

TITLE**HYDROCYANATION PROCESS AND MULTIDENTATE PHOSPHITE
AND NICKEL CATALYST COMPOSITION THEREFOR**FIELD OF THE INVENTION

5 The invention relates to a process and catalyst composition for the hydrocyanation of monoethylenically unsaturated compounds wherein zero-valent nickel and a multidentate phosphite ligand are used in the presence of a Lewis acid promoter.

BACKGROUND OF THE INVENTION

10 Hydrocyanation catalyst systems, particularly pertaining to the hydrocyanation of ethylenically unsaturated compounds, are known in the art. For example, systems useful for the hydrocyanation of butadiene to form pentenenitrile (PN) and in the subsequent hydrocyanation of pentenenitrile to form adiponitrile (ADN), are known in the commercially important nylon synthesis field.

15 The hydrocyanation of ethylenically unsaturated compounds using transition metal complexes with monodentate phosphite ligands is documented in the prior art. See, for example, U.S. Patents 3,496,215; 3,631,191; 3,655,723; and 3,766,237, and Tolman et al., Advances in Catalysis, 33, 1, 1985. The hydrocyanation of activated ethylenically unsaturated compounds, such as with
20 conjugated ethylenically unsaturated compounds (e.g., butadiene and styrene), and strained ethylenically unsaturated compounds (e.g., norbornene) proceeds without the use of a Lewis acid promoter, while hydrocyanation of unactivated ethylenically unsaturated compounds, such as 1-octene and 3-pentenenitrile, requires the use of a Lewis acid promoter.

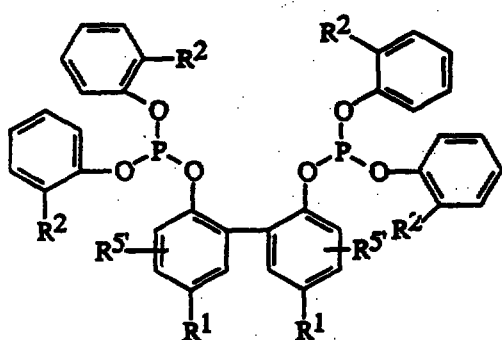
25 Teachings regarding the use of a promoter in the hydrocyanation reaction appear, for example, in U.S. Patent 3,496,217. This patent discloses an improvement in hydrocyanation using a promoter selected from a large number of metal cation compounds with a variety of anions as catalyst promoters. U.S. Patent 3,496,218 discloses a nickel hydrocyanation catalyst promoted with various
30 boron-containing compounds, including triphenylboron and alkali metal borohydrides. U.S. Patent 4,774,353 discloses a process for the preparation of dinitriles, including ADN, from unsaturated nitriles, including PN, in the presence of a zero-valent nickel catalyst and a triorganotin catalyst promoter. Moreover, U.S. Patent 4,874,884 discloses a process for producing ADN by the zero-valent
35 nickel-catalyzed hydrocyanation of pentenenitriles in the presence of a synergistic combination of promoters selected in accordance with the reaction kinetics of the ADN synthesis.

Phosphite ligands have been shown to be useful ligands in the hydrocyanation of activated ethylenically unsaturated compounds. See, for example, Baker, M. J., and Pringle, P. G., J. Chem. Soc., Chem. Commun., 1292, 1991; Baker et al., J. Chem. Soc., Chem. Commun., 803, 1991; Union Carbide,
 5 WO 93,03839. Also, phosphite ligands have been disclosed with rhodium in the hydroformylation of functionalized ethylenically unsaturated compounds: see, Cuny et al., J. Am. Chem. Soc., 1993, 115, 2066.

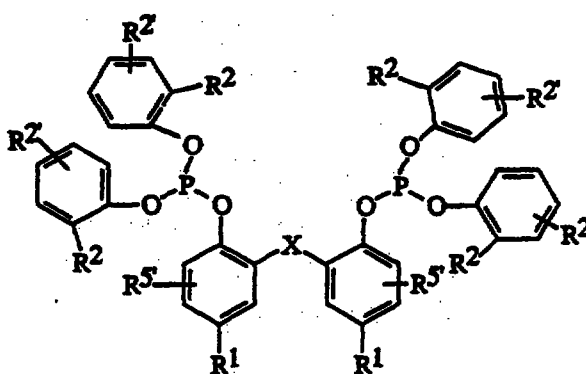
The present invention provides a novel process and catalyst precursor complex which is more rapid, selective, efficient and stable than current processes
 10 and catalyst complexes employed in the hydrocyanation of monoethylenically unsaturated compounds. Other objects and advantages of the present invention will become apparent to those skilled in the art upon reference to the detailed description of the invention which hereinafter follows.

SUMMARY OF THE INVENTION

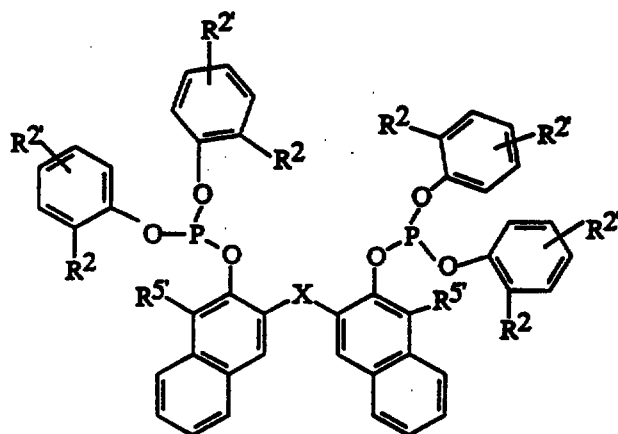
15 The present invention provides a hydrocyanation process, comprising reacting an acyclic, aliphatic, monoethylenically unsaturated compound in which the ethylenic double bond is not conjugated to any other olefinic group in the molecule, or a monoethylenically unsaturated compound in which the ethylenic double bond is conjugated to an organic ester group, with a source of HCN in the
 20 presence of a catalyst precursor composition comprising a Lewis acid, a zero-valent nickel, and at least one multidentate phosphite ligand selected from the group represented by the following Formulas I, II, III, IV, V, VI, and VII, in which all like reference characters have the same meaning, except as further explicitly limited.



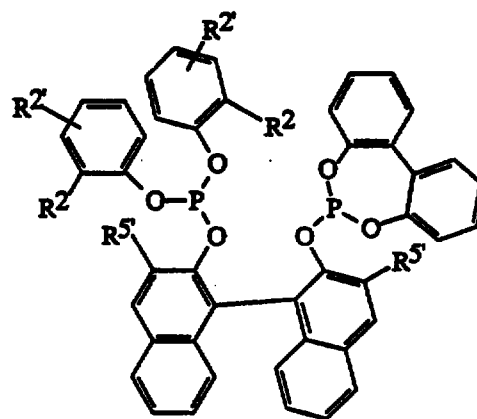
Formula I



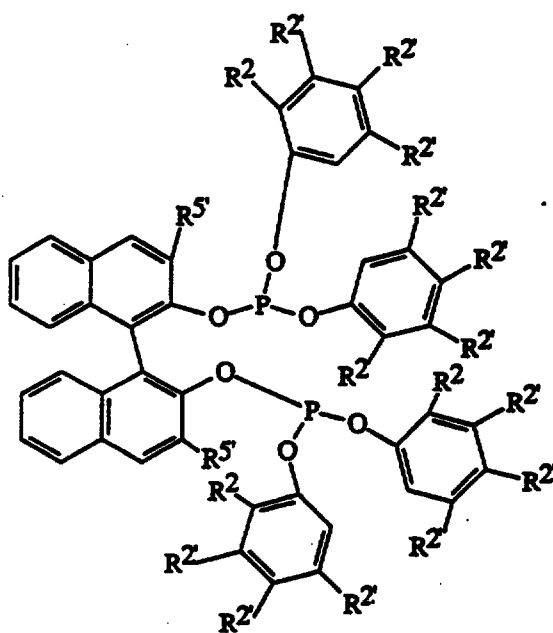
Formula II



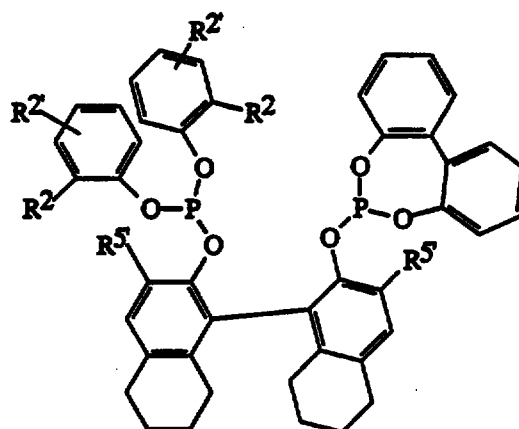
Formula III



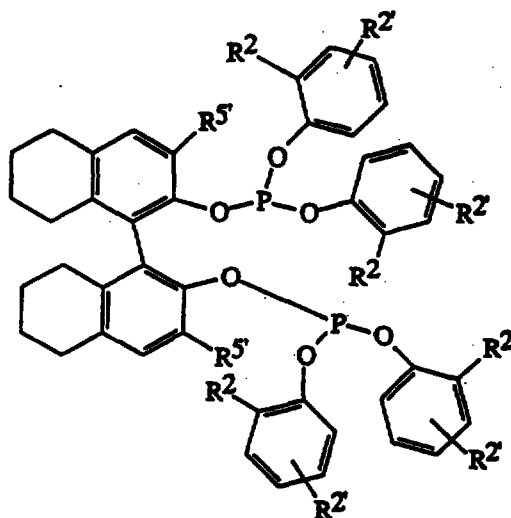
Formula IV



Formula V



Formula VI



Formula VII

wherein

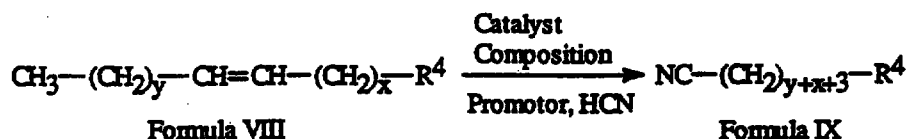
- each R^1 is independently, H, halogen, a C_1 to C_6 alkyl, or OR^3 wherein R^3 is a C_1 to C_6 alkyl;
- each R^2 is independently a secondary or tertiary hydrocarbyl of 3 to 6 carbon atoms;
- each $R^{2'}$ is independently H, halogen, OR^3 wherein R^3 is a C_1 to C_6 alkyl or a primary, secondary or tertiary hydrocarbyl of 1 to 6 carbon atoms; for Formulas II, III, IV, VI and VII, $R^{2'}$ is at either the meta or para position to the oxygen;
- each $R^{5'}$ is independently H or a primary or secondary hydrocarbyl of 1 to 3 carbon atoms in either the ortho or meta position to the oxygen or $CO_2R^{3'}$ wherein $R^{3'}$ is a C_1 to C_4 alkyl; and
- each X is independently O or $CH(R^{4'})$, wherein $R^{4'}$ is H, a substituted phenyl, or a C_1 to C_6 alkyl;
- with the proviso that the terms "secondary" and "tertiary" herein refer to the carbon atom bonded to an aromatic ring;
- and with the further proviso that in Formulas I, II, and V at least one R^2 cannot be a tertiary hydrocarbyl.

In the above catalyst compositions, the Lewis acid is considered to be a promoter.

