Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2357805 C 2003/02/04

(11)(21) 2 357 805

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 1996/05/21
(41) Mise à la disp. pub./Open to Public Insp.: 1996/11/24
(45) Date de délivrance/Issue Date: 2003/02/04
(62) Demande originale/Original Application: 2 177 008
(30) Priorité/Priority: 1995/05/23 (08/447,887) US

(51) Cl.Int.^{7}/Int.Cl.^{7} C08F 4/42, C08F 4/69, C08F 4/68, C07F 11/00, C07F 15/04, C07C 11/02, C08F 4/64, C07F 9/50, C07F 9/30, C07C 2/26

(72) Inventeurs/Inventors:
SOMOGYVARI, ARPAD F., CA;
CREED, BETH LORRAINE, CA;
NICOLA, ANTONIO PIETRO, CA;
SANGER, ALAN RODNEY, CA;
LAW, DAVID JOHN, CA;
CAVELL, RONALD GEORGE, CA

(73) Propriétaire/Owner:
THE GOVERNORS OF THE UNIVERSITY OF ALBERTA, CA

(74) Agent: G. RONALD BELL & ASSOCIATES

(54) Titre : PRECURSEUR DE CATALYSEUR D'OLIGOMERISATION
(54) Title: OLIGOMERIZATION CATALYST PRECURSOR

(57) Abrégé/Abstract:
The present invention relates to the oligomerization of lower alpha olefins, and particularly ethylene, to higher olefins in the presence of a catalyst precursor having either or both of a dithiophosphinate complex and a heterobifunctional ligand having a phosphine center and an imine or similar center, in the presence of an activator. The catalysts have a high reactivity and a good selectivity.

ABSTRACT OF THE DISCLOSURE

The present invention relates to the oligomerization of lower alpha olefins, and particularly ethylene, to higher olefins in the presence of a catalyst precursor having either or both of a dithiophosphinate complex and a heterobifunctional ligand having a phosphine center and an imine or similar center, in the presence of an activator. The catalysts have a high reactivity and a good selectivity.

OLIGOMERIZATION CATALYST PRECURSOR

This application is a division of Canadian Patent Application Serial Number 2,177,008 filed on May 21, 1996. The claims of the present application are directed to a catalyst precursor. However, for a ready understanding of the overall invention including all features which are inextricably bound up in one and the same inventive concept, the teachings of those features are all retained in the present application.

The parent application describes and claims a process for the oligomerization of lower olefins to one or more higher olefins, preferably alpha olefins. The oligomerization is carried out in the presence of a homogeneous catalyst comprising:

a) a catalyst precursor selected from the group consisting of:

1) dithiophosphinate (sometimes also called dithiophosphonates, typically when the P is substituted by an alkoxy radical) complexes of Ni, Cr, Ti, Zr, Hf, V, W, and Mo; and

2) complexes of Ni, Cr, Ti, Ni, Zr, Hf, V, W, and Mo with a heterobifunctional ligand having a phosphine center and an imine or similar center; and

3) complexes of Cr, Ti, Ni, Zr, Hf, V, W, and Mo having one or more ligands selected from the group consisting of dithiophosphinate ligands and hetero-bifunctional ligands having a phosphine center and an imine or similar center; and

b) an activator.

The oligomerization has a high conversion and a high degree of selectivity to the target product.

The oligomerization of lower alpha olefins is of industrial concern as many polymers of alpha olefins such as ethylene and propylene comprise a higher alpha olefin such as butene, hexene or octene. If ethylene could be selectively oligomerized at relatively high conversion to a higher alpha olefin such as butene, hexene or octene it would mean that a plant need only have one monomer, such as ethylene, from which co-monomers could be produced.

There have been a number of attempts to oligomerize alpha olefins into higher alpha olefins.

There are a number of papers and patents in which Kingsley John Cavell and/or Anthony J. Masters is/are named as an author(s) (e.g. WO 8302907) in which square planar complexes of Ni^{2+} are used to oligomerize alpha olefins. The complexes contain triphenyl phosphine and 2,4-pentanedithione (sacsac) or 4-thioxo-2-pentanone. These compounds are not the dithiophosphinate precursors of the present invention.

United States Patent 4,533,651 issued Aug. 6, 1985 assigned to Commonwealth Scientific and Industrial Research Organization, Australia, also discloses oligomerization of ethylene with a nickel complex which contains a phosphine. The patent does not suggest the use of a ligand which contains both a phosphine and an imine or a dithiophosphinate ligand of the present invention. Related United States Patent 5,286,696 issued Feb. 14, 1994 and 5,210,360 issued May 11, 1993 both assigned to Phillips disclose the oligomerization of ethylene using a nickel complex which contains a phosphine. The patents do not disclose the presence of both a phosphine and an imine group or a dithiophosphinate in the ligand.

United States Patent 5,334,791 issued Aug. 2, 1994 to Ligands, Inc. discloses that some of the catalyst precursors of the present invention may be used to hydrogenate non-aromatic unsaturated hydrocarbons. United States Patent 5,352,813 issued Oct. 4, 1994 to the University of Alberta discloses that some of the catalyst precursors of the present invention may be used to carbonylate methanol. However, these patents do not disclose that such compounds in conjunction with an activator of a compound such as aluminum or boron could be used to oligomerize alpha olefins.

Further these references do not teach or suggest that such an oligomerization if possible would have a high conversion and a controllable selectivity.

The invention described and claimed inthe parent application provides a process for the oligomerization of one or more C_{2-4} olefins to one or more higher olefins comprising;

i) forming a dissolved catalyst system comprising:

a) a dissolved catalyst precursor selected from the group consisting of:

1) dithiophosphinate complexes of Cr, Ti, Ni, Zr, Hf, V, W, and Mo;

2) complexes of Cr, Ti, Ni, Zr, Hf, V, W, and Mo with a heterobifunctional ligand having a phosphine center and an imine or similar center; and

3) complexes of Cr, Ti, Ni, Zr, Hf, V, W, and Mo having one or more ligands selected from the group consisting of dithiophosphinate ligands and heterobifunctional ligands having a phosphine center and an imine or similar center; and

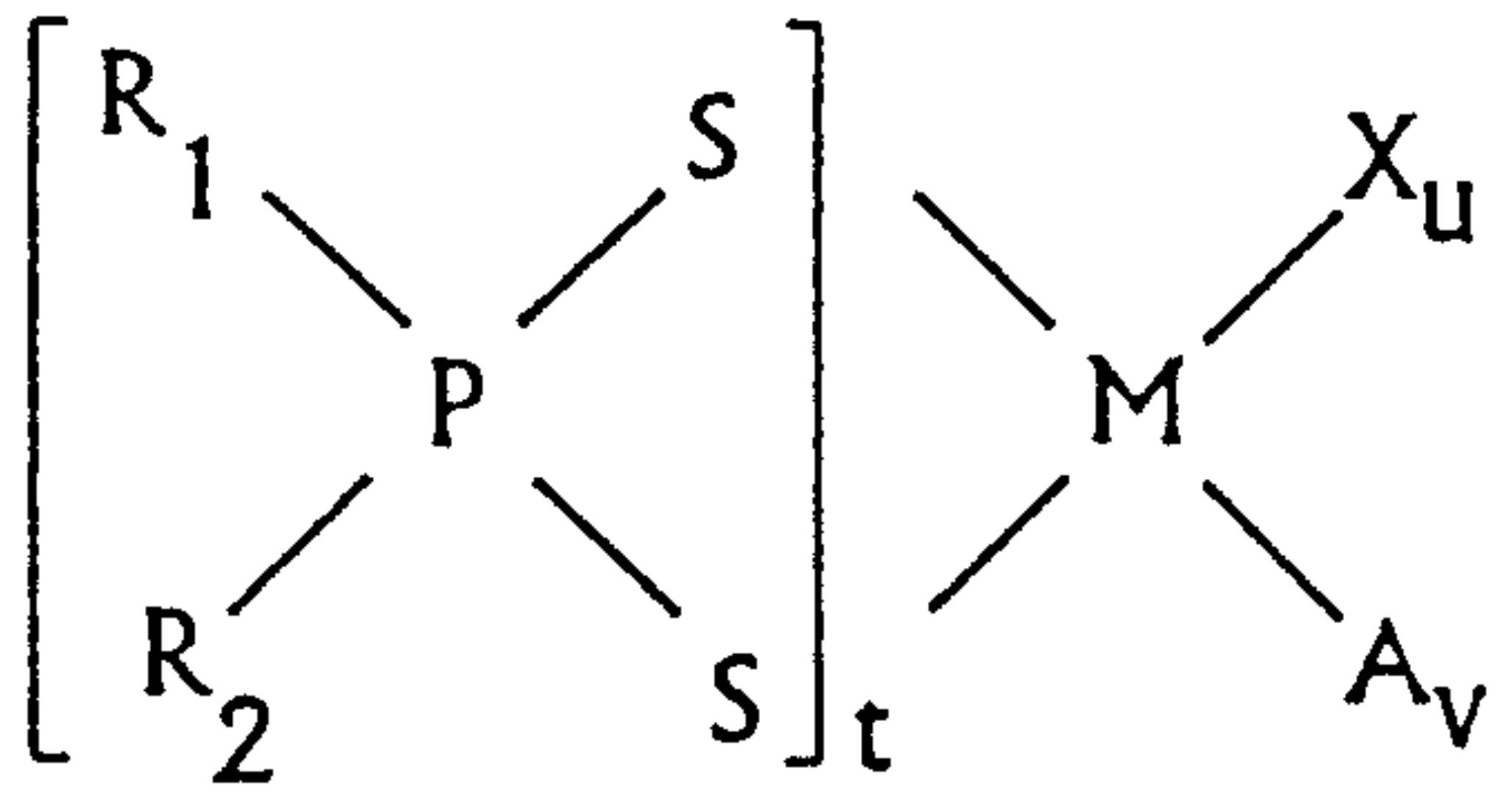
b) a soluble activator selected from the group consisting of activators of the formula $AlR_{3-n}X_n$ in which R is a C_{1-8} alkyl radical, X is a halogen atom and n is 0, 1, or 2; alkyl aluminoxane compounds in which the alkyl group has from 1 to 8 carbon atoms and boron trihalide, tetraphenylborate and tri- or tetra(penta fluorophenyl) boron compounds or complexes, in a mole ratio of activator to catalyst precursor from 1:2 to 500:1 in a solvent selected from the group comprising C_{6-12} cyclic aliphatic and aromatic compounds which are unsubstituted or substituted with a C_{1-4} alkyl radical; and

ii) contacting said olefin in liquid form with the solution of the catalyst at a temperature from -15°C to 250°C; and at a pressure from 15 to 1500 psi.

The catalyst precursor includes a source of a transition metal selected from the group consisting of Cr, Ti, Ni, Zr, Hf, V, W, and Mo, most preferably Ni, Cr, and Ti and either a dithiophosphinate ligand or a heterobifunctional ligand having a phosphine center and an imine center, or both. Preferred transition metals are nickel (Ni) and chromium (Cr).

The catalyst precursor may be a dithiophosphinate complex (i.e. a) 1).

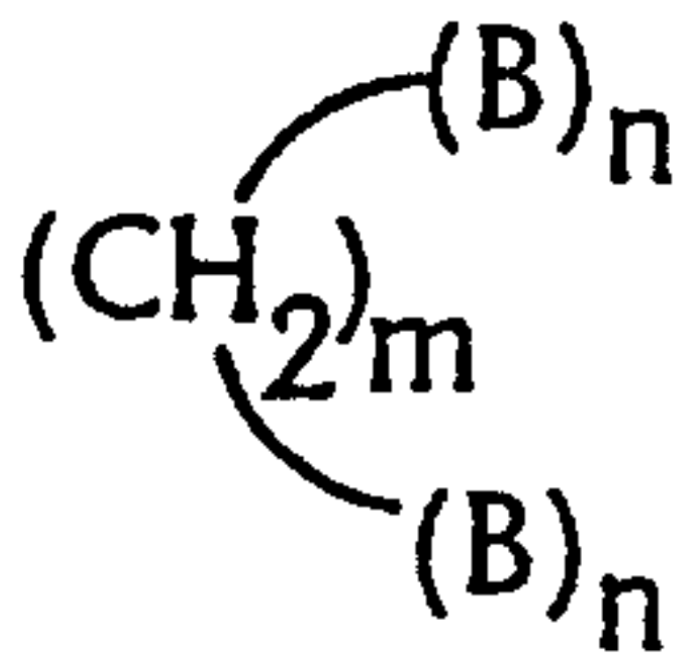
The dithiophosphinate catalyst precursor according to an aspect of the present invention has the formula:



COMPLEX I

wherein:

M is selected from the group consisting of the above noted metals, preferably Ni, Cr, Ti, V, and Zr, t, u, and v are integers and the sum of 2t+u+v is the coordination number of M and t is an integer from 1 to half the coordination number of M and u and v may be 0 or integers, and the sum of u+v is from 0 to two less than the coordination number of M, R_1,and R_2, are independently selected from the group consisting of C_{1-10} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three substituents selected from the group consisting of C_{1-8} alkyl radicals; C_{1-6} alkoxy or thioalkyl radicals; C_{6-12} aryloxy radicals; C_{6-12} arylthio radicals; CF_3; and fluorine; or if taken together R_1 and R_2 form a cyclic diradical (e.g. a divalent radical) of the formula:



$(CH_2)_m$ with $(B)_n$ at each end

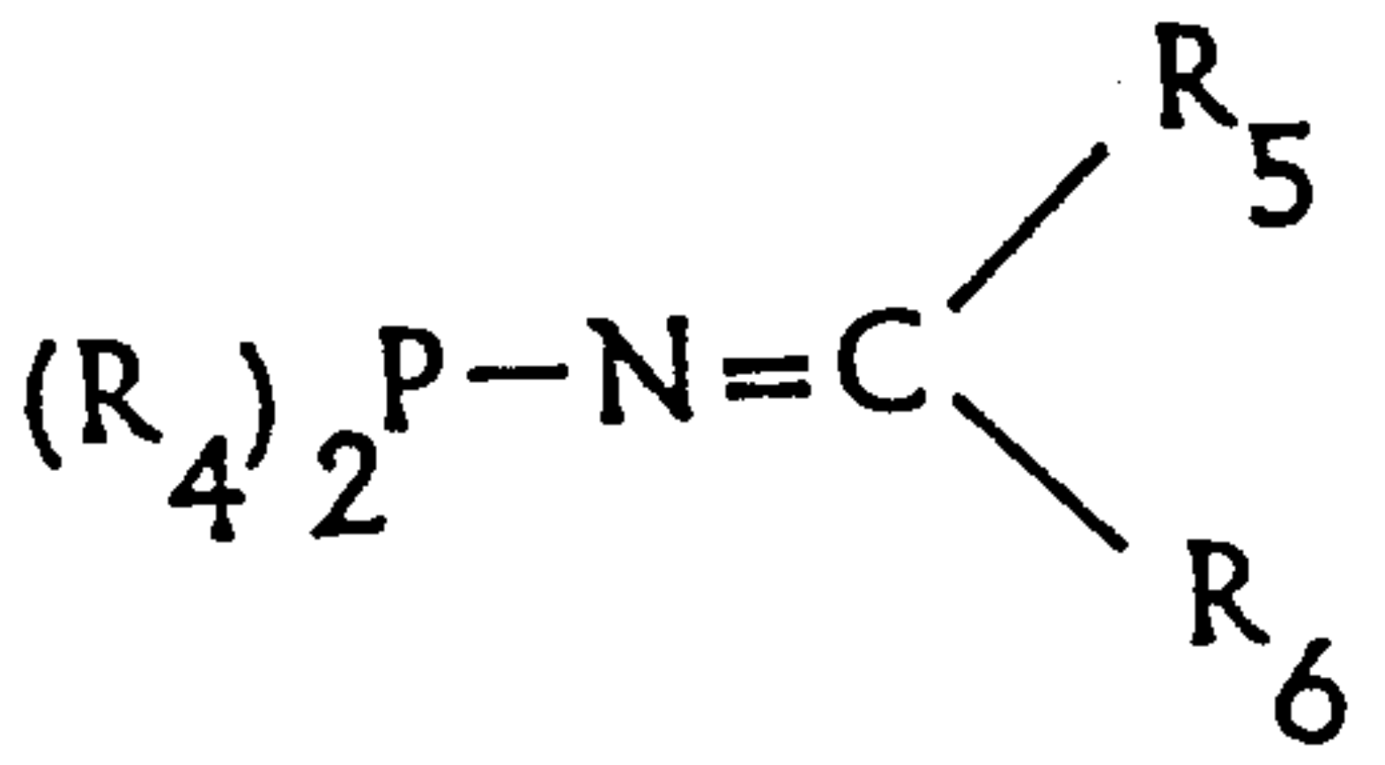
wherein n may independently be 0 or 1, m is an integer from 1 to 10, preferably 2 to 10, and each B may be independently selected from the group consisting of O or S;

