



DINITRILE PREPARATION METHOD

The present invention relates to a process for the preparation of dinitriles by hydrocyanation of
5 unsaturated nitrile compounds in the presence of a catalyst based on a metal element in the zero oxidation state and on organophosphorus ligands.

It relates more particularly to a process for the
10 recovery from the hydrocyanation medium of a catalyst for the hydrocyanation of unsaturated nitriles to dinitriles.

The hydrocyanation reaction is used industrially for
15 the synthesis of compounds comprising nitrile function groups from compounds comprising unsaturations. Thus, adiponitrile, which is an important chemical intermediate, in particular in the manufacture of hexamethylenediamine, a monomer for a number of
20 polymers, such as polyamide, is manufactured by hydrocyanation in two stages of butadiene or of a hydrocarbon cut, known as the C4 cut, comprising butadiene. In this manufacturing process, the two
25 reactions are carried out with catalytic systems composed essentially of the same entities, namely an organometallic coordination complex and at least one organophosphorus ligand of monodentate organophosphite type, such as tritolyl phosphite.

30 Numerous patents disclose this process for the manufacture of adiponitrile, and processes for the manufacture of the catalysts.

Furthermore, for the economics of the process, it is
35 important to be able to recover the catalytic system and to recycle it in the hydrocyanation stages.

Thus, Patent US 4 539 302 discloses a process for the recovery of the catalyst from the reaction medium obtained in the second stage of the process of the



preparation of adiponitrile, namely hydrocyanation of unsaturated nitriles to dinitriles.

5 This process for recovery by settling makes it possible to limit the losses of metal element and facilitates the control of the organophosphorus ligand/metal element ratio, which is low for the hydrocyanation of unsaturated nitriles. Thus, it is also possible to recover a catalytic system with a high ligand/metal
10 element ratio, which makes possible recycling and reuse of the catalytic system in stages for the manufacture of catalyst and/or in stages for the hydrocyanation of butadiene or the isomerization of branched pentenenitriles.

15 Numerous other organophosphorus ligands have been provided for the catalysis of these hydrocyanation reactions.

20 Thus, bidentate ligands of organophosphite, organophosphinite, organophosphonite and organophosphine type have been disclosed in numerous patents, such as, for example, Patents WO 99/06355, WO 99/06356, WO 99/06357, WO 99/06358, WO 99/52632, WO 99/65506,
25 WO 99/62855, US 5 693 843, WO 96/1182, WO 96/22968, US 5 981 772, WO 01/36429, WO 99/64155 or WO 02/13964.

Finally, provision has also been made, by Patent WO 03/11457, to use a mixture of mono- and bidentate
30 ligands for the catalysis of hydrocyanation reactions. The use of such a mixture makes it possible to facilitate the synthesis of the catalyst and the formation of the organometallic complex, in particular with respect to processes for the synthesis of
35 organometallic complexes with bidentate ligands.

In the case of mixtures of ligands, it is also important to be able to recover the catalyst without losing ligands or metal element.