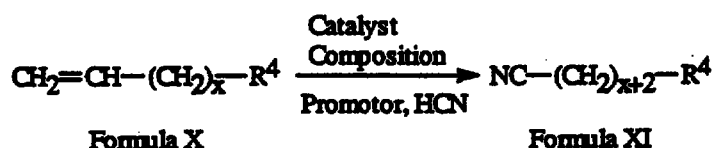
The present invention further provides a catalyst composition consisting essentially of zero-valent nickel and at least one multidentate phosphite ligand selected from one of Formulas I, II, III, IV, V, VI and VII, as defined above.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Representative ethylenically unsaturated compounds which are useful in the process of this invention are shown in Formulas VIII or X, and the corresponding terminal nitrile compounds produced are illustrated by Formulas IX or XI, respectively, wherein like reference characters have same meaning.



or



wherein

R^4 is H, CN, CO_2R^5 , or perfluoroalkyl;

y is an integer of 0 to 12;

x is an integer of 0 to 12 when R^4 is H, CO_2R^5 or perfluoroalkyl;

x is an integer of 1 to 12 when R^4 is CN; and

R^5 is alkyl.

One of the ligands useful in the catalyst compositions of the present invention is illustrated above by Formula I, as defined. Alkyl groups in Formula I can be either straight chain or branched. When R^1 is OR^3 , R^3 can be primary, secondary or tertiary; examples include methyl, ethyl, isopropyl and t-butyl. In the preferred ligand, both R^1 groups are H, methoxy groups, or chlorine. As stated in the definitions of the reference characters, all of the R^2 groups in Formula I cannot be tertiary hydrocarbyls; see Comparative Example 3 for Ligand "A2". The term "hydrocarbyl" is well known to the art and designates a hydrocarbon molecule from which one hydrogen atom has been removed. Such structure can contain single, double, or triple bonds. In the preferred Formula I ligand, R^2 in each occurrence is isopropyl, R^1 is methoxy, and R^5 is hydrogen. In Formula II, X preferably is $\text{CH}(\text{Et})$, where Et stands for ethyl, R^2 in each occurrence is isopropyl, $\text{R}^{2'}$ is hydrogen, and each one of R^1 and $\text{R}^{5'}$ is methyl, where each $\text{R}^{5'}$ is in a position ortho to the oxygen atom. Again, all of the R^2 groups cannot be tertiary hydrocarbyls; see Comparative Example 13 for Ligand "J2". In the preferred Formula III ligand, each R^2 is isopropyl, each $\text{R}^{2'}$ is hydrogen, X is $\text{CHR}^{4'}$, where $\text{R}^{4'}$ is 4-methoxyphenyl, and each $\text{R}^{5'}$ is hydrogen. In the preferred Formula IV

ligand, each R^2 group is isopropyl, and each R^2 and R^5 is hydrogen. In the preferred Formula V ligand, each R^2 group is isopropyl, each R^2 group is para to R^2 methyl with the other R^2 being hydrogens and each R^5 is hydrogen. In the preferred Formula VI ligand, each R^2 group is isopropyl, each R^2 is hydrogen, and each R^5 is hydrogen. In the preferred Formula VII ligand, each R^2 group is isopropyl, and each R^2 group is hydrogen and each R^5 group is hydrogen.

The catalyst composition of the invention may be considered a "precursor" composition in that the zero-valent nickel at some point becomes complexed to the multidentate phosphite ligand, and, further in all likelihood, additional reactions occur during hydrocyanation, such as, for example, complexing of the initial catalyst composition to an ethylenically unsaturated compound.

These ligands can be prepared by a variety of methods known in the art, for example, see descriptions in European Patent Application 92109599.8 of Mitsubishi Kasei Corporation and the corresponding U.S. Patent 5,235,113 to Sato et al. The reaction of 2-isopropylphenol with phosphorus trichloride gives the phosphorochloridite. The reaction of this phosphorochloridite with 2,2'-dihydroxy-5,5'-dimethoxy-1,1'-biphenyl in the presence of triethylamine gives the above-identified preferred ligand of Formula I.

The zero-valent nickel compounds can be prepared or generated according to techniques well known in the art, as described, for example, in U.S. Patents 3,496,217; 3,631,191; 3,846,461; 3,847,959; and 3,903,120, which are incorporated herein by reference. Zero-valent nickel compounds that contain ligands which can be displaced by the organophosphorus ligand are a preferred source of zero-valent nickel. Two such preferred zero-valent nickel compounds are $Ni(COD)_2$ (COD is 1,5-cyclooctadiene) and $Ni\{P(O-o-C_6H_4CH_3)_3\}_2(C_2H_4)$, both of which are known in the art. Alternatively, divalent nickel compounds may be combined with a reducing agent, to serve as a source of zero-valent nickel in the reaction. Suitable divalent nickel compounds include compounds of the formula NiY_2 where Y is halide, carboxylate, or acetylacetonate. Suitable reducing agents include metal borohydrides, metal aluminum hydrides, metal alkyls, Zn, Fe, Al, Na, or H_2 . Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Patent 3,903,120, is also a suitable source of zero-valent nickel.

The nonconjugated acyclic, aliphatic, monoethylenically unsaturated starting materials useful in this invention include unsaturated organic compounds containing from 2 to approximately 30 carbon atoms. 3-pentenitrile and 4-pentenitrile are especially preferred. As a practical matter, when the nonconjugated acyclic aliphatic monoethylenically unsaturated compounds are used

in accordance with this invention, up to about 10% by weight of the monoethylenically unsaturated compound may be present in the form of a conjugated isomer, which itself may undergo hydrocyanation. For example, when 3-pentenitrile is used, as much as 10% by weight thereof may be 2-pentenitrile. (As
5 used herein, the term "pentenenitrile" is intended to be identical with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups which do not attack the catalyst, such as cyano. These unsaturated compounds include monoethylenically unsaturated compounds containing from 2 to 30 carbons such as
10 ethylene, propylene, butene-1, pentene-2, hexene-2, etc., nonconjugated diethylenically unsaturated compounds such as allene, substituted compounds such as 3-pentenitrile, 4-pentenitrile, methyl pent-3-enoate, and ethylenically unsaturated compounds having perfluoroalkyl substituents such as, for example, C_zF_{2z+1} , where z is an integer of up to 20. The monoethylenically unsaturated
15 compounds may also be conjugated to an ester group such as methyl pent-2-enoate.

The starting ethylenically unsaturated compounds useful in this invention and the hydrocyanation products thereof are those shown above in Formulas VIII through XI. Those of Formula VIII yield terminal nitriles of Formula IX, while
20 those of Formula X yield terminal nitriles of Formula XI.

Preferred are nonconjugated linear alkenes, nonconjugated linear alkene-nitriles, nonconjugated linear alkenoates, linear alk-2-enoates and perfluoroalkyl ethylenes. Most preferred substrates include 3- and 4-pentenitrile, alkyl 2-, 3-, and 4-pentenoates, and $C_zF_{2z+1}CH=CH_2$ (where z is 1 to 12).

25 The preferred products are terminal alkanenitriles, linear dicyanoalkylenes, linear aliphatic cyanoesters, and 3-(perfluoroalkyl)propionitrile. Most preferred products are adiponitrile, alkyl 5-cyanovalerate, and $C_zF_{2z+1}CH_2CH_2CN$, where z is 1 to 12.

The present hydrocyanation process may be carried out, for example, by
30 charging a reactor with the reactants, catalyst composition, and solvent, if any; but preferably, the hydrogen cyanide is added slowly to the mixture of the other components of the reaction. Hydrogen cyanide may be delivered as a liquid or as a vapor to the reaction. Another suitable technique is to charge the reactor with the catalyst and the solvent to be used, and feed both the unsaturated compound and
35 the HCN slowly to the reaction mixture. The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 2000:1.

Preferably, the reaction medium is agitated, for example, by stirring or shaking. The reaction product can be recovered by conventional techniques such

as, for example, by distillation. The reaction may be run either batchwise or in a continuous manner.

The hydrocyanation reaction can be carried out with or without a solvent. The solvent, if used, should be liquid at the reaction temperature and pressure and
5 inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons, such as benzene or xylene, and nitriles, such as acetonitrile or benzonitrile. In some cases, the unsaturated compound to be hydrocyanated may itself serve as the solvent.

The exact temperature is dependent to a certain extent on the particular
10 catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25°C to 200°C can be used, the range of 0°C to 150°C being preferred.

Atmospheric pressure is satisfactory for carrying out the present invention and hence pressures of from about 0.05 to 10 atmospheres (50.6 to 1013 kPa) are
15 preferred. Higher pressures, up to 10,000 kPa or more, can be used, if desired, but any benefit that may be obtained thereby would probably not justify the increased cost of such operations.

HCN can be introduced to the reaction as a vapor or liquid. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example,
20 U.S. Patent 3,655,723.

The process of this invention is carried out in the presence of one or more Lewis acid promoters which affect both the activity and the selectivity of the catalyst system. The promoter may be an inorganic or organometallic compound in which the cation is selected from scandium, titanium, vanadium, chromium,
25 manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include 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 , $\text{FeCl}_2(\text{THF})_2$, $\text{TiCl}_4(\text{THF})_2$, TiCl_4 , TiCl_3 , $\text{CITi}(\text{OiPr})_3$, 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 ,
30 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 . Suitable promoters are further described in U.S. Patents 3,496,217; 3,496,218; and 4,774,353. These include 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 or aryl group). U.S. Patent 4,874,884 describes how
35 synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl_2 , ZnCl_2 , $\text{B}(\text{C}_6\text{H}_5)_3$, and $(\text{C}_6\text{H}_5)_3\text{SnX}$, where $\text{X} = \text{CF}_3\text{SO}_3$, $\text{CH}_3\text{C}_6\text{H}_5\text{SO}_3$, or $(\text{C}_6\text{H}_5)_3\text{BCN}$.

The mole ratio of promoter to nickel present in the reaction can be within the range of about 1:16 to about 50:1.

EXAMPLES

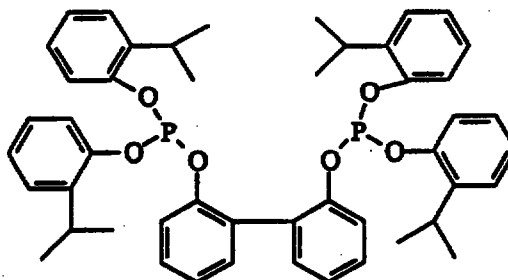
The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

The mixtures were heated in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N₂ gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0°C. This provided a vapor stream which was about 35% HCN (vol/vol). Samples were periodically analyzed by gas chromatography (GC). In the examples, ADN stands for adiponitrile, MGN stands for 2-methylglutaronitrile, and ESN stands for ethylsuccinonitrile. COD stands for bis(1,5-cyclooctadiene) and THF stands for tetrahydrofuran.

EXAMPLE 1

Synthesis of the ligand of Formula I

where each R² is isopropyl and each R¹ is H (Ligand "A")



Ligand "A"

To a solution of 2.0 g of phosphochloridite derived from PCl₃ and 2-isopropylphenol in 20 ml of toluene was added 0.55 g (2.95 mmoles) of 2,2'-biphenol and 1.1 g (10.9 mmoles) of NEt₃ in 20 ml of toluene. After stirring overnight under nitrogen, the mixture was filtered through Celite® (a product of Johns-Manville Company), and washed with toluene. The remaining solvent was removed in a rotary evaporator. Thus was obtained 2.163 g of product as an opaque liquid. ³¹P (1H) (121.4 MHz, C₆D₆): 130.96 ppm. ¹H (300 MHz, C₆D₆): 7.51 (d, J = 8 Hz, 2H), 7.39 (dd, J = 1.6, 7.5 Hz, 2H), 7.2-6.9 (m, 20H), 3.43 (septet, J = 6.9 Hz, 4H), 1.19 (d, J = 6.9 Hz, 24H) along with a small amount of toluene. HRMS (High Resolution Mass Spectroscopy) calculated for C₄₈H₅₂O₆P₂: 786.3239; Found: 786.3208.