X is selected from the group consisting of Cl, Br, I, and H; and

A is a ligand selected from the group consisting of:

i) ligands of the formula $P(R_3)_3$ wherein R_3 may be independently selected from the group of radicals consisting of C_{1-10} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three, preferably one, substituents selected from the group consisting of C_{1-8} alkyl radicals; and

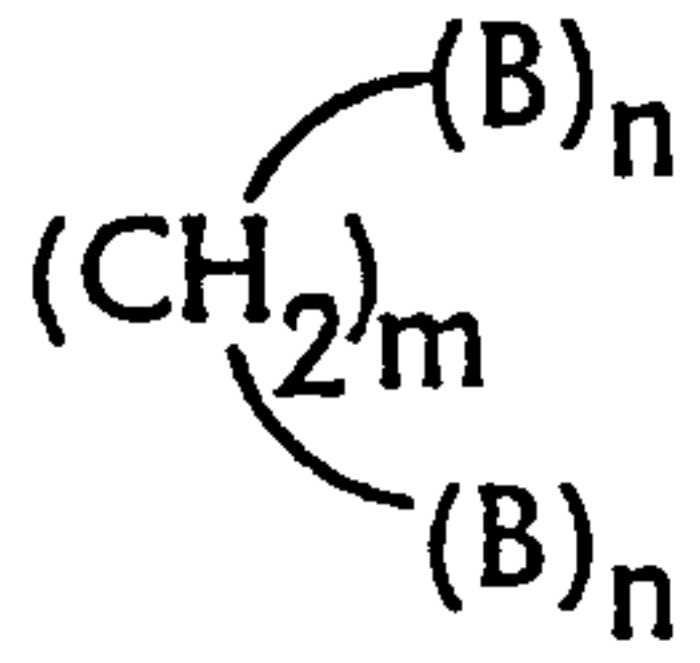
ii) ligands of the formula



wherein R_4 may be a radical selected from the group of radicals from which R_3 is selected and R_5 and R_6 may independently be a hydrogen atom or a radical selected from the group consisting of C_{1-10} straight chained, or branched alkyl radicals; C_{5-8} cyclic alkyl radicals, C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three, substituents selected from the group consisting of C_{1-8} alkyl radicals.

In the above catalyst precursors, preferably X is Cl or Br.

If R_1 and R_2 are taken together to form a diradical of the formula:

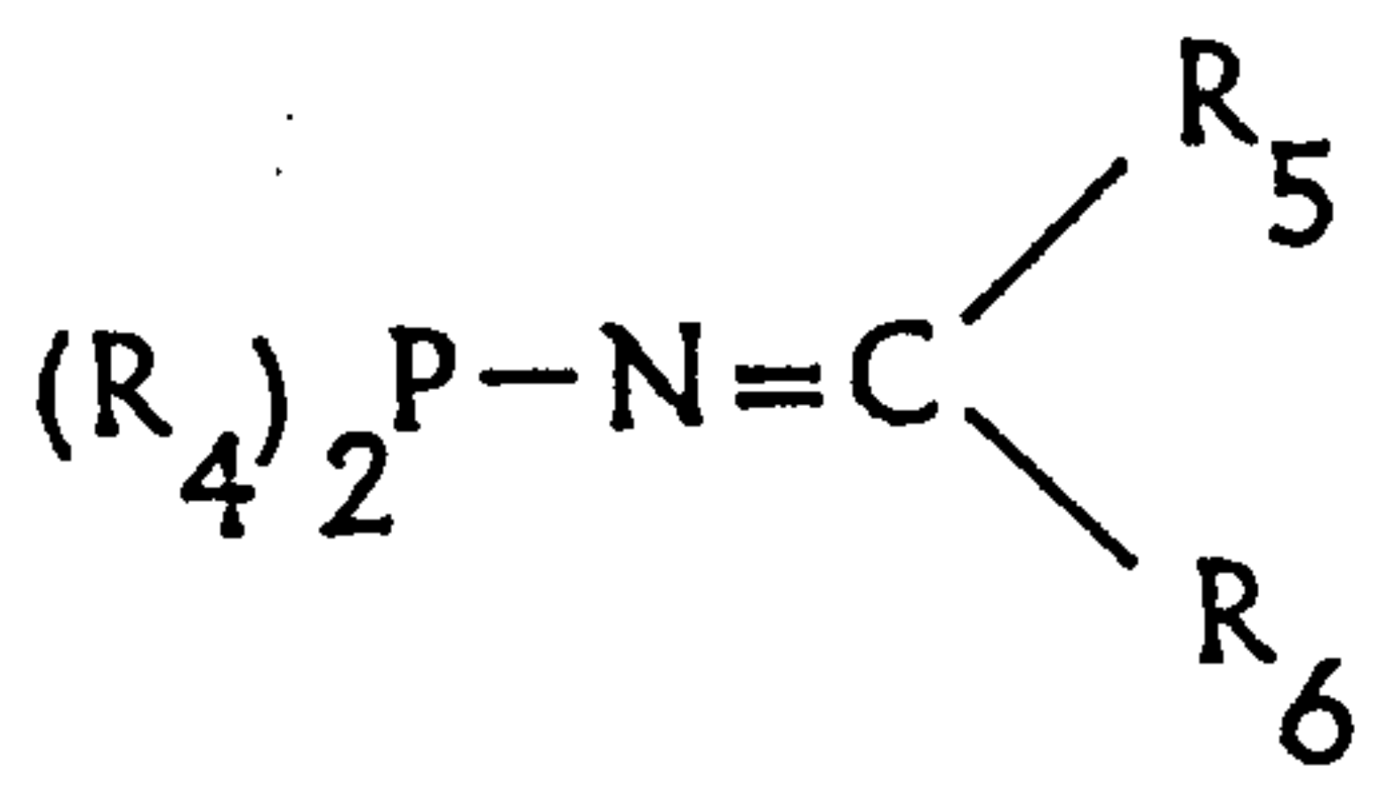


wherein n may independently be 0 or 1, m is an integer from 1 to 10, preferably 2 to 10 and each B may be independently selected from the group consisting of O or S, preferably R_1 and R_2 are independently selected from the group consisting of C_{1-8} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical; C_{1-6} alkoxy or thioalkyl radicals; CF_3; and fluorine.

In the above complexes the ligand A is preferably selected from the group of ligands consisting of:

i) ligands of the formula $P(R_3)_3$ where in R_3 may be independently selected from the group of radicals consisting of C_{1-8} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical;

ii) ligands of the formula:

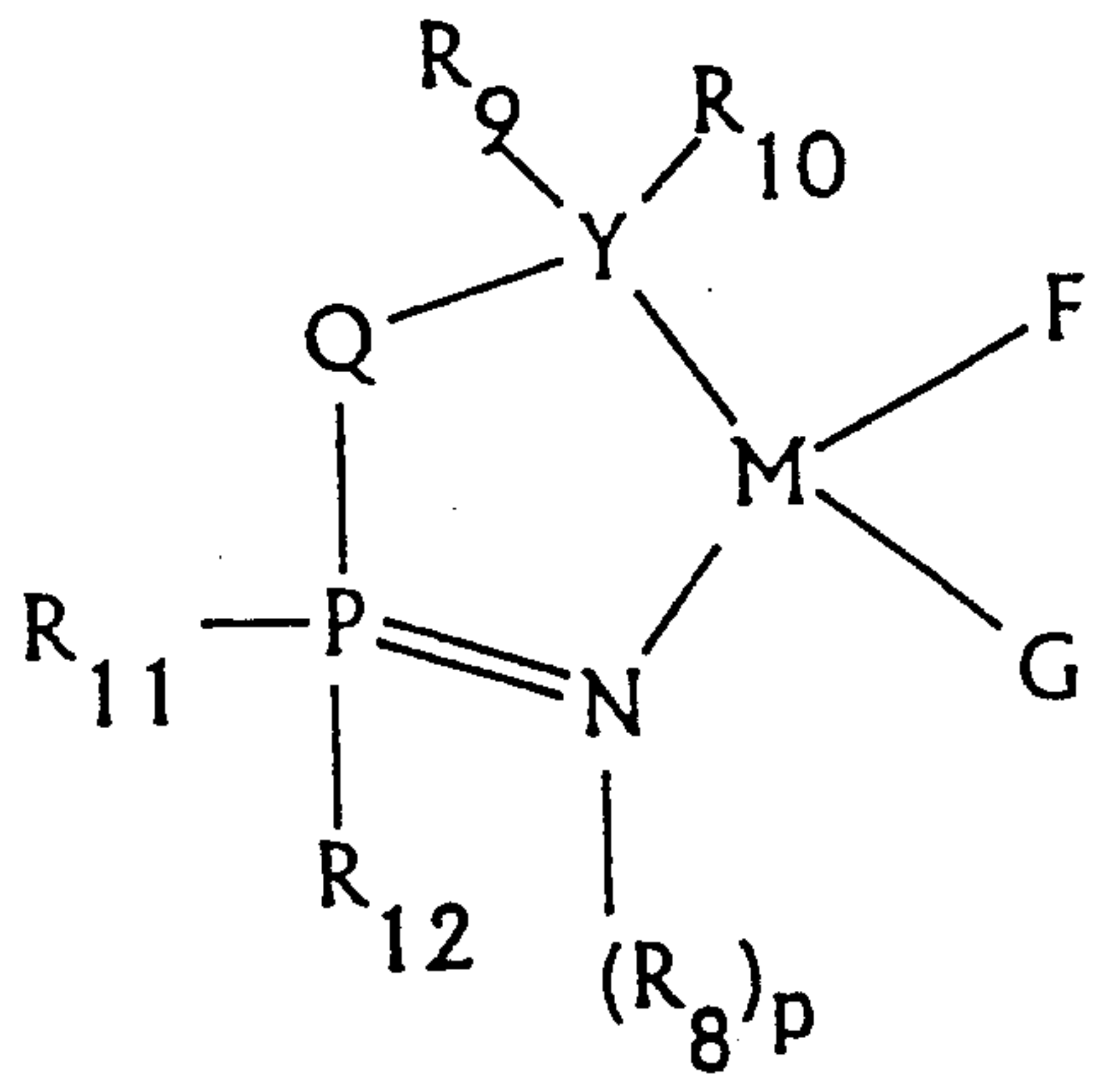


wherein R_4 may be a radical selected from the group consisting of radicals from the group consisting of C_{1-8} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical and R_5 and R_6 may independently be a hydrogen atom or a radical selected from the group consisting of C_{1-8} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical.

The catalyst precursor may contain a heterobifunctional ligand (i.e. i) a) 2).

The catalyst precursor having a heterobifunctional ligand having a phosphine center or an arsenic and an imine center has the general formula:

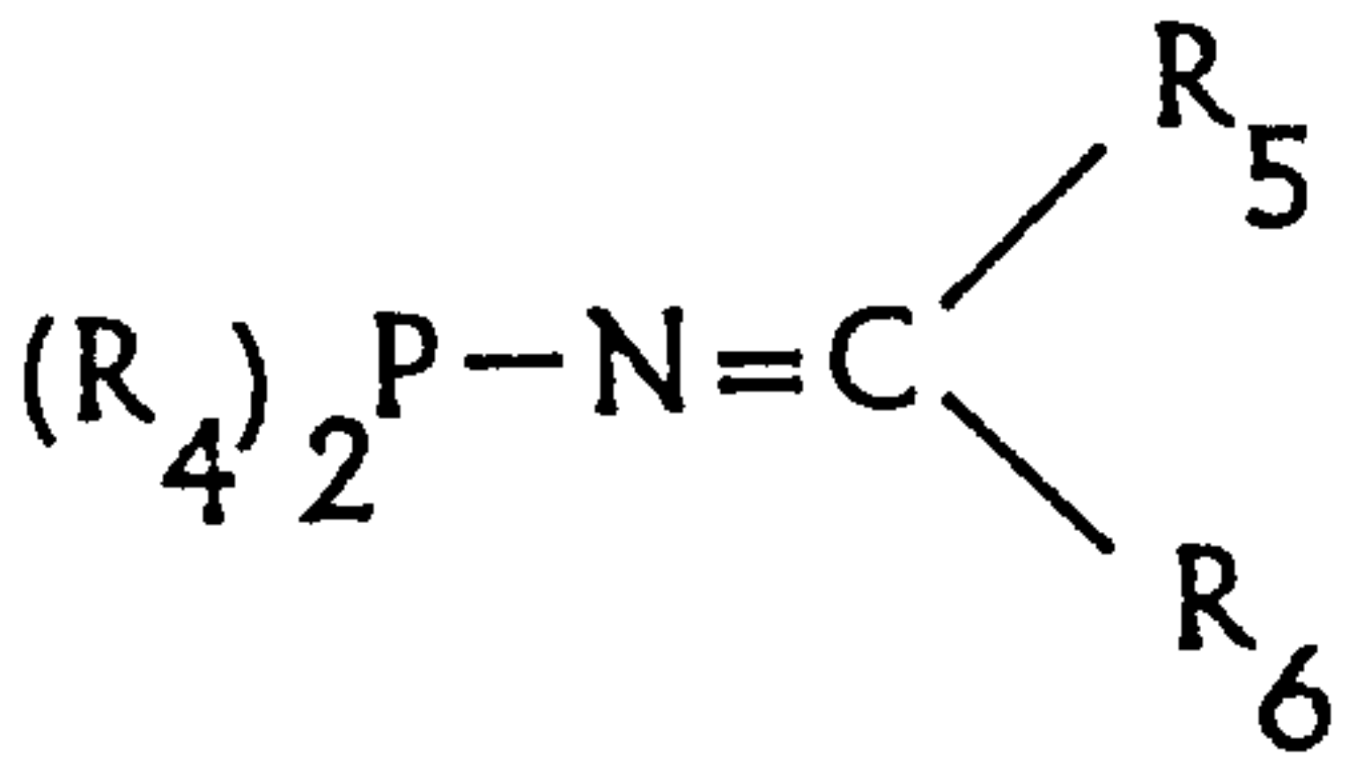
COMPLEX II



wherein M, is as defined above; R_9, R_{10}, R_{11}, and R_{12} are independently selected from the group consisting of C_{1-10} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three substituents, preferably one, selected from the group consisting of C_{1-8} preferably C_{1-4} alkyl radicals; F and G are independently selected from the group consisting of Cl, Br, I, and H, and ligands selected from the group consisting of:

i) ligands of the formula $P(R_3)_3$ wherein R_3 is independently selected from the group of radicals consisting of C_{1-10} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three preferably one, substituents selected from the group consisting of C_{1-8} preferably C_{1-4} alkyl radicals; and