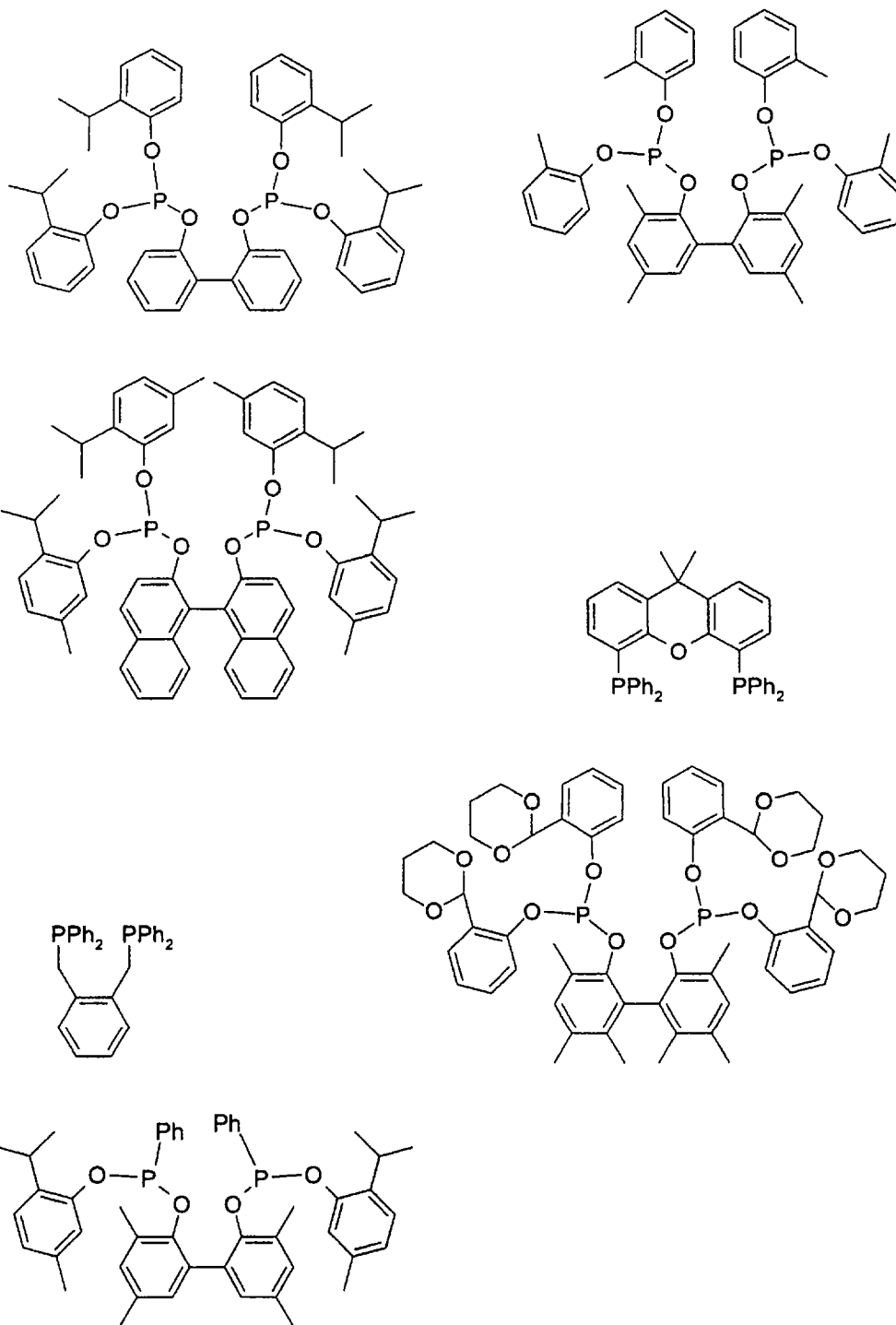
One of the aims of the present invention is to provide, in a process for the preparation of dinitriles, a process for the recovery of a catalyst formed by a mixture of mono- and bidentate ligands and to be able to reuse the catalyst thus recovered in the hydrocyanation and/or isomerization stages.

To this end, the invention provides a process for the preparation of dinitrile compounds by hydrocyanation of unsaturated mononitrile compounds in the presence of a catalytic system comprising an organometallic complex formed from a metal element and from a mixture of organophosphorus ligands comprising at least one monodentate organophosphite compound and at least one bidentate organophosphorus compound chosen from the group consisting of organophosphites, organophosphinites, organophosphonites and organophosphines, and optionally a promoter, the said process comprising a recovery of the catalytic system, characterized in that the process consists in controlling the concentration of unsaturated nitriles in the reaction medium resulting from the hydrocyanation reaction in order to obtain a concentration by weight of unsaturated nitriles of less than 20% in the said medium, in feeding the said medium to a stage of settling into two upper and lower phases, and in separating the two phases, the lower phase being at least partially recycled to the said hydrocyanation stage and the upper phase being subjected to a liquid/liquid extraction in order to separate the organometallic complex and the organophosphorus compounds present in the said upper phase from the dinitriles.

Mention may be made, as monodentate organophosphite ligand suitable for the invention, by way of examples, of triphenyl phosphite, tritolyl phosphite (TTP) or tricymenyl phosphite.