EXAMPLE 1A**Hydrocyanation of 3-Pentenitrile
with Ligand "A"/Ni(COD)₂; ZnCl₂ promoter**

342 mg of Ligand "A" and 40 mg Ni(COD)₂ were dissolved in 5 ml THF.

- 5 The solvent was removed by vacuum evaporation and 5 ml of 3PN (3-pentenitrile) and 20 mg of ZnCl₂ were added. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 12 ml/min at 50°C for 15 minutes. After this time, the temperature controller was set at 60°C. At 15 minute intervals, the temperature was increased to 70, 80, and 100°C. Fifteen minutes after a
- 10 temperature of 100°C was set, GC analysis indicated 46.7% ADN, 8.0% MGN, and 1.0% ESN.

EXAMPLE 1B**Hydrocyanation of 3-Pentenitrile
with Ligand "A"/Ni(COD)₂; ZnCl₂ promoter**

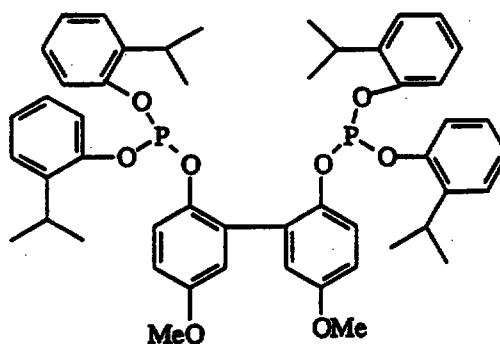
- 15 Ligand "A", 332 mg, and 40 mg of Ni(COD)₂ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation; then, 5 ml of 3PN and 20 mg of ZnCl₂ were added. The mixture was treated with HCN with a nitrogen carrier gas flow rate of 12 ml/min at 70°C for 2 hrs. GC analysis indicated 70.0% ADN, 11.6% MGN and 1.4% ESN (selectivity to ADN: 84%).

EXAMPLE 1C**Hydrocyanation of 3-Pentenitrile
with Ligand "A"/Ni(COD)₂; ZnCl₂ promoter**

- 20 Ligand "A", 330 mg, and 40 mg of Ni(COD)₂ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation, and 5 ml of 3PN and
- 25 20 mg of ZnCl₂ were added. The mixture was treated with HCN with a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. After this time, GC analysis indicated 26.4% ADN, 4.5% MGN and 0.6% ESN (selectivity to ADN: 84).

EXAMPLE 2

Synthesis of the ligand of Formula I where each R^2 is isopropyl, each R^5 is H, and each R^1 is OCH_3 (Ligand "B")



Ligand "B"

2,2'-Dihydroxyl-5,5'-dimethoxy-1,1'-biphenyl was prepared by the
 5 dealkylation of 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5'-dimethoxy-1,1'-biphenyl using a
 procedure described in the literature (Tashiro et al., Organic Preparations and
 Procedures Int., 8, 263, 1976). Ten grams of $AlCl_3$ and 10 g of 2,2'-dihydroxy-
 3,3'-di-*t*-butyl-5,5'-dimethoxy-1,1'-biphenyl were mixed in 125 ml of benzene and
 heated at 40°C for 3 hours. The mixture was cooled in ice, and 125 ml of 10%
 10 aqueous HCl was added slowly. The organic layer was separated and washed with
 three 125-ml portions of 10% NaOH. The basic solution was neutralized with
 concentrated HCl and extracted three times with 100 ml portions of ether. The
 ether layer was dried over Na_2SO_4 . After filtering and removing the solvent by
 vacuum evaporation, the brown oil was washed with hexane; the product
 15 crystallized from CH_2Cl_2 /hexane, yielding 2.202 g of 2,2'-dihydroxyl-5,5'-
 dimethoxy-1,1'-biphenyl, which was obtained as a white solid. ^1H (300 MHz,
 CD_2Cl_2): 6.9-6.8 (m, 6H), 5.71 (s, 2H), 3.78 (s, 6H).

To 2 g of phosphochloridite derived from PCl_3 and 2-isopropylphenol in
 20 ml of toluene was added 660 mg of the 2,2'-dihydroxy-5,5'-dimethoxy-1,1'-
 biphenyl prepared above and 1.01 g of NEt_3 in 20 ml of toluene. The mixture was
 stirred overnight and filtered through Celite®, and washed with toluene. The
 solvent was removed to give 2.588 g of the desired product as an orange oil.
 ^{31}P {1H} (121.4 MHz, C_6D_6): 131.41. ^1H -NMR (Nuclear Magnetic Resonance)
 (C_6D_6): 7.4-6.4 (22H), 3.3 (m, 4H), 3.1 (s, 6H), 1.0 (m, 24H) along with a small
 25 amount of toluene. FBMS (Fast Atom Bombardment Mass Spectroscopy):
 calculated $M-OCH_3$: 815.36; Found: 815.07.

EXAMPLE 2A

Hydrocyanations of 3-Pentenenitrile
with Ligand "B"/Ni(o-TTP)₂(C₂H₄),

where o-TTP is P(O-o-C₆H₄CH₃)₃; ZnCl₂ promoter

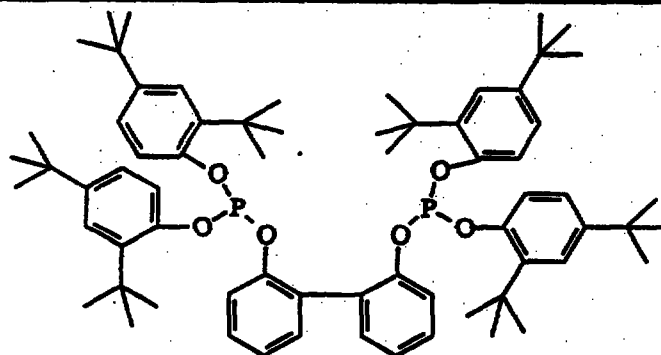
- 5 Ligand "B", 346 mg, 0.111 g of Ni(o-TTP)₂(C₂H₄), and 20 mg of ZnCl₂ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 61.2% ADN, 9.9% MGN and 1.3% ESN (selectivity to ADN: 84.5%).

COMPARATIVE EXAMPLES 3-4A

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BIPHENOL BACKBONE**COMPARATIVE EXAMPLE 3**

Synthesis of the Ligand of Formula I where all R² are t-butyl,
a t-butyl group is meta to each R², and R¹ and R⁵ are H (Ligand "A2")



Ligand "A2"

- To 3.8 g of the chlorodite derived from PCl₃ and 2,4-di-t-butylphenol in
15 20 ml of toluene there was added 0.75 g of 2,2'-biphenol and 0.809 g of NEt₃ in
20 ml of toluene. The mixture was stirred overnight and then filtered through
Celite® and washed with toluene. The solvent was removed in a rotary
evaporator. The residue was washed with acetonitrile, and filtered to give 1.381 g
of the product as a white solid. ³¹P {1H} (121.4 MHz, C₆D₆): 132.46 ppm.
20 Also, small peaks at 161.57 and 139.88 due to impurities.

COMPARATIVE EXAMPLE 3A

Hydrocyanation using Ligand "A2" and Ni(o-TTP)₂(C₂H₄)

- Ligand "A2", 448 mg, and 0.111 g of Ni(o-TTP)₂(C₂H₄) and 20 mg of
ZnCl₂ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a
25 nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis
indicated 0.0% ADN, 0.05% MGN and 0.1% ESN.

COMPARATIVE EXAMPLE 3B

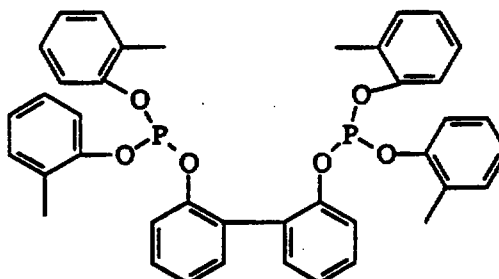
Hydrocyanation using Ligand "A2" and Ni(COD)₂

- Ligand "A2", 452 mg, 0.040 g of Ni(COD)₂, and 20 mg of ZnCl₂ were
30 dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier

gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 0.0% ADN, 0.0% MGN, and 0.1% ESN.

COMPARATIVE EXAMPLE 4

Synthesis of the Ligand of Formula I where
R² is -CH₃ and R¹ and R⁵ are H (Ligand "A3")



Ligand "A3"

The phosphachloridite was prepared in the usual manner by the reaction of PCl₃ with o-cresol at 0°C in toluene, followed by fractional distillation at reduced pressure. It (1.85 g; 6.6 mmol) was dissolved in toluene (30 ml), and the solution was cooled to 0°C. Triethylamine (3 ml) was added, followed by 2,2'-biphenol (0.56 g, 3.0 mmols). The mixture was stirred overnight at room temperature. The solids were filtered, and the solvent was removed at a reduced pressure to give 2.26 g of a lightly orange-colored liquid. ³¹P NMR (CDCl₃): δ 133.1. Also, smaller peaks at 144.5, 131.2, and 3.2 due to impurities. ¹H NMR also indicated a small amount of Et₃N/salts.

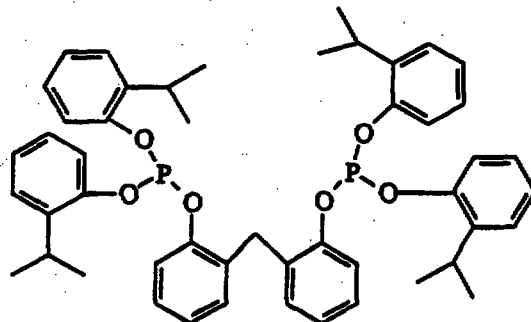
COMPARATIVE EXAMPLE 4A

Hydrocyanation using Ligand "A3"

Ligand "A3", 346 mg, 0.111 g of Ni(o-TTP)₂(C₂H₄), and 20 mg of ZnCl₂ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 0.0% ADN, 0.05% MGN and 0.0% ESN.

EXAMPLE 5

Synthesis of the ligand of Formula II where each R^2 is isopropyl, each R^1 , R^2 and R^5 is H, and X is $-CH_2-$ (Ligand "C")



Ligand "C"

To 2 g of the phosphochloridite derived from PCl_3 with 2-isopropylphenol
 5 in 20 ml of toluene there was added 595 mg of bis(2-hydroxyphenyl)methane and
 1.01 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered
 through Celite[®], and washed with toluene. The solvent was removed, to give
 2.514 g of the desired product as a pale yellow oil. ^{31}P (1H) (121.4 MHz, C_6D_6):
 131.33. ^1H NMR (C_6D_6): 4.11 (s, 2H), 3.2 (m, 4H), 0.98 (d, 24H) along with
 10 aromatic resonances and a little toluene. HRMS: calculated $C_{49}H_{54}O_6P_2$:
 800.3396; Found: 800.3017.

EXAMPLE 5A

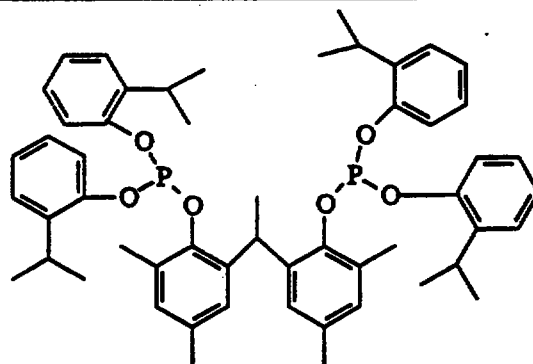
Hydrocyanation of 3-Pentenitrile with

Ligand "C"/Ni(o-TTP)₂(C₂H₄); ZnCl₂ promoter

15 Ligand "C", 337 mg, 0.111 g of Ni(o-TTP)₂(C₂H₄), and 20 mg of ZnCl₂
 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen
 flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 52.4% ADN,
 11.3% MGN and 1.6% ESN (selectivity to ADN: 80%).

