Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2454912 A1 2003/02/13

(21) 2 454 912

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2002/07/16
(87) Date publication PCT/PCT Publication Date: 2003/02/13
(85) Entrée phase nationale/National Entry: 2004/01/23
(86) N° demande PCT/PCT Application No.: EP 2002/007888
(87) N° publication PCT/PCT Publication No.: 2003/011457
(30) Priorité/Priority: 2001/07/27 (101 36 488.1) DE

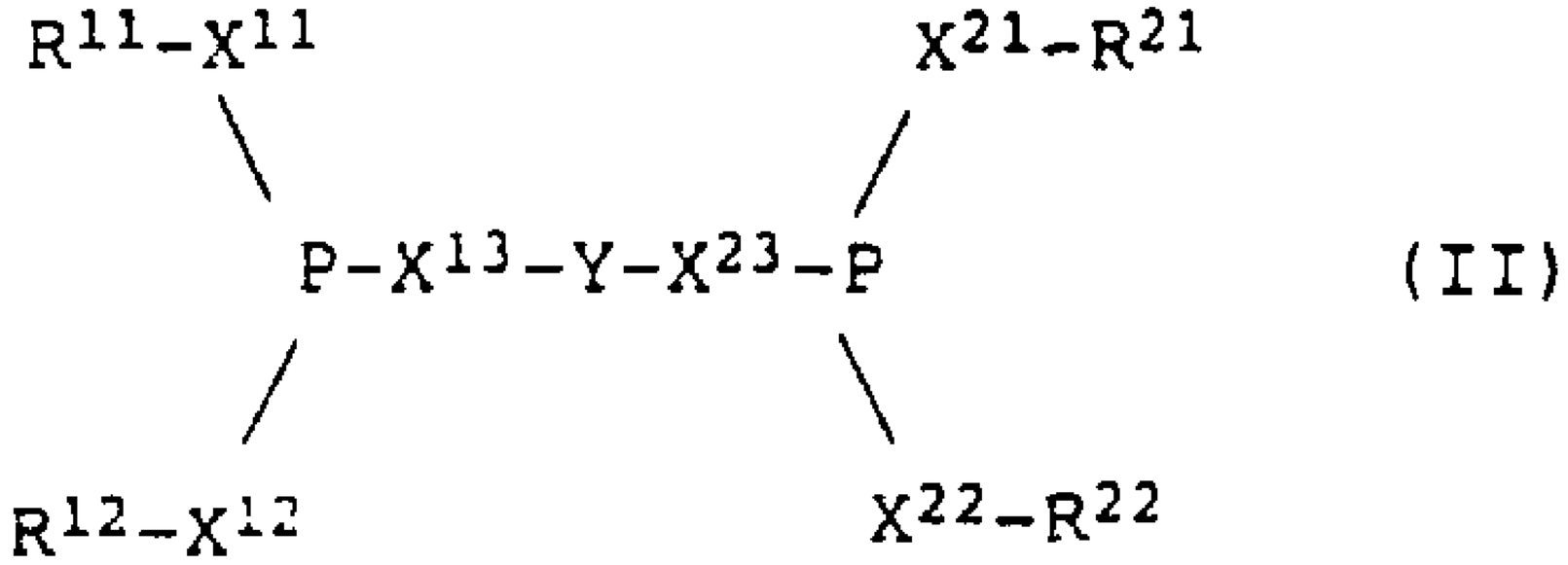
(51) Cl.Int.^{7}/Int.Cl.^{7} B01J 31/18, B01J 31/24, C07C 253/10

(71) Demandeur/Applicant:
BASF AKTIENGESELLSCHAFT, DE

(72) Inventeurs/Inventors:
BARTSCH, MICHAEL, DE;
BAUMANN, ROBERT, DE;
KUNSMANN-KEITEL, DAGMAR PASCALE, DE;
HADERLEIN, GERD, DE;
JUNGKAMP, TIM, DE;
ALTMAYER, MARCO, DE;
SIEGEL, WOLFGANG, DE

(74) Agent: ROBIC

(54) Titre : SYSTEME CATALYSEUR CONTENANT NI(0) POUR HYDROCYANATION
(54) Title: CATALYST SYSTEM CONTAINING NI(0) FOR HYDROCYANATION



(II)

(57) Abrégé/Abstract:
A catalyst system containing a) Ni (0), b) 4 -10 mol per mol Ni (0) according to a) a compound (I) of formula P (X^1R^1) (X^2R^2) (X^3R^3) (I) wherein X^1, X^2, X^3 independently represent oxygen or a single bond R^1, R^2, R^3 represent independently, the same or different organic radicals, and c) 1 -4 mol per mol Ni (0) according to a) a compound (II) of formula (II) wherein X^{11}, X^{12}, X^{13}, X^{21}, X^{22}, X^{23} independnetly represent oxygen or a single bond, R^{11}, R^{12} independently represent the same or different individual or bridged organic radicals, R^{21}, R^{22} independently represent the same or different, individual or bridged organic radicals, Y represents a bridge group. The invention also relates to a method for the production of mixtures of monoolefin C_5-mononitrils with a n-conjugated C=C and C=N bond by hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene in the presence of at least one such system and to a method for the production of a dinitrile by hydrocyanation of a mixture of monoolefin C_5-mononitriles with a non-conjugated C=C- and C=N bond in the presence of at least one such system.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
13. Februar 2003 (13.02.2003)

PCT

(10) Internationale Veröffentlichungsnummer
WO 03/011457 A1

(51) Internationale Patentklassifikation[7]: B01J 31/18, 31/24, C07C 253/10

(21) Internationales Aktenzeichen: PCT/EP02/07888

(22) Internationales Anmeldedatum:
16. Juli 2002 (16.07.2002)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
101 36 488.1 27. Juli 2001 (27.07.2001) DE

(71) Anmelder *(für alle Bestimmungsstaaten mit Ausnahme von US)*: **BASF AKTIENGESELLSCHAFT** [DE/DE]; 67056 Ludwigshafen (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder *(nur für US)*: **BARTSCH, Michael** [DE/DE]; Konrad-Adenauer-Strasse 38, 67433 Neustadt (DE). **BAUMANN, Robert** [DE/DE]; U 4, 18, 68161 Mannheim (DE). **KUNSMANN-KEITEL, Dagmar, Pascale** [DE/DE]; Neuhofener Str. 1, 67117 Limburgerhof (DE). **HADERLEIN, Gerd** [DE/DE]; Saalbaustr. 27, 64283 Darmstadt (DE). **JUNGKAMP, Tim** [DE/DE]; Kirchstr. 20, 69221 Dossenheim (DE). **ALTMAYER, Marco** [DE/DE]; Schulstrasse 1, 68199 Mannheim (DE). **SIEGEL, Wolfgang** [DE/DE]; Goethestr. 34b, 67117 Limburgerhof (DE).

(74) Gemeinsamer Vertreter: **BASF AKTIENGESELLSCHAFT**; 67056 Ludwigshafen (DE).

