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Phosphonites

The present invention relates to novel phosphonites, in particular chelating phosphonites, methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, a process for preparing the complexes, their use as catalyst and processes carried out in the presence of such transition metal complexes as catalysts.

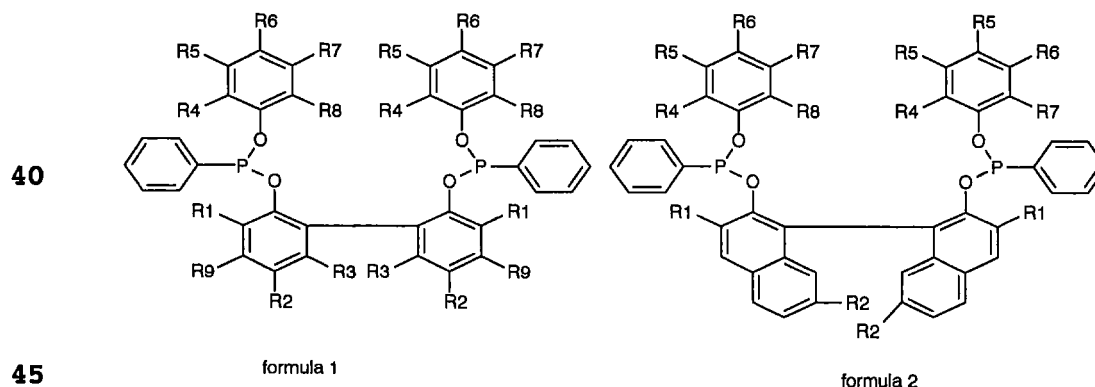
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Chelating phosphonites, nickel complexes containing such phosphonites as ligands and the use of such complexes as catalysts are known.

15 WO 99/13983 and WO 99/64155 describe a process for the hydrocyanation of unsaturated organic compounds and the isomerization of nitriles in the presence of nickel(0) complexes containing chelating phosphonites as ligands. The chelating phosphonites described do have a good stability under the
20 corresponding reaction conditions. It would be desirable to improve the stability of the chelating phosphonite ligands to increase the operating life of the catalyst. Furthermore, an improvement in the selectivity of the catalyst, for example to 3-pentenitrile in the hydrocyanation of butadiene or to
25 adiponitrile in the hydrocyanation of 3-pentenitrile, and an improvement in the space-time yield are desirable.

It is an object of the present invention to provide phosphonites which are suitable as chelating phosphonites and display high
30 stability, high reactivity and high selectivity when used as catalysts in the hydrocyanation of unsaturated organic compounds. We have found that this object is achieved by phosphonites I of the formula 1 or 2

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where

R1, R2 are each, independently of one another, hydrogen, an alkyl or alkylene group having from 1 to 8 carbon atoms or an alkoxy
5 group having from 1 to 8 carbon atoms, with the proviso that R1 and R2 are not simultaneously H,

R3 is H or methyl,

10 R4 is t-butyl,

R5, R6, R7, R8, R9 are each, independently of one another, H or an alkyl or alkylene group having from 1 to 8 carbon atoms.

15 The present invention also provides methods of preparing them, provides for their use as ligands in transition metal complexes, provides novel transition metal complexes and processes for preparing them, provides for their use as catalyst and provides processes carried out in the presence of such transition metal
20 complexes as catalyst.

According to the present invention, the radicals R1 and R2 are each, independently of one another, hydrogen, an alkyl or alkylene group having from 1 to 8 carbon atoms, or an alkoxy
25 group having from 1 to 8 carbon atoms, with the proviso that R1 and R2 are not simultaneously H.

As alkyl or alkylene group having from 1 to 8 carbon atoms, preference is given to an alkyl group having from 1 to 8 carbon
30 atoms, in particular from 1 to 4 carbon atoms, advantageously selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, i-butyl and t-butyl, in particular from the group consisting of methyl, ethyl, n-propyl, i-propyl and t-butyl.

35 As alkoxy group having from 1 to 8 carbon atoms, preference is given to an alkoxy group having from 1 to 4 carbon atoms, advantageously selected from the group consisting of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, s-butoxy, i-butoxy and
40 t-butoxy, in particular methoxy.

In the case of a phosphonite I of the formula 1, an advantageous, preferred embodiment provides for R1 and R2 each to be, independently of one another, an alkyl group which has from 1 to
45 4 carbon atoms and is preferably selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl,

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s-butyl, i-butyl and t-butyl, in particular from the group consisting of methyl, ethyl, n-propyl, i-propyl and t-butyl.

In the case of a phosphonite I of the formula 2, an advantageous,
 5 preferred embodiment provides for R1 and R2 each to be, independently of one another, hydrogen, an alkyl group which has from 1 to 4 carbon atoms and is preferably selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, i-butyl and t-butyl, in particular from the group
 10 consisting of methyl, ethyl, n-propyl, i-propyl and t-butyl, or an alkoxy group which has from 1 to 4 carbon atoms and is advantageously selected from the group consisting of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, s-butoxy, i-butoxy and t-butoxy, in particular methoxy. In a particularly preferred
 15 embodiment, R1 can be an alkyl group which has from 1 to 4 carbon atoms and is preferably selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, i-butyl and t-butyl, in particular from the group consisting of methyl, ethyl, n-propyl, i-propyl and t-butyl, particularly preferably
 20 methyl, and R2 can be hydrogen or an alkoxy group which has from 1 to 4 carbon atoms and is advantageously selected from the group consisting of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, s-butoxy, i-butoxy and t-butoxy, in particular methoxy.