ii) ligands of the formula

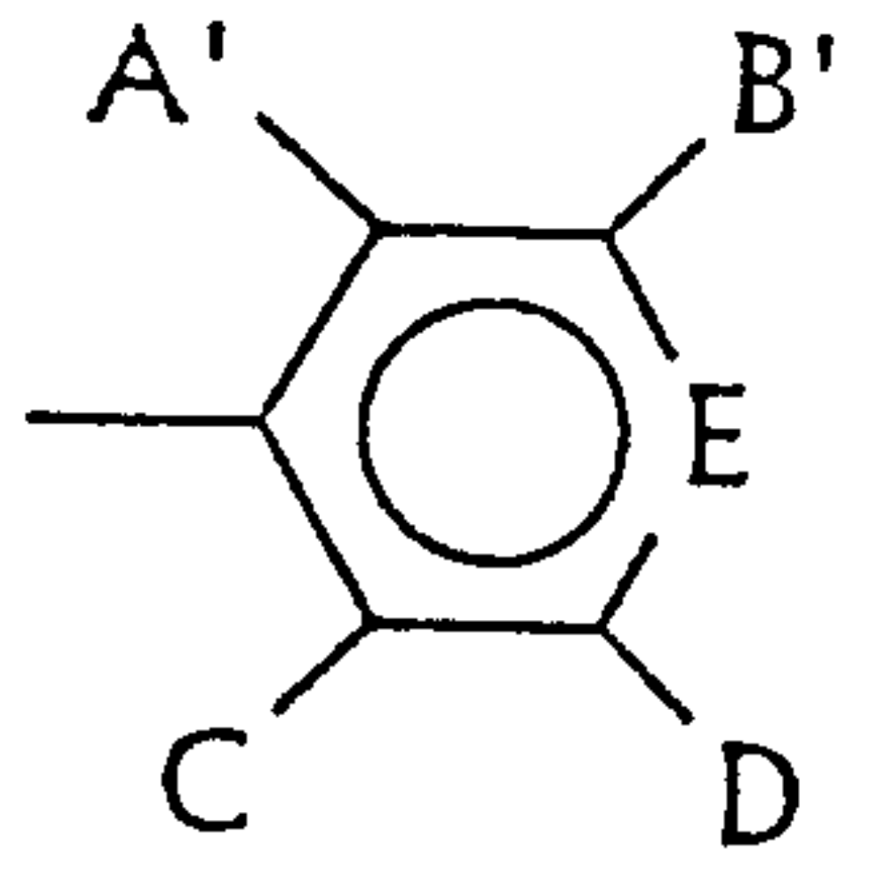


$$(R_4)_2P{-}N{=}C(R_5)(R_6)$$

wherein R_4 may be a radical selected from the group of radicals from which R_3 is selected and R_5 and R_6 are independently a hydrogen atom or a radical selected from the group consisting of C_{1-10} preferably C_{1-4} straight chained, or branched alkyl radicals; C_{5-8} cyclic alkyl radicals, C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a up to three, preferably only one, substituents selected from the group consisting of C_{1-8} preferably C_{1-4} alkyl radicals;

Y is P or As (preferably P), Q is selected from the group consisting of $(CH_2)_n$ wherein n is 1, 2, or 3, a C_{2-4} alkyl radical, a disubstituted C_6 aryl radical, and R_7N wherein R_7 is selected from the group consisting of C_{1-6} straight chained or branched alkyl radicals, C_{6-10} aryl radicals which are either unsubstituted or substituted by a C_{1-4} alkyl radical, and p is 0 or 1. If present, R_8 is selected from the group consisting of:

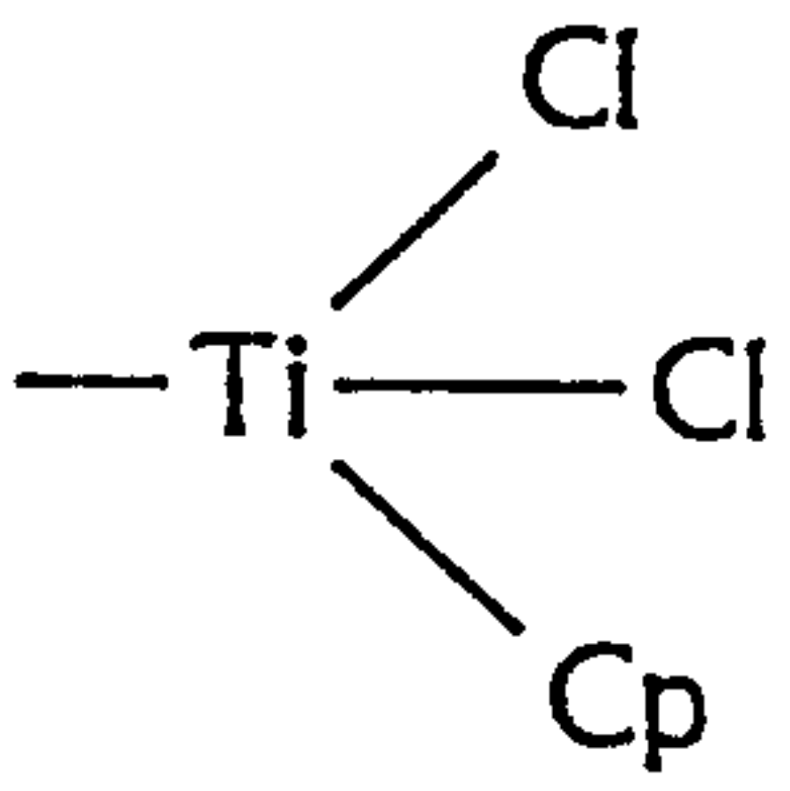
i) a radical of the formula



wherein A′, B′, C, D, are independently selected from the group consisting of F, H, NO_2, a C_{1-6} alkyl radical, and a C_{8-12} aryl radical, and E is an endocyclic nitrogen atom or a C-CN radical or isomers thereof,

ii) $SiR^1R^2R^3$ wherein R^1, R^2, and R^3 are independently selected from the group consisting of C_{1-4} alkyl radicals; and

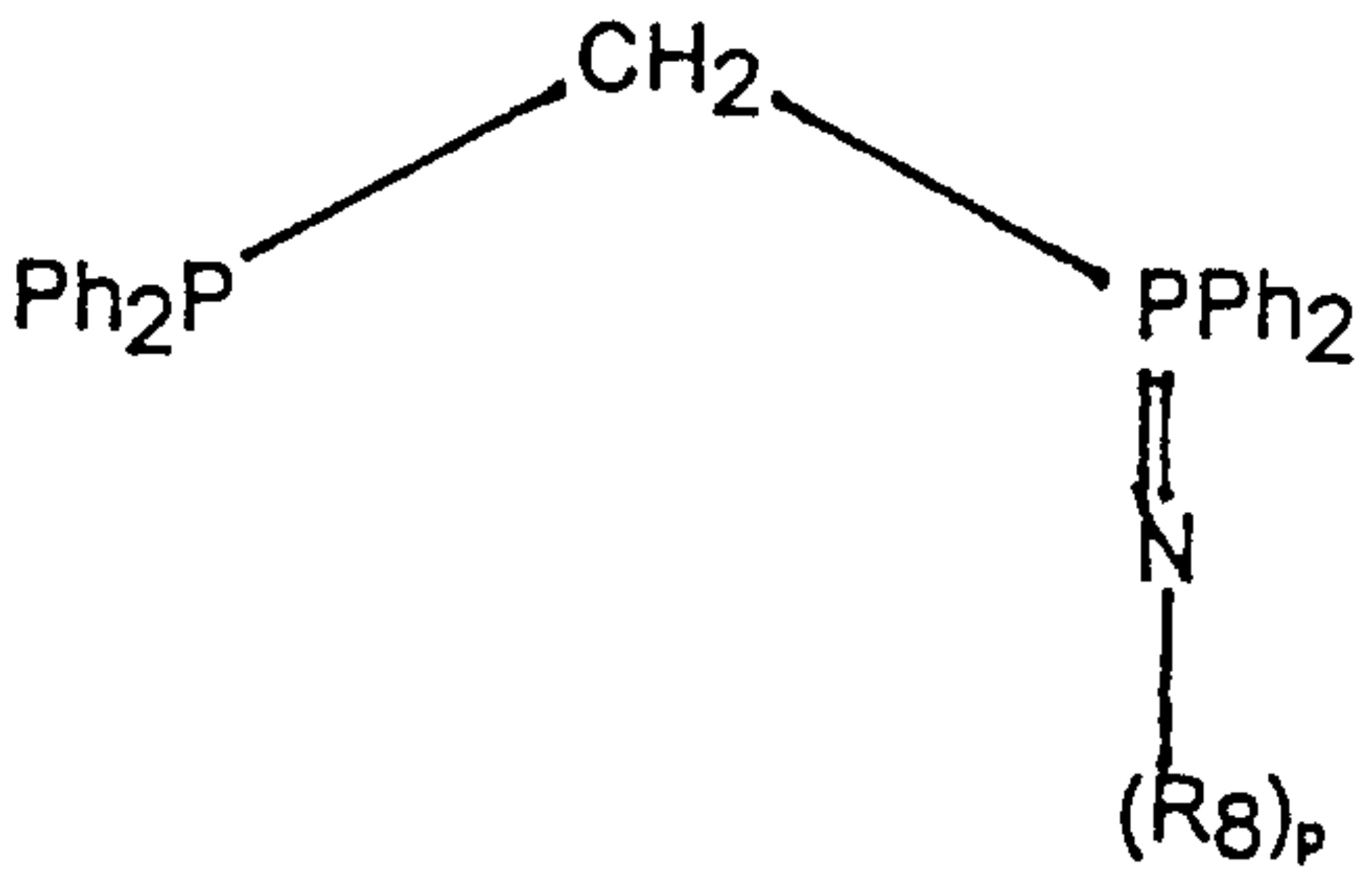
iii) a group of the formula



in which Cp is a cyclopentadienyl radical.

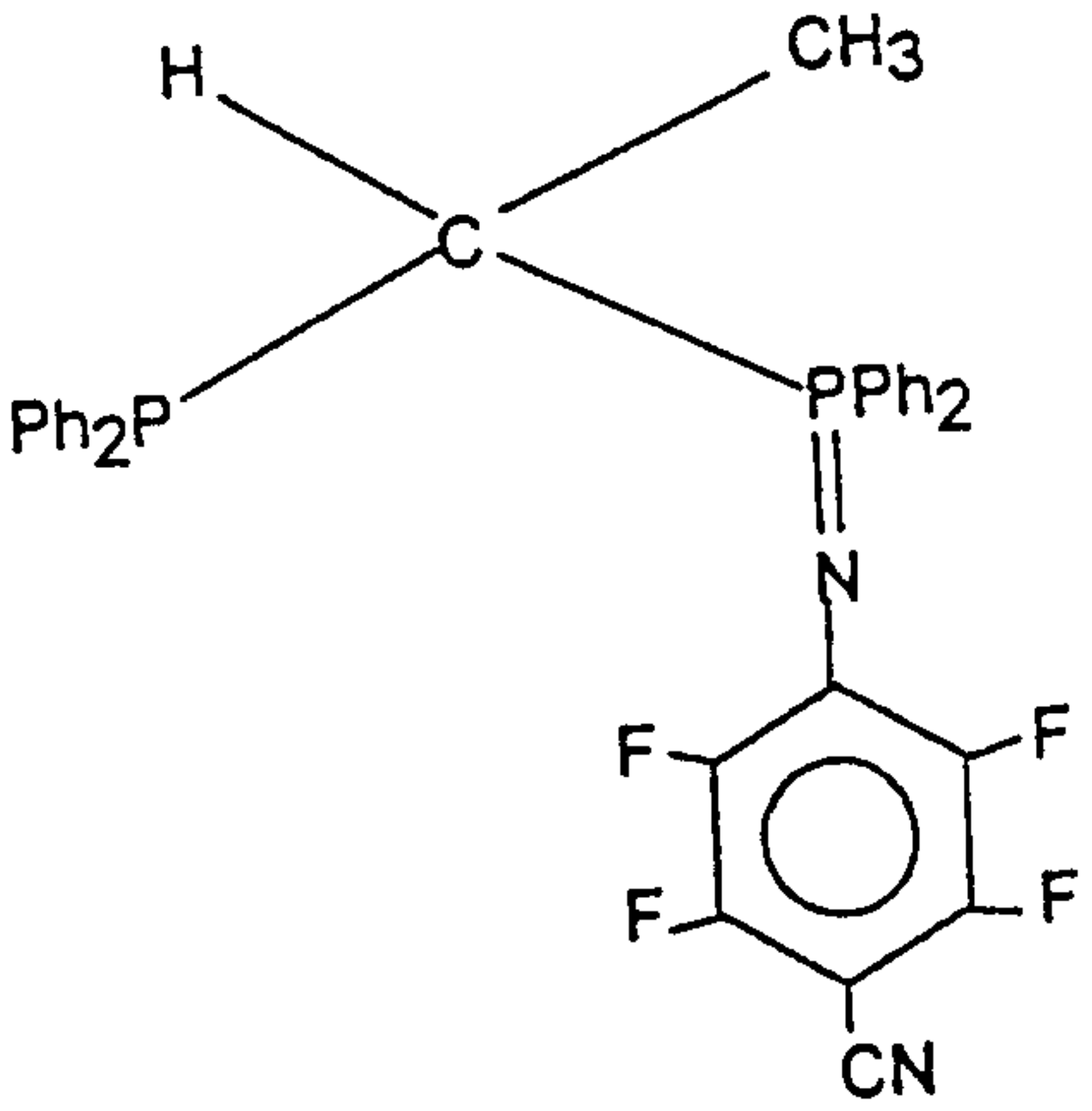
In the above ligands/complexes preferably M is Cr, Ti and Ni.

Suitable ligands include those of the formula $Ph_2PCH_2CH_2PPh_2{=}NSiMe_3$ (i.e. Y is P, Q is $-CH_2CH_2-$, and R_8 is trimethyl silyl); and

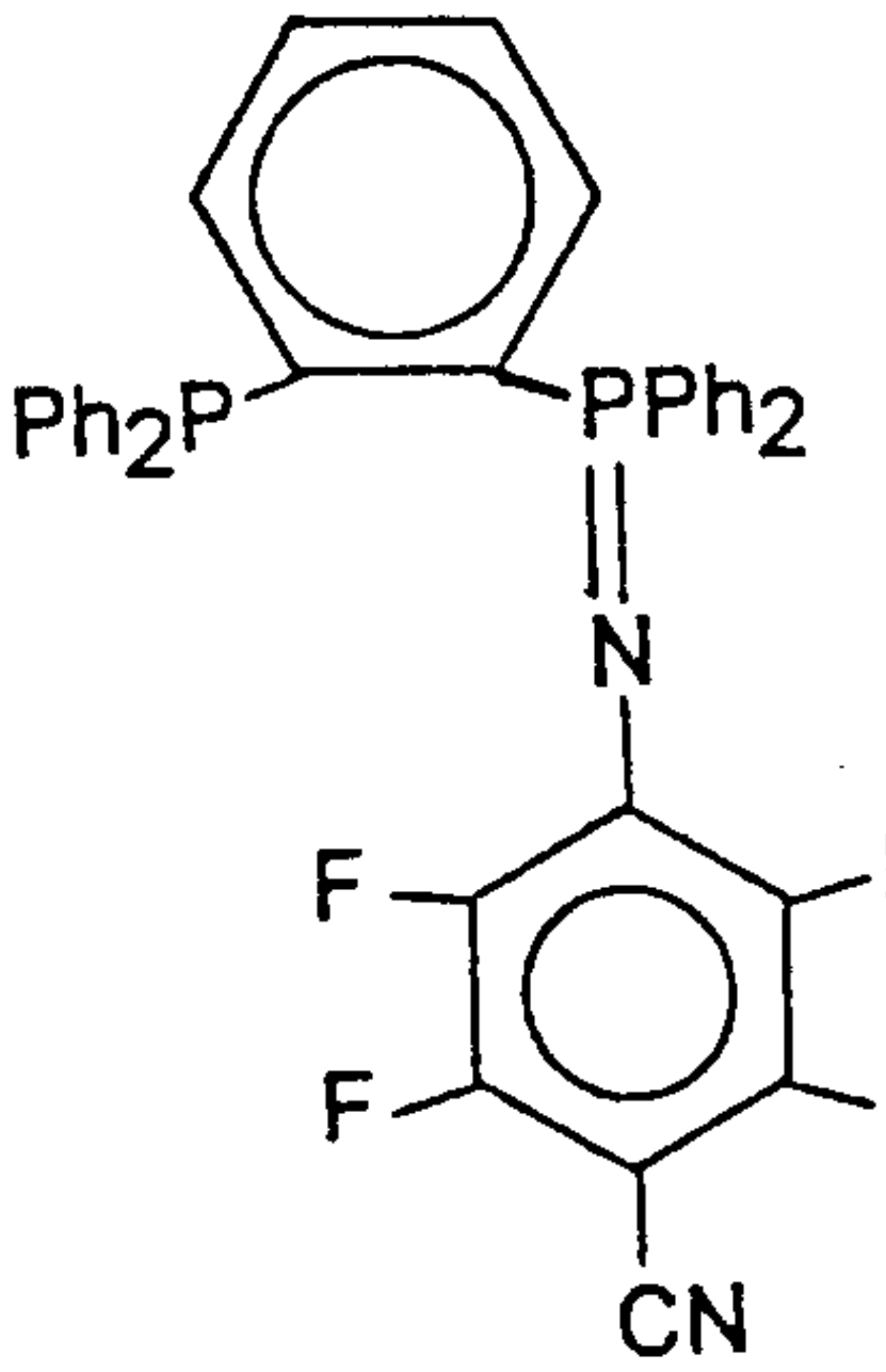


wherein p is 0 or 1, Q is CH_2 and if present R_8 is selected from the group as defined above.