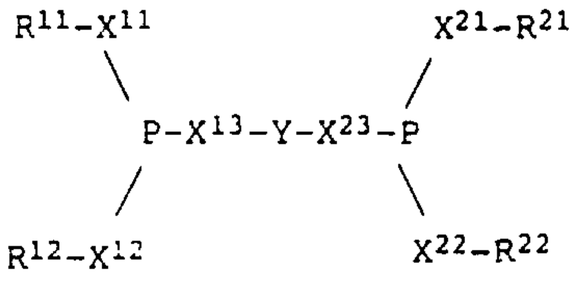
(81) Bestimmungsstaaten *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Bestimmungsstaaten *(regional)*: ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT,

[Fortsetzung auf der nächsten Seite]

(54) Title: CATALYST SYSTEM CONTAINING NI(0) FOR HYDROCYANATION

(54) Bezeichnung: NI(0) ENTHALTENDES KATALYSATORSYSTEM FÜR HYDROCYANIERUNG



(II)

(57) Abstract: A catalyst system containing a) Ni (0), b) 4 -10 mol per mol Ni (0) according to a) a compound (I) of formula P (X^1R^1) (X^2R^2) (X^3R^3) (I) wherein X^1, X^2, X^3 independently represent oxygen or a single bond R^1, R^2, R^3 represent independently, the same or different organic radicals, and c) 1 -4 mol per mol Ni (0) according to a) a compound (II) of formula (II) wherein X^{11}, X^{12}, X^{13}, X^{21}, X^{22}, X^{23} independnetly represent oxygen or a single bond, R^{11}, R^{12} independently represent the same or different individual or bridged organic radicals, R^{21}, R^{22} independently represent the same or different, individual or bridged organic radicals, Y represents a bridge group. The invention also relates to a method for the production of mixtures of monoolefin C_5-mononitrils with a n-conjugated C=C and C=N bond by hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene in the presence of at least one such system and to a method for the production of a dinitrile by hydrocyanation of a mixture of monoolefin C_5-mononitriles with a non-conjugated C=C- and C=N bond in the presence of at least one such system.

(57) Zusammenfassung: Als Katalysator geeignetes System enthaltend a) Ni (0), b) 4 bis 10 mol pro mol Ni (0) gemäss a) eine Verbindung (I) der Formel P(X^1R^1) (X^2R^2) (X^3R^3) (I) mit X^1, X^2, X^3 unabhängig voneinander Sauerstoff oder Einzelbindung R^1, R^2, R^3 unabhängig voneinander gleiche oder unterschiedliche organische Reste , und c) 1 bis 4 mol pro mol Ni (0) gemäss a) eine Verbindung (II) der Formel (II) mit X^{11}, X^{12}, X^{13}, X^{21}, X^{22}, X^{23} unabhängig voneinander Sauerstoff oder Einzelbindung R^{11}, R^{12} unabhängig voneinander gleiche oder unterschiedliche, einzelne oder verbrückte organische Reste R^{21}, R^{22} unabhängig voneinander gleiche oder unterschiedliche, einzelne oder verbrückte organische Reste Y Brückengruppe sowie Verfahren zur Herstellung von Gemischen monoolefinischer C_5-Mononitrile mit nichtkonjugierter C=C- und C=N-Bindung durch Hydrocyanierung eines 1,3-Butadien-haltigen Kohlenwasserstoffgemisches in Gegenwart mindestens eines solchen Systems und Verfahren zur Herstellung eines Dinitrils durch Hydrocyanierung eines Gemischs monooelfinischer C_5-Mononitrile mit nichtkonjugierter C=C- und C=N-Bindung in Gegenwart mindestens eines solchen Systems.

WO 03/011457 A1

WO 03/011457 A1

SE, SK, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

— *mit internationalem Recherchenbericht*

— *vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen*

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

CATALYST SYSTEM CONTAINING NI(0) FOR HYDROCYANATION

The present invention relates to a system comprising

a) Ni(0)

b) from 4 to 10 mol per mol of Ni(0) in a) of a compound (I) of the formula

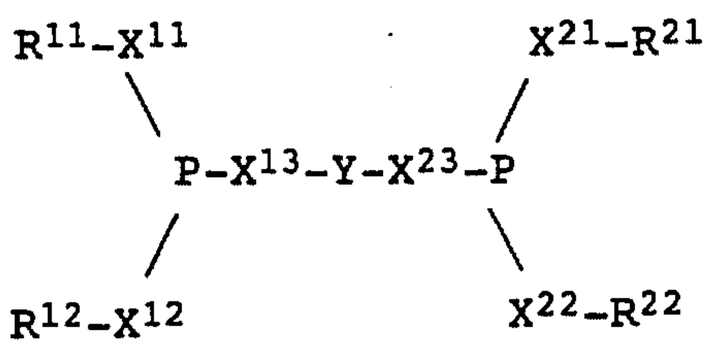
$P(X^1R^1)(X^2R^2)(X^3R^3)$ (I)

where

X^1, X^2, X^3 are each oxygen
R^1, R^2, R^3 are, independently of one another,

and

c) from 1 to 4 mol per mol of Ni(0) in a) of a compound (II) of the formula



where

X^{11}, X^{12}, X^{13} X^{21}, X^{22}, X^{23} are each oxygen

R^{11}, R^{12} are identical or different, individual or bridged organic radicals

R^{21}, R^{22} are identical or different, individual or bridged organic radicals and

Y is a bridging group

R^1, R^2, R^3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group,

which is suitable as catalyst and to processes for preparing such systems.

Systems comprising Ni(0) and a compound (II) which are suitable as catalysts for the hydrocyanation of butadiene to form a mixture of isomeric pentenenitriles and of pentenenitrile to form adiponitrile and processes for preparing them are known per se, for example from US 3,903,120, US 5,523,453, US 5,981,772, US 6,127,567, US 5,693,843, US 5,847,191, WO 01/14392.

The preparation of these catalyst systems is technically complicated and expensive. This applies particularly since the catalyst systems are gradually decomposed during use and thus have to be discharged and replaced by fresh catalyst.

The direct reaction of metallic nickel as Ni(0) source with compound (II) in the presence or absence of a liquid diluent or hydrogen halide as catalyst leads to a large extent to decomposition of compound (II).

The use of bis-1,4-cyclooctadieneNi as Ni(0)-containing starting compounds does make it possible to prepare the system comprising Ni(0) and compound (II), but this process suffers from the disadvantage of the complicated and expensive preparation of the bis-1,4-cyclooctadieneNi.

The same applies to the use of $Ni(p(O\text{-}o\text{-}C_6H_4CH_3)_3)_2(C_2H_4)$ as Ni(0)-containing starting compound.

The preparation of the system comprising Ni(0) and compound (II) starting from nickel chloride and zinc as Ni(0) source is known. A disadvantage of this process is the simultaneous formation of the specified catalyst system and zinc chloride.

If the use of the pure catalyst system is envisaged, the zinc chloride firstly has to be removed before use, which is costly.

If the mixture of catalyst system and zinc chloride is used instead of the pure catalyst system, then the work-up of the mixture of exhausted catalyst system and zinc chloride poses a great problem.