Mention may be made, as bidentate ligands which are suitable for the invention, of the compounds with the following structures, in which Ph means phenyl:

5



According to a preferred characteristic of the
10 invention, the catalyst present in the reaction medium

generally comprises a number of moles of bidentate ligand, expressed as number of phosphorus atoms with respect to a metal element atom, of between 1 and 4, while that of monodentate ligand, expressed as number of phosphorus atoms, is between 4 and 7.

In the present text, the expression "ligand/nickel" always refers to the ratio of all the molecules of mono- and/or bidentate ligands with respect to the number of nickel atoms, unless expressly indicated otherwise.

The metal elements exhibiting a catalytic effect in a hydrocyanation reaction are, for example, nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium or cerium. Nickel is the preferred catalytic element. For greater clarity, the metal element will be denoted by the term "nickel" in the continuation of the present text, without this being a limiting meaning.

Furthermore, in the hydrocyanation reaction of the unsaturated nitriles, a promoter or cocatalyst is generally used. Lewis acids are generally used as preferred promoters.

Use may in particular be made, by way of examples, of the Lewis acids cited in the work edited by G. A. Olah, "Friedel-Crafts and Related Reactions", Volume I, pages 191 to 197 (1963).

The Lewis acids which can be employed as cocatalysts in the present process are advantageously chosen from compounds of the elements from Groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements. These compounds are generally salts, in particular halides, such as chlorides or bromides, sulphates, sulphonates, haloalkylsulphonates, perhaloalkylsulphonates, in particular fluoroalkylsulphonates or perfluoroalkyl-

sulphonates, haloacetates, perhaloacetates,
carboxylates and phosphates.

Mention may be made, as non-limiting examples of such
5 Lewis acids, of zinc chloride, zinc bromide, zinc
iodide, manganese chloride, manganese bromide, cadmium
chloride, cadmium bromide, stannous chloride, stannous
bromide, stannous sulphate, stannous tartrate, indium
chloride, indium trifluoromethylsulphonate, indium
10 trifluoroacetate, the chlorides or bromides of rare
earth elements, such as lanthanum, cerium,
praseodymium, neodymium, samarium, europium,
gadolinium, terbium, dysprosium, hafnium, erbium,
thulium, ytterbium and lutetium, cobalt chloride,
15 ferrous chloride or yttrium chloride.

Use may also be made, as Lewis acid, of compounds such
as triphenylborane or titanium tetraisopropoxide.

20 It is possible, of course, to employ mixtures of
several Lewis acids.

Preference is very particularly given, among Lewis
acids, to zinc chloride, zinc bromide, stannous
25 chloride, stannous bromide, triphenylborane, indium
trifluoromethylsulphonate, indium trifluoroacetate and
zinc chloride/stannous chloride mixtures.

The Lewis acid cocatalyst employed generally represents
from 0.005 to 50 mol per mole of nickel.

30 According to a preferred characteristic of the
invention, the medium fed to the settling stage is
cooled to a temperature of between 25°C and 75°C,
advantageously between 30°C and 55°C.

35 In order to obtain settling and separation into two
phases of the reaction medium, it is advantageous for
the concentration by weight of nickel in the reaction

medium fed to the settling stage to be between 0.2 and 2%.

In order to obtain such a nickel concentration, it may
5 be necessary to add a certain amount of catalytic
system to the reaction medium exiting from the
hydrocyanation stage. This is because the concentration
of nickel used in the reaction medium when the nickel
is used in combination with a bidentate ligand may be
10 very low, such as, for example, of the order of 100 to
2000 mg of nickel/kg of reaction medium.

According to a preferred embodiment of the invention,
the concentration of nickel in the medium resulting
15 from the hydrocyanation stage is adjusted to a suitable
and desired value by introduction of at least a portion
of the lower phase obtained in the settling stage.

According to yet another preferred characteristic of
20 the invention, the concentration of unsaturated
nitriles in the medium fed to the settling stage is
less than or equal to 20% by weight, advantageously
between 4 and 20% by weight.

25 The control or the production of such a concentration
can be carried out in different ways:

- A first possibility is to control and define the
degree of conversion of the unsaturated nitriles in the
30 hydrocyanation stage in order to obtain, in the
reaction medium at the end of the reaction or exiting
from the said reactor, a concentration of unsaturated
nitriles of less than or equal to 20% by weight.