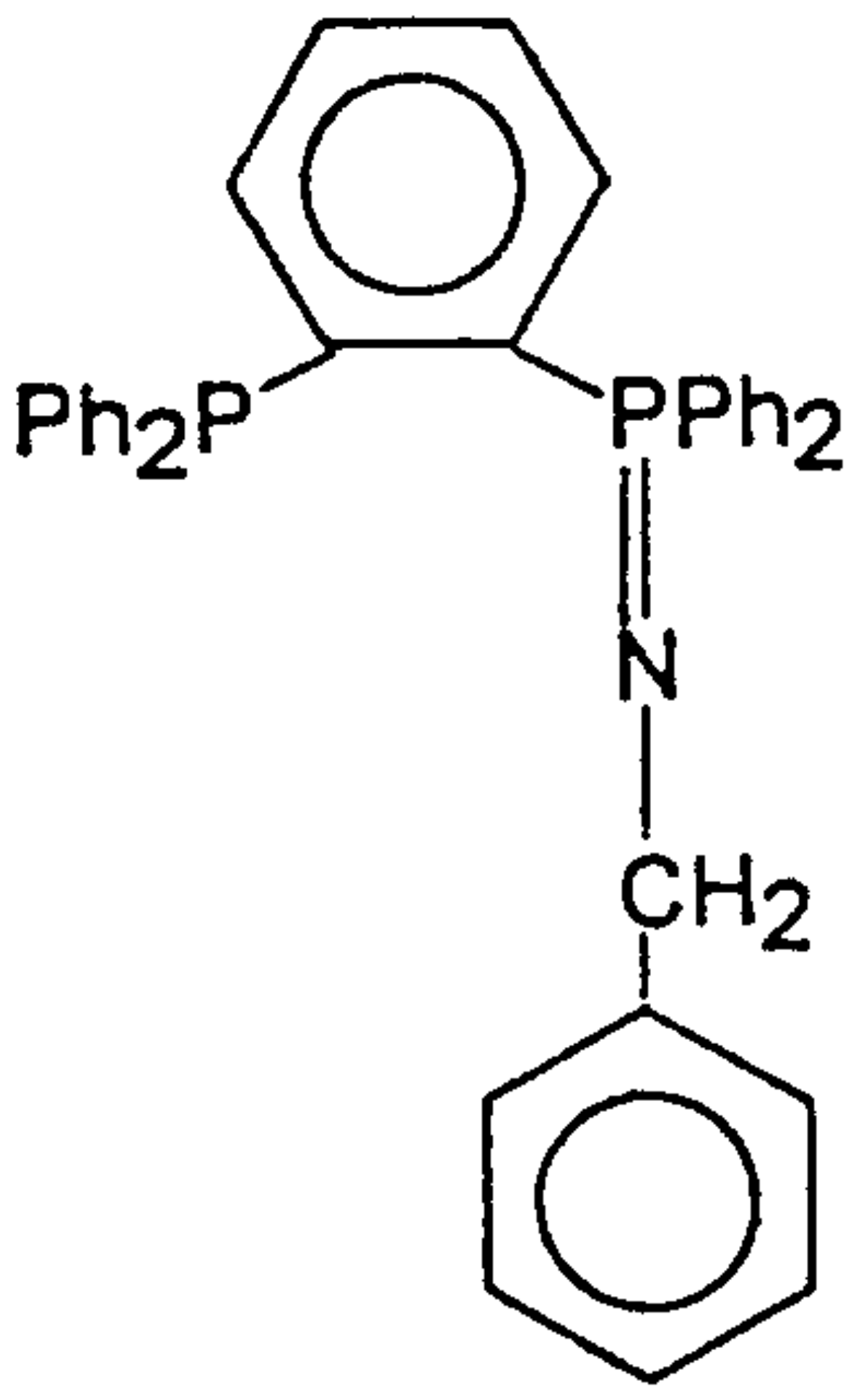
Suitable ligands also include:



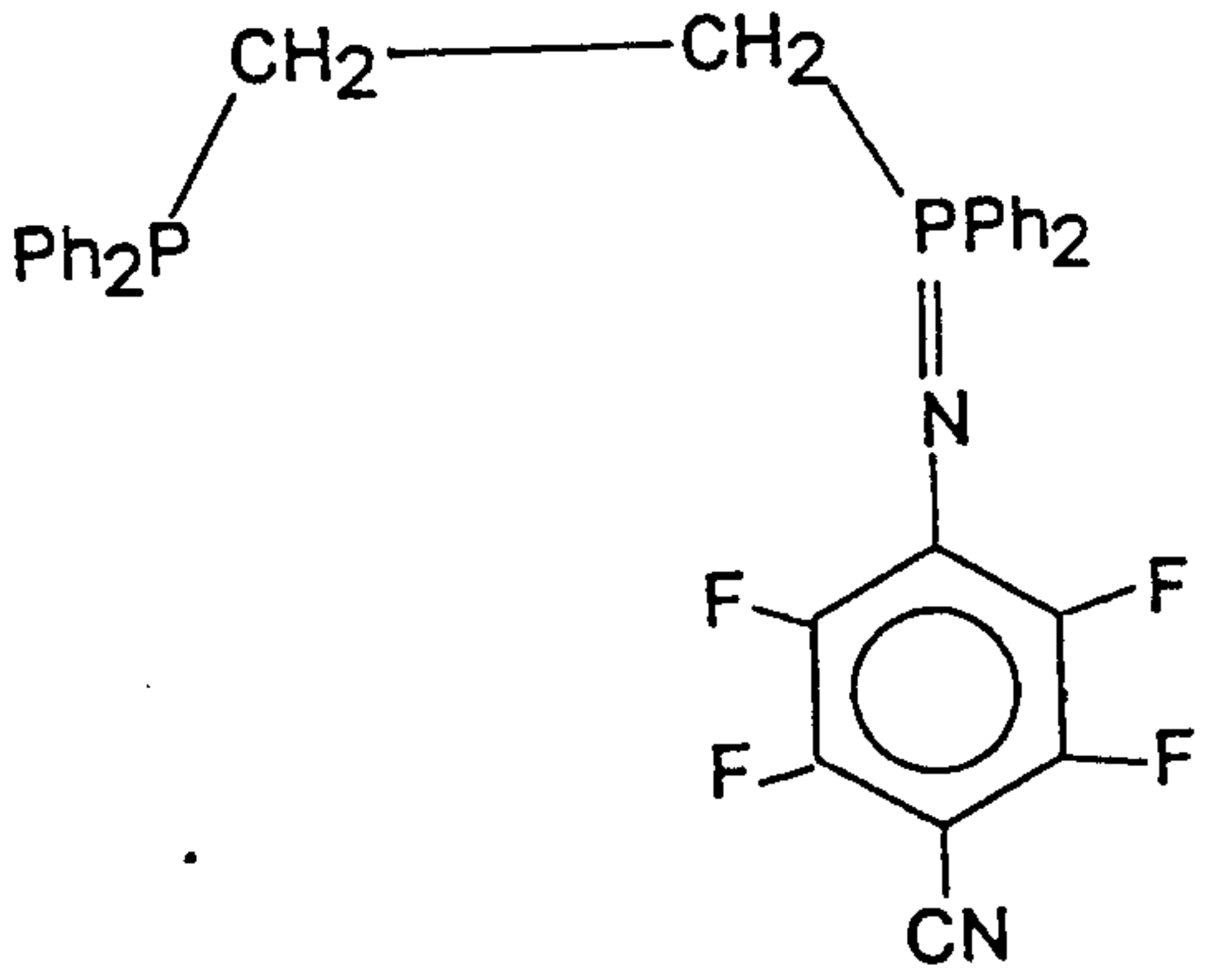
1-(N-4-cyanotetrafluorophenyl-diphenylphosphoranimine)-1-(diphenylphosphino)ethane (i.e. Q is CH-CH_3, p is 1 and R_8 is tetrafluorocyanophenyl);



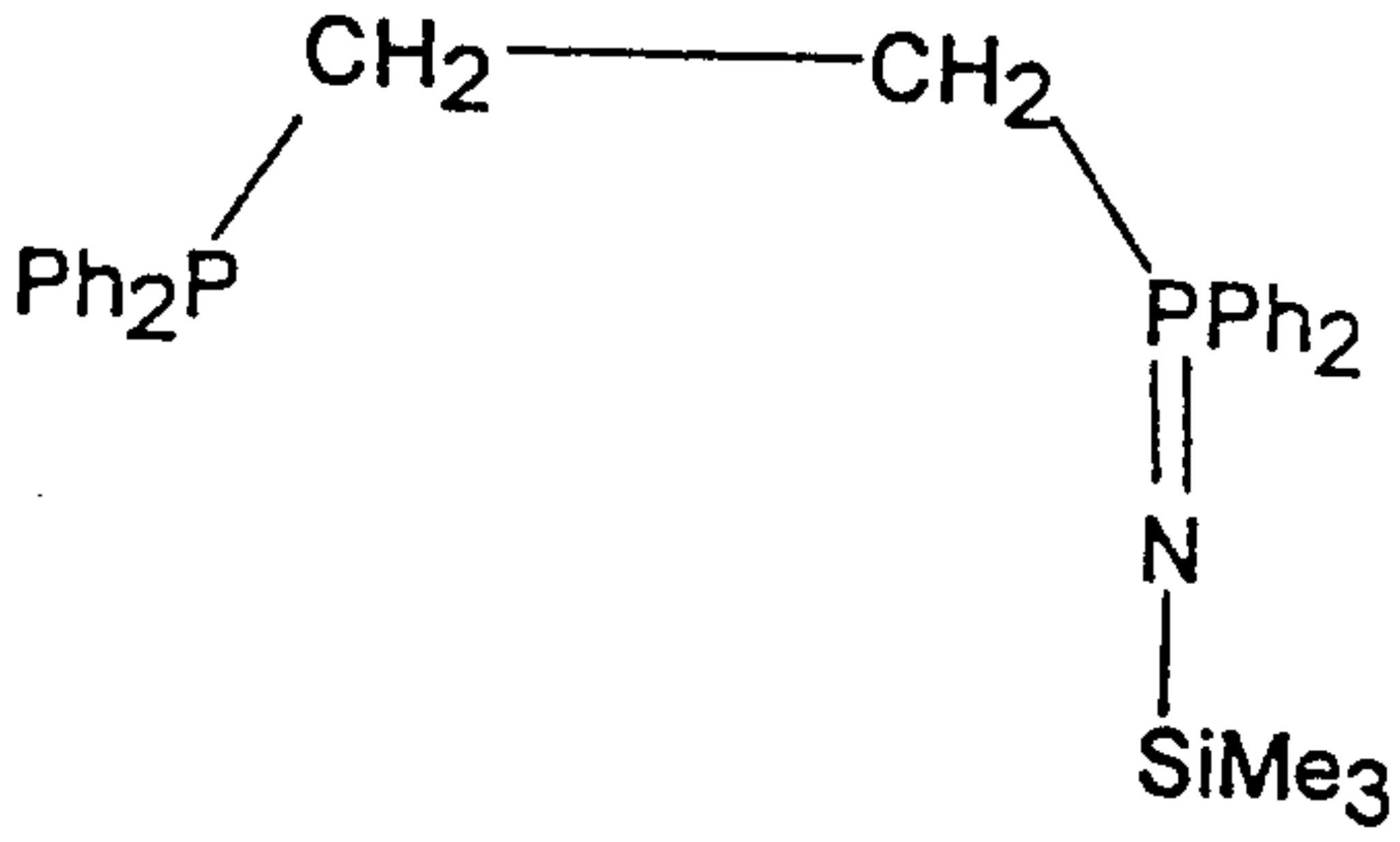
1-(N-4-cyanotetrafluorophenyldiphenylphosphoranimine)-2-(diphenylphosphino)benzene (i.e. p is 1, Q is a disubstituted (divalent) phenyl radical, and R_8 is tetrafluorocyanophenyl);



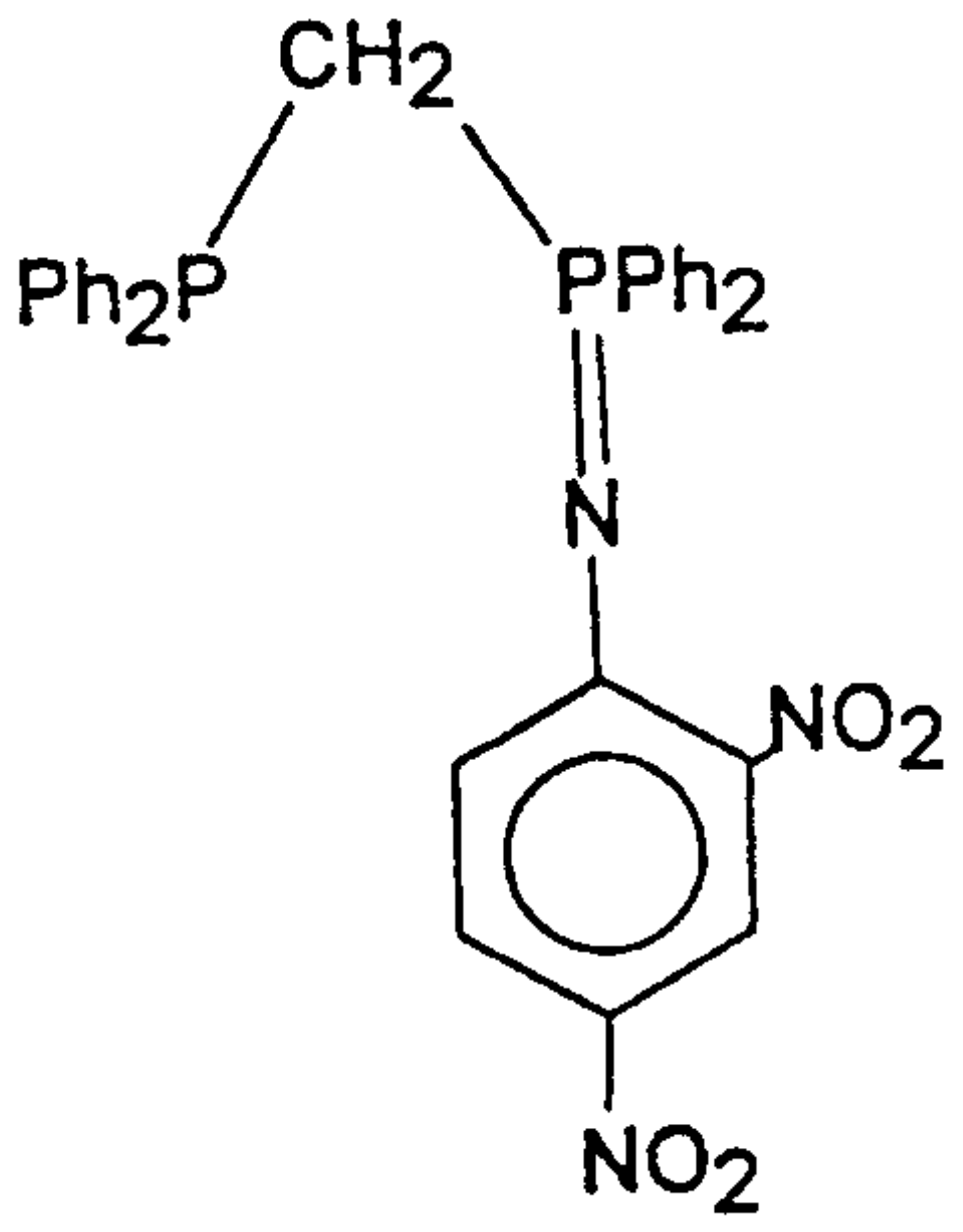
1-(N-benzyldiphenylphosphoranimine)-2-(diphenylphosphino)-benzene (i.e. p is 1, Q is a disubstituted (divalent) phenyl radical, and R_8 is benzyl);