EXAMPLE 6

Synthesis of the ligand of Formula II
 where each R^2 is isopropyl, each $R^{2'}$ is H, each
 R^1 and $R^{5'}$ is $-\text{CH}_3$, and X is $-\text{C}(\text{H})(\text{CH}_3)-$ (Ligand "D")



Ligand "D"

- 5 To 2 g of the chlorodite derived from PCl_3 and 2-isopropylphenol in 20 ml of toluene there was added 803 mg of 2,2'-ethyldienebis(4,6-dimethylphenol), prepared according to Yamada et al., Bull. Chem. Soc. Jpn., 62, 3603 (1989), and 0.900 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite®, and washed with toluene. The solvent was removed to give
- 10 2.603 g of the desired product as a very light-yellow oil. ^{31}P {1H} (121.4 MHz, C_6D_6): 133.53. Also, minor peaks due to impurities at 133.19, 131.25 and 130.36, 127.59 and 105.81 ppm. FBMS calculated for M + H: 871.43; Found: 871.40.

EXAMPLE 6A

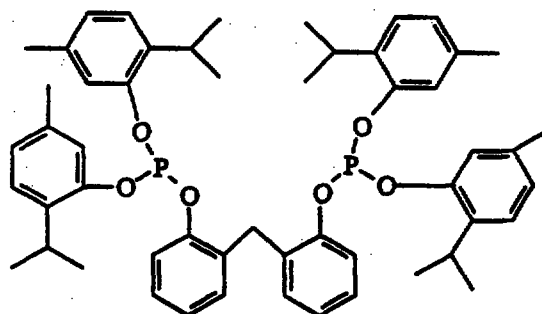
- 15 Hydrocyanation of 3-Pentenenitrile
 with Ligand "D"/ $\text{Ni}(\text{COD})_2$; ZnCl_2 promoter

Ligand "D", 366 mg, 0.040 g of $\text{Ni}(\text{COD})_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 55.6% ADN, 7.8%

20 MGN and 1.4% ESN (selectivity to ADN: 86%).

EXAMPLE 7

Synthesis of the ligand of Formula II where each R^2 is isopropyl, $R^{2'}$ is methyl, R^1 and $R^{5'}$ are H, and X is $-CH_2-$ (Ligand "E")



Ligand "E"

To 2 g of the chlorodite derived from PCl_3 and thymol in 20 ml of toluene there was added 549 mg of bis(2-hydroxyphenyl)methane and 0.910 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite®, and washed with toluene. The solvent was removed to give 2.379 g of the desired product as a light yellow oil. ^{31}P (1H) (121.4 MHz, C_6D_6): 131.69. Also, minor peaks due to impurities at 132.24 and 130.9. FBMS: calculated $C_{53}H_{62}O_6P_2$: 856.41; Found: 855.63.

EXAMPLE 7A

Hydrocyanation of 3-Pentenitrile with
Ligand "E"/ $Ni(COD)_2$; $ZnCl_2$ promoter

Ligand "E", 360 mg, and 0.040 g of $Ni(COD)_2$ were dissolved in 5 ml of THF. The solvent was removed, and 20 mg of $ZnCl_2$ and 5 ml of 3PN were added. The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 5.8% ADN, 1.4% MGN and 0.2% ESN (selectivity to ADN: 78%).

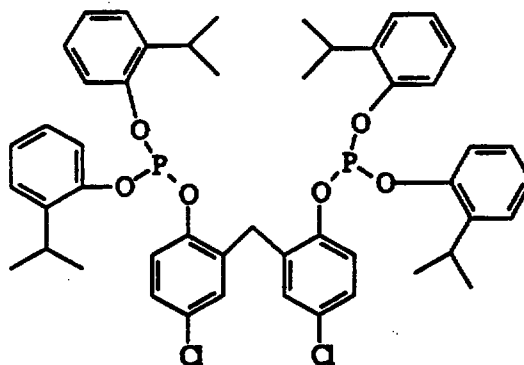
EXAMPLE 7B

Hydrocyanation of 3-Pentenitrile with
Ligand "E"/ $Ni(COD)_2$; $ZnCl_2$ promoter

Ligand "E", 360 mg, 40 mg of $Ni(COD)_2$ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation. To the residue was added 5 ml of 3PN and 20 mg of $ZnCl_2$. The mixture was treated with HCN at a nitrogen flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 27.4% ADN, 5.3% MGN, and 0.7% ESN (selectivity to ADN: 82.1%).

EXAMPLE 8

Synthesis of the ligand of Formula II where each R^2 is isopropyl, each R^1 is Cl, R^2 and R^5 are H, and X is $-CH_2-$ (Ligand "F")



Ligand "F"

To 2 g of the phosphochloridite derived from PCl_3 and 2-isopropylphenol
 5 in 20 ml of toluene there was added 799 mg of 2,2'-methylenebis(4-chlorophenol)
 and 900 mg of NEt_3 in 20 ml of toluene. The mixture was stirred overnight,
 filtered through Celite®, and washed with toluene. The solvent was removed, to
 give 2.678 g of the desired product as a light-yellow opaque oil. ^{31}P {1H}
 (121.4 MHz, C_6D_6): 131.6. ^1H NMR (C_6D_6): 4.16 (s, 2H), 3.51 (m, 4H), 1.3
 10 (d, 24H) along with aromatic resonances and a little toluene. FBMS: calculated
 M+H: 869.27; Found: 868.96.

EXAMPLE 8A

Hydrocyanation of 3-Pentenenitrile with
Ligand "F"/Ni(o-TTP) $_2$ (C $_2$ H $_4$); ZnCl $_2$ promoter

15 Ligand "F", 337 mg, 0.111 g of Ni(o-TTP) $_2$ (C $_2$ H $_4$), and 20 mg of ZnCl $_2$
 were dissolved in 5 ml of 3PN. The solution was treated with HCN at a nitrogen
 flow rate of 30 ml/min at 70°C for one hour. After this time, GC analysis indicated
 23.6% ADN, 5.3% MGN and 1.2% ESN (selectivity to ADN: 79%).

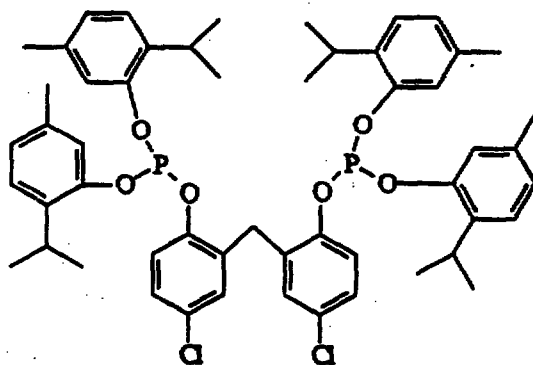
EXAMPLE 8B

Hydrocyanation of 3-Pentenenitrile with
Ligand "F"/Ni(COD) $_2$; ZnCl $_2$ promoter

20 Ligand "F", 365 mg, 40 mg of Ni(COD) $_2$ were dissolved in 5 ml of THF.
 The solvent was removed by vacuum evaporation. To the residue was added 5 ml
 of 3PN and 20 mg of ZnCl $_2$. The mixture was treated with HCN at a nitrogen
 25 flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 51.4% ADN,
 11.5% MGN, and 2.4% ESN (selectivity to ADN: 82.6%).

EXAMPLE 9

Synthesis of the ligand of Formula II where each R^2 is isopropyl; each R^2 para to R^2 is methyl, each R^1 is Cl, each R^5 is H, and X is $-CH_2-$ (Ligand "G")



Ligand "G"

To 1.42 g of the chlorodite derived from PCl_3 and 2-isopropylphenol in
 5 20 ml of toluene there was added 523 mg of 2,2'-methylenebis(4-chlorophenol) and
 0.607 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered
 through Celite®, and washed with toluene. The solvent was removed to give
 2.07 g of the desired product as a colorless oil. ^{31}P (1H) (121.4 MHz, C_6D_6):
 131.87. FBMS: calculated M + H ($M = C_{53}H_{60}O_6P_2Cl_2$): 925.33; Found:
 10 925.25.

EXAMPLE 9A

Hydrocyanation of 3-Pentenenitrile with
Ligand "G"/Ni(COD) $_2$; $ZnCl_2$ promoter

Ligand "G", 389 mg, and 40 mg of $Ni(COD)_2$ were dissolved in 5 ml of
 15 THF. The solvent was removed, and 5 ml of 3PN and 20 mg of $ZnCl_2$ were
 added. The mixture was treated with HCN at a nitrogen carrier gas flow rate of
 30 ml/min at 70°C for one hour. GC analysis indicated 6.1% ADN, 1.7% MGN
 and 0.25% ESN (selectivity to ADN: 76%).

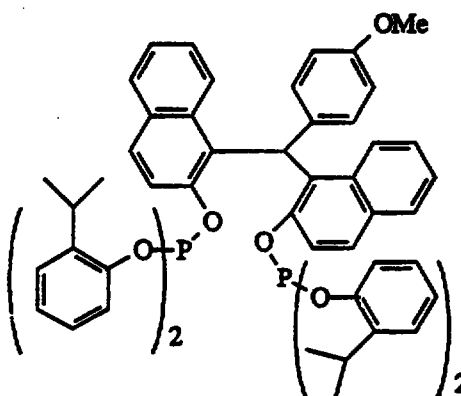
EXAMPLE 9B

Hydrocyanation of 3-Pentenenitrile with
Ligand "G"/Ni(COD) $_2$; $ZnCl_2$ promoter

Ligand "G", 389 mg, 40 mg of $Ni(COD)_2$ were dissolved in 5 ml of THF.
 The solvent was removed by vacuum evaporation. To the residue was added 5 ml
 of 3PN and 20 mg of $ZnCl_2$. The mixture was treated with HCN at a nitrogen
 25 flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 21.2% ADN,
 3.1% MGN, and 0.5% ESN (selectivity to ADN: 82.7%).

EXAMPLE 10

Synthesis of the Ligand of Formula III, where each R^2 is isopropyl, each R^2 and R^5 is H, and X is -CH(p-methoxyphenyl)- (Ligand "H")



Ligand "H"

To 2 g of the chlorodite derived from PCl_3 and 2-isopropylphenol in 20 ml of toluene was added 1.207 g of commercial p-anisylidene 1,1'-(bis(2-naphthol) and 1.01 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite®, and washed with toluene. The solvent was removed, to give 2.916 g of the desired product as a light-yellow oil. ^{31}P (1H) (121.4 MHz, C_6D_6): 130.10. Also, a minor peak due to an impurity at 132.52 ppm.

EXAMPLE 10A**Hydrocyanation using Ligand "H"**

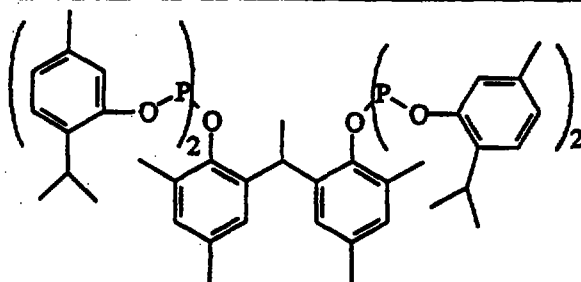
Ligand "H", 423 mg, 0.040 g of $\text{Ni}(\text{COD})_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 16.9% ADN, 2.8% MGN and 0.5% ESN (selectivity to ADN: 83%).

EXAMPLE 10B**Hydrocyanation using Ligand "H"**

Ligand "H", 423 mg, 40 mg of $\text{Ni}(\text{COD})_2$ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation. To the residue was added 5 ml of 3PN and 20 mg of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 36.8% ADN, 6.6% MGN, and 1.0% ESN (selectivity to ADN: 82.6%).