35 - According to another embodiment of the invention,
the reaction medium exiting from the hydrocyanation
stage is fed to a stage of distillation under reduced
pressure or flashing of the unconverted unsaturated
nitriles. This stage makes it possible to control the

concentration of the unsaturated nitriles in the medium fed to the settling stage.

To avoid losses of nickel by precipitation in the distillation bottoms, it is advantageous for the bottom temperature of this distillation stage to be less than 140°C. The term "distillation bottom temperature" is understood to mean the temperature of the medium which is found in the boiler but also the temperature of the walls of the said boiler.

In this embodiment comprising the stage of distillation of a portion of the unsaturated nitriles, the adjusting or control of the concentration of nickel in the distillation bottoms fed to the settling stage can be carried out by recycling a portion of the lower phase from the settling. This recycling is advantageously carried out before feeding the medium to the distillation stage.

According to the process of the invention, the lower phase obtained in the decanter or heavy phase comprises most of the nickel and of the bidentate ligand, and a portion of the monodentate ligand. However, as the coefficients for partition of the metal element and of the organophosphorus ligands between the two phases are different, the molar ratio of ligands/metal element atoms will be low in the lower phase and high in the upper phase. In addition, the process of the invention makes it possible to use most of the bidentate ligand preferentially in the stage of hydrocyanation of the unsaturated nitriles to thus obtain a high selectivity for linear dinitriles.

According to another characteristic of the process of the invention, the upper phase recovered in the settling stage comprises a ligand/nickel molar ratio, expressed as number of phosphorus atoms, advantageously of greater than 8.

According to the invention, the total recovery of the catalyst and of the ligands is carried out by a liquid/liquid extraction of these using an extraction
5 solvent which is immiscible with the dinitriles.

Mention may be made, as suitable extraction solvent, by way of examples, of saturated, linear or cyclic, aliphatic hydrocarbons, such as hexane, heptane,
10 octane, cyclohexane, cyclopentane, cycloheptane and more generally cycloparaffins or analogues. Cyclohexane is the preferred extraction solvent.

After extraction, the cyclohexane solution of the organometallic complex and of the ligands is fed to a
15 stage of evaporation or distillation of the extraction solvent. To limit the loss of nickel by precipitation, it is important for the ligand/nickel molar ratio, expressed as number of phosphorus atoms with respect to
20 the number of nickel atoms, to be high and in particular greater than 8. This high ratio is, in the process of the invention, obtained in the settling stage by virtue of the coefficients of partition of the various chemical entities between the two upper and
25 lower phases.

In addition, in order to limit losses of nickel, the bottom temperature of the stage of distillation or evaporation at atmospheric pressure or under a pressure
30 of greater than atmospheric pressure is advantageously less than 180°C. The term "bottom temperature" is understood to mean the temperature of the medium present in the boiler of the said stage and the temperature of the walls of the said boiler.

35

The process for recovery of the catalyst of the invention thus makes possible complete recovery of the catalyst and of the organophosphorus ligands.

The invention applies generally to a process for the conversion of unsaturated mononitriles to dinitriles which constitutes the second stage of a process for the manufacture of dinitrile compounds by double
5 hydrocyanation of diolefins, such as butadiene. This process comprises a first stage of hydrocyanation of the diolefin to unsaturated nitriles carried out with a catalyst which is advantageously composed of the same compounds as those of the catalytic system used in the
10 second stage with, possibly, different ratios between the compounds. This first stage is generally combined with an isomerization reaction of the branched mononitriles formed in order to convert them to linear unsaturated mononitriles which will be fed to the
15 second stage. This isomerization is carried out with a catalytic system equivalent to that of the first stage and in the absence of hydrogen cyanide.

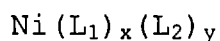
In such a process comprising the two stages, the
20 catalyst and the ligands recovered after evaporation of the extraction solvent are advantageously recycled, either in a stage of hydrocyanation of the diolefins (or of a C4 hydrocarbon cut) or in a stage of preparation of the catalyst, and/or to the
25 isomerization of the branched unsaturated nitriles or alternatively added to the catalyst recovered from the lower settling phase before introduction into the stage of hydrocyanation of the unsaturated nitrile compounds.