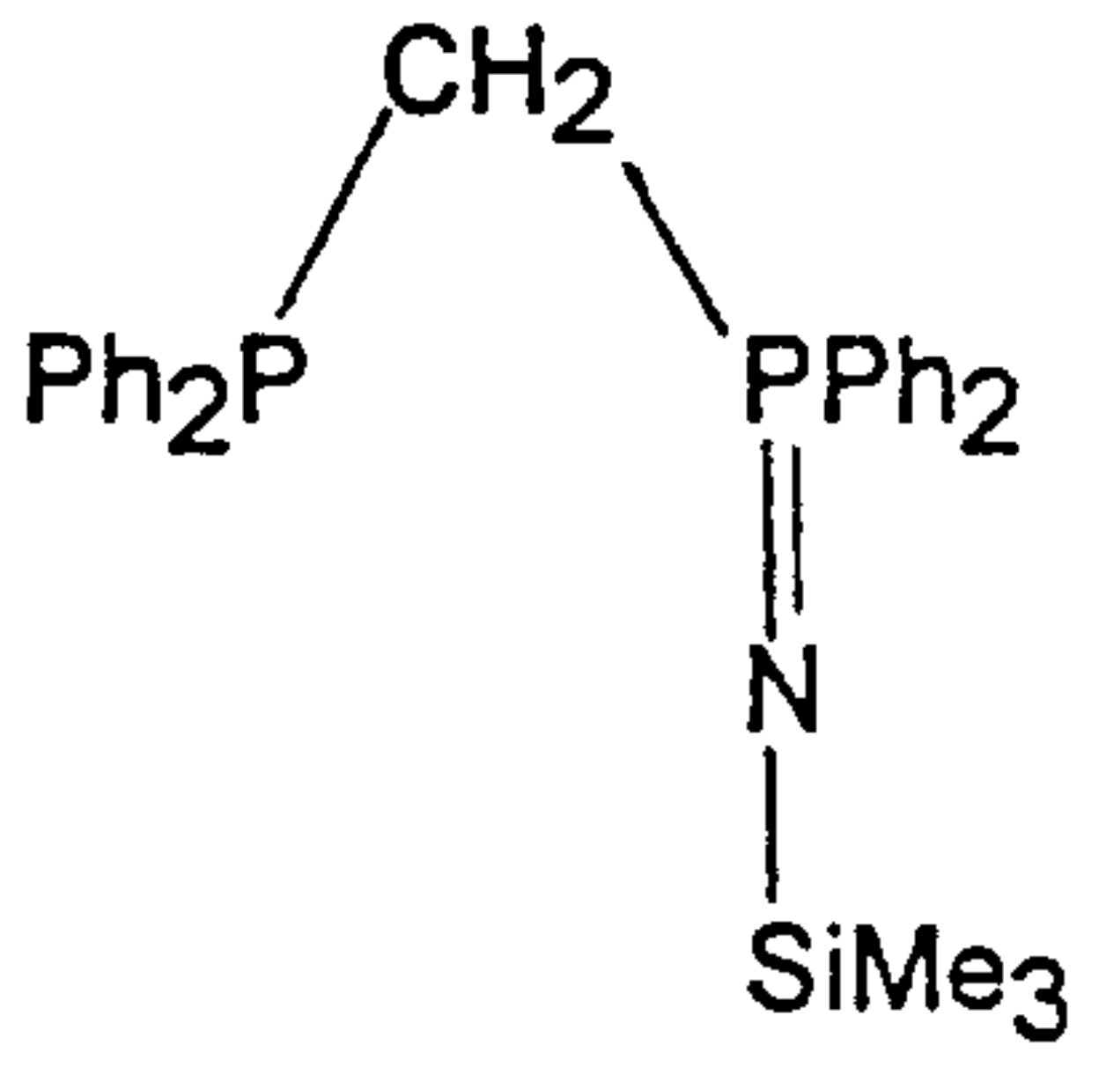
1-(N-4-cyanotetrafluorophenyldiphenylphosphoranimine)-2-(diphenylphosphino)ethane (i.e. p is 1, Q is $-CH_2CH_2-$ (e.g. an ethylene diradical), and R_8 is tetrafluorocyanophenyl);



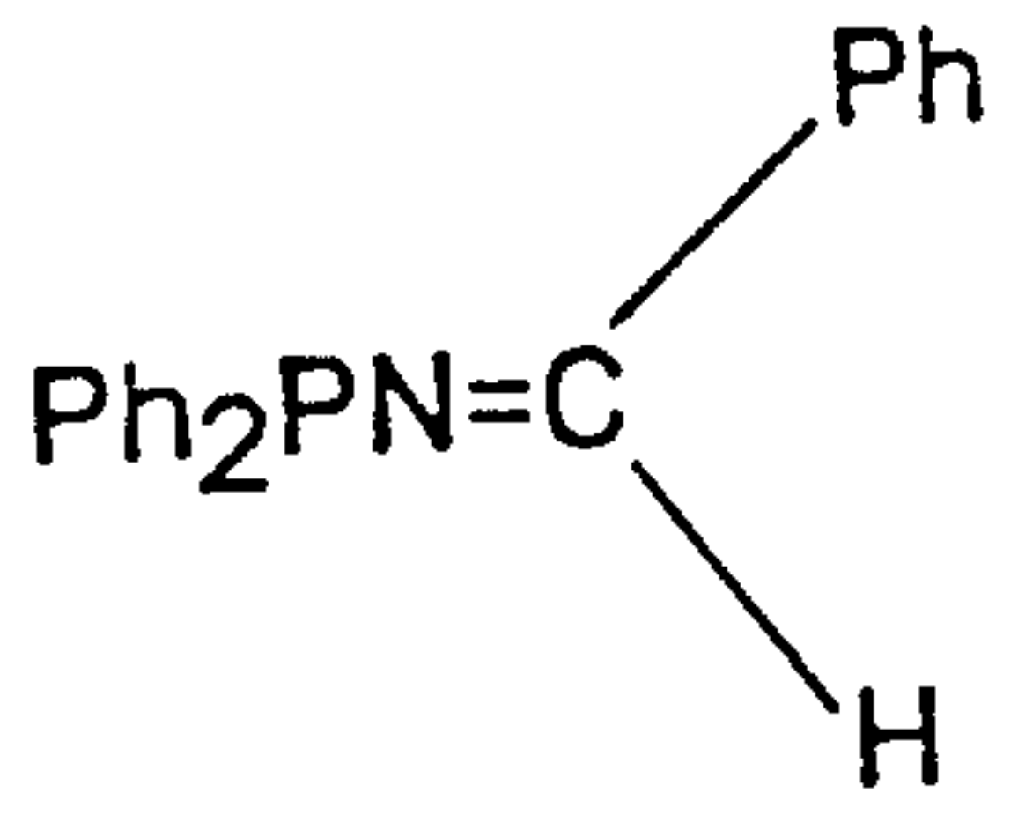
1-diphenylphosphino-2-(N-trimethylsilyldiphenylphosphoranimine)ethane (i.e. Q is $-CH_2CH_2-$, p is 1 and R_8 is trimethyl silyl);



N-2,4-di(nitro)phenyl(diphenylphosphoranimine)-methylene-diphenylphosphine (i.e. Q is $-CH_2-$, p is 1 and R_8 is 2,4-dinitrophenyl)

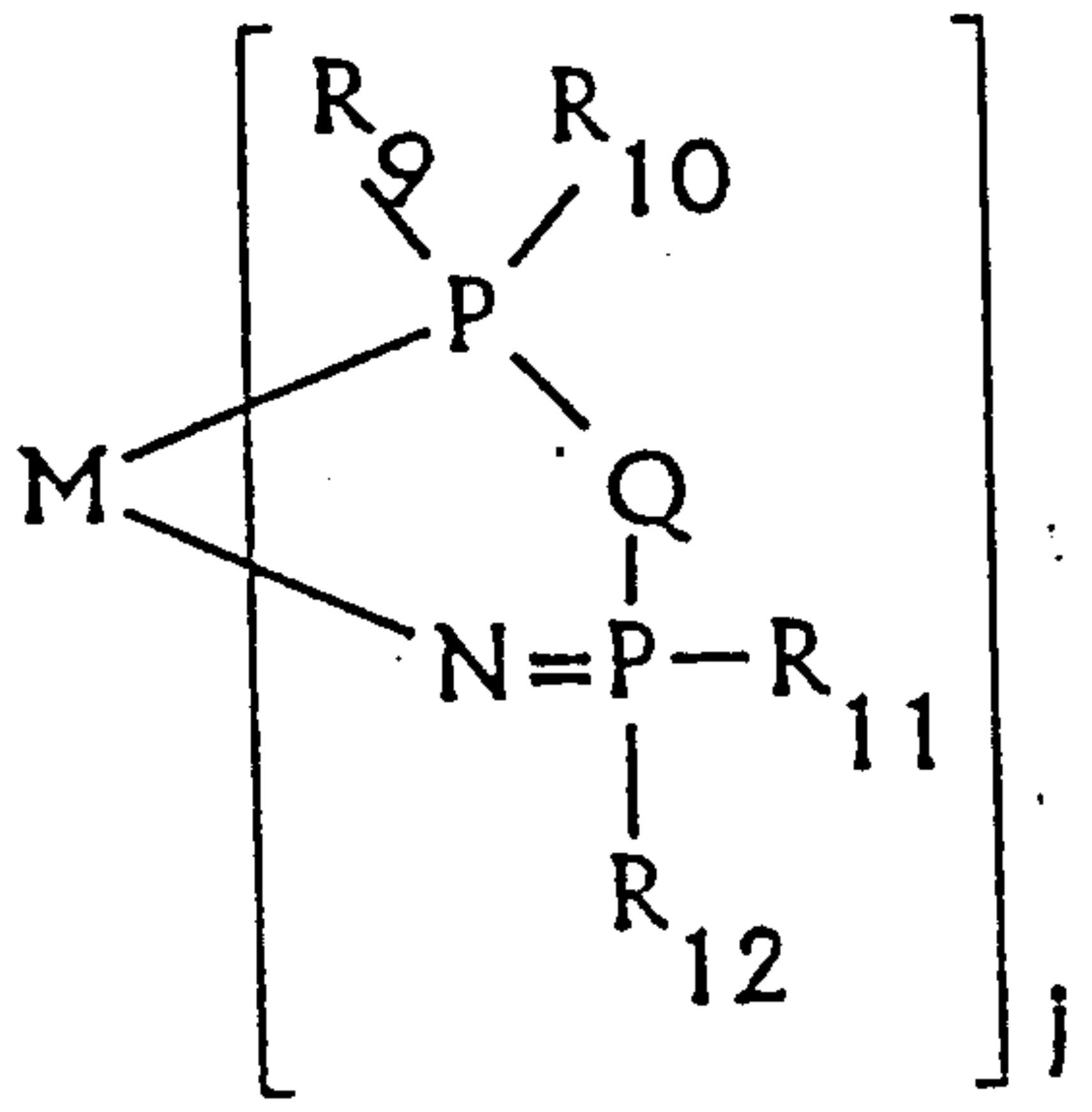


1-diphenylphosphino-1-(N-trimethylsilyldiphenylphosphoranimine)methane (i.e. Q is $-CH_2-$, p is 1 and R_8 is trimethyl silyl)(in the above specific formulae R_9, R_{10}, R_{11}, and R_{12} are all phenyl radicals); and



N-diphenylphosphinobenzylimine.

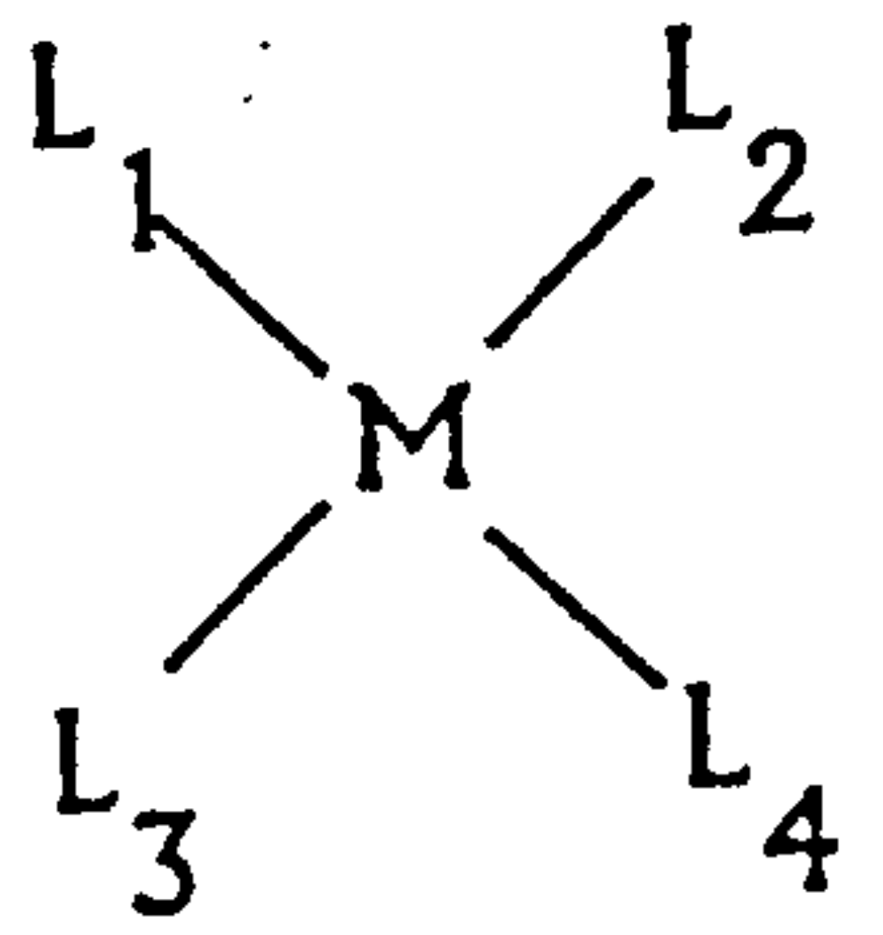
The catalyst precursor according to another aspect of the invention may be of the formula



COMPLEX III

wherein M and Q are as defined above; j is 2 or 3 depending on the coordination number of M; and R_9, R_{10}, R_{11}, and R_{12} are independently selected from the group consisting of C_{1-10} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three substituents, preferably one, selected from the group consisting of C_{1-8}, preferably C_{1-4}, alkyl radicals.