A further disadvantage of the catalyst system comprising Ni(0) and compound (II) is that compound (II) can be obtained only by way of a technically complicated and expensive synthesis.

It is an object of the present invention to provide a catalyst system which can be synthesized in a technically simple and economical way and displays selectivities and activities comparable to those of a catalyst system comprising Ni(0) and compound (II), especially in the hydrocyanation of compounds having conjugated olefinic double bonds, e.g. butadiene, and of compounds having one olefinic double bond and another unsaturated group, e.g. 2-pentenenitrile, 3-pentenenitrile, 4-pentenenitrile, 2-pentenoic esters, 3-pentenoic esters or 4-pentenoic esters.

We have found that this object is achieved by the system defined at the outset and a process for its preparation.

According to the present invention, Ni(0) is used as compound a).

It is advantageous to use metallic nickel as Ni(0), in which case further elements can be alloyed with the metallic nickel. In a preferred embodiment, pure metallic nickel can be used. For the purposes of the present invention, the pure metallic nickel can contain the impurities which are usual in commercial product.

The geometric form of the metallic nickel is not critical per se. However, it has been found to be advantageous to use metallic nickel having a large surface area per unit weight so as to achieve a high reaction rate in step a) of the process of the present invention. Suitable forms of nickel are, for example, nickel sponge or preferably finely divided nickel powder. Such high surface area metallic nickel is known per se and is commercially available.

According to the present invention, compound (I) has the formula

$$P(X^1R^1)\ (X^2R^2)\ (X^3R^3) \qquad (I)$$

For the purposes of the present invention, compound (I) is either a single compound or a mixture of various compounds having the abovementioned formula.

According to the invention, all of the groups X^1, X^2 and X^3 are oxygen, so that compound (I) is a phosphite of the formula $P(OR^1)(OR^2)(OR^3)$ in which R^1, R^2 and R^3 are as defined in this description.

According to the present invention, R^1, R^2, R^3 are, independently of one another, identical or different organic radicals.

According to the invention, the groups R^1, R^2 and R^3 are radicals selected from the group consisting of phenyl, o-tolyl, m-tolyl and p-tolyl.

In a particularly preferred embodiment, not more than two of the groups R^1, R^2 and R^3 are phenyl groups.

In another preferred embodiment, not more than two of the groups R^1, R^2 and R^3 are o-tolyl groups.

Particularly preferred compounds (I) are those of the formula
$(o\text{-tolyl-O-})_w\ (m\text{-tolyl-O-})_x\ (p\text{-tolyl-O-})_y\ (phenyl\text{-O-})_z\ P$

where w, x, y, z are each a natural number
and w + x + y + z = 3 and
w, z are each less than or equal to 2,

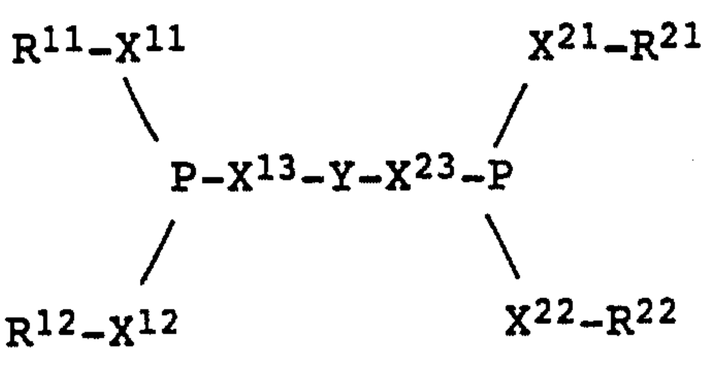
for example $(p\text{-tolyl-O-})(phenyl)_2P$, $(m\text{-tolyl-O-})(phenyl)_2P$, $(o\text{-tolyl-O-})(phenyl)_2P$, $(p\text{-tolyl-O-})_2(phenyl)P$, $(m\text{-tolyl-O-})_2(phenyl)P$, $(o\text{-tolyl-O-})_2(phenyl)P$, $(m\text{-tolyl-O-})(p\text{-tolyl-O-})(phenyl)P$, $(o\text{-tolyl-O-})(p\text{-tolyl-O-})(phenyl)P$, $(o\text{-tolyl-O-})(m\text{-tolyl-O-})(phenyl)P$, $(p\text{-tolyl-O-})_3P$, $(m\text{-tolyl-O-})(p\text{-tolyl-O-})_2P$, $(o\text{-tolyl-O-})(p\text{-tolyl-O-})_2P$, $(m\text{-tolyl-O-})_2(p\text{-tolyl-O-})P$, $(o\text{-tolyl-O-})_2(p\text{-tolyl-O-})P$, $(o\text{-tolyl-O-})(m\text{-tolyl-O-})(p\text{-tolyl-O-})P$, $(m\text{-tolyl-O-})_3P$, $(o\text{-tolyl-O-})(m\text{-tolyl-O-})_2P$ $(o\text{-tolyl-O-})_2(m\text{-tolyl-O-})P$ or mixtures of such compounds.

Thus, for example, mixtures comprising $(m\text{-tolyl-O-})_3P$, $(m\text{-tolyl-O-})_2(p\text{-tolyl-O-})P$, $(m\text{-tolyl-O-})(p\text{-tolyl-O-})_2P$ and $(p\text{-tolyl-O-})_3P$ can be obtained by reacting a mixture comprising m-cresol and p-cresol, in particular in a molar ratio of 2:1, as is obtained in the refining of petroleum by distillation, with a phosphorus trihalide such as phosphorus trichloride.

Such compounds (I) and their preparation are known per se.

According to the present invention, the system has a molar ratio of compound (I) to Ni(0) in the range from 4:1 to 10:1, preferably from 4:1 to 8:1, in particular from 4:1 to 6:1.

According to the present invention, compound (II) has the formula



where

X^{11}, X^{12}, X^{13} X^{21}, X^{22}, X^{23} are each oxygen,

R^{11}, R^{12} are identical or different, individual or bridged organic radicals,

R^{21}, R^{22} are identical or different, individual or bridged organic radicals

Y is a bridging group.

For the purposes of the present invention, compound (II) is a single compound or a mixture of various compounds of the abovementioned formula.

Suitable bridging groups Y are advantageously substituted, for example by C_1-C_4-alkyl, halogen such as fluorine, chlorine, bromine, halogenated alkyl such as trifluoromethyl, aryl such as phenyl, or unsubstituted aryl groups, preferably those having from 6 to 20 carbon atoms in the aromatic system, in particular pyrocatechol, bis(phenol) or bis(naphthol).

The radicals R^{11} and R^{12} can be identical or different organic radicals. Advantageous radicals R^{11} and R^{12} are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or monosubstituted or polysubstituted, in particular by C_1-C_4-alkyl, halogen such as fluorine, chlorine, bromine, halogenated alkyl such as trifluoromethyl, aryl such as phenyl, or unsubstituted aryl groups.