30 In one embodiment of the invention, at least a portion of the catalyst recovered after evaporation of the extraction solvent is introduced into the stage of isomerization of the branched nitriles and then optionally into the stage of hydrocyanation of the
35 dienes. The catalyst recovered after the latter stage can be recycled directly in the liquid/liquid extraction stage or the settling stage.

In this embodiment, the catalyst used in the isomerization stage and the stage of hydrocyanation of

the dienes comprises a low proportion of bidentate ligand, thus making it possible to reduce the losses of this ligand due, for example, to a hydrolysis reaction or to a reaction with compounds present in the dienes, such as tert-butylcatechol (TBC) present in butadiene.

The present invention preferably applies to the hydrocyanation of unsaturated nitriles comprising from 3 to 8 carbon atoms and more preferably of 3-pentenitrile and/or 4-pentenitrile for the production of adiponitrile with use of a catalyst of the type represented by the following formula:



in which L_1 represents a monodentate ligand and L_2 a bidentate ligand,

x and y represent decimal numbers ranging from 0 to 4, the sum $x + 2y$ being equal to 3 or 4.

The catalyst can be composed of a mixture of complexes corresponding to the above general formula.

The catalytic system or the reaction medium can also comprise an amount of mono- and/or bidentate organophosphorus ligand in the free form, that is to say not bonded to the nickel.

This reaction is disclosed in particular in Patent US 4 371 474.

This hydrocyanation can be carried out starting from pentenenitriles synthesized by hydrocyanation of butadiene in a separate plant or in a first stage positioned in series with the stage of hydrocyanation of the pentenenitriles, as described above.

It is possible to use the catalytic system described above solely in the stage of hydrocyanation of the unsaturated nitriles, the catalytic system used in the first stage of hydrocyanation of butadiene and the

isomerization stage being different. However, it is preferable to use in these different stages a catalytic system composed of the same compounds, such as metal element and organophosphorus ligands, optionally
5 according to different ratios between the compounds with different concentrations.

The catalytic systems of the invention can be obtained by formation in a first stage of an organometallic
10 complex between the nickel and the monodentate ligand. Processes for the formation of such complexes are disclosed, for example, in Patents US 3 903 120 and US 4 416 825.

In a second stage, the bidentate ligand is added to the
15 medium comprising the said organometallic complex.

Other details and advantages of the invention will become more clearly apparent in the light of the examples given below solely by way of indication and
20 illustration.

Abbreviations:

PN: pentenenitriles

DN: dinitriles (mixtures of dinitriles AdN, MGN and ESN, predominantly comprising AdN)

AdN: adiponitrile

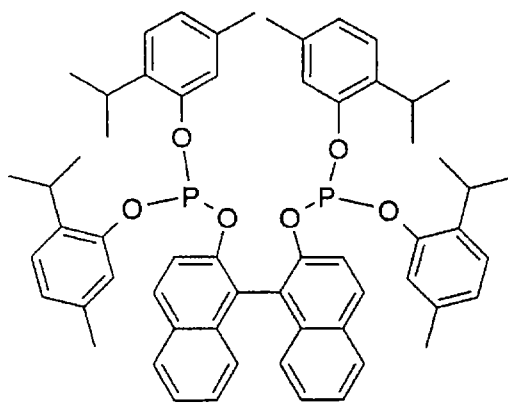
MGN methylglutaronitrile

ESN: ethylsuccinonitrile

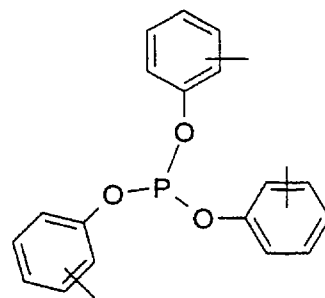
Example 1:

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Hydrocyanation of pentenenitriles was carried out using a catalytic system comprising an organometallic complex obtained from nickel in the zero oxidation state, from a promoter ZnCl_2 and from organophosphorus compounds
30 with the following formulae:



A



TTP

After flashing the PNs, the reaction medium obtained has the following composition (% expressed by weight; the ratios are molar ratios):