25 According to the present invention, R3 is H or a methyl group.

According to the present invention, R4 is a t-butyl group.

According to the present invention, the radicals R5, R6, R7, R8
 30 and R9 are each, independently of one another, hydrogen or an alkyl or alkylene group having from 1 to 8 carbon atoms.

Particularly preferred phosphonites I of the formula 1 are those in which the radicals R1, R2, R3, R4, R5, R6, R7, R8 and R9 are
 35 as shown in Table 1 below.

No.	R1	R2	R3	R4	R5	R6	R7	R8	R9
1	Me	Me	H	t-Bu	H	H	H	H	H
2	Et	Et	H	t-Bu	H	H	H	H	H
40 3	n-Pr	n-Pr	H	t-Bu	H	H	H	H	H
4	t-Bu	t-Bu	H	t-Bu	H	H	H	H	H
5	Et	Me	H	t-Bu	H	H	H	H	H
6	n-Pr	Me	H	t-Bu	H	H	H	H	H
7	t-Bu	Me	H	t-Bu	H	H	H	H	H
8	Me	Me	H	t-Bu	H	H	H	H	Me
45 9	t-Bu	Me	Me	t-Bu	H	H	H	H	H
10	Me	Me	H	t-Bu	H	t-Bu	H	H	H
11	Et	Et	H	t-Bu	H	t-Bu	H	H	H

	12	n-Pr	n-Pr	H	t-Bu	H	t-Bu	H	H	H
	13	t-Bu	t-Bu	H	t-Bu	H	t-Bu	H	H	H
	14	Et	Me	H	t-Bu	H	t-Bu	H	H	H
	15	n-Pr	Me	H	t-Bu	H	t-Bu	H	H	H
5	16	t-Bu	Me	H	t-Bu	H	t-Bu	H	H	H
	17	Me	Me	H	t-Bu	H	t-Bu	H	H	Me
	18	t-Bu	Me	Me	t-Bu	H	t-Bu	H	H	H
	19	Me	Me	H	t-Bu	H	Me	H	H	H
	20	Et	Et	H	t-Bu	H	Me	H	H	H
10	21	n-Pr	n-Pr	H	t-Bu	H	Me	H	H	H
	22	t-Bu	t-Bu	H	t-Bu	H	Me	H	H	H
	23	Et	Me	H	t-Bu	H	Me	H	H	H
	24	n-Pr	Me	H	t-Bu	H	Me	H	H	H
	25	t-Bu	Me	H	t-Bu	H	Me	H	H	H
	26	Me	Me	H	t-Bu	H	Me	H	H	Me
15	27	t-Bu	Me	Me	t-Bu	H	Me	H	H	H
	28	Me	Me	H	t-Bu	H	H	Me	H	H
	29	Et	Et	H	t-Bu	H	H	Me	H	H
	30	n-Pr	n-Pr	H	t-Bu	H	H	Me	H	H
	31	t-Bu	t-Bu	H	t-Bu	H	H	Me	H	H
20	32	Et	Me	H	t-Bu	H	H	Me	H	H
	33	n-Pr	Me	H	t-Bu	H	H	Me	H	H
	34	t-Bu	Me	H	t-Bu	H	H	Me	H	H
	35	Me	Me	H	t-Bu	H	H	Me	H	Me
	36	t-Bu	Me	Me	t-Bu	H	H	Me	H	H
	37	Me	Me	H	t-Bu	H	H	H	Me	H
25	38	Et	Et	H	t-Bu	H	H	H	Me	H
	39	n-Pr	n-Pr	H	t-Bu	H	H	H	Me	H
	40	t-Bu	t-Bu	H	t-Bu	H	H	H	Me	H
	41	Et	Me	H	t-Bu	H	H	H	Me	H
	42	n-Pr	Me	H	t-Bu	H	H	H	Me	H
30	43	t-Bu	Me	H	t-Bu	H	H	H	Me	H
	44	Me	Me	H	t-Bu	H	H	H	Me	Me
	45	t-Bu	Me	Me	t-Bu	H	H	H	Me	H
	46	Me	Me	H	t-Bu	H	Me	H	Me	H
	47	Et	Et	H	t-Bu	H	Me	H	Me	H
	48	n-Pr	n-Pr	H	t-Bu	H	Me	H	Me	H
35	49	t-Bu	t-Bu	H	t-Bu	H	Me	H	Me	H
	50	Et	Me	H	t-Bu	H	Me	H	Me	H
	51	n-Pr	Me	H	t-Bu	H	Me	H	Me	H
	52	t-Bu	Me	H	t-Bu	H	Me	H	Me	H
	53	Me	Me	H	t-Bu	H	Me	H	Me	Me
40	54	t-Bu	Me	Me	t-Bu	H	Me	H	Me	H

Table 1

Particularly preferred phosphonites I of the formula 2 are those in which the radicals R1, R2, R4, R5, R6, R7 and R8 are as shown in Table 1 below.

