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(54) **Titre :** POLYMERES D'OLEFINES ET DE α -OLEFINES ET PROCEDES DE POLYMERISATION

(54) **Title:** α -OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR

(57) **Abrégé/Abstract:**

Disclosed herein are processes for polymerizing ethylene, acyclic olefins, and/or selected cyclic olefins, and optionally selected olefinic esters or carboxylic acids, and other monomers. The polymerizations are catalysed by selected transition metal compounds, and sometimes other co-catalysts. Since some of the polymerizations exhibit some characteristics of living polymerizations, block copolymers can be readily made. Many of the polymers produced are often novel, particularly in regard to their microstructure, which gives some of them unusual properties. Numerous novel catalysts are disclosed, as well as some novel processes for making them. The polymers made are useful as elastomers, molding resins, in adhesives, etc. Also described herein is the synthesis of linear α -olefins by the oligomerization of ethylene using as a catalyst system a combination of a nickel compound having a selected α -diimine ligand and a selected Lewis or Bronsted acid, or by contacting selected α -diimine nickel complexes with ethylene.

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08/378,044 24 January 1995 (24.01.95) US 08/415,283 3 April 1995 (03.04.95) US 08/473,590 7 June 1995 (07.06.95) US 60/007,375 8 August 1995 (08.08.95) US 60/002,654 22 August 1995 (22.08.95) US			
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(54) Title: α -OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR

(57) Abstract

Disclosed herein are processes for polymerizing ethylene, acyclic olefins, and/or selected cyclic olefins, and optionally selected olefinic esters or carboxylic acids, and other monomers. The polymerizations are catalysed by selected transition metal compounds, and sometimes other co-catalysts. Since some of the polymerizations exhibit some characteristics of living polymerizations, block copolymers can be readily made. Many of the polymers produced are often novel, particularly in regard to their microstructure, which gives some of them unusual properties. Numerous novel catalysts are disclosed, as well as some novel processes for making them. The polymers made are useful as elastomers, molding resins, in adhesives, etc. Also described herein is the synthesis of linear α -olefins by the oligomerization of ethylene using as a catalyst system a combination of a nickel compound having a selected α -diimine ligand and a selected Lewis or Bronsted acid, or by contacting selected δ (a)-diimine nickel complexes with ethylene.

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THIS SECTION OF THE APPLICATION/PATENT CONTAINS MORE
THAN ONE VOLUME

THIS IS VOLUME 1 OF 2

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TITLE

α -OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR

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FIELD OF THE INVENTION

15 The invention concerns novel homo- and copolymers
of ethylene and/or one or more acyclic olefins, and/or
selected cyclic olefins, and optionally selected ester,
carboxylic acid, or other functional group containing
olefins as comonomers; selected transition metal
20 containing polymerization catalysts; and processes for
making such polymers, intermediates for such catalysts,
and new processes for making such catalysts. Also
disclosed herein is a process for the production of
linear alpha-olefins by contacting ethylene with a
25 nickel compound of the formula $[DAB]NiX_2$, wherein DAB is
a selected α -diimine and X is chlorine, bromine, iodine
or alkyl, and a selected Lewis or Bronsted acid, or by
contacting ethylene with other selected α -diimine
nickel complexes

30

BACKGROUND OF THE INVENTION

 Homo- and copolymers of ethylene (E) and/or one or
more acyclic olefins, and/or cyclic olefins, and/or
substituted olefins, and optionally selected olefinic
esters or carboxylic acids, and other types of
35 monomers, are useful materials, being used as plastics
for packaging materials, molded items, films, etc., and
as elastomers for molded goods, belts of various types,
in tires, adhesives, and for other uses. It is well

known in the art that the structure of these various polymers, and hence their properties and uses, are highly dependent on the catalyst and specific conditions used during their synthesis. In addition to these factors, processes in which these types of polymers can be made at reduced cost are also important. Therefore, improved processes for making such (new) polymers are of interest. Also disclosed herein are uses for the novel polymers.

α -Olefins are commercial materials being particularly useful as monomers and as chemical intermediates. For a review of α -olefins, including their uses and preparation, see B. Elvers, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 238-251. They are useful as chemical intermediates and they are often made by the oligomerization of ethylene using various types of catalysts. Therefore catalysts which are capable of forming α -olefins from ethylene are constantly sought.

SUMMARY OF THE INVENTION

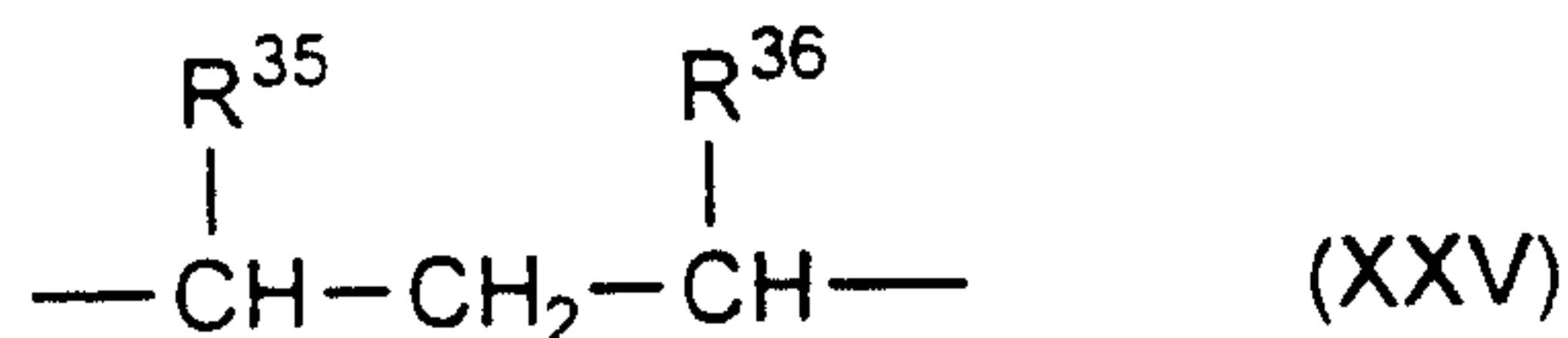
This invention concerns a polyolefin, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.

This invention also concerns a polyolefin which contains about 20 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, about 1 to about 12 propyl branches, about 1 to about 12 butyl branches, about 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches.

Disclosed herein is a polymer, consisting essentially of repeat units derived from the monomers,

ethylene and a compound of the formula
 $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$, wherein R^1 is hydrogen, hydrocarbyl or
 substituted hydrocarbyl, and m is 0 or an integer from
 1 to 16, and which contains about 0.01 to about 40 mole
 5 percent of repeat units derived from said compound, and
 provided that said repeat units derived from said
 compound are in branches of the formula $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}^1$,
 in about 30 to about 70 mole percent of said branches n
 is 5 or more, in about 0 to about 20 mole percent n is
 10 4, in about 3 to 60 mole percent n is 1, 2 and 3, and
 in about 1 to about 60 mole percent n is 0.

This invention concerns a polymer of one or more
 alpha-olefins of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$ wherein a is
 an integer of 2 or more, which contains the structure
 15 (XXV)

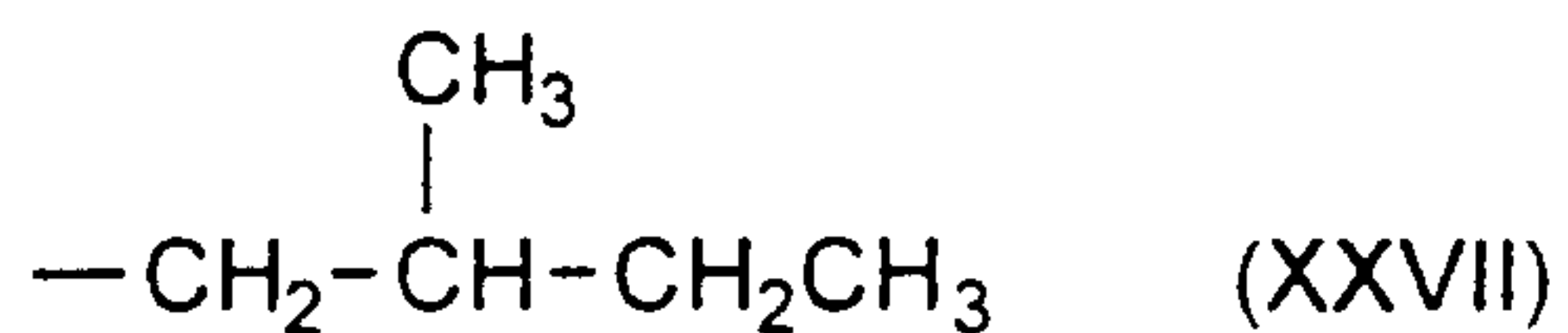


wherein R^{35} is an alkyl group and R^{36} is an alkyl group
 20 containing two or more carbon atoms, and provided that
 R^{35} is methyl in about 2 mole percent or more of the
 total amount of (XXV) in said polymer.

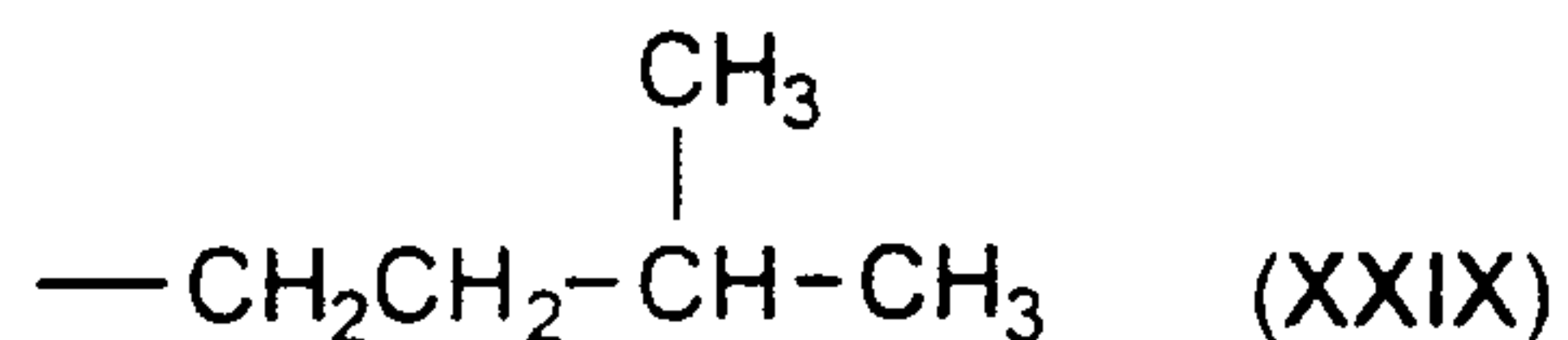
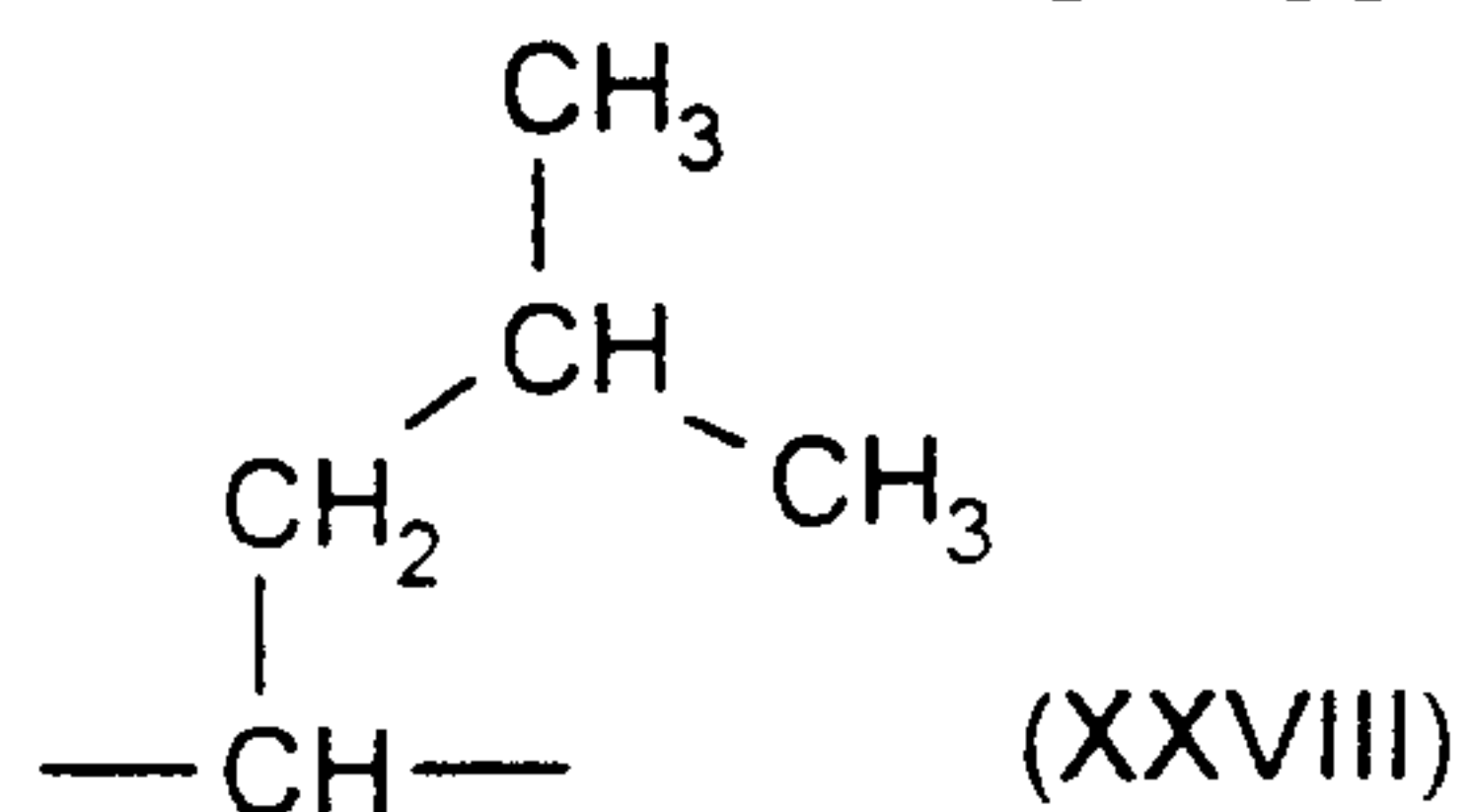
This invention also includes a polymer of one or
 more alpha-olefins of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$ wherein
 25 a is an integer of 2 or more, wherein said polymer
 contains methyl branches and said methyl branches
 comprise about 25 to about 75 mole percent of the total
 branches.

This invention also concerns a polyethylene
 30 containing the structure (XXVII) in an amount greater
 than can be accounted for by end groups, and preferably
 at least 0.5 or more of such branches per 1000
 methylene groups than can be accounted for by end
 groups.

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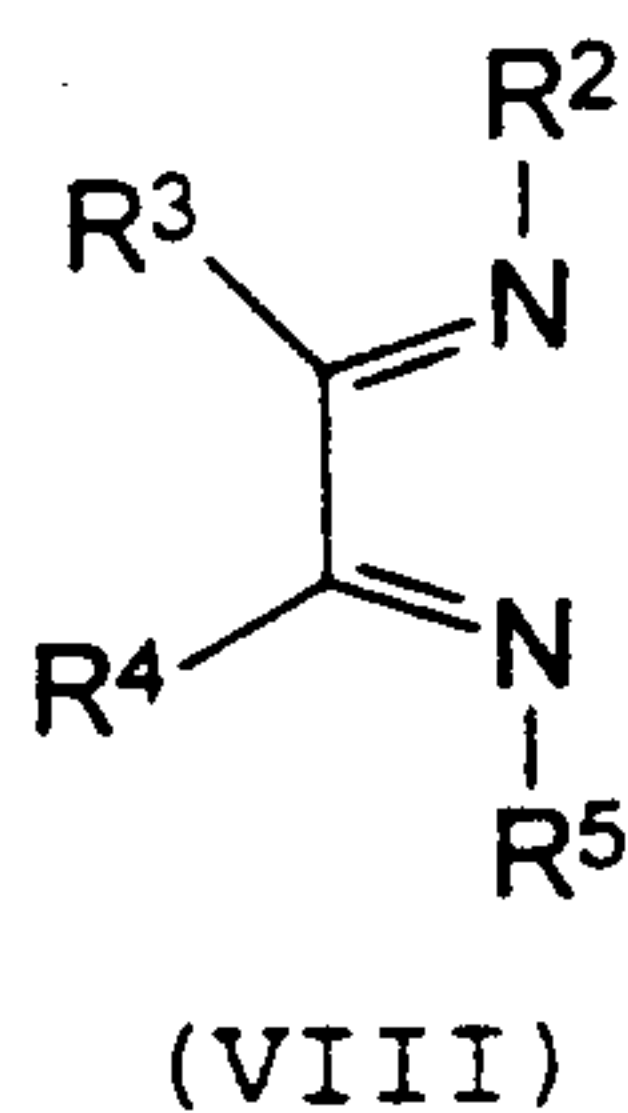


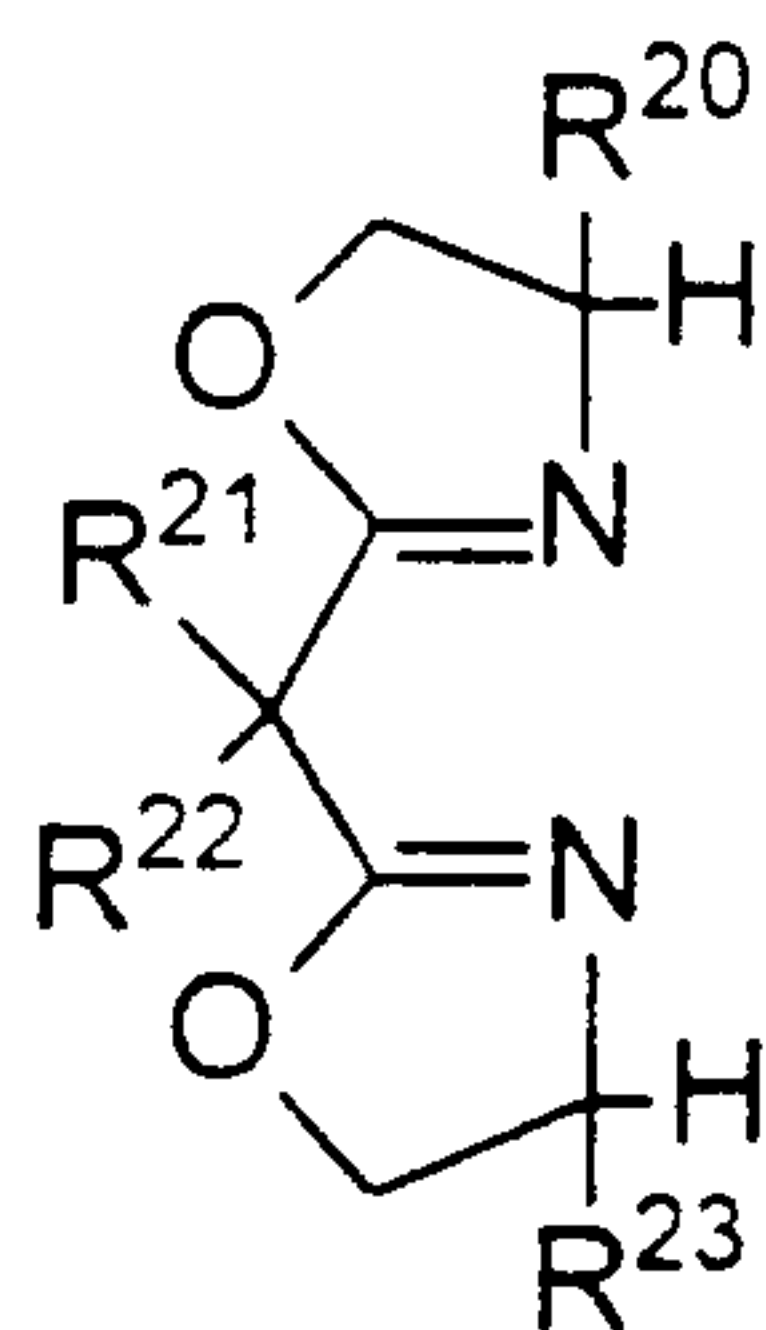
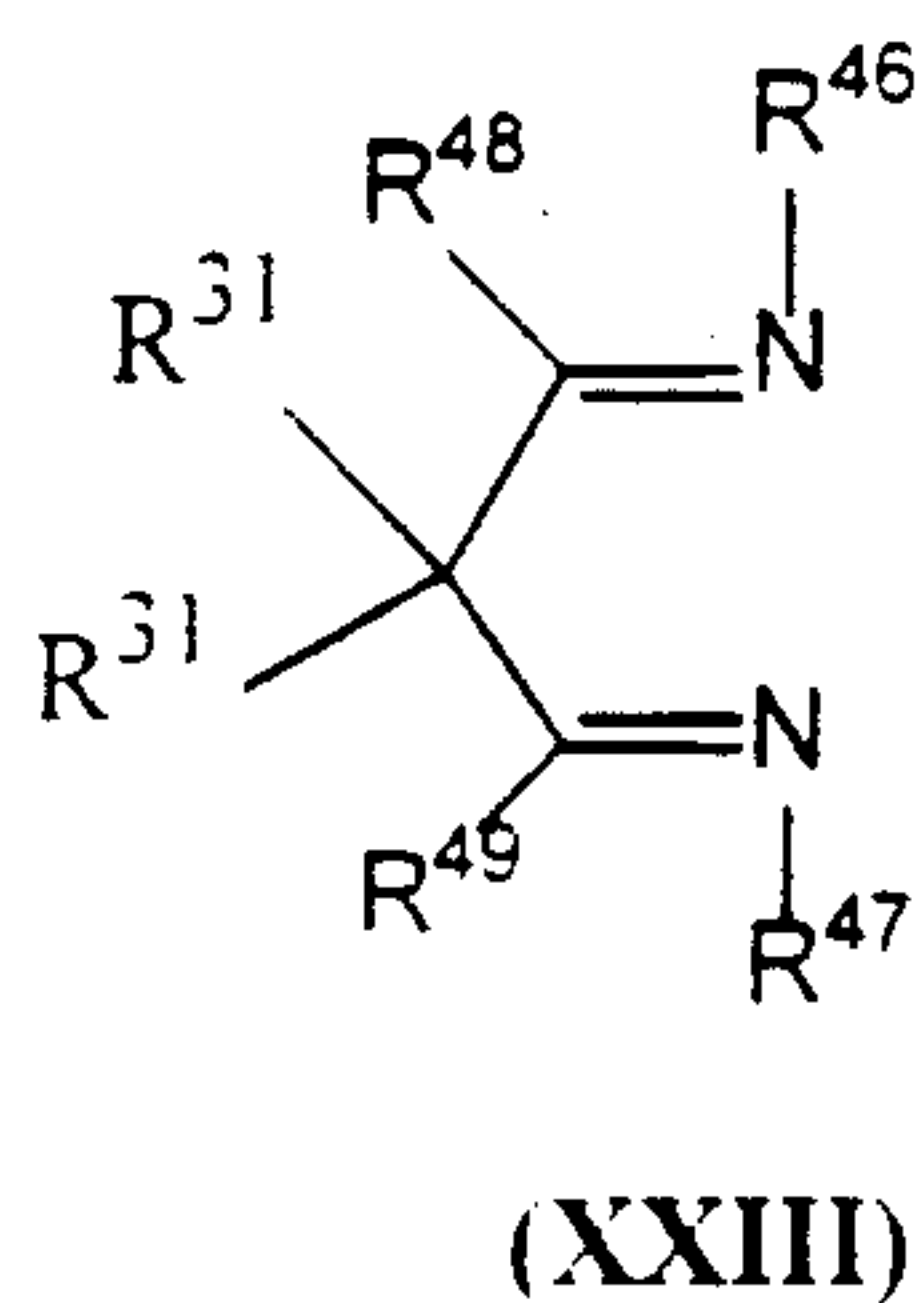
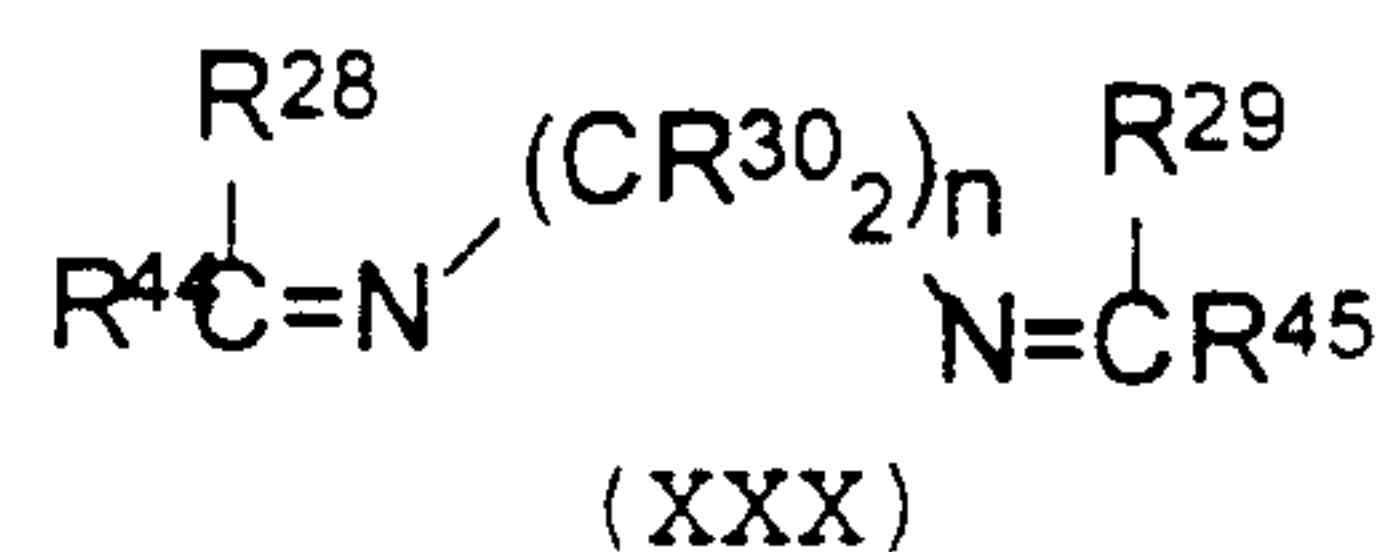
This invention also concerns a polypropylene containing one or both of the structures (XXVIII) and (XXIX) and in the case of (XXIX) in amounts greater than can be accounted for by end groups. Preferably at least 0.5 more of (XXIX) branches per 1000 methylene groups than can be accounted for by end groups, and/or at least 0.5 more of (XXVIII) per 1000 methylene groups are present in the polypropylene.



Also described herein is an ethylene homopolymer with a density of 0.86 g/ml or less.

Described herein is a process for the polymerization of olefins, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of





(XXXII)

5

with an olefin wherein:

said olefin is selected from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclobutene, cyclopentene, norbornene, or substituted norbornene;

10

said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd;

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

15

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4

taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring;

R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring; each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

R^{21} and R^{22} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

n is 2 or 3;

R^1 is hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

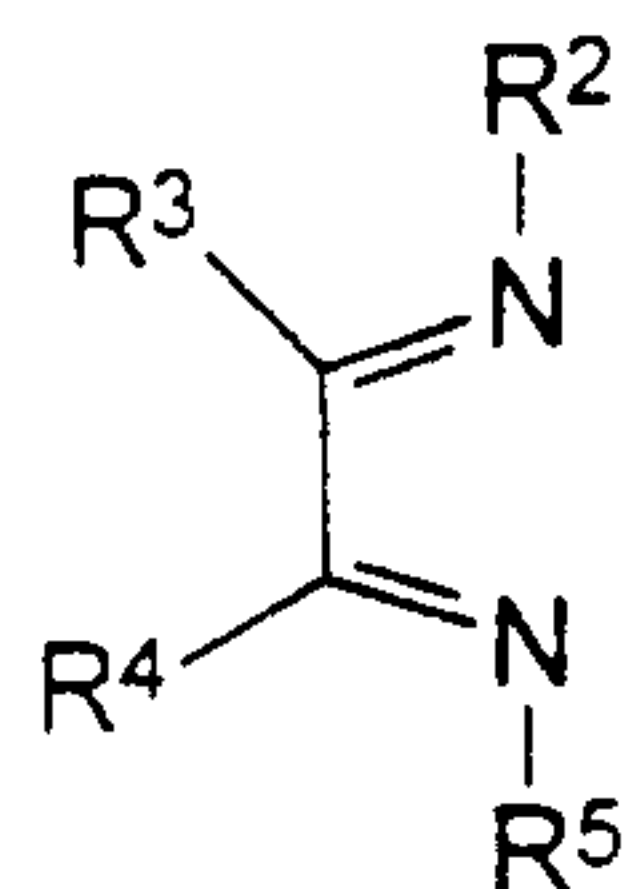
said transition metal also has bonded to it a ligand that may be displaced by said olefin or added to said olefin;

when M is Pd, said bidentate ligand is (VIII), (XXXII) or (XXIII);

when M is Pd a diene is not present; and

when norbornene or substituted norbornene is used no other olefin is present.

Described herein is a process for the copolymerization of an olefin and a fluorinated olefin, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of



(VIII)

with an olefin, and a fluorinated olefin wherein:

5 said olefin is selected from the group
consisting of ethylene and an olefin of the formula
 $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$;

 said transition metal is selected from the
group consisting of Ni and Pd;

10 said fluorinated olefin is of the formula
 $H_2C=CH(CH_2)_aR_fR^{42}$;

 a is an integer of 2 to 20; R_f is
perfluoroalkylene optionally containing one or more
ether groups;

15 R^{42} is fluorine or a functional group;

R^2 and R^5 are each independently hydrocarbyl or
substituted hydrocarbyl, provided that the carbon atom
bound to the imino nitrogen atom has at least two
carbon atoms bound to it;

20 R^3 and R^4 are each independently hydrogen,
hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4
taken together are hydrocarbylene substituted
hydrocarbylene to form a carbocyclic ring;

 each R^{17} is independently saturated
25 hydrocarbyl;

 and provided that said transition metal also has
bonded to it a ligand that may be displaced by said
olefin or add to said olefin.

 This invention also concerns a copolymer of an
30 olefin of the formula $R^{17}CH=CHR^{17}$ and a fluorinated
olefin of the formula $H_2C=CH(CH_2)_aR_fR^{42}$, wherein:

 each R^{17} is independently hydrogen or saturated
hydrocarbyl;

a is an integer of 2 to 20; R_f is perfluoroalkylene optionally containing one or more ether groups; and

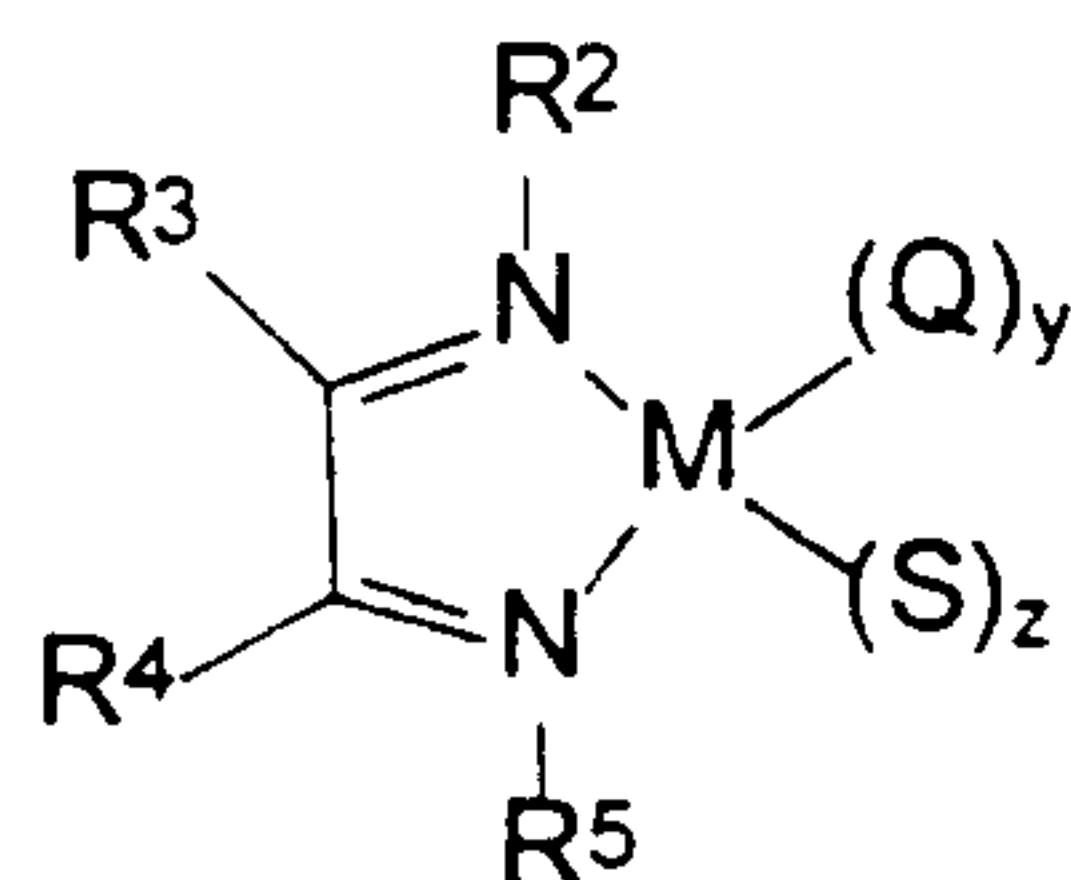
R^{42} is fluorine or a functional group;

5 provided that when both of R^{17} are hydrogen and R^{42} is fluorine, R_f is $-(CF_2)_b-$ wherein b is 2 to 20 or perfluoroalkylene containing at least one ether group.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a
10 temperature of about -100°C to about $+200^\circ\text{C}$:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q^- or S^- to form WQ^- or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted
15 acid whose counterion is a weakly coordinating anion;

a second compound of the formula



(XI)

20

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

25 wherein:

M is Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd the m oxidation state;

$$y + z = m$$

30 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

5 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

10 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

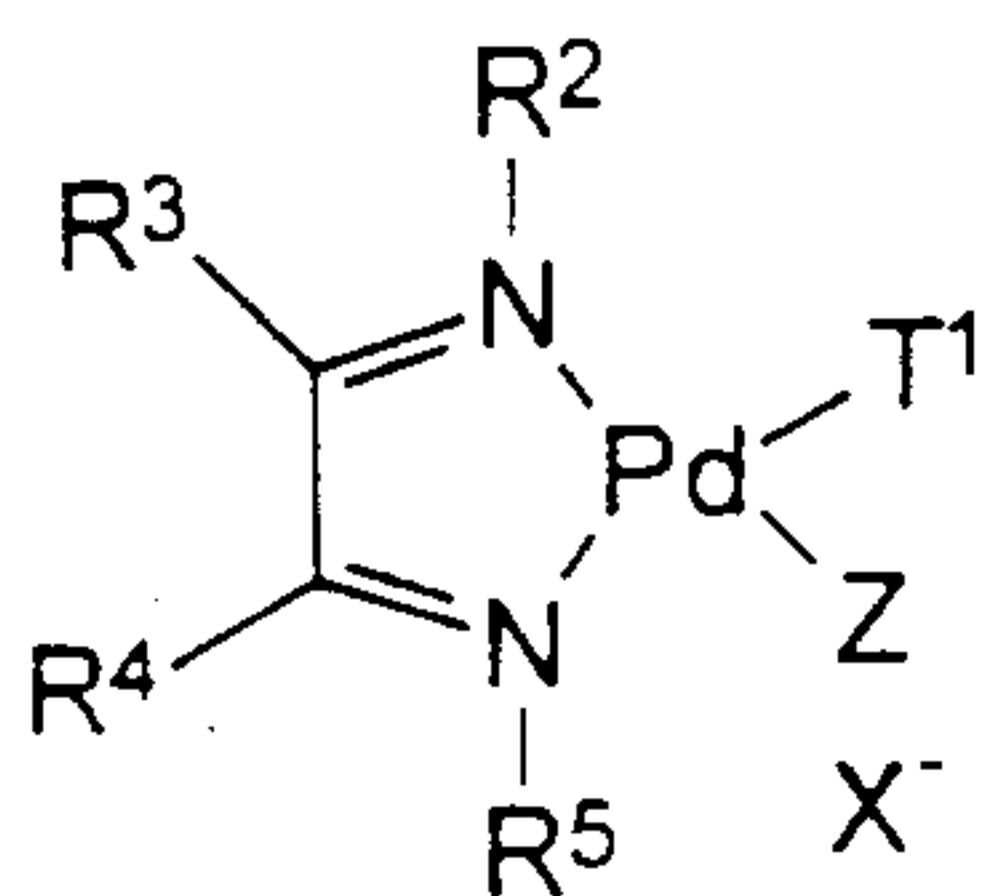
provided that:

15 when norbornene or substituted norbornene is present, no other monomer is present;

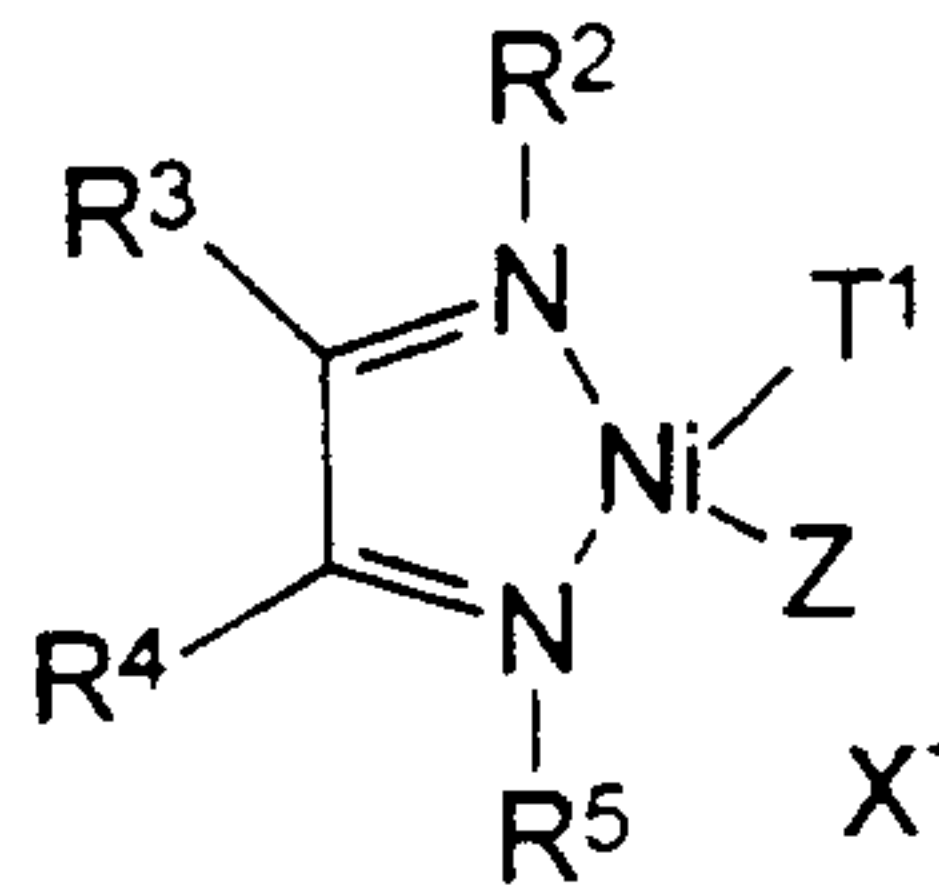
when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable
20 of transferring a hydride or alkyl group to M.

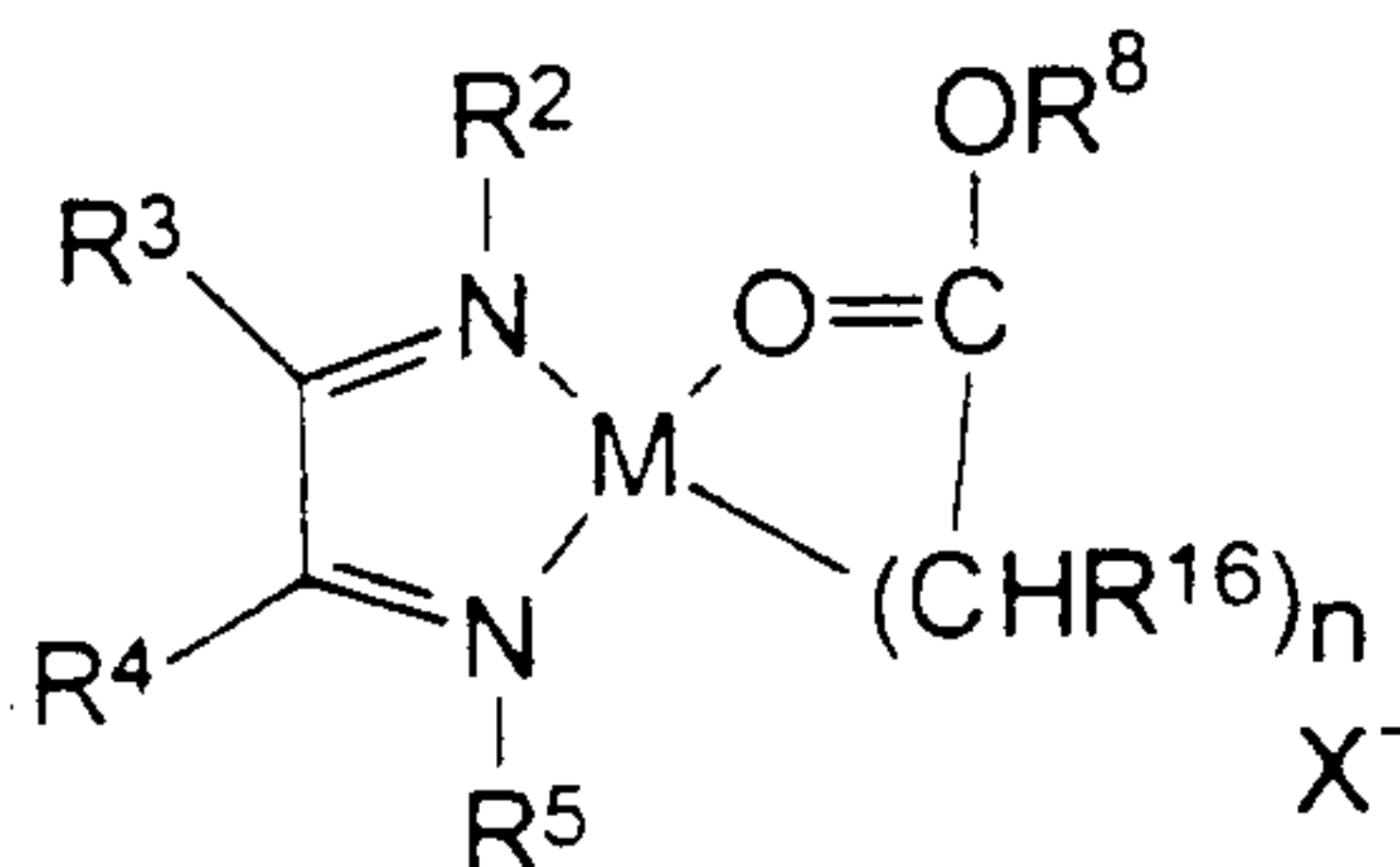
This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, one or more monomers selected from the group consisting of
25 ethylene, an olefin of the formula $R^{17}\text{CH}=\text{CH}_2$ or $R^{17}\text{CH}=\text{CHR}^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula



(II)



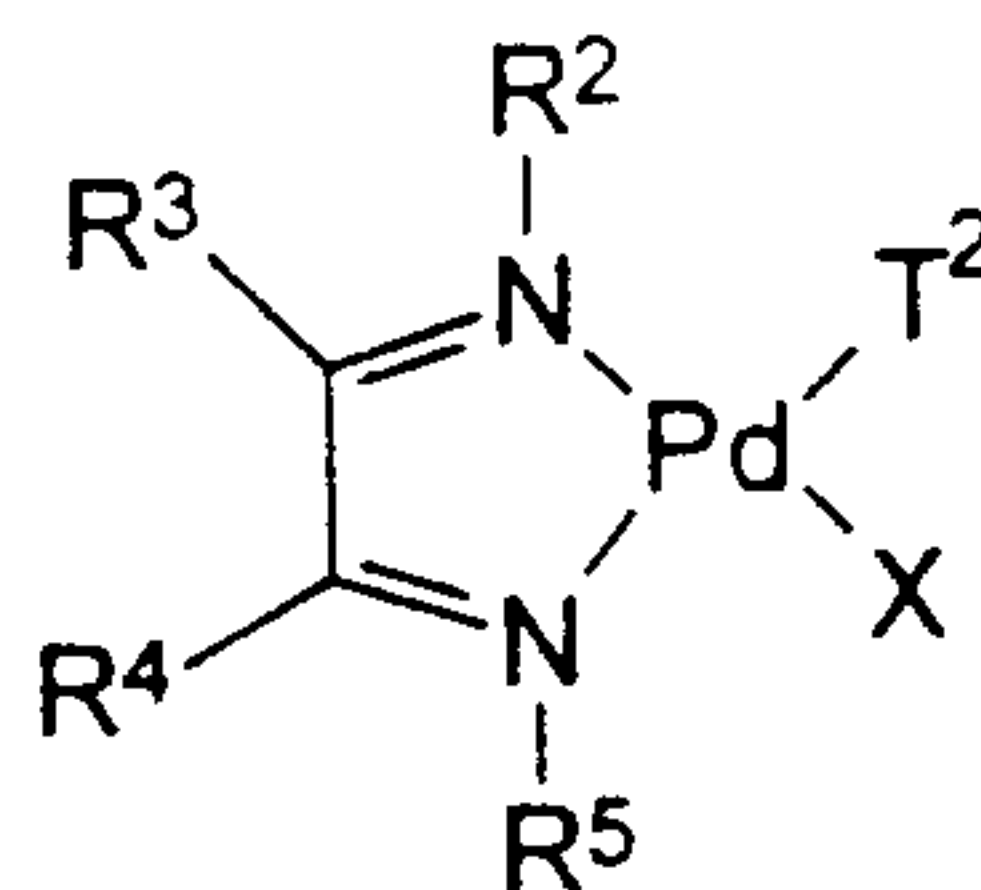
(III)



(IV)

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or



(VII)

wherein:

10 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

15 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

20 n is 2 or 3;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pK_a of the conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion;

R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

each R^{16} is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

R^8 is hydrocarbyl; and

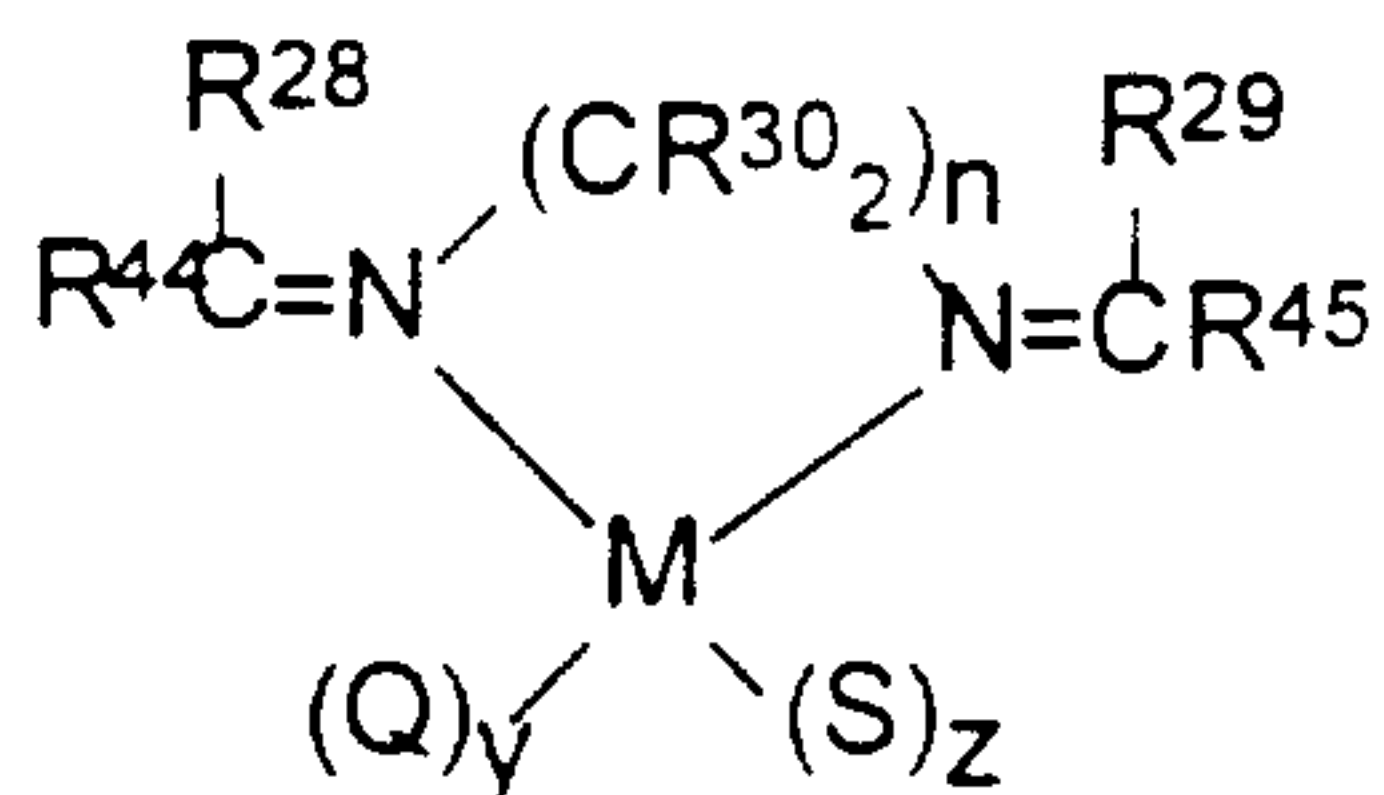
T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

and provided that:

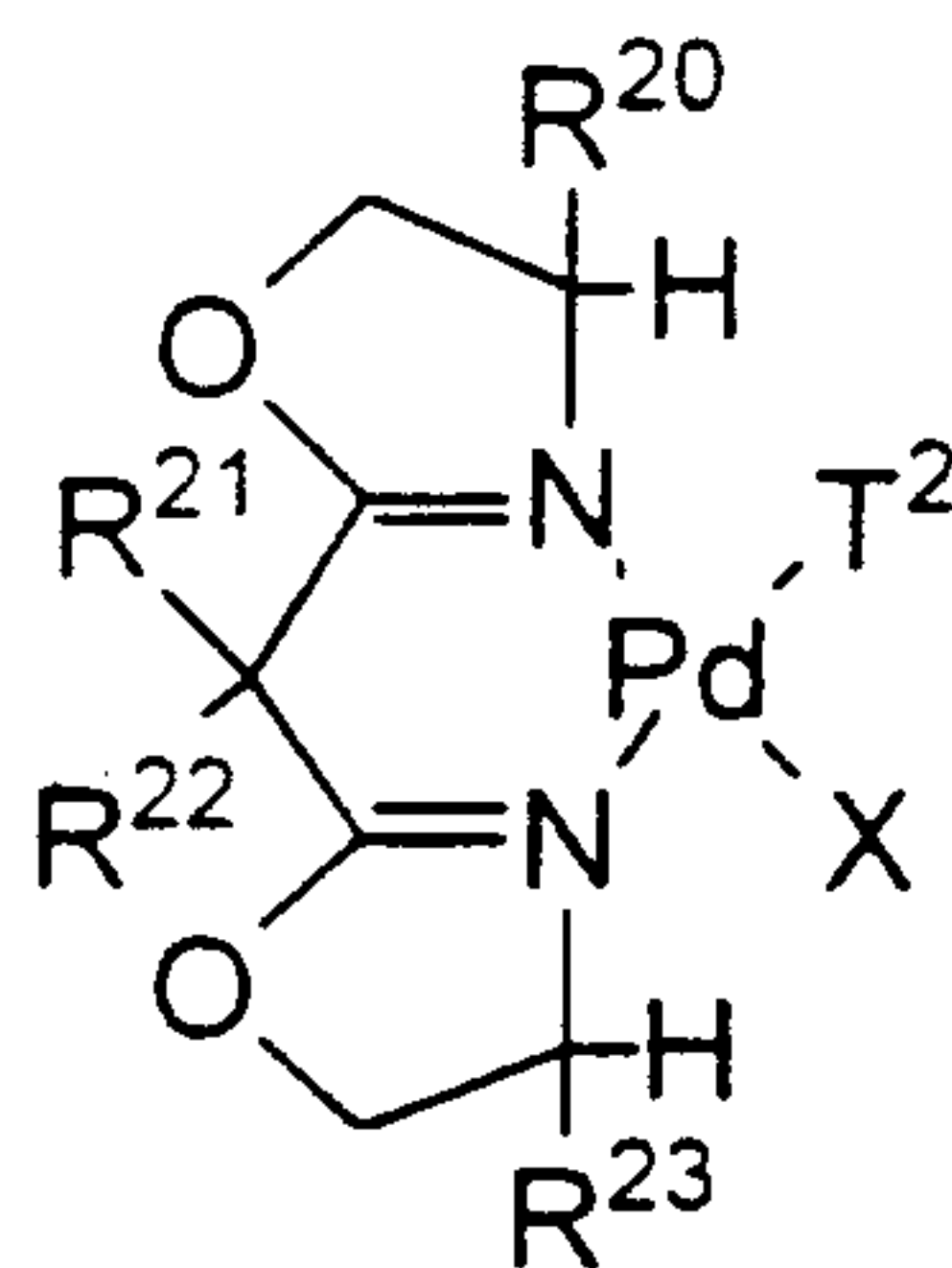
when M is Pd a diene is not present; and

when norbornene or substituted norbornene is used no other monomer is present.