Ni = 0.58%

TTP/Ni = 5

Ligand **A**/Ni = 1.2

10 P/Ni = 7.4

DN = 64.0%

PN = 6.4%

ZnCl₂ = 0.16%

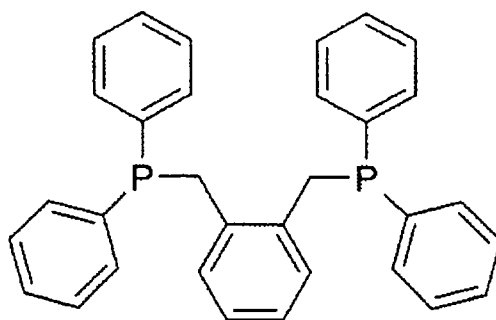
15 The mixture is cooled to 50°C: separation into two liquid phases is observed. The dense phase comprises approximately 83% of the Ni(0) and approximately 73% of the ligand **A**. The TTP/Ni ratio is approximately 3 in the lower phase and approximately 15 in the upper phase. 20 The TTP/ligand **A** molar ratio is close to 8 in the upper phase.

The upper phase, which comprises more than 90% by weight of adiponitrile, is subjected to a liquid/liquid extraction with cyclohexane. The cyclohexane solution 25 obtained is evaporated. The recovery of the catalytic system as residue from the evaporation is quantitative.

Example 2: Settling of the TTP/ligand **B** mixed system

Example 1 is repeated but replacing the ligand **A** by the ligand **B** with the following formula:

5



B

After flashing the PN_s, the reaction medium obtained has the following composition (% expressed by weight; the ratios are molar ratios):

10

Ni = 0.70%

TTP/Ni = 4

Ligand **B**/Ni = 1

15 P/Ni = 6

DN = 67.7%

PN = 6.7%

ZnCl₂ = 0.17%

20 The medium is cooled to 50°C: separation into two liquid phases is observed. The dense phase comprises approximately 70% of the Ni(0) and approximately 70% of the ligand **B**. The TTP/Ni ratio is less than 2 in the dense phase and approximately equal to 9 in the light phase.

25 phase. The TTP/ligand **B** ratio is close to 9 in the light phase.

The upper phase is subjected to a liquid/liquid extraction with cyclohexane. The cyclohexane solution is evaporated. The recovery of the catalytic system as

30 residue from the evaporation is quantitative.

CLAIMS

1. Process for the preparation of dinitrile compounds by hydrocyanation of unsaturated mononitrile compounds in the presence of a catalytic system comprising an organometallic complex formed from a metal element and from a mixture of organophosphorus ligands comprising at least one monodentate organophosphite compound and at least one bidentate organophosphorus compound chosen from the group consisting of organophosphites, organophosphinites, organophosphonites and organophosphines, and optionally a promoter, the said process comprising a recovery of the catalytic system, characterized in that the process consists in controlling the concentration of unsaturated nitriles in the reaction medium resulting from the hydrocyanation reaction in order to obtain a concentration by weight of unsaturated nitriles of less than 20% in the said medium, in feeding the said medium to a stage of settling into two upper and lower phases, and in separating the two phases, the lower phase being at least partially recycled to a hydrocyanation stage and the upper phase being subjected to a liquid/liquid extraction in order to extract the organometallic complex and the organophosphorus compounds present in the said phase.
2. Process according to Claim 1, characterized in that the reaction medium is cooled to a temperature of between 25°C and 75°C before being introduced into the settling stage.
3. Process according to either of Claims 1 and 2, characterized in that the concentration by weight of nickel in the medium fed to the settling stage is between 0.2 and 2%.

4. Process according to one of the preceding claims, characterized in that the concentration by weight of unsaturated nitriles in the medium fed to the settling stage is between 4% and 20% by weight.
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5. Process according to one of the preceding claims, characterized in that the concentration of unsaturated nitriles in the reaction medium resulting from the hydrocyanation stage is less
10 than 20% by weight.
6. Process according to one of Claims 1 to 5, characterized in that the reaction medium resulting from the hydrocyanation stage is fed to
15 a stage of distillation of the unsaturated nitriles, the distillation bottoms being fed to the settling stage.
7. Process according to one of Claims 1 to 6,
20 characterized in that the lower phase from the settling stage is at least partially recycled in the reaction medium resulting from the hydrocyanation.
- 25 8. Process according to Claim 7, characterized in that a portion of the said lower phase is recycled in the reaction medium resulting from the hydrocyanation, before the stage of distillation of the unsaturated nitriles.
30
9. Process according to one of the preceding claims, characterized in that the number of moles of bidentate ligand, expressed as number of phosphorus atoms with respect to a metal element
35 atom, is between 1 and 4 in the hydrocyanation medium.
10. Process according to one of the preceding claims, characterized in that the number of moles of

monodentate ligand, expressed as number of phosphorus atoms with respect to a metal element atom, in the hydrocyanation medium is between 4 and 7.