The radicals R^{21} and R^{22} can be identical or different organic radicals. Advantageous radicals R^{21} and R^{22} are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or monosubstituted or polysubstituted, in

particular by C_1-C_4-alkyl, halogen such as fluorine, chlorine, bromine, halogenated alkyl such as trifluoromethyl, aryl such as phenyl, or unsubstituted aryl groups.

The radicals R^{11} and R^{12} may be individual or bridged. The radicals R^{21} and R^{22} may be individual or bridged.

It is possible for the radicals R^{11}, R^{12}, R^{21} and R^{22} all to be individual, for two to be bridged and two to be individual or for all four to be bridged in the manner described.

In a particularly preferred embodiment, the compounds of the formulae I, II, III, IV and V mentioned in US 5,723,641 can be employed.

In a particularly preferred embodiment, the compounds of the formulae I, II, III, IV, V, VI and VII mentioned in US 5,512,696, in particular the compounds used there in Examples 1 to 31, can be employed.

In a particularly preferred embodiment, the compounds of the formulae I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV and XV mentioned in US 5,821,378, in particular the compounds used there in Examples 1 to 73, can be employed.

In a particularly preferred embodiment, the compounds of the formulae I, II, III, IV, V and VI mentioned in US 5,512,695, in particular the compounds used there in Examples 1 to 6, can be employed.

In a particularly preferred embodiment, the compounds of the formulae I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII and XIV mentioned in US 5,981,772, in particular the compounds used there in Examples 1 to 66, can be employed.

In a particularly preferred embodiment, the compounds mentioned in US 6,127,567 and the compounds used there in Examples 1 to 29 can be employed.

In a particularly preferred embodiment, the compounds of the formulae I, II, III, IV, V, VI, VII, VIII, IX and X mentioned in US 6,020,516, in particular the compounds used there in Examples 1 to 33, can be employed.

In a particularly preferred embodiment, the compounds mentioned in US 5,959,135 and the compounds used there in Examples 1 to 13 can be employed.

In a particularly preferred embodiment, the compounds of the formulae I, II and III mentioned in US 5,847,191 can be employed.

In a particularly preferred embodiment, the compounds mentioned in US 5,523,453, in particular the compounds shown there in formulae 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 12, 13, 14, 15, 16, 17, 18, 19, 20 and 21, can be employed.

In a particularly preferred embodiment, the compounds mentioned in WO 01/14392, preferably the compounds shown there in formulae V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII, XXI, XXII, XXIII, can be employed.

In a particularly preferred embodiment, the compounds mentioned in WO 98/27054 can be employed.

Such compounds (II) and their preparation are known per se.

According to the present invention, the system has a molar ratio of compound (II) to Ni(0) in the range from 1:1 to 4:1, preferably from 1:1 to 3:1. In a particular embodiment, it is possible, especially in the case of compounds (II) which are difficult to prepare or are expensive, to employ a molar ratio of compound (II) to Ni(0) in the range from 1:1 to 2:1.

Compound (I) and compound (II) should advantageously be capable of forming complexes with Ni(0). In general, compound (I) has only one coordination position capable of bonding to Ni(0), while compound (II) generally has, depending on geometry, bond strength and the presence of other compounds which can coordinate to Ni(0), e.g. compound (I), one or two coordination positions capable of bonding to Ni(0).

In a preferred embodiment, the system of the present invention comprises an Ni(0) complex of the formula Ni(0)(compound(I))$_x$(compound(II)), where x = 1, 2.

According to the present invention, the systems can be obtained by

a) reacting Ni(0) with a compound (I) in the presence of a liquid diluent to give a first system comprising Ni(0) and compound (I)
and then

b) reacting this first system with a compound (II) in the presence of a liquid diluent to give a system.

According to the present invention, Ni(0) is used as compound a).

It is advantageous to use metallic nickel as Ni(0), in which case further elements can be alloyed with the metallic nickel. In a preferred embodiment, pure metallic nickel can be used. For the purposes of the present invention, the pure metallic nickel can contain the impurities which are usual in commercial product.

The geometric form of the metallic nickel is not critical per se. However, it has been found to be advantageous to use metallic nickel having a large surface area per unit weight so as to achieve a high reaction rate in step a) of the process of the present invention. Suitable forms of nickel are, for example, nickel sponge or preferably finely divided nickel powder. Such high surface area metallic nickel is known per se and is commercially available.

According to the present invention, from 4 to 10 mol, preferably from 4 to 8 mol, in particular from 4 to 6 mol, of compound (I) are used per mol of Ni(0) in step a).

In an advantageous embodiment, the liquid diluent used in step a) can be a compound of the formula (I), an olefinically unsaturated nitrile, preferably a pentenenitrile such as cis-2-pentenenitrile, trans-2-pentenenitrile, cis-3-pentenenitrile, trans-3-pentenenitrile, 4-pentenenitrile, 2-methyl-3-butenenitrile, cis-2-methyl-2-butenenitrile, trans-2-methyl-2-butenenitrile, a dinitrile such as adiponitrile, methylglutaronitrile, an aromatic such as benzene, toluene, o-xylene, m-xylene, p-xylene, an aliphatic such as cyclohexane or a mixture of such compounds.

The preparation of the first system in step a) can advantageously be carried out in the presence of a homogeneous or heterogeneous, preferably homogeneous, catalyst.

As homogeneous catalyst, it is advantageous to use a protic acid or a mixture of such protic acids, for example hydrochloric acid.

An advantageous homogeneous catalyst is a compound of the formula

(R^1X^1) $(R^2X^2)PCl$ or $(R^1X^1)PCl_2$

where R^1, R^2, X^1, X^2 are as defined above,

or a mixture of such compounds.

The catalyst used in step a) can be carried over from step a) to step b). It has been found to be advantageous to remove the catalyst from step a) between steps a) and b).

In an advantageous embodiment, from 1 to 4 mol, preferably from 1 to 3 mol, of compound (II) are used per mol of Ni(0). In a particular embodiment, a molar ratio of compound (II) to Ni(0) in the range from 1:1 to 2:1 can be employed, especially in the case of compounds (II) which are difficult to prepare or are expensive.

In an advantageous embodiment, the liquid diluent used in step b) can be a compound of the formula (I), an olefinically unsaturated nitrile, preferably a pentenenitrile such as cis-2-pentenenitrile, trans-2-pentenenitrile, cis-3-pentenenitrile, trans-3-pentenenitrile, 4-pentenenitrile, 2-methyl-3-butenenitrile, cis-2-methyl-2-butenenitrile, trans-2-methyl-2-butenenitrile, a dinitrile such as adiponitrile, methylglutaronitrile, an aromatic such as benzene, toluene, o-xylene, m-xylene, p-xylene, an aliphatic such as cyclohexane or a mixture of such compounds.

In a particularly preferred embodiment, the same liquid diluent is used in step a) and step b).

The present invention further provides a process for preparing mixtures of monoolefinic C_5-mononitriles having nonconjugated C=C and C=N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the above-described systems according to the present invention.