This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about $-100^{\circ}C$ to about $+200^{\circ}C$, one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

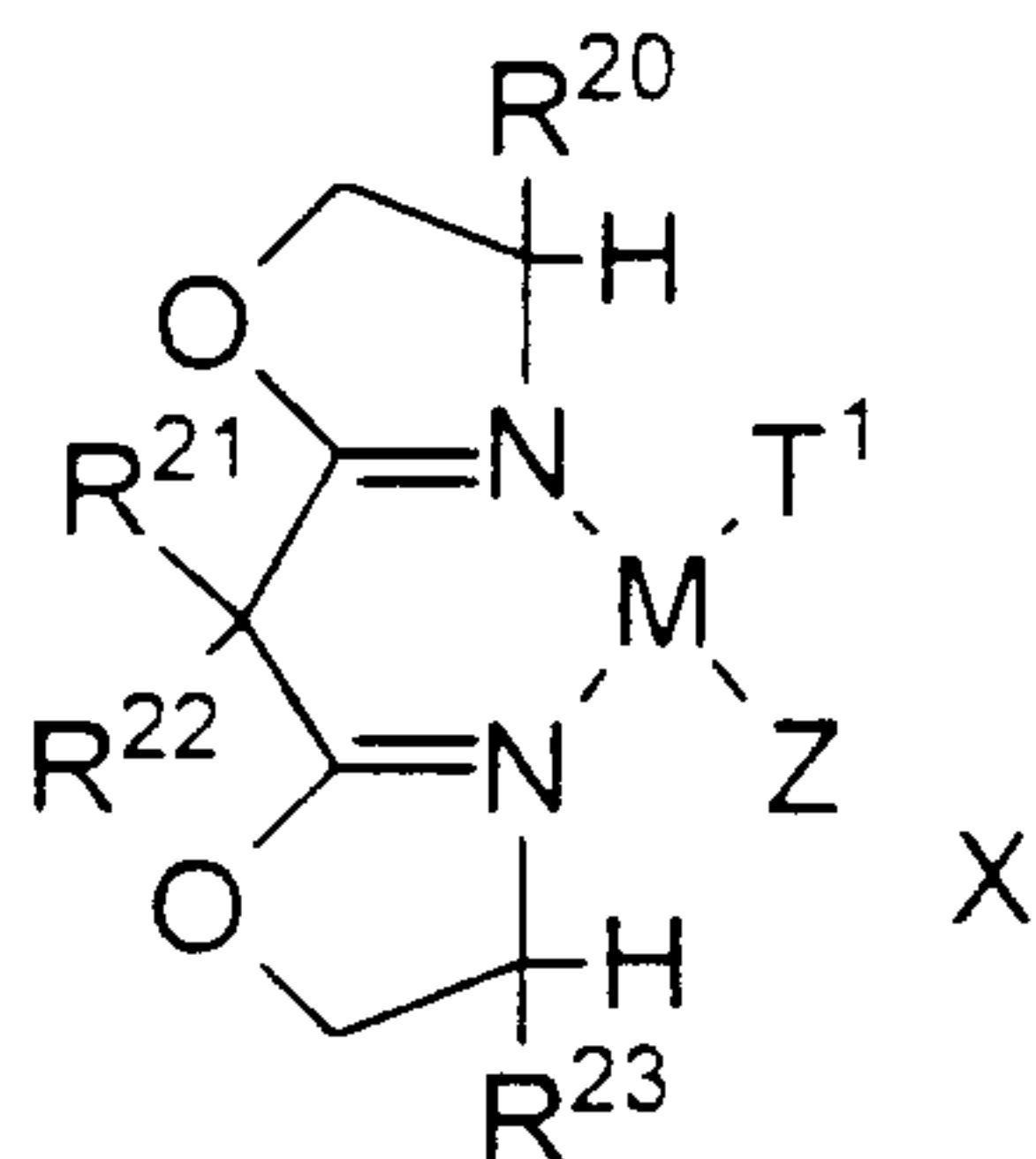


(XVII)



(XVIII)

or



(XIII)

wherein:

- 5 R^{44} is hydrocarbyl or substituted hydrocarbyl,
and R^{28} is hydrogen, hydrocarbyl or substituted
hydrocarbyl or R^{44} and R^{28} taken together form a ring;
 R^{45} is hydrocarbyl or substituted hydrocarbyl,
and R^{29} is hydrogen, substituted hydrocarbyl or
10 hydrocarbyl, or R^{45} and R^{29} taken together form a ring;
each R^{30} is independently hydrogen, substituted
hydrocarbyl or hydrocarbyl, or two of R^{30} taken
together form a ring;
each R^{17} is independently hydrocarbyl or
15 substituted hydrocarbyl provided that any olefinic bond
in said olefin is separated from any other olefinic
bond or aromatic ring by a quaternary carbon atom or at
least two saturated carbon atoms;
 R^{20} and R^{23} are independently hydrocarbyl or
20 substituted hydrocarbyl;
 R^{21} and R^{22} are each independently hydrogen,
hydrocarbyl or substituted hydrocarbyl;

T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}CC(=O)-$;

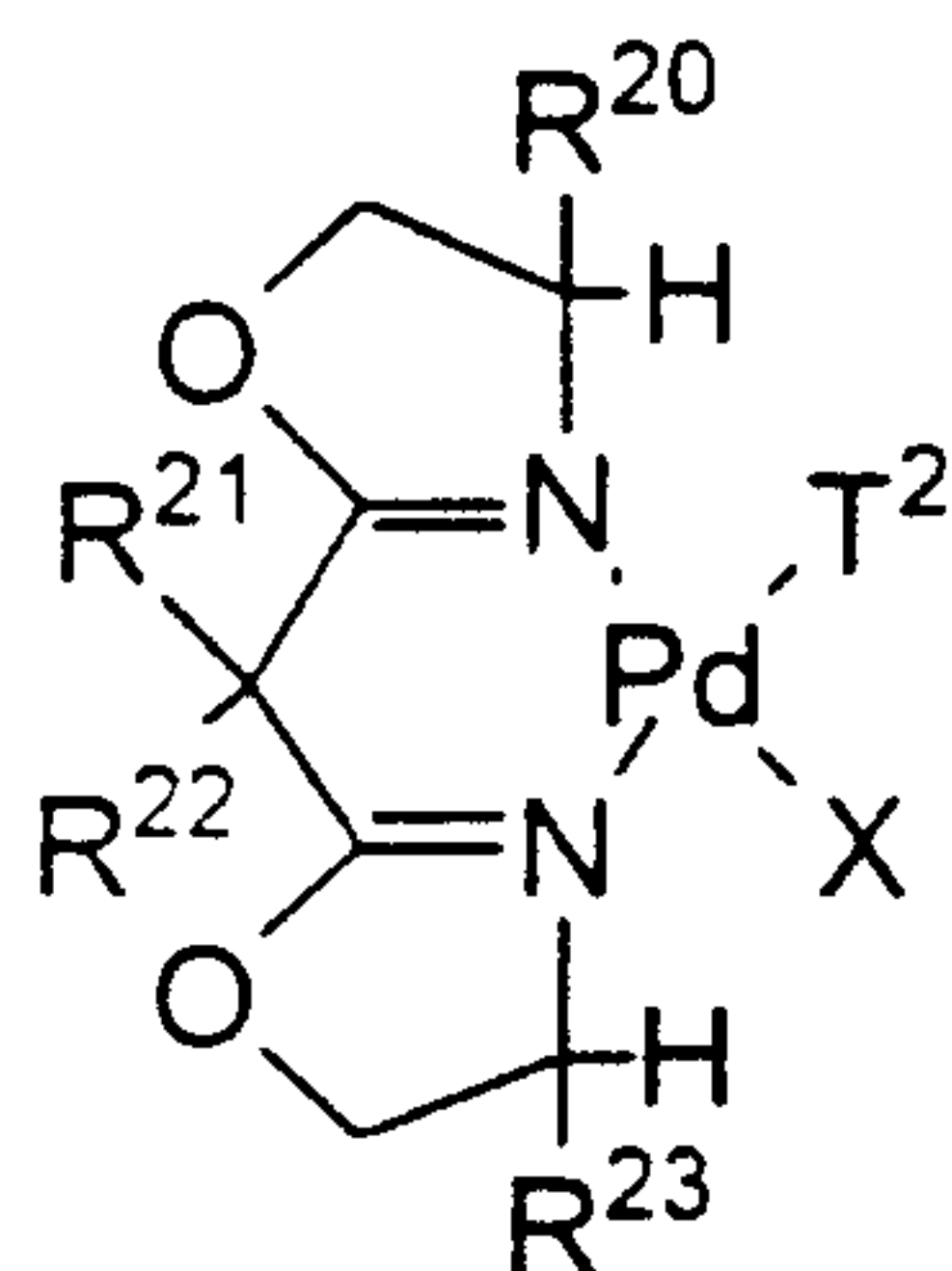
Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if
 5 the donating atom is nitrogen then the pK_a of the conjugate acid of that compound is less than about 6; and

X is a weakly coordinating anion; and provided that:

10 when M is Pd or (XVIII) is used a diene is not present; and

in (XVII) M is not Pd.

This invention includes a process for the production of polyolefins, comprising contacting, at a
 15 temperature of about -100°C to about $+200^\circ\text{C}$, one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, 4-vinylcyclohexene, cyclobutene, cyclopentene, substituted norbornene, and norbornene;
 20 with a compound of the formula



(XVIII)

wherein:

25 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

R^{21} and R^{22} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

T^1 is hydrogen, hydrocarbyl not containing
 30 olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

5 X is a weakly coordinating anion;

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond
10 in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

T² is hydrogen, hydrocarbyl not containing
15 olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, R¹⁵C(=O)- or R¹⁵OC(=O)-;

and provided that:

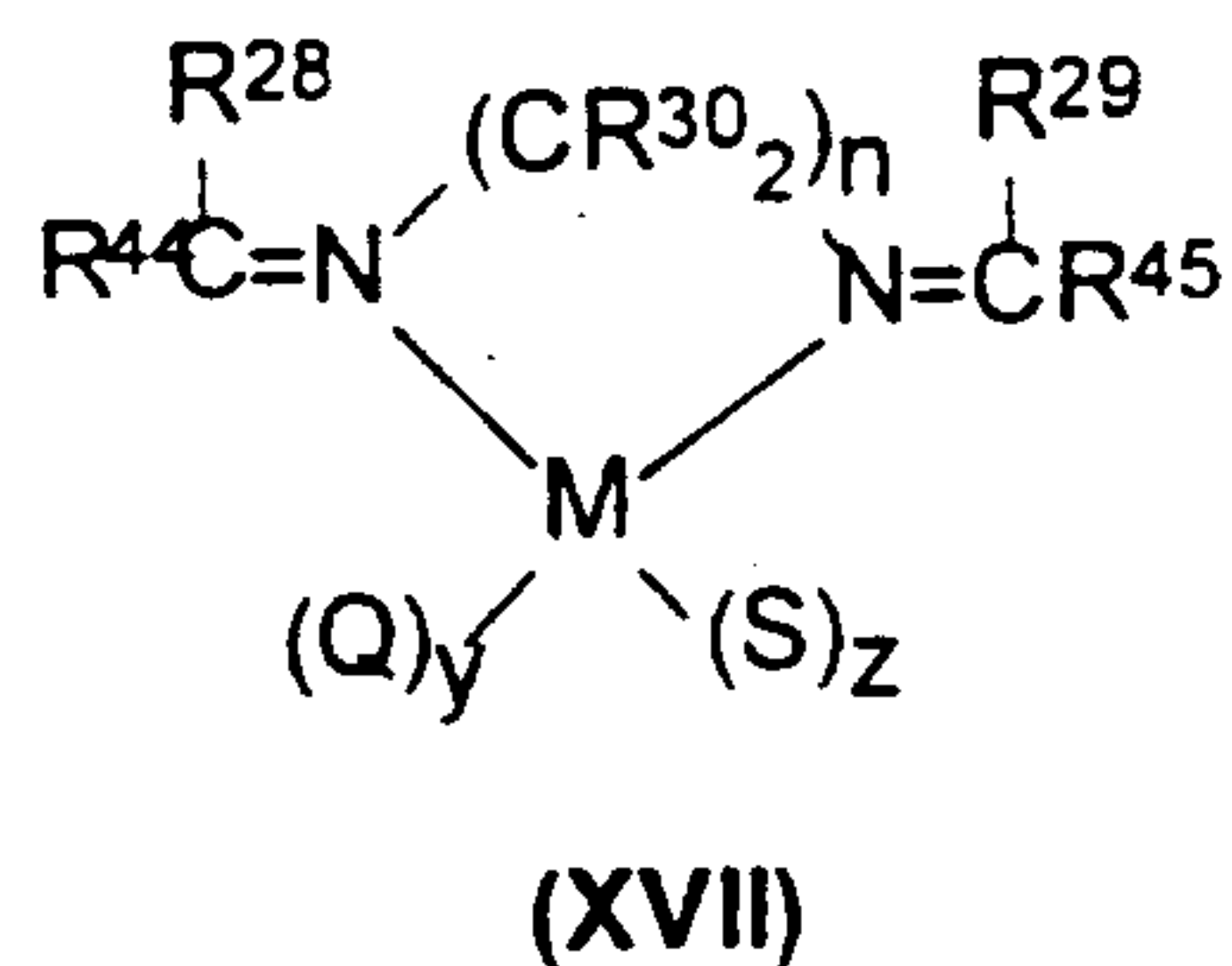
when M is Pd a diene is not present; and

20 when norbornene or substituted norbornene is used no other monomer is present.

Described herein is a process for the production for polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C,

25 a first compound W, which is a neutral Lewis acid capable of abstracting either Q⁻ or S⁻ to form WQ⁻ or WS⁻, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

30 a second compound of the formula



and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

M is Ti, Zr, V, Cr, a rare earth metal, Co, Fe, Sc, or Ni, of oxidation state m;

R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

n is 2 or 3;

y and z are positive integers;

y+z = m;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

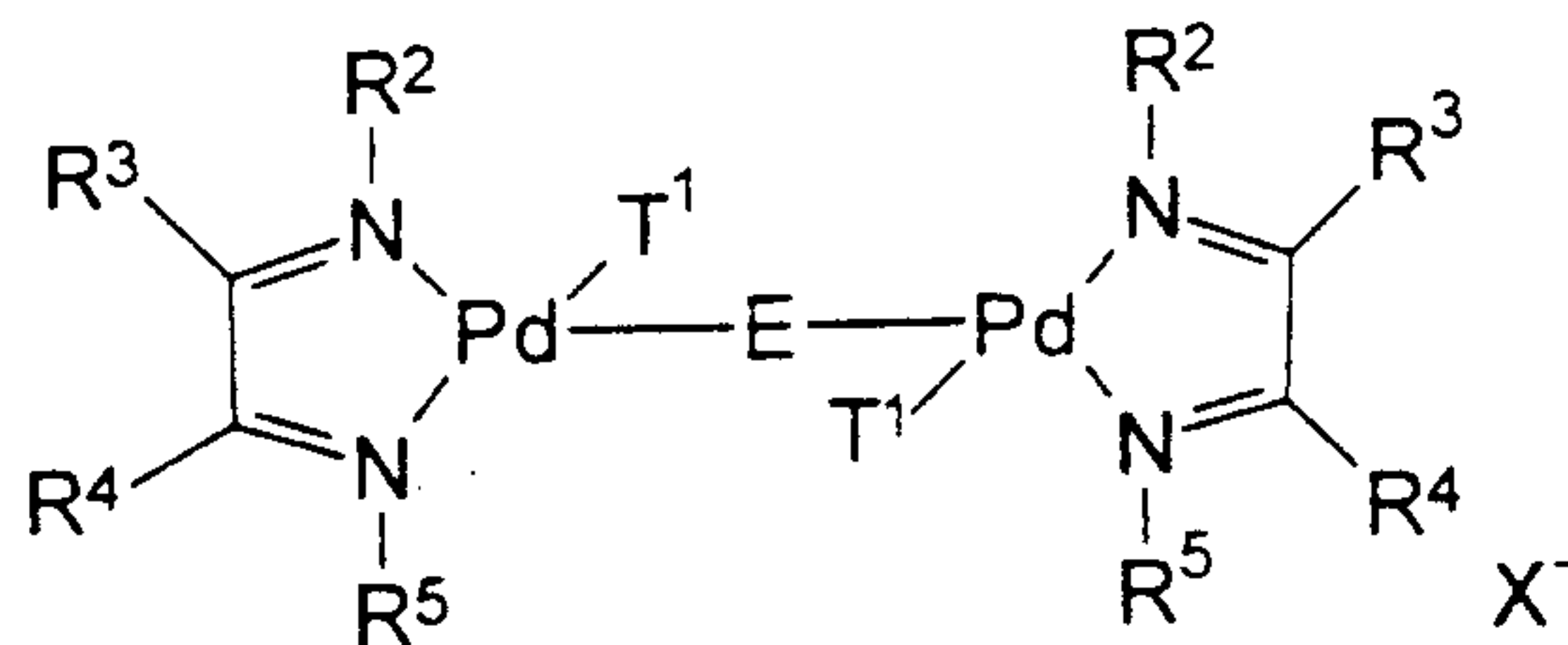
S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is present, no other monomer is present.

Disclosed herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about $-100^{\circ}C$ to about $+200^{\circ}C$, one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted

norbornene, and norbornene; optionally a source of X^- ; with a compound of the formula



5

(V)

wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom
10 bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene substituted hydrocarbylene
15 to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds;

T^1 is hydrogen, hydrocarbyl not containing
20 olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

E is halogen or $-OR^{18}$;

R^{18} is hydrocarbyl not containing olefinic or
25 acetylenic bonds; and

X is a weakly coordinating anion;

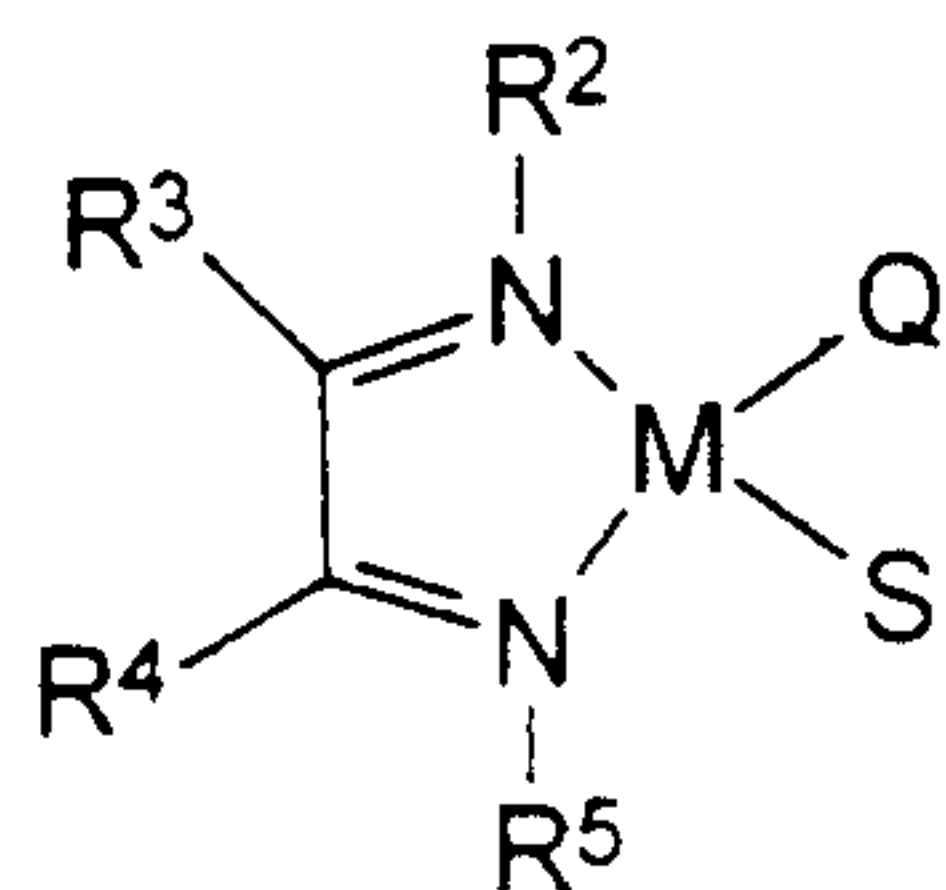
provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a process for the
30 polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about $+200^\circ\text{C}$:

a first compound W , which is a neutral Lewis acid capable of abstracting either Q^- or S^- to form WQ^-

or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; a second compound of the formula

5



(I)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, 4-vinylcyclohexene, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

15 M is Ni(II), Co(II), Fe(II), or Pd(II);

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

20 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

25 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

30 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

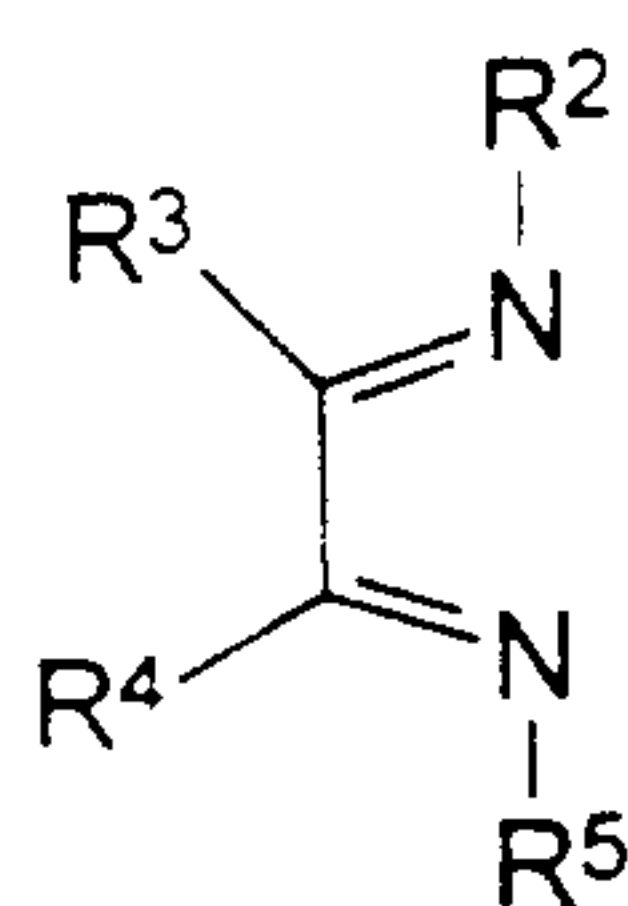
provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

Included herein is a polymerization process, comprising, contacting a compound of the formula $[\text{Pd}(\text{R}^{13}\text{CN})_4]\text{X}_2$ or a combination of $\text{Pd}[\text{OC}(\text{O})\text{R}^{40}]_2$ and HX; a compound of the formula



(VIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds;

R^{13} is hydrocarbyl;

R^{40} is hydrocarbyl or substituted hydrocarbyl

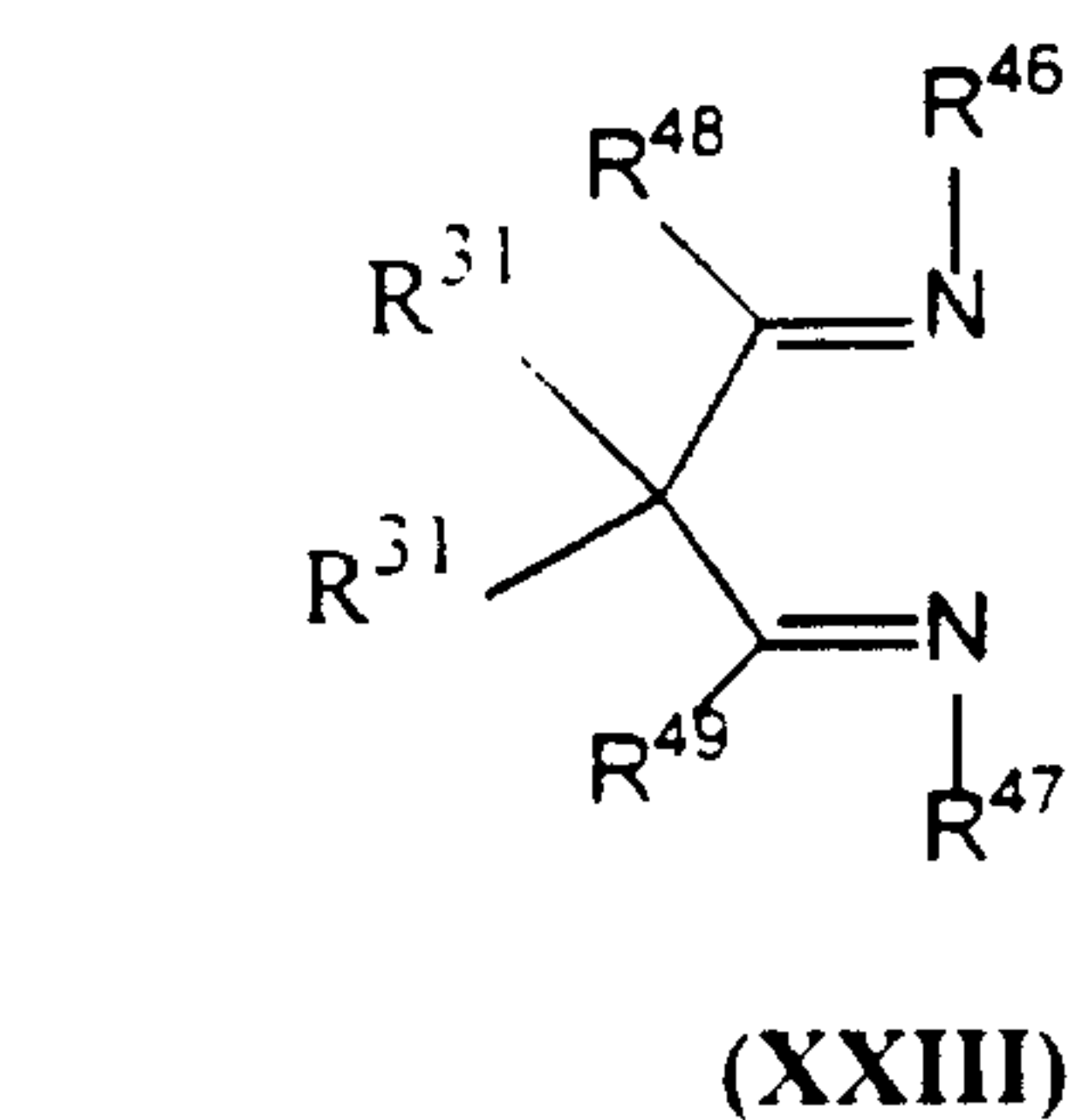
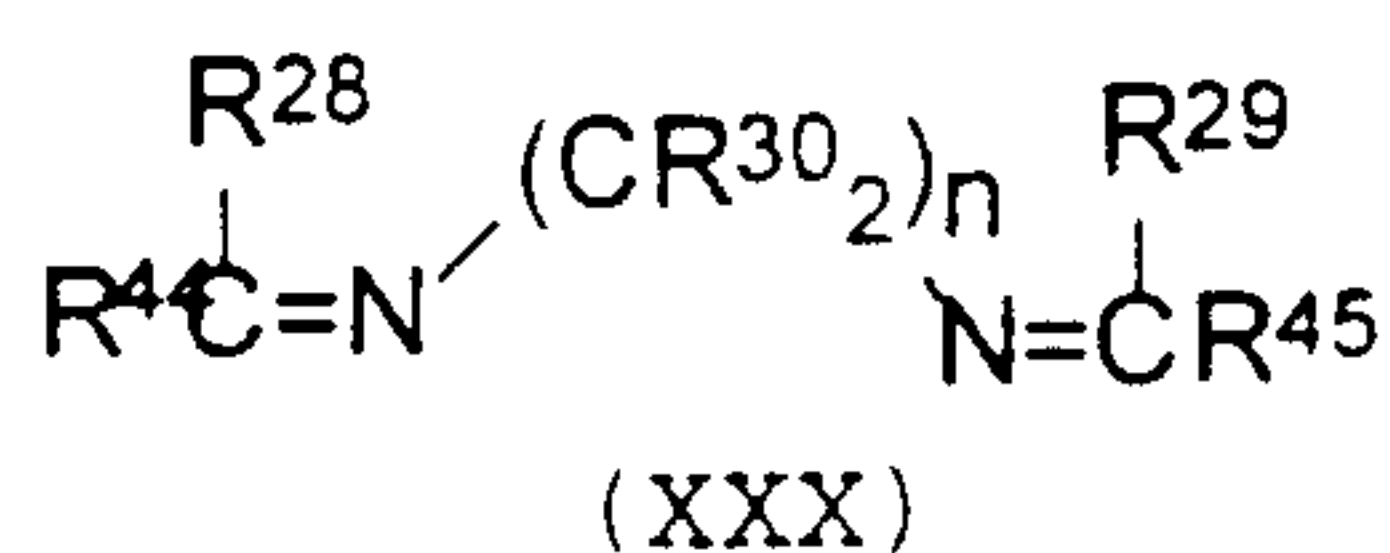
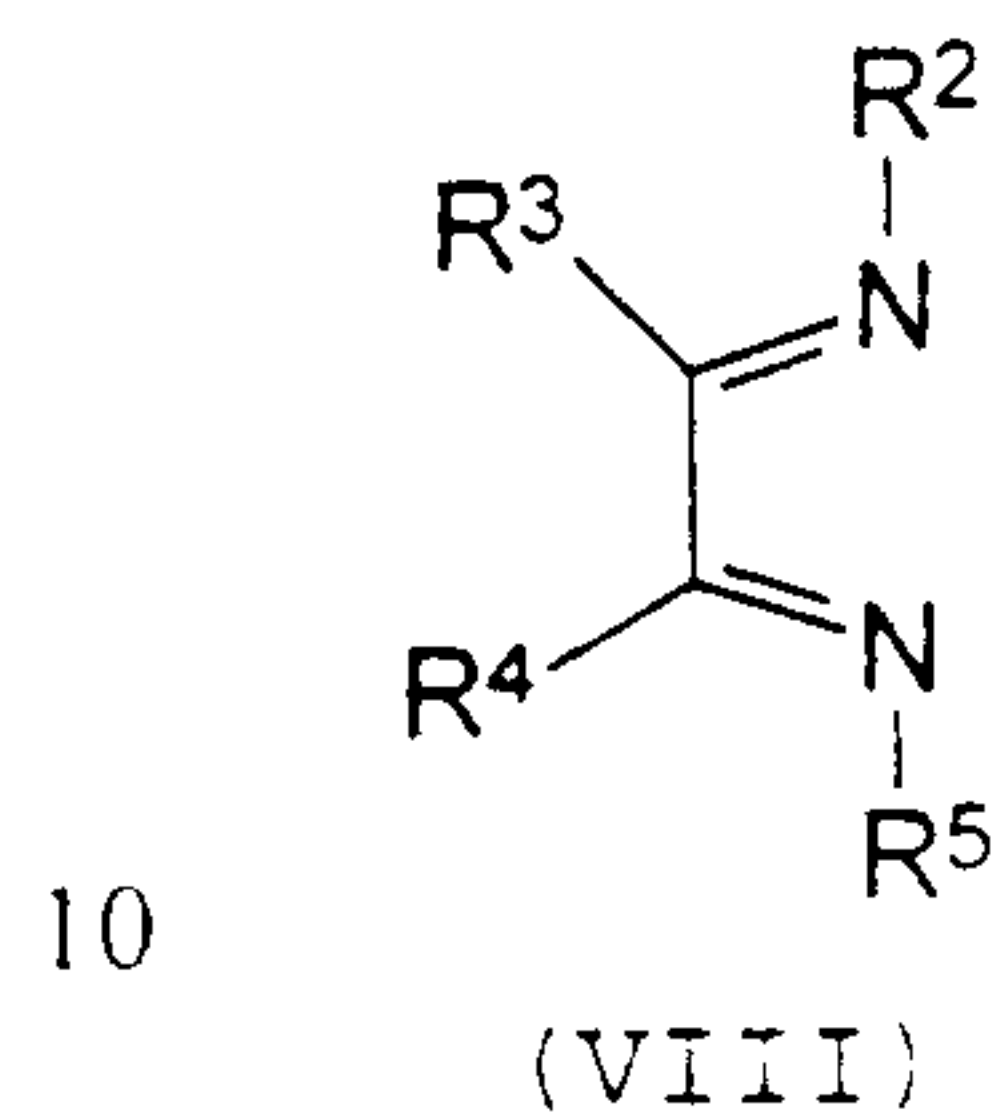
and

X is a weakly coordinating anion;

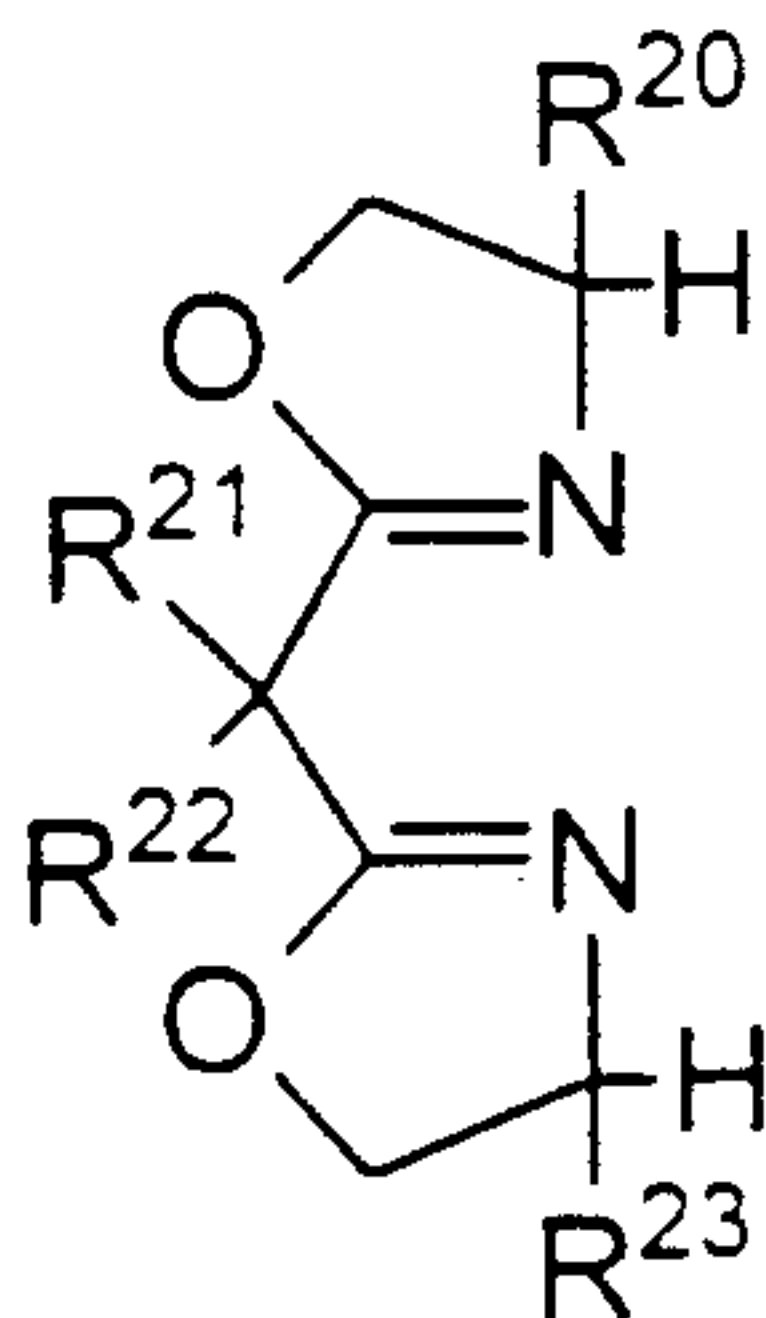
provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Also described herein is a polymerization process, comprising;

- 5 contacting Ni[0], Pd[0] or Ni[I] compound containing a ligand which may be displaced by a ligand of the formula (VIII), (XXX), (XXXII) or (XXIII);
- a second compound of the formula



or



(XXXII)

an oxidizing agent;

a source of a relatively weakly coordinating anion;

- 5 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene;

wherein:

- 10 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

- R^3 and R^4 are each independently hydrogen, 15 hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

- each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond 20 in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R^{13} is hydrocarbyl;

R^{44} is hydrocarbyl or substituted hydrocarbyl,

- 25 and R^{26} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

R^{31} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{48} and R^{49} are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

n is 2 or 3;

R^{21} and R^{22} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

X is a weakly coordinating anion;

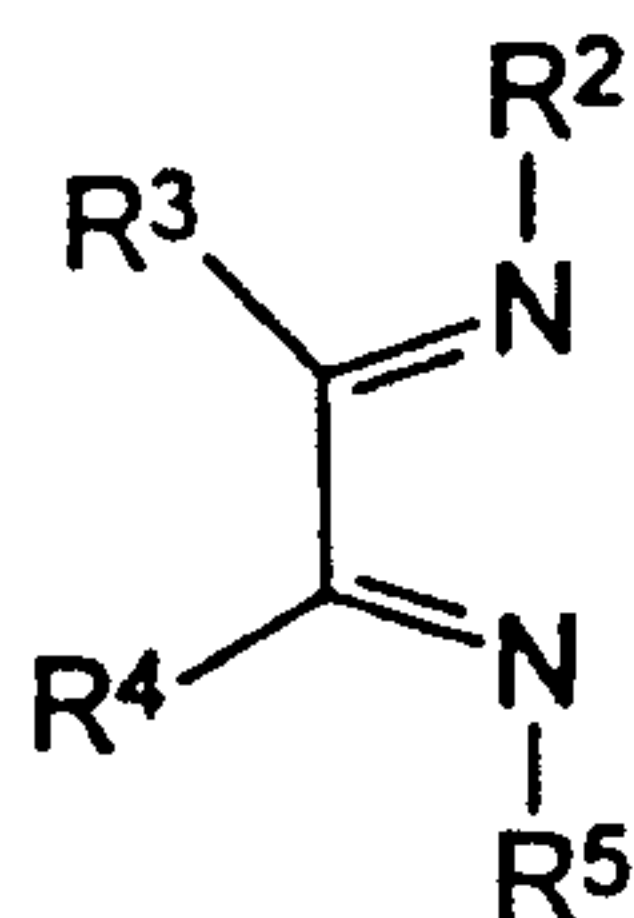
provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when said $Pd[0]$ compound is used, a diene is not present; and

when said second compound is (XXX) only an $Ni[0]$ or $Ni[I]$ compound is used.