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11. Process according to one of the preceding claims, characterized in that the solvent used for carrying out the liquid/liquid extraction of the catalyst and of the organophosphorus compounds present in the upper phase is chosen from the group consisting of saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbons.

12. Process according to one of the preceding claims, characterized in that the catalyst and the organophosphorus ligands extracted in the liquid/liquid extraction stage are recovered by evaporation of the extraction solvent.

13. Process according to Claim 11 and Claim 12, characterized in that the extraction solvent is chosen from the group consisting of hexane, heptane, octane, cyclohexane, cyclopentane and cycloheptane.

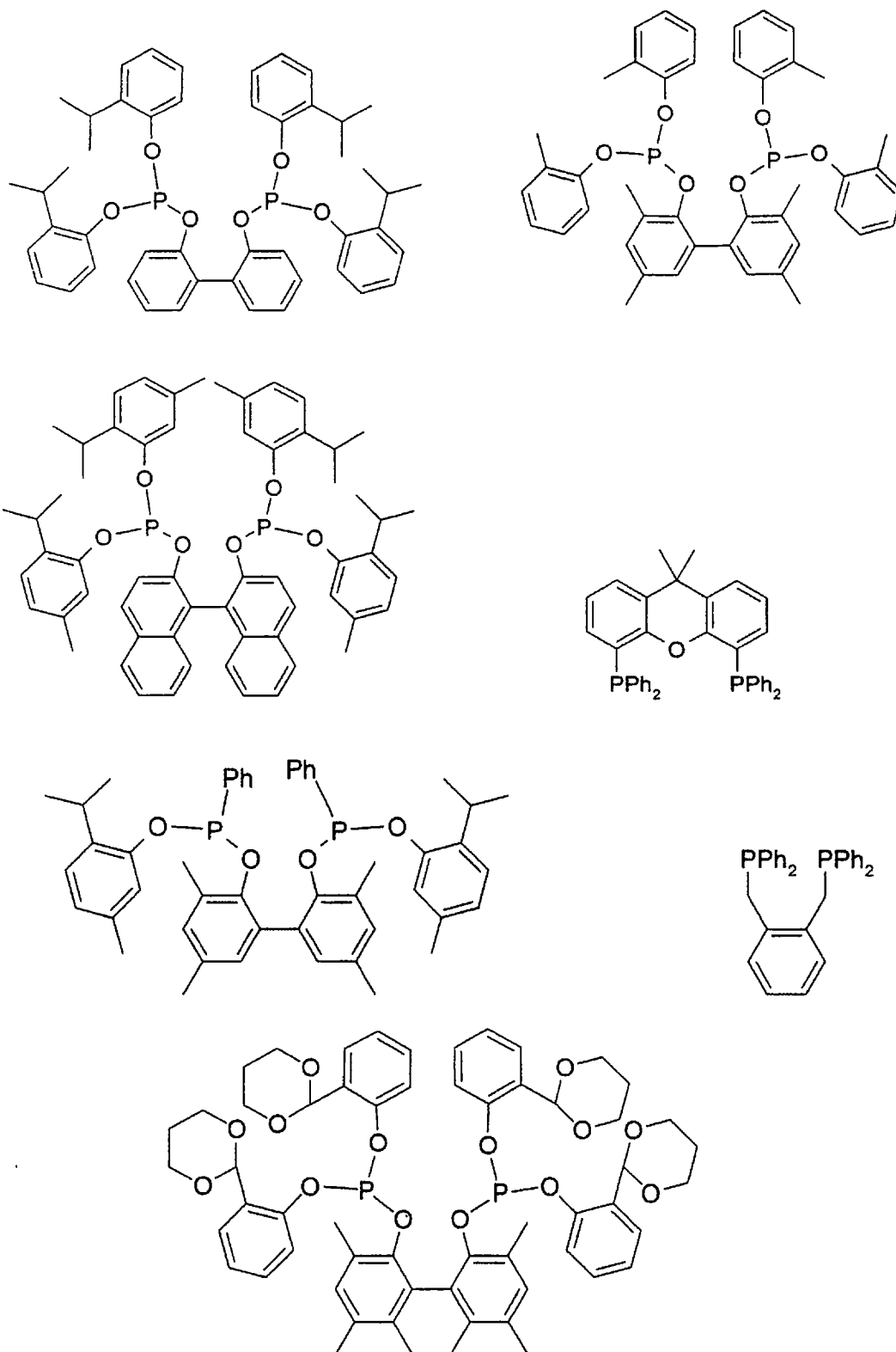
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14. Process according to one of the preceding claims, characterized in that the number of moles of organophosphorus ligands, expressed as number of phosphorus atoms, in the medium fed to the liquid/liquid extraction stage with respect to a metal element atom is greater than 8.