EXAMPLE 11

Synthesis of the Ligand of Formula II where each R^2 is isopropyl; each $R^{2'}$ para to R^2 , R^1 and $R^{5'}$ is methyl, and X is $-\text{CH}(\text{CH}_3)-$ (Ligand "I")



Ligand "I"

- To 2 g of the chlorodite derived from PCl_3 and thymol in 20 ml of toluene there was added 0.741 g of 2,2'-ethyldienebis(4,6-dimethylphenol), prepared according to Yamada et al., Bull. Chem. Soc. Jpn., 62, 3603 (1989), and 1.0 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite®, and washed with toluene. The solvent removed to give 2.427 g of the desired product as a light yellow oil. ^{31}P (1H) (121.4 MHz, C_6D_6): 135.15. Also, minor peaks due to impurities at 137.10, 132.5, 132.0 and 106.4 ppm. FBMS: calculated for M + H: 927.48; Found: medium-intensity ion-cluster at 925.41.

EXAMPLE 11A**Hydrocyanation using Ligand "I"**

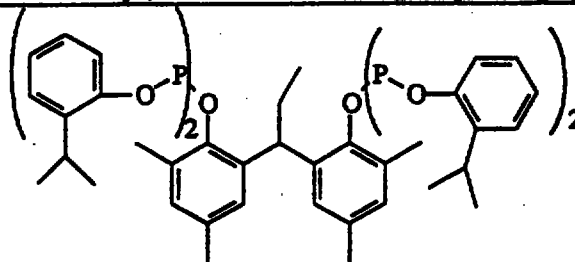
- Ligand "I", 389 mg, 0.040 g of $\text{Ni}(\text{COD})_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 31% ADN, 2.7% MGN and 0.4% ESN (selectivity to ADN: 91%).

EXAMPLE 11B**Hydrocyanation using Ligand "I"**

- Ligand "I", 389 mg, 40 mg of $\text{Ni}(\text{COD})_2$ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation. To the residue was added 5 ml of 3PN and 20 mg of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 48.3% ADN, 4.2% MGN, and 0.5% ESN (selectivity to ADN: 91.1%).

EXAMPLE 12**Synthesis of the Ligand of Formula II**

where each R^2 is isopropyl, each $R^{2'}$ is H, each R^1 and $R^{5'}$ is methyl, and X is $-\text{CH}(\text{CH}_2\text{CH}_3)-$ (Ligand "J")



Ligand "J"

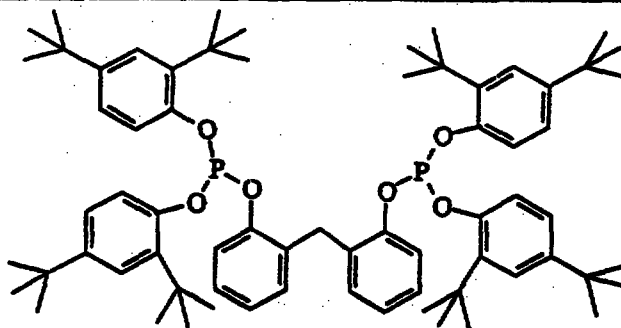
- 5 To 2 g of the chlorodite derived from PCl_3 and 2-isopropylphenol in 20 ml of toluene there was added 0.845 g of 2,2'-propylidenebis(4,6-dimethylphenol) (prepared according to Yamada et al. *loc. cit.*) and 1.0 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight and filtered through Celite®, and washed with toluene. The solvent was removed, to give 2.77 g of the desired
- 10 product as a yellow oil. ^{31}P {1H} (121.4 MHz, C_6D_6): 134.68. Also, minor peaks due to impurities at 136.22, 132.26, 128.6 and 105.29 ppm. FBMS: calculated for M + H: 885.44; Found: 885.39.

EXAMPLE 12A**Hydrocyanation using Ligand "J"**

- 15 Ligand "J", 372 mg, 0.040 g of $\text{Ni}(\text{COD})_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 67% ADN, 7.2% MGN and 0.9% ESN (selectivity to ADN: 89%).

COMPARATIVE EXAMPLES 13-13B**DIPHENYLMETHANE BACKBONE****COMPARATIVE EXAMPLE 13**

Synthesis of the ligand of Formula II where each R^2 and R^2
 para to R^2 is t-butyl, each R^1 and R^5 is H, and X is $-CH_2-$ (Ligand "J2")



Ligand "J2"

To 2 g of the chlorodite derived from PCl_3 and 2,4-di-t-butylphenol in 20 ml of toluene was added 420 mg of bis(2-hydroxyphenyl)methane and 607 mg of NEt_3 in 20 ml of toluene. The mixture was stirred overnight and filtered through Celite®, and washed with toluene. The solvent removed to give 2.238 g of the desired product as a pale yellow oil. ^{31}P (1H) (121.4 MHz, C_6D_6); 131.35. Also, minor peaks due to impurities at 132.6, 132.0, 131.7, 131.6, 130.3, and 121.8.ppm.

COMPARATIVE EXAMPLE 13A

Hydrocyanations of 3-Pentenenitrile with Ligand

"J2"/ $Ni(o-TTP)_2(C_2H_4)$, where o-TTP is $P(O-o-C_6H_4CH_3)_3$; $ZnCl_2$ promoter

Ligand "J2", 454 mg, 0.111 g of $Ni(o-TTP)_2(C_2H_4)$, and 20 mg of $ZnCl_2$ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 2.0% ADN, 0.8% MGN and 0.2% ESN (selectivity to ADN: 67%).

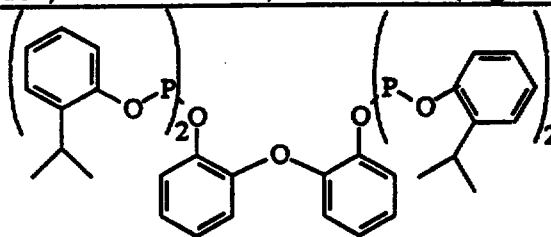
COMPARATIVE EXAMPLE 13B

Hydrocyanation with Ligand "J2"/ $Ni(COD)_2$

Ligand "J2", 454 mg, 0.040 g of $Ni(COD)_2$, and 20 mg of $ZnCl_2$ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. After this time, GC analysis indicated 0.9% ADN, 0.4% MGN and 0.2% ESN.

EXAMPLE 14

Synthesis of the Ligand of Formula II where each R^2 is isopropyl, each R^2 , R^5 and R^1 is H, and X is -O- (Ligand "K")



Ligand "K"

To 2 g of the chlorodite derived from PCl_3 and 2-isopropylphenol in 20 ml of toluene was added 0.601 g of 2,2'-dihydroxyphenyl ether and 1.0 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite®, and washed with toluene. The solvent was removed to give 2.44 g of the desired product as a colorless oil. ^{31}P {1H} (121.4 MHz, C_6D_6): 131.6. Also, minor peaks due to an impurities at 132.12, and 131.8 ppm.

10

EXAMPLE 14A**Hydrocyanation using Ligand "K"**

Ligand "K", 369 mg, 0.040 g of $\text{Ni}(\text{COD})_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 30% ADN, 7.1% MGN and 1.0% ESN (selectivity to ADN: 79%).

15

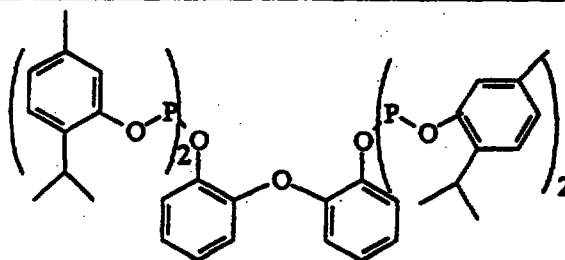
EXAMPLE 14B**Hydrocyanation using Ligand "K"**

Ligand "K", 337 mg, 40 mg of $\text{Ni}(\text{COD})_2$ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation. To the residue was added 5 ml of 3PN and 20 mg of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 68.2% ADN, 15.4% MGN, and 3.2% ESN (selectivity to ADN: 78.6%).

20

EXAMPLE 15

Synthesis of the Ligand of Formula II where each R^2 is isopropyl, each $R^{2'}$ para to R^2 is methyl, each R^5 and R^1 is H, and X is -O- (Ligand "L")



Ligand "L"

To 2 g of the chlorodite derived from PCl_3 and thymol in 20 ml of toluene was added 0.554 g of 2,2'-dihydroxyphenyl ether and 1.0 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite[®], and washed with toluene. The solvent removed, to give 2.46 g of the desired product as a colorless oil. ^{31}P (1H) (121.4 MHz, C_6D_6): 131.81. Also, minor peaks due to impurities at 132.3 and 132.0 ppm.

10

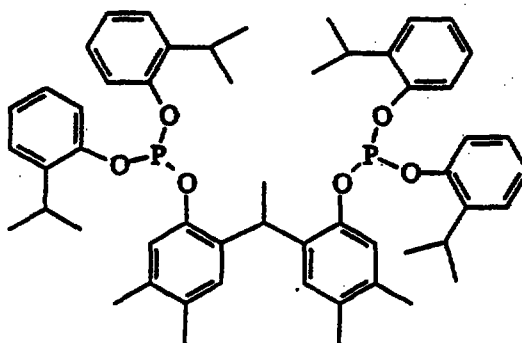
EXAMPLE 15A**Hydrocyanation using Ligand "L"**

Ligand "L", 359 mg, 0.040 g of $Ni(COD)_2$, and 20 mg of $ZnCl_2$ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier gas flow rate of 30 ml/min at 70°C for one hour. After this time, GC analysis indicated 55% ADN, 12.0% MGN and 1.0% ESN (selectivity to ADN: 80%).

15

EXAMPLE 16

Synthesis of the ligand of Formula II where each R^2 is isopropyl, each $R^{2'}$ is H, each R^5 and R^1 is methyl, and X is -CH(CH₃)- (Ligand "D2")



Ligand "D2"

20

To 2 g of the chlorodite derived from PCl_3 and 2-isopropylphenol in 20 ml of toluene was added 803 mg of 2,2'-ethyldienebis(4,5-dimethylphenol), prepared according to Yamada et al., *op. cit.*, and 1 g of NEt_3 in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite[®], and washed with toluene. The solvent was removed, to give 2.541 g of the desired product as an opaque oil.

^{31}P {1H} (121.4 MHz, C_6D_6): 130.7. Minor peaks at 132.06, 131.14, and 130.14.

EXAMPLE 16A

Hydrocyanation of 3-Pentenenitrile with
Ligand "D2"/Ni(COD) $_2$; ZnCl_2 promoter

370 mg of Ligand "D2", 0.040 g of Ni(COD) $_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 24.7% ADN, 6.0% MGN and 0.7% ESN (selectivity to ADN: 79%).

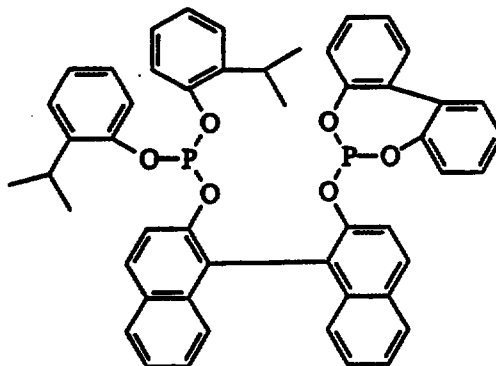
EXAMPLE 16B

Hydrocyanation of 3-Pentenenitrile
with Ligand "D2"/Ni(COD) $_2$; ZnCl_2 promoter

Ligand "D2", 366 mg, 40 mg of Ni(COD) $_2$ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation. To the residue was added 5 ml of 3PN and 20 mg of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 36.2% ADN, 8.7% MGN, and 1.0% ESN (selectivity to ADN: 79.0%).