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No.	R1	R2	R4	R5	R6	R7	R8
55	Me	H	t-Bu	H	H	H	H
56	Me	H	t-Bu	H	t-Bu	H	H
57	Me	H	t-Bu	H	Me	H	H
58	Me	H	t-Bu	H	H	Me	H
59	Me	H	t-Bu	H	H	H	Me
60	Me	H	t-Bu	H	Me	H	Me
61	Me	OMe	t-Bu	H	H	H	H
62	Me	OMe	t-Bu	H	t-Bu	H	H
63	Me	OMe	t-Bu	H	Me	H	H
64	Me	OMe	t-Bu	H	H	Me	H
65	Me	OMe	t-Bu	H	H	H	Me
66	Me	OMe	t-Bu	H	Me	H	Me

Table 2

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In Table 1 and Table 2, the abbreviations have the following meanings:

- H: hydrogen
 20 Me: methyl
 Et: ethyl
 n-Pr: n-propyl
 t-Bu: t-butyl
 OMe: methoxy

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The preparation of phosphonite I can be carried out using a method analogous to that described in WO 99/64155 for the phosphonite ligands of the formula 1 described there by firstly reacting a phenylphosphorus(III) dihalide, preferably

- 30 phenylphosphorus(III) dichloride, with a phenol bearing the radicals R4, R5, R6, R7 and R8 to eliminate hydrogen halide and give a phenyl(R4, R5, R6, R7, R8-phenoxy)phosphorus(III) halide. If desired, this reaction product can be isolated and/or purified by known methods, e.g. by distillation, before being reacted
 35 further. The phenyl(R4, R5, R6, R7, R8-phenoxy)phosphorus(III) halide can then be reacted with a 2,2'-bisphenol bearing the radicals R1, R2, R3 and R9 in the case of formula 1 or a 2,2'-bisnaphthol bearing the radicals R1 and R2 to eliminate hydrogen halide and give a phosphonite I.

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Both reactions can advantageously be carried out at from about 40 to about 200°C. Both reactions can be carried out in the presence of a base such as an aliphatic amine, for example diethylamine, dipropylamine, dibutylamine, trimethylamine,
 45 triethylamine or tripropylamine, or pyridine, preferably triethylamine or pyridine. Preference is given to a purely

thermal elimination of hydrogen halide in the first reaction step.

The preparation of the phosphonites I is advantageously carried out without use of organomagnesium or organolithium compounds. The simple reaction sequence makes it possible to prepare a wide range of phosphonites I. The preparation can thus be carried out efficiently and economically from readily available starting materials.

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The phosphonites I can be used as ligands in transition metal complexes.

Transition metals which can advantageously be used are the metals of transition groups I, II and VI to VIII of the Periodic Table, preferably transition group VIII of the Period Table, particularly preferably iron, cobalt and nickel, in particular nickel.

20 If nickel is used, it can be present in various oxidation states such as 0, +1, +2, +3. Preference is given to nickel(0) and nickel(+2), in particular nickel(0).

To prepare the transition metal complexes, a chemical compound of a transition metal or preferably a transition metal can be reacted with a phosphonite I, with the phosphonite I used being able to be either a single phosphonite I or a mixture of a plurality of phosphonites I.

30 Prior to the reaction, the transition metal can be obtained from suitable chemical compounds, e.g. salts such as chlorides, for example by reduction with base metals such as zinc.

If a transition metal compound is used for preparing the transition metal complexes, advantageous compounds are salts such as chlorides, bromides, acetylacetonates, sulfates, nitrates, for example nickel(2) chloride, or Ni(0) complexes such as bis(1,5-cyclooctadiene)Ni(0).

40 After the reaction of the transition metal compound or the transition metal with a phosphonite I, the oxidation state of the transition metal in the complex can be altered by means of suitable oxidizing or reducing agents, for example base metals such as zinc or hydrogen in chemically bound form, e.g. sodium borohydride, or in molecular form, or electrochemically.

In a particularly preferred embodiment, a complex of Ni(0) with organic monophosphine, monophosphonite, monophosphonite or monophosphite ligands can be reacted with a phosphonite I using a method based on that described in the German patent application 5 10136488.1.

In the transition metal complexes, the molar ratio of transition metal to phosphonite I can be in the range from 1 to 6, preferably from 2 to 5, in particular 2, 3 or 4.

10 The transition metal complexes can be free of ligands other than the phosphonites I.

The transition metal complexes may further comprise other ligands in addition to the phosphonites I, for example nitriles such as 15 acetonitrile, adiponitrile, 3-pentenitrile, 4-pentenitrile, 2-methyl-3-butenitrile, olefins such as butadiene or phosphorus compounds such as organic monophosphines, monophosphonites, monophosphonites or monophosphites.

20 The preparation of such transition metal complexes can be carried out by methods analogous to those described in the literature, for example in DE-A-2 237 703, US-A-3,850,973, US-A-3,766,237 or US-A-3,903,120, for preparing transition metal complexes containing tri-o-tolyl phosphite, tri-m-tolyl phosphite or 25 tri-p-tolyl phosphite ligands by replacing these phosphites partly or completely by the phosphonites I of the present invention.

The transition metal complexes of the present invention can be 30 used as catalysts, in particular as homogeneous catalysts.

It has been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the addition of hydrocyanic acid onto olefinic double bonds, 35 in particular double bonds which are conjugated with a further olefinic double bond, for example onto a double bond of butadiene to give a mixture comprising 2-methyl-3-butenitrile and 3-pentenitrile. It is equally advantageous to use the transition metal complexes of the invention as catalysts in the 40 addition of hydrocyanic acid onto olefinic double bond which are not conjugated with a further olefinic double bond, for example onto the double bond of 3-pentenitrile or 4-pentenitrile or mixtures thereof, preferably 3-pentenitrile, to give adiponitrile, or onto 3-pentenoic esters or 4-pentenoic esters or 45 mixtures thereof, preferably 3-pentenoic esters, to give 5-cyanovaleric esters.

It has likewise been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles, in particular ones in which the nitrile group is not conjugated with an
5 olefinic double bond, for example the isomerization of 2-methyl-3-butenenitrile to give 3-pentenenitrile. It is equally advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles in which the nitrile group is conjugated with an olefinic double
10 bond.