Described herein is a polymerization process, comprising, contacting an $Ni[0]$ complex containing a ligand or ligands which may be displaced by (VIII), oxygen, an alkyl aluminum compound, and a compound of the formula



(VIII)

and one or more monomers selected from the group
consisting of ethylene, an olefin of the formula

21a

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$R^{17}CH=CH_2$, or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

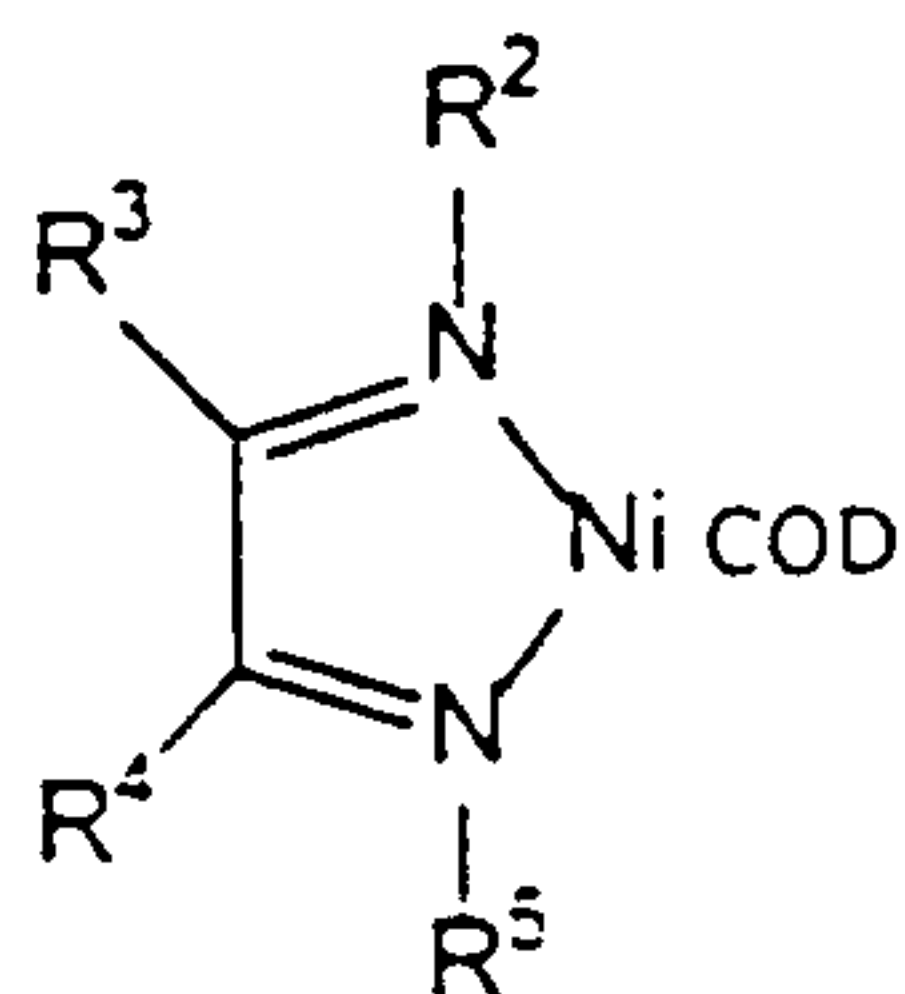
R^3 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^1 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

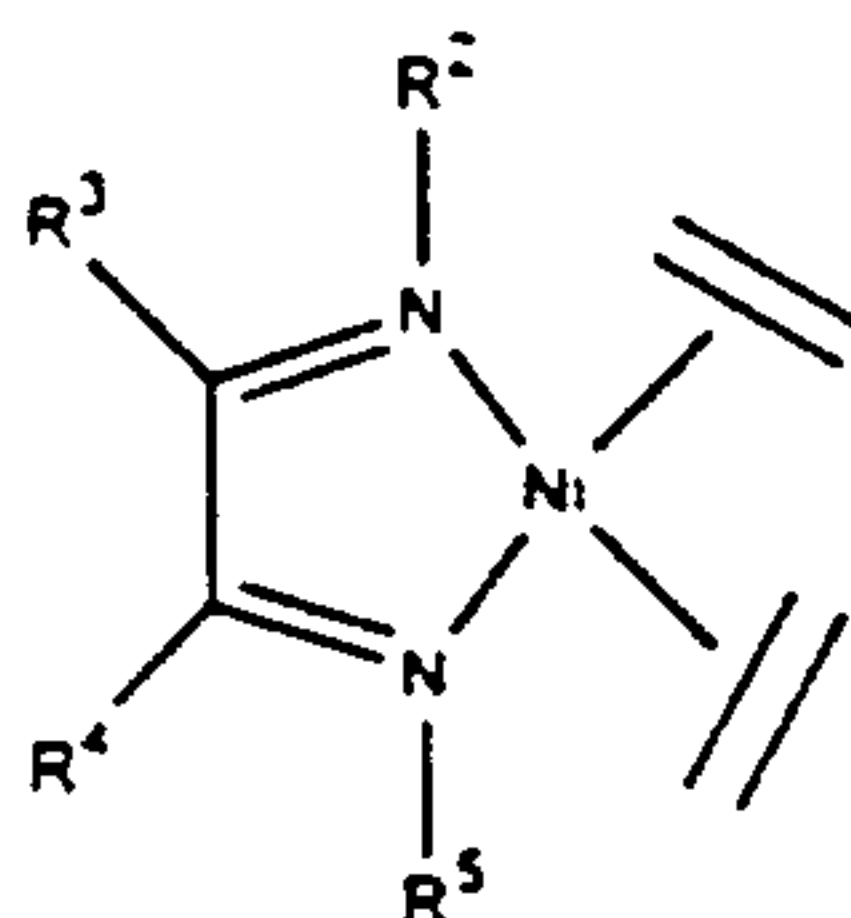
each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

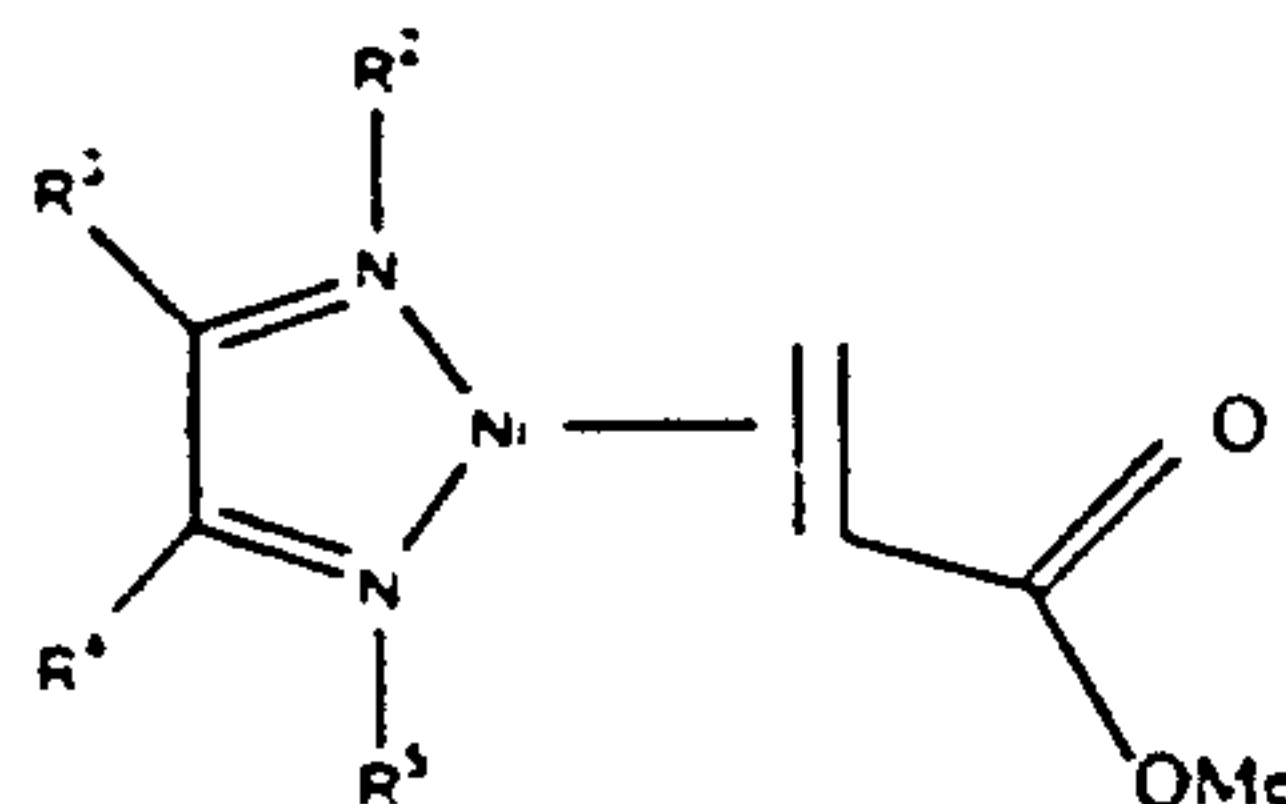
A polymerization process, comprising, contacting oxygen and an alkyl aluminum compound, or a compound of the formula HX, and a compound of the formula



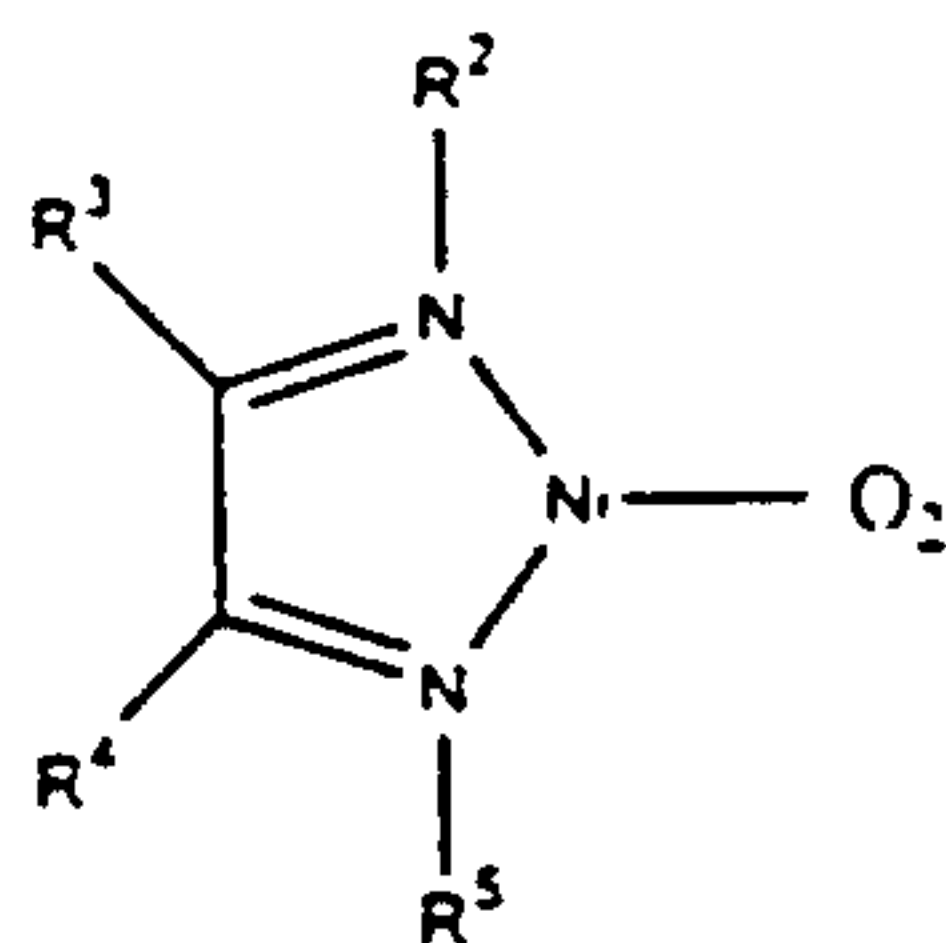
(XXXIII)



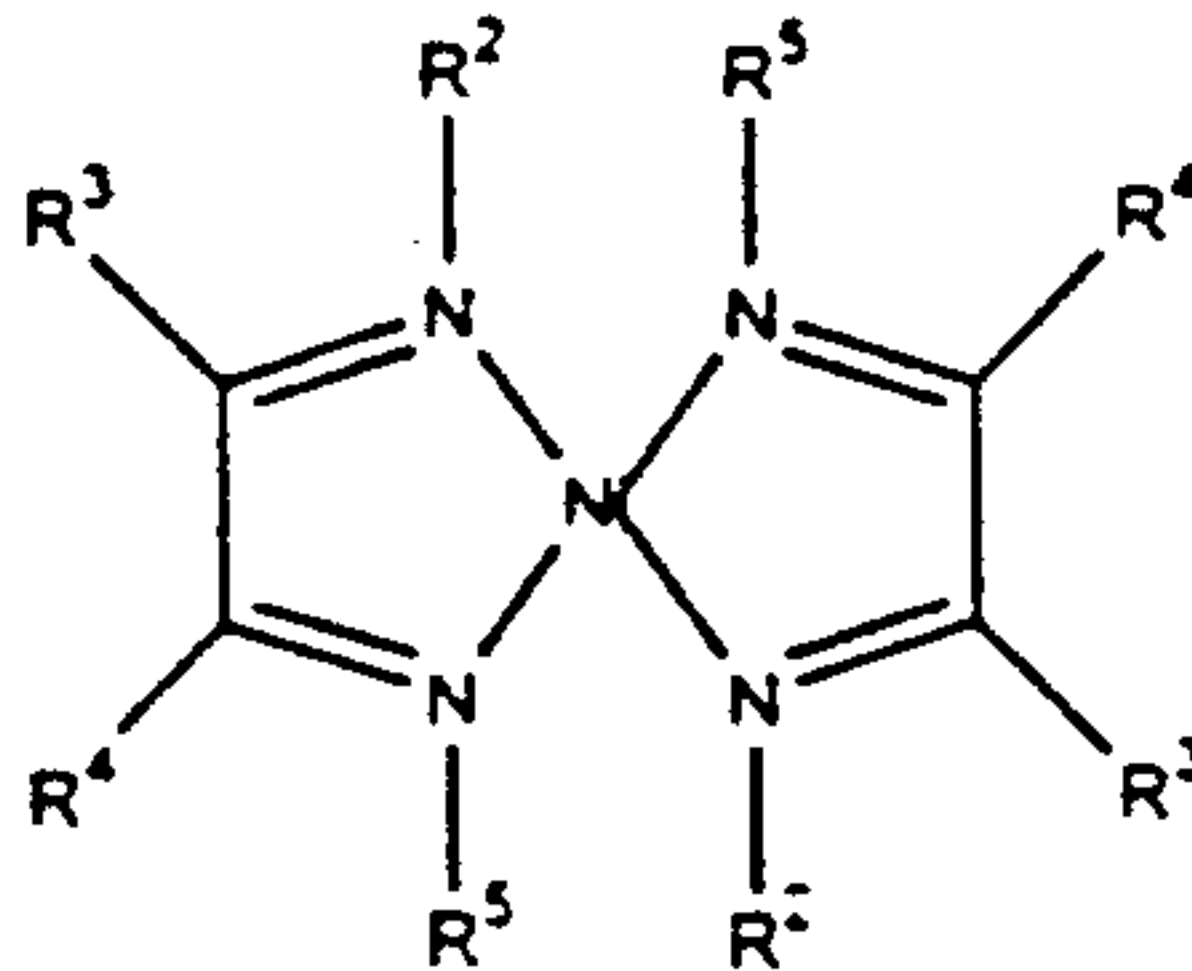
(XXXXII)



(XXXXIII)



(XXXXIV)



(XXXXV)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$, or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

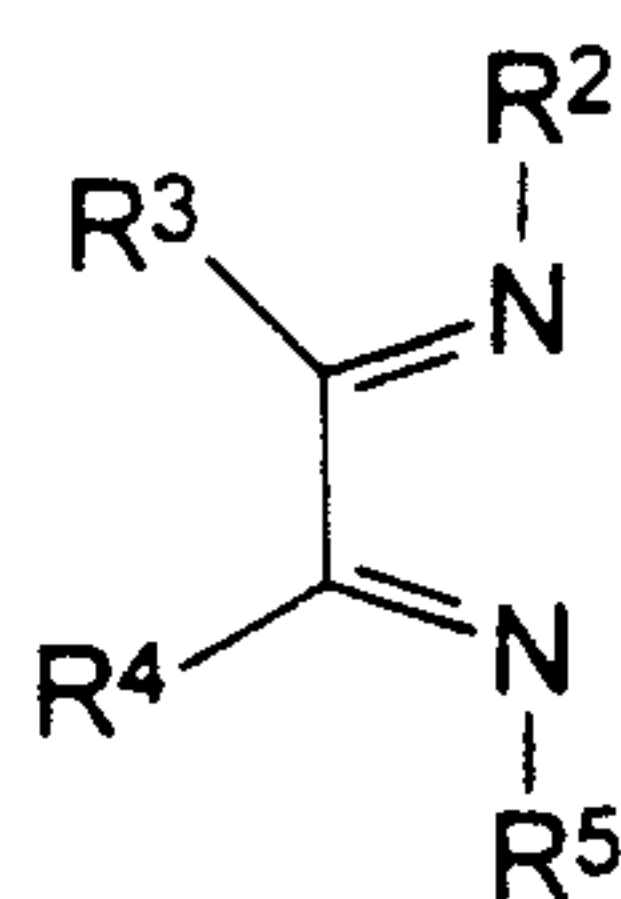
R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

each R^{17} is independently hydrocarbyl or
10 substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

X is a weakly coordinating anion; and
15 provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a polymerization process, comprising, contacting an Ni[0] complex containing a ligand or ligands which may be displaced by (VIII), HX
20 or a Bronsted acidic solid, and a compound of the formula



(VIII)

25

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

30 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

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R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

5 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; and

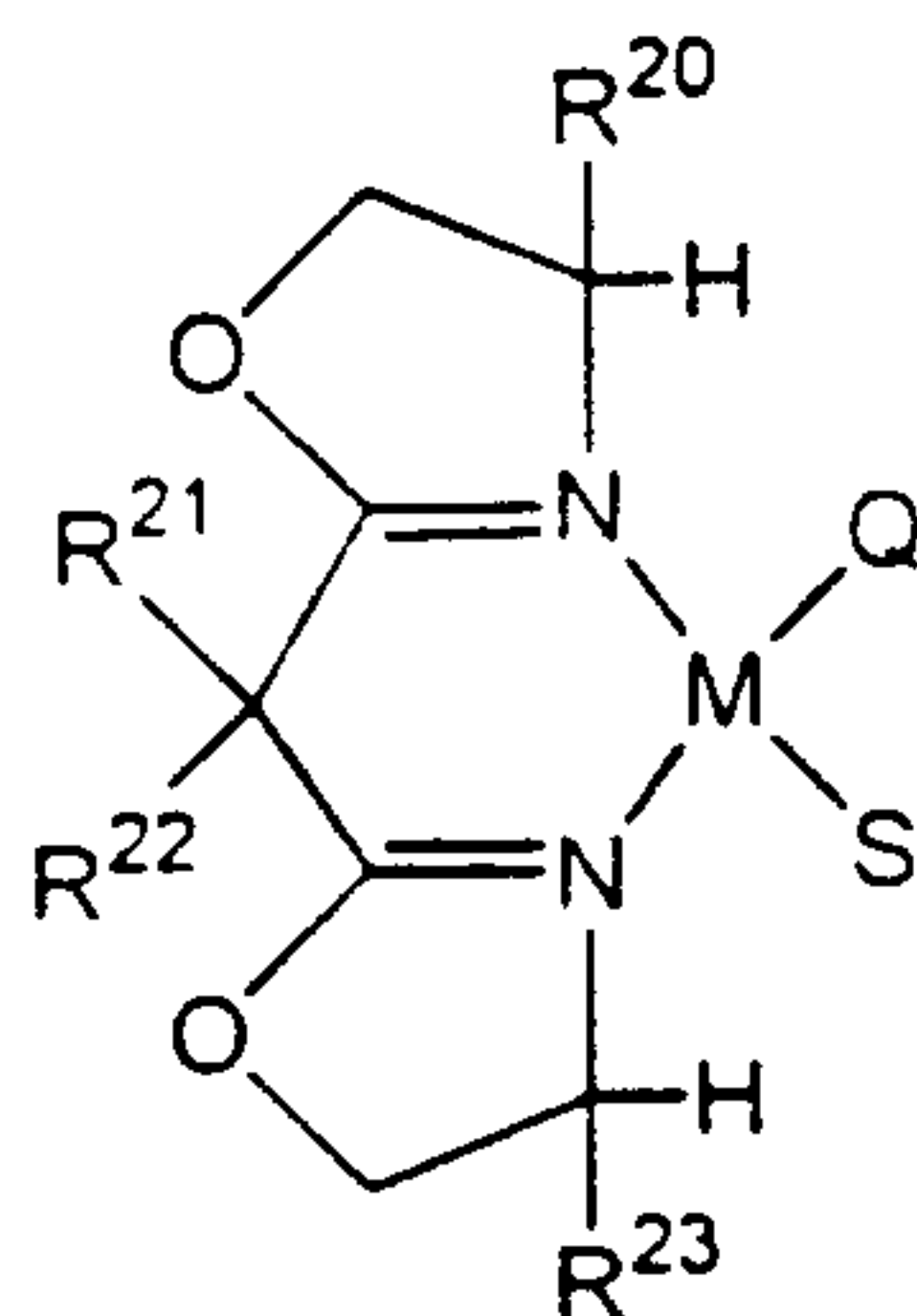
10 X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present

Described herein is a process for the polymerization of olefins, comprising, contacting, at a
15 temperature of about -100°C to about $+200^{\circ}\text{C}$:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q^- or S^- to form WQ^- or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted
20 acid whose counterion is a weakly coordinating anion;

a second compound of the formula



XIX

25 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}\text{CH}=\text{CH}_2$ or $R^{17}\text{CH}=\text{CHR}^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

30 M is Ni(II) or Pd(II);

R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

R^{21} and R^{22} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

5 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

10 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

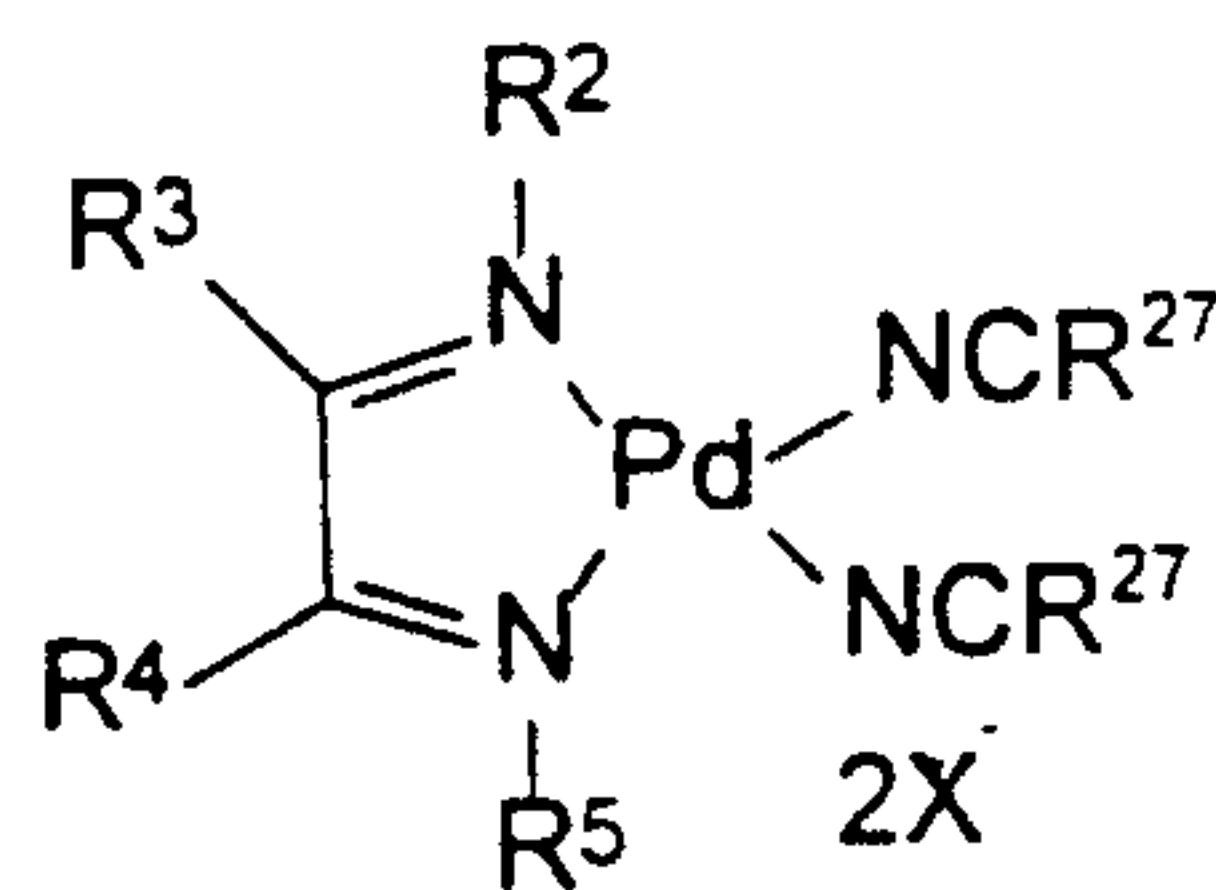
15 when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable
20 of transferring a hydride or alkyl group to M.

This invention also concerns a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, a compound of the formula

25



(XIV)

30 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}\text{CH}=\text{CH}_2$ or $R^{17}\text{CH}=\text{CHR}^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds; and

each R^{27} is independently hydrocarbyl;

each X is a weakly coordinating anion;

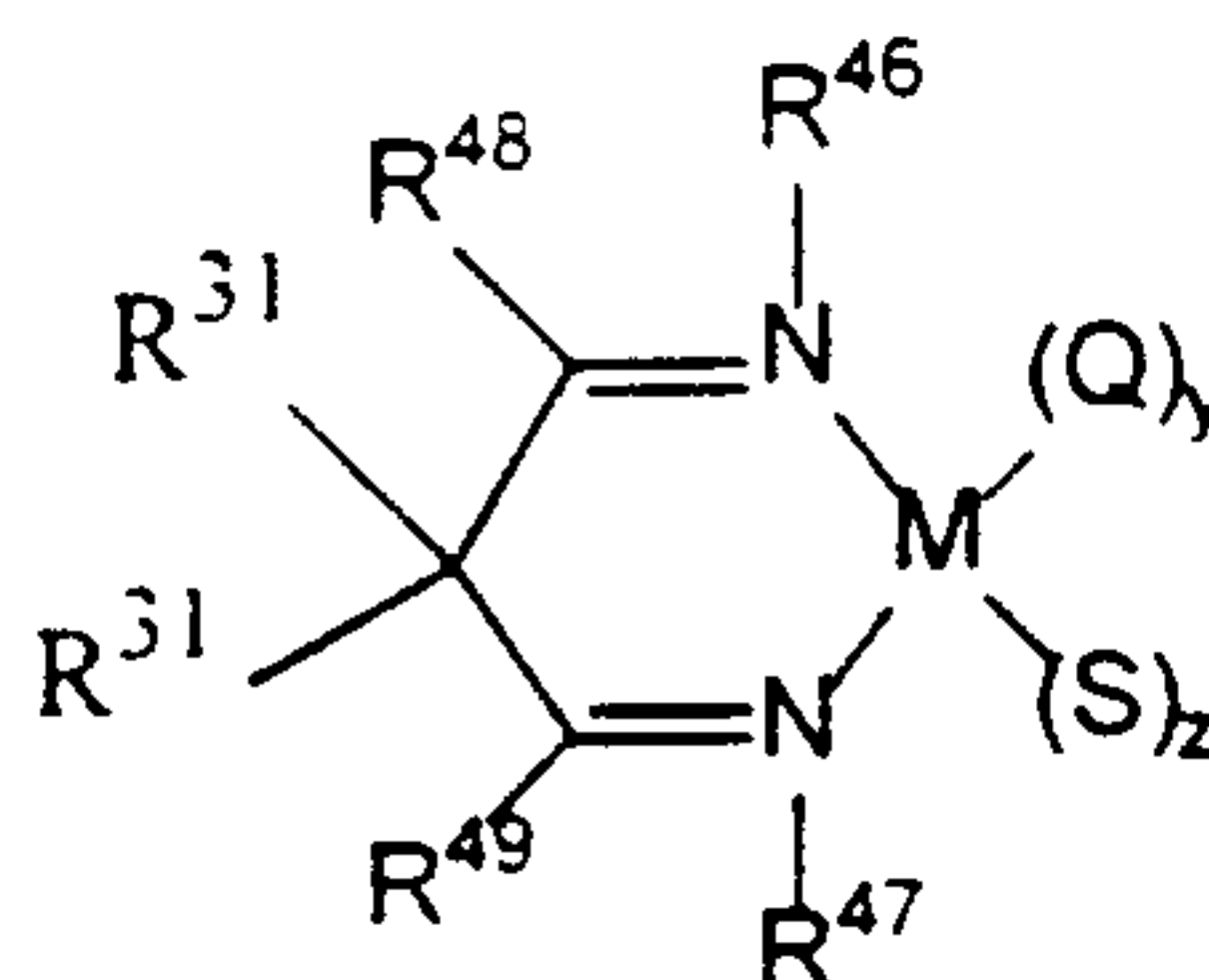
provided that, when norbornene or substituted norbornene is present, no other monomer is present.

This invention also concerns a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$:

20 a first compound W, which is a neutral Lewis acid capable of abstracting either Q^- or S^- to form WQ^- or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

25



(XV)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

30

R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

5 R^{48} and R^{49} are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

each R^{31} is independently hydrocarbyl, substituted hydrocarbyl or hydrogen;

10 M is Ti, Zr, Co, V, Cr, a rare earth metal, Fe, Sc, Ni, or Pd of oxidation state m;

y and z are positive integers;

$y+z = m$;

15 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

20 S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

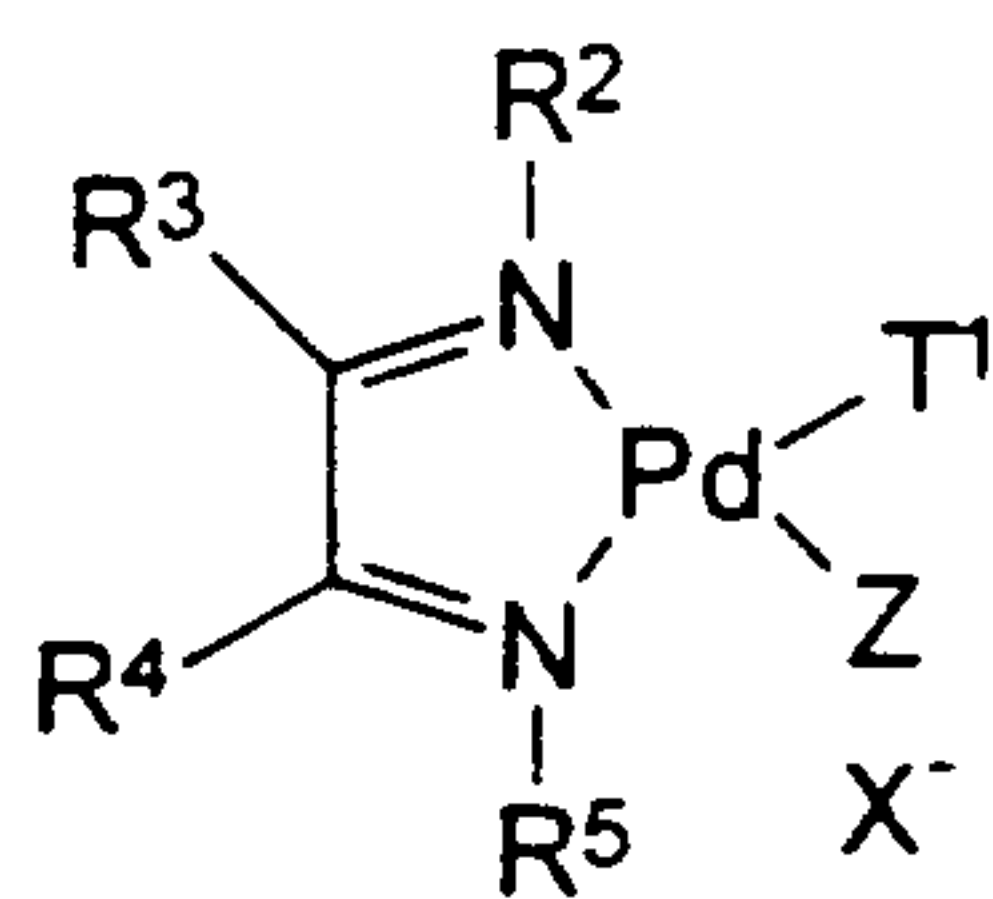
when norbornene or substituted norbornene is present, no other monomer is present;

25 when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

Disclosed herein is a compound of the formula

30



(II)

wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two
5 carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

10 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

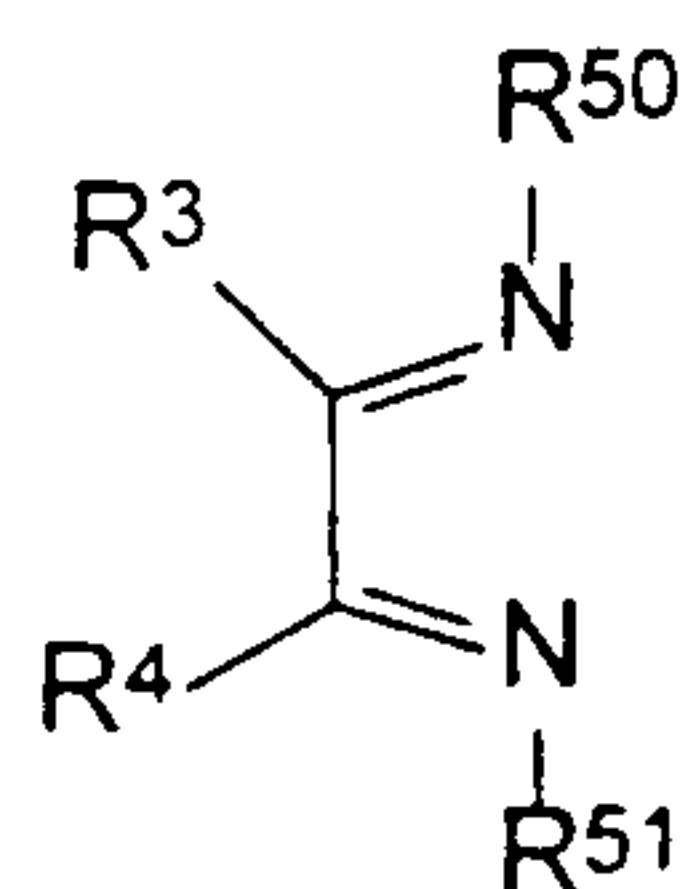
Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pK_a of the
15 conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion; and

R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

provided that when R^3 and R^4 taken together are
20 hydrocarbylene to form a carbocyclic ring, Z is not an organic nitrile.

Described herein is a compound of the formula



wherein:

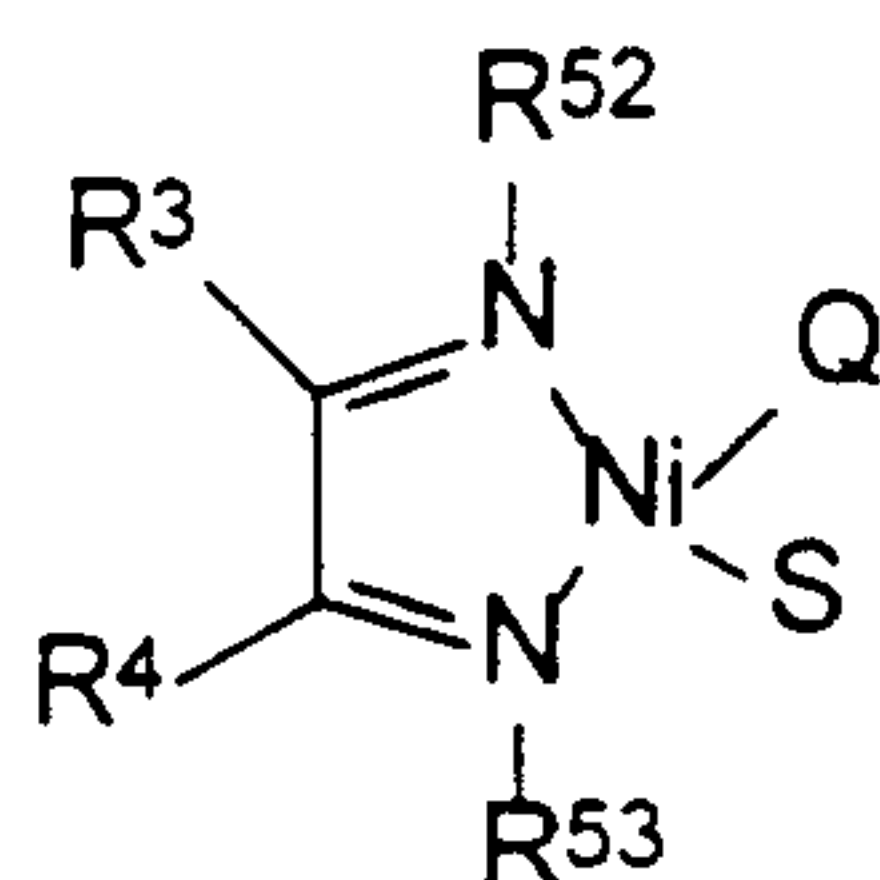
25 R^{50} is substituted phenyl;

R^{51} is phenyl or substituted phenyl;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted
30 hydrocarbylene to form a ring;

and provided that groups in the 2 and 6 positions of R^{50} have a difference in E_s of about 0.60 or more.

Described herein is a compound of the formula

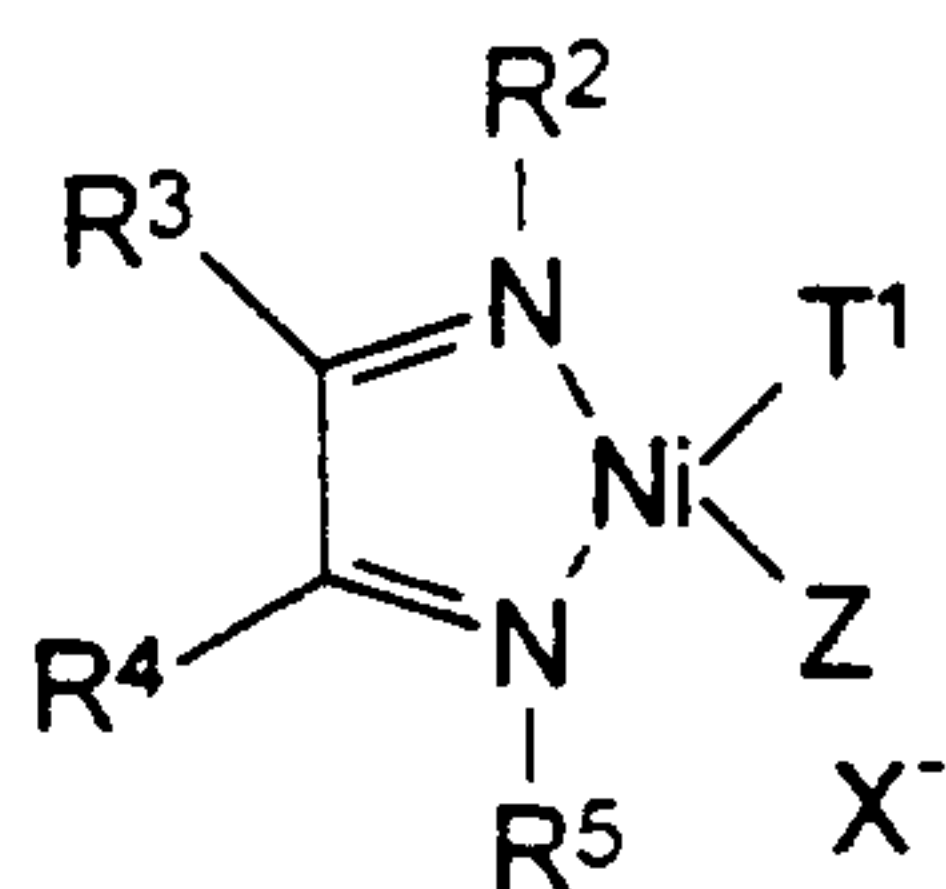


(XXXVI)

wherein:

- 5 R⁵² is substituted phenyl;
 R⁵³ is phenyl or substituted phenyl;
 R³ and R⁴ are each independently hydrogen,
 hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken
 together are hydrocarbylene or substituted
 10 hydrocarbylene to form a ring;
 Q is alkyl, hydride, chloride, bromide or
 iodide;
 S is alkyl, hydride, chloride, bromide or
 iodide;
 15 and provided that;
 groups in the 2 and 6 positions of R⁵² have a
 difference in E_s of 0.15 or more; and
 when both Q and S are each independently chloride,
 bromide or iodide W is capable of transferring a
 20 hydride or alkyl group to Ni.

This invention includes a compound of the formula



(III)

25

wherein:

- R² and R⁵ are each independently hydrocarbyl or
 substituted hydrocarbyl, provided that the carbon atom

bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

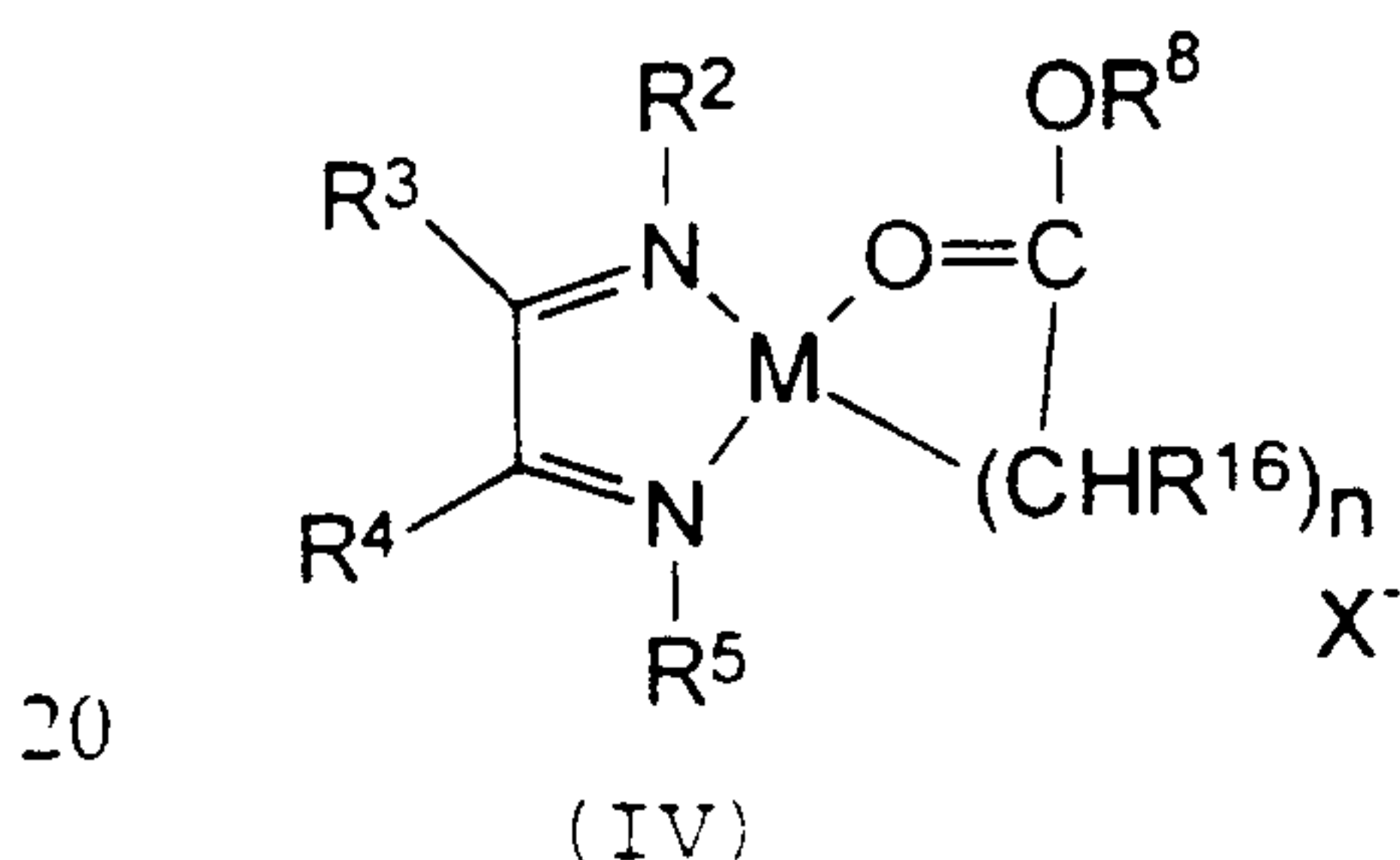
T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

R^{15} is hydrocarbyl not containing an olefinic or acetylenic bond;

Z is a neutral Lewis acid wherein the donating atom is nitrogen, sulfur or oxygen, provided that, if the donating atom is nitrogen, then the pKa of the conjugate acid of that compound is less than about 6; and

X is a weakly coordinating anion.

This invention also concerns a compound of the formula



wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

M is Ni(II) or Pd(II);

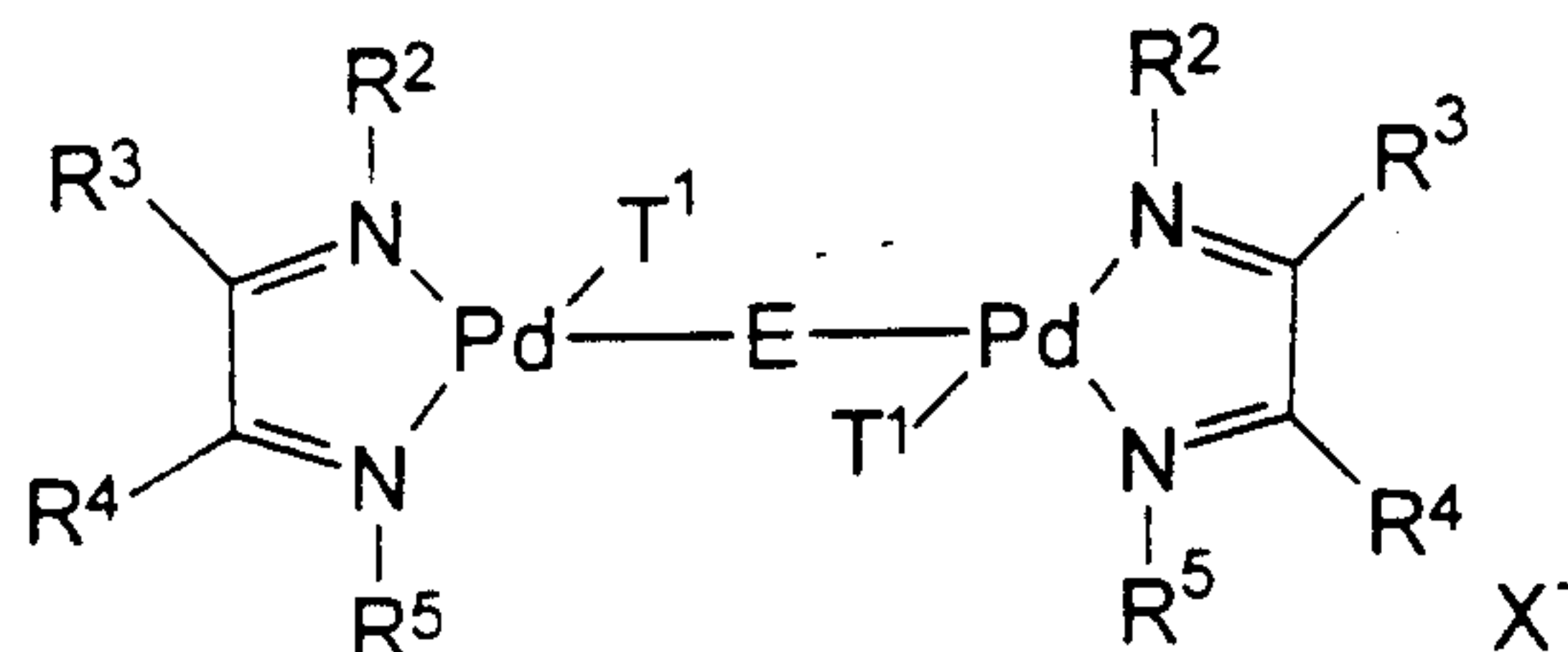
each R^{16} is independently hydrogen or alkyl
containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

X is a weakly coordinating anion; and

5 R^8 is hydrocarbyl.

Also disclosed herein is a compound of the formula



(V)

10

wherein:

R^2 and R^5 are each independently hydrocarbyl or
substituted hydrocarbyl, provided that the carbon atom
bound directly to the imino nitrogen atom has at least
15 two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen,
hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken
together are hydrocarbylene or substituted
hydrocarbylene to form a ring;

20 E is halogen or $-OR^{18}$;

R^{18} is hydrocarbyl not containing olefinic or
acetylenic bonds;

T^1 is hydrogen, hydrocarbyl not containing
olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

25 R^{15} is hydrocarbyl not containing olefinic or
acetylenic bonds; and

X is a weakly coordinating anion.