The preparation of monoolefinic C_5-mononitriles by the process of the present invention is preferably carried out using a hydrocarbon mixture which has a 1,3-butadiene content of at least 10% by volume, preferably at least 25% by volume, in particular at least 40% by volume.

To prepare mixtures of monoolefinic C_5-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 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 refining of petroleum by steam cracking of naphtha produces a hydrocarbon mixture known as C_4 fraction which has a high total olefin content of which about 40% is 1,3-butadiene and the remainder is made up of monoolefins and multiply unsaturated hydrocarbons together with alkanes. These streams always contain small proportions of generally up to 5% of alkynes, 1,2-dienes and vinylacetylene.

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

C_4 fractions are, if appropriate, substantially free of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, products in which a C=C double bond is conjugated with the C=N bond may be obtained. It is known from "Applied Homogeneous Catalysis with Organometalic Compounds", vol. 1, VCH Weinheim, p. 479, that the conjugated 2-pentenenitrile formed in the isomerization of 2-methyl-3-butenenitrile and 3-pentenenitrile 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 C_4 fraction also act as catalyst poisons for the first reaction step of the production of adipic acid, viz. the monoaddition of hydrogen cyanide.

For this reason, those components which act as catalyst poisons in catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof, are advantageously removed completely or partially from the hydrocarbon mixture. To remove these components, the C_4 fraction is subjected to a catalytic partial hydrogenation prior to 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 oxides, in particular silicon and aluminum

oxides, aluminosilicates, zeolites, carbides, nitrides, etc, customary for this purpose and mixtures thereof. Preferred supports are Al_2O_3, SiO_2 and mixtures thereof. 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 C_4 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 the continuous reaction 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. 743 ff. The continuous variant of the process of the present invention is preferably carried out using a 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 semicontinuously.

The semicontinuous process comprises:

a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired one produced in situ, and, if desired, a solvent,

b) reacting the mixture at elevated temperature and superatmospheric pressure, with hydrogen cyanide being fed in at the rate at which it is consumed,

c) completing the reaction by provision of an after-reaction time and subsequently working up the mixture.

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 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):
The pressure-rated reactor is charged with the partially hydrogenated C_4 fraction, 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 present invention, preferably aromatic hydrocarbons such as toluene and xylene or tetrahydrofuran.

Step b):
The reaction of the mixture is generally carried out at elevated temperature and 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 particulur 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 from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, during which no more hydrogen cycanide is fed into the autoclave. The temperature during this time is kept essentially constant at the level of the reaction temperature previously set. 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 scrubbing or extraction, and working up the remaining reaction mixture by distillation to separate off the desired product and to recover the still active catalyst.

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, the reaction conditions employed are essentially those described for the semicontinuous process, but no additional hydrogen cyanide is fed in in step b); all the hydrogen cycanide for the reaction is present 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 subdivided into three steps:

1. Preparation of C_5-monoolefin mixtures having a nitrile function.

2. Isomerization of the 2-methyl-3-butenenitrile present in these mixtures to form 3-pentenenitrile and isomerization of the 3-pentenenitrile formed in this way and that already present in the mixture from step 1 to form various n-pentenenitriles. Here, a very high proportion of 3-pentenenitrile or 4-pentenenitrile and a very low proportion of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.

3. Preparation of adiponitrile by addition of hydrogen cyanide onto the 3-pentenenitrile which has been formed in step 2 and is isomerized beforehand "in situ" to 4-pentenenitrile. By-products which occur are, for example, 2-methylglutaronitrile from the Markovnikov addition of hydrogen cyanide onto 4-pentenenitrile or the anti-Markovnikov addition of hydrogen cyanide onto 3-pentenenitrile and ethylsuccinonitrile from the Markovnikov addition of hydrogen cyanide onto 3-pentenenitrile.

Advantageously, the catalysts of the present invention based on phosphonite ligands are also suitable for the structural isomerization and double bond isomerization in step 2 and/or the second addition of hydrogen cyanide in step 3.

In a useful embodiment of the process of the present invention, the ratio of 3-pentenenitrile to 2-methyl-3-butenenitrile obtained in the monoaddition reaction of hydrogen cyanide with the 1,3-butadiene-containing hydrocarbon mixture is at least 1.9:1, preferably at least 2.1:1.

Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures but they can also be admixed with an excess of hydrogen cyanide in the hydrocyanation without appreciable precipitation 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 catalysts of the formula 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 generally present. Thus, the catalysts used according to the present invention and the hydrocyanation processes based on them generally allow greater recirculation of catalysts and display longer catalyst operating lives than do known processes. This is advantageous both in terms of improved economics and also from an ecological point of view, since the nickel cyanide formed from the active catalyst by reaction with hydrogen cyanide is highly toxic and has to be worked up or disposed of, which is very costly.

Apart from the hydrocyanation of 1,3-butadiene-containing 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 nonactivated olefins, e.g. styrene and 3-pentenenitrile.

A further advantageous embodiment of hydrocyanation and isomerization can be derived from US 6,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

A further advantageous embodiment of hydrocyanation and isomerization can be derived from 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 systems is used in place of the catalysts mentioned in that patent.

A further advantageous embodiment of a hydrocyanation process can be derived from 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 systems is used in place of the catalysts mentioned in that patent.

A further advantageous embodiment of a hydrocyanation process can be derived from 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 systems is used in place of the catalysts mentioned in that patent.

The invention is illustrated by the following nonlimiting examples.

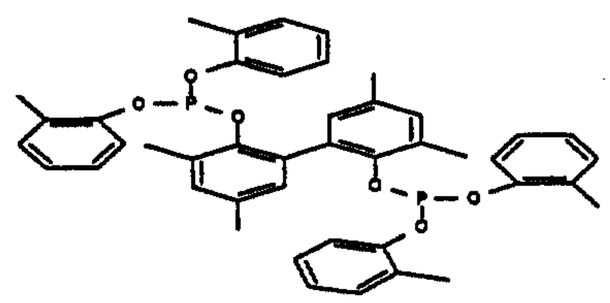
Examples

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 chromatography: Hewlett Packard HP 5890)

All examples were carried out under a protective argon atmosphere.

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

Chelating ligands used were:



Ligand 1

$Ni(COD)_2$ is bis(1,4-cyclooctadiene)Ni(0).

In the tables, 2M3BN is 2-methyl-3-butenenitrile, t2M2BN is trans-2-methyl-2-butenenitrile, c2M2BN is cis-2-methyl-2-butenenitrile, t2PN is trans-2-pentenenitrile, 4PN is 4-pentenenitrile, t3PN is trans-3-pentenenitrile, c3PN is cis-3-pentenenitrile, MGN is methylglutaronitrile and ADN is adiponitrile.

Examples 1-18: Use of ligand 1 as compound (II)

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

Example 1 (comparison)

1 molar equivalent of Ni(0)-(m/p-tolyl phosphite) (0.5 mmol of Ni(0)) was admixed with 465 molar equivalents of 2-methyl-3-butenenitrile and the mixture was heated to 115°C.