Processes for the addition of hydrocyanic acid onto an olefinic double bond or for the isomerization of organic nitriles can be carried out in a manner analogous to that described, for example,
15 in WO 99/13983 or WO 99/64155, by partly or completely replacing the phosphonites described there by the phosphonites I of the present invention.

The invention also provides a process for preparing mixtures of
20 monoolefinic C₅-mononitriles having nonconjugated C=C and C=N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of at least one of the above described systems according to the present invention as catalyst.

25 The preparation of monoolefinic C₅-mononitriles by the process of the present invention is preferably carried out using a hydrocarbon mixture having a 1,3-butadiene content of at least 10% by volume, preferably at least 25% by volume, in particular at least 40% by volume.

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To prepare mixtures of monoolefinic C₅-mononitriles which comprise, for example, 3-pentenenitrile and 2-methyl-3-butenenitrile and are suitable as intermediates for further processing to produce adiponitrile, it is possible to use
35 pure butadiene or 1,3-butadiene-containing hydrocarbon mixtures.

1,3-Butadiene-containing hydrocarbon mixtures are available on an industrial scale. Thus, for example, the processing of petroleum by steam cracking of naphtha produces a hydrocarbon mixture known
40 as C₄ fraction which has a high total olefin content, with about 40% being 1,3-butadiene and the remainder being made up of monoolefins and multiply unsaturated hydrocarbons and also alkanes. These streams always contain small proportions of generally up to 5% of alkynes, 1,2-dienes and vinylacetylene.

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Pure 1,3-butadiene can be isolated from industrially available hydrocarbon mixtures by, for example, extractive distillation.

C₄ fractions are, if desired, substantially freed of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, the products in which a C=C double bond is conjugated with the C≡N bond are sometimes obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, VCH Weinheim, p. 479, that the conjugated 2-pentenitrile formed in the isomerization of 2-methyl-3-butenitrile and 3-pentenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C₄ fraction also act as catalyst poisons for the first reaction step of the preparation of adipic acid, namely the monoaddition of hydrogen cyanide.

For this reason, it may be useful to free the hydrocarbon mixture partly or completely of components which form catalyst poisons in the catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof. To remove these components, the C₄ fraction is subjected to a catalytic partial hydrogenation before the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.

Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the customary oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. Preference is given to using Al₂O₃, SiO₂ and mixtures thereof as supports. In particular, the heterogeneous catalysts used are those described in US-A-4,587,369; US-A-4,704,492 and US-A-4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.

The addition reaction of hydrogen cyanide with 1,3-butadiene or a 1,3-butadiene-containing hydrocarbon mixture, e.g. a pretreated, partially hydrogenated C₄ fraction, can be carried out continuously, semicontinuously or batchwise.

In a useful variant of the process of the present invention, the addition reaction of the hydrogen cyanide is carried out continuously. Suitable reactors for a continuous reaction are

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known to those skilled in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, vol. 1, 3rd edition, 1951, p. 743 ff. The continuous variant of the process of the present invention is preferably carried out using a
5 cascade of stirred vessels or a tube reactor.

In a preferred variant of the process of the present invention, the addition reaction of hydrogen cyanide with 1,3-butadiene or a 1,3-butadiene-containing hydrocarbon mixture is carried out
10 semicontinuously.

The semicontinuous process comprises

- a) charging a reactor with the hydrocarbon mixture, if desired
15 part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired produced in situ, and, if desired, a solvent,
- b) reacting the mixture at elevated temperature and
20 superatmospheric pressure, with hydrogen cyanide being fed in at the rate at which it is consumed,
- c) completing the conversion by a period of after-reaction and subsequently working up the mixture.

25 Suitable pressure-rated reactors are known to those skilled in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, vol. 1, 3rd edition, 1951, p. 769 ff. In general, the process of the present invention is carried out
30 using an autoclave which may, if desired, be provided with a stirrer and an internal lining. For the above steps, the following procedures/conditions are preferred:

Step a):

- 35 The pressure-rated reactor is charged with the partially hydrogenated C₄ fraction or butadiene, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the
40 present invention, preferably aromatic hydrocarbons such as toluene and xylene, or tetrahydrofuran.

Step b):

- The mixture is generally reacted at elevated temperature and
45 superatmospheric pressure. The reaction temperature is generally in a range from about 0 to 200°C, preferably from about 50 to 150°C. The pressure is generally in a range from about 1 to 200

bar, preferably from about 1 to 100 bar, in particular from 1 to 50 bar, particularly preferably from 1 to 20 bar. During the reaction, hydrogen cyanide is fed in at a rate corresponding to that at which it is consumed, with the pressure in the autoclave remaining essentially constant. The reaction time is from about 30 minutes to 5 hours.

Step c):

To complete the conversion, the reaction time can be followed by an after-reaction time of up to about 5 hours, preferably from about 1 hour to 3.5 hours, during which no more hydrogen cyanide is fed into the autoclave. During this time, the temperature is kept essentially constant at the reaction temperature set during the addition of hydrogen cyanide. Work-up is carried out by customary methods and comprises separating off the unreacted 1,3-butadiene and the unreacted hydrogen cyanide, e.g. by washing or extraction, and fractionally distilling the remaining reaction mixture to separate off the product of value and recover the still active catalyst.

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In a further useful variant of the process of the present invention, the addition reaction of the hydrogen cyanide with the 1,3-butadiene-containing hydrocarbon mixture is carried out batchwise. Here, essentially the same reaction conditions as described for the semicontinuous process are maintained, but no additional hydrogen cyanide is fed in step b). All of the hydrogen cyanide is included in the initial charge.