15. Process according to one of the preceding claims, characterized in that the monodentate ligand is a compound chosen from the group consisting of triphenyl phosphite, tritolyl phosphite and tricymenyl phosphite.

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16. Process according to one of the preceding claims,
characterized in that the bidentate
organophosphorus ligand is chosen from the group
consisting of organophosphites,
5 organophosponites, organophosphinites and
organophosphines.
17. Process according to Claim 16, characterized in
that the bidentate organophosphorus ligand is
10 chosen from the group consisting of the compounds
with the following structures, in which Ph means
phenyl:



18. Process according to one of the preceding claims,
 5 characterized in that the catalytic system
 comprises a promoter or cocatalyst composed of a
 Lewis acid.

19. Process according to Claim 18, characterized in that the promoter is chosen from the group consisting of compounds of the elements from Groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements. These compounds are generally salts, in particular halides, such as chlorides or bromides, sulphates, sulphonates, haloalkylsulphonates, perhaloalkylsulphonates, in particular fluoroalkylsulphonates or perfluoroalkylsulphonates, haloacetates, perhaloacetates, carboxylates and phosphates, zinc chloride, arylboranes, fluoroacetates and perfluoroacetates, fluoroalkylsulphonates and perfluoroalkylsulphonates.
20. Process according to Claim 19, characterized in that the Lewis acid is chosen from the group consisting of zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium chloride, indium trifluoromethylsulphonate, indium trifluoroacetate, the chlorides or bromides of rare earth elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride, yttrium chloride, triphenylborane, titanium tetraisopropoxide and their mixtures.
21. Process according to one of Claims 6 to 20, characterized in that the column bottom temperature in the stage of distillation of the unsaturated nitriles is less than 140°C.

22. Process according to one of the preceding claims, characterized in that the unsaturated nitrile is a linear or branched aliphatic compound comprising from 3 to 8 carbon atoms.
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23. Process according to Claim 22, characterized in that the unsaturated nitrile is a pentenenitrile.
24. Process according to one of the preceding claims, characterized in that the catalytic system solution recovered after the stage of liquid/liquid extraction is subjected to distillation of the extraction solvent, the bottom temperature of this distillation being less than 180°C.
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- 15
25. Process for the manufacture of dinitrile compounds from diolefins, comprising a first stage of hydrocyanation of the diolefin to give unsaturated mononitriles, optionally an isomerization reaction of the branched unsaturated mononitriles formed in the first stage, and a second stage of hydrocyanation of the unsaturated mononitriles to give dinitrile compounds according to one of Claims 1 to 24.
- 20
- 25
26. Process according to Claim 25, characterized in that the catalyst recovered from the upper phase of the settling stage is at least partially recycled in the isomerization reaction and/or to the first hydrocyanation stage.
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27. Process according to Claim 26, characterized in that the catalyst recovered from the upper phase of the settling stage is at least partially recycled in the isomerization reaction and then in the first hydrocyanation stage.
- 35

28. Process according to Claim 27, characterized in that the catalyst recovered from the hydrocyanation medium of the first stage is fed to the settling stage or to the liquid/liquid extraction stage.
- 5