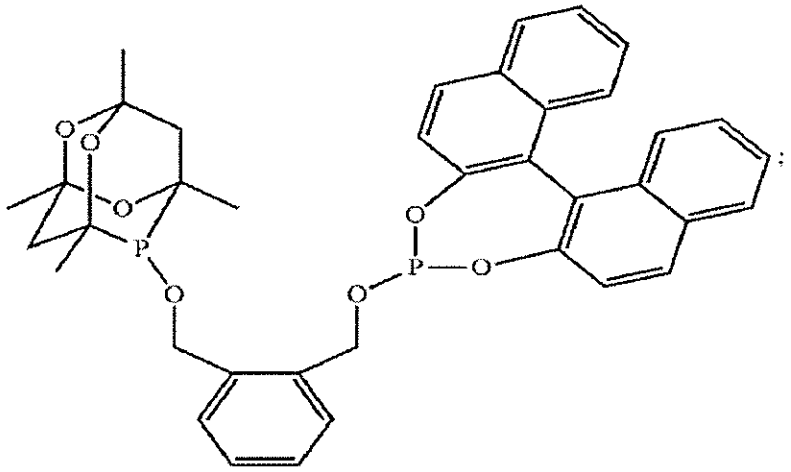
in which:

R_1, R_2, R_3, R_4, R_6 and R_7, which may can be identical or different, represent a hydrogen atom, a linear or branched alkyl radical having from 1 to 12 carbon atoms which can comprise heteroatoms, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic ring 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

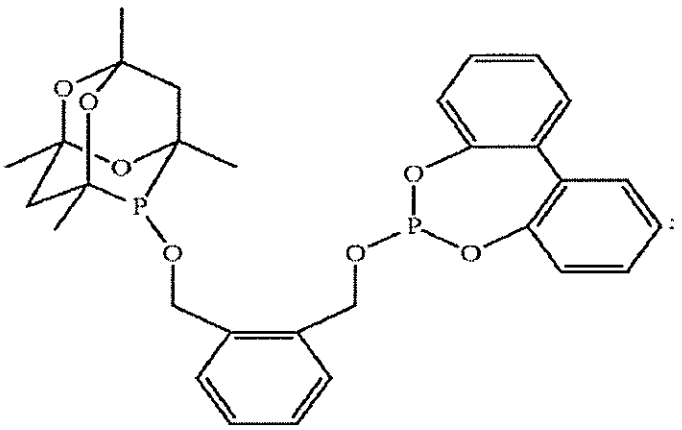
R_5 and R_8, which can be identical or different, represent a linear or branched aliphatic radical having from 1 to 12 carbon atoms which can comprise heteroatoms, a radical comprising a substituted or unsubstituted aromatic or cycloaliphatic ring which can comprise heteroatoms or several aromatic rings, condensed or joined together.