In general, the preparation of adiponitrile from a butadiene-containing mixture by addition of 2 molar equivalents of hydrogen cyanide can be divided into three steps:

1. Preparation of mixtures of C₅-monoolefins having a nitrile function.
2. Isomerization of the 2-methyl-3-butenenitrile present in these mixtures to form 3-pentenitrile and isomerization of the 3-pentenitrile formed in this way and the 3-pentenitrile already present in the mixtures from step 1 to form various n-pentenitriles. A very high proportion of 3-pentenitrile or 4-pentenitrile and a very small proportion of conjugated 2-pentenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.

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3. Preparation of adiponitrile by addition of hydrogen cyanide onto the 4-pentenitrile which has previously been formed in situ by isomerization of the 3-pentenitrile formed in step 2. By-products formed are, for example,
- 5 2-methylglutaronitrile from the Markovnikov addition of hydrogen cyanide onto 4-pentenitrile or the anti-Markovnikov addition of hydrogen cyanide onto 3-pentenitrile and ethyl succinonitrile from the Markovnikov addition of hydrogen cyanide onto
- 10 3-pentenitrile.

The novel catalysts based on phosphonite ligands can also be used advantageously for the structural isomerization and double bond isomerization in step 2 and/or the second addition of hydrogen

15 cyanide in step 3.

Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation of

20 1,3-butadiene-containing hydrocarbon mixtures but they can also be admixed with an excess of hydrogen cyanide without appreciable deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the

25 catalysts comprising a phosphonite I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is

30 generally present. The catalysts used according to the present invention and the hydrocyanation processes based on them generally display higher catalyst recycle rates and longer catalyst operating times than do known processes. Apart from the economic aspect, this is also a advantageous for ecological

35 reasons since the nickel cyanide formed by reaction of the active catalyst with hydrogen cyanide is highly toxic and has to be worked up or disposed of at high costs.

Apart from the hydrocyanation of 1,3-butadiene-containing

40 hydrocarbon mixtures, the systems of the present invention are generally suitable for all customary hydrocyanation processes. Particular mention may be made of the hydrocyanation of unactivated olefins, e.g. styrene and 3-pentenitrile.

45 The addition of hydrocyanic acid onto an olefinic double bond in the presence of a catalyst system according to the present invention, in particular the addition onto butadiene or onto

- 3-pentenitrile, 4-pentenitrile or a mixture of such pentenenitriles or the isomerization of organic nitriles in the presence of a catalyst system according to the present invention, in particular the isomerization of 2-methyl-3-butenitrile to
- 5 3-pentenitrile, can advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the catalyst system of the present invention. Possible promoters are inorganic and organic compounds in which the cation is selected from the group
- 10 consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples which may be mentioned are ZnBr_2 , ZnI_2 , ZnCl_2 , ZnSO_4 , CuCl_2 , CuCl , $\text{Cu}(\text{O}_3\text{SCF}_3)_2$, CoCl_2 , CoI_2 , FeI_2 , FeCl_3 , FeCl_2 , $\text{FeCl}_2(\text{THF})_2$,
- 15 $\text{TiCl}_4(\text{THF})_2$, TiCl_4 , TiCl_3 , $\text{ClTi}(\text{O-iso-Pr})_3$, MnCl_2 , ScCl_3 , AlCl_3 , $(\text{C}_8\text{H}_{17})\text{AlCl}_2$, $(\text{C}_8\text{H}_{17})_2\text{AlCl}$, $(\text{iso-C}_4\text{H}_9)_2\text{AlCl}$, Ph_2AlCl , PhAlCl_2 , ReCl_5 , ZrCl_4 , ZrCl_2 , NbCl_5 , VCl_3 , CrCl_2 , MoCl_5 , YCl_3 , CdCl_2 , LaCl_3 , $\text{Er}(\text{O}_3\text{SCF}_3)_3$, $\text{Yb}(\text{O}_2\text{CCF}_3)_3$, SmCl_3 , $\text{B}(\text{C}_6\text{H}_5)_3$, TaCl_5 , as are generally described, for example in US 6,171,996 B1. Further suitable
- 20 promoters are described in the patents US 3,496,217, US 3,496,218 and US 4,774,353. These comprise metal salts such as ZnCl_2 , CoI_2 and SnCl_2 , and organometallic compounds such as RAlCl_2 , $\text{R}_3\text{SnO}_3\text{SCF}_3$ and R_3B , where R is an alkyl group or aryl groups. US Patent No. 4,874,884 describes the selection of synergistically effective
- 25 combinations of promoters to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl_2 , FeCl_2 , ZnCl_2 , $\text{B}(\text{C}_6\text{H}_5)_3$ and $(\text{C}_6\text{H}_5)_3\text{SnZ}$, where Z is CF_3SO_3 , $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$ or $(\text{C}_6\text{H}_5)_3\text{BCN}$.
- 30 The molar ratio of promoter to nickel in the catalyst system can be in the range from 1:16 to 50:1.

A further advantageous embodiment of hydrocyanation and isomerization may be found in US 5,981,772, whose contents are

35 hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

40 A further advantageous embodiment of hydrocyanation and isomerization may be found in US 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts

45 mentioned in the patent cited.

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A further advantageous embodiment of hydrocyanation may be found in US 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is
5 used in place of the catalyts mentioned in the patent cited.

A further advantageous embodiment of hydrocyanation may be found in US 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is
10 used in place of the catalyts mentioned in the patent cited.
The invention is illustrated by the following nonlimiting examples.