Included herein is a compound of the formula $[(\eta^4-1,5-COD)PdT^1Z]^+X^-$, wherein:

30 T^1 is hydrocarbyl not containing olefinic or
acetylenic bonds;

X is a weakly coordinating anion;

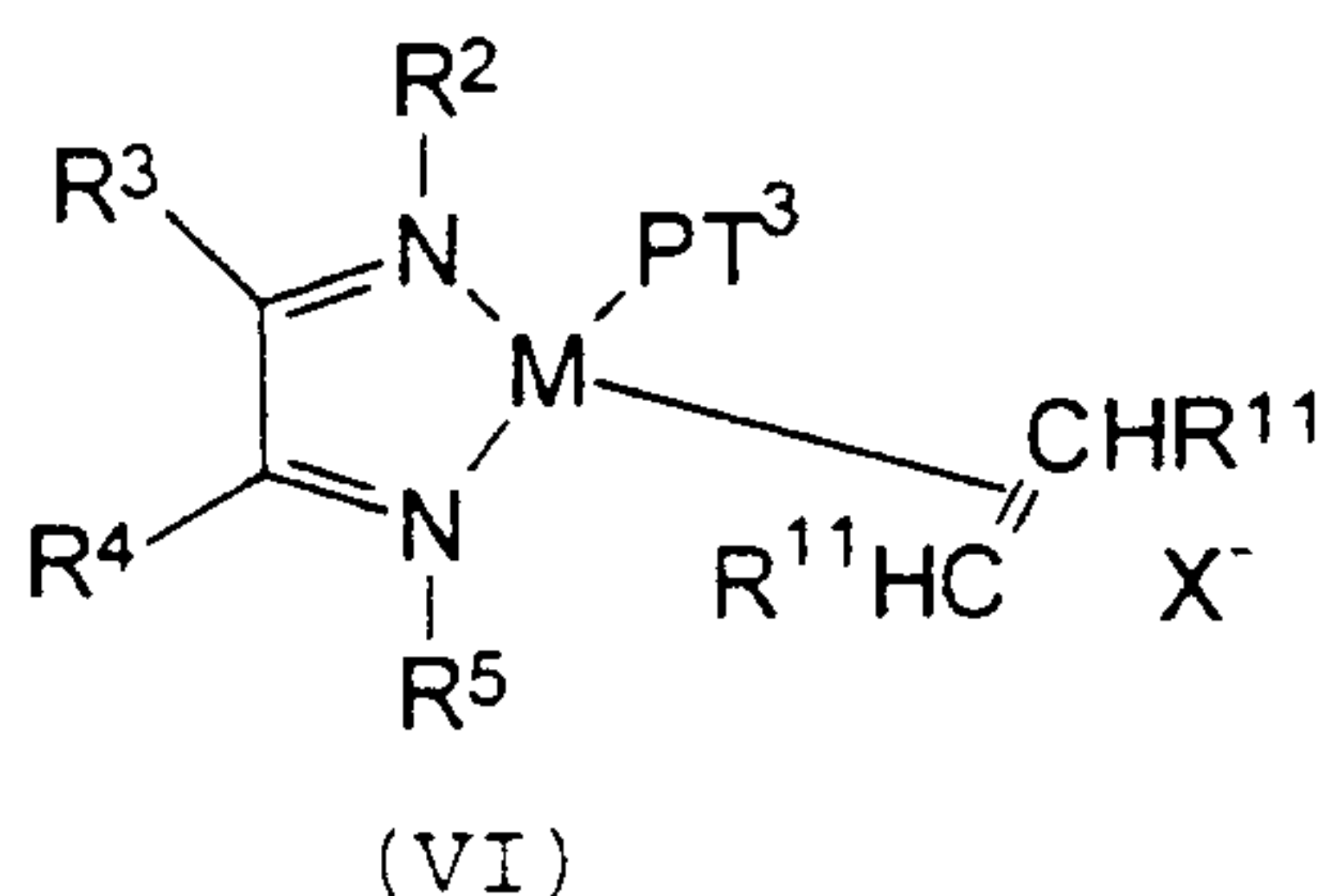
COD is 1,5-cyclooctadiene;

Z is $R^{10}CN$; and

R^{10} is hydrocarbyl not containing olefinic or acetylenic bonds.

Also included herein is a compound of the formula

5



wherein:

10

M is Ni(II) or Pd(II);

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

15

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, alkyl or
20 $-(CH_2)_mCO_2R^1$;

T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-CH_2CH_2CH_2CO_2R^6$;

P is a divalent group containing one or more repeat units derived from the polymerization of one or
25 more of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene and, when M is Pd(II), optionally one or more of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, CO, or a vinyl ketone;

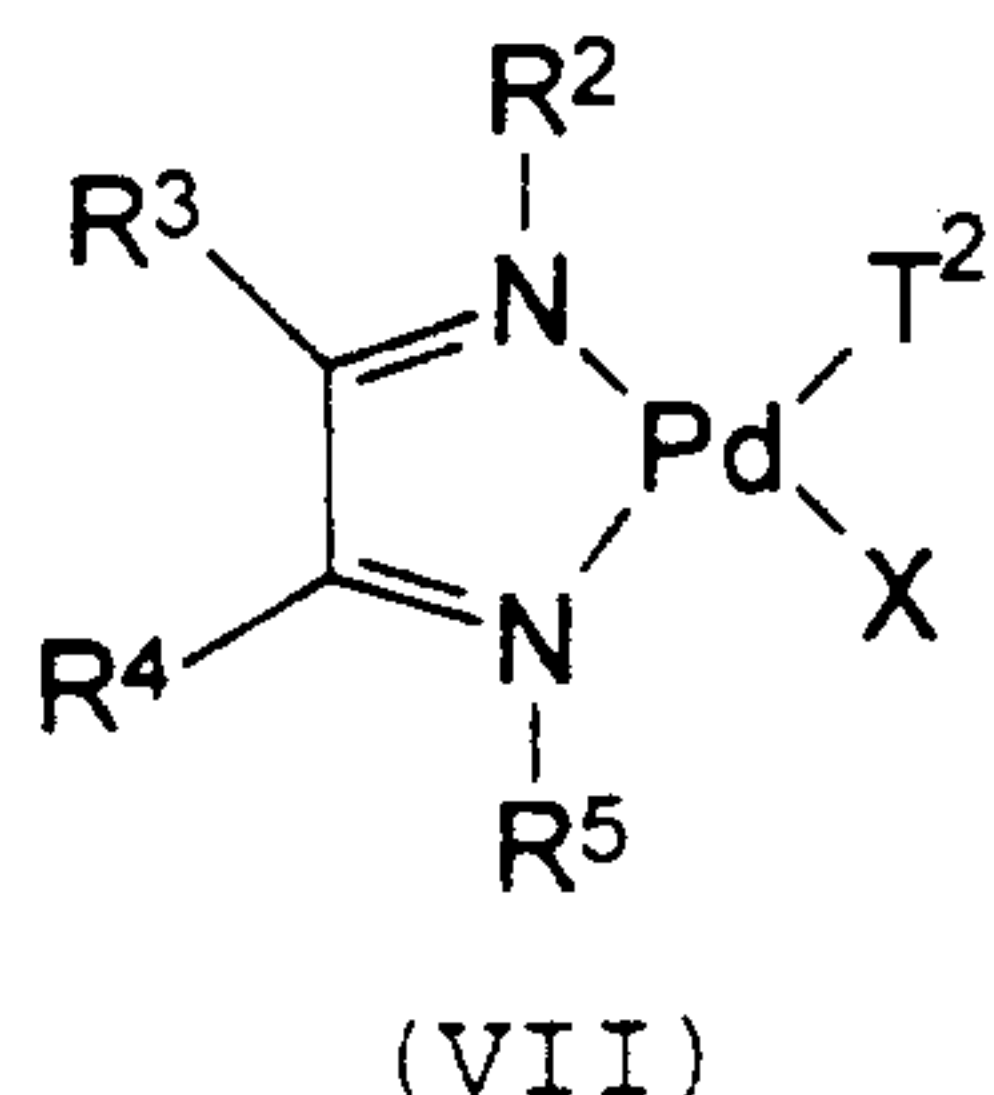
30

R^8 is hydrocarbyl;

m is 0 or an integer from 1 to 16;

R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion;
 provided that, when M is Ni(II), R¹¹ is not -CO₂R⁸.
 Also described herein is a compound of the formula



wherein:

R² and R⁵ are each independently hydrocarbyl or
 10 substituted hydrocarbyl, provided that the carbon atom
 bound to the imino nitrogen atom has at least two
 carbon atoms bound to it;

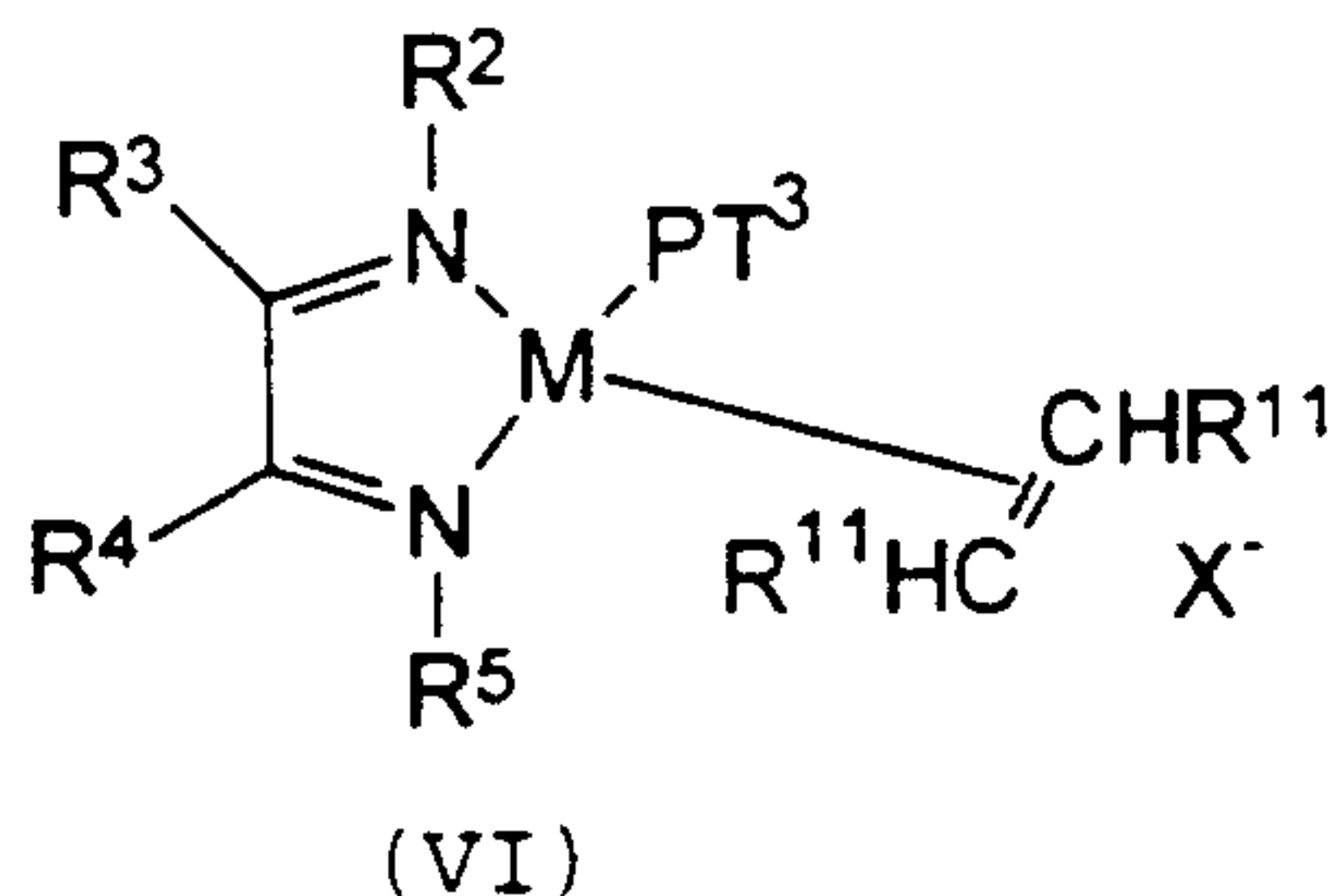
R³ and R⁴ are each independently hydrogen,
 hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken
 15 together are hydrocarbylene or substituted
 hydrocarbylene to form a ring;

T² is hydrogen, hydrocarbyl not containing
 olefinic or acetylenic bonds, hydrocarbyl substituted
 with keto or ester groups but not containing olefinic
 20 or acetylenic bonds, R¹⁵C(=O)- or R¹⁵OC(=O)-;

R¹⁵ is hydrocarbyl not containing olefinic or
 acetylenic bonds; and

X is a weakly coordinating anion.

Included herein is a process for the production of
 25 polyolefins, comprising, contacting, at a temperature
 of about -100°C to about +200°C, a compound of the
 formula



and one or more monomers selected from the group
consisting of ethylene, an olefin of the formula
 $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene,
5 substituted norbornene, and norbornene,

wherein:

M is Ni(II) or Pd(II);

R^2 and R^5 are each independently hydrocarbyl or
substituted hydrocarbyl, provided that the carbon atom
10 bound directly to the imino nitrogen atom has at least
two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen,
hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken
together are hydrocarbylene or substituted
15 hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, alkyl or
- $(CH_2)_mCO_2R^1$;

T^3 is hydrogen, hydrocarbyl not containing
olefinic or acetylenic bonds, or $-CH_2CH_2CH_2CO_2R^8$;

20 P is a divalent group containing one or more
repeat units derived from the polymerization of one or
monomers selected from the group consisting of
ethylene, an olefin of the formula $R^{17}CH=CH_2$ or
 $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted
25 norbornene, and norbornene, and, when M is Pd(II),
optionally one or more of: a compound of the formula
 $CH_2=CH(CH_2)_mCO_2R^1$, CO or a vinyl ketone;

R^8 is hydrocarbyl;

each R^{17} is independently hydrocarbyl or
30 substituted hydrocarbyl provided that any olefinic bond
in said olefin is separated from any other olefinic
bond or aromatic ring by a quaternary carbon atom or at
least two saturated carbon atoms; R^1 is hydrogen, or
hydrocarbyl or substituted hydrocarbyl containing 1 to
35 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion;

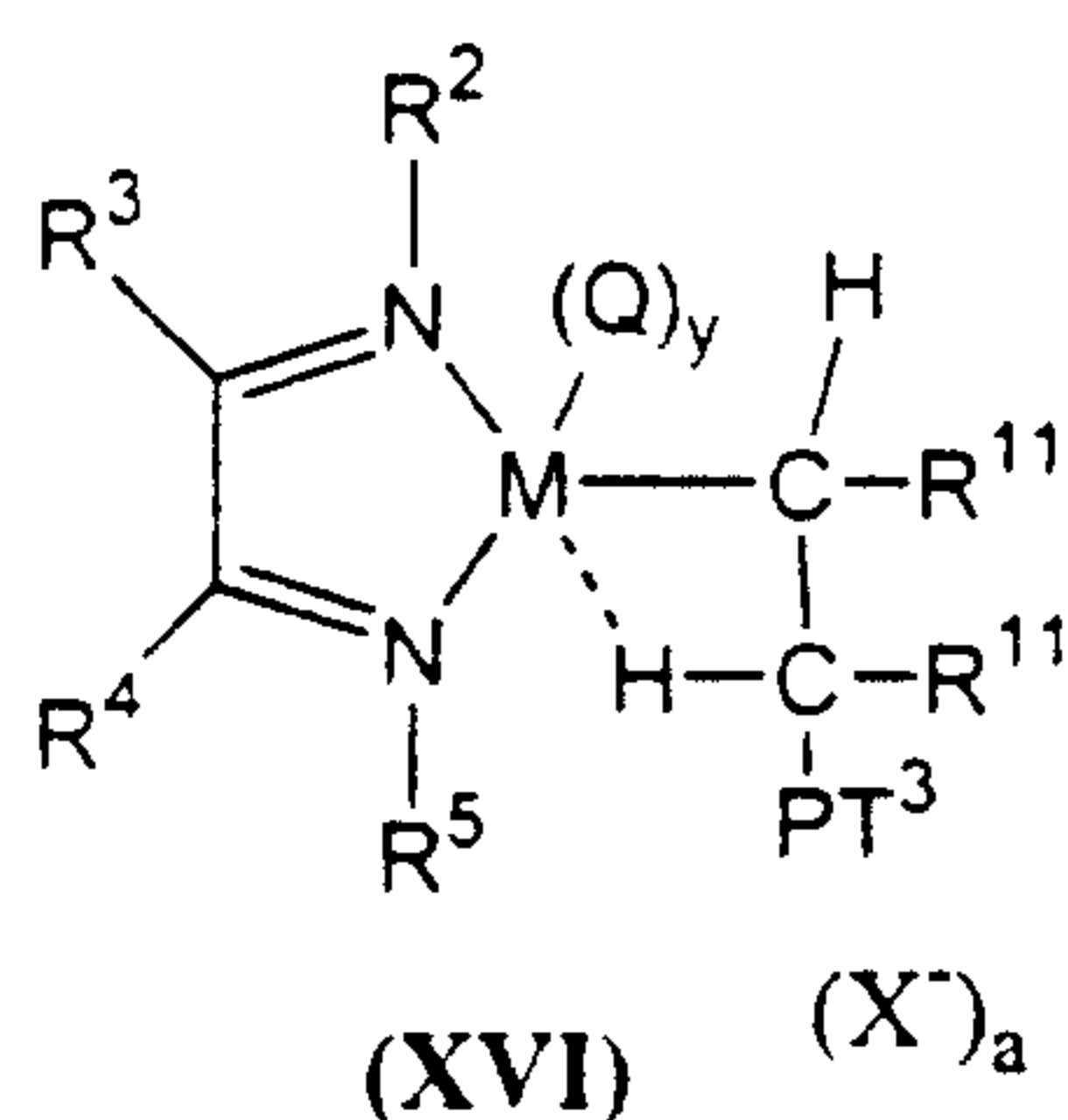
provided that:

when M is Pd a diene is not present;

when norbornene or substituted norbornene is present, no other monomer is present; and

5 further provided that, when M is Ni(II), R^{11} is not $-\text{CO}_2\text{R}^8$.

Included herein is a process for the production of polyolefins, comprising, contacting, at a temperature
10 of about -100°C to about $+200^\circ\text{C}$, a compound of the formula



15 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

20 M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least
25 two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

30 each R^{11} is independently hydrogen, or alkyl, or both of R^{11} taken together are hydrocarbylene to form a carbocyclic ring;

T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^6$;

P is a divalent group containing one or more repeat units derived from the polymerization of one or
 5 monomers selected from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula
 10 $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$, CO, or a vinyl ketone;

R^6 is hydrocarbyl;

a is 1 or 2;

$y + a + 1 = m$;

each R^{17} is independently hydrocarbyl or
 15 substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to
 20 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion;

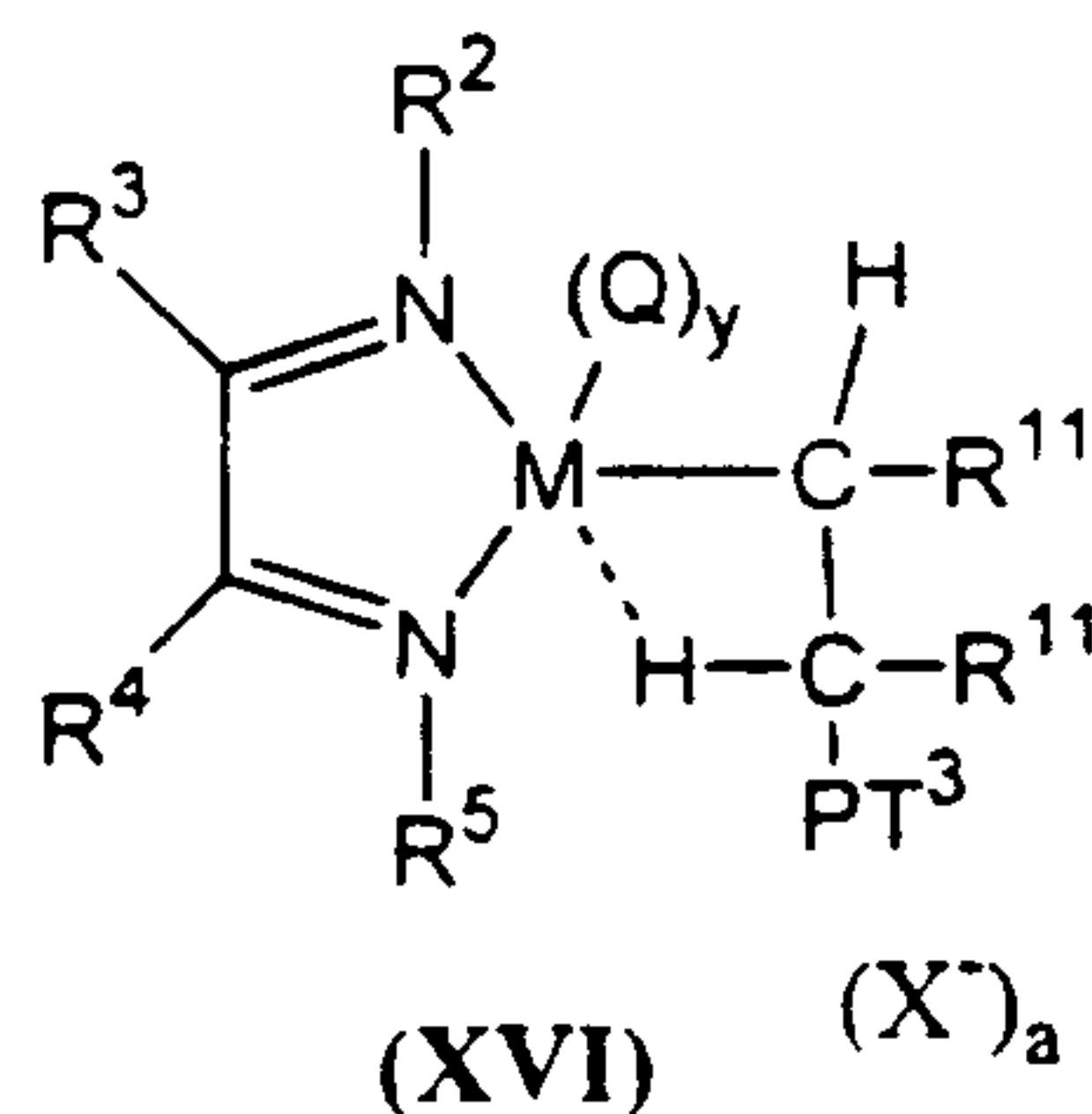
provided that:

when norbornene or substituted norbornene is
 25 present, no other monomer is present;

when M is Pd a diene is not present; and

further provided that, when M is Ni(II), R^{11} is not
 $-\text{CO}_2\text{R}^6$.

30 Also described herein is a compound of the formula



wherein:

M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

5 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, 10 hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, or alkyl, or both of R^{11} taken together are hydrocarbylene to 15 form a carbocyclic ring;

T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^6$;

P is a divalent group containing one or more repeat units derived from the polymerization of one or 20 monomers selected from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and optionally, when M is Pd(II), one or more of: a compound of the formula 25 $\text{CH}_2=\text{CH}(\text{CH}_2)_y\text{CO}_2\text{R}^1$, CO, or a vinyl ketone;

Q is a monovalent anion;

R^6 is hydrocarbyl;

a is 1 or 2;

$y + a + 1 = m$;

30 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

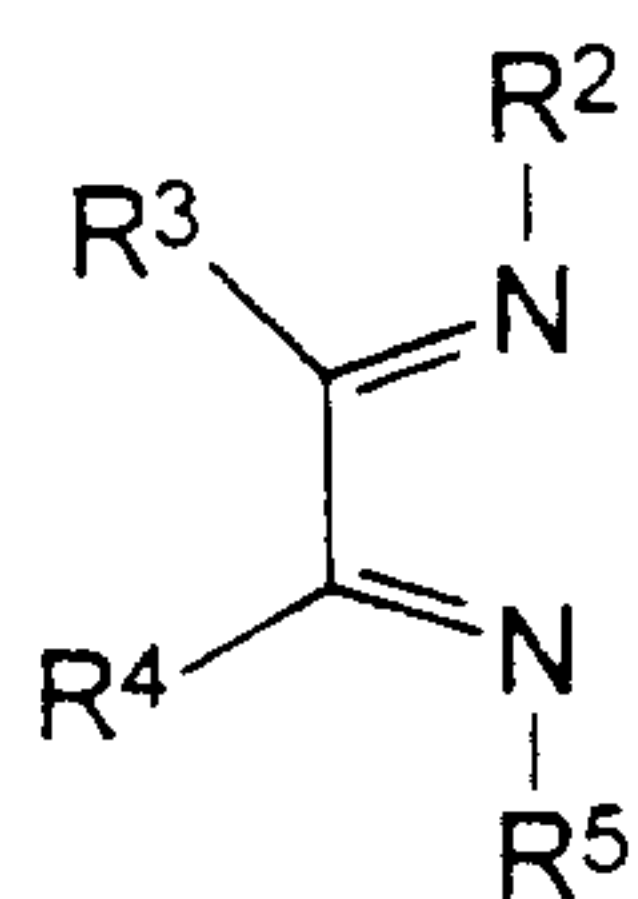
35 R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and

and X is a weakly coordinating anion;

and provided that when M is Pd a diene is not present.

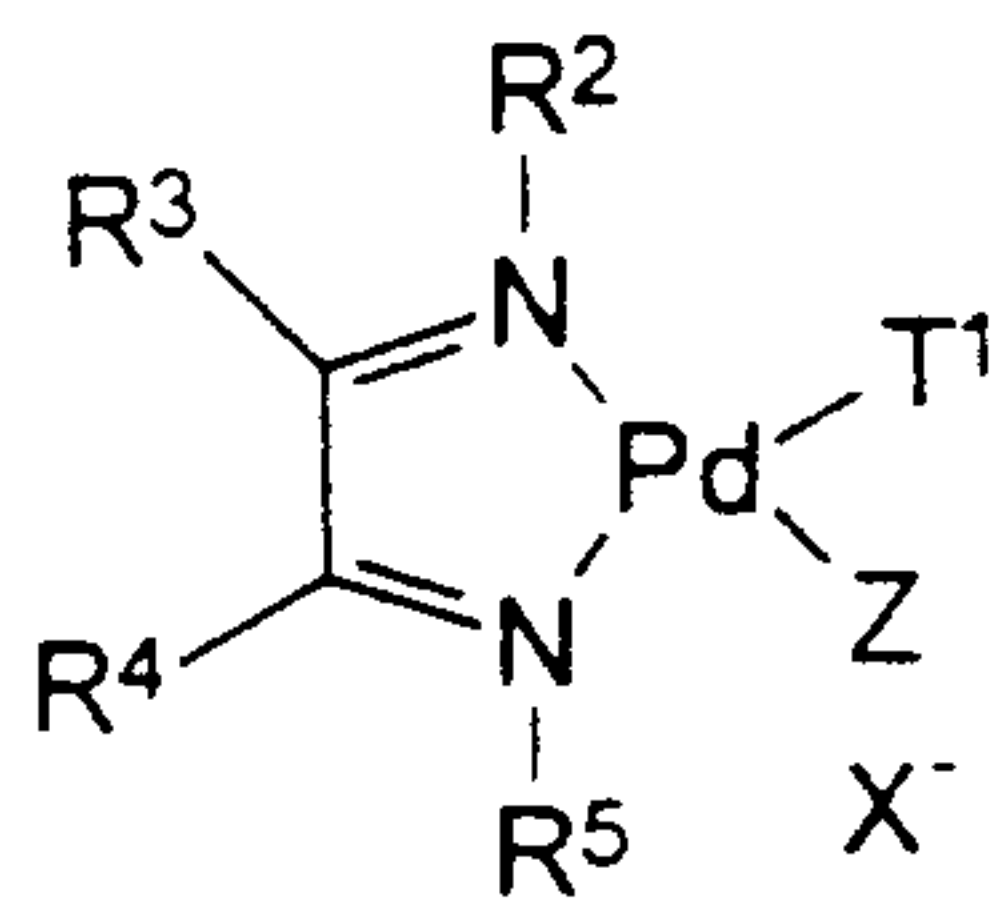
Described herein is a process, comprising, contacting, at a temperature of about -40°C to about
5 $+60^{\circ}\text{C}$, a compound of the formula $[(\eta^4\text{-}1,5\text{-COD})\text{Pd}^{\text{T}^1}\text{Z}]^+\text{X}^-$ and a diimine of the formula



(VIII)

10

to produce a compound of the formula



(II)

15

wherein:

T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $\text{R}^{15}\text{C}(=\text{O})-$ or $\text{R}^{15}\text{OC}(=\text{O})-$;

X is a weakly coordinating anion;

20

COD is 1,5-cyclooctadiene;

Z is R^{10}CN ;

R^{10} is hydrocarbyl not containing olefinic or acetylenic bonds;

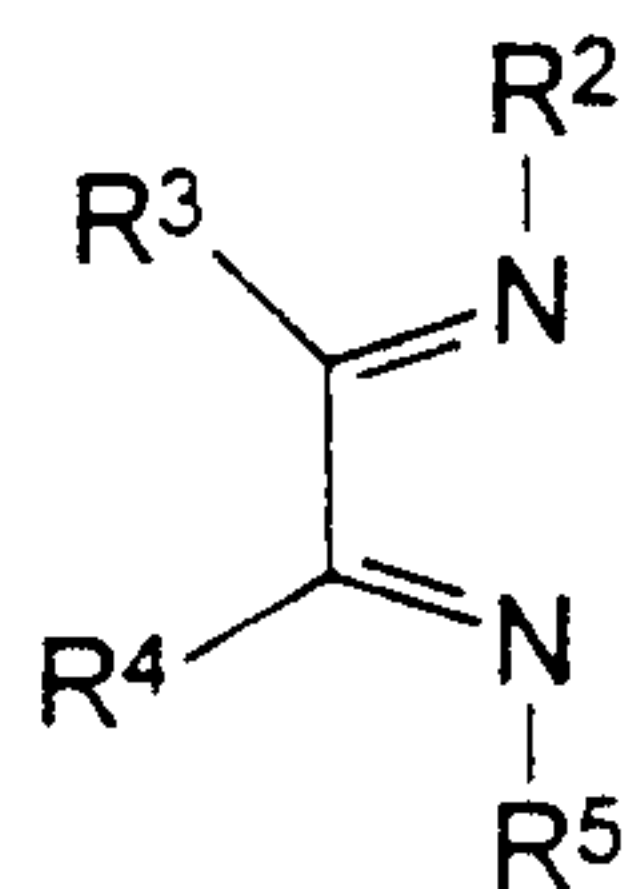
25

R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

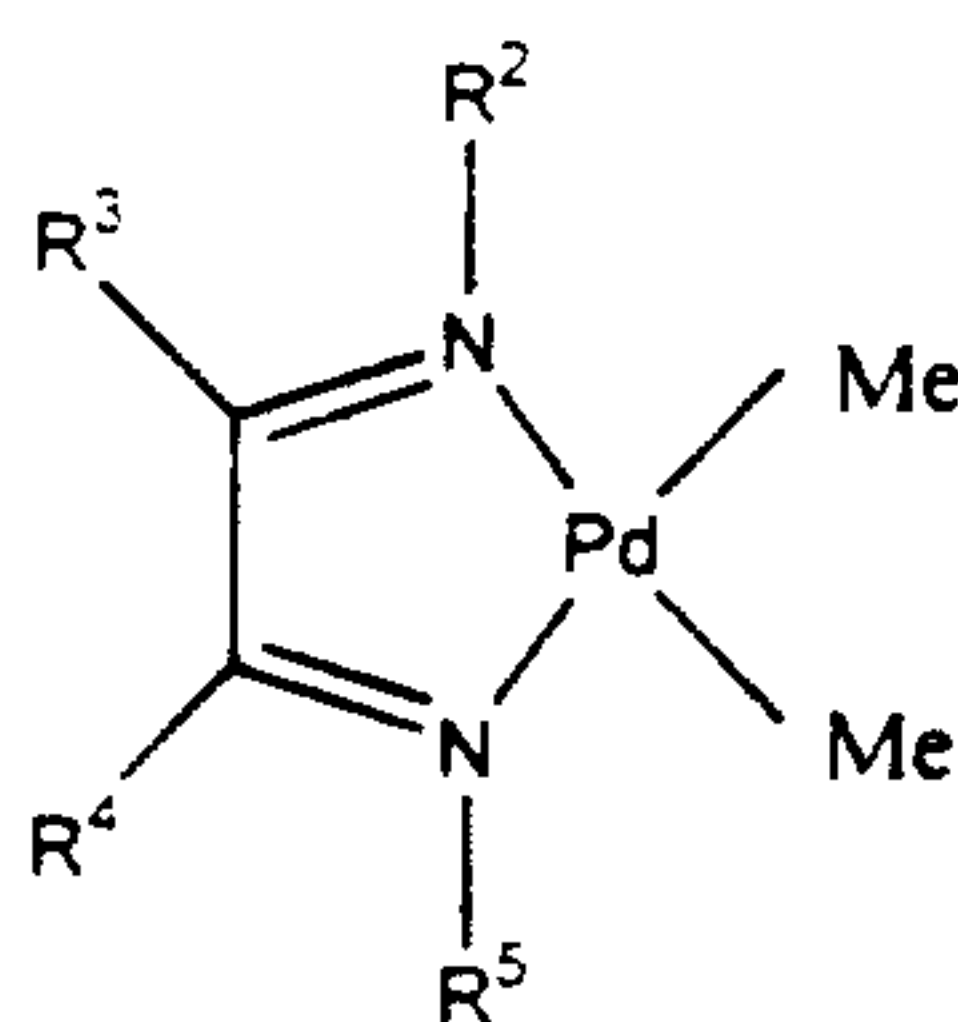
5 Described herein is a process, comprising, contacting, at a temperature of about -80°C to about $+20^{\circ}\text{C}$, a compound of the formula $(\eta^4\text{-}1,5\text{-COD})\text{PdMe}_2$ and a diimine of the formula



10

(VIII)

to produce a compound of the formula



15

(XXXXI)

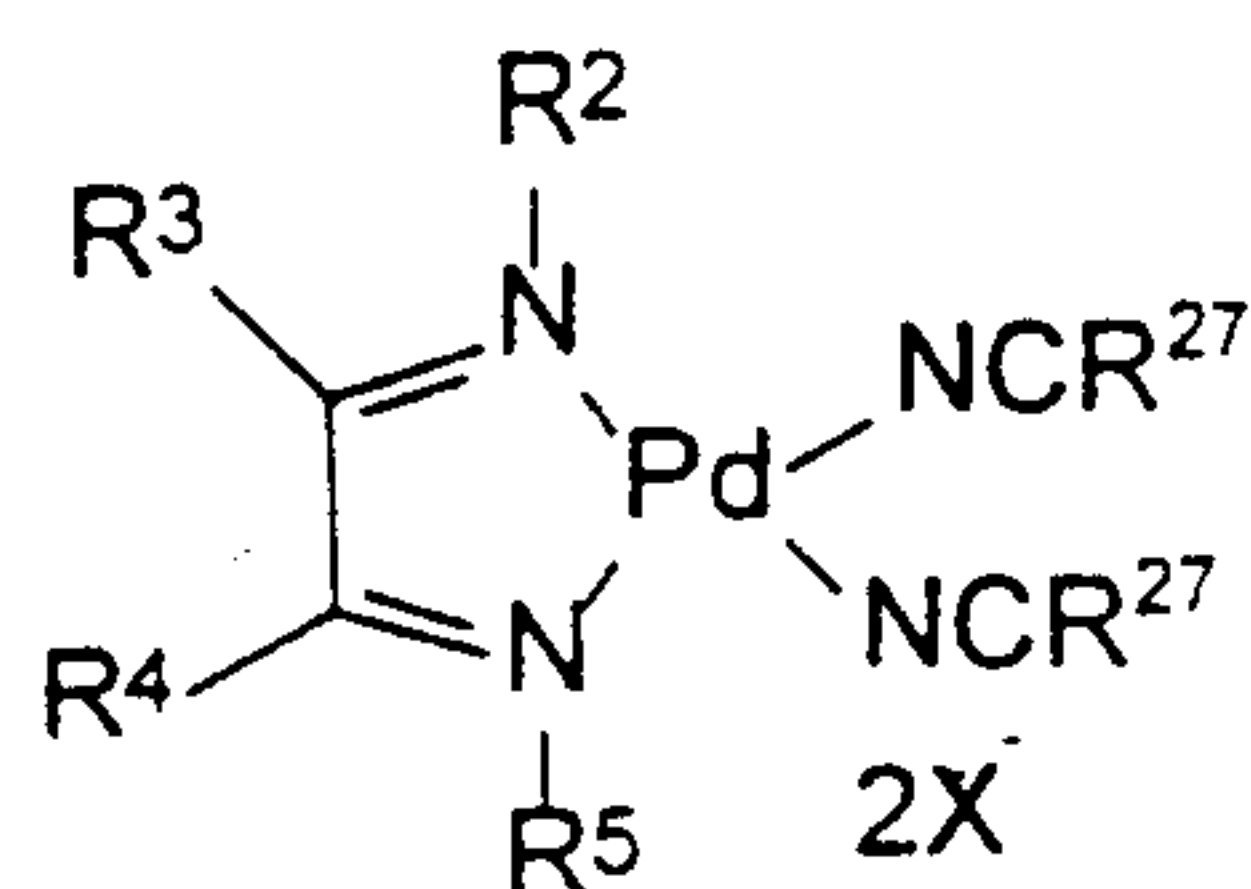
wherein:

COD is 1,5-cyclooctadiene;

20 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

25 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

Also disclosed herein is a compound of the formula



(XIV)

5

wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

10

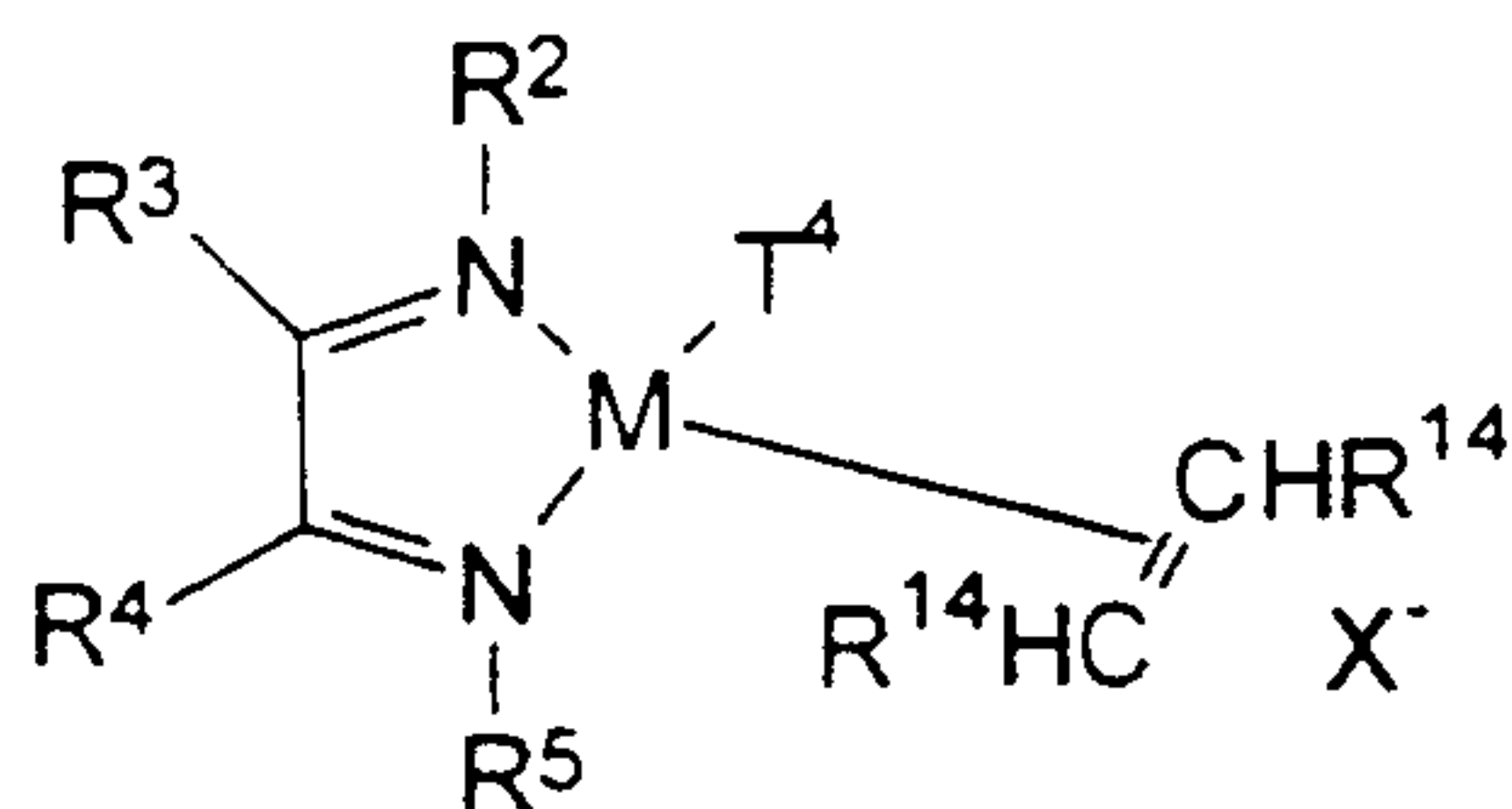
R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

15

each R^{27} is hydrocarbyl; and

each X is a weakly coordinating anion.

This invention includes a compound of the formula



20

(IX)

wherein:

M is Ni(II) or Pd(II);

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

25

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken

together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{14} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

5 R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

T^4 is alkyl, $-R^{60}C(O)OR^8$, $R^{15}(C=O)-$ or $R^{15}OC(=O)-$

;

10 R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

R^{60} is alkylene not containing olefinic or acetylenic bonds;

R^8 is hydrocarbyl;;

and X is a weakly coordinating anion;

15 and provided that when R^{14} is $-(CH_2)_mCO_2R^1$, or T^4 is not alkyl, M is Pd(II).

Described herein is a homopolypropylene with a glass transition temperature of -30°C or less, and containing at least about 50 branches per 1000 methylene groups.

20 This invention also concerns a homopolymer of cyclopentene having a degree of polymerization of about 30 or more and an end of melting point of about 100°C to about 320°C , provided that said homopolymer has less than 5 mole percent of enchaind linear olefin containing pentylene units.

In addition, disclosed herein is a homopolymer or copolymer of cyclopentene that has an X-ray powder diffraction pattern that has reflections at approximately 17.3° , 19.3° , 24.2° , and 40.7° 2θ .

30 Another novel polymer is a homopolymer of cyclopentene wherein at least 90 mole percent of enchaind cyclopentylene units are 1,3-cyclopentylene units, and said homopolymer has an average degree of polymerization of 30 more.

Described herein is a homopolymer of cyclopentene wherein at least 90 mole percent of enchaind cyclopentylene units are cis-1,3-cyclopentylene, and

said homopolymer has an average degree of polymerization of about 10 or more.

Also described is a copolymer of cyclopentene and ethylene wherein at least 75 mole percent of enchain-
5 cyclopentylene units are 1,3-cyclopentylene units.

This invention concerns a copolymer of cyclopentene and ethylene wherein there are at least 20 branches per 1000 methylene carbon atoms.

Described herein is a copolymer of cyclopentene
10 and ethylene wherein at least 50 mole percent of the repeat units are derived from cyclopentene.

Disclosed herein is a copolymer of cyclopentene and an α -olefin.

This invention also concerns a polymerization
15 process, comprising, contacting an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, wherein each R^{17} is independently hydrogen, hydrocarbyl, or substituted hydrocarbyl provided that any olefinic bond in said
20 aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms with a catalyst, wherein said catalyst:

contains a nickel or palladium atom in a positive oxidation state;

25 contains a neutral bidentate ligand coordinated to said nickel or palladium atom, and wherein coordination to said nickel or palladium atom is through two nitrogen atoms or a nitrogen atom and a phosphorous atom; and

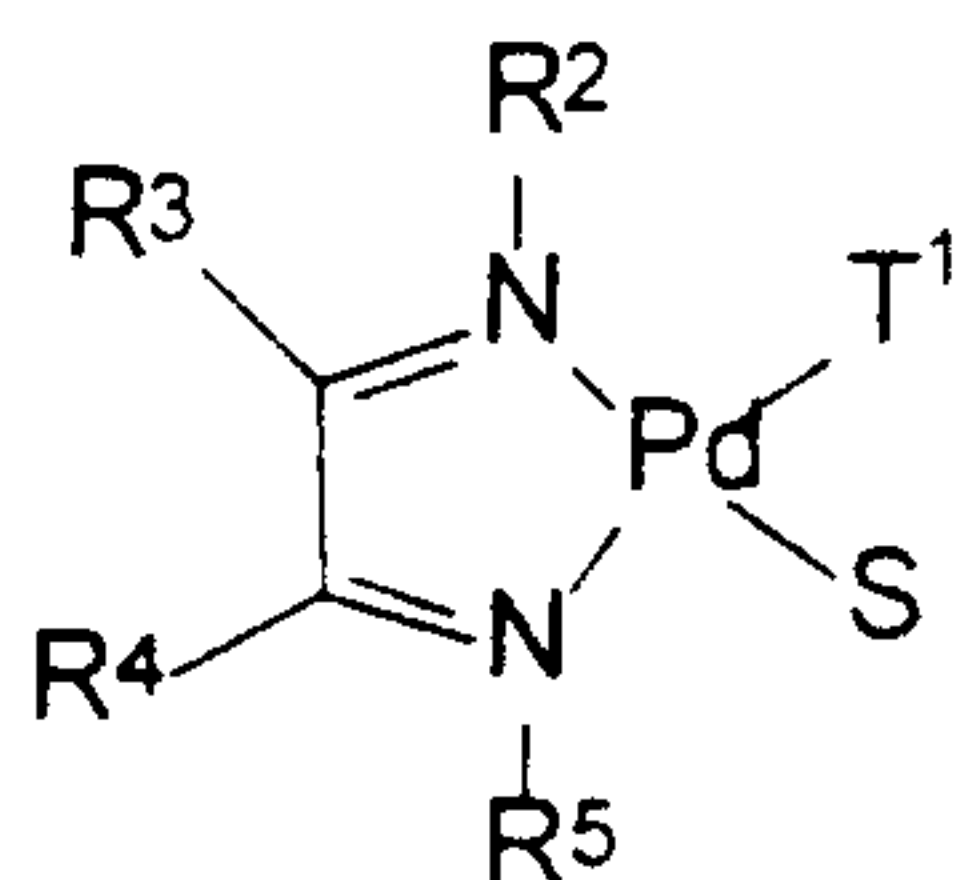
30 said neutral bidentate ligand, has an Ethylene Exchange Rate of less than $20,000 \text{ L-mol}^{-1}\text{s}^{-1}$ when said catalyst contains a palladium atom, and less than $50,000 \text{ L-mol}^{-1}\text{s}^{-1}$ when said catalyst contains a nickel atom;

35 and provided that when Pd is present a diene is not present.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$:

a first compound which is a salt of an alkali metal cation and a relatively noncoordinating monoanion;

a second compound of the formula



(XX)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bond;

T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $\text{R}^{15}\text{C}(=\text{O})-$ or $\text{R}^{15}\text{OC}(=\text{O})-$;

S is chloride, iodide, or bromide; and

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula $H_2C=CH(CH_2)_eG$ by contacting said monomers with a transition metal containing coordination

5 polymerization catalyst, wherein:

each G is independently hydrogen or $-CO_2R^1$;

each e is independently 0 or an integer of 1 to 20;

each R^1 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G is hydrogen; and

except when no branches should be theoretically present, the number of branches per 1000 methylene groups is 90% or less than the number of theoretical branches per 1000 methylene groups, or the number of branches per 1000 methylene groups is 110% or more of theoretical branches per 1000 methylene groups, and

when there should be no branches theoretically present, said polyolefin has 50 or more branches per 1000 methylene groups;

25 and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

Also described herein is a polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula $H_2C=CH(CH_2)_eG$ by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or $-CO_2R^1$;

each e is independently 0 or an integer of 1 to 20;

R^1 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G is hydrogen;

5 said polymer has at least 50 branches of the formula $-(CH_2)_fG$ per 1000 methylene groups, wherein when G is the same as in a monomer and $e \neq f$, and/or for any single monomer of the formula $H_2C=CH(CH_2)_eG$ there are less than 90% of the number of theoretical branches per 1000 methylene groups, or more than 110% of the theoretical branches per 1000 methylene groups of the formula $-(CH_2)_fG$ and $f=e$, and wherein f is 0 or an integer of 1 or more;

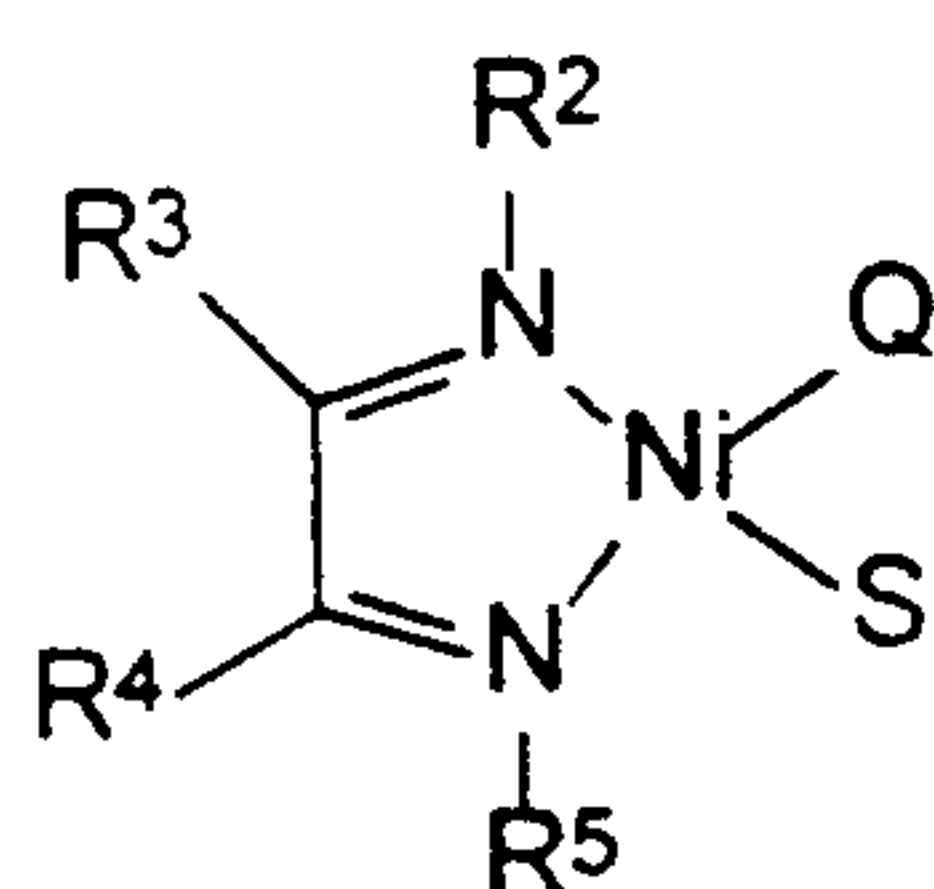
10 and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms.