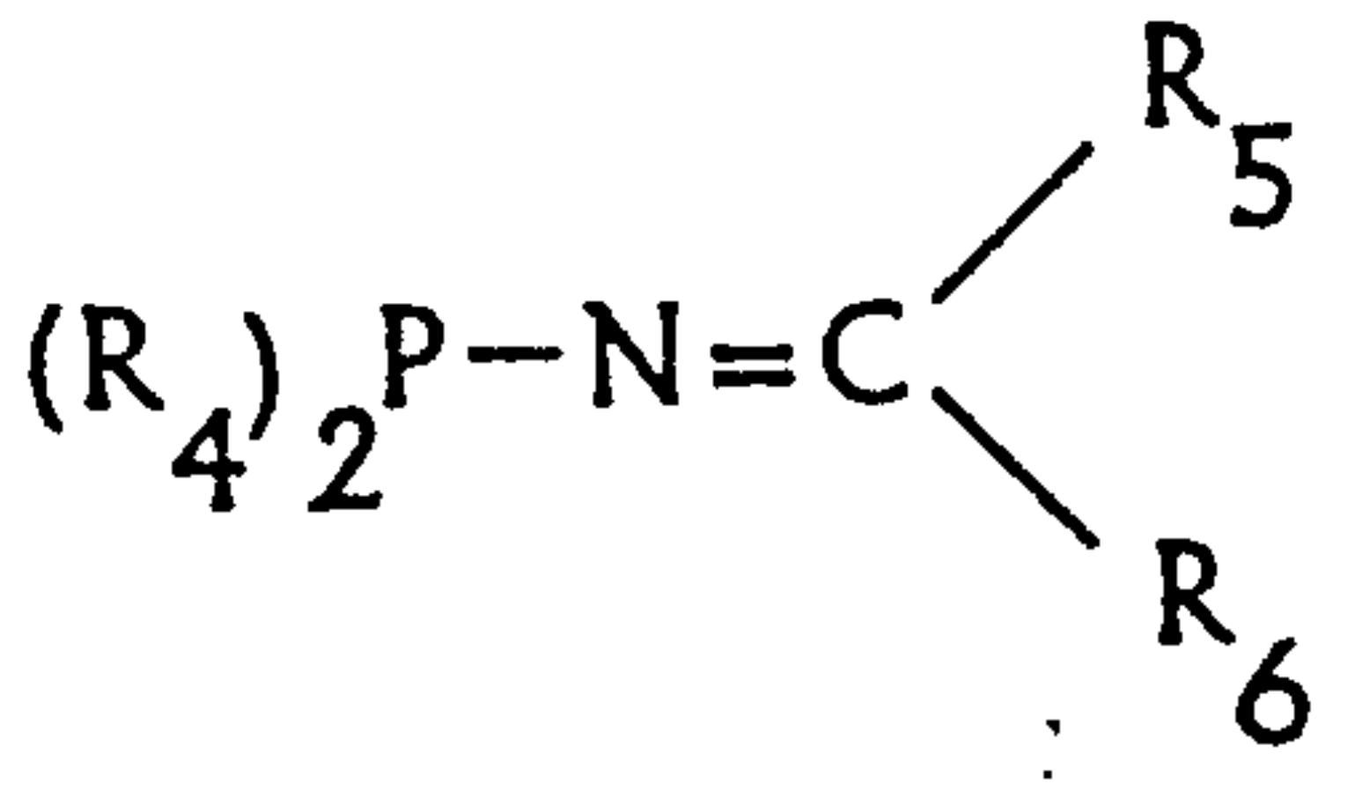
The catalyst precursor may be of the formula



COMPLEX IV

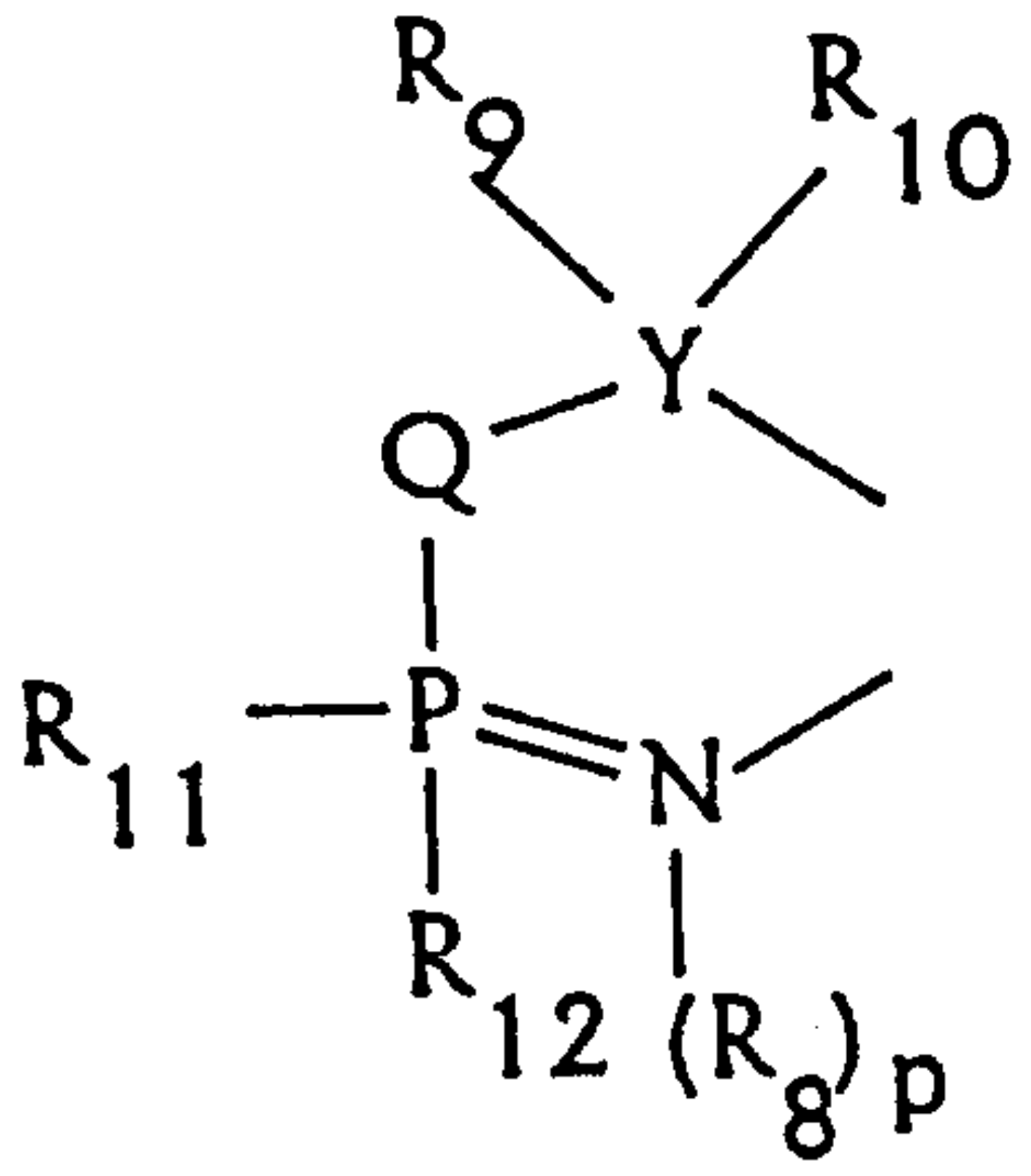
wherein M is as defined above and L_1, L_2, L_3, and L_4 are independently selected from the group consisting of

i) ligands of the formula



wherein R_4 may be a radical selected from the group of radicals from which R_3 is selected and R_5 and R_6 may independently be a hydrogen atom or a radical selected from the group consisting of C_{1-10}, straight chained, or branched alkyl radicals; C_{5-8} cyclic alkyl radicals, C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three, preferably one, substituents selected from the group consisting of C_{1-8}, preferably C_{1-4} alkyl radicals;

ii) or L_1 and L_2, or L_3 and L_4, or both, may be taken together to form a ligand of the formula



wherein Y, Q, R_8, R_9, R_{10}, R_{11}, and R_{12}, and p are as defined above:

iii) ligands of the formula $P(R_3)_3$ where in R_3 may be independently selected from the group of radicals consisting of C_{1-10} straight chained, branched or cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three, preferably one, substituents selected from the group consisting of C_{1-8}, alkyl radicals; and provided at least one of L_1, L_2, L_3, and L_4 is a ligand of formulas i) or ii) above;

iv) olefins selected from the group consisting of C_{2-4} olefins, and C_{6-8} cyclic, nonconjugated diolefins; and provided at least one of L_1, L_2, L_3, and L_4 is a ligand of formulas i) or ii) above.

Suitable olefins include ethylene, 1,5-cyclooctadiene (cod); and norbornadiene (nbd).

Preferably the catalyst precursor is a complex of the transition metal, preferably Ni, Cr, Ti, V, and Zr, most preferably Ni.

The catalyst precursor is dissolved in a solvent in which the co-catalyst and the alpha olefin are also soluble or a solvent which is miscible with solvents for the co-catalyst and alpha olefin. Typically the solvent is a C_{6-12} cyclic aliphatic or aromatic compound which is unsubstituted or substituted by up to six substituents selected from the group consisting of C_{1-4} alkyl radicals and halogen atoms. Suitable solvents include cyclohexane, toluene and chlorobenzene.

The activator for the catalyst is typically an aluminum alkyl compound such as are used in Ziegler-Natta catalysts. The activator may be selected from the group of activators consisting of:

i) activators of the formula $AlR_{3-n}X_n$ wherein R is a C_{1-8}, preferably C_{1-4}, alkyl radical, most preferably an ethyl radical, X is halogen, preferably chlorine, and n is 0, 1 or 2;

ii) C_{1-8}, preferably C_{1-4} alkyl, most preferably methyl aluminoxane compounds; and

iii) boron trifluoride.

The activator is advantageously selected from the group consisting of triethyl aluminum, diethyl aluminum chloride (DEAC), ethyl aluminum dichloride (EADC), methyl aluminoxane (MAO), boron trifluoride, tetraphenylborate and tri- or tetra(penta fluorophenyl) boron compounds and complexes.

Commercially available activators include DEAC, EADC, MAO and boron trifluoride.

The degree of oligomerization is controlled by the mole ratio of activator to catalyst precursor which may range from 1:2 to 500:1, preferably from 5:1 to 250:1.

The olefin may be used in the form of a condensed liquid depending on the pressure and temperature (i.e. for ethylene the temperature must be below 9°C for the monomer to be a liquid) of the process or more generally in the form of a solution of olefin in a solvent as noted above. Ethylene and propylene are preferred olefins.

The solution of catalyst precursor, activator and olefin are then reacted in a pressurized vessel (a Parr bomb, autoclave or a reactor (CSTR)) at a temperature from -15°C to 250°C, preferably from 0 to 250°C, and for the nickel complexes most preferably from 0 to 30°C. The pressure in the reactor may be from 15 to 1500 psi, preferably from 60 to 1200 psi. If the pressure and temperature are such to maintain the olefin in a liquid form then the olefin need not be dissolved in a solvent.

Typically the residence time in the reactor will be at least a half an hour. The reactants are all liquids and the process is homogeneous. On exiting the reactor the liquid phase may be subjected to conventional separation techniques such as distillation to separate the oligomerized olefin from the feed olefin.

One particular advantage of the process of the present invention is "high reactivity". The activity is typically not less than 1500 g of olefin per gram of catalyst per hour of residence time in the reactor. Further by selecting the catalyst precursor and activator it is possible to control the product distribution. For example, starting with ethylene the product may be 90+% of 1-butene.

The invention will be illustrated by the following non-limiting examples. In the examples unless otherwise indicated parts means parts by weight (e.g. grams). In the examples Ph is phenyl, Me is methyl, OEt is ethoxide, and Bu is butyl.

Catalyst Precursors

Dithiophosphinate Complexes:

$[NiCl(PPh_3)(S_2PPh_2)]$ (A)

$NiCl_2(PPh_3)_2$ (1.645 g, 2.5 mmol) in ethanol (150 cm^3) was stirred under argon with $NH_4[S_2PPh_2]$ (0.672 g, 2.5 mmol) for 0.5 hours. Fifty cm^3 of diethyl ether was added to the resulting solution which was then stirred for a further 10 minutes, after which the solution was filtered and washed with degassed diethyl ether (3 X 20cm^3). One hundred and fifty cm^3 of CH_2Cl_2 was added to the filtrate and the resulting mixture was further filtered to remove any inorganic salts. The compound was then recrystallized using a mixture of CH_2Cl_2/hexane. The yield was 1.18 g (76%).

$[NiCl(PPh_3)(S_2PMe_2)]$ (B)

$NiCl_2(PPh_3)_2$ (10.00 g, 15 mmol) in toluene (300 cm^3) was stirred under argon with $NaS_2PMe_2.2H_2O$ (2.67 g, 15 mmol) for 2.5 hours. The solution was cooled to -20°C and filtered, the solid residue was washed with degassed diethyl ether (3 X 20cm^3) and dried under vacuum for 0.5 hours. One hundred and fifty cm^3 of CH_2Cl_2 was added to the filtrate and the resulting mixture was further filtered to remove any inorganic salts. The compound was then recrystallized using a mixture of CH_2Cl_2/hexane. The yield was 3.46 g (47%).

$[Ni(PPh_3)(S_2P(OEt)_2)_2]$ (C)

$NiCl_2(PPh_3)_2$ (1.00 g, 1.5 mmol) in dichloromethane (150 cm^3) was stirred under argon with $NH_4[S_2P(OEt)_2]$ (2.76 g, 1.5 mmol) for 0.5 hours. The solution was filtered to remove inorganic salts. The dichloromethane was removed under vacuum and the resulting solid was redissolved in diethyl ether (20 cm^3). Slow evaporation of the solvent to approximately 5 cm^3 at room temperature resulted in the precipitation of the desired product. The compound was recrystallized using this method to remove any excess PPh_3. (Yield 0.69 g, 65%)

$[Ni(S_2P(OEt)_2)_2]$ (D)

$NiCl_2 . 6H_2O$ (0.238 g, 1.0 mmol) in absolute ethanol (50 cm^3) was stirred under argon with $NH_4[S_2P(OEt)_2]$ (0.406 g, 2.0 mmol) for 1 hour. The resulting solution was filtered and the precipitate was dissolved in dichloromethane. The solution was washed with degassed water (3 X 20 cm^3) to remove inorganic salts. The organic layer was separated and the solvent removed under vacuum and the resulting solid was redissolved in hexane (20 cm^3). Slow evaporation of the solvent resulted in the precipitation of the desired product. The compound was recrystallized from hexane (cooling to -40°C). (Yield 0.25 g, 58%)

$[Ni(PPh_3)_2\ S_2PMe_2]^+\ BPh_4-$ (E)

$[NiCl_2(PPh_3)_2]$ (1 g, 1.53 mmol) NaS_2PMe_2 (0.116 g, 1.53 mmol) and $NaBPh_4$ (0.523 g, 1.53 mmol) were stirred in an acetonitrile solution (30 cm^3) under argon for 1 hour. The solution was filtered to remove NaCl and the solvent was removed under vacuum. Vigorous stirring of the residue with dry degassed hexane gave the product as a brown precipitate. (Yield 0.96 g, 63%)

$[NiCl(PBu_3)(S_2PPh_2)]$ (F)

$[NiCl_2(PPh_3)_2]$ (1.657 g, 3 mmol) in 150 cm^3 of toluene was stirred under argon with $NH_4[S_2PPh_2]$ (0.802 g, 3 mmol) for 0.5

hours. The solution was then filtered to remove inorganic salts. The toluene was removed under reduced pressure to yield a purple oil. The yield is nearly quantitative.