Examples

15

The yields were determined by gas chromatography (column: 30 m Stabil-Wachs, temperature program: 5 minutes isothermal at 50°C, then heating at a rate of 5°C/min to 240°C, gas chromatograph: Hewlett Packard HP 5890)

20

All examples were carried out under a protective argon atmosphere.

The abbreviation nickel(0)-(m/p-tolyl phosphite) is used for a
25 mixture comprising 2.35% by weight of Ni(0), 19% by weight of 3-pentenitrile and 78.65% by weight of m/p-tolyl phosphite having an m/p ratio of 2:1.

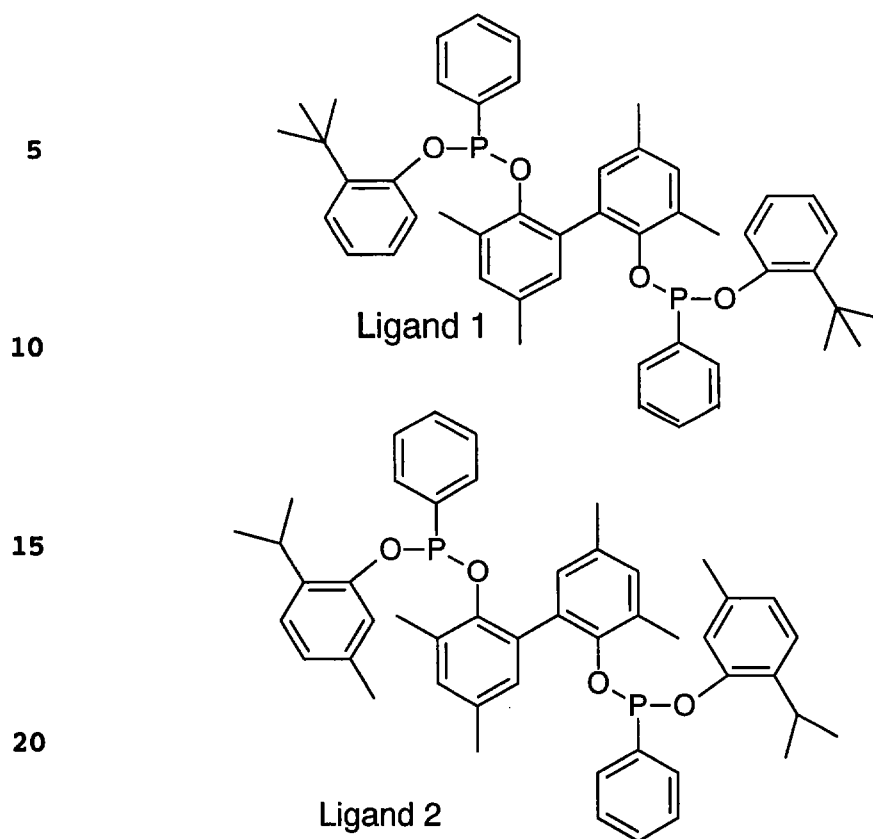
Chelating ligands used were:

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25 $\text{Ni}(\text{COD})_2$ is used as an abbreviation for bis(1,4-cyclo-octadiene) $\text{Ni}(0)$, 2M3BN for 2-methyl-3-butenenitrile, t2M2BN for trans-2-methyl-2-butenenitrile, c2M2BN for cis-2-methyl-2-butenenitrile, t2PN for trans-2-pentenitrile, 4PN for 4-pentenitrile, t3PN for trans-3-pentenitrile, c3PN for

30 cis-3-pentenitrile, MGN for methylglutaronitrile, BD for 1,3-butadiene, HCN for hydrocyanic acid, ADN for adiponitrile and THF for tetrahydrofuran.

Examples 1-3: Isomerization of 2-methyl-3-butenenitrile to form

35 3-pentenitrile

Example 1 (comparison) (0.5 mmol of $\text{Ni}(0)$)

1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with

40 465 equivalents of 2M3BN and heated to 115°C. GC samples were taken from the reaction mixture after 90 minutes and after 180 minutes and analyzed by gas chromatography (GC percent by area). The following results were obtained:

16

Time	2M3BN	t2M2BN	c2M2BN	t2PN	4PN	c,t-3PN	3PN/2M3BN
90 min	84.5	1.3	0.3			13.0	0.15
180 min	72.4	1.5	0.5			24.4	0.34

5

Example 2 (according to the present invention) (0.51 mmol of Ni(0))

- 10 1 equivalent of Ni(COD)₂ was admixed with 3 equivalents of ligand 1 and 465 equivalents of 2M3BN, stirred at 25°C for 1 hour and then heated to 115°C. GC samples were taken from the reaction mixture after 90 minutes and after 180 minutes and analyzed by gas chromatography (GC percent by area). The following results
15 were obtained:

Time	2M3BN	t2M2BN	c2M2BN	t2PN	4PN	t3PN	c3PN	3PN/2M3BN
90 min	52.54	0.05	0.13	0	0.02	42.14	2.13	0.84
180 min	11.92	0.08	0.25	0	0.13	81.05	3.18	7.07

20

Example 3 (according to the present invention) (0.44 mmol of Ni(0))

- 1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with
25 3 equivalents of ligand 1 and 465 equivalents of 2M3BN, stirred at 25°C for 12 hours and then heated to 115°C. GC samples were taken from the reaction mixture after 90 minutes and after 180 minutes and analyzed by gas chromatography (GC percent by area). The following results were obtained:

30

Time	2M3BN	t2M2BN	c2M2BN	t2PN	4PN	t3PN	c3PN	3PN/2M3BN
90 min	56.99	0.16	0.27	0.01	0.03	37.39	2.58	0.71
180 min	28.35	0.31	0.48	0.03	0.11	65.22	2.7	2.40