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

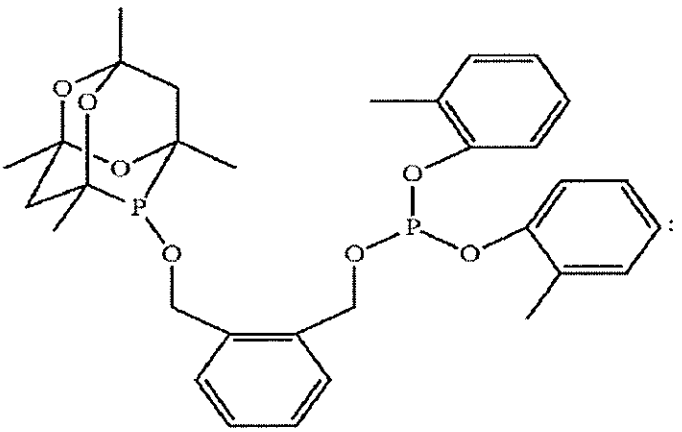
Ligand A



Ligand B

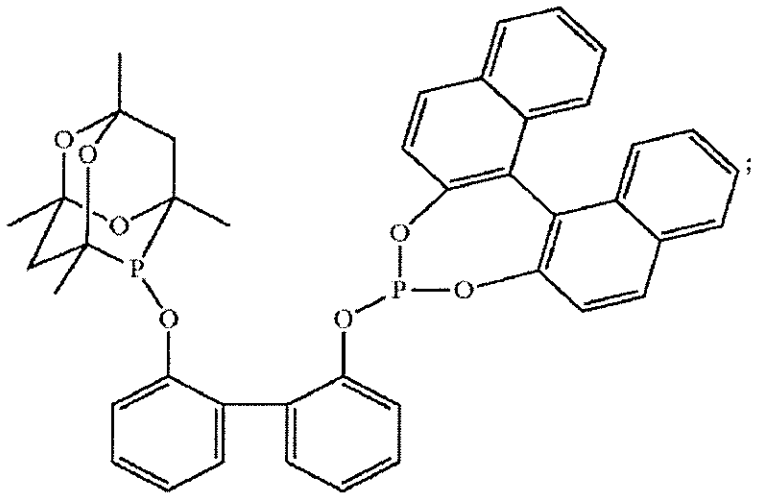


Ligand C

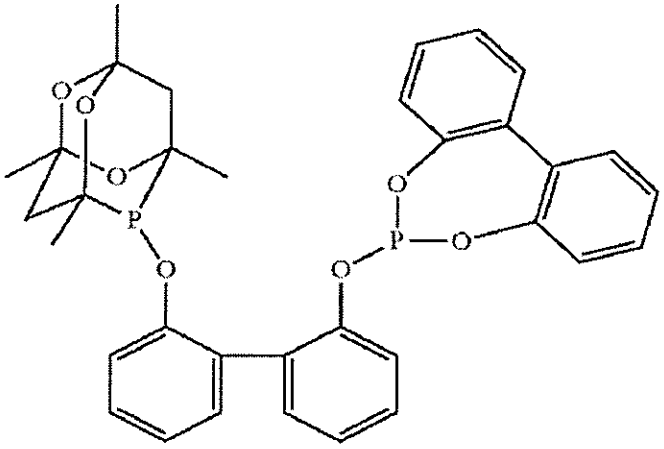


-continued

Ligand D

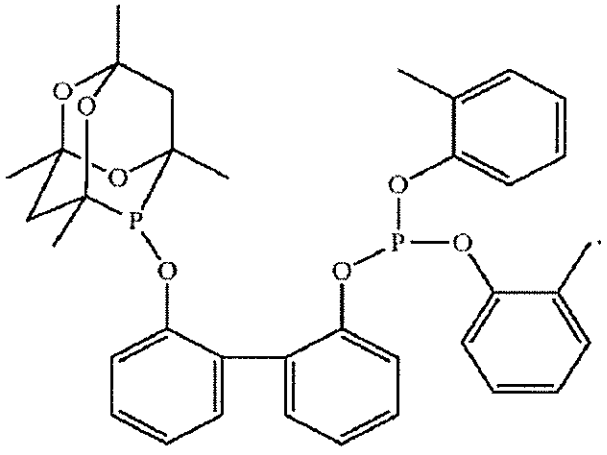


Ligand E



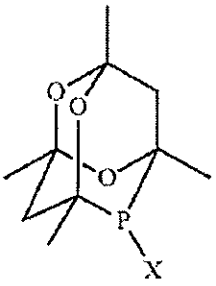
; and

Ligand F

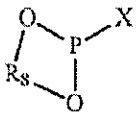


3. A method of preparing a compound according to claim 1, the method comprising reacting a compound obtained by reacting a compound of formula OH—R_5—OH with an organo-alkali metal compound with a CgPX compound of formula (1) below where X represents a halogen atom and reacting the resulting compound, with a halogenated organophosphite corresponding to the phosphite residue linked to R5 in general formulae I and II, of formula (2) or (3)

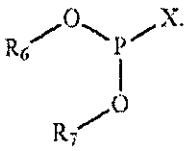
(1)



(2)



(3)



4. The method according to claim 3, wherein the compound obtained by reaction of the compound of formula OH—R_5—OH with an organoalkali metal compound is reacted with a CgPX compound of formula (1) in a first stage, and then the product of reaction with the a halogenated organophosphite corresponding to a phosphite residue linked to R5 in formulae I and II, of formula (2) or (3), is reacted in a second stage.

5. A catalytic system comprising a metallic element forming a complex with an organophosphorus compound according to claim 1, wherein the complex corresponds to the following formula (III):

$$M\,[L_f]_t \qquad \text{(III)}$$

in which:

M is a transition metal

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

t represents a number between 1 and 10 (inclusive).

6. The catalytic system according to claim 5, 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.

7. A method of hydrocyanation of a hydrocarbon compound, the method comprising performing the hydrocyanation of the hydrocarbon compound, wherein the hydrocarbon compound comprises at least one ethylenic unsaturation by reaction in a liquid medium with hydrogen cyanide in the presence of a catalytic system according to claim 5, wherein the metallic element is nickel.

8. The method according to claim 7, wherein the organic compound bearing at least one ethylenic unsaturation is a diolefin selected from the group consisting of butadiene, isoprene, hexadiene-1,5, and cyclooctadiene-1,5, an ethylenically unsaturated aliphatic nitrile, a monoolefin or a mixture of several of these compounds.

9. The method according to claim 7, wherein 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.

10. The method according to claim 7, wherein the ethylenically unsaturated compound is an ethylenically unsaturated nitrile compound 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 phosphinite-phosphite of formula (I) or (II) and a cocatalyst comprising at least one Lewis acid.

11. The method according to claim 10, wherein the ethylenically unsaturated nitrile compound is an ethylenically unsaturated aliphatic nitrile comprising a linear pentenenitrile or mixtures thereof.

12. The method according t claim 10, wherein the Lewis acid employed as cocatalyst is a compound of an element selected from the group consisting of group Ib, group IIb, group IIIa, group IIIb, group IVa, group IVb, group Va, group Vb, group VIb, group VIIb and group VIII of the periodic table.

13. The method according to claim **10**, wherein the Lewis acid is selected from the group consisting of cobalt chloride, ferrous chloride zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethyl-sulphonate, chloride of rare earth element, bromide of rare earth element, and an organometallic compound or a mixture thereof of Lewis acids.

14. The method according to claim **7**, further comprising, when hydrocyanating butadiene, a step of isomerizing methyl-2-butene-3-nitrile, present in the reaction mixture resulting from the hydrocyanation of butadiene, in the absence of hydrogen cyanide, in the presence of a catalyst bearing at least one compound of formula (I) or (II) and at least one compound of a transition metal.

15. The method according to claim **8**, wherein the ethyl-enically unsaturated aliphatic nitrile is a linear pentenenitrile.

16. The method according to claim **15**, wherein the linear pentenenitrile is pentene-3-nitrile or pentene-4-nitrile.

17. The method according to claim **8**, wherein the monoolefin is selected from the group consisting of styrene, methylstyrene, vinylnaphthalene, cyclohexene, and methyl-cyclohexene.

18. The method according to claim **11**, wherein the linear pentenenitrile is pentene-3-nitrile or pentene-4-nitrile.

19. The method according to claim **13**, wherein the rare earth element is selected from the group consisting of lantha-num, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium

20. The method according to claim **13**, wherein the Lewis acid is cobalt chloride, ferrous chloride, yttrium chloride or an organometallic compound selected from the group con-sisting of triphenylborane, and titanium isopropylate.