$[NiCl(PBu_3)(S_2PMe_2)]$ (G)

$[NiCl_2(PBu_3)_2]$ (1.657 g, 3 mmol) in 150 cm^3 of toluene were stirred under argon with $NaS_2PMe_2.2H_2O$ (0.553 g, 3 mmol) for 2 hours. The solution was then filtered to remove inorganic salts. The toluene was removed under reduced pressure to give a high yield (80-90%) of a purple oil.

Phosphine Imine Complexes:

$[Ni(Ph_2P\text{-}N{=}CHPh)_4]$ (H)

Bis(1,5-cyclooctadiene)nickel (0.48 g, 1.76 mmol) and $Ph_2P\text{-}N{=}CHPh$ (2.023 g, 6.99 mmol) were stirred as a suspension in hexane in a flask under an argon atmosphere at 0°C. Dichloromethane was slowly added to the suspension until solution occurred and immediately a brown precipitate formed. After allowing the mixture to come to room temperature the precipitate was filtered and dried under vacuum to give a product sensitive to air and moisture:

$[Ni(Ph_2P\text{-}N{=}CHPh)_4]$ NMR ^{31}P $\{^1H\}$ CD_2Cl_2 δ 74.0 ppm.

[Ni(cod)($Ph_2P-N=CHPh)_2$] (cod = cyclooctadiene) (I)

Bis(1,5-cyclooctadiene)nickel (1.377 g, 5 mmol) and $Ph_2P-N=CHPh$ (2.9 g, 10 mmol) were stirred as a suspension in hexane in a flask under an argon atmosphere at 0°C. Dichloromethane was slowly added to the suspension until solution occurred and immediately a brown precipitate formed. After allowing the mixture to come to room temperature the precipitate was filtered and dried under vacuum to give a product sensitive to air and moisture: [Ni(cod)($Ph_2P-N=CHPh)_2$] NMR ^{31}P $\{^1H\}$ CD_2Cl_2 δ 73.15 ppm.

[Ni($Ph_2PCH_2P(Ph)_2N-C_6F_4CN)_2$].$CH_2Cl_2$ (J)

Bis(1,5-cyclooctadiene)nickel (0.387 g, 1.4 mmol) and $Ph_2PCH_2P(Ph)_2=N-C_6F_4CN$ (1.53 g, 2.67 mmol) were stirred as a suspension in hexane (15 cm^3) in a flask under an argon atmosphere at 0°C. Dichloromethane (5 cm^3) was slowly added to the suspension until a brown solution formed from which there formed a red precipitate. After allowing the mixture to come to room temperature the precipitate was filtered and dried under vacuum to give an analytically pure product.

[Ni(cod)$Ph_2PCH_2P(Ph_2)=N-C_6F_4CN$].$CH_2Cl_2$ (K)

Bis(1,5-cyclooctadiene)nickel (1.347 g, 4.9 mmol) and $Ph_2PCH_2P(Ph_2)=N-C_6F_4CN$ (2.8 g, 4.9 mmol) were stirred as a suspension in hexane (15 cm^3) in a flask under an argon atmosphere at 0°C. Dichloromethane (15 cm^3) was slowly added to the suspension until the suspension changed from yellow to red/brown. After allowing the mixture to come to room temperature the precipitate was filtered and dried under vacuum to give a pale red powder.

A series of oligomerizations was then carried out with some of the above catalyst precursors and diethyl aluminum chloride (DEAC) or ethyl aluminum dichloride (EADC) as the activator. The oligomerizations were carried out under a nitrogen containing olefin atmosphere. The yields of C_4, C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, and polymer C_{18+} expressed as percentages were measured. The results are set forth in Table 1. In the table: PRE is the catalyst precursor; ACT is the activator; PPE is ethylene partial pressure in pounds per square inch gauge (PSIG); Temp is the reaction temperature in °C; Ti is reaction time in hours; PPN is the nitrogen partial pressure in PSIG; Rato is the mol/mol ratio of activator to catalyst precursor; C followed by a number is the wt% of that cut of carbon atoms in the product; and C_{18+} is the "polymer cut" (which was filtered out of the solution).

Table 1

RUN	1	2	3	4	5	6	7	8	9	10	11	12
PRE	A	A	A	A	H	H	H	H	H	H	I	A
ACT	DEAC	DEAC	DEAC	EADC	DEAC	DEAC	DEAC	DEAC	EADC	DEAC	DEAC	DEAC
PPE	30	60	30	60	30	60	30	60	60	400	400	100
Temp	15	15	25	15	15	15	15	25	25	22	22	15
Ti	1	1	1	1	1	1	1	1	1	2	2	1
PPN	20	20	20	20	20	20	20	20	20	10	10	10
Rato	147	153	120	162	147	168	135	146	152	5.26	5.30	4.86
C_4	43.65	89.73	84.88	76.27	77.65	93.18	90.49	28.34	19.27	94.55	97.85	98.2
C_6	2.08	8.53	13.61	3.75	4.92	2.52	8.23	1.79	1.50	0.32	1.22	1.6
C_8	1.89	0.91	0.89	2.08	1.73	0.24	0.46	0.45	0.51	3.40	0.49	0.2
C_{10}	6.32	0.25	0.15	2.94	8.37	0.58	0.13	39.87	8.05	1.26	0.41	0.0
C_{12}	11.63	0.22	0.19	7.79	4.94	0.82	0.22	6.51	37.18	(1)	(1)	(1)
C_{14}	14.36	0.10	0.08	3.60	0.86	0.59	0.11	12.24	20.37	(1)	(1)	(1)
C_{16}	18.26	0.14	0.08	2.85	0.43	1.73	0.17	9.52	12.13	(1)	(1)	(1)
C_{18}	1.20	0.00	0.00	0.21	0.00	0.00	0.00	0.53	0.69	(1)	(1)	(1)
C_{18+}	0.58	0.13	0.13	0.51	1.09	0.34	0.19	0.22	0.30	1.26	0.02	0.1

(1) not determined

The initial activity of the catalyst system could exceed 400,000 moles of C_2 consumed per mole of catalyst per hour. In some cases the C_{10+} fraction may contain aromatic components possibly from a reaction with the solvent.

A further series of experiments was then run. The results of these experiments are set out in Tables 2 and 3 in which the same abbreviations are used.

Table 2

RUN	1	2	3	4	$5^{(2)}$	$6^{(3)}$	7	$8^{(4)}$	$9^{(5)}$	10	11	12
PRE	H	A	H	A	H	H	H	A	A	A	A	H
ACT	EADC	EADC	DEAC	EADC	DEAC	EADC	DEAC	DEAC	EADC	DEAC	DEAC	EADC
PPE	30	60	60	30	30	60	30	30	60	60	60	30
Temp	15	25	15	25	15	25	25	25	15	15	25	25
Ti	1	0.5	0.5	1	1	1	0.5	1	1	1	0.5	0.5
PPN	20	20	20	20	20	20	20	20	20	20	20	20
Rato	159	144	155	143	140	141	148	153	153	135	144	150
C_4	73.09	76.89	95.99	73.75	91.39	33.09	91.70	88.74	87.01	91.96	92.46	67.3
C_6	6.47	5.02	2.97	6.26	5.35	3.18	6.55	9.79	5.96	6.71	6.46	6.47
C_8	1.12	1.83	0.26	2.39	0.65	0.61	0.83	0.67	0.60	0.66	0.51	0.99
C_{10}	2.74	4.04	0.02	4.04	0.04	8.08	0.03	0.16	1.82	0.23	0.07	6.70
C_{12}	7.16	5.98	0.24	7.80	1.07	39.65	0.33	0.23	2.08	0.17	0.18	9.62
C_{14}	3.46	3.03	0.10	3.18	0.47	9.90	0.10	0.14	1.21	0.12	0.09	4.24
C_{16}	4.50	2.27	0.19	2.35	0.75	4.94	0.14	0.11	1.06	0.12	0.13	3.86
C_{18}	0.13	0.21	0.00	0.06	0.00	0.24	0.00	0.00	0.09	0.00	0.00	0.14
C_{18+}	1.33	0.72	0.22	0.18	0.27	0.32	0.31	0.17	0.16	0.02	0.11	0.73

(2) repeat of Table 1 #5,
(3) repeat of Table 1 #6,
(4) repeat of Table 1 #3, and
(5) repeat of Table 1 #4.

Table 3

RUN	13	14	15 (6)	16
PRE	A	H	H	A
ACT	EDAC	EADC	DEAC	DEAC
PPE	30	60	60	30
Temp	15	15	25	15
Ti	0.5	0.5	1	0.5
PPN	20	20	20	20
Rato	134	144	146	157
C_4	64.96	69.44	94.03	91.2
C_6	2.82	3.41	5.01	7.90
C_8	0.88	0.69	0.32	0.37
C_{10}	6.20	7.86	0.04	0.05
C_{12}	16.37	8.62	0.18	0.12
C_{14}	4.84	2.69	0.08	0.05
C_{16}	3.48	2.87	0.17	0.06
C_{18}	0.04	0.00	0.00	0.00
C_{18+}	0.39	4.42	0.17	0.19

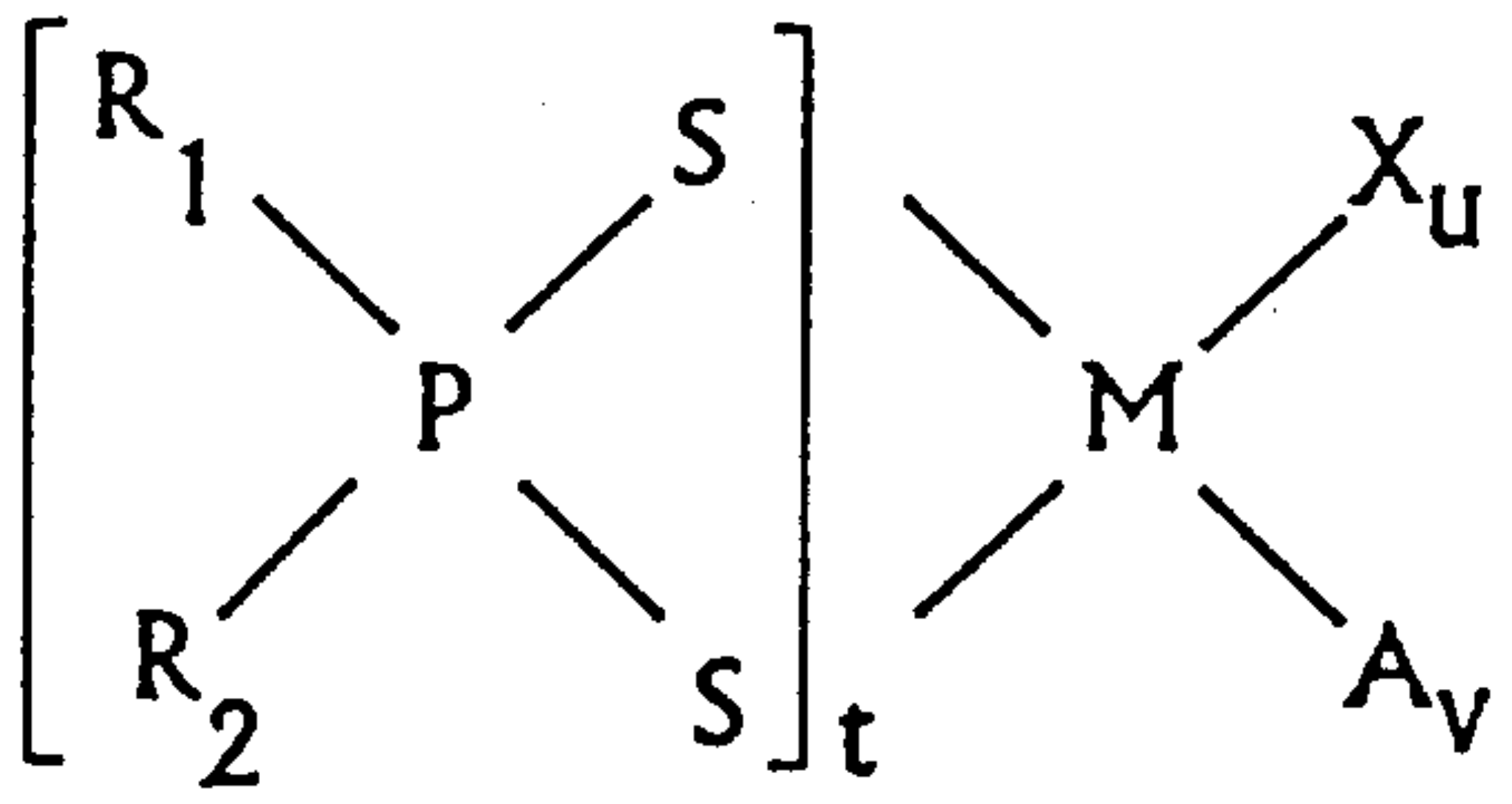
(6) the amount of catalyst is double that of Table 1 #8.

In the examples of the subject matter of the present invention it was observed that isomerization could be controlled to some extent by pressure. That is at ethylene pressures greater than 100 psig, typically from 100 to 400 psig, preferably from 100 to 200 psig, there tended to be higher amounts of the 1- higher olefin. Typically in the runs of oligomerization using the catalysts of the present invention the lowest selectivity for the preparation of 1-butene was from about 3 to 10% (runs 1, 2, 3, 4, and 7 from Table 1, runs 2, 4, 7, 8, 9, and 10 from Table 2, and run 13 and 16 from Table 3. The selectivity of the other runs except for runs 10 and 11 of Table 1 ranged from 10 to 25%, while in runs 10 and 11 of Table 1 the selectivity of 1-butene was about 80% and 60%, respectively. For comparative purposes the catalyst of example 1 of United States Patent 4,533,651 was prepared and activated over a comparable ratio of DEAC and EADC (105 to 199) and oligomerization of ethylene was carried out under comparable times, temperatures and pressures. In all of the comparative runs using the catalyst of example 1 of United States Patent 4,533,651, the selectivity for 1-butene was in the 2 to 5% range.

The catalysts of the present invention can be controlled by pressure and the ratio of the activator to the catalysts to produce higher amounts of higher olefins and to be more selective in producing 1- or alpha olefins.