This invention concerns a process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about $+200^\circ\text{C}$:

20 ethylene;

a first compound W, which is a neutral Lewis acid capable of abstracting X^- to form WX^- , provided that the anion formed is a weakly coordinating anion, or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; and

a second compound of the formula



(XXXI)

wherein:

30 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken

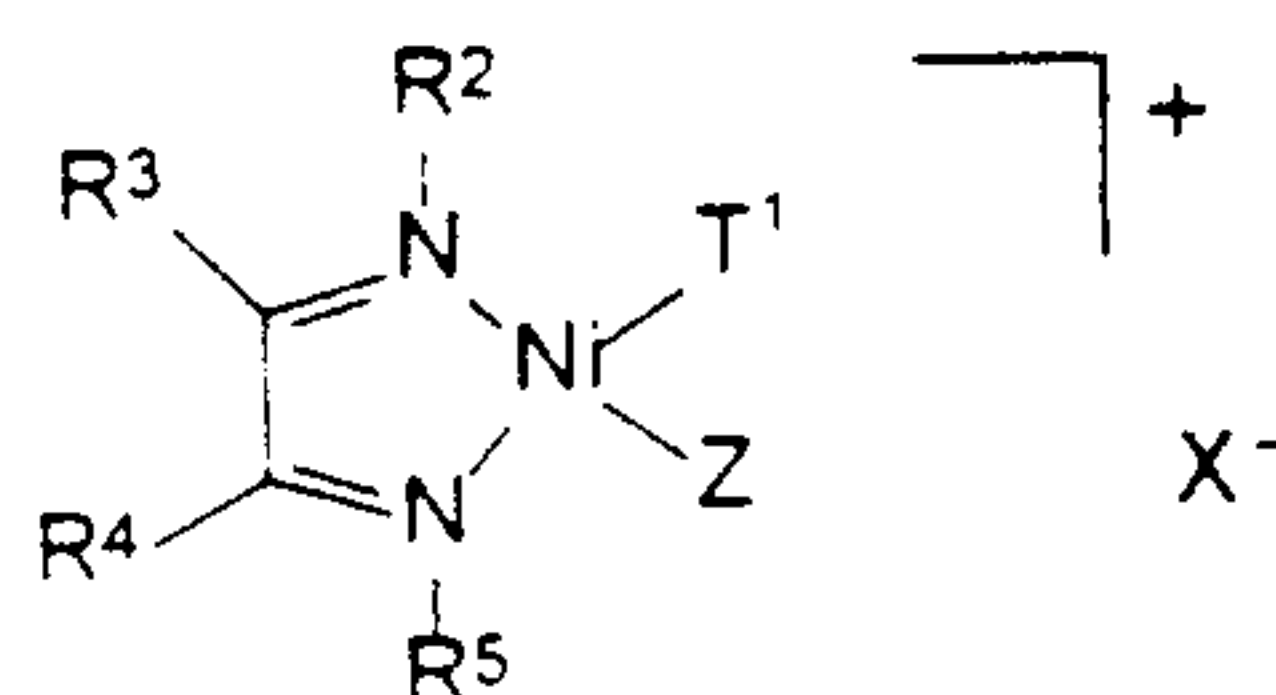
together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

Q and S are each independently chlorine, bromine, iodine or alkyl; and

5 wherein an α -olefin containing 4 to 40 carbon atoms is produced.

This invention also concerns a process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$:

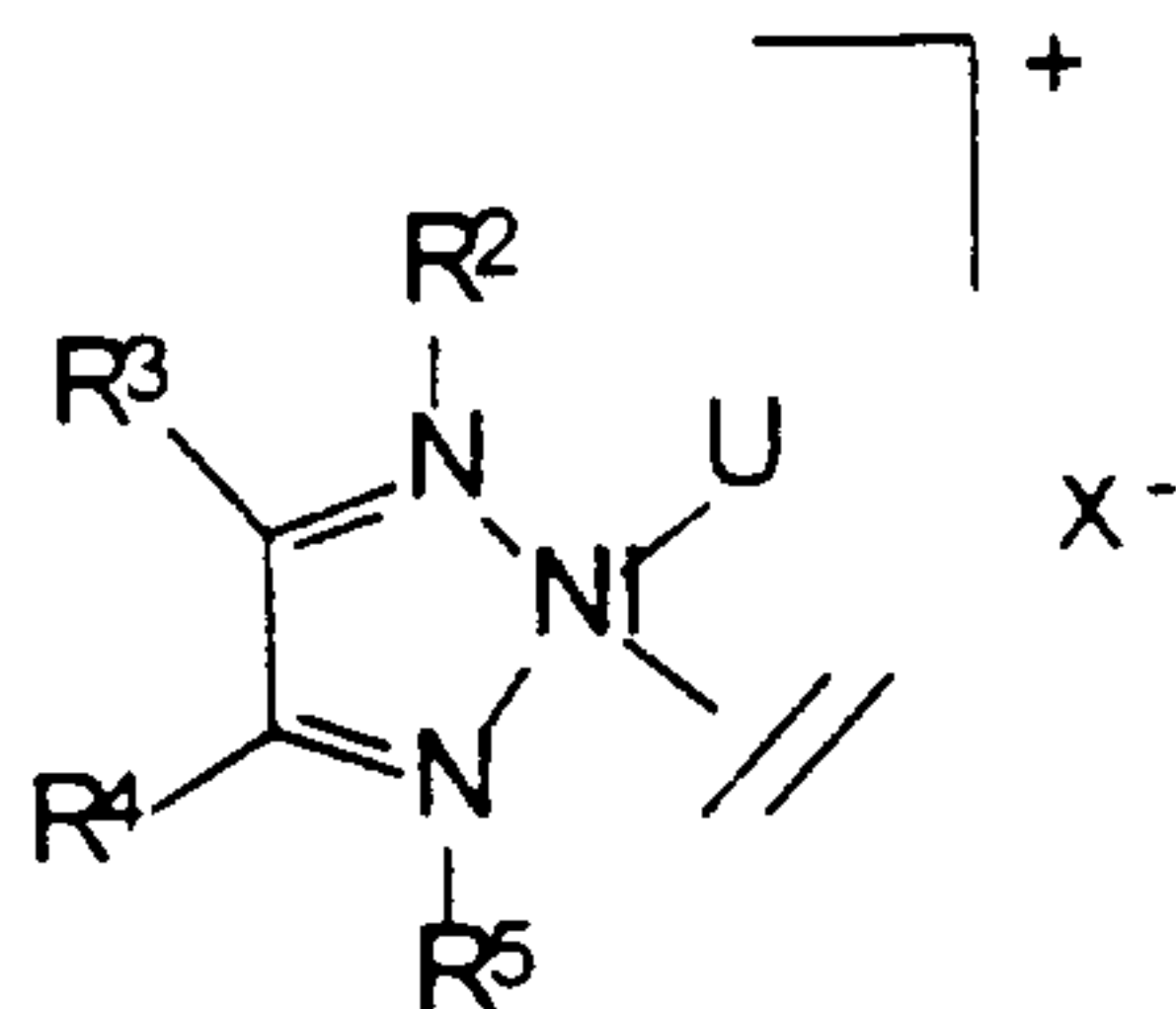
10 ethylene and a compound of the formula



(III)

or

15



(XXXIV)

wherein:

20 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted

25 hydrocarbylene to form a ring;

T^1 is hydrogen or n-alkyl containing up to 38 carbon atoms;

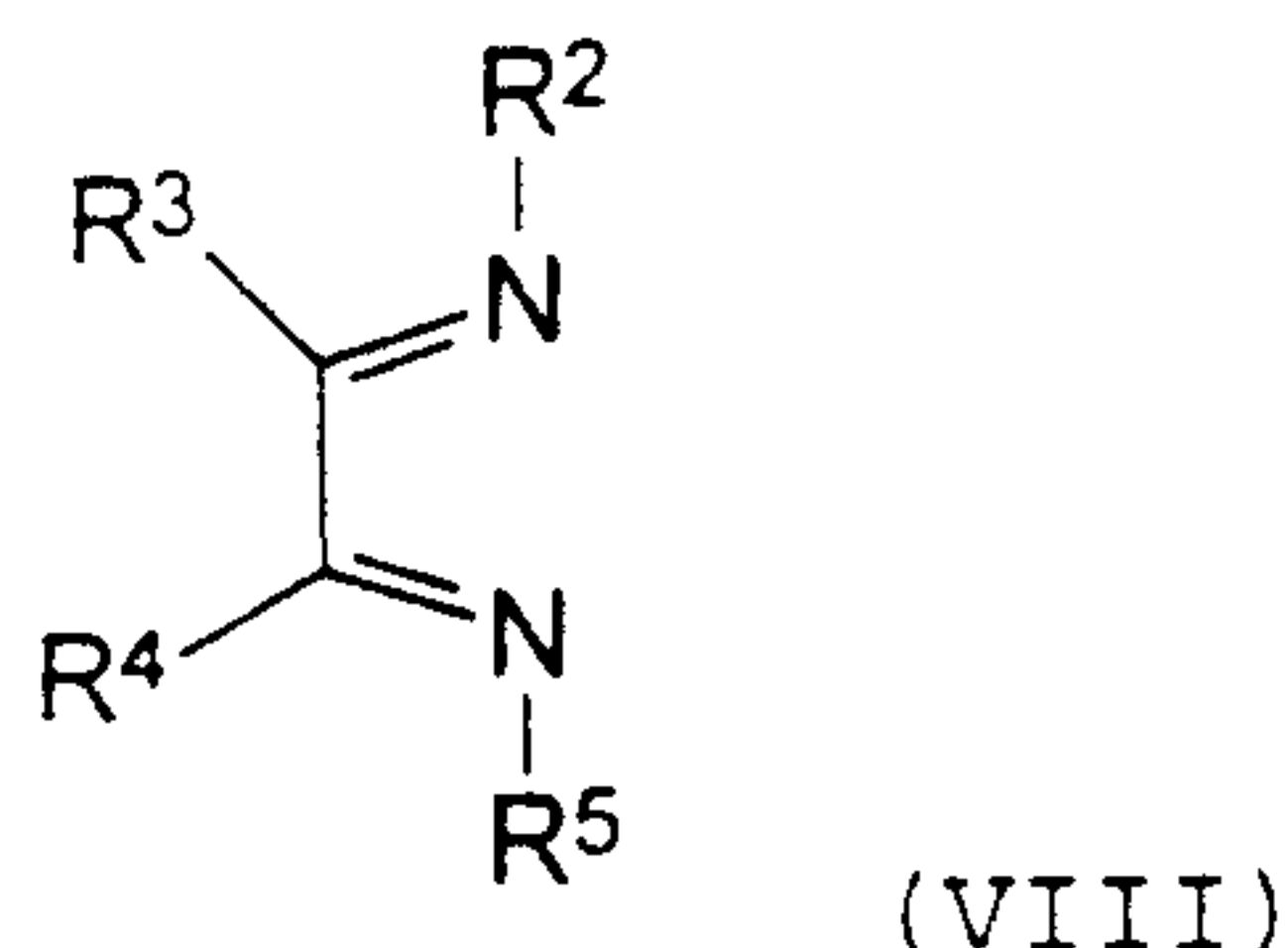
Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if

the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6;

U is n-alkyl containing up to 38 carbon atoms;
5 and

X is a noncoordinating anion;
and wherein an α -olefin containing 4 to 40 carbon atoms is produced.

Another novel process is a process for the
10 formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$:
ethylene;
and a Ni[III] of



15

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

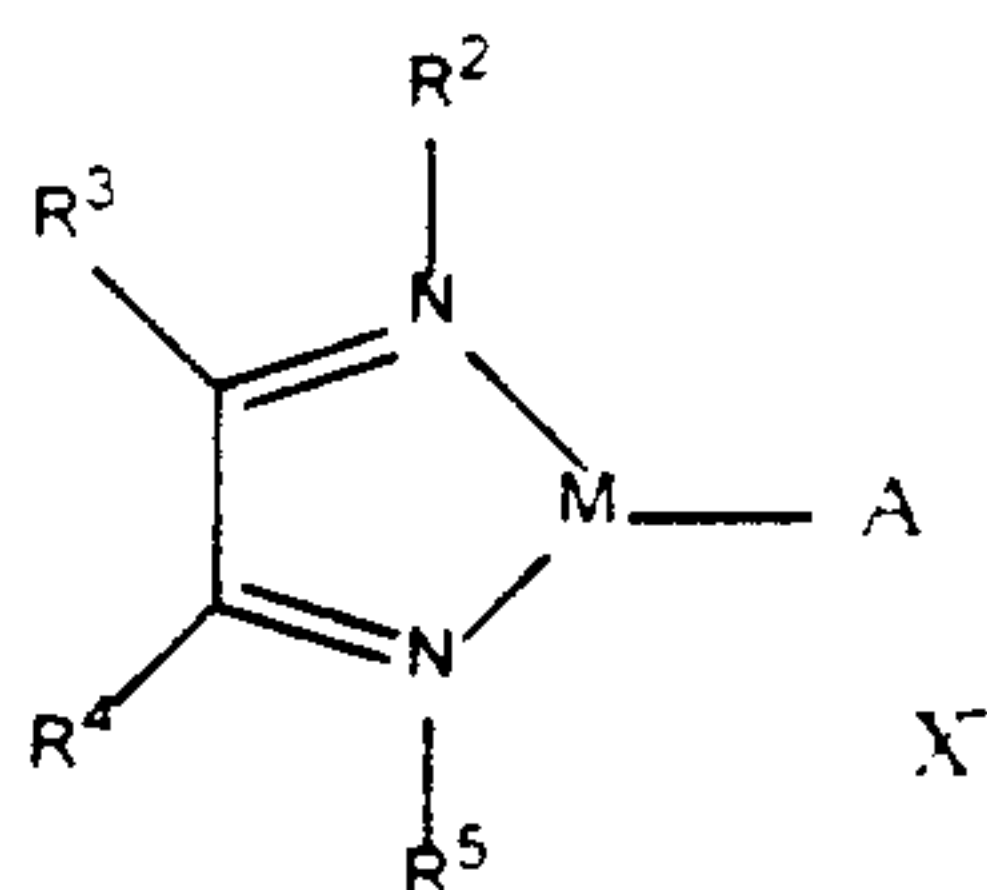
20

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring and

wherein an α -olefin containing 4 to 40 carbon
25 atoms is produced.

Also described herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about 0°C to about $+200^{\circ}\text{C}$, a compound of the formula

30



XXXVII

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula
 5 $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

M is Ni(II) or Pd(II);

A is a π -allyl or π -benzyl group;

10 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

15 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

20 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

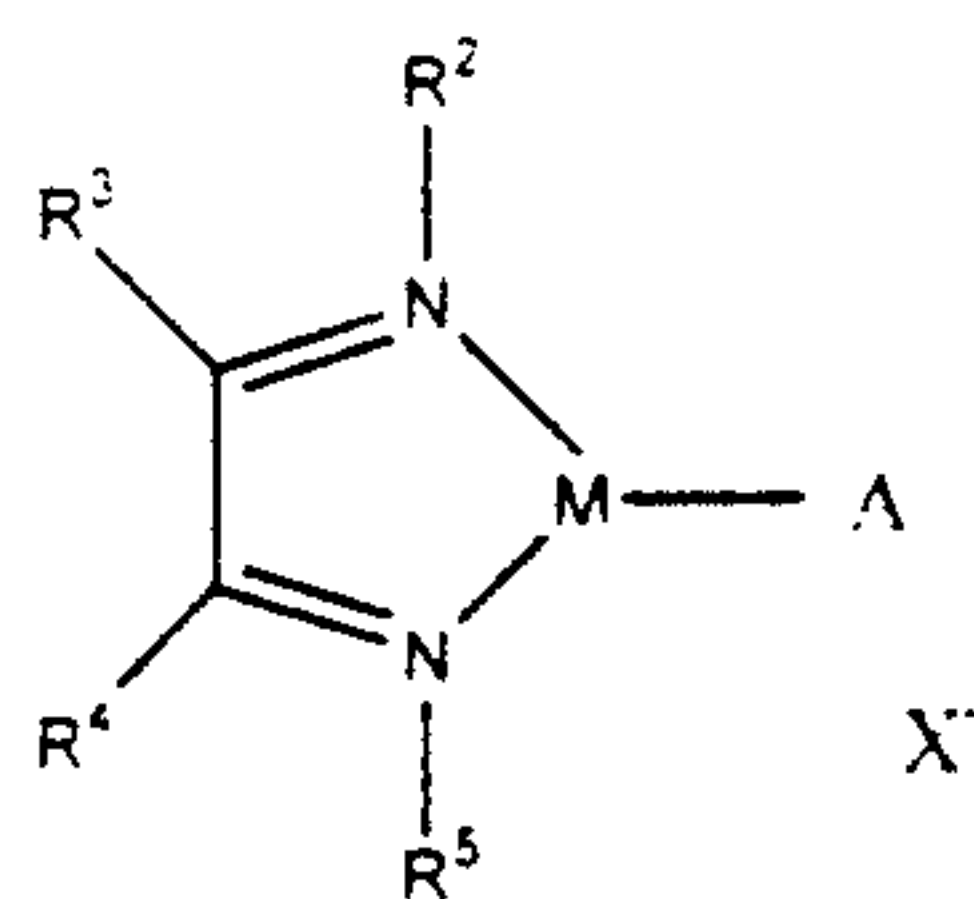
and X is a weakly coordinating anion;

and provided that:

25 when M is Pd a diene is not present; and
 when norbornene or substituted norbornene is present, no other monomer is present.

The invention also includes a compound of the formula

30



XXXVII

wherein:

M is Ni(II) or Pd(II);

A is a π -allyl or π -benzyl group;

5 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

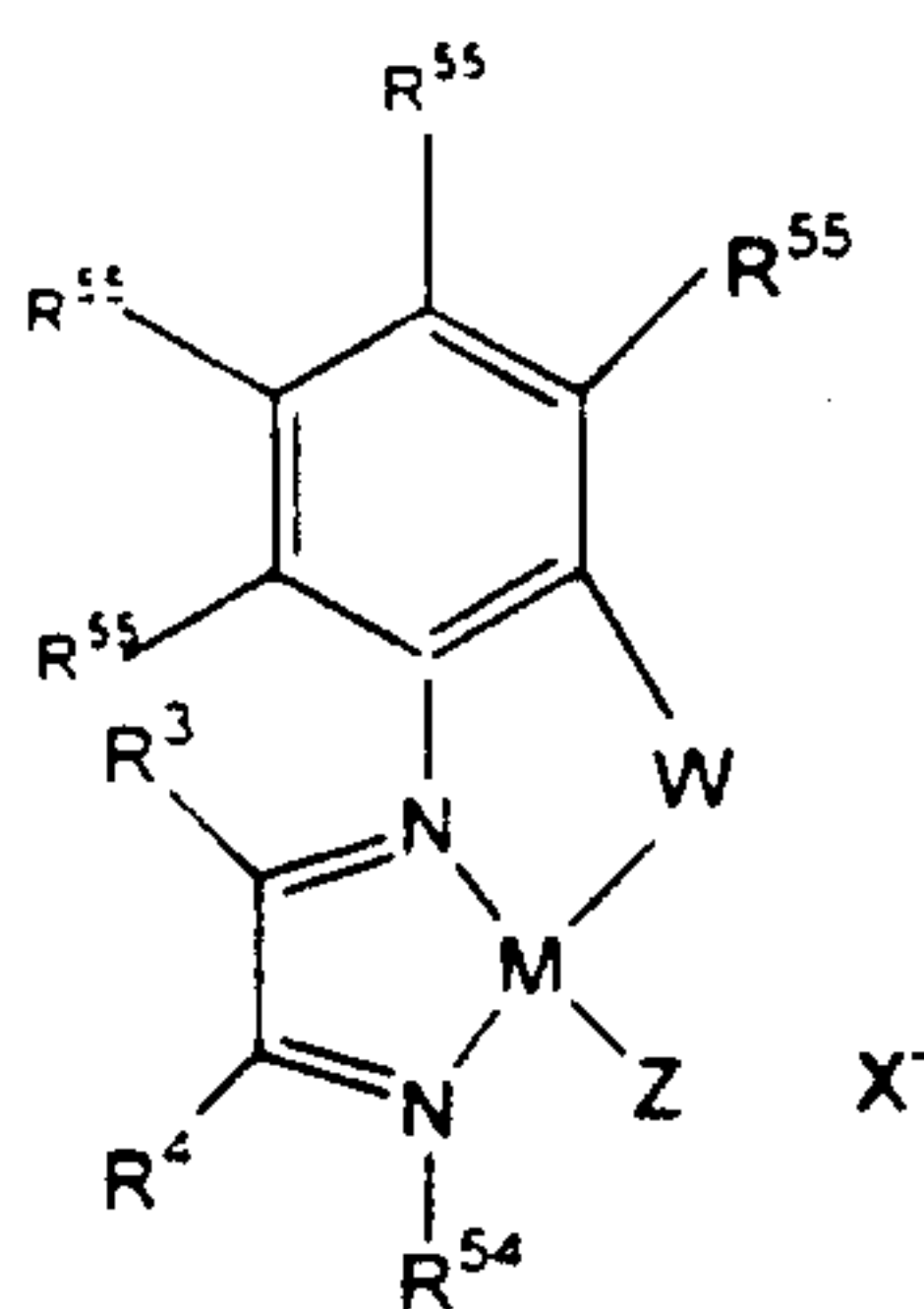
10 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

15 each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

and X is a weakly coordinating anion;

20 and provided that when M is Pd a diene is not present.

This invention also includes a compound of the formula



(XXXVIII)

25

wherein:

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken
5 together are hydrocarbylene or substituted hydrocarbylene to form a ring;

R^{54} is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound
10 to it;

each R^{55} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene
15 containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is
20 less than about 6, or an olefin of the formula $R^{17}CH=CHR^{17}$;

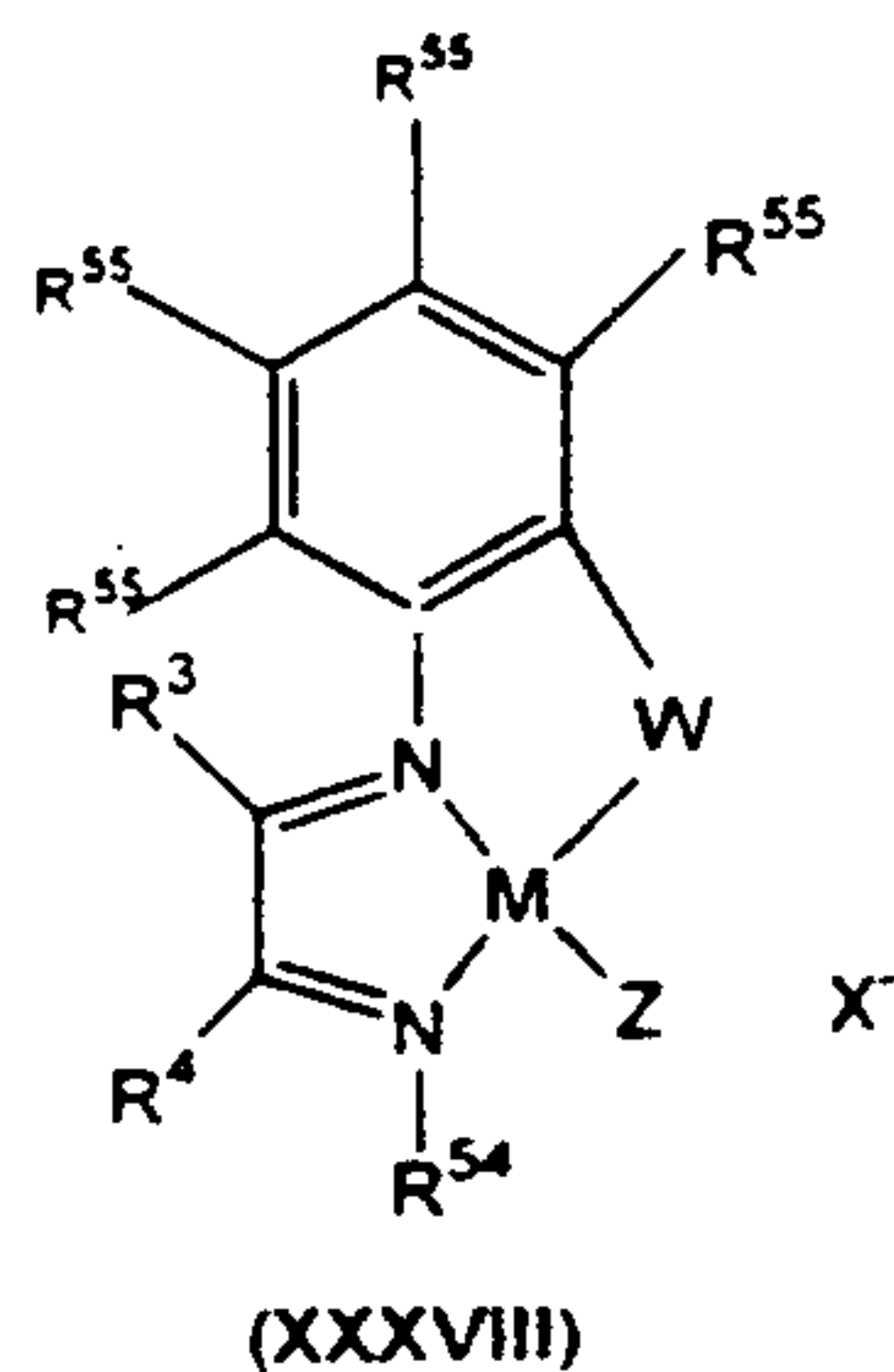
each R^{17} is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and

X is a weakly coordinating anion;

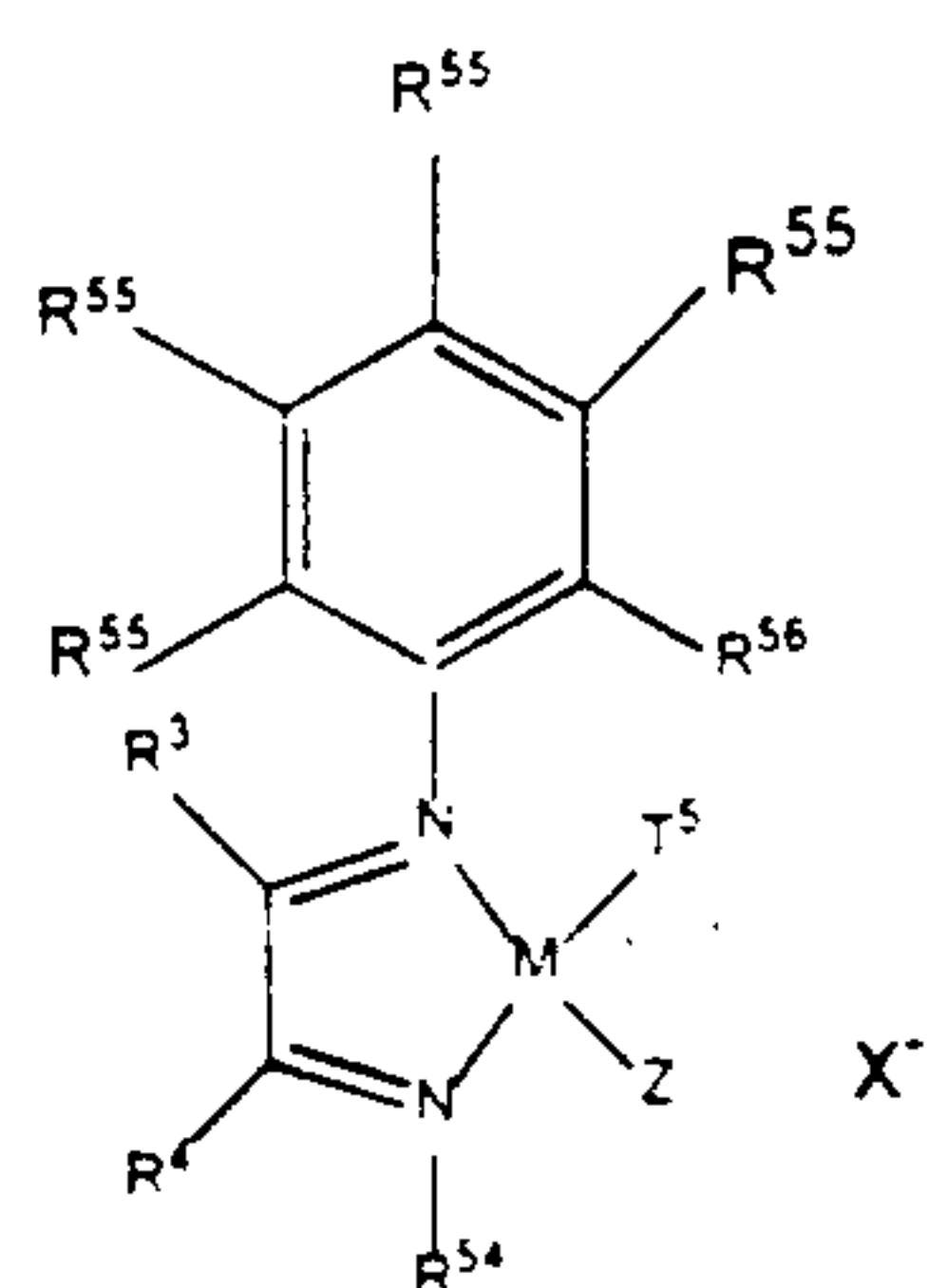
25 and provided that when M is Ni, W is alkylene and each R^{17} is independently hydrogen or saturated hydrocarbyl.

This invention also includes a process for the production of a compound of the formula

30



comprising, heating a compound of the formula



(XXXIX)

at a temperature of about -30°C to about $+100^{\circ}$ for a
 5 sufficient time to produce (XXXVIII), and wherein:

R^3 and R^4 are each independently hydrogen,
 hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken
 together are hydrocarbylene or substituted
 hydrocarbylene to form a ring;

10 R^{54} is hydrocarbyl or substituted hydrocarbyl,
 provided that the carbon atom bound directly to the
 imino nitrogen atom has at least two carbon atoms bound
 to it;

each R^{55} is independently hydrogen,
 15 hydrocarbyl, substituted hydrocarbyl, or a functional
 group;

R^{56} is alkyl containing 2 to 30 carbon atoms;

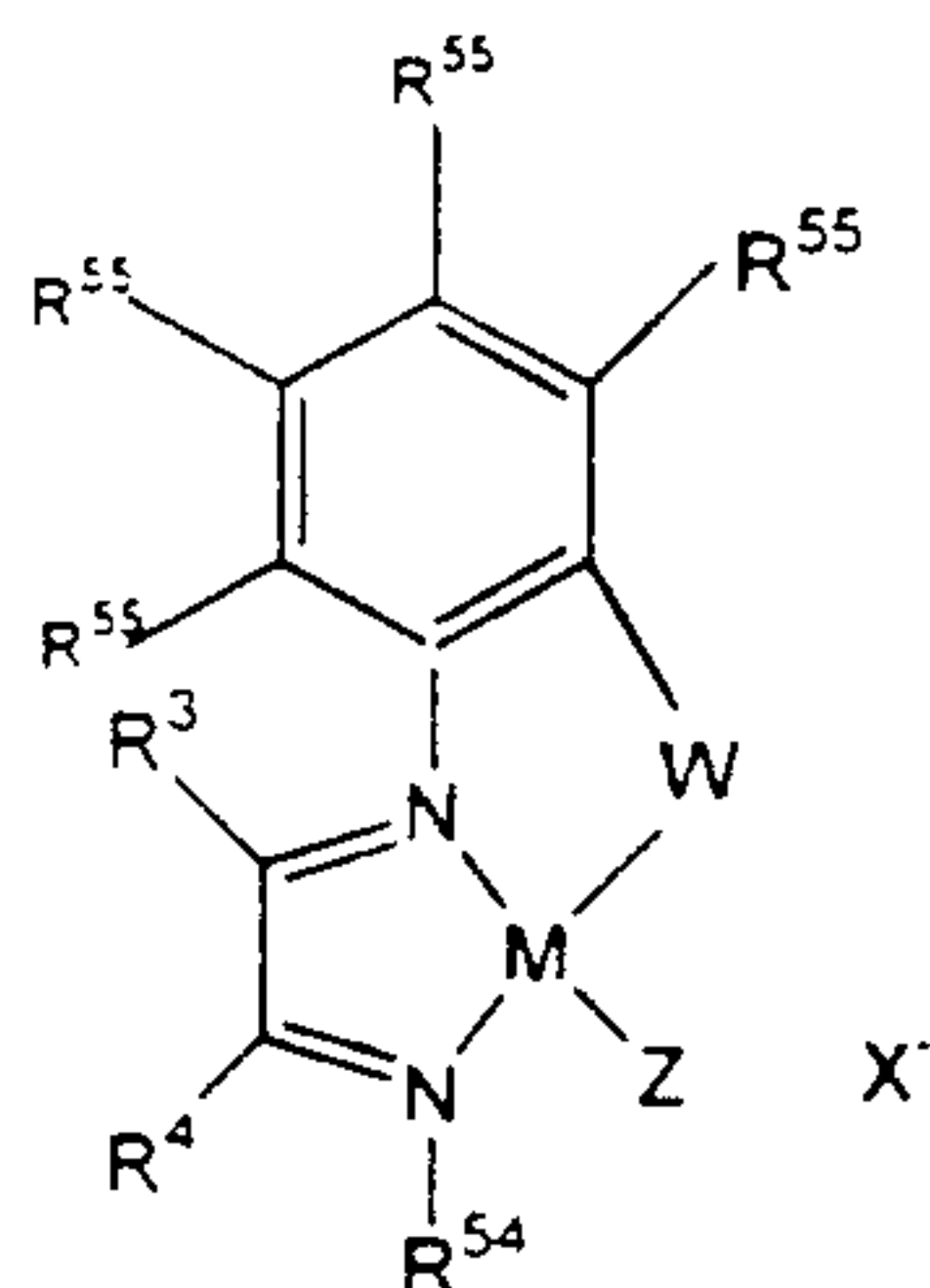
T^5 is alkyl;

W is alkylene containing 2 to 30 carbon atoms;

20 Z is a neutral Lewis base wherein the donating
 atom is nitrogen, sulfur, or oxygen, provided that if
 the donating atom is nitrogen then the pKa of the
 conjugate acid of that compound (measured in water) is
 less than about 6; and

25 X is a weakly coordinating anion.

This invention also concerns a process for the
 polymerization of olefins, comprising, contacting a
 compound of the formula



(XXXVIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

R^{54} is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each R^{55} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula $R^{17}CH=CHR^{17}$;

each R^{17} is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and

X is a weakly coordinating anion;

and provided that:

when M is Ni, W is alkylene and each R^{17} is independently hydrogen or saturated hydrocarbyl;

and when norbornene or substituted norbornene is present, no other monomer is present.

This invention also concerns a homopolypropylene containing about 10 to about 700 δ^+ methylene groups per 1000 total methylene groups in said homopolypropylene.

Described herein is a homopolypropylene wherein the ratio of $\delta^+:\gamma$ methylene groups is about 0.5 to about 7.

Also included herein is a homopolypropylene in which about 30 to about 85 mole percent of the monomer units are enchaind in an $\omega,1$ fashion.

DETAILS OF THE INVENTION

Herein certain terms are used to define certain chemical groups or compounds. These terms are defined below.

- A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

- By "not containing olefinic or acetylenic bonds" is meant the grouping does not contain olefinic carbon-carbon double bonds (but aromatic rings are not excluded) and carbon-carbon triple bonds.

- By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.

- By an alkyl aluminum compound is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide,

- By "hydrocarbylene" herein is meant a divalent group containing only carbon and hydrogen.



10

• By "substituted hydrocarbylene" herein is meant a hydrocarbylene group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbylene groups herein contain 1 to about 30 carbon atoms. Included within the meaning of "substituted" are heteroaromatic rings.

• By "saturated hydrocarbonyl" is meant a univalent group containing only carbon and hydrogen which contains no unsaturation, such as olefinic, acetylenic, or aromatic groups. Examples of such groups include alkyl and cycloalkyl. If not otherwise

stated, it is preferred that saturated hydrocarbonyl groups herein contain 1 to about 30 carbon atoms.

- By "neutral Lewis base" is meant a compound, which is not an ion, which can act as a Lewis base.

5 Examples of such compounds include ethers, amines, sulfides, and organic nitriles.

- By "cationic Lewis acid" is meant a cation which can act as a Lewis acid. Examples of such cations are sodium and silver cations.

10

- By " α -olefin" is meant a compound of the formula $\text{CH}_2=\text{CHR}^{19}$, wherein R^{19} is n-alkyl or branched alkyl, preferably n-alkyl.

- By "linear α -olefin" is meant a compound of the formula $\text{CH}_2=\text{CHR}^{19}$, wherein R^{19} is n-alkyl. It is preferred that the linear α -olefin have 4 to 40 carbon atoms.

- By a "saturated carbon atom" is meant a carbon atom which is bonded to other atoms by single bonds only. Not included in saturated carbon atoms are carbon atoms which are part of aromatic rings.

- By a quaternary carbon atom is meant a saturated carbon atom which is not bound to any hydrogen atoms. A preferred quaternary carbon atom is bound to four other carbon atoms.

25

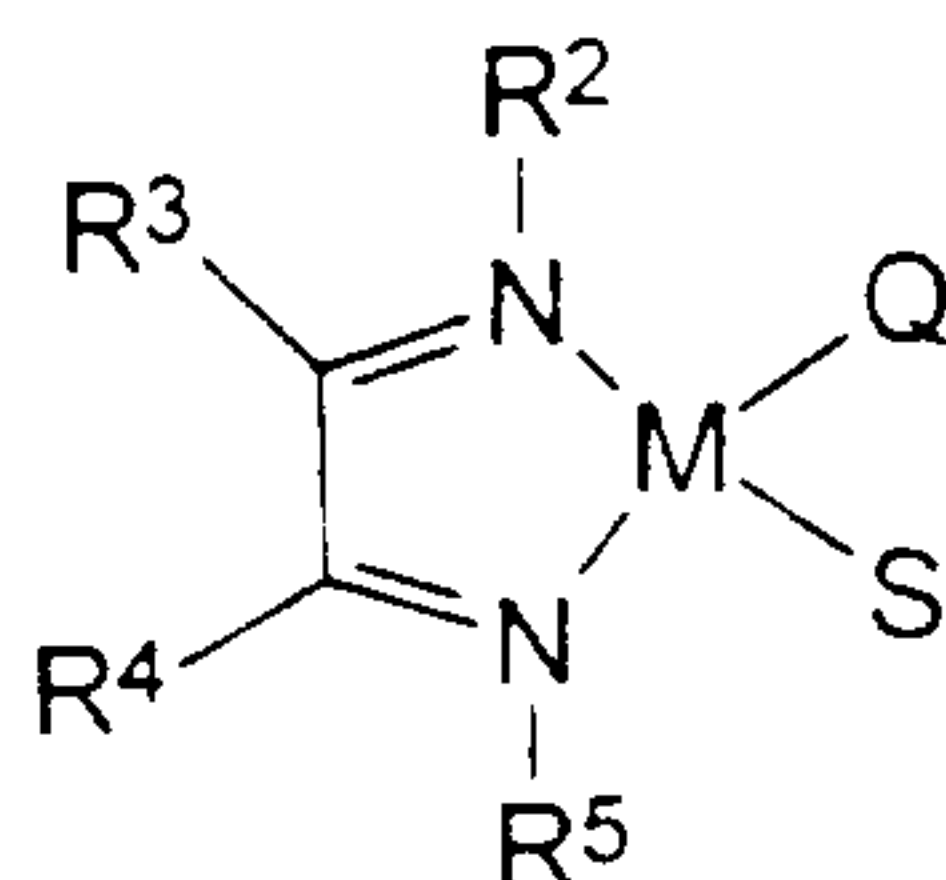
- By an olefinic bond is meant a carbon-carbon double bond, but does not include bonds in aromatic rings.

- By a rare earth metal is meant one of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or lutetium.

This invention concerns processes for making polymers, comprising, contacting one or more selected olefins or cycloolefins, and optionally an ester or carboxylic acid of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^2$, and other selected monomers, with a transition metal containing catalyst (and possibly other catalyst

components). Such catalysts are, for instance, various complexes of a diimine with these metals. By a "polymerization process herein (and the polymers made therein)" is meant a process which produces a polymer with a degree of polymerization (DP) of about 20 or more, preferably about 40 or more [except where otherwise noted, as in P in compound (VI)] By "DP" is meant the average number of repeat (monomer) units in the polymer.

One of these catalysts may generally be written as

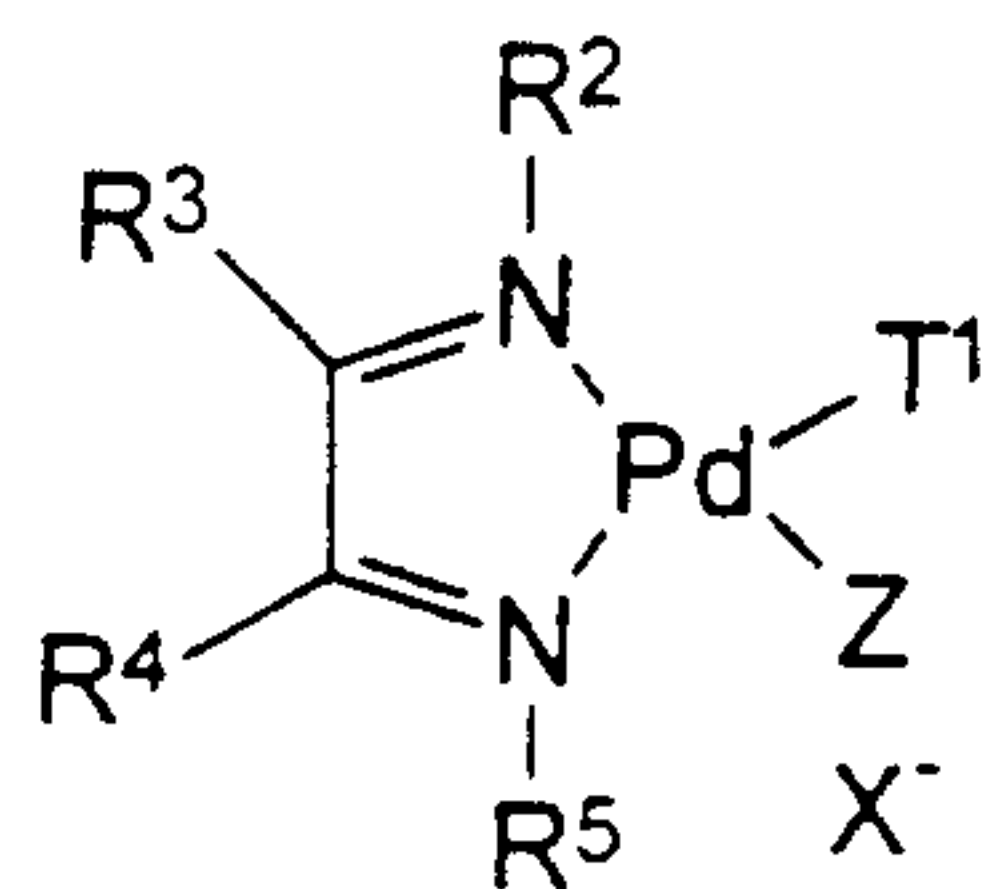


(I)

wherein: M is Ni(II), Co(II), Fe(II) or Pd(II); R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; Q is alkyl, hydride, chloride, iodide, or bromide; and S is alkyl, hydride, chloride, iodide, or bromide. Preferably M is Ni(II) or Pd(II).

In a preferred form of (I), R³ and R⁴ are each independently hydrogen or hydrocarbyl. If Q and/or S is alkyl, it is preferred that the alkyl contains 1 to 4 carbon atoms, and more preferably is methyl.

Another useful catalyst is

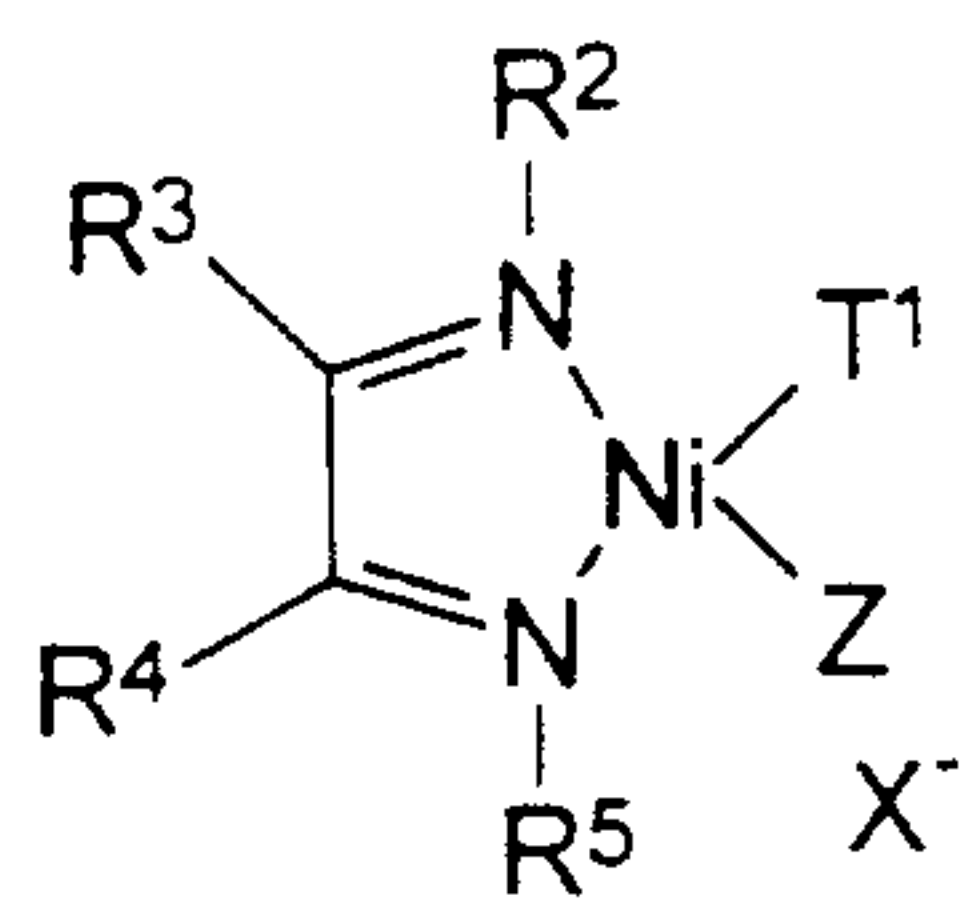


(II)

wherein: R^2 and R^5 are each independently hydrocarbyl
 5 or substituted hydrocarbyl, provided that the carbon
 atom bound to the imino nitrogen atom has at least two
 carbon atoms bound to it; R^3 and R^4 are each
 independently hydrogen, hydrocarbyl, substituted
 hydrocarbyl or R^3 and R^4 taken together are
 10 hydrocarbylene or substituted hydrocarbylene to form a
 ring; T^1 is hydrogen, hydrocarbyl not containing
 olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$; Z
 is a neutral Lewis base wherein the donating atom is
 nitrogen, sulfur or oxygen, provided that, if the
 15 donating atom is nitrogen, then the pKa of the
 conjugate acid of that compound is less than about 6; X^-
 is a weakly coordinating anion; and R^{15} is hydrocarbyl
 not containing olefinic or acetylenic bonds.