Samples were taken from the reaction mixture after 90 minutes and after 180 minutes and the following yields (in percent) were determined:

Time	2M3BN	t2M2BN	c2M2BN	t2PN	4PN	t3PN	c3PN	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

Example 2 (comparison)

1 molar equivalent of $Ni(COD)_2$ (0.58 mmol of Ni(0)) was admixed with 3 molar equivalents of ligand 1 and 465 molar equivalents of 2-methyl-3-butenenitrile, the mixture was stirred at 25°C for 1 hour and then heated to 115°C. Samples were taken from the reaction mixture after 90 minutes and after 180 minutes and the following yields (in percent) were determined:

Time	2M3BN	t2M2BN	c2M2BN	t2PN	4PN	t3PN	c3PN	3PN/2M3BN
90 min	4.69	1.4	0.22	0.3	0.78	87.82	4.80	19.74
180 min	4.52	1.34	0.16	0.23	1.41	85.3	7.0	20.42

Example 3 (according to the present invention)

1 molar equivalent of Ni(0)-(m/p-tolyl phosphite) (0.4 mmol of Ni(0)) was admixed with 1 molar equivalent of ligand 1 and 465 molar equivalents of 2-methyl-3-butenenitrile, the mixture was stirred at 25°C for 12 hours and then heated to 115°C. Samples were taken from the reaction mixture after 90 minutes and after 180 minutes and the following yields (in percent) were determined:

Time	2M3BN	T2M2BN	c2M2BN	t2PN	4PN	T3PN	c3PN	3PN/2M3BN
90 min	28.81	1.5			0.1	57.6		2
180 min	13.31	1.3			0.1	75.5		5.68

Examples 4-15: Hydrocyanation of 3-pentenenitrile to adiponitrile

Example 4 (comparison)

1 molar equivalent of nickel(0)-(m/p-tolyl phosphite) (0.6 mmol of Ni(0)) was admixed with 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for 1 hour and

heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 94 molar equivalents of HCN/hour*Ni in an argon carrier gas stream were passed in. Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

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

Example 5 (comparison)

The procedure of Example 4 was repeated using 1 molar equivalent of $Ni(COD)_2$ (0.27 mmol of Ni(0)) and 1 molar equivalent of ligand 1 in place of 1 molar equivalent of nickel(0)-(m/p-tolyl phosphite).

Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	0.68	2.19	76.2
60 min	0.99	6.17	86.2
120 min	1.01	7.28	87.8

Example 6 (comparison)

The procedure of Example 5 (using 0.64 mmol of Ni(0)) was repeated, except that only 38 molar equivalents of HCN/hour*Ni were passed in instead of 94 molar equivalents of HCN/hour*Ni. Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	0.88	1.33	60.0
60 min	1.71	8.69	83.5
120 min	2.01	15.90	88.7

Example 7 (according to the present invention)

1 molar equivalent of $Ni(COD)_2$ (0.61 mmol of Ni(0)) was admixed with 1 molar equivalent of ligand 1, 4 molar equivalents of m/p-tolyl phosphite (m:p = 2:1) and 365 molar equivalents of

3-pentenenitrile, the mixture was stirred at 25°C for 1 hour and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 133 molar equivalents of HCN/hour*Ni in an argon carrier gas stream were passed in.

Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	2.86	17.50	85.9
60 min	3.96	36.86	90.3
120 min	6.88	77.27	91.8

Example 8 (according to the present invention)

The procedure of Example 7 was repeated (using 0.53 mmol of Ni(0)), except that 28 molar equivalents of HCN/hour*Ni were passed in instead of 133 molar equivalents of HCN/hour*Ni.

Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	0.49	8.02	94.2
60 min	1.10	19.73	94.7
120 min	1.88	33.54	94.7

Example 9 (according to the present invention)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (0.6 mmol of Ni(0)) was admixed with 1.2 molar equivalents of ligand 1 and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for 12 hours and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 131 molar equivalents of HCN/h*Ni in an Ar carrier gas stream were then passed in.

Samples were taken after 30 minutes, 60 minutes and 120 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.67	15.21	90.1
60 min	3.13	39.05	92.6
120 min	5.15	65.04	92.7

Example 10 (comparison)

1 molar equivalent of $Ni(COD)_2$ (0.49 mmol of Ni(0)) was admixed with 3 molar equivalents of ligand 1 and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for 1 hour and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 43 molar equivalents of HCN/h*Ni in an Ar carrier gas stream were then passed in.

Samples were taken after 60 minutes and 120 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
60 min	2.41	11.73	83.0
120 min	3.21	29.14	90.1

Example 11 (comparison)

The procedure of Example 10 was repeated (using 0.58 mmol of Ni(0)), except that 95 molar equivalents of HCN/h*Ni were passed in instead of 43 molar equivalents of HCN/h*Ni.

Samples were taken after 30 minutes, 60 minutes and 120 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.40	13.32	90.5
60 min	2.26	31.96	93.4
120 min	3.69	58.46	94.0

Example 12 (comparison)

The procedure of Example 10 was repeated (using 0.58 mmol of Ni(0)), except that the catalyst mixture was stirred at 25°C for 12 hours instead of 1 hour and 122 molar equivalents of HCN/h*Ni were passed in instead of 43 molar equivalents of HCN/h*Ni.

Samples were taken after 30 minutes, 60 minutes and 180 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.71	18.50	91.5
60 min	2.52	36.10	93.5
180 min	5.92	91.04	93.9

Example 13 (comparison)

The procedure of Example 12 was repeated (using 0.4 mmol of Ni(0)), except that 150 molar equivalents of HCN/h*Ni were passed in instead of 43 molar equivalents of HCN/h*Ni.

Samples were taken after 30 minutes, 60 minutes and 120 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	3.47	42.03	92.4
60 min	4.90	67.36	93.2
120 min	5.96	83.92	93.4

Example 14 (according to the present invention)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (0.6 mmol of Ni(0)) was admixed with 3 molar equivalents of ligand 1 and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for 12 hours and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 111 molar equivalents of HCN/h*Ni in an Ar carrier gas stream were then passed in.

Samples were taken after 30 minutes, 60 minutes and 120 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.11	16.31	93.6
60 min	2.11	36.31	94.5
120 min	4.14	70.50	94.5

Example 15 (according to the present invention)

The procedure of Example 14 (using 0.6 mmol of Ni(0)) was repeated, except that 109 molar equivalents of HCN/h*Ni were passed in instead of 111 molar equivalents of HCN/h*Ni.

Samples were taken after 30 minutes, 60 minutes and 120 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.03	15.79	93.9
60 min	2.00	34.31	94.5
120 min	4.58	77.68	94.4

Examples 16-18: Hydrocyanation of 1,3-butadiene to 3-pentenenitrile

Example 16 (comparison)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (1 mmol of Ni(0)) was admixed with 500 molar equivalents of 1,3-butadiene and 420 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

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

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was 9.8%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 1/3.4.