EXAMPLE 17

Synthesis of the ligand of Formula IV,
where each R^2 is isopropyl, and each R^2 and R^5 is H (Ligand "M")



Ligand "M"

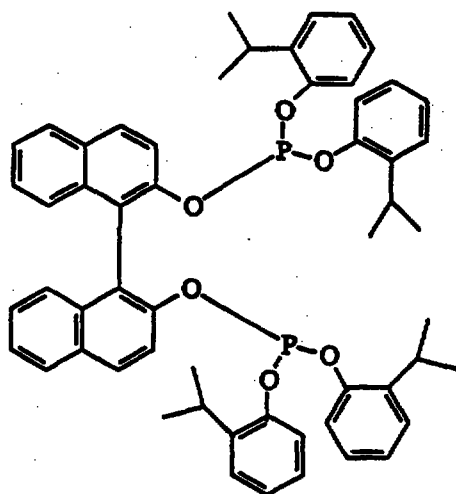
To 20 ml of a toluene solution containing 1.145 g of 2,2'-binaphthol and 1.21 g of NEt_3 at -40°C was added 1.0 g of 1,1'-biphenyl-2,2'-diyl phosphorochloridite in 20 ml of toluene. The mixture was warmed to room temperature and stirred overnight. A 20 ml toluene solution containing the chloridite derived from PCl_3 and 2-isopropylphenol was added thereto. After stirring for two days, the mixture was filtered through Celite®, and washed with toluene. The solvent was removed, to give 3.382 g of tan solid. ^{31}P {1H} (121.4 MHz, C_6D_6): 145.3 δ , 131.2 δ . Also minor peaks due to impurities at 146.6, 146.4, 146.3, 132.2, and 131.0. FBMS: Found: 885.30. The FBMS data is inconsistent with the structure shown for Ligand "M" due to the possible presence of an impurity.

EXAMPLE 17A**Hydrocyanation of 3-Pentenenitrile with
Ligand "M"/Ni(o-TTP)₂(C₂H₄); ZnCl₂ promoter**

Ligand "M", 331 mg, 0.111 g of Ni(o-TTP)₂(C₂H₄), and 20 mg of ZnCl₂ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. After this time, GC analysis indicated 19.2% ADN, 3.7% MGN and 0.7% ESN (selectivity to ADN: 81%).

EXAMPLE 17B**Hydrocyanation of 3-Pentenenitrile
with Ligand "M"/Ni(COD)₂; ZnCl₂ promoter**

344 mg of Ligand "M" and 0.040 g of Ni(COD)₂ and 20 mg of ZnCl₂ were dissolved in 5 ml of 3PN. The mixture was treated with HCN with a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 41% ADN, 7.1% MGN and 1.1% ESN (selectivity to ADN: 83%).

EXAMPLE 18**Synthesis of the ligand of Formula V,
where each R² is isopropyl, and each R^{2'} and R^{5'} is H (Ligand "N")****Ligand "N"**

To 2 g of the phosphochloridite derived from PCl₃ and 2-isopropylphenol in 20 ml of toluene was added 850 mg of 1,1'-bi-2-naphthol and 1.2 g of NEt₃ in 20 ml of toluene. The mixture was stirred overnight, filtered through Celite®, and washed with toluene. The solvent was removed, to give 2.711 g of the desired product as a yellow liquid. ³¹P {¹H} (121.4 MHz, C₆D₆): 131.51. FBMS calculated for M + 1 for the desired product C₅₆H₅₆O₆P₂: 887.36; Found: 887.37.

EXAMPLE 18A

Hydrocyanation of 3-Pentenenitrile with
Ligand "N"/Ni(COD)₂; ZnCl₂ promoter

Ligand "N", 373 mg, and 0.040 g of Ni(COD)₂ were dissolved in 5 ml of
5 3PN containing 20 mg of ZnCl₂. The mixture was treated with HCN at a nitrogen
flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 21.5% ADN,
3.3% MGN and 0.5% ESN (selectivity to ADN: 85%).

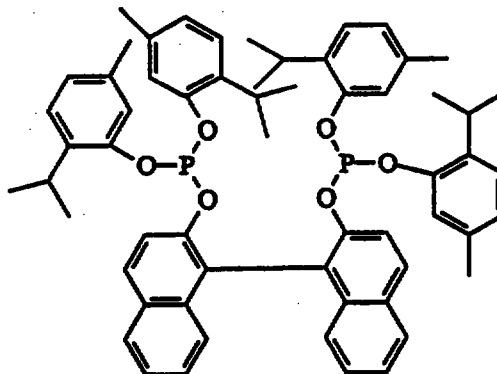
EXAMPLE 18B

Hydrocyanation of 3-Pentenenitrile with
Ligand "N"/Ni(COD)₂; ZnCl₂ promoter

10 Ligand "N", 373 mg, 40 mg of Ni(COD)₂ were dissolved in 5 ml of THF.
The solvent was removed by vacuum evaporation. To the residue was added 5 ml
of 3PN and 20 mg of ZnCl₂. The mixture was treated with HCN at a nitrogen
flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 58.9% ADN,
15 9.2% MGN, and 1.1% ESN (selectivity to ADN: 83.3%).

EXAMPLE 19

Synthesis of the ligand of Formula V, where each R² is isopropyl, each R^{2'}
para to R² is methyl and the other R^{2'} is H, and each R⁵ is H (Ligand "O")



Ligand "O"

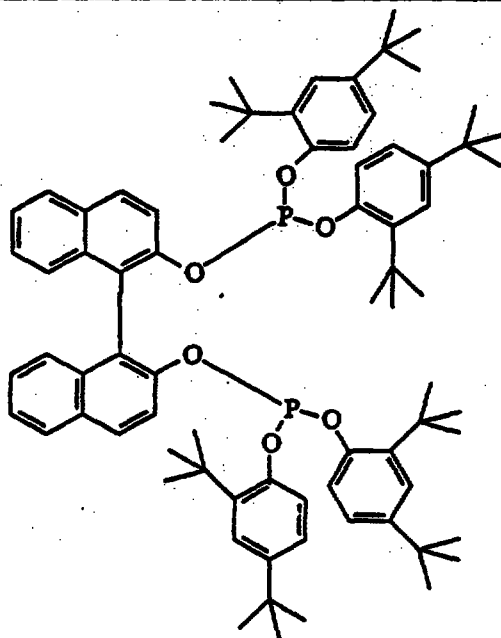
To 20 ml of toluene solution containing 2.0 g of the phosphorochloridite
20 derived from PCl₃ and thymol were added 0.785 g of 1,1'-bi-2-naphthol and
0.910 g of NEt₃ in 20 ml of toluene. The mixture was stirred overnight. The
mixture was filtered through Celite®, and washed with toluene. The solvent was
removed, to give 2.569 g of an orange oil. ³¹P {1H} (121.4 MHz, C₆D₆):
131.246. Also minor peaks due to impurities at 145.73 and 132.31. FBMS:
25 Found: 941.64; calculate for C₆₀H₆₄O₆P₂: 942.42.

EXAMPLE 19A**Hydrocyanations of 3-Pentenitrile with Ligand****"O"/Ni(COD)₂; ZnCl₂ promoter**

Ligand "O", 396 mg, 0.040 g of Ni(COD)₂, and 20 mg of ZnCl₂ were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 63% ADN, 8.0% MGN and 0.8% ESN (selectivity to ADN: 88%).

COMPARATIVE EXAMPLE 20

Synthesis of the ligand of Formula V, where each R² and R^{2'} para to R² is t-butyl, other R^{2'} is H and each R^{5'} is H (Ligand "P")



Ligand "P"

Phosphorus trichloride (0.55 g, 4.0 mmols) was dissolved in toluene (10 ml) and cooled in an ice/salt bath. 2,6-Di-*t*-butyl phenol (1.65 g, 8.0 mmols) and triethylamine (2.1 ml; 15 mmols) were dissolved in toluene (10 ml). This solution was added dropwise to the cold PCl₃ solution. After 30 min, the mixture was heated to reflux for 75 minutes. The mixture was again cooled in the ice bath, and a solution of 1,1'-bi-(2-naphthol) (0.57 g; 2.0 mmol) in toluene was added dropwise. The reaction mixture was heated to reflux for 1.5 hours. The mixture was cooled, and the solids were removed by filtration. The solvent was removed in vacuo, leaving a sticky yellow solid. Recrystallization from acetonitrile was unsuccessful because the material was fairly soluble. The acetonitrile was removed to give a pale yellow solid. ³¹P NMR (CDCl₃): δ 129.7. Also, small peaks at 130.8 and 145.6 due to impurities.

COMPARATIVE EXAMPLE 20AHydrocyanation using Ligand P

Ligand "P", 490 mg, 0.040 g of $\text{Ni}(\text{COD})_2$, and 20 mg of ZnCl_2 were dissolved in 5 ml of 3PN. The mixture was treated with HCN at a nitrogen carrier
5 gas flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 3.7% ADN, 0.7% MGN and 0.4% ESN (selectivity to ADN: 77%).

EXAMPLES 22-31Hydrocyanation of 3-Pentenenitrile

Table 1 shows hydrocyanations using a variety of ligands of the invention,
10 prepared in accordance with the general procedures described in the previous examples. The specific conditions for each hydrocyanation are described as Method A, B or C.

COMPARATIVE EXAMPLES A-C2Hydrocyanation of 3-Pentenenitrile using *p*-tritolylphosphite

15

COMPARATIVE EXAMPLE ACompares to Method A of Table 1

To 5 ml of THF was added 0.296 g (0.84 mmoles) of *p*-tritolylphosphite and 0.040 g (0.14 mmoles) of $\text{Ni}(\text{COD})_2$. The solvent was removed by vacuum
20 evaporation. To the residue was added 5 ml of 3PN and 20 mg of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 37.5% ADN, 8.4% MGN and 1.3% ESN (selectivity to ADN: 79.4%).

COMPARATIVE EXAMPLE BCompares to Method B of Table 1

25 To 5 ml of 3PN was added 0.306 g (0.89 mmoles) of *p*-tritolylphosphite and 0.115 g (0.14 mmoles) of $(\text{oTTP})_2\text{Ni}(\text{ethylene})$ (oTTP = *o*-tritolylphosphite) and 0.020 g of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 30 ml/min at 70°C for one hour. GC analysis indicated 28.6% ADN, 5.9% MGN and 0.9% ESN (selectivity to ADN: 80.7%).

30

COMPARATIVE EXAMPLE C1Compares to Method C of Table 1

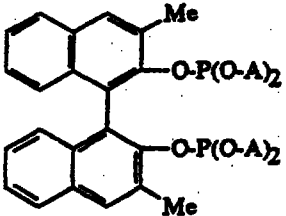
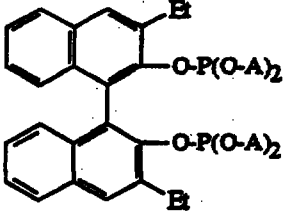
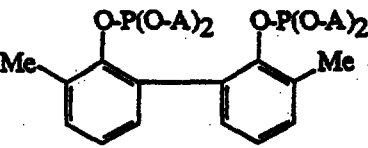
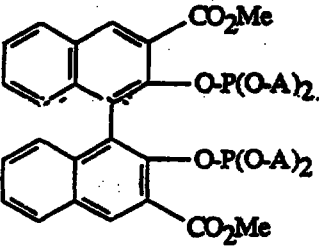
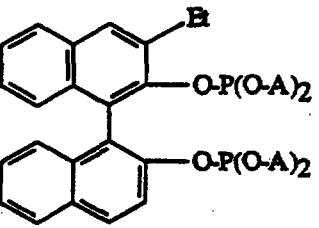
296 mg of *p*-tritolylphosphite and 40 mg of $\text{Ni}(\text{COD})_2$ were dissolved in 5 ml of THF. The solvent was removed by vacuum evaporation. To the residue
35 was added 5 ml of 3PN and 20 mg of ZnCl_2 . The mixture was treated with HCN at a nitrogen flow rate of 12 ml/min at 70°C for two hours. GC analysis indicated 22.7% ADN, 5.1% MGN, and 0.8% ESN (selectivity to ADN: 79.4%).