- 35 Examples 4-8: Hydrocyanation of 3-pentenitrile to form adiponitrile

Example 4 (comparison) (0.6 mmol of Ni(0))

- 40 1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with 365 equivalents of 3PN, stirred at 25°C for one hour and heated to 70°C. 1 equivalent of ZnCl₂ was added to this mixture and the mixture was stirred for a further 5 minutes. 94 equivalents of HCN/h*Ni in a stream of argon carrier gas were then introduced.
45 GC samples were taken from the reaction mixture after 30 minutes,

17

60 minutes and 150 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

5	Time	MGN	ADN	ADN selectivity (%)
	30 min	3.35	10.75	76.2
	60 min	6.87	26.39	79.3
	150 min	7.11	27.82	79.6

10 Example 5 (comparison) (0.55 mmol of Ni(0))

1 equivalent of Ni(COD)₂ was admixed with 3 equivalents of ligand 2 and 365 equivalents of 3PN, stirred at 25°C for one hour and heated to 70°C. 1 equivalent of ZnCl₂ was added to this

15 mixture and the mixture was stirred for a further 5 minutes.

142 equivalents of HCN/h*Ni in a stream of argon carrier gas were then introduced. GC samples were taken from the reaction mixture after 30 minutes and after 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard:

20 ethylbenzene). The following results were obtained:

	Time	MGN	ADN	ADN selectivity (%)
	30 min	1.80	18.91	91.3
	60 min	2.51	32.57	92.9

25

** The amount of 2PN formed after 60 minutes was 2.80%.

Example 6 (comparison) (0.49 mmol of Ni(0))

30 1 equivalent of Ni(COD)₂ was admixed with 1.2 equivalents of ligand 2, 4 equivalents of m-/p-tolyl phosphite (m:p ratio = 2:1) and 365 equivalents of 3PN, stirred at 25°C for one hour and heated to 70°C. 1 equivalent of ZnCl₂ was added to this mixture and the mixture was stirred for a further 5 minutes.

35 125 equivalents of HCN/h*Ni in a stream of argon carrier gas were then introduced. GC samples were taken from the reaction mixture after 45 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

40

	Time	MGN	ADN	ADN selectivity (%)
	45 min	1.85	21.51	92.1
	60 min	2.29	27.58	92.3

45 The amount of 2PN formed after 60 minutes was 2.41%.

18

Example 7 (according to the present invention) (0.63 mmol of Ni(0))

1 equivalent of Ni(COD)₂ was admixed with 3 equivalents of
 5 ligand 1 and 365 equivalents of 3PN, stirred at 25°C for one hour
 and heated to 70°C. 1 equivalent of ZnCl₂ was added to this
 mixture and the mixture was stirred for a further 5 minutes.
 125 equivalents of HCN/h*Ni in a stream of argon carrier gas were
 then introduced. GC samples were taken from the reaction mixture
 10 after 30 minutes and after 60 minutes and analyzed by gas
 chromatography (GC percent by weight, internal standard:
 ethylbenzene). The following results were obtained:

15	Time	MGN	ADN	ADN selectivity (%)
	30 min	1.28	17.11	93.1
	60 min	2.29	37.90	94.3

The amount of 2PN formed after 60 minutes was 1.69%.

20 Example 8 (according to the present invention) (0.58 mmol of Ni(0))

1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with
 3 equivalents of ligand 1 and 365 equivalents of 3PN, stirred at
 25 25°C for one hour and heated to 70°C. 1 equivalent of ZnCl₂ was
 added to this mixture and the mixture was stirred for a further
 5 minutes. 113 equivalents of HCN/h*Ni in a stream of argon
 carrier gas were then introduced. GC samples were taken from the
 reaction mixture after 30 minutes and after 60 minutes and
 30 analyzed by gas chromatography (GC percent by weight, internal
 standard: ethylbenzene). The following results were obtained:

35	Time	MGN	ADN	ADN selectivity (%)
	30 min	1.1	17.52	94.1
	60 min	2.26	34.15	93.8

The amount of 2PN formed after 60 minutes was 1.49%.

Examples 9-13: Hydrocyanation of butadiene to form
 40 3-pentenitrile

Example 9 (comparison) (1 mmol of Ni(0))

45 1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with
 500 equivalents of BD and 420 equivalents of HCN in THF, placed
 in a glass autoclave at 25°C and heated to 80°C. The temperature
 during the reaction (slightly exothermic reaction) was determined

19

by means of an internal thermometer and after 180 minutes the conversion of HCN into 2M3BN and 3PN was determined by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

5

Time	Internal temperature
30 min	80.3
50 min	80.5
60 min	80.4
180 min	80.3

10

Virtually no temperature increase occurs. This means that the catalyst is not very active.

- 15 The conversion of HCN into 2M3BN/3PN was 9.8%. The ratio of 2M3BN/3PN was 1/3.4.

Example 10 (comparison) (1 mmol of Ni(0))

- 20 1 equivalent of Ni(COD)₂ was stirred with 3 equivalents of ligand 2 in THF for 20 minutes. This solution was admixed with 557 equivalents of BD and 433 equivalents of HCN in THF, placed in a glass autoclave at 25°C and heated to 80°C. The temperature during the reaction (slightly exothermic reaction) was determined
- 25 by means of an internal thermometer and after 180 minutes the conversion of HCN into 2M3BN and 3PN was determined by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

30

Time	Internal temperature
15 min	82.2
30 min	82.1
120 min	81.1

- 35 Virtually no temperature increase occurs. This means that the catalyst is not very active.