Example 17 (comparison)

1 molar equivalent of $Ni(COD)_2$ (0.32 mmol of Ni(0)) was stirred with 3 molar equivalents of ligand 1 in THF for 20 minutes. This solution was admixed with 696 molar equivalents of 1,3-butadiene and 580 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

Time	Internal temperature
30 min	81.9
45 min	82
60 min	81.9
90 min	81.3
180 min	80.8

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was 94.4%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 1/1.3.

Example 18 (according to the present invention)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (1 mmol of Ni(0)) was stirred with 1.2 molar equivalents of ligand 1 in THF for 12 hours. This solution was admixed with 480 molar equivalents of 1,3-butadiene and 400 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

Time	Internal temperature
30 min	86
45 min	88.6
60 min	86.9
120 min	80

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was above 99%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 1/1.5.

Examples 19-25: Use of ligand 2 as compound (II)
Examples 19-20: Isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile

Example 19 (comparison)

1 molar equivalent of $Ni(COD)_2$ (0.58 mmol of Ni(0)) was admixed with 3 molar equivalents of ligand 2 and 465 molar equivalents of 2-methyl-3-butenenitrile, the mixture was stirred at 25°C for 1 hour and then heated to 115°C..
Samples were taken from the reaction mixture after 90 minutes and after 180 minutes and the following yields (in percent) were determined:

Time	2M3BN	t2M2BN	c2M2	t2PBNN	4PN	t3PN	c3PN	3PN/2 M3BN
90 min	11.96	1.81	0.30	0.27		82.75	2.48	
180 min	4.77	1.81	0.33	0.18	1.32	86.6	4.88	

Example 20 (according to the present invention)

1 molar equivalent of Ni(0)-(m/p-tolyl phosphite) (0.4 mmol of Ni(0)) was admixed with 1 molar equivalent of ligand 2 and 465 molar equivalents of 2-methyl-3-butenenitrile, the mixture was stirred at 25°C for 12 hours and heated to 115°C.

Samples were taken from the reaction mixture after 90 minutes and after 180 minutes and the following yields (in percent) were determined:

Time	2M3BN	t2M2BN	c2M2BN	t2PN	4PN	t3PN	c3PN	3PN/2 M3BN
90 min	59.96	1.78		0.32	0.1	26.45		0.44
180 min	44.09	2.30		0.36	0.1	40.84		0.93

Examples 21-23: Hydrocyanation of 3-pentenenitrile to adipodinitrile

Example 21 (comparison)

1 molar equivalent of $Ni(COD)_2$ (0.55 mmol of Ni(0)) was admixed with 3 molar equivalents of ligand 2 and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for one hour and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 142 molar equivalents of HCN/h*Ni in an Ar carrier gas stream were then passed in.

Samples were taken after 30 minutes and 60 minutes and the following yields (in percent) were determined:

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

Example 22 (according to the present invention)

1 molar equivalent of $Ni(COD)_2$ (0.49 mmol of Ni(0)) was admixed with 1.2 molar equivalents of ligand 2, 4 molar equivalents of m-/p-tolyl phosphite (m/p = 2:1) and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for one hour and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 125 molar equivalents of HCN/h*Ni in an Ar carrier gas stream were then passed in.

Samples were taken after 45 minutes and 60 minutes and the following yields (in percent) were determined:

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

Example 23 (according to the present invention)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (0.6 mmol of Ni(0)) was admixed with 1 molar equivalent of ligand 2 and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25°C for 12 hours and heated to 70°C. 1 molar equivalent of $ZnCl_2$ was added to this mixture and the mixture was stirred for a further 5 minutes. 120 molar equivalents of HCN/h*Ni in an Ar carrier gas stream were then passed in.

Samples were taken after 30 minutes and 60 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.22	11.49	90.4
60 min	2.88	26.12	90.0

Examples 24-25: Hydrocyanation of 1,3-butadiene to 3-pentenenitrile

Example 24 (comparison)

1 molar equivalent of $Ni(COD)_2$ (1 mmol of Ni(0)) was stirred with 3 molar equivalents of ligand 2 in THF for 20 minutes. This solution was admixed with 557 molar equivalents of 1,3-butadiene and 433 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

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

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was 97.5%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 1.5/1.

Example 25 (according to the present invention)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (1 mmol of Ni(0)) was stirred with 1.2 molar equivalents of ligand 2 in THF for 12 hours. This solution was admixed with 480 molar equivalents of 1,3-butadiene and 400 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

Time	Internal temperature
30 min	83.6
60 min	84.6
120 min	84.4
180 Min	80.5

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was above 99%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 1.35/1.

Examples 26-28: Use of ligand 3 as compound (II)

Example 26 (comparison)

1 molar equivalent of $Ni(COD)_2$ (1 mmol of Ni(0)) was stirred with 1.2 molar equivalents of ligand 3 in THF for 20 minutes. This solution was admixed with 480 molar equivalents of 1,3-butadiene and 400 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

Time	Internal temperature
5 min	85
10 min	89
15 min	92.9
20 min	90.3
30 min	86.1
60 min	82
120 min	81

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was 88.0%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 3/1.

Example 27 (according to the present invention)

1 molar equivalent of nickel(0)-(m-/p-tolyl phosphite) (1 mmol of Ni(0)) was stirred with 1.2 molar equivalents of ligand 3 in THF for 12 hours. This solution was admixed with 462 molar equivalents of 1,3-butadiene and 390 molar equivalents of HCN in THF, and the mixture was placed in a glass autoclave at 25°C and heated to 80°C.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

Time	Internal temperature
30 min	91
40 min	122
50 min	84
60 min	80.2
120 min	80.2

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was above 99%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 2.5/1.

Example 28 (according to the present invention)

The procedure of Example 28 (using 1 mmol of Ni(0)) was repeated, except that 720 molar equivalents of 1,3-butadiene and 600 molar equivalents of HCN were used instead of 462 molar equivalents of 1,3-butadiene and 390 molar equivalents of HCN.

By means of an internal thermometer, the following pressures and temperatures were measured as a function of time during the reaction (slightly exothermic reaction):

Time	Internal temperature
25 min	84
45 min	89.1
65 min	90.5
80 min	80.5
120 min	80.2

After 180 minutes, the HCN conversion into 2-methyl-3-butenenitrile and 3-pentenenitrile was 96/6%. The molar ratio of 2-methyl-3-butenenitrile to 3-pentenenitrile was 2.8/1.