In one preferred form of (II), R^3 and R^4 are each
 20 independently hydrogen or hydrocarbyl. In a more
 preferred form of (II), T^1 is alkyl, and T^1 is
 especially preferably methyl. It is preferred that Z
 is R^6_2O or R^7CN , wherein each R^6 is independently
 hydrocarbyl and R^7 is hydrocarbyl. It is preferred that
 25 R^6 and R^7 are alkyl, and it is more preferred that they
 are methyl or ethyl. It is preferred that X^- is BAF ,
 SbF_6 , PF_6 or BF_4 .

Another useful catalyst is



(III)

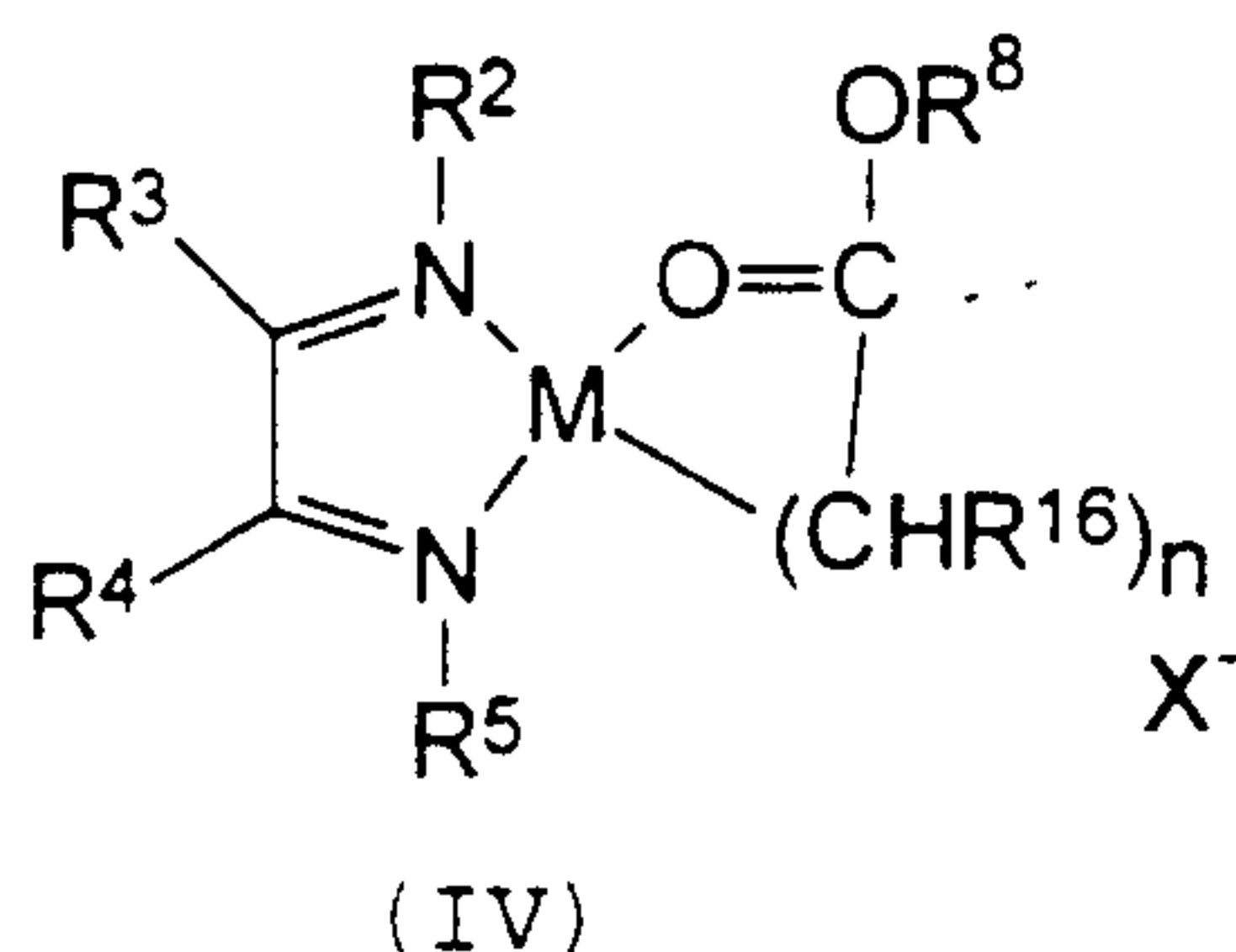
wherein: R^2 and R^5 are each independently hydrocarbyl
 5 or substituted hydrocarbyl, provided that the carbon
 atom bound to the imino nitrogen atom has at least two
 carbon atoms bound to it; R^3 and R^4 are each
 independently hydrogen, hydrocarbyl, or substituted
 hydrocarbylene, or R^3 and R^4 taken together are
 10 hydrocarbylene or substituted hydrocarbylene to form a
 ring; T^1 is hydrogen, hydrocarbyl not containing
 olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$; Z
 is a neutral Lewis base wherein the donating atom is
 nitrogen, sulfur or oxygen, provided that if the
 15 donating atom is nitrogen then the pK_a of the conjugate
 acid of that compound is less than about 6; X is a
 weakly coordinating anion; and R^{15} is hydrocarbyl not
 containing olefinic or acetylenic bonds.

In one preferred form of (III), R^3 and R^4 are each
 20 independently hydrogen, hydrocarbyl. In a more
 preferred form of (III) T^1 is alkyl, and T^1 is
 especially preferably methyl. It is preferred that Z
 is R^6_2O or R^7CN , wherein each R^6 is independently
 hydrocarbyl and R^7 is hydrocarbyl. It is preferred
 25 that R^6 and R^7 are alkyl, and it is especially preferred
 that they are methyl or ethyl. It is preferred that X^-
 is BAF^- , SbF_6^- , PF_6^- or BF_4^- .

Relatively weakly coordinating anions are known to
 the artisan. Such anions are often bulky anions,
 30 particularly those that may delocalize their negative
 charge. Suitable weakly coordinating anions in this
 Application include $(Ph)_4B^-$ (Ph = phenyl),
 tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (herein

abbreviated BAF), PF_6^- , BF_4^- , SbF_6^- , trifluoromethanesulfonate, p-toluenesulfonate, $(\text{R}_f\text{SO}_2)_2\text{N}^-$, and $(\text{C}_6\text{F}_5)_4\text{B}^-$. Preferred weakly coordinating anions include BAF^- , PF_6^- , BF_4^- , and SbF_6^- .

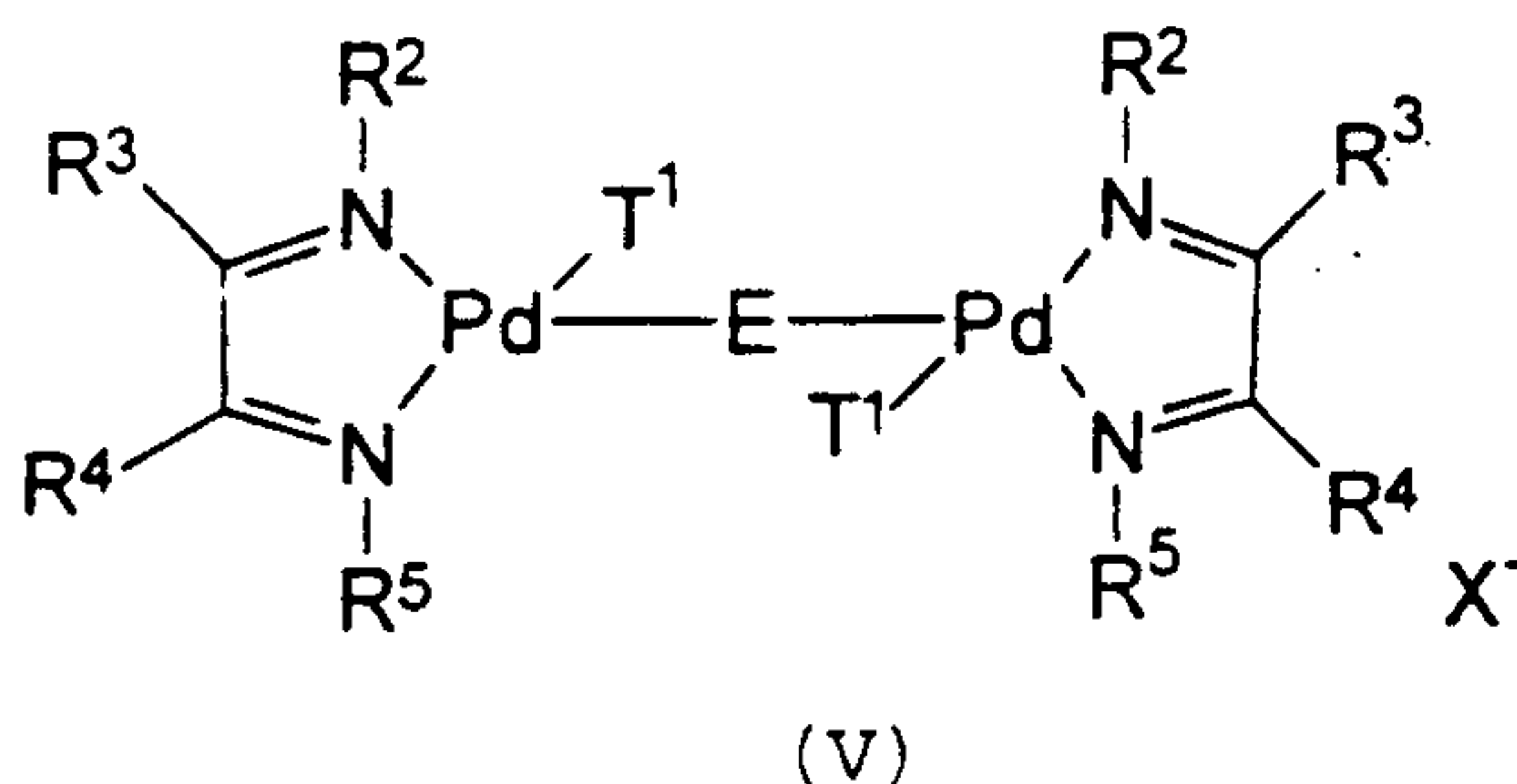
- 5 Also useful as a polymerization catalyst is a compound of the formula



- 10 wherein: R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R^3 and R^4 are each
 15 independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; M is $\text{Ni}(\text{II})$ or $\text{Pd}(\text{II})$; each R^{16} is independently hydrogen or alkyl containing 1 to 10 carbon atoms; n is
 20 1, 2, or 3; X is a weakly coordinating anion; and R^8 is hydrocarbyl.

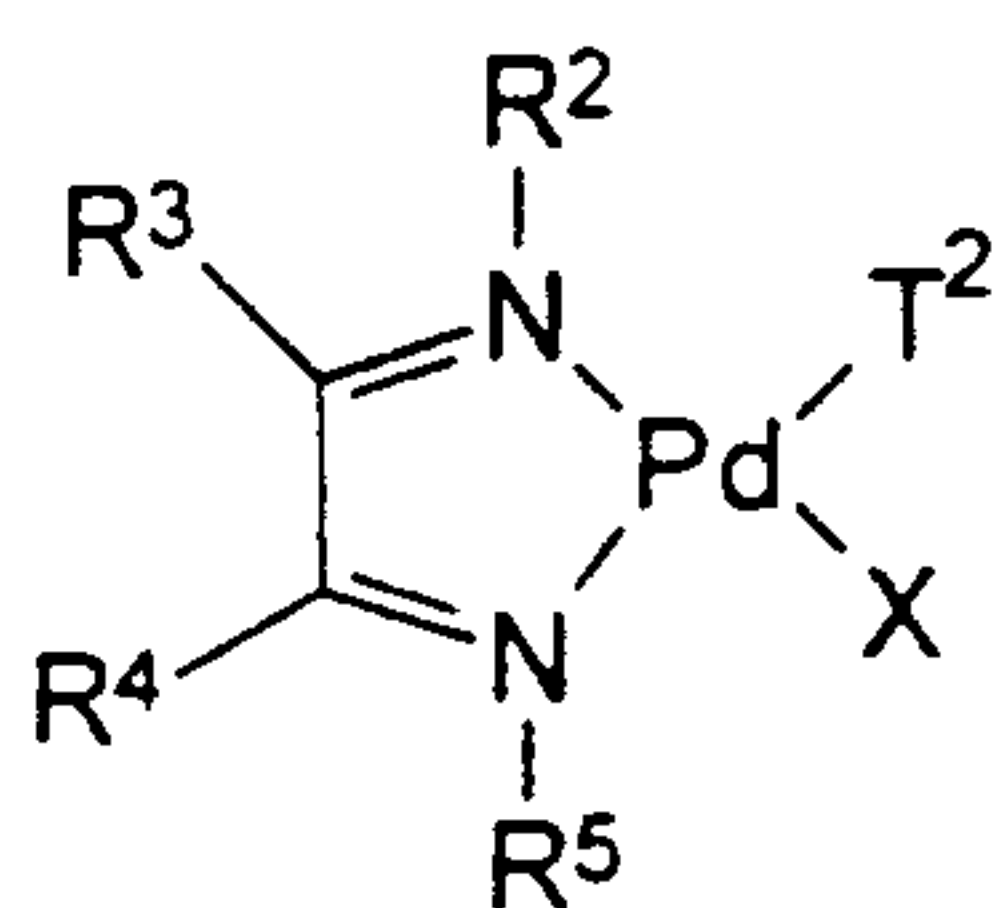
- It is preferred that n is 3, and all of R^{16} are hydrogen. It is also preferred that R^8 is alkyl or substituted alkyl, especially preferred that it is
 25 alkyl, and more preferred that R^8 is methyl.

Another useful catalyst is



wherein: R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$; R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds; E is halogen or $-OR^{18}$; R^{18} is hydrocarbyl not containing olefinic or acetylenic bonds; and X is a weakly coordinating anion. It is preferred that T^1 is alkyl containing 1 to 4 carbon atoms, and more preferred that it is methyl. In other preferred compounds (V), R^3 and R^4 are methyl or hydrogen and R^2 and R^5 are 2,6-diisopropylphenyl and X is BAF. It is also preferred that E is chlorine.

Another useful catalyst is a compound of the formula



(VII)

25

wherein: R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a

ring; T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$; R^{15} is
5 hydrocarbyl not containing olefinic or acetylenic bonds; and X is a weakly coordinating anion. In a more preferred form of (VII), T^2 is alkyl containing 1 to 4 carbon atoms and T^2 is especially preferably methyl. It is preferred that X is perfluoroalkylsulfonate,
10 especially trifluoromethanesulfonate (triflate). If X^- is an extremely weakly coordinating anion such as BAF^- , (VII) may not form. Thus it may be said that (VII) forms usually with weakly, but perhaps not extremely weakly, coordinating anions.

15 In all compounds, intermediates, catalysts, processes, etc. in which they appear it is preferred that R^2 and R^5 are each independently hydrocarbyl, and in one form it is especially preferred that R^2 and R^5 are both 2,6-diisopropylphenyl, particularly when R^3
20 and R^4 are each independently hydrogen or methyl. It is also preferred that R^3 and R^4 are each independently hydrogen, hydrocarbyl or taken together hydrocarbylene to form a carbocyclic ring.

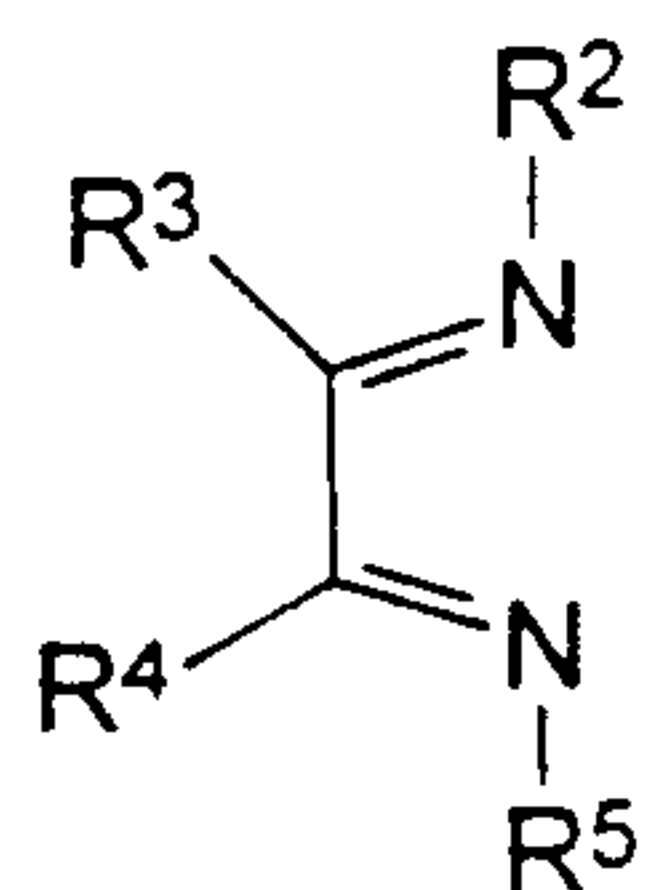
Compounds of the formula (I) wherein M is Pd, Q is
25 alkyl and S is halogen may be made by the reaction of the corresponding 1,5-cyclooctadiene (COD) Pd complex with the appropriate diimine. When M is Ni, (I) can be made by the displacement of a another ligand, such as a dialkylether or a polyether such as 1,2-
30 dimethoxyethane, by an appropriate diimine.

Catalysts of formula (II), wherein X^- is BAF^- , may be made by reacting a compound of formula (I) wherein Q is alkyl and S is halogen, with about one equivalent of an alkali metal salt, particularly the sodium salt, of
35 $HBAF$, in the presence of a coordinating ligand, particularly a nitrile such as acetonitrile. When X^- is an anion such as BAF^- , SbF_6^- or BF_4^- the same

starting palladium compound can be reacted with the silver salt AgX.

However, sometimes the reaction of a diimine with a 1,5-COD Pd complex as described above to make compounds of formula (II) may be slow and/or give poor conversions, thereby rendering it difficult to make the starting material for (II) using the method described in the preceding paragraph. For instance when:
 5 $R^2=R^5=Ph_2CH-$ and $R^3=R^4=H$; $R^2=R^5=Ph-$ and $R^3=R^4=Ph$; $R^2=R^5=2-$
 10 t -butylphenyl and $R^3=R^4=CH_3$; $R^2=R^5=\alpha$ -naphthyl and $R^3=R^4=CH_3$; and $R^2=R^5=2$ -phenylphenyl and $R^3=R^4=CH_3$, difficulty may be encountered in making a compound of formula (II).

In these instances it has been found more convenient to prepare (II) by reacting $[(\eta^4-1,5-COD)PdT^+Z]^+X^-$, wherein T^+ and X^- are as defined above and Z is an organic nitrile ligand, preferably in an organic nitrile solvent, with a diimine of the formula



20

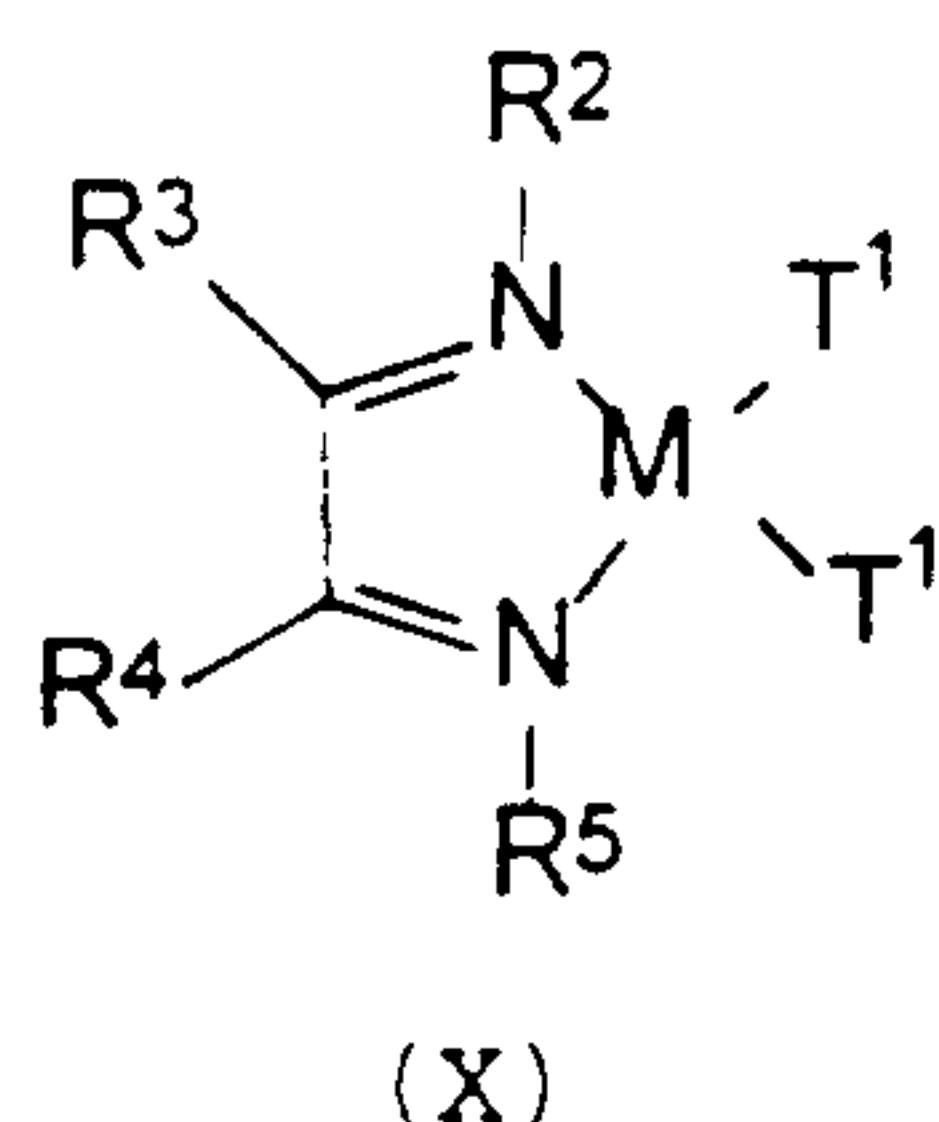
(VIII)

By a "nitrile solvent" is meant a solvent that is at least 20 volume percent nitrile compound. The product of this reaction is (II), in which the Z ligand is the nitrile used in the synthesis. In a preferred synthesis, T^+ is methyl and the nitrile used is the same as in the starting palladium compound, and is more preferably acetonitrile. The process is carried out in solution, preferably when the nitrile is substantially all of the solvent, at a temperature of about $-40^\circ C$ to about $+60^\circ C$, preferably about $0^\circ C$ to about $30^\circ C$. It is

preferred that the reactants be used in substantially equimolar quantities.

The compound $[(\eta^4-1,5-COD)PdT^1Z]^+X^-$, wherein T^1 is alkyl, Z is an organic nitrile and X is a weakly coordinating anion may be made by the reaction of $[(\eta^4-1,5-COD)PdT^1A]$, wherein A is Cl, Br or I and T^1 is alkyl with the silver salt of X^- , AgX, or if X is BAF with an alkali metal salt of HBAF, in the presence of an organic nitrile, which of course will become the ligand T^1 . In a preferred process A is Cl, T^1 is alkyl, more preferably methyl, and the organic nitrile is an alkyl nitrile, more preferably acetonitrile. The starting materials are preferably present in approximately equimolar amounts, except for the nitrile which is present preferably in excess. The solvent is preferably a non-coordinating solvent such as a halocarbon. Methylene chloride is useful as such a solvent. The process preferably is carried out at a temperature of about $-40^\circ C$ to about $+50^\circ C$. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen.

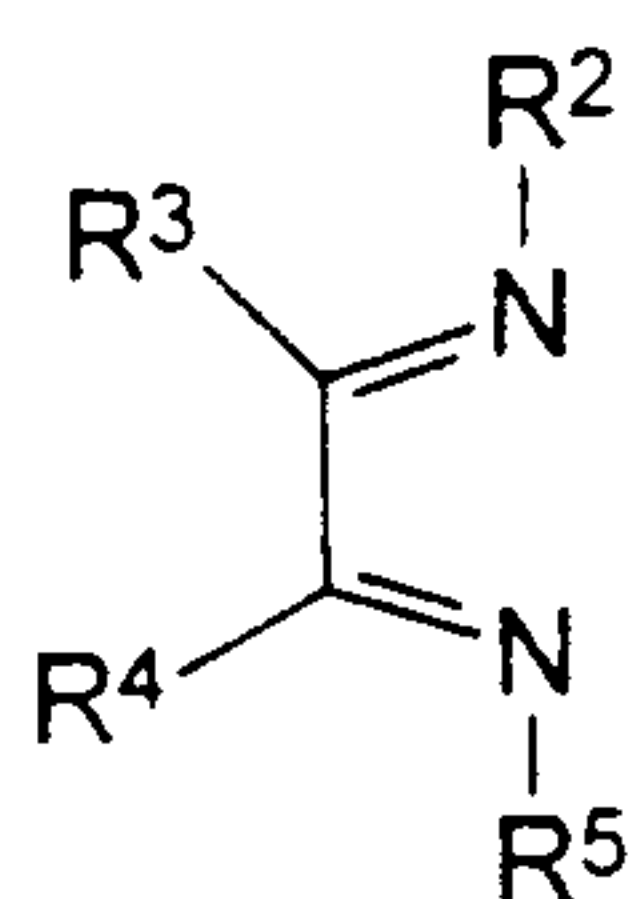
Compounds of formula (II) [or (III) when the metal is nickel] can also be made by the reaction of



with a source of the conjugate acid of the anion X, the acid HX or its equivalent (such as a trityl salt) in the presence of a solvent which is a weakly coordinating ligand such as a dialkyl ether or an alkyl

nitrile. It is preferred to carry out this reaction at about -80°C to about 30°C .

Compounds of formula (XXXXI) can be made by a process, comprising, contacting, at a temperature of about -80°C to about $+20^{\circ}\text{C}$, a compound of the formula (η^4 -1,5-COD)PdMe₂ and a diimine of the formula



(VIII)

10

wherein: COD is 1,5-cyclooctadiene; R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring. It is preferred that the temperature is about -50°C to about $+10^{\circ}\text{C}$. It is also preferred that the two starting materials be used in approximately equimolar quantities, and/or that the reaction be carried out in solution. It is preferred that R^2 and R^5 are both 2-t-butylphenyl or 2,5-di-t-butylphenyl and that R^3 and R^4 taken together are An, or R^3 and R^4 are both hydrogen or methyl.

Compounds of formula (IV) can be made by several routes. In one method a compound of formula (II) is reacted with an acrylate ester of the formula $\text{CH}_2=\text{CHCO}_2\text{R}^1$ wherein R^1 is as defined above. This reaction is carried out in a non-coordinating solvent such as methylene chloride, preferably using a greater than 1 to 50 fold excess of the acrylate ester. In a

30

preferred reaction, Q is methyl, and R⁺ is alkyl containing 1 to 4 carbon atoms, more preferably methyl. The process is carried out at a temperature of about -100°C to about +100°C, preferably about 0°C to about 50°C. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen

Alternatively, (IV) may be prepared by reacting (I), wherein Q is alkyl and S is Cl, Br or I with a source of an appropriate weakly coordinating anion such as AgX or an alkali metal salt of BAF and an acrylate ester (formula as immediately above) in a single step. Approximately equimolar quantities of (I) and the weakly coordinating anion source are preferred, but the acrylate ester may be present in greater than 1 to 50 fold excess. In a preferred reaction, Q is methyl, and R⁺ is alkyl containing 1 to 4 carbon atoms, more preferably methyl. The process is preferably carried out at a temperature of about -100°C to about +100°C, preferably about 0°C to about 50°C. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen.

In another variation of the preparation of (IV) from (I) the source of the weakly coordinating anion is a compound which itself does not contain an anion, but which can combine with S [of (I)] to form such a weakly coordinating anion. Thus in this type of process by "source of weakly coordinating anion" is meant a compound which itself contains the anion which will become X⁻, or a compound which during the process can combine with other process ingredients to form such an anion.

Catalysts of formula (V), wherein X⁻ is BAF⁻, may be made by reacting a compound of formula (I) wherein Q

is alkyl and S is halogen, with about one-half or an equivalent of an alkali metal salt, particularly the sodium salt, of HBAF. Alternatively, (V) containing other anions may be prepared by reacting (I), wherein Q
5 is alkyl and S is Cl, Br or I with one-half equivalent of a source of an appropriate weakly coordinating anion such as AgX.

Some of the nickel and palladium compounds described above are useful in processes for
10 polymerizing various olefins, and optionally also copolymerizing olefinic esters, carboxylic acids, or other functional olefins, with these olefins. When (I) is used as a catalyst, a neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a
15 weakly coordinating anion is also present as part of the catalyst system (sometimes called a "first compound" in the claims). By a "neutral Lewis acid" is meant a compound which is a Lewis acid capable for abstracting Q⁻ or S⁻ from (I) to form a weakly
20 coordination anion. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF₅, Ar₃B (wherein Ar is aryl), and BF₃. By a cationic Lewis acid is meant a cation with a positive charge such as Ag⁺, H⁺, and Na⁺.

25 In those instances in which (I) (and similar catalysts which require the presence of a neutral Lewis acid or a cationic Lewis or Bronsted acid), does not contain an alkyl or hydride group already bonded to the metal (i.e., neither Q or S is alkyl or hydride), the
30 neutral Lewis acid or a cationic Lewis or Bronsted acid also alkylates or adds a hydride to the metal, i.e., causes an alkyl group or hydride to become bonded to the metal atom.

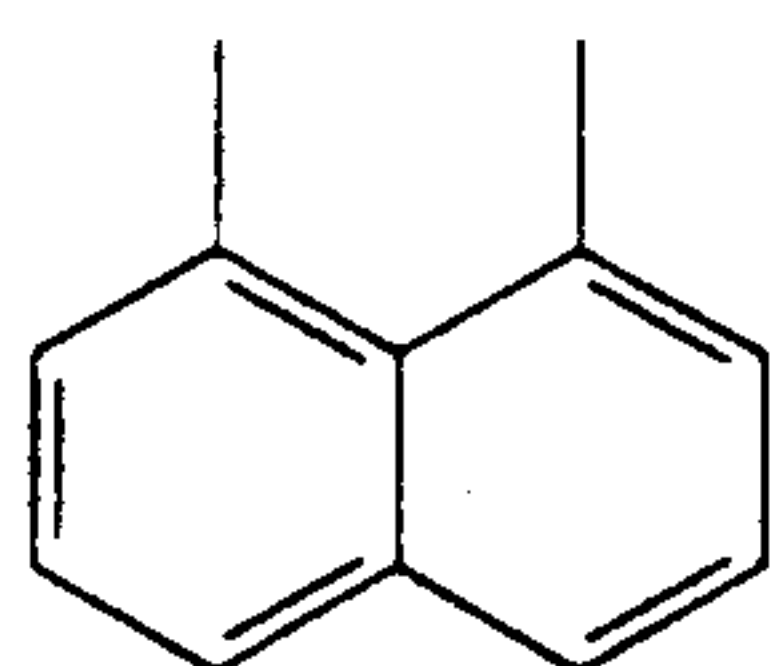
A preferred neutral Lewis acid, which can alkylate
35 the metal, is a selected alkyl aluminum compound, such as R⁹₃Al, R⁹₂AlCl, R⁹AlCl₂, and "R⁹AlO" (alkylaluminoxanes), wherein R⁹ is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms.

Suitable alkyl aluminum compounds include methylaluminoxane (which is an oligomer with the general formula $[\text{MeAlO}]_n$), $(\text{C}_2\text{H}_5)_2\text{AlCl}$, $\text{C}_2\text{H}_5\text{AlCl}_2$, and $[(\text{CH}_3)_2\text{CHCH}_2]_3\text{Al}$.

5 Metal hydrides such as NaBH_4 may be used to bond hydride groups to the metal M.

The first compound and (I) are contacted, usually in the liquid phase, and in the presence of the olefin, and/or 4-vinylcyclohexene, cyclopentene, cyclobutene, substituted norbornene, or norbornene. The liquid
10 phase may include a compound added just as a solvent and/or may include the monomer(s) itself. The molar ratio of first compound:nickel or palladium complex is about 5 to about 1000, preferably about 10 to about
15 100. The temperature at which the polymerization is carried out is about -100°C to about $+200^\circ\text{C}$, preferably about -20°C to about $+80^\circ\text{C}$. The pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa, or more, being a
20 suitable range. The pressure may affect the microstructure of the polyolefin produced (see below).

When using (I) as a catalyst, it is preferred that R^3 and R^4 are hydrogen, methyl, or taken together are



25

(An)

It is also preferred that both R^2 and R^5 are 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 4-methylphenyl, phenyl, 2,4,6-trimethylphenyl, and 2-t-butylphenyl. When M is
30 Ni(II), it is preferred that Q and S are each independently chloride or bromide, while when M is Pd(II) it is preferred that Q is methyl, chloride, or
35 bromide, and S is chloride, bromide or methyl. In

addition, the specific combinations of groups in the catalysts listed in Table I are especially preferred.

Table I

5

R ²	R ³	R ⁵	R ⁵	Q	S	M
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	Cl	Pd
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	Cl	Pd
2,6-i-PrPh	An	An	2,6-i-PrPh	Me	Cl	Pd
2,6-MePh	H	H	2,6-MePh	Me	Cl	Pd
4-MePh	H	H	4-MePh	Me	Cl	Pd
4-MePh	Me	Me	4-MePh	Me	Cl	Pd
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	Me	Pd
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	Me	Pd
2,6-MePh	H	H	2,6-MePh	Me	Me	Pd
2,6-i-PrPh	H	H	2,6-i-PrPh	Br	Br	Ni
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Br	Br	Ni
2,6-MePh	H	H	2,6-MePh	Br	Br	Ni
Ph	Me	Me	Ph	Me	Cl	Pd
2,6-EtPh	Me	Me	2,6-EtPh	Me	Cl	Pd
2,4,6-MePh	Me	Me	2,4,6-MePh	Me	Cl	Pd
2,6-MePh	Me	Me	2,6-MePh	Br	Br	Ni
2,6-i-PrPh	An	An	2,6-i-PrPh	Br	Br	Ni
2,6-MePh	An	An	2,6-MePh	Br	Br	Ni
2-t-BuPh	An	An	2-t-BuPh	Br	Br	Ni
2,5-t-BuPh	An	An	2,5-t-BuPh	Br	Br	Ni
2-i-Pr-6-MePh	An	An	2-i-Pr-6-MePh	Br	Br	Ni
2-i-Pr-6-MePh	Me	Me	2-i-Pr-6-MePh	Br	Br	Ni
2,6-t-BuPh	H	H	2,6-t-BuPh	Br	Br	Ni
2,6-t-BuPh	Me	Me	2,6-t-BuPh	Br	Br	Ni
2,6-t-BuPh	An	An	2,6-t-BuPh	Br	Br	Ni
2-t-BuPh	Me	Me	2-t-BuPh	Br	Br	Ni

Note - In Tables I and II, and elsewhere herein, the following convention and abbreviations are used. For R² and R⁵, when a substituted phenyl ring is present, the amount of substitution is indicated by the number of numbers indicating positions on the phenyl

ring, so that, for example, 2,6-i-PrPh is 2,6-diisopropylphenyl. The following abbreviations are used: i-Pr = isopropyl; Me = methyl; Et = ethyl; t-Bu = t-butyl; Ph = phenyl; Np = naphthyl; An = 1,8-naphthylylene (a divalent radical used for both R^3 and R^4 , wherein R^3 and R^4 taken together form a ring, which is part of an acenaphthylene group); OTf = triflate; and BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

10

Preferred olefins in the polymerization are one or more of ethylene, propylene, 1-butene, 2-butene, 1-hexene 1-octene, 1-pentene, 1-tetradecene, norbornene, and cyclopentene, with ethylene, propylene and cyclopentene being more preferred. Ethylene (alone as a homopolymer) is especially preferred.

The polymerizations with (I) may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, monomer(s), and polymer may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, toluene and benzene.

Whether such a liquid is used, and which and how much liquid is used, may affect the product obtained. It may affect the yield, microstructure, molecular weight, etc., of the polymer obtained.

Compounds of formulas (XI), (XIII), (XV) and (XIX) may also be used as catalysts for the polymerization of the same monomers as compounds of formula (I). The polymerization conditions are the same for (XI), (XIII), (XV) and (XIX) as for (I), and the same Lewis and Bronsted acids are used as co-catalysts. Preferred groupings R^2 , R^3 , R^4 , and R^5 (when present) in (XI) and (XIII) are the same as in (I), both in a polymerization process and as compounds in their own right.

Preferred (XI) compounds have the metals Sc(III), Zr(IV), Ni(II), Ni(I), Pd(II), Fe(II), and Co(II). When M is Zr, Ti, Fe, and Sc it is preferred that all of Q and S are chlorine or bromine more preferably
5 chlorine. When M is Ni or Co it is preferred that all of Q and S are chlorine, bromine or iodine, more preferably bromine.

In (XVII) preferred metals are Ni(II) and Ti(IV). It is preferred that all of Q and S are halogen. It is
10 also preferred that all of R^{28} , R^{29} , and R^{30} are hydrogen, and/or that both R^{44} and R^{45} are 2,4,6-trimethylphenyl or 9-anthracenyl.

In (XV) it is preferred that both of R^{31} are hydrogen.

15 In (XIII), (XXIII) and (XXXII) (as polymerization catalysts and as novel compounds) it is preferred that all of R^{20} , R^{21} , R^{22} and R^{23} are methyl. It is also preferred that T^1 and T^2 are methyl. For (XIII), when M is Ni(I) or (II), it is preferred that both Q and S
20 are bromine, while when M is Pd it is preferred that Q is methyl and S is chlorine.

Compounds (II), (IV) or (VII) will each also cause the polymerization of one or more of an olefin, and/or a selected cyclic olefin such as cyclobutene, cyclopentene or norbornene, and, when it is a Pd(II)
25 complex, optionally copolymerize an ester or carboxylic acid of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein m is 0 or an integer of 1 to 16 and R^1 is hydrogen or hydrocarbyl or substituted hydrocarbyl, by themselves (without
30 cocatalysts). However, (III) often cannot be used when the ester is present. When norbornene or substituted norbornene is present no other monomer should be present.

Other monomers which may be used with compounds
35 (II), (IV) or (VII) (when it is a Pd(II) complex) to form copolymers with olefins and selected cycloolefins are carbon monoxide (CO), and vinyl ketones of the general formula $H_2C=CHC(O)R^{25}$, wherein R^{25} is alkyl

containing 1 to 20 carbon atoms, and it is preferred that R^{25} is methyl. In the case of the vinyl ketones, the same compositional limits on the polymers produced apply as for the carboxylic acids and esters described as comonomers in the immediately preceding paragraph.

CO forms alternating copolymers with the various olefins and cycloolefins which may be polymerized with compounds (II), (IV) or (VII). The polymerization to form the alternating copolymers is done with both CO and the olefin simultaneously in the process mixture, and available to the catalyst. It is also possible to form block copolymers containing the alternating CO/(cyclo)olefin copolymers and other blocks containing just that olefin or other olefins or mixtures thereof. This may be done simply by sequentially exposing compounds (II), (IV) or (VII), and their subsequent living polymers, to the appropriate monomer or mixture of monomers to form the desired blocks. Copolymers of CO, a (cyclo)olefin and a saturated carboxylic acid or ester of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein m is 0 or an integer of 1 to 16 and R^1 is hydrogen or hydrocarbyl or substituted hydrocarbyl, may also be made by simultaneously exposing the polymerization catalyst or living polymer to these 3 types of monomers.

The polymerizations may be carried out with (II), (III), (IV) or (VII), and other catalyst molecules or combinations, initially in the solid state [assuming (II), (III) (IV) or (VII) is a solid] or in solution. The olefin and/or cycloolefin may be in the gas or liquid state (including gas dissolved in a solvent). A liquid, which may or may not be a solvent for any or all of the reactants and/or products may also be present. Suitable liquids include alkanes, cycloalkanes, halogenated alkanes and cycloalkanes, ethers, water, and alcohols, except that when (III) is used, hydrocarbons should preferably be used as solvents. Specific useful solvents include methylene

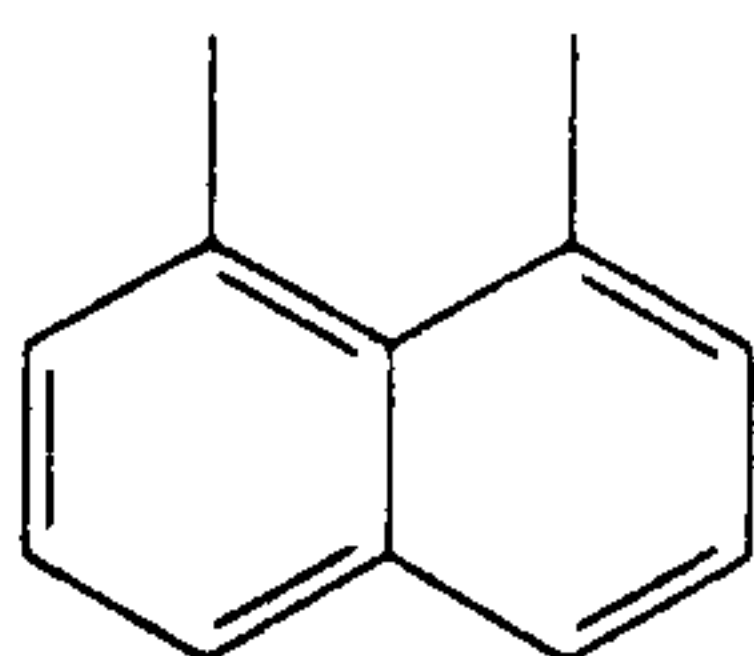
chloride, hexane, CO₂, chloroform, perfluorō(n-butyltetrahydrofuran) (herein sometimes called FC-75), toluene, dichlorobenzene, 2-ethylhexanol, and benzene.

It is particularly noteworthy that one of the liquids which can be used in this polymerization process with (II), (III), (IV) or (VII) is water, see for instance Examples 213-216. Not only can water be present but the polymerization "medium" may be largely water, and various types of surfactants may be employed so that an emulsion polymerization may be done, along with a suspension polymerization when surfactants are not employed.

Preferred olefins and cycloolefins in the polymerization using (II), (III) or (IV) are one or more of ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-butene, cyclopentene, 1-tetradecene, and norbornene; and ethylene, propylene and cyclopentene are more preferred. Ethylene alone is especially preferred.

Olefinic esters or carboxylic acids of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$, wherein R¹ is hydrogen, hydrocarbyl, or substituted hydrocarbyl, and m is 0 or an integer of 1 to 16. It is preferred if R¹ hydrocarbyl or substituted hydrocarbyl and it is more preferred if it is alkyl containing 1 to 10 carbon atoms, or glycidyl. It is also preferred if m is 0 and/or R¹ is alkyl containing 1 to 10 carbon atoms. It is preferred to make copolymers containing up to about 60 mole percent, preferably up to about 20 mole percent of repeat units derived from the olefinic ester or carboxylic acid. Total repeat unit units in the polymer herein refer not only to those in the main chain from each monomer unit, but those in branches or side chains as well.

When using (II), (III), (IV) or (VII) as a catalyst it is preferred that R³ and R⁴ are hydrogen, methyl, or taken together are



(An)

It is also preferred that both R^2 and R^5 are 2,6-
5 diisopropylphenyl, 2,6-dimethylphenyl, 4-methylphenyl,
phenyl, 2,6-diethylphenyl, 2,4,6-trimethylphenyl and 2-
t-butylphenyl. When (II) is used, it is preferred that
 T^1 is methyl, R^6 is methyl or ethyl and R^7 is methyl.
When (III) is used it is preferred that T^1 is methyl
10 and said Lewis base is R^6_2O , wherein R^6 is methyl or
ethyl. When (IV) is used it is preferred that R^8 is
methyl, n is 3 and R^{16} is hydrogen. In addition in
Table II are listed all particularly preferred
combinations as catalysts for (II), (III), (IV) and
15 (VII).