The conversion of HCN into 2M3BN/3PN was 97.5%. The ratio of 2M3BN/3PN was 1.5/1.

40

Example 11 (comparison) (1 mmol of Ni(0))

- 1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was stirred with 1.2 equivalents of ligand 2 in THF for 12 hours. This solution
- 45 was admixed with 480 equivalents of BD and 400 equivalents of HCN in THF, placed in a glass autoclave at 25°C and heated to 80°C. The temperature during the reaction (slightly exothermic

20

reaction) was determined by means of an internal thermometer and after 180 minutes the conversion of HCN into 2M3BN and 3PN was determined by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

5

Time	Internal temperature
30 min	83.6
60 min	84.5
120 min	84.4
180 min	80.5

10

The conversion of HCN into 2M3BN/3PN was > 99%. The ratio of 2M3BN/3PN was 1.35/1.

15 Example 12 (according to the present invention) (1 mmol of Ni(0))

1 equivalent of Ni(COD)₂ was stirred with 3 equivalents of ligand 1 in THF for 20 minutes. This solution was admixed with 480 equivalents of BD and 400 equivalents of HCN in THF, placed in a glass autoclave at 25°C and heated to 80°C. The temperature during the reaction (slightly exothermic reaction) was determined by means of an internal thermometer and after 180 minutes the conversion of HCN into 2M3BN and 3PN was determined by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

25

Time	Internal temperature
5 min	84.8
10 min	86.7
20 min	88.0
90 min	81.2

30

The conversion of HCN into 2M3BN/3PN was > 98%. The ratio of 2M3BN/3PN was 1.34/1.

35

Example 13 (according to the present invention) (1 mmol of Ni(0))

1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was stirred with 1.2 equivalents of ligand 1 in THF for 12 hours. This solution was admixed with 480 equivalents of BD and 400 equivalents of HCN in THF, placed in a glass autoclave at 25°C and heated to 80°C.

40

Time	Internal temperature
5 min	84.4
10 min	87.3
20 min	88.7
90 min	81.2

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The conversion of HCN into 2M3BN/3PN was > 95%. The ratio of 2M3BN/3PN was 1.3/1.

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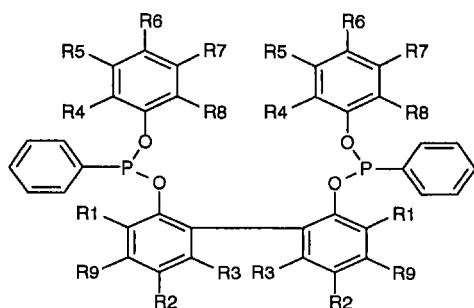
We claim:

1. A phosphonite I of the formula 1 or 2

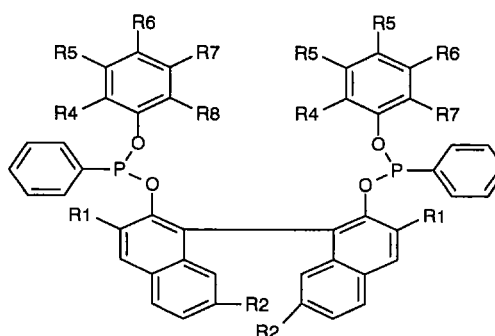
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formula 1



formula 2

where

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R1, R2 are each, independently of one another, hydrogen, an alkyl or alkylene group having from 1 to 8 carbon atoms or an alkoxy group having from 1 to 8 carbon atoms, with the proviso that R1 and R2 are not simultaneously H,

25

R3 is H or methyl,

R4 is t-butyl,

30

R5, R6, R7, R8, R9 are each, independently of one another, H or an alkyl or alkylene group having from 1 to 8 carbon atoms.

35

2. A phosphonite I as claimed in claim 1 in which R1, R2 are selected independently from the group consisting of H, methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, i-butyl, t-butyl and methoxy.

40

3. A phosphonite I as claimed in claim 1 in which R1, R2 are selected independently from the group consisting of H, methyl, ethyl, n-propyl, i-propyl, t-butyl and methoxy.

4. The use of a phosphonite I as claimed in any of claims 1 to 3 as ligand in transition metal complexes.

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5. A transition metal complex comprising a phosphonite I as claimed in any of claims 1 to 3 as ligand.
6. A transition metal complex as claimed in claim 5, wherein the transition metal used is nickel.
7. A process for preparing transition metal complexes as claimed in claim 5 or 6, which comprises reacting an elemental transition metal or a chemical compound containing a transition metal with a phosphonite I.
8. The use of a transition metal complex as claimed in claim 5 or 6 as catalyst.
9. The use as claimed in claim 8 as catalyst for the addition of hydrocyanic acid onto an olefinic double bond.
10. The use as claimed in claim 8 as catalyst for the isomerization of organic nitriles.
11. A process for the addition of hydrocyanic acid onto an olefinic double bond in the presence of a transition metal complex as claimed in claim 5 or 6 as catalyst.
12. A process as claimed in claim 11, wherein hydrocyanic acid is added onto butadiene to give a compound selected from the group consisting of 2-methyl-3-butenenitrile and 3-pentenitrile.
13. A process for the isomerization of organic nitriles in the presence of a transition metal complex as claimed in claim 5 or 6 as catalyst.
14. A process as claimed in claim 13, wherein 2-methyl-3-butenitrile is isomerized to 3-pentenitrile.
15. A process as claimed in claim 11, wherein hydrocyanic acid is added onto 3-pentenitrile, 4-pentenitrile or a mixture thereof to give adiponitrile.

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