We claim:

1. A system comprising

a) Ni(0)

b) from 4 to 10 mol per mol of Ni(0) in a) of a compound (I) of the formula

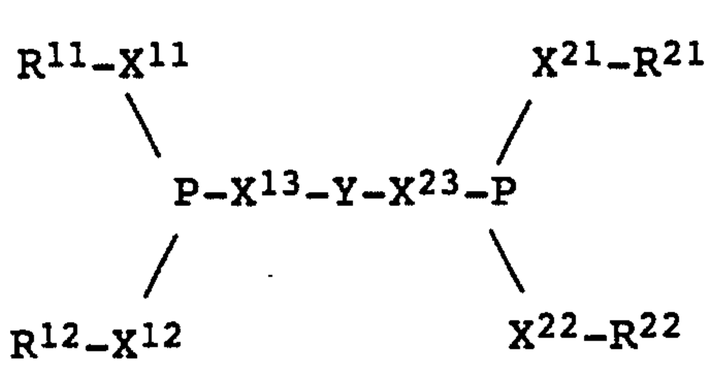
$$P(X^1R^1)(X^2R^2)(X^3R^3) \qquad (I)$$

where

X^1, X^2, X^3 are each oxygen,
R^1, R^2, R^3 are, independently of one another,

and

c) from 1 to 4 mol per mol of Ni(0) in a) of a compound (II) of the formula



where

X^{11}, X^{12}, X^{13} X^{21}, X^{22}, X^{23} are each oxygen,

R^{11}, R^{12} are identical or different, individual or bridged organic radicals,

R^{21}, R^{22} are identical or different, individual or bridged organic radicals,

Y is a bridging group and

R^1, R^2, R^3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group,

which is suitable as catalyst.

2. A system as claimed in claim 1, wherein R^1, R^2 and R^3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group, with the proviso that the number of phenyl groups in compound (I) is not more 2 and the number of o-tolyl groups in compound (I) is not more than 2.

3. A system as claimed in claim 1, wherein the compound (I) used is a compound of the formula

$$(\text{o-Tolyl-O-})_w\ (\text{m-Tolyl-O-})_x\ (\text{p-Tolyl-O-})_y\ (\text{Phenyl-O-})_z\ \text{P}$$

where w, x, y, z are each a natural number
and $w + x + y + z = 3$ and
w, z are each less than or equal to 2.

4. A system as claimed in any of claims 1 to 3, wherein Y is a substituted or unsubstituted pyrocatechol, bis(phenol) or bis(naphthol).

5. A system as claimed in any of claims 1 to 4, comprising an Ni(0) complex of the formula

$$\text{Ni(0)}\ (\text{compound (I)})_x(\text{compound(II)})$$

where x = 1, 2.

6. A process for preparing a system as claimed in any of claims 1 to 5, which comprises

a) reacting Ni(0) with a compound (I) in the presence of a liquid diluent to give a first system comprising Ni(0) and compound (I)
and then

b) reacting this first system with a compound (II) in the presence of a liquid diluent to give a system as claimed in any of claims 1 to 10.

7. A process as claimed in claim 6, wherein metallic nickel is used as Ni(0) in step a).

8. A process as claimed in claim 6 or 7, wherein from 4 to 10 mol of compound (I) are used per mol of Ni(0) in step a).

9. A process as claimed in any of claims 6 to 8, wherein the liquid diluent used in step a) is a compound of the formula (I), 3-pentenenitrile, 4-pentenenitrile, 2-methyl-3-butenenitrile, adiponitrile, methylglutaronitrile, an aromatic, an aliphatic or a mixture thereof.

10. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a catalyst.

11. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a homogeneous catalyst.

12. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a protic acid as homogeneous catalyst.

13. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of hydrogen chloride as homogeneous catalyst.

14. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a compound of the formula $(R^1X^1)(R^2X^2)PCl$ or $(R^1X^1)PCl_2$, where X^1, X^2, R^1, R^2 are as defined in any of claims 1 to 8, as homogeneous catalyst.

15. A process as claimed in any of claims 6 to 14, wherein the catalyst is removed between step a) and step b).

16. A process as claimed in any of claims 6 to 15, wherein from 1 to 4 mol of compound (II) are used per mol Ni(0) in step b).

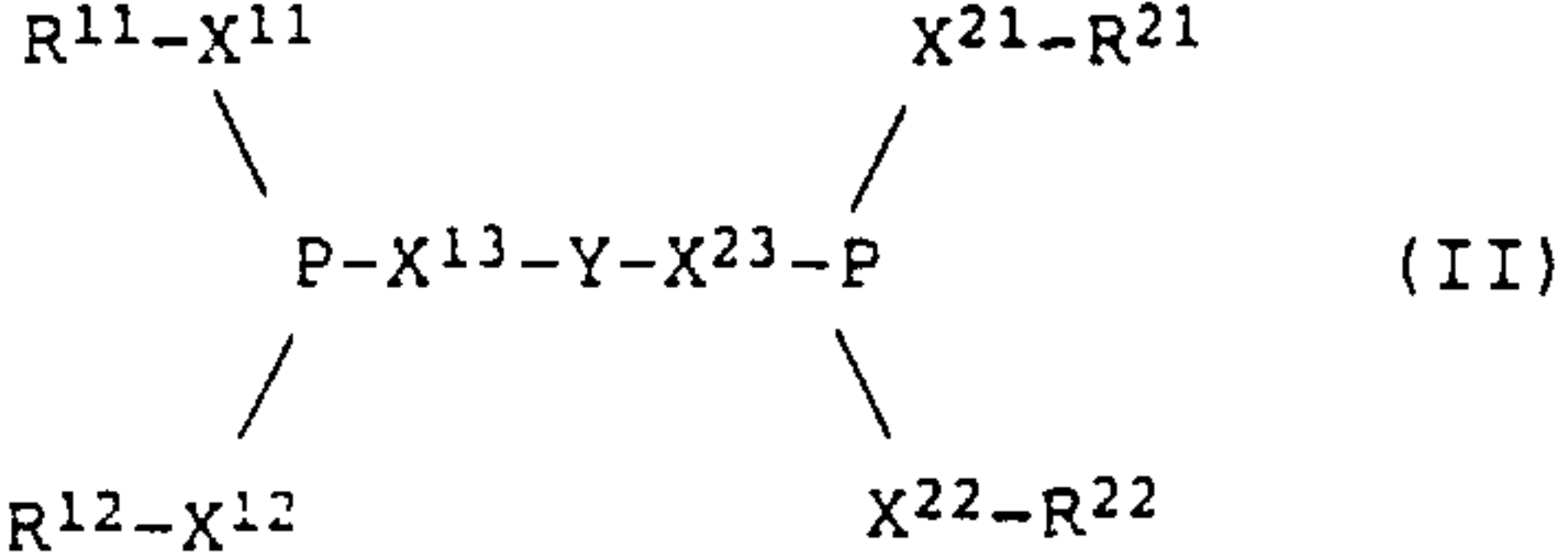
17. A process as claimed in any of claims 6 to 16, wherein the liquid diluent used in step b) is a compound of the formula (I), 3-pentenenitrile, 4-pentenenitrile, 2-methyl-3-butenenitrile, adiponitrile, methylglutaronitrile, an aromatic, an aliphatic or a mixture thereof.

18. A process as claimed in any of claims 6 to 17, wherein the same liquid diluent is used in step a) and in step b).

19. A process for preparing mixtures of monoolefinic C_5-mononitriles having nonconjugated C=C and C=N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

20. A process for preparing a dinitrile by hydrocyanation of a mixture of monoolefinic C_5-mononitriles having nonconjugated C=C and C=N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

21. A process for preparing adiponitrile by hydrocyanation of a mixture of monoolefinic C_5-mononitriles having nonconjugated C=C and C=N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.



(II)