Table II

Com- pound	R ²	R ³	R ⁴	R ⁵	T ¹ /T ² / R ⁸	Z	M	X
Type								
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt ₂	Pd	BAF
(II)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	OEt ₂	Pd	BAF
(III)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt ₂	Ni	BAF
(III)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	OEt ₂	Ni	BAF
(II)	2,6- MePh	H	H	2,6-MePh	Me	OEt ₂	Pd	BAF
(II)	2,6- MePh	Me	Me	2,6-MePh	Me	OEt ₂	Pd	BAF
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt ₂	Pd	SbF ₆
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt ₂	Pd	BF ₄
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	OEt ₂	Pd	PF ₆
(II)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	OEt ₂	Pd	SbF ₆
(II)	2,4,6- MePh	Me	Me	2,4,6- MePh	Me	OEt ₂	Pd	SbF ₆
(II)	2,6-i- PrPh	An	An	2,6-i- PrPh	Me	OEt ₂	Pd	SbF ₆
(II)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	NCMe	Pd	SbF ₆
(II)	Ph	Me	Me	Ph	Me	NCMe	Pd	SbF ₆
(II)	2,6- EtPh	Me	Me	2,6-EtPh	Me	NCMe	Pd	BAF
(II)	2,6- EtPh	Me	Me	2,6-EtPh	Me	NCMe	Pd	SbF ₆
(II)	2-t- BuPh	Me	Me	2-t-BuPh	Me	NCMe	Pd	SbF ₆

(II)	1-Np	Me	Me	1-Np	Me	NCMe	Pd	SbF ₆
(II)	Ph ₂ CH	H	H	Ph ₂ CH	Me	NCMe	Pd	SbF ₆
(II)	2-PhPh	Me	Me	2-PhPh	Me	NCMe	Pd	SbF ₆
(II)	Ph	a	a	Ph	Me	NCMe	Pd	BAF
(IV)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	b	Pd	SbF ₆
(IV)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	b	Pd	BAF
(IV)	2,6-i- PrPh	H	H	2,6-i- PrPh	Me	b	Pd	SbF ₆
(IV)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	b	Pd	B(C ₆ F ₅) ₃ C 1
(II)	Ph	Me	Me	Ph	Me	NCMe	Pd	SbF ₆
(VII)	2,6-i- PrPh	Me	Me	2,6-i- PrPh	Me	-	Pd	OTf
(II)	Ph	Ph	Ph	Ph	Me	NCMe	Pd	BAF
(II)	Ph ₂ CH	H	H	Ph ₂ CH	Me	NCMe	Pd	SbF ₆

^a This group is -CMe₂CH₂CMe₂-

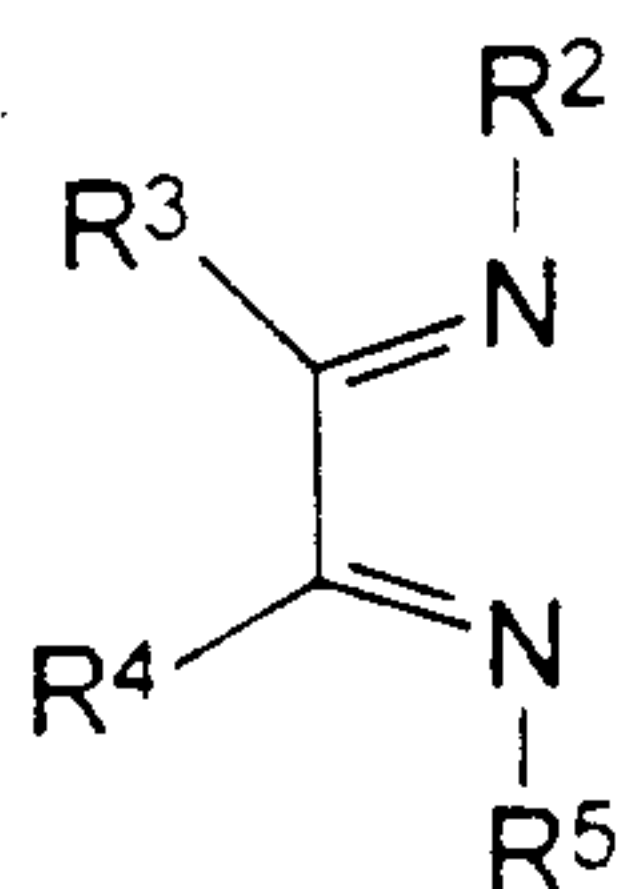
^b This group is -(CH₂)₃CO₂Me

When using (II), (III), (IV) or (VII) the
 5 temperature at which the polymerization is carried out
 is about -100°C to about +200°C, preferably about 0°C to
 about 150°C, more preferably about 25°C to about 100°C.
 The pressure at which the polymerization is carried out
 is not critical, atmospheric pressure to about 275 MPa
 10 being a suitable range. The pressure can affect the
 microstructure of the polyolefin produced (see below).

Catalysts of the formulas (II), (III), (IV) and
 (VII) may also be supported on a solid catalyst (as
 opposed to just being added as a solid or in solution),
 15 for instance on silica gel (see Example 98). By
 supported is meant that the catalyst may simply be
 carried physically on the surface of the solid support,
 may be adsorbed, or carried by the support by other
 means.

When using (XXX) as a ligand or in any process or reaction herein it is preferred that n is 2, all of R^{30} , R^{28} and R^{29} are hydrogen, and both of R^{44} and R^{45} are 9-anthracenyl.

5 Another polymerization process comprises contacting a compound of the formula $[Pd(R^{13}CN)_4]X_2$ or a combination of $Pd[OC(O)R^{40}]_2$ and HX , with a compound of the formula



10

(VIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula
 15 $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene and norbornene, wherein: R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound
 20 to it; R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring; each R^{17} is
 25 independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds; R^{40} is hydrocarbyl or substituted hydrocarbyl; and X is a weakly coordinating anion; provided that when norbornene or substituted norbornene is present no other monomer is present.

30 It is believed that in this process a catalyst similar to (II) may be initially generated, and this then causes the polymerization. Therefore, all of the conditions, monomers (including olefinic esters and

carboxylic acids), etc., which are applicable to the process using (II) as a polymerization catalyst are applicable to this process. All preferred items are also the same, including appropriate groups such as R^2 , R^3 , R^4 , R^5 , and combinations thereof. This process however should be run so that all of the ingredients can contact each other, preferably in a single phase. Initially at least, it is preferred that this is done in solution. The molar ratio of (VIII) to palladium compound used is not critical, but for most economical use of the compounds, a moderate excess, about 25 to 100% excess, of (VIII) is preferably used.

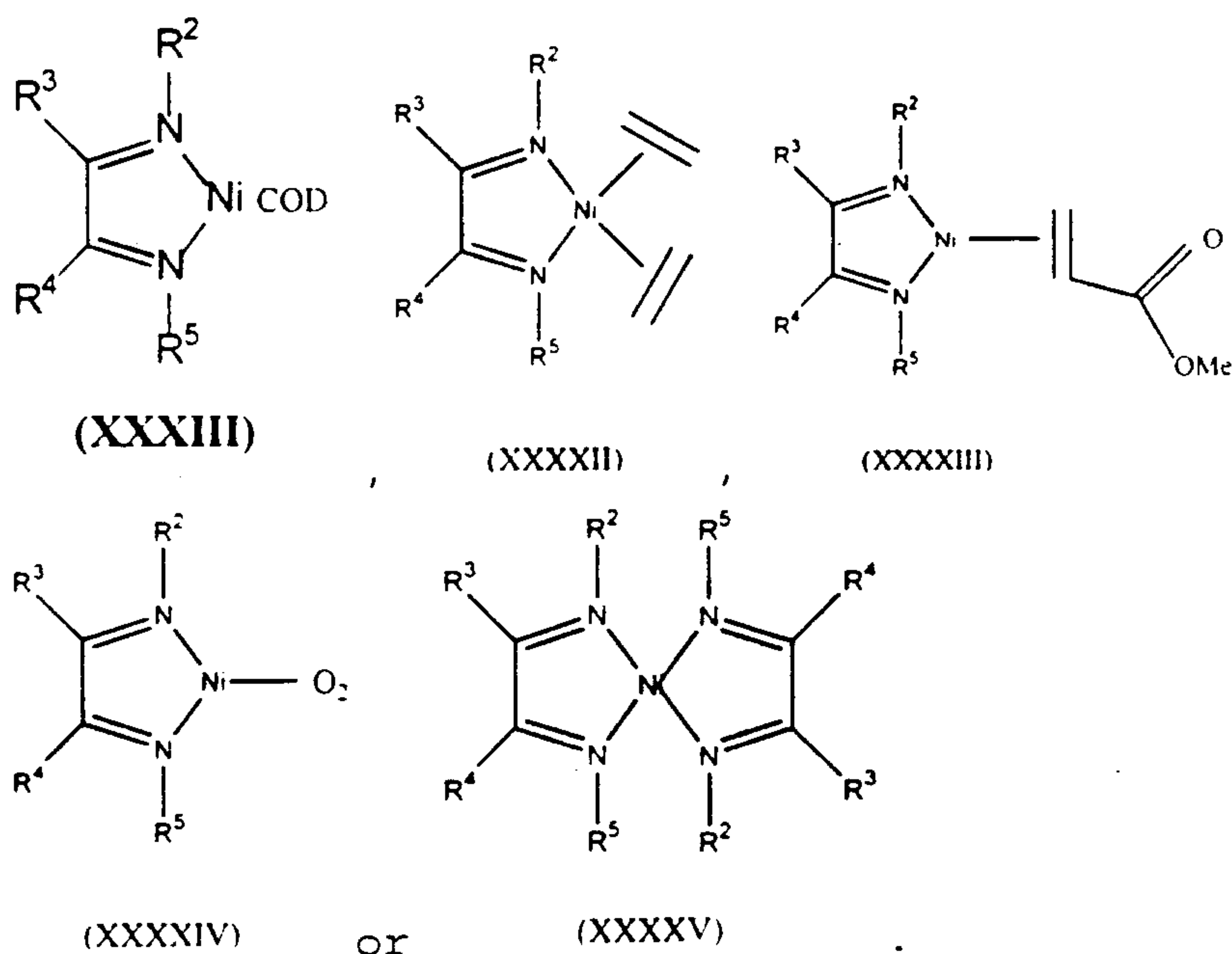
As mentioned above, it is believed that in the polymerization using (VIII) and $[Pd(R^{13}CN)_4]X_2$ or a Pd(II) carboxylate a catalyst similar to (II) is formed. Other combinations of starting materials that can combine into catalysts similar to (II), (III), (IV) and (VII) often also cause similar polymerizations, see for instance Examples 238 and 239. Also combinations of α -diimines or other diimino ligands described herein with: a nickel [0] or nickel [I] compound, oxygen, an alkyl aluminum compound and an olefin; a nickel [0] or nickel [I] compound, an acid such as HX and an olefin; or an α -diimine Ni[0] or nickel [I] complex, oxygen, an alkyl aluminum compound and an olefin. Thus active catalysts from α -diimines and other bidentate imino compounds can be formed beforehand or in the same "pot" (in situ) in which the polymerization takes place. In all of the polymerizations in which the catalysts are formed in situ, preferred groups on the α -diimines are the same as for the preformed catalysts.

In general Ni[0], Ni[I] or Ni(II) compounds may be used as precursors to active catalyst species. They must have ligands which can be displaced by the appropriate bidentate nitrogen ligand, or must already contain such a bidentate ligand already bound to the nickel atom. Ligands which may be displaced include

1,5-cyclooctadiene and tris(o-tolyl)phosphite, which may be present in Ni[0] compounds, or dibenzylideneacetone, as in the useful Pd[0] precursor tris(dibenzylideneacetone)dipalladium[0]. These lower
 5 valence nickel compounds are believed to be converted into active Ni[II] catalytic species. As such they must also be contacted (react with) with an oxidizing agent and a source of a weakly coordinating anion (X^-). Oxidizing agents include oxygen, HX (wherein X is a
 10 weakly coordinating anion), and other well known oxidizing agents. Sources of X^- include HX, alkylaluminum compounds, alkali metal and silver salts of X^- . As can be seen above, some compounds such as HX may act as both an oxidizing agent and a source of X^- .
 15 Compounds containing other lower valent metals may be converted into active catalyst species by similar methods.

When contacted with an alkyl aluminum compound or HX useful Ni[0] compounds include

20



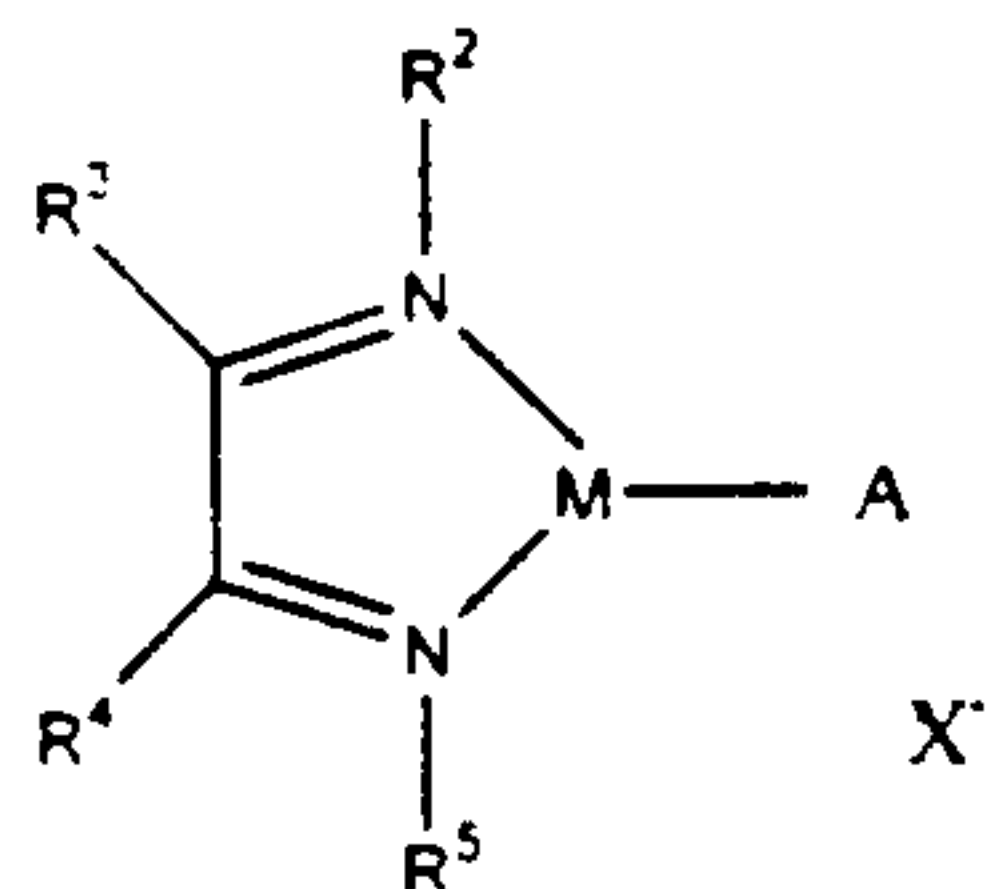
Various types of Ni[0] compounds are known in the literature. Below are listed references for the types
 25 shown immediately above.

- (XXXIII) G. van Koten, et al., ~~Adv.~~ Organometal. Chem., vol. 21, p. 151-239 (1982).
- (XXXXII) W. Bonrath, et al., Angew. Chem. Int. Ed. Engl., vol. 29, p. 298-300 (1990).
- 5 • (XXXXIV) H. tom Dieck, et al., Z. Naturforsch., vol. 366, p. 823-832 (1981); and M. Svoboda, et al., J. Organometal. Chem., vol. 191, p. 321-328 (1980).
- (XXXXV) G. van Koten, et al., Adv. Organometal. Chem., vol. 21, p. 151-239 (1982).

In polymerizations using (XIV), the same preferred monomers and groups (such as R^2 , R^3 , R^4 , R^5 and X) as are preferred for the polymerization using (II) are used and preferred. Likewise, the conditions used and preferred for polymerizations with (XIV) are similar to those used and preferred for (II), except that higher olefin pressures (when the olefin is a gas) are preferred. Preferred pressures are about 2.0 to about 20 MPa. (XIV) may be prepared by the reaction of one mole of $[Pd(R^{13}CN)_4]X_2$ with one mole of (VIII) in acetonitrile or nitromethane.

Novel compound (XIV) is used as an olefin polymerization catalyst. In preferred forms of (XIV), the preferred groups R^2 , R^3 , R^4 , R^5 and X are the same as are preferred for compound (II).

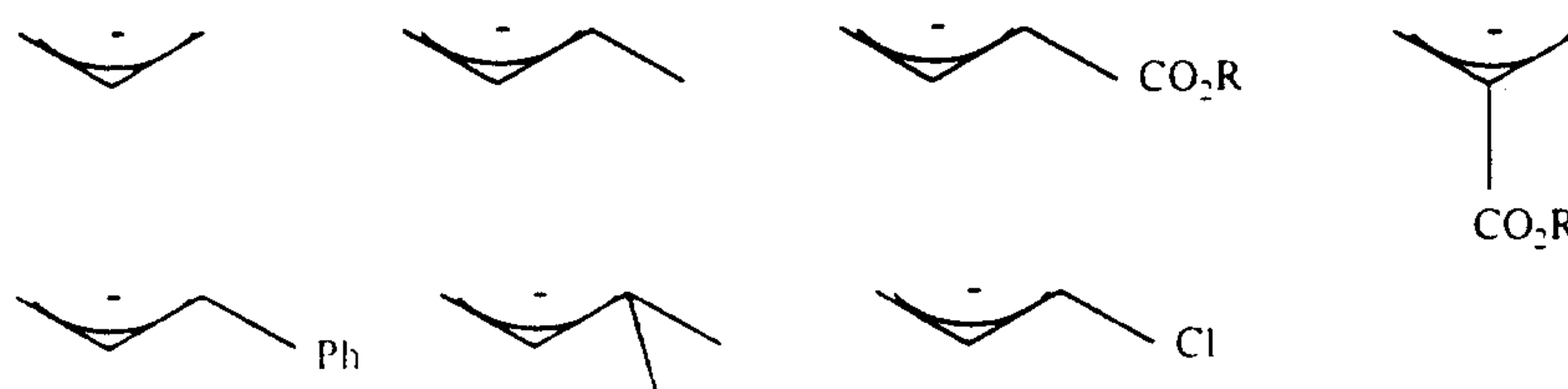
Another type of compound which is an olefin polymerization catalyst are π -allyl and π -benzyl compounds of the formula



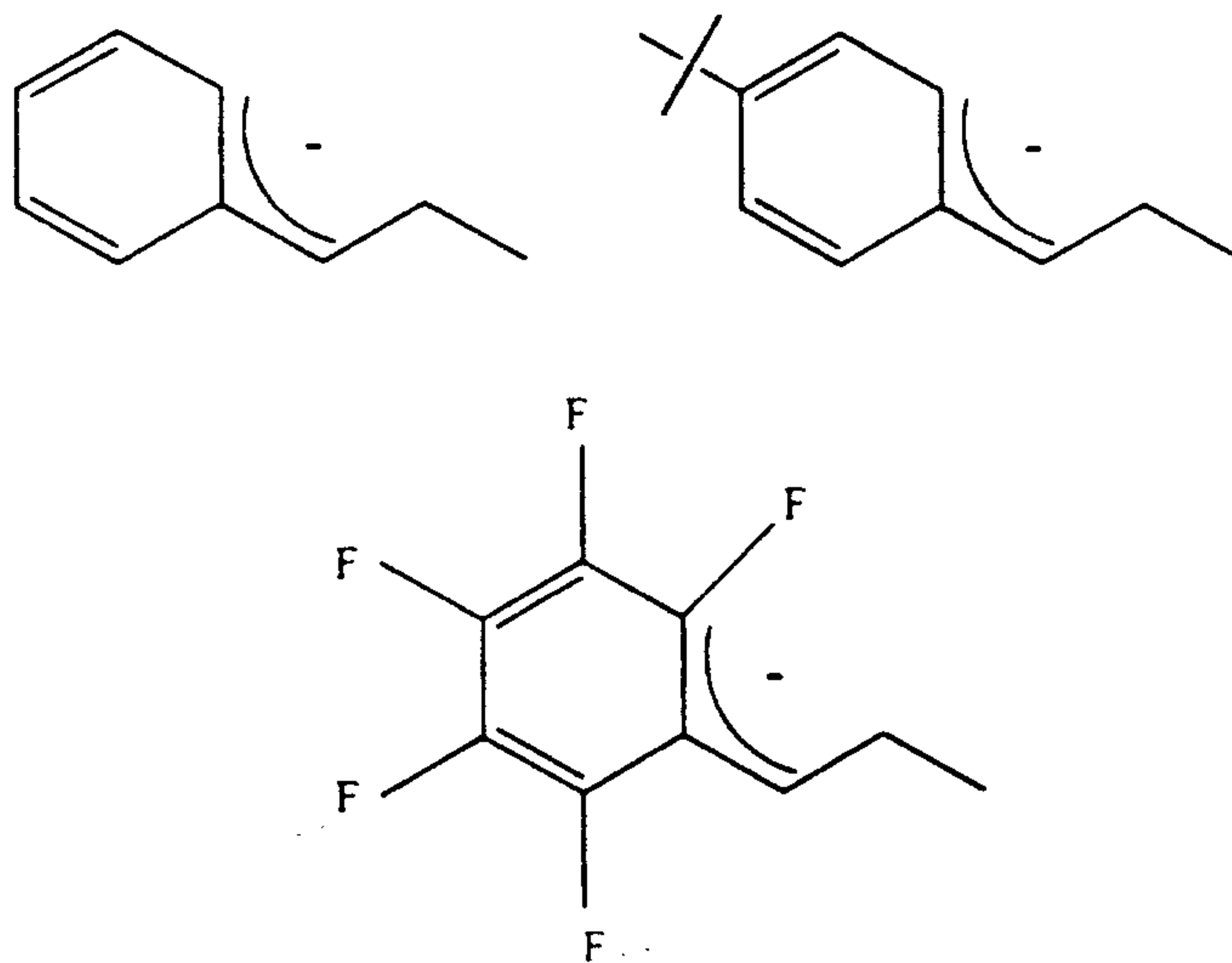
XXXVII

wherein M is Ni(II) or Pd(II); R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen

atom has at least two carbon atoms bound to it; R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a
 5 ring; X is a weakly coordinating anion; and A is a π -allyl or π -benzyl group. By a π -allyl group is meant a monoanionic with 3 adjacent sp^2 carbon atoms bound to a metal center in an η^3 fashion. The three sp^2 carbon atoms may be substituted with other hydrocarbyl groups
 10 or functional groups. Typical π -allyl groups include



wherein R is hydrocarbyl. By a π -benzyl group is meant
 15 π -allyl ligand in which two of the sp^2 carbon atoms are part of an aromatic ring. Typical π -benzyl groups include



20

π -Benzyl compounds usually initiate polymerization of the olefins fairly readily even at room temperature, but π -allyl compounds may not necessarily do so.

Initiation of π -allyl compounds can be improved by using one or more of the following methods:

- Using a higher temperature such as about 80°C.

5 • Decreasing the bulk of the α -diimine ligand, such as R² and R⁵ being 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl.

- Making the π -allyl ligand more bulky, such as using

10



rather than the simple π -allyl group itself.

- Having a Lewis acid present while using a functional π -allyl or π -benzyl group. Relatively weak

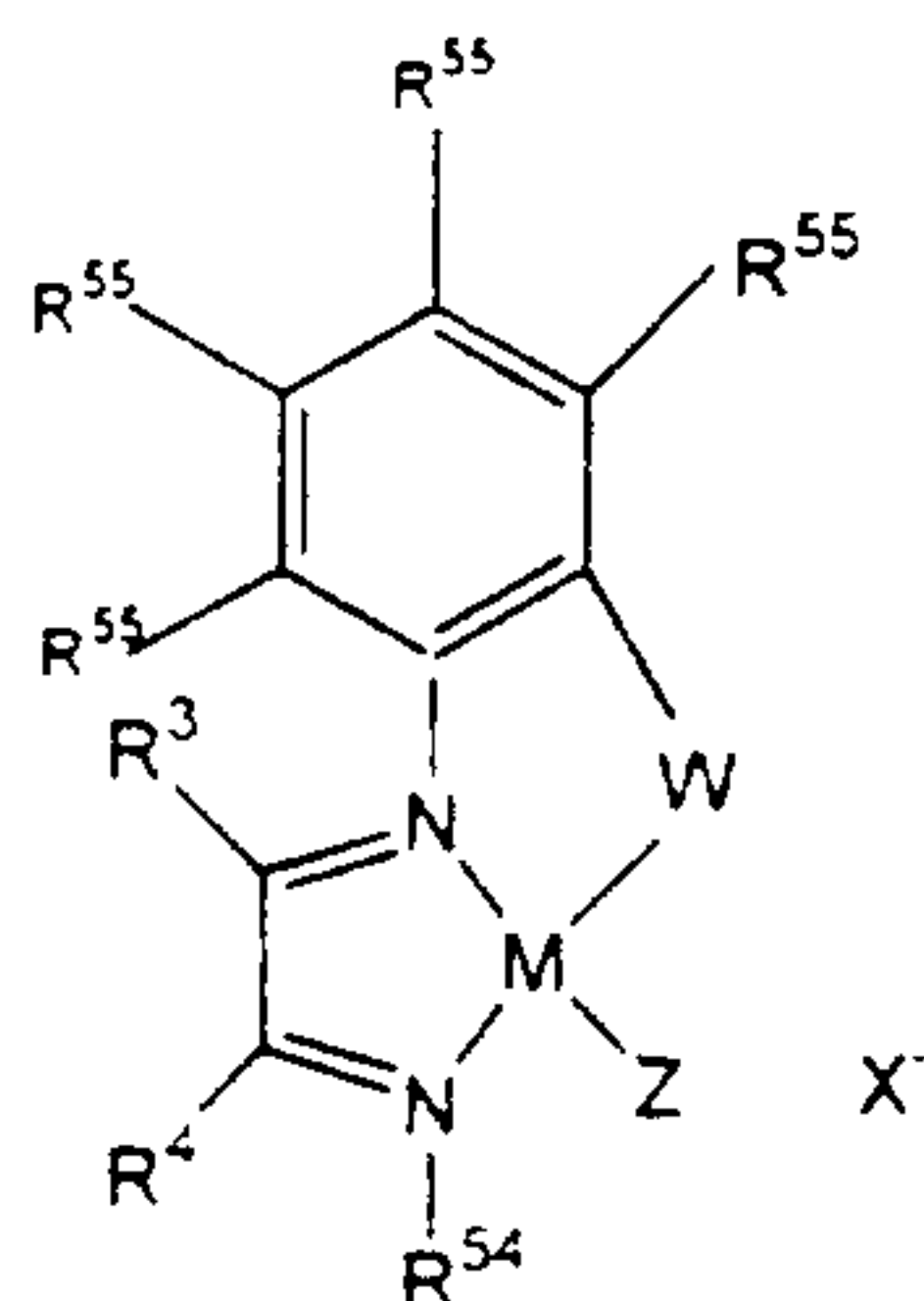
15 Lewis acids such as triphenylborane, tris(pentafluorophenyl)borane, and tris(3,5-trifluoromethylphenyl)borane, are preferred. Suitable functional groups include chloro and ester. "Solid" acids such as montmorillonite may also be used.

20 When using (XXXVII) as a polymerization catalyst, it is preferred that ethylene and/or a linear α -olefin is the monomer, or cyclopentene, more preferred if the monomer is ethylene and/or propylene, and ethylene is especially preferred. A preferred temperature for the

25 polymerization process using (XXXVII) is about +20°C to about 100°C. It is also preferred that the partial pressure due to ethylene or propylene monomer is at least about 600 kPa. It is also noted that (XXXVII) is a novel compound, and preferred items for (XXXVII) for

30 the polymerization process are also preferred for the compound itself.

Another catalyst for the polymerization of olefins is a compound of the formula



(XXXVIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein: R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; R^{54} is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; each R^{55} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group; W is alkylene or substituted alkylene containing 2 or more carbon atoms; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula $R^{17}CH=CHR^{17}$; each R^{17} is independently alkyl or substituted alkyl; and X is a weakly coordinating anion. It is preferred that in compound (XXXVIII) that: R^{54} is phenyl or substituted phenyl, and preferred substituents are alkyl groups; each R^{55} is independently hydrogen or alkyl containing 1 to 10 carbon atoms; W contains 2 carbon atoms between the phenyl ring and metal atom it is bonded to or W is a divalent polymeric group derived from the polymerization of $R^{17}CH=CHR^{17}$, and it is especially preferred that it is $-CH(CH_3)CH_2-$ or $-C(CH_3)_2CH_2-$; and Z is a dialkyl ether or an olefin of the formula

$R^{17}CH=CHR^{17}$; and combinations thereof. W is an alkylene group in which each of the two free valencies are to different carbon atoms of the alkylene group.

When W is a divalent group formed by the polymerization of $R^{17}CH=CHR^{17}$, and Z is $R^{17}CH=CHR^{17}$, the compound (XXXVIII) is believed to be a living ended polymer. That end of W bound to the phenyl ring actually is the original fragment from R^{56} from which the "bridge" W originally formed, and the remaining part of W is formed from the olefin(s) $R^{17}CH=CHR^{17}$. In a sense this compound is similar in function to compound (VI).

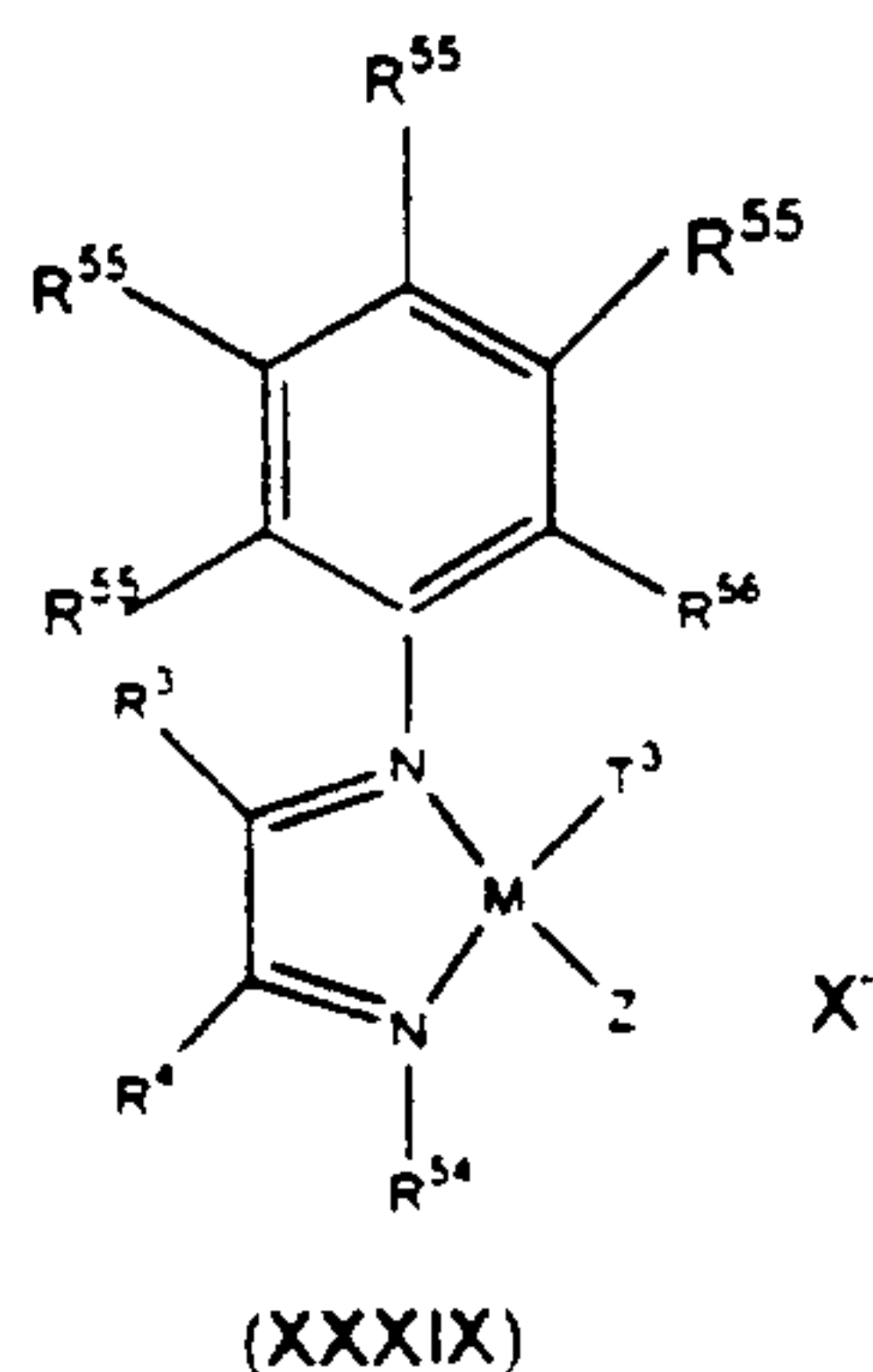
By substituted phenyl in (XXXVIII) and (XXXIX) is meant the phenyl ring can be substituted with any grouping which does not interfere with the compound's stability or any of the reactions the compound undergoes. Preferred substituents in substituted phenyl are alkyl groups, preferably containing 1 to 10 carbon atoms.

Preferred monomers for this polymerization are ethylene and linear α -olefins, or cyclopentene, particularly propylene, and ethylene and propylene or both are more preferred, and ethylene is especially preferred.

It is noted that (XXXVIII) is a novel compound, and preferred compounds and groupings are the same as in the polymerization process.

Compound (XXXVIII) can be made by heating compound (XXXIX),

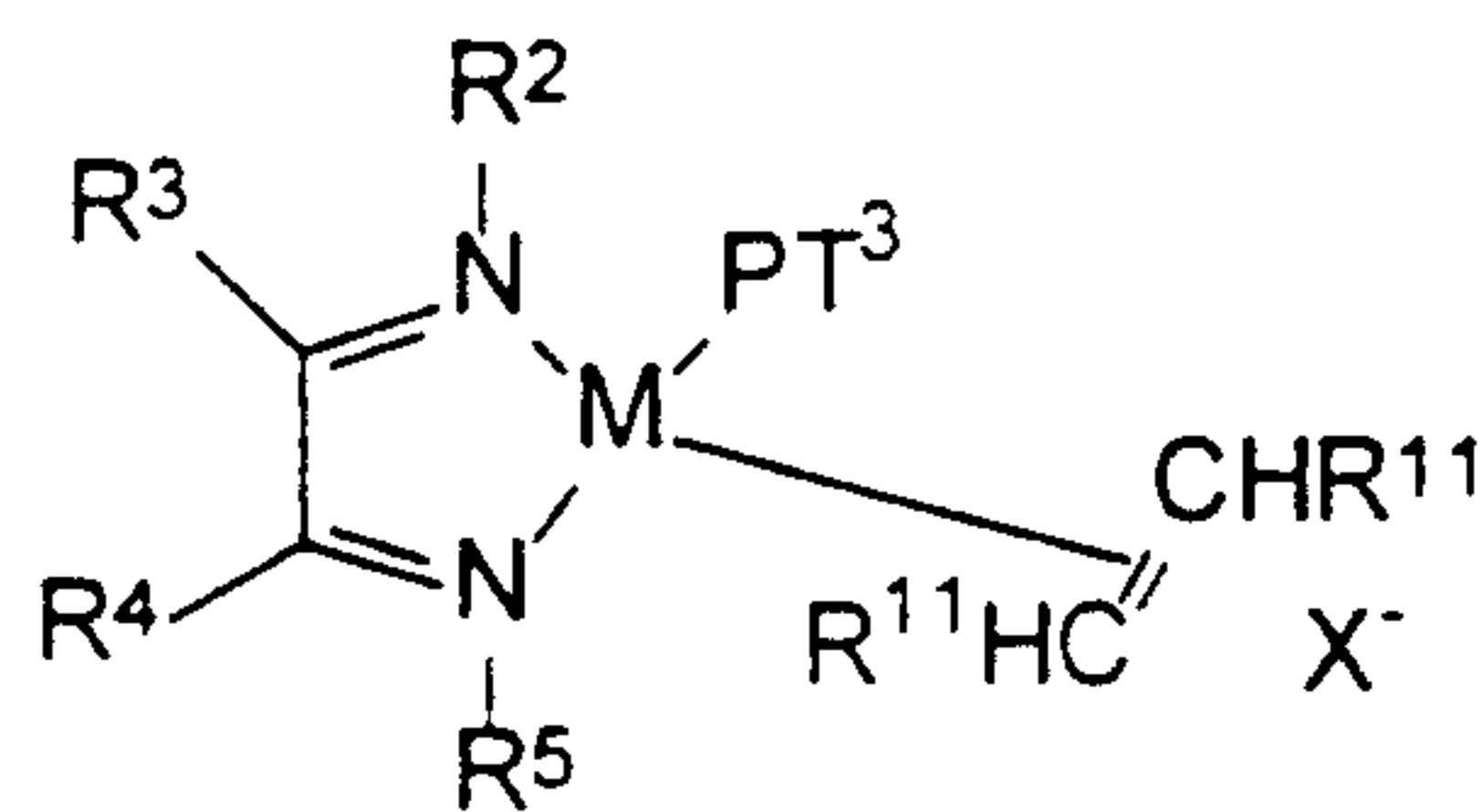
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wherein: R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; R^{54} is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; each R^{55} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group; R^{56} is alkyl containing 2 to 30 carbon atoms; T^3 is alkyl; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6; and X is a weakly coordinating anion. Preferred groups are the same as those in (XXXVIII). In addition it is preferred that T^5 contain 1 to 10 carbon atoms, and more preferred that it is methyl. A preferred temperature for the conversion of (XXXIX) to (XXXVIII) is about -30°C to about 50°C . Typically the reaction takes about 10 min. to about 5 days, the higher the temperature, the faster the reaction. Another factor which affects the reaction rate is the nature of Z. The weaker the Lewis basicity of Z, the faster the desired reaction will be.

When (II), (III), (IV), (V), (VII), (VIII) or a combination of compounds that will generate similar compounds, (subject to the conditions described above) is used in the polymerization of olefins, cycloolefins, and optionally olefinic esters or carboxylic acids, polymer having what is believed to be similar to a "living end" is formed. This molecule is that from which the polymer grows to its eventual molecular weight. This compound may have the structure

35



(VI)

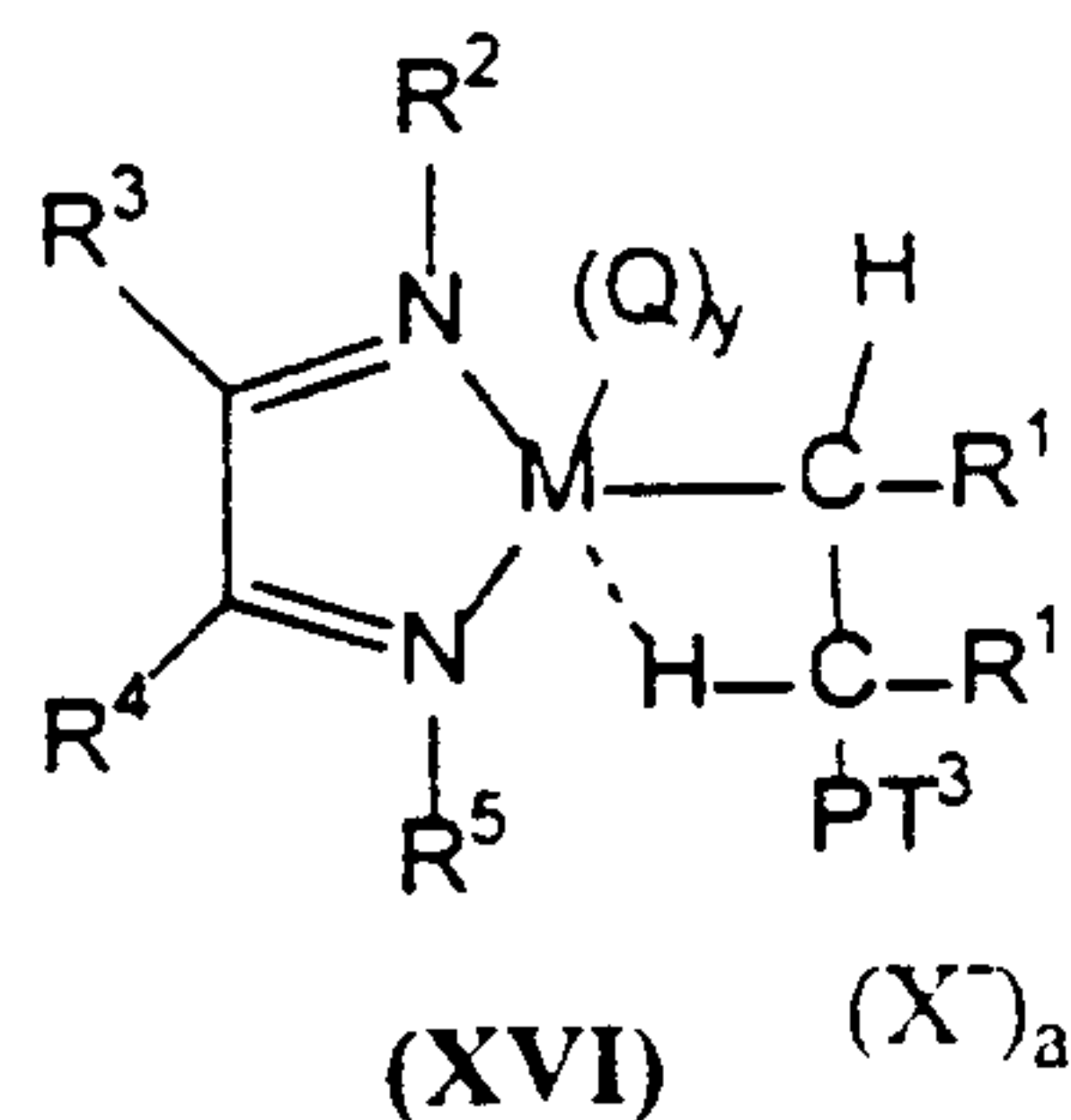
- wherein: M is Ni(II) or Pd(II); R² and R⁵ are
- 5 hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are
- 10 hydrocarbylene or substituted hydrocarbylene to form a ring; each R¹² is independently hydrogen, alkyl or -(CH₂)_mCO₂R¹; T³ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵(C=O)-, R¹⁵O(C=O)-, or -CH₂CH₂CH₂CO₂R⁸; R¹⁵ is hydrocarbyl not containing
- 15 olefinic or acetylenic unsaturation; P is a divalent group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, or
- 20 norbornene and, when M is Pd(II), optionally one or more compounds of the formula CH₂=CH(CH₂)_mCO₂R¹; R⁶ is hydrocarbyl; each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic
- 25 bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; m is 0 or an integer from 1 to 16; R¹ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms; and X is a weakly coordinating anion; and that
- 30 when M is Ni(II), R¹¹ is not -CO₂R⁸ and when M is Pd a diene is not present. By an "olefinic ester or carboxylic acid" is meant a compound of the formula

$\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$, wherein m and R^1 are as defined immediately above.

This molecule will react with additional monomer (olefin, cyclic olefin, olefinic ester or olefinic carboxylic acid) to cause further polymerization. In other words, the additional monomer will be added to P, extending the length of the polymer chain. Thus P may be of any size, from one "repeat unit" to many repeat units, and when the polymerization is over and P is removed from M, as by hydrolysis, P is essentially the polymer product of the polymerization. Polymerizations with (VI), that is contact of additional monomer with this molecule takes place under the same conditions as described above for the polymerization process using (II), (III), (IV), (V), (VII) or (VIII), or combinations of compounds that will generate similar molecules, and where appropriate preferred conditions and structures are the same.

The group T^3 in (VI) was originally the group T^1 in (II) or (III), or the group which included R^8 in (IV). It in essence will normally be one of the end groups of the eventual polymer product. The olefinic group which is coordinated to M, $\text{R}^{11}\text{CH}=\text{CHR}^{11}$ is normally one of the monomers, olefin, cyclic olefin, or, if $\text{Pd}(\text{II})$ is M, an olefinic ester or carboxylic acid. If more than one of these monomers is present in the reaction, it may be any one of them. It is preferred that T^3 is alkyl and especially preferred that it is methyl, and it is also preferred that R^{11} is hydrogen or n-alkyl. It is also preferred that M is $\text{Pd}(\text{II})$.

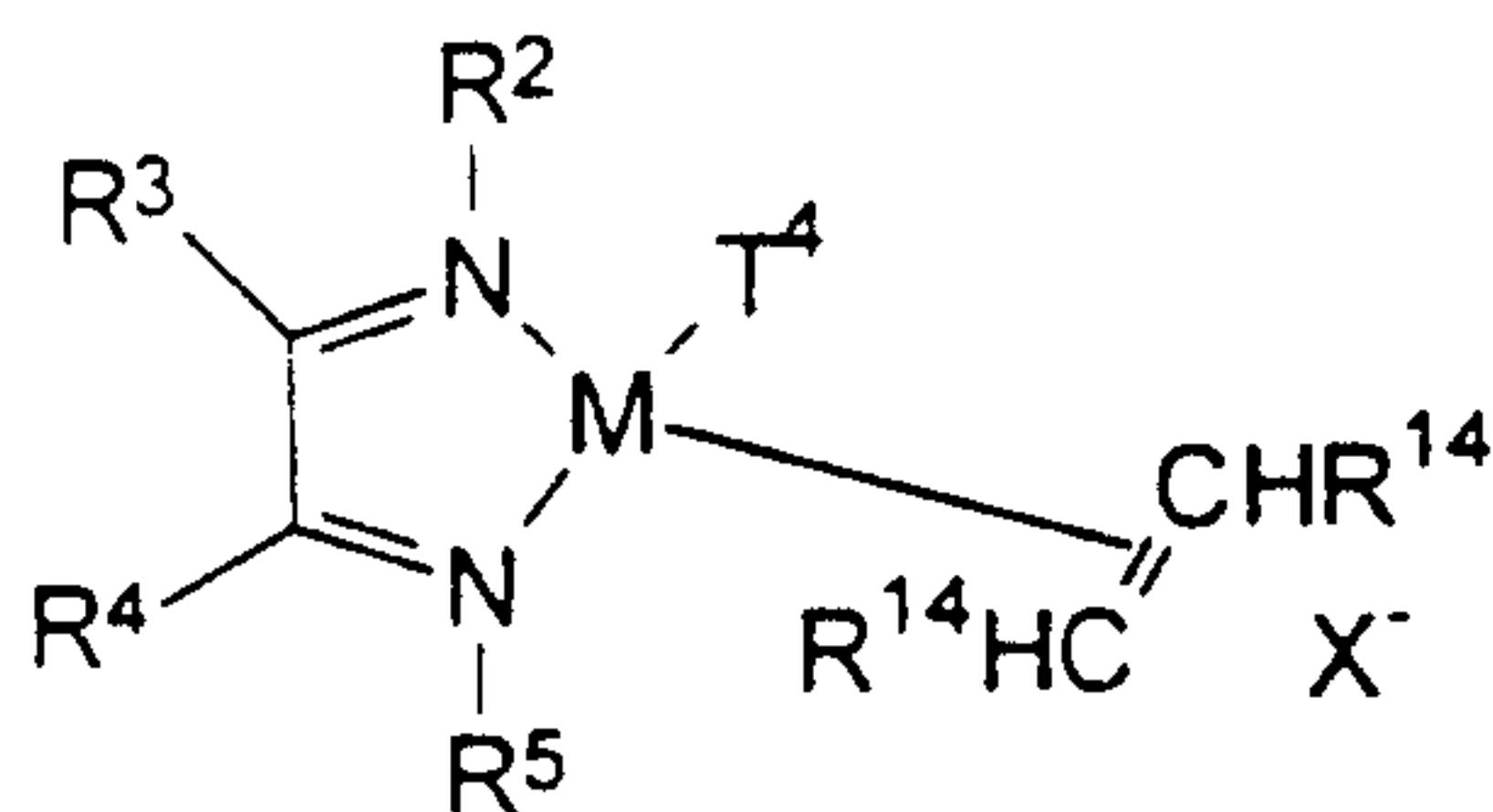
Another "form" for the living end is (XVI).



This type of compound is sometimes referred to as a compound in the "agostic state". In fact both (VI) and (XVI) may coexist together in the same polymerization, both types of compound representing living ends. It is believed that (XVI)-type compounds are particularly favored when the end of the growing polymer chain bound to the transition metal is derived from a cyclic olefin such as cyclopentene. Expressed in terms of the structure of (XVI) this is when both of R^{11} are hydrocarbylene to form a carbocyclic ring, and it is preferred that this be a five-membered carbocyclic ring.

For both the polymerization process using (XVI) and the structure of (XVI) itself, the same conditions and groups as are used and preferred for (VI) are also used and preferred for (XVI), with the exception that for R^{11} it is preferred in (XVI) that both of R^{11} are hydrocarbylene to form a carbocyclic ring.