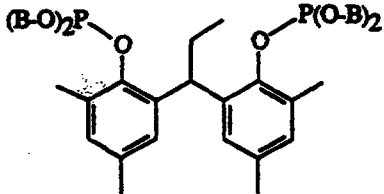
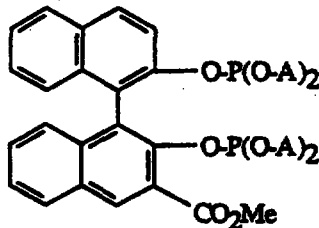
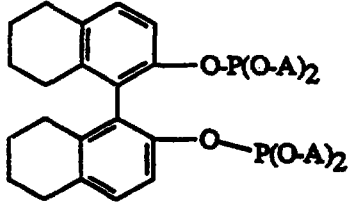
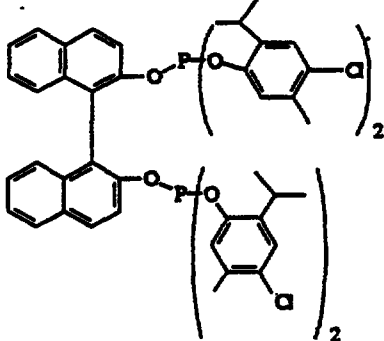
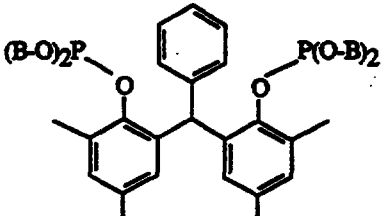
COMPARATIVE EXAMPLE C2**Compares to Method C of Table 1**

To 5 ml of 3PN was added 0.099 g (0.28 mmoles) of *p*-tritolylphosphite, 0.205 g (0.14 mmoles) of tetrakis(*p*-tritolylphosphite)nickel and 20 mg of ZnCl₂.

- 5 The mixture was treated with HCN at a nitrogen flow rate of 12 cc/min. After 1 hr of reaction, GC analysis indicated 26.5% ADN, 5.9% MGN and 0.8% ESN (selectivity to ADN: 79.8%). After 2 hr of reaction, GC analysis indicated 27.6% ADN, 6.1% MGN, 0.9% ESN (selectivity to ADN: 79.8%).

TABLE 1

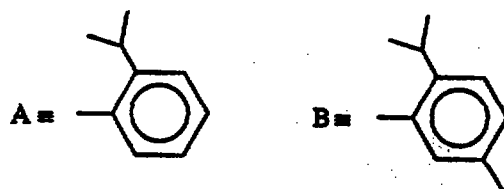
Example No.	Ligand Structure	Conversion	% ADN	Hydrocyanation Method
22		19.0	92.4	A
23		6.7	88.3	A
24		28.7	91.6	A
25		6.3	91.2	A
26		77.5	90.1	A

27		25.9	89.1	C
28		24.3	89.9	A
29		41.0	83.9	B
30		46.9	84.8	A
31		15.8	86.1	C

Method A: 0.42 mmoles ligand, 0.14 mmoles Ni(COD)₂ in 5 ml THF. Remove solvent. 5 ml 3PN and 20 mg ZnCl₂. HCN at 30 ml/min for 1 hr.

Method B: 0.42 mmoles ligand, 0.14 mmoles Ni(COD)₂ in 5 ml 3PN and 20 mg ZnCl₂. HCN at 30 ml/min for 1 hr.

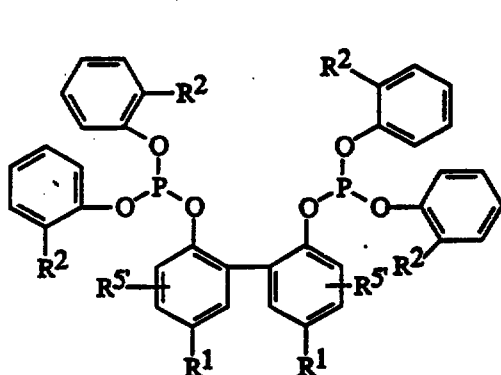
Method C: 0.42 mmoles ligand, 0.14 mmoles Ni(COD)₂ in 5 ml THF. Remove solvent. 5 ml 3PN and 20 mg ZnCl₂. HCN at 12 ml/min for 2 hrs.



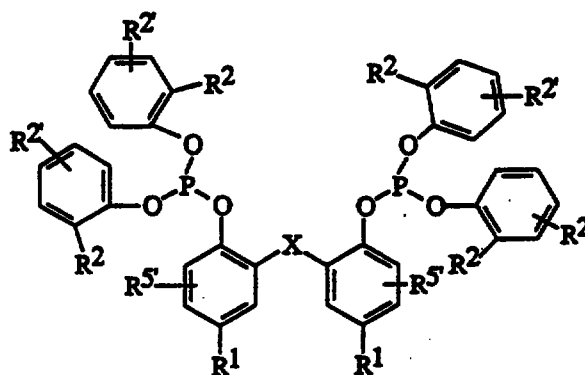
Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

We Claim:

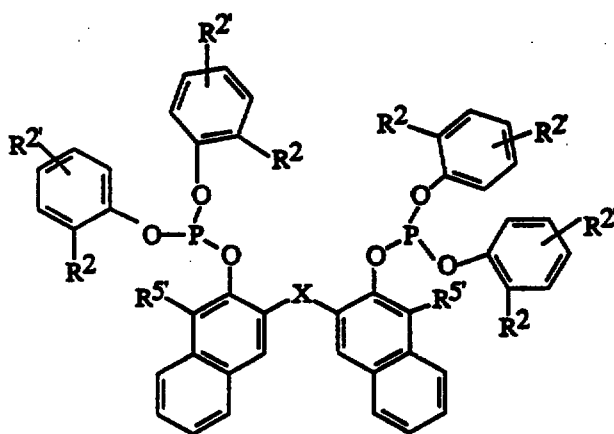
1. A hydrocyanation process comprising reacting an acyclic, aliphatic, monoethylenically unsaturated compound in which the ethylenic double bond is not conjugated to any other olefinic group in the molecule, or a monoethylenically
- 5 unsaturated compound in which the ethylenic double bond is conjugated to an organic ester group, with a source of HCN in the presence of a catalyst composition comprising a Lewis acid, a zero-valent nickel, and at least one multidentate phosphite ligand selected from the group represented by the following Formulas I, II, III, IV, V, VI and VII:



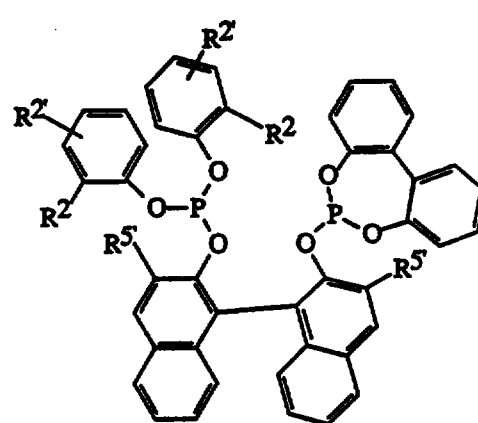
Formula I



Formula II

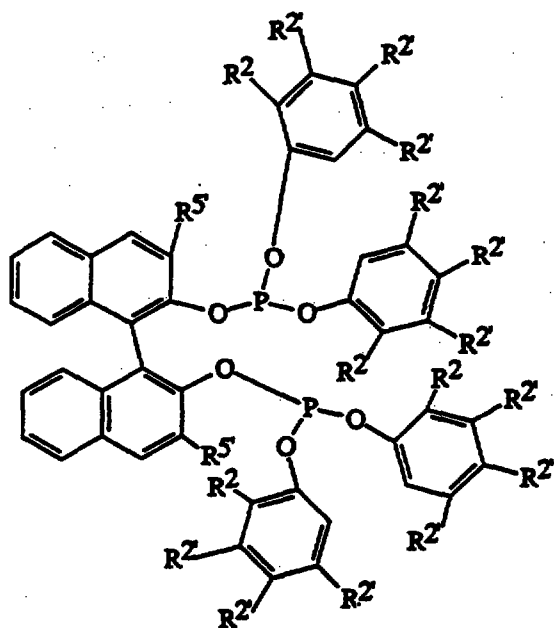


Formula III

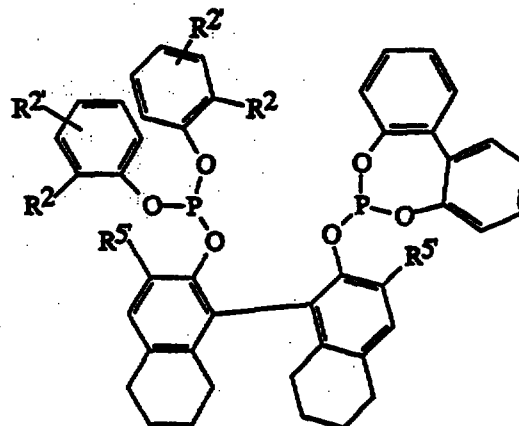


Formula IV

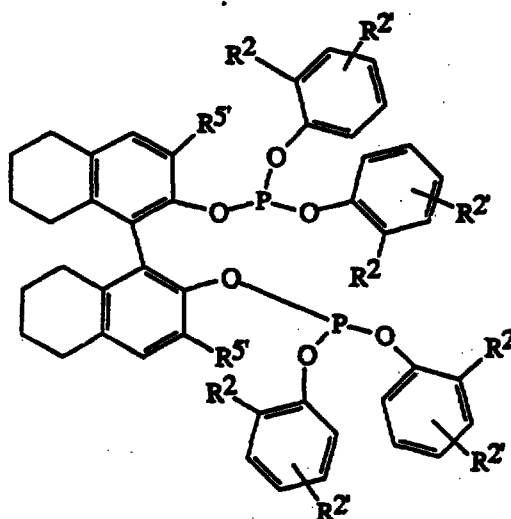




Formula V



Formula VI



Formula VII

wherein

each R^1 is independently, H, halogen, a C_1 to C_6 alkyl, or OR^3 wherein R^3 is a C_1 to C_6 alkyl;

each R^2 is independently a secondary or tertiary hydrocarbyl of 3 to 6 carbon atoms;

each $R^{2'}$ is independently H, halogen, OR^3 wherein R^3 is a C_1 to C_6 alkyl or a primary, secondary or tertiary hydrocarbyl of 1 to 6 carbon atoms; for Formulas II, III, IV, VI and VII, $R^{2'}$ is at either the meta or para position to the oxygen;

5



each R^5 is independently H or a primary or secondary hydrocarbyl of 1 to 3 carbon atoms in either the ortho or meta position to the oxygen or CO_2R^3 wherein R^3 is a C_1 to C_4 alkyl; and

each X is independently O or $CH(R^4)$, wherein R^4 is H, a substituted phenyl, or a C_1 to C_6 alkyl;

with the proviso that the terms "secondary" and "tertiary"

herein refer to the carbon atom bonded to an aromatic ring;

and with the further proviso that in Formulas I, II, and V at least one R^2 cannot be a tertiary hydrocarbyl.