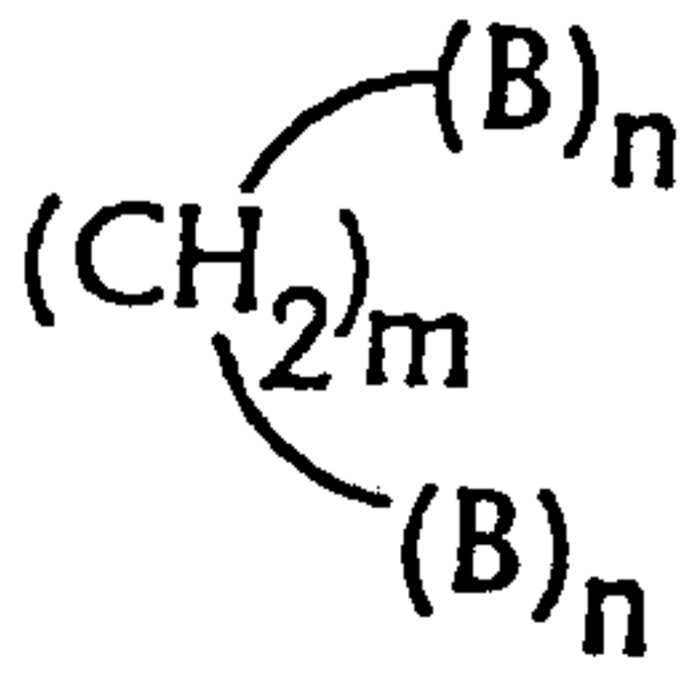
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A catalyst precursor comprising a dithiophosphinate transition metal complex of the formula:



COMPLEX I

wherein M is selected from the group consisting of Ni, Cr, Ti, V, and Zr; t is an integer from 1 to half the coordination number of M; u and v are each 0 or an integer; the sum of u+v is from 0 to two less than the coordination number of M; and the sum of 2t+u+v is the coordination number of M; R_1 and R_2 are independently selected from the group consisting of C_{1-10} straight chained, branched and cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three C_{1-8} alkyl radicals; C_{1-6} alkoxy and thioalkyl radicals; C_{6-12} aryloxy radicals; C_{6-12} arylthio radicals; CF_3; and fluorine; or if taken together, R_1 and R_2 form a diradical of the formula:



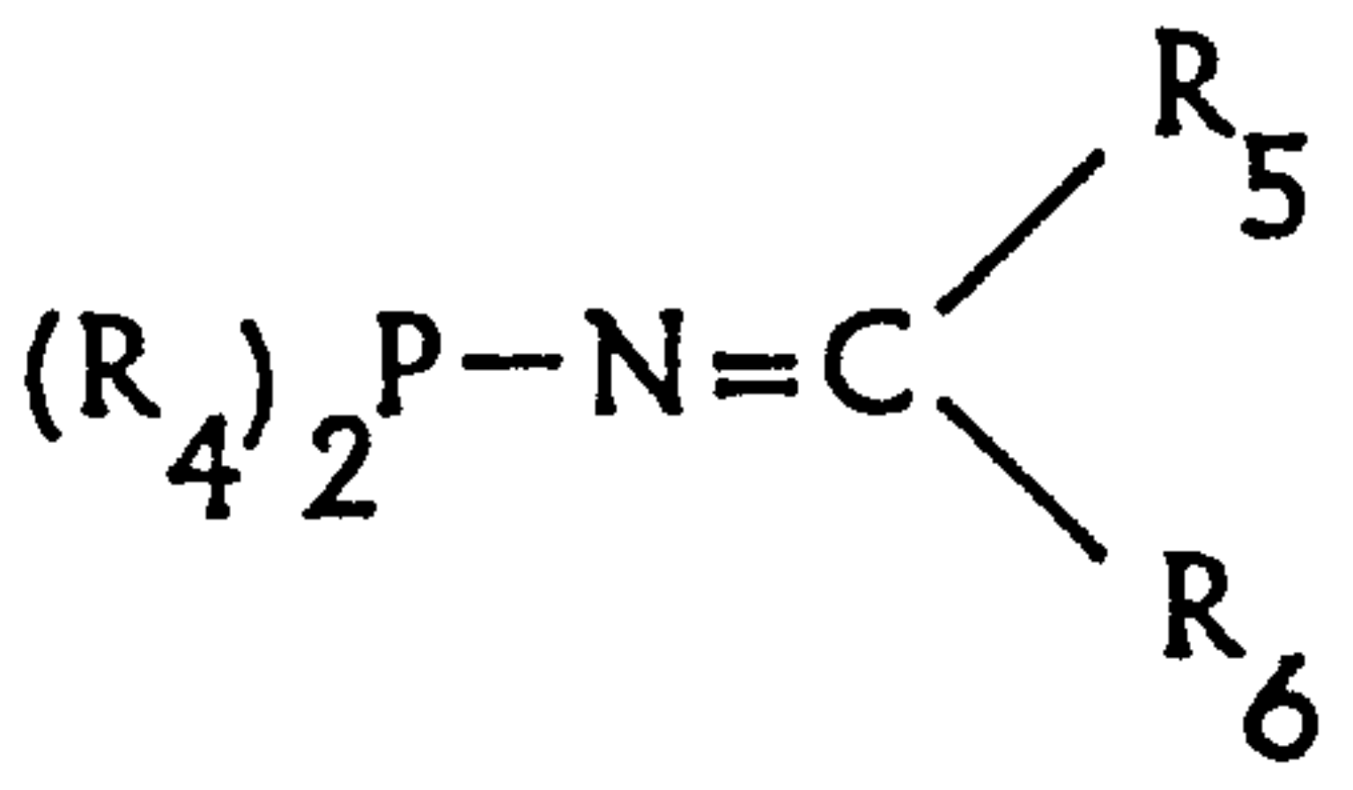
wherein each n is independently 0 or 1, m is an integer from 1 to 10 and each B independently denotes O or S;

X is selected from the group consisting of Cl, Br, I, and H; and

A is a ligand selected from the group consisting of:

i) ligands of the formula $P(R_3)_3$ wherein R_3 is independently selected from the group of radicals consisting of C_{1-10} straight chained, branched and cyclic alkyl radicals; and C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three C_{1-8} alkyl radicals; and

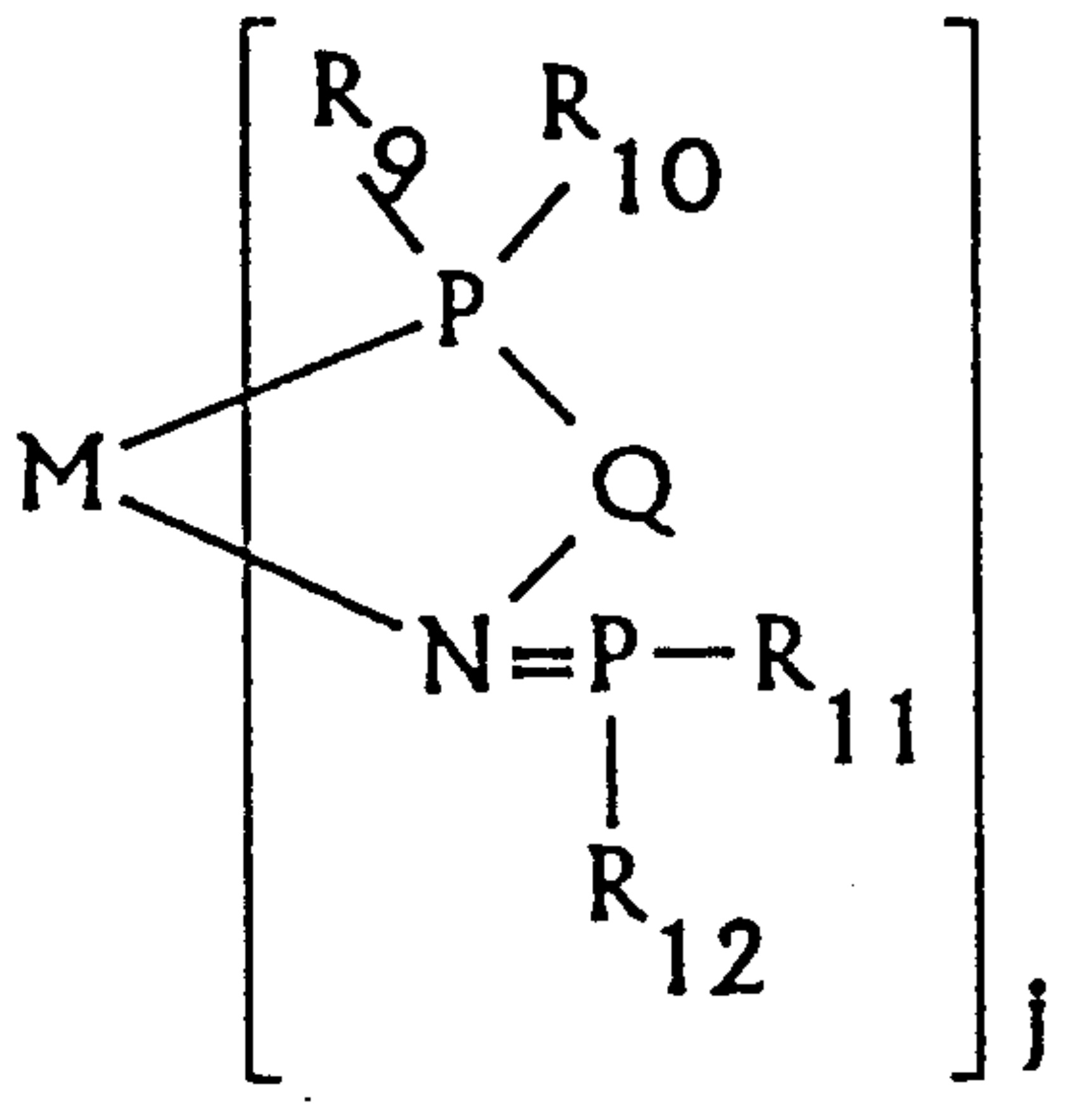
ii) ligands of the formula



$$(R_4)_2P-N=C(R_5)(R_6)$$

wherein R_4 is selected from the group of radicals from which R_3 is selected; and R_5 and R_6 are independently a hydrogen atom or a radical selected from the group consisting of C_{1-10} straight chained or branched alkyl radicals; C_{5-8} cyclic alkyl radicals; and C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three C_{1-8} alkyl radicals.

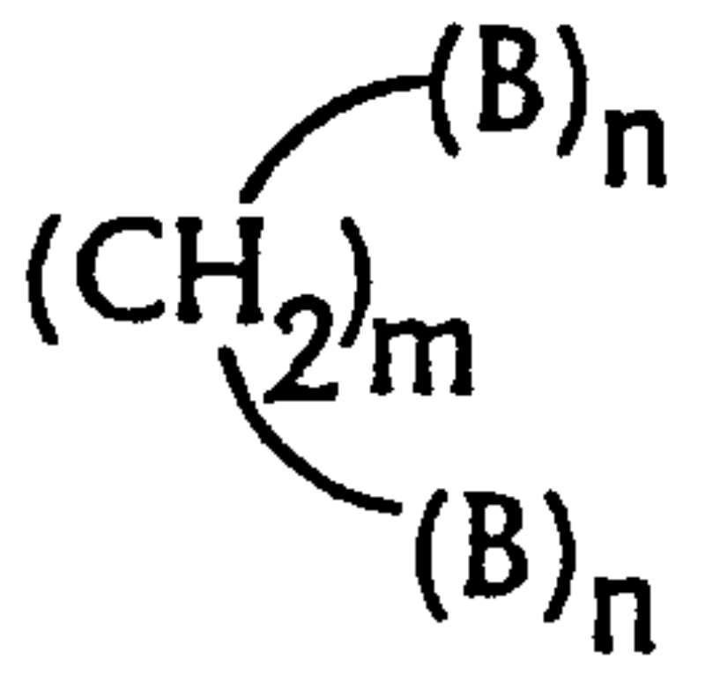
2. A catalyst precursor of the formula:



COMPLEX III

wherein M is selected from the group consisting of Ni, Cr, Ti, V, and Zr; Q is selected from the group consisting of $(CH_2)_n$ wherein n is 1, 2 or 3; a C_{2-4} alkyl radical; a disubstituted C_6 aryl radical; and R_7N wherein R_7 is selected from the group consisting of C_{1-6} straight chained and branched alkyl radicals and C_{6-10} aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical; j is 2 or 3 depending on the coordination number of M; and R_9, R_{10}, R_{11}, and R_{12} are independently selected from the group consisting of C_{1-10} straight chained, branched and cyclic alkyl radicals; and C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by up to three C_{1-8} alkyl radicals.

3. The catalyst precursor according to claim 1, wherein X is Cl or Br, and R_1 and R_2 are independently selected from the group consisting of C_{1-8} straight chained, branched and cyclic alkyl radicals; C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical; C_{1-6} alkoxy and thioalkyl radicals; CF_3; and fluorine, or if taken together, R_1 and R_2 form a diradical of the formula:

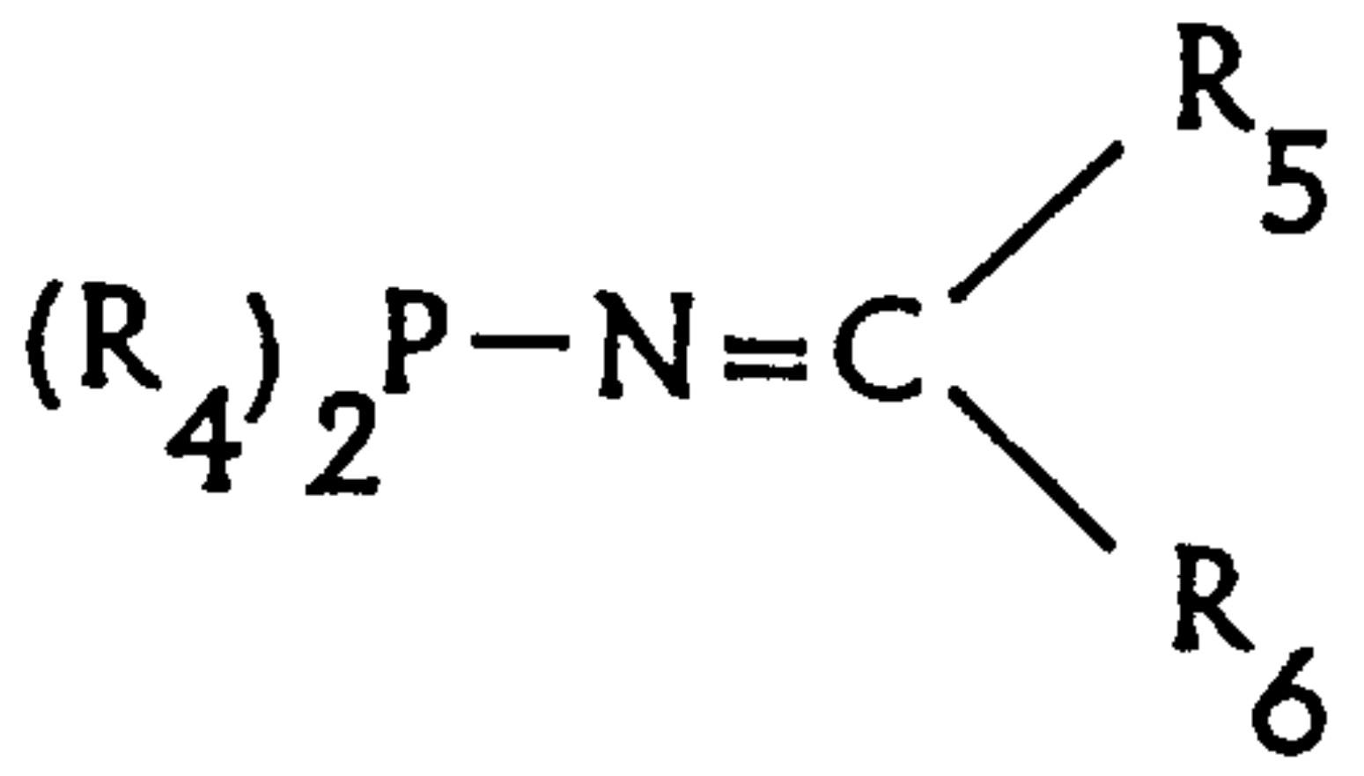


wherein each n is independently 0 or 1, m is an integer from 2 to 10 and each B is independently O or S.

4. The catalyst precursor according to claim 3, wherein A is a ligand of the formula $P(R_3)_3$ wherein R_3 is independently selected from the group of radicals consisting of C_{1-8} straight chained, branched and cyclic alkyl radicals; and C_{6-8}

monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical.

5. The catalyst precursor according to claim 1, wherein A is a ligand of the formula:



$$(R_4)_2P-N=C(R_5)(R_6)$$

wherein R_4 is selected from the group of radicals consisting of C_{1-8} straight chained, branched and cyclic alkyl radicals; and C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical; and R_5 and R_6 independently represent a hydrogen atom or a radical selected from the group consisting of C_{1-8} straight chained, branched and cyclic alkyl radicals; and C_{6-8} monoaromatic aryl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical.

6. A catalyst precursor according to claim 2, wherein Q is $(CH_2)_n$, wherein n is 1 or 2, or a C_{2-4} alkyl radical.