This invention also concerns a compound of the formula



(IX)

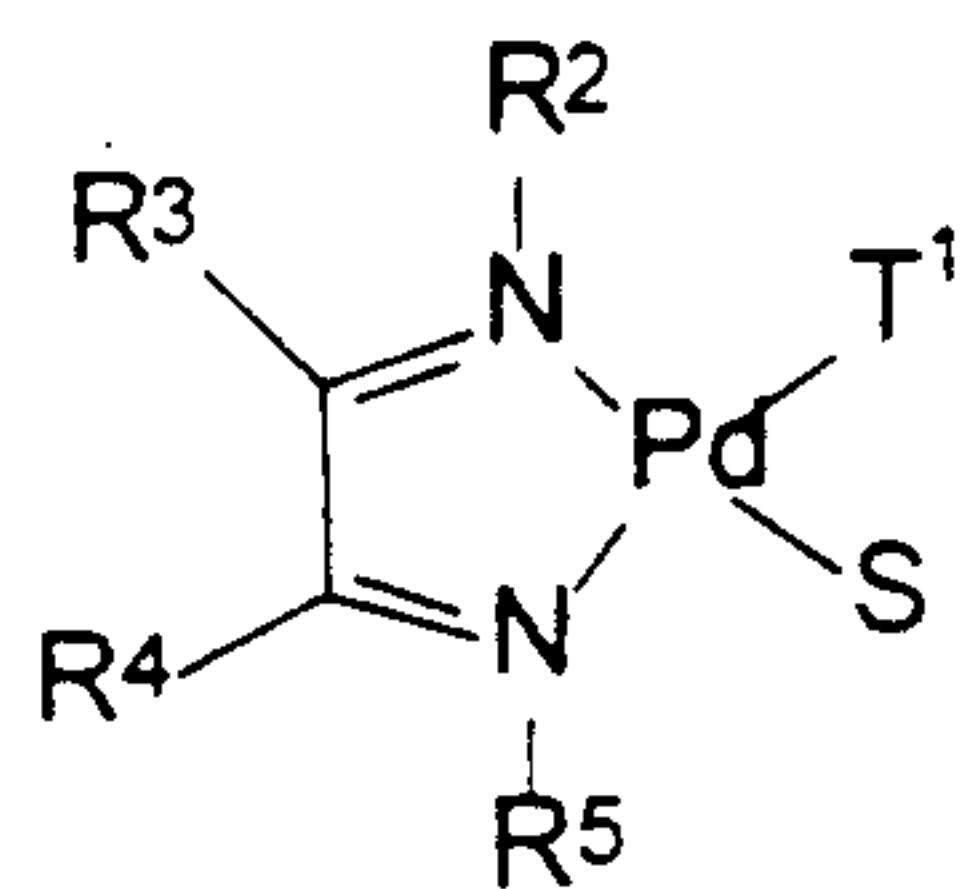
wherein: M is Ni(II) or Pd(II); R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a

ring; each R^{14} is independently hydrogen, alkyl or
[when M is Pd(II)] $-(CH_2)_mCO_2R^1$; R^1 is hydrogen, or
hydrocarbyl or substituted hydrocarbyl containing 1 to
10 carbon atoms; T^4 is alkyl, $-R^{60}C(O)OR^8$, $R^{15}(C=O)-$ or
5 $R^{15}OC(=O)-$; R^{15} is hydrocarbyl not containing olefinic
or acetylenic bonds; R^{60} is alkylene not containing
olefinic or acetylenic bonds; R^8 is hydrocarbyl; and X
is a weakly coordinating anion.

(IX) may also be used to polymerize olefins,
10 cyclic olefins, and optionally olefinic esters and
carboxylic acids. The same conditions (except as noted
below) apply to the polymerizations using (IX) as they
do for (VI). It is preferred that M is Pd(II) and T^4
is methyl.

15 A compound of formula (V) may also be used as a
catalyst for the polymerization of olefins, cyclic
olefins, and optionally olefinic esters and/or
carboxylic acids. In this process (V) is contacted
with one or more of the essential monomers. Optionally
20 a source of a relatively weakly coordinating anion may
also be present. Such a source could be an alkali
metal salt of BAF or AgX (wherein X is the anion), etc.
Preferably about 1 mole of the source of X, such as
AgX, will be added per mole of (V). This will usually
25 be done in the liquid phase, preferably in which (V)
and the source of the anion are at least partially
soluble. The conditions of this polymerization are
otherwise the same as described above for (II), (III),
(IV) and (VII), including the preferred conditions and
30 ingredients.

In polymerizations using (XX) as the catalyst,
a first compound which is a source of a relatively
noncoordinating monoanion is present. Such a source
can be an alkali metal or silver salt of the monoanion.
35



(XX)

It is preferred that the alkali metal cation is sodium
 5 or potassium. It is preferred that the monoanion is
 SbF_6^- , BAF^- , PF_6^- , or BF_4^- , and more preferred that it is
 BAF^- . It is preferred that T^1 is methyl and/or S is
 chlorine. All other preferred groups and conditions
 10 for these polymerizations are the same as for
 polymerizations with (II).

In all of the above polymerizations, and the
 catalysts for making them it is preferred that R^2 and
 R^5 , if present, are 2,6-diisopropylphenyl and R^3 and R^4
 are hydrogen or methyl. When cyclopentene is
 15 polymerized, is preferred that R^2 and R^5 (if present)
 are 2,6-dimethylphenyl or 2,4,6-trimethylphenyl and
 that R^3 and R^4 taken together are An. R^2 , R^3 , R^4 and R^5
 and other groups herein may also be substituted
 hydrocarbyl. As previously defined, the substituent
 20 groups in substituted hydrocarbyl groups (there may be
 one or more substituent groups) should not
 substantially interfere with the polymerization or
 other reactions that the compound is undergoing.
 Whether a particular group will interfere can first be
 25 judged from the artisans general knowledge and the
 particular polymerization or other reaction that is
 involved. For instance, in polymerizations where an
 alkyl aluminum compound is used may not be compatible
 with the presence of groups containing an active
 30 (relatively acidic) hydrogen atom, such as hydroxyl or
 carboxyl because of the known reaction of alkyl
 aluminum compounds with such active hydrogen containing
 groups (but such polymerizations may be possible if

enough "extra" alkyl aluminum compound is added to react with these groups). However, in very similar polymerizations where alkyl aluminum compounds are not present, these groups containing active hydrogen may be present. Indeed many of the polymerization processes described herein are remarkably tolerant to the presence of various functional groups. Probably the most important considerations as to the operability of compounds containing any particular functional group are the effect of the group on the coordination of the metal atom (if present), and side reaction of the group with other process ingredients (such as noted above). Therefore of course, the further away from the metal atom the functional group is, the less likely it is to influence, say, a polymerization. If there is doubt as to whether a particular functional group, in a particular position, will affect a reaction, simple minimal experimentation will provide the requisite answer. Functional groups which may be present in R^2 , R^3 , R^4 , R^5 , and other similar radicals herein include hydroxy, halo (fluoro, chloro, bromo and iodo), ether, ester, dialkylamino, carboxy, oxo (keto and aldehydo), nitro, amide, thioether, and imino. Preferred functional groups are hydroxy, halo, ether and dialkylamino.

Also in all of the polymerizations, the (cyclo)olefin may be substituted hydrocarbyl. Suitable substituents include ether, keto, aldehyde, ester, carboxylic acid.

In all of the above polymerizations, with the exceptions noted below, the following monomer(s), to produce the corresponding homo- or copolymers, are preferred to be used: ethylene; propylene; ethylene and propylene; ethylene and an α -olefin; an α -olefin; ethylene and an alkyl acrylate, especially methyl acrylate; ethylene and acrylic acid; ethylene and carbon monoxide; ethylene, and carbon monoxide and an acrylate ester or acrylic acid, especially methyl

acrylate; propylene and alkyl acrylate, especially methyl acrylate; cyclopentene; cyclopentene and ethylene; cyclopentene and propylene. Monomers which contain a carbonyl group, including esters, carboxylic acids, carbon monoxide, vinyl ketones, etc., can be polymerized with Pd(II) containing catalysts herein, with the exception of those that require the presence of a neutral or cationic Lewis acid or cationic Bronsted acid, which is usually called the "first compound" in claims describing such polymerization processes.

Another useful "monomer" for these polymerization processes is a C₄ refinery catalytic cracker stream, which will often contain a mixture of n-butane, isobutane, isobutene, 1-butene, 2-butenes and small amounts of butadiene. This type of stream is referred to herein as a "crude butenes stream". This stream may act as both the monomer source and "solvent" for the polymerization. It is preferred that the concentration of 1- and 2-butenes in the stream be as high as possible, since these are the preferred compounds to be polymerized. The butadiene content should be minimized because it may be a polymerization catalyst poison. The isobutene may have been previously removed for other uses. After being used in the polymerization (during which much or most of the 1-butene would have been polymerized), the butenes stream can be returned to the refinery for further processing.

In many of the these polymerizations certain general trends may be noted, although for all of these trends there are exceptions. These trends (and exceptions) can be gleaned from the Examples.

Pressure of the monomers (especially gaseous monomers such as ethylene) has an effect on the polymerizations in many instances. Higher pressure often affects the polymer microstructure by reducing branching, especially in ethylene containing polymers. This effect is more pronounced for Ni catalysts than Pd

catalysts. Under certain conditions higher pressures also seem to give higher productivities and higher molecular weight. When an acrylate is present and a Pd catalyst is used, increasing pressure seems to decrease
5 the acrylate content in the resulting copolymer.

Temperature also affects these polymerizations. Higher temperature usually increases branching with Ni catalysts, but often has little such effect using Pd catalysts. With Ni catalysts, higher temperatures
10 appear to often decrease molecular weight. With Pd catalysts, when acrylates are present, increasing temperature usually increases the acrylate content of the polymer, but also often decreases the productivity and molecular weight of the polymer.

15 Anions surprisingly also often affect molecular weight of the polymer formed. More highly coordinating anions often give lower molecular weight polymers. Although all of the anions useful herein are relatively weakly coordinating, some are more strongly
20 coordinating than others. The coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which
25 may be referred to. The results found herein in which the molecular weight of the polymer produced is related to the coordinating ability of the anion used, is in line with the coordinating abilities of these anions as described in Beck (p. 1411) and
30 Strauss (p. 932, Table II).

In addition to the "traditional" weakly coordinating anions cited in the paragraph immediately above, heterogeneous anions may also be employed. In these cases, the true nature of the counterion is
35 poorly defined or unknown. Included in this group are MAO, MMAO and related aluminoxanes which do not form true solutions. The resulting counterions are thought to bear anionic aluminate moieties related to those

cited in the paragraph immediately above. Polymeric anionic materials such as Nafion™ polyfluorosulfonic acid can function as non-coordinating counterions. In addition, a wide variety of heterogeneous inorganic materials can be made to function as non-coordinating counterions. Examples would include aluminas, silicas, silica/aluminas, cordierites, clays, $MgCl_2$, and many others utilized as traditional supports for Ziegler-Natta olefin polymerization catalysts. These are generally materials which have Lewis or Bronsted acidity. High surface area is usually desired and often these materials will have been activated through some heating process. Heating may remove excess surface water and change the surface acidity from Bronsted to Lewis type. Materials which are not active in the role may often be made active by surface treatment. For instance, a surface-hydrated silica, zinc oxide or carbon can be treated with an organoaluminum compound to provide the required functionality.

The catalysts described herein can be heterogenized through a variety of means. The heterogeneous anions in the paragraph immediately above will all serve to heterogenize the catalysts. Catalysts can also be heterogenized by exposing them to small quantities of a monomer to encapsulate them in a polymeric material through which additional monomers will diffuse. Another method is to spray-dry the catalyst with its suitable non-coordinating counterion onto a polymeric support. Heterogeneous versions of the catalyst are particularly useful for running gas-phase polymerizations. The catalyst is suitably diluted and dispersed on the surface of the catalyst support to control the heat of polymerization. When applied to fluidized-bed polymerizations, the heterogeneous supports provide a convenient means of catalyst introduction.

Another item may effect the incorporation of polar monomers such as acrylic esters in olefin copolymers. It has been found that catalysts containing less bulky α -diimines incorporate more of the polar monomer into the polymer (one obtains a polymer with a higher percentage of polar monomer) than a catalyst containing a more bulky α -diimine, particularly when ethylene is the olefin comonomer. For instance, in an α -diimine of formula (VIII), if R^2 and R^5 are 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl, more acrylic monomer will be incorporated into the polymer. However, another common effect of using a less bulky catalyst is to produce a polymer with lower molecular weight. Therefore one may have to make a compromise between polar monomer content in the polymer and polymer molecular weight.

When an olefinic carboxylic acid is polymerized into the polymer, the polymer will of course contain carboxyl groups. Similarly in an ester containing polymer, some or all of the ester groups may be hydrolyzed to carboxyl groups (and vice versa). The carboxyl groups may be partially or completely converted into salts such as metallic salts. Such polymeric salts are termed ionomers. Ionomers are useful in adhesives, as ionomeric elastomers, and as molding resins. Salts may be made with ions of metals such as Na, K, Zn, Mg, Al, etc. The polymeric salts may be made by methods known to the artisan, for instance reaction of the carboxylic acid containing polymers with various compounds of the metals such as bases (hydroxides, carbonates, etc.) or other

compounds, such as acetylacetonates. Novel polymers that contain carboxylic acid groups herein, also form novel ionomers when the carboxylic acid groups are partially or fully converted to carboxylate salts.

5 When copolymers of an olefinic carboxylic acid or olefinic ester and selected olefins are made, they may be crosslinked by various methods known in the art, depending on the specific monomers used to make the polymer. For instance, carboxyl or ester containing
10 polymers may be crosslinked by reaction with diamines to form bisamides. Certain functional groups which may be present on the polymer may be induced to react to crosslink the polymer. For instance epoxy groups (which may be present as glycidyl esters) may be
15 crosslinked by reaction of the epoxy groups, see for instance Example 135.

It has also been found that certain fluorinated olefins, some of them containing other functional groups may be polymerized by nickel and palladium
20 catalysts. Note that these fluorinated olefins are included within the definition of $H_2C=CHR^{17}$, wherein R^{17} can be considered to be substituted hydrocarbyl, the substitution being fluorine and possibly other substituents. Olefins which may be polymerized include
25 $H_2C=CH(CH_2)_aR_fR^{42}$ wherein a is an integer of 2 to 20, R_f is perfluoroalkylene optionally containing one or more ether groups, and R^{42} is fluorine or a functional group. Suitable functional groups include hydrogen, chlorine, bromine or iodine, ester, sulfonic acid (-
30 SO_3H), and sulfonyl halide. Preferred groups for R^{42} include fluorine, ester, sulfonic acid, and sulfonyl fluoride. A sulfonic acid group containing monomer does not have to be polymerized directly. It is preferably made by hydrolysis of a sulfonyl halide
35 group already present in an already made polymer. It is preferred that the perfluoroalkylene group contain 2 to 20 carbon atoms and preferred perfluoroalkylene groups are $-(CF_2)_b-$ wherein b is 2 to 20, and -

(CF₂)_dOCF₂CF₂- wherein d is 2 to 20. A preferred olefinic comonomer is ethylene or a linear α-olefin, and ethylene is especially preferred. Polymerizations may be carried out with many of the catalysts described
5 herein, see Examples 284 to 293.

As described herein, the resulting fluorinated polymers often don't contain the expected amount of branching, and/or the lengths of the branches present are not those expected for a simple vinyl
10 polymerization.

The resulting polymers may be useful for compatibilizing fluorinated and nonfluorinated polymers, for changing the surface characteristics of fluorinated or nonfluorinated polymers (by being mixed
15 with them), as molding resins, etc. Those polymers containing functional groups may be useful where those functional groups may react or be catalysts. For instance, if a polymer is made with a sulfonyl fluoride group (R⁴² is sulfonyl fluoride) that group may be
20 hydrolyzed to a sulfonic acid, which being highly fluorinated is well known to be a very strong acid. Thus the polymer may be used as an acid catalyst, for example for the polymerization of cyclic ethers such as tetrahydrofuran.

25 In this use it has been found that this polymer is more effective than a completely fluorinated sulfonic acid containing polymer. For such uses the sulfonic acid content need not be high, say only 1 to 20 mole percent, preferably about 2 to 10 mole percent of the
30 repeat units in the polymer having sulfonic acid groups. The polymer may be crosslinked, in which case it may be soluble in the medium (for instance tetrahydrofuran), or it may be crosslinked so it swollen but not dissolved by the medium, Or it may be
35 coated onto a substrate and optionally chemically attached and/or crosslinked, so it may easily be separated from the other process ingredients.

One of the monomers that may be polymerized by the above catalysts is ethylene (E), either by itself to form a homopolymer, or with α -olefins and/or olefinic esters or carboxylic acids. The structure of the polymer may be unique in terms of several measurable properties.

These polymers, and others herein, can have unique structures in terms of the branching in the polymer. Branching may be determined by NMR spectroscopy (see the Examples for details), and this analysis can determine the total number of branches, and to some extent the length of the branches. Herein the amount of branching is expressed as the number of branches per 1000 of the total methylene ($-\text{CH}_2-$) groups in the polymer, with one exception. Methylene groups that are in an ester grouping, i.e. $-\text{CO}_2\text{R}$, are not counted as part of the 1000 methylenes. These methylene groups include those in the main chain and in the branches. These polymers, which are E homopolymers, have a branch content of about 80 to about 150 branches per 1000 methylene groups, preferably about 100 to about 130 branches per 1000 methylene groups. These branches do not include polymer end groups. In addition the distribution of the sizes (lengths) of the branches is unique. Of the above total branches, for every 100 that are methyl, about 30 to about 90 are ethyl, about 4 to about 20 are propyl, about 15 to about 50 butyl, about 3 to about 15 are amyl, and about 30 to about 140 are hexyl or longer, and it is preferred that for every 100 that are methyl, about 50 to about 75 are ethyl, about 5 to about 15 are propyl, about 24 to about 40 are butyl, about 5 to 10 are amyl, and about 65 to about 120 are hexyl or larger. These E homopolymers are often amorphous, although in some there may be a small amount of crystallinity.

Another polyolefin, which is an E homopolymer that can be made by these catalysts has about 20 to about 150 branches per 1000 methylene groups, and, per 100

methyl groups, about 4 to about 20 ethyl groups, about 1 to about 12 propyl groups, about 1 to about 12 butyl group, about 1 to about 10 amyl groups, and 0 to about 20 hexyl or larger groups. Preferably this polymer has about 40 to about 100 methyl groups per 1000 methylene groups, and per 100 methyl groups, about 6 to about 15 ethyl groups, about 2 to about 10 propyl groups, about 2 to about 10 butyl groups, about 2 to about 8 amyl groups, and about 2 to about 15 hexyl or larger groups.

Many of the polyolefins herein, including homopolyethylenes, may be crosslinked by various methods known in the art, for instance by the use of peroxide or other radical generating species which can crosslink these polymers. Such crosslinked polymers are novel when the uncrosslinked polymers from which they are derived are novel, because for the most part the structural feature(s) of the uncrosslinked polymers which make them novel will be carried over into the crosslinked forms.

In addition, some of the E homopolymers have an exceptionally low density, less than about 0.86 g/mL, preferably about 0.85 g/mL or less, measured at 25°C. This density is based on solid polymer.

Homopolymers of polypropylene (P) can also have unusual structures. Similar effects have been observed with other α -olefins (e.g. 1-hexene). A "normal" P homopolymer will have one methyl group for each methylene group (or 1000 methyl groups per 1000 methylene groups), since the normal repeat unit is -CH(CH₃)CH₂-. However, using a catalyst of formula (I) in which M is Ni(II) in combination with an alkyl aluminum compound it is possible to produce a P homopolymer with about 400 to about 600 methyl groups per 1000 methylene groups, preferably about 450 to about 550 methyl groups per 1000 methylene groups. Similar effects have been observed with other α -olefins (e.g. 1-hexene).

In the polymerization processes described herein olefinic esters and/or carboxylic acids may also be present, and of course become part of the copolymer formed. These esters may be copolymerized with one or
5 more of E and one or more α -olefins. When copolymerized with E alone polymers with unique structures may be formed.

In many such E/olefinic ester and/or carboxylic acid copolymers the overall branching level and the
10 distribution of branches of various sizes are unusual. In addition, where and how the esters or carboxylic acids occur in the polymer is also unusual. A relatively high proportion of the repeat units derived from the olefinic esters are at the ends of branches.
15 In such copolymers, it is preferred that the repeat units derived from the olefinic esters and carboxylic acids are about 0.1 to 40 mole percent of the total repeat units, more preferably about 1 to about 20 mole percent. In a preferred ester, m is 0 and R^1 is
20 hydrocarbyl or substituted hydrocarbyl. It is preferred that R^1 is alkyl containing 1 to 20 carbon atoms, more preferred that it contains 1 to 4 carbon atoms, and especially preferred that R^1 is methyl.

One such preferred dipolymer has about 60 to 100
25 methyl groups (excluding methyl groups which are esters) per 1000 methylene groups in the polymer, and contains, per 100 methyl branches, about 45 to about 65 ethyl branches, about 1 to about 3 propyl branches, about 3 to about 10 butyl branches, about 1 to about 3
30 amyl branches, and about 15 to about 25 hexyl or longer branches. In addition, the ester and carboxylic acid containing repeat units are often distributed mostly at the ends of the branches as follows. If the branches, and the carbon atom to which they are attached to the
35 main chain, are of the formula $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}^1$, wherein the CH is part of the main chain, then in some of these polymers about 40 to about 50 mole percent of ester groups are found in branches where n is 5 or more,

about 10 to about 20 mole percent when n is 4, about 20 to 30 mole percent when n is 1, 2 and 3 and about 5 to about 15 mole percent when n is 0. When n is 0, an acrylate ester has polymerized "normally" as part of the main chain, with the repeat unit $-\text{CH}_2-\text{CHCO}_2\text{R}^1-$.

These branched polymers which contain olefin and olefinic ester monomer units, particularly copolymers of ethylene and methyl acrylate and/or other acrylic esters are particularly useful as viscosity modifiers for lubricating oils, particularly automotive lubricating oils.

Under certain polymerization conditions, some of the polymerization catalysts described herein produce polymers whose structure is unusual, especially considering from what compounds (monomers) the polymers were made, and the fact that polymerization catalysts used herein are so-called transition metal coordination catalysts (more than one compound may be involved in the catalyst system, one of which must include a transition metal). Some of these polymers were described in a somewhat different way above, and they may be described as "polyolefins" even though they may contain other monomer units which are not olefins (e.g., olefinic esters). In the polymerization of an unsaturated compound of the formula $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_e\text{G}$, wherein e is 0 or an integer of 1 or more, and G is hydrogen or $-\text{CO}_2\text{R}^1$, the usual ("normal") polymeric repeat unit obtained would be $-\text{CH}_2-\text{CH}[(\text{CH}_2)_e\text{G}]$ -, wherein the branch has the formula $-(\text{CH}_2)_e\text{G}$. However, with some of the instant catalysts a polymeric unit may be $-\text{CH}_2-\text{CH}[(\text{CH}_2)_f\text{G}]$ -, wherein $f \neq e$, and f is 0 or an integer of 1 or more. If $f < e$, the "extra" methylene groups may be part of the main polymer chain. If $f > e$ (parts of) additional monomer molecules may be incorporated into that branch. In other words, the structure of any polymeric unit may be irregular and different for monomer molecules incorporated into the polymer, and the structure of such a polymeric unit obtained could

be rationalized as the result of "migration of the active polymerizing site" up and down the polymer chain, although this may not be the actual mechanism. This is highly unusual, particularly for polymerizations employing transition metal coordination catalysts.

For "normal" polymerizations, wherein the polymeric unit $-\text{CH}_2-\text{CH}[(\text{CH}_2)_e\text{G}] -$ is obtained, the theoretical amount of branching, as measured by the number of branches per 1000 methylene ($-\text{CH}_2-$) groups can be calculated as follows which defines terms "theoretical branches" or "theoretical branching" herein:

$$\text{Theoretical branches} = \frac{1000 \cdot \text{Total mole fraction of } \alpha\text{-olefins}}{\{[\Sigma(2 \cdot \text{mole fraction } e=0)] + [\Sigma(\text{mole fraction } \alpha\text{-olefin} \cdot e)]\}}$$

In this equation, an α -olefin is any olefinic compound $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_e\text{G}$ wherein $e \neq 0$. Ethylene or an acrylic compound are the cases wherein $e=0$. Thus to calculate the number of theoretical branches in a polymer made from 50 mole percent ethylene ($e=0$), 30 mole percent propylene ($e=1$) and 20 mole percent methyl 5-heptenoate ($e=4$) would be as follows:

$$\text{Theoretical branches} = \frac{1000 \cdot 0.5}{\{[(2 \cdot 0.5)] + [(0.30 \cdot 1) + (0.20 \cdot 4)]\}} = 238 \text{ (branches/1000 methylenes)}$$

The "1000 methylenes" include all of the methylene groups in the polymer, including methylene groups in the branches.

For some of the polymerizations described herein, the actual amount of branching present in the polymer is considerably greater than or less than the above theoretical branching calculations would indicate. For instance, when an ethylene homopolymer is made, there should be no branches, yet there are often many such branches. When an α -olefin is polymerized, the

branching level may be much lower or higher than the theoretical branching level. It is preferred that the actual branching level is at 90% or less of the theoretical branching level, more preferably about 80% or less of the theoretical branching level, or 110% or more of the theoretical branching level, more preferably about 120% or more of the theoretical branching level. The polymer should also have at least about 50 branches per 1000 methylene units, preferably about 75 branches per 1000 methylene units, and more preferably about 100 branches per 1000 methylene units. In cases where there are "0" branches theoretically present, as in ethylene homopolymers or copolymers with acrylics, excess branches as a percentage cannot be calculated. In that instance if the polymer has 50 or more, preferably 75 or more branches per 1000 methylene groups, it has excess branches (i.e. in branches in which $f > 0$).

These polymers also have "at least two branches of different lengths containing less than 6 carbon atoms each." By this is meant that branches of at least two different lengths (i.e. number of carbon atoms), and containing less than 6 carbon atoms, are present in the polymer. For instance the polymer may contain ethyl and butyl branches, or methyl and amyl branches.

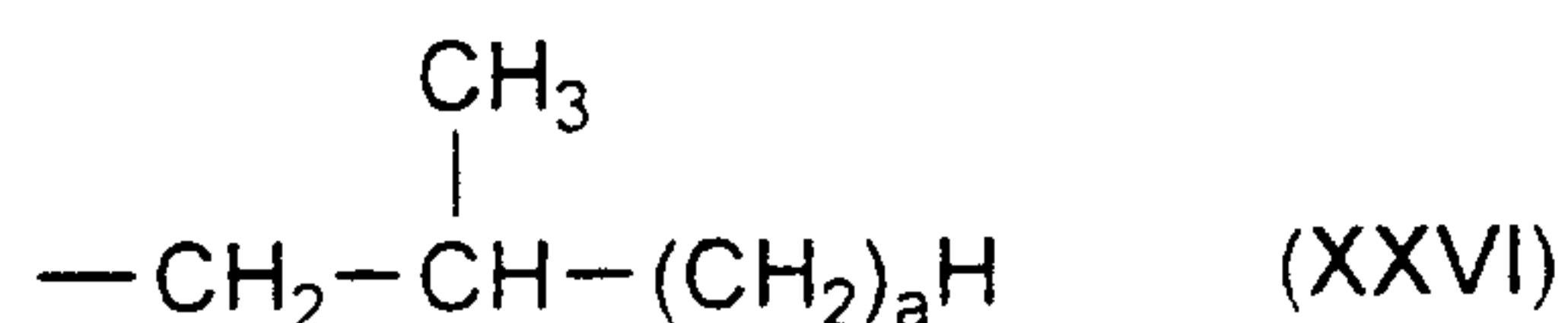
As will be understood from the above discussion, the lengths of the branches ("f") do not necessarily correspond to the original sizes of the monomers used ("e"). Indeed branch lengths are often present which do not correspond to the sizes of any of the monomers used and/or a branch length may be present "in excess". By "in excess" is meant there are more branches of a particular length present than there were monomers which corresponded to that branch length in the polymer. For instance, in the copolymerization of 75 mole percent ethylene and 25 mole percent 1-butene it would be expected that there would be 125 ethyl branches per 1000 methylene carbon atoms. If there

were more ethyl branches than that, they ~~would be in~~ excess compared to the theoretical branching. There may also be a deficit of specific length branches. If there were less than 125 ethyl branches per 1000 methylene groups in this polymer there would be a deficit. Preferred polymers have 90% or less or 110% or more of the theoretical amount of any branch length present in the polymer, and it is especially preferred if these branches are about 80% or less or about 120% or more of the theoretical amount of any branch length. In the case of the 75 mole percent ethylene/25 mole percent 1-butene polymer, the 90% would be about 113 ethyl branches or less, while the 110% would be about 138 ethyl branches or more. Such polymers may also or exclusively contain at least 50 branches per 1000 methylene atoms with lengths which should not theoretically (as described above) be present at all.

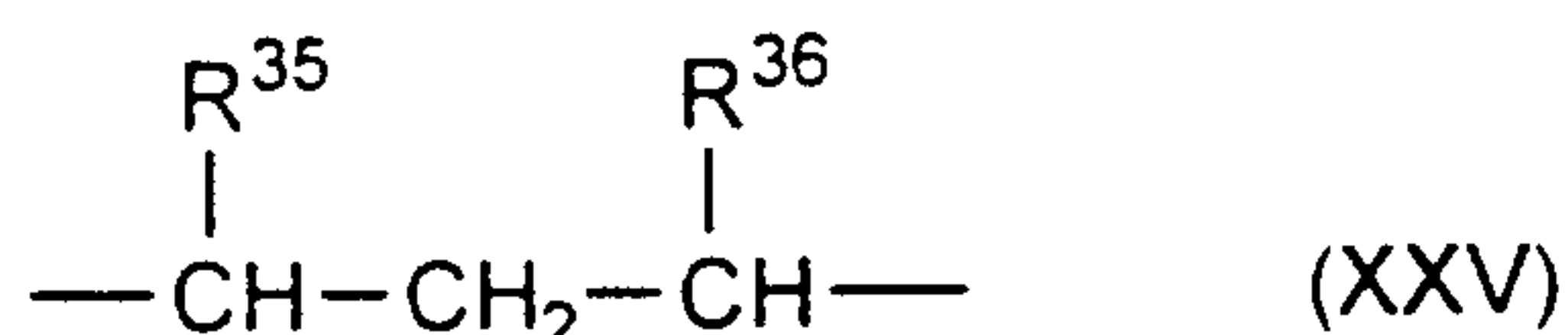
These polymers also have "at least two branches of different lengths containing less than 6 carbon atoms each." By this is meant that branches of at least two different lengths (i.e. number of carbon atoms), and containing less than 6 carbon atoms, are present in the polymer. For instance the polymer may contain ethyl and butyl branches, or methyl and amyl branches.

Some of the polymers produced herein are novel because of unusual structural features. Normally, in polymers of alpha-olefins of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$ wherein a is an integer of 2 or more made by coordination polymerization, the most abundant, and often the only, branches present in such polymers have the structure $-(\text{CH}_2)_a\text{H}$. Some of the polymers produced herein are novel because methyl branches comprise about 25% to about 75% of the total branches in the polymer. Such polymers are described in Examples 139, 162, 173 and 243-245. Some of the polymers produced herein are novel because in addition to having a high percentage (25-75%) of methyl branches (of the total branches present), they also contain linear branches of the

structure $-(CH_2)_nH$ wherein n is an integer of six or greater. Such polymers are described in Examples 139, 173 and 243-245. Some of the polymers produced herein are novel because in addition to having a high
 5 percentage (25-75%) of methyl branches (of the total branches present), they also contain the structure (XXVI), preferably in amounts greater than can be accounted for by end groups, and more preferably greater than 0.5 (XXVI) groups per thousand methyl
 10 groups in the polymer greater than can be accounted for by end groups.



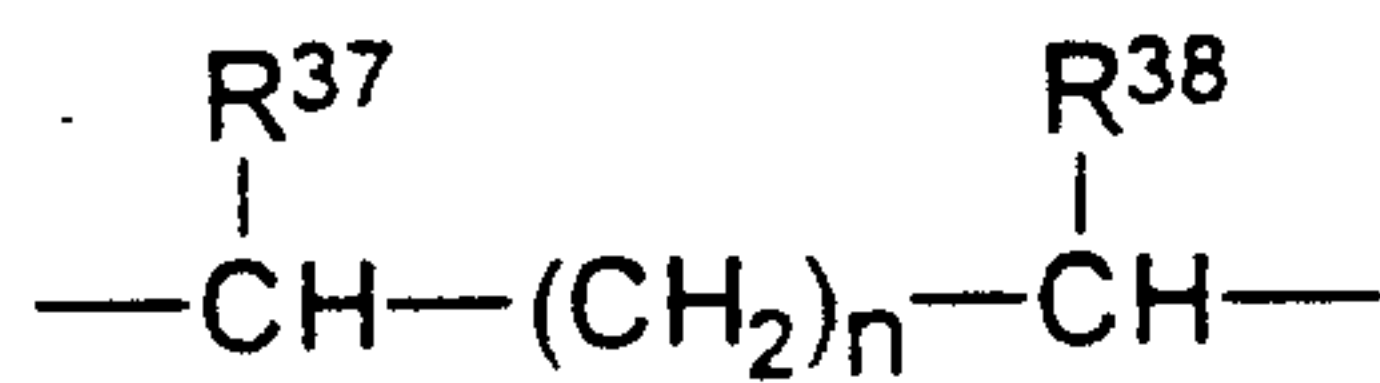
15 Normally, homo- and copolymers of one or more alpha-olefins of the formula $CH_2=CH(CH_2)_aH$ wherein a is an integer of 2 or more contain as part of the polymer backbone the structure (XXV)



20 wherein R^{35} and R^{36} are alkyl groups. In most such polymers of alpha-olefins of this formula (especially those produced by coordination-type polymerizations), both of R^{35} and R^{36} are $-(CH_2)_aH$. However, in certain of these polymers described herein, about 2 mole percent or more, preferably about 5 mole percent or more and more preferably about 50 mole percent or more of the total amount of (XXV) in said polymer consists
 30 of the structure where one of R^{35} and R^{36} is a methyl group and the other is an alkyl group containing two or more carbon atoms. Furthermore, in certain of these polymers described herein, structure (XXV) may occur in side chains as well as in the polymer backbone.
 35 Structure (XXV) can be detected by ^{13}C NMR. The signal

for the carbon atom of the methylene group between the two methine carbons in (XXV) usually occurs in the ^{13}C NMR at 41.9 to 44.0 ppm when one of R^{35} and R^{36} is a methyl group and the other is an alkyl group containing two or more carbon atoms, while when both R^{35} and R^{36} contain 2 or more carbon atoms, the signal for the methylene carbon atom occurs at 39.5 to 41.9 ppm. Integration provides the relative amounts of these structures present in the polymer. If there are interfering signals from other carbon atoms in these regions, they must be subtracted from the total integrals to give correct values for structure (XXV).

Normally, homo- and copolymers of one or more alpha-olefins of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$ wherein a is an integer of 2 or more (especially those made by coordination polymerization) contain as part of the polymer backbone structure (XXIV) wherein n is 0, 1, or 2. When n is 0, this structure is termed "head to head" polymerization. When n is 1, this structure is termed "head to tail" polymerization. When n is 2, this structure is termed "tail to tail" polymerization. In most such polymers of alpha-olefins of this formula (especially those produced by coordination-type polymerizations), both of R^{37} and R^{38} are $-(\text{CH}_2)_a\text{H}$. However some of the polymers of alpha-olefins of this formula described herein are novel in that they also contain structure (XXIV) wherein $n = a$, R^{37} is a methyl group, and R^{38} is an alkyl group with 2 or more carbon atoms.

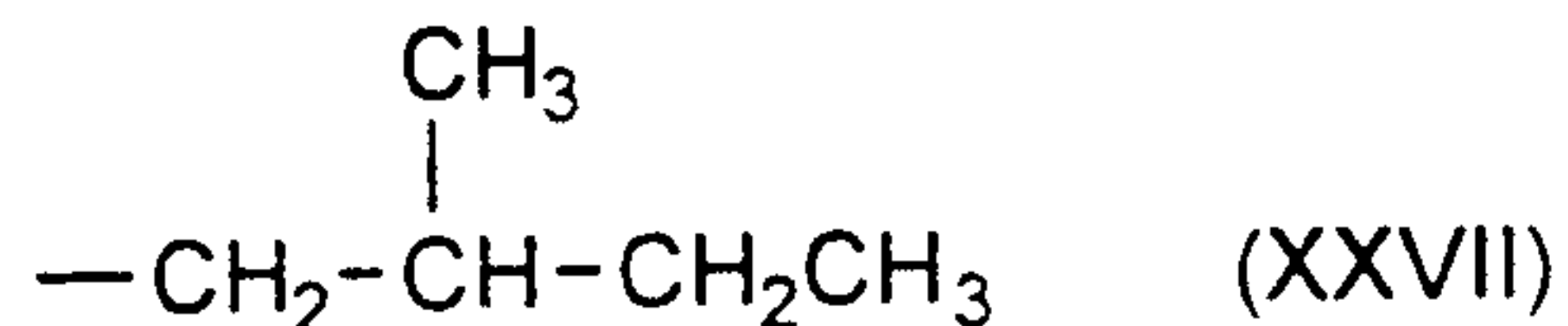


(XXIV)

Normally polyethylene made by coordination polymerization has a linear backbone with either no

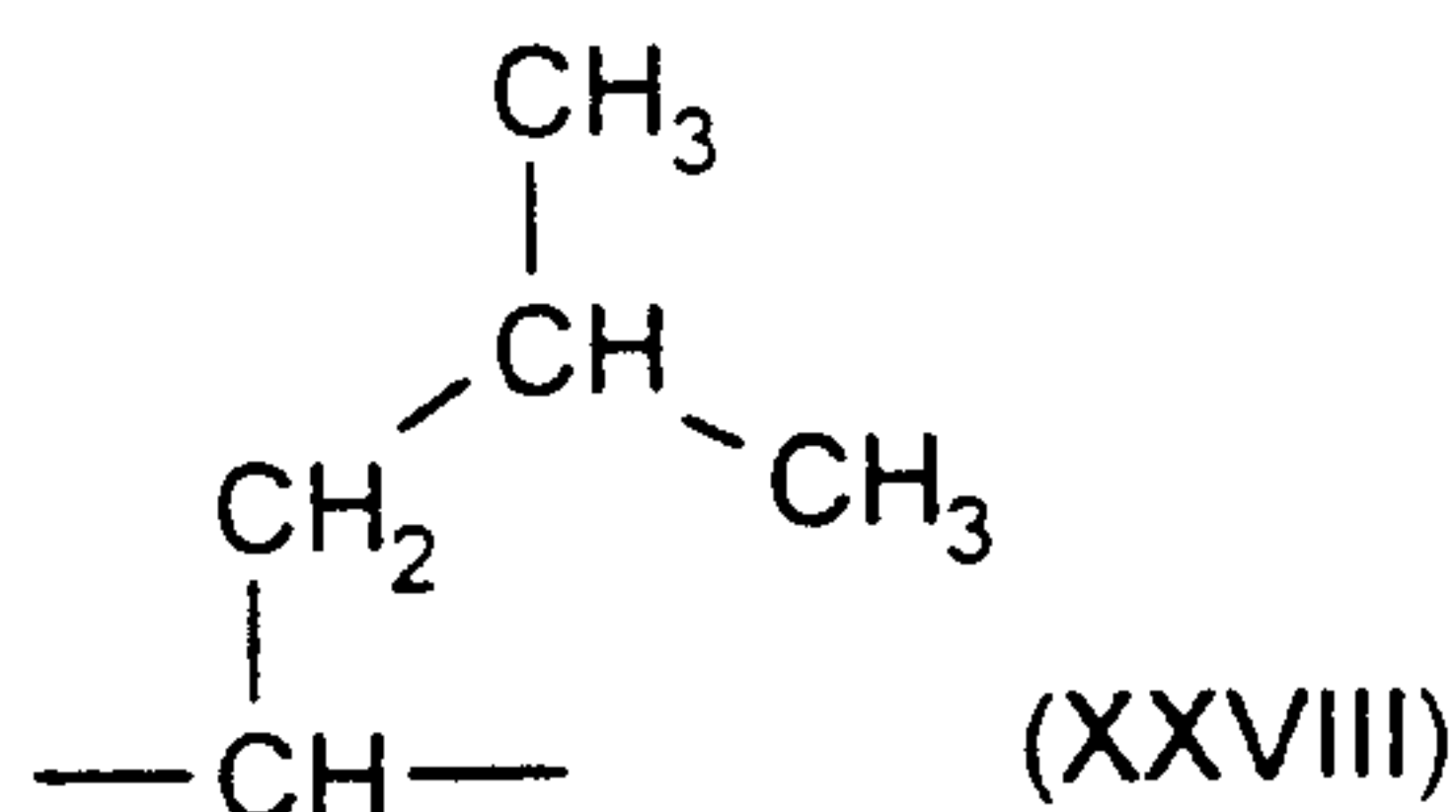
branching, or small amounts of linear branches. Some of the polyethylenes described herein are unusual in that they contain structure (XXVII) which has a methine carbon that is not part of the main polymer backbone.

5

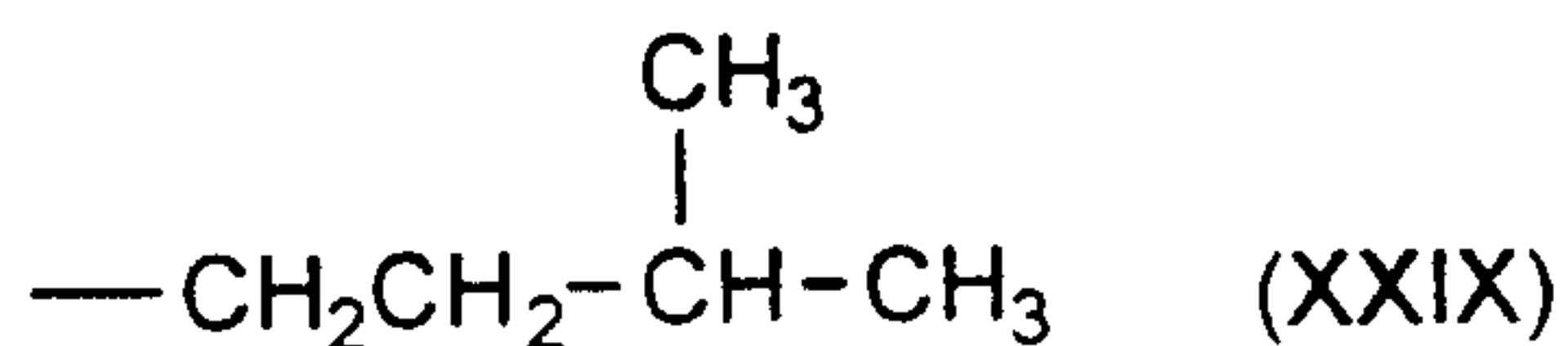


Normally, polypropylene made by coordination polymerization has methyl branches and few if any branches of other sizes. Some of the polypropylenes described herein are unusual in that they contain one or both of the structures (XXVIII) and (XXIX).

10

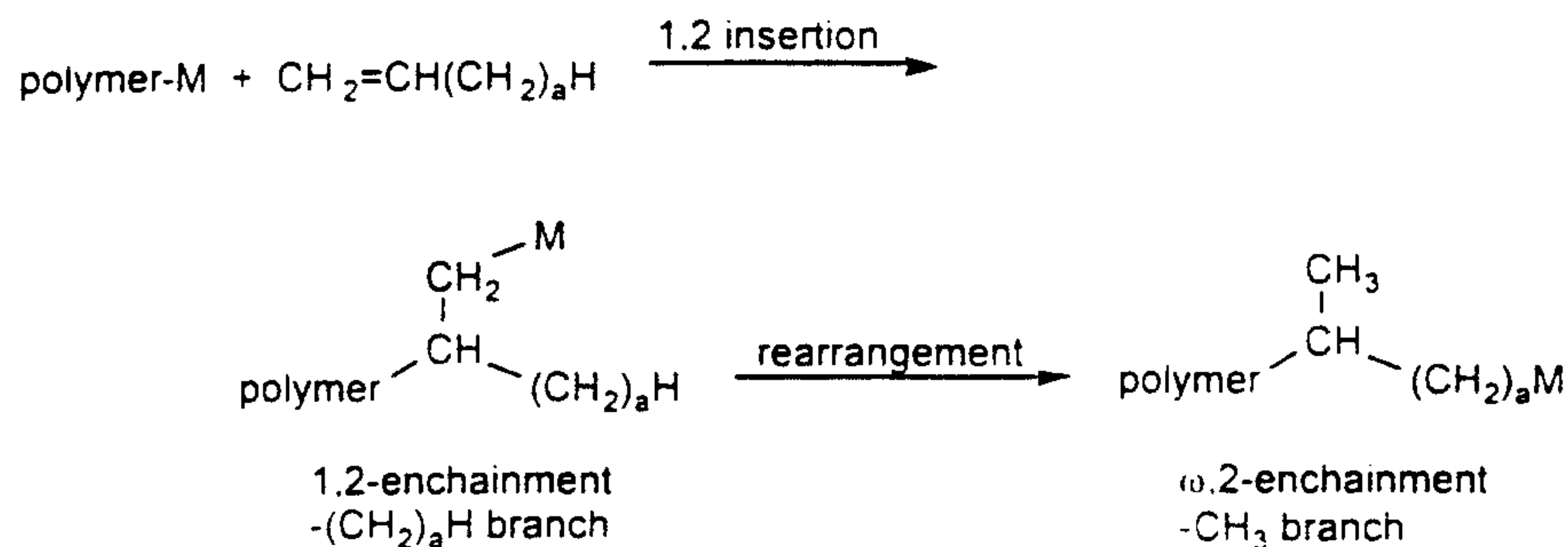


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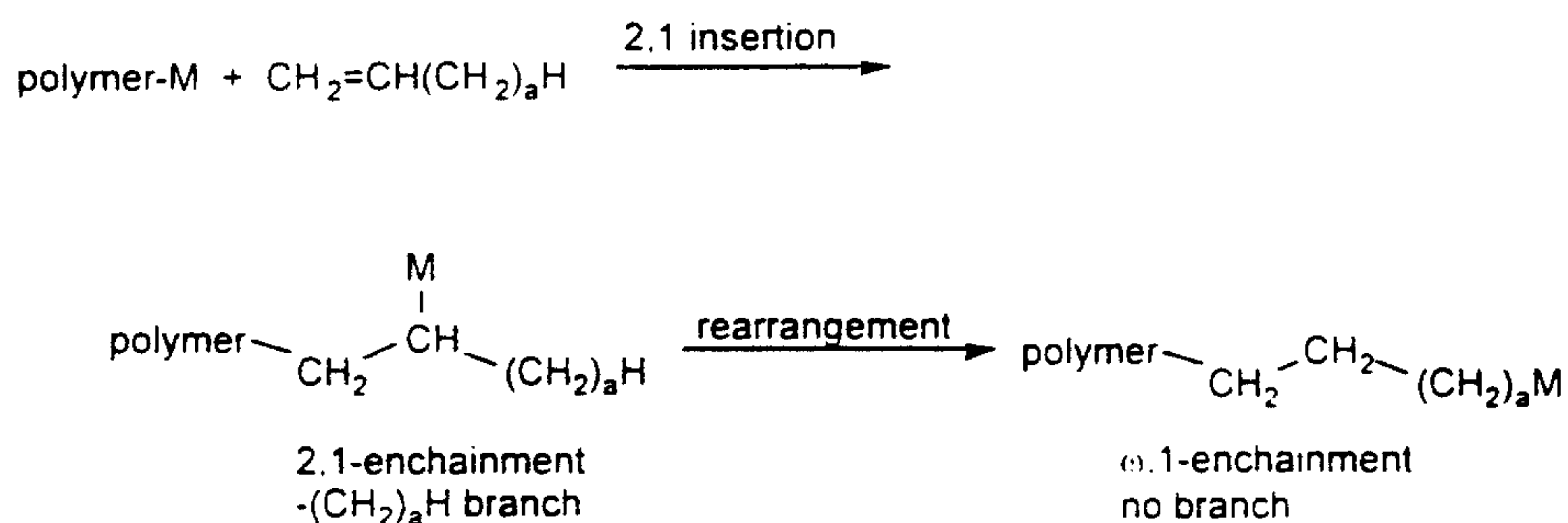


As the artisan understands, in coordination polymerization alpha-olefins of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$ may insert into the growing polymer chain in a 1,2 or 2,1 manner. Normally these insertion steps lead to 1,2- enchainment or 2,1-enchainment of the monomer. Both of these fundamental steps form a - $(\text{CH}_2)_a\text{H}$ branch. However