- 10 2. The process of Claim 1 wherein the starting ethylenically unsaturated compound is selected from the group consisting of the compounds of the following formulas VIII and X:



15 wherein

R^4 is H, CN, CO_2R^5 , or perfluoroalkyl;

y is an integer of 0 to 12;

x is an integer of 0 to 12 when R^4 is H, CO_2R^5 or perfluoroalkyl;

x is an integer of 1 to 12 when R^4 is CN; and

20 R^5 is alkyl.

3. The process of Claim 1 wherein the starting ethylenically unsaturated compound is selected from the group consisting of 3-pentenitrile, 4-pentenitrile; alkyl 2-, 3-, and 4-pentenoates, and $C_zF_{2z+1}CH=CH_2$, where z is an integer of 1 to 12.

25 4. The process of Claim 3 wherein the starting ethylenically unsaturated compound is 3-pentenitrile or 4-pentenitrile.

5. The process of Claim 1 which is carried out at a temperature of $-25^\circ C$ to $200^\circ C$ and at a pressure of 50.6 to 1013 kPa.

30 6. The process of Claim 5 which is carried out at atmospheric pressure and at a temperature of $0^\circ C$ to $150^\circ C$.

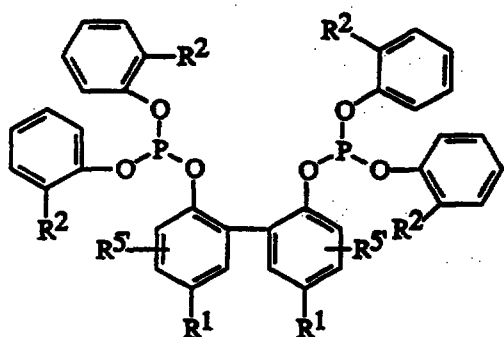
7. The process of Claim 1 wherein the Lewis acid is selected from the group consisting of inorganic or organometallic compounds in which the cation is selected from scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, 35 cadmium, rhenium and tin.

8. The process of Claim 7 wherein the Lewis acid is selected from the group consisting of $ZnBr_2$, ZnI_2 , $ZnCl_2$, $ZnSO_4$, $CuCl_2$, $CuCl$, $Cu(O_3SCF_3)_2$, $CoCl_2$, CoI_2 , FeI_2 , $FeCl_3$, $FeCl_2(tetrahydrofuran)_2$, $TiCl_4(tetrahydrofuran)_2$, $TiCl_4$,

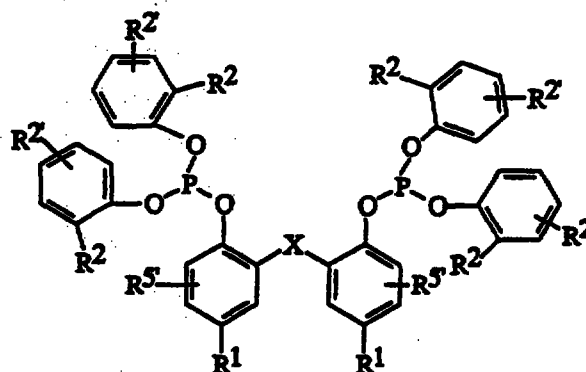


TiCl_3 , $\text{ClTi}(\text{O}i\text{Pr})_3$, MnCl_2 , ScCl_3 , AlCl_3 , $(\text{C}_8\text{H}_{17})\text{AlCl}_2$, $(\text{C}_8\text{H}_{17})_2\text{AlCl}$, $(\text{iso-C}_4\text{H}_9)_2\text{AlCl}$, $(\text{phenyl})_2\text{AlCl}$, phenylAlCl_2 , ReCl_5 , ZrCl_4 , NbCl_5 , VCl_3 , CrCl_2 , MoCl_5 , YCl_3 , CdCl_2 , LaCl_3 , $\text{Er}(\text{O}_3\text{SCF}_3)_3$, $\text{Yb}(\text{O}_2\text{CCF}_3)_3$, SmCl_3 , TaCl_5 , CdCl_2 , $\text{B}(\text{C}_6\text{H}_5)_3$, and $(\text{C}_6\text{H}_5)_3\text{SnX}$, where $\text{X} = \text{CF}_3\text{SO}_3$, $\text{CH}_3\text{C}_6\text{H}_5\text{SO}_3$, or $(\text{C}_6\text{H}_5)_3\text{BCN}$.

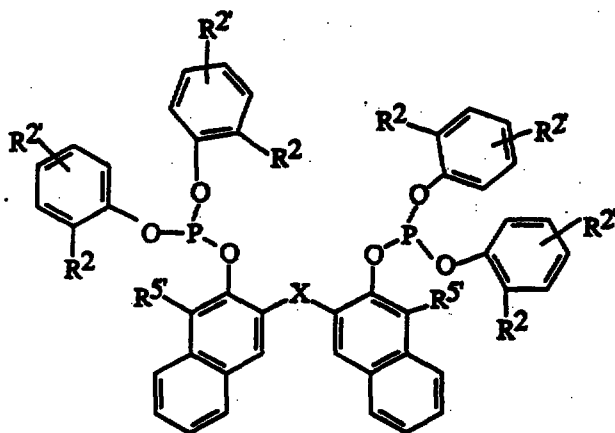
- 5 9. A catalyst composition consisting essentially of a zero-valent nickel, and at least one multidentate phosphite ligand selected from the group represented by the following Formulas I, II, III, IV, V, VI and VII:



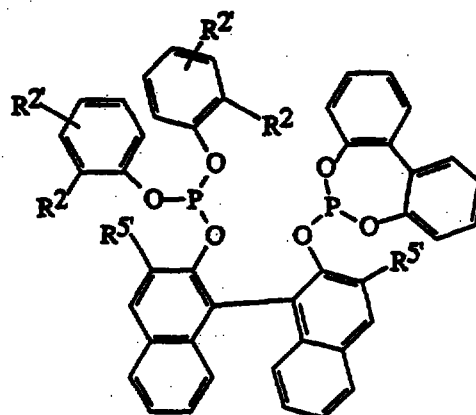
Formula I



Formula II

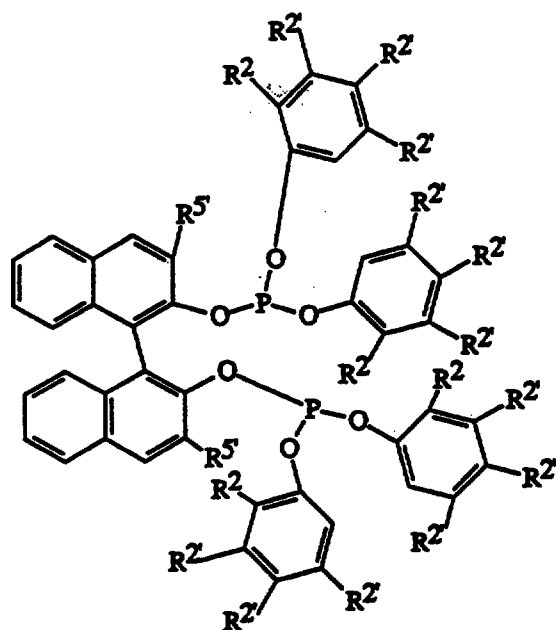


Formula III

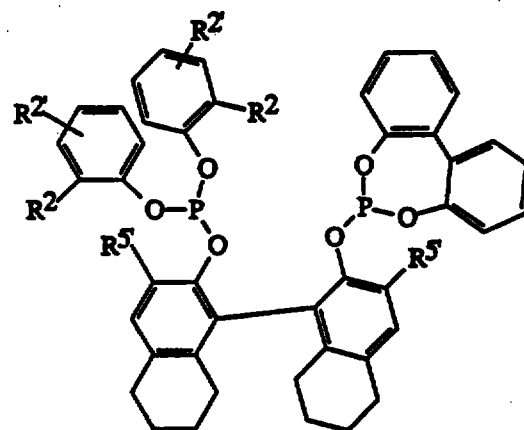


Formula IV

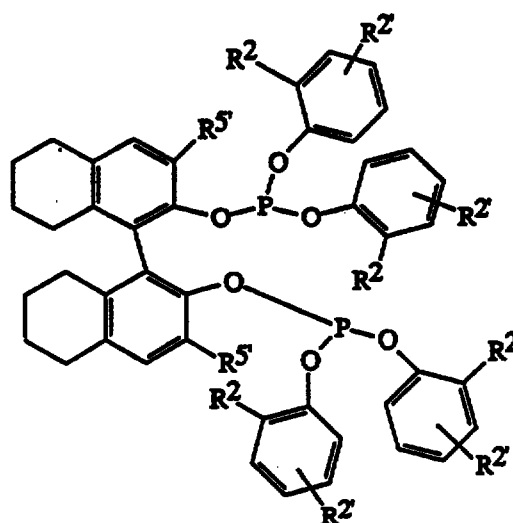




Formula V



Formula VI



Formula VII

wherein

each R^1 is independently, H, halogen, a C_1 to C_6 alkyl, or OR^3 wherein R^3 is a C_1 to C_6 alkyl;

each R^2 is independently a secondary or tertiary hydrocarbonyl of 3 to 6 carbon atoms;

each $R^{2'}$ is independently H, halogen, OR^3 wherein R^3 is a C_1 to C_6 alkyl or a primary, secondary or tertiary hydrocarbonyl of 1 to 6 carbon atoms; for Formulas II, III, IV, VI and VII, $R^{2'}$ is at either the meta or para position to the oxygen;

5



each R^5 is independently H or a primary or secondary hydrocarbyl of 1 to 3 carbon atoms in either the ortho or meta position to the oxygen or CO_2R^3 wherein R^3 is a C_1 to C_4 alkyl; and

each X is independently O or $CH(R^4)$, wherein R^4 is H, a substituted phenyl, or a C_1 to C_6 alkyl;

with the proviso that the terms "secondary" and "tertiary"

herein refer to the carbon atom bonded to an aromatic ring;

and with the further proviso that in Formulas I, II, and V at

least one R^2 cannot be a tertiary hydrocarbyl.

10 10. The catalyst composition of Claim 9 wherein a Lewis acid is also present.

11. The catalyst composition of Claim 10 wherein the Lewis acid is selected from the group consisting of $ZnBr_2$, ZnI_2 , $ZnCl_2$, $ZnSO_4$, $CuCl_2$, $CuCl$, $Cu(O_3SCF_3)_2$, $CoCl_2$, CoI_2 , FeI_2 , $FeCl_3$, $FeCl_2(tetrahydrofuran)_2$, $TiCl_4(tetrahydrofuran)_2$, $TiCl_4$, $TiCl_3$, $ClTi(OiPr)_3$, $MnCl_2$, $ScCl_3$, $AlCl_3$, $(C_8H_{17})AlCl_2$, $(C_8H_{17})_2AlCl$, $(iso-C_4H_9)_2AlCl$, $(phenyl)_2AlCl$, $phenylAlCl_2$, $ReCl_5$, $ZrCl_4$, $NbCl_5$, VCl_3 , $CrCl_2$, $MoCl_5$, YCl_3 , $CdCl_2$, $LaCl_3$, $Er(O_3SCF_3)_3$, $Yb(O_2CCF_3)_3$, $SmCl_3$, $TaCl_5$, $CdCl_2$, $B(C_6H_5)_3$, and $(C_6H_5)_3SnX$, where $X = CF_3SO_3$, $CH_3C_6H_5SO_3$, or $(C_6H_5)_3BCN$.

20 12. The catalyst composition of Claim 9 wherein the zero-valent nickel and the multidentate phosphite ligand are bonded to each other.

13. The catalyst of Claim 9 wherein the zero-valent nickel and the multidentate phosphite ligand are supported on the same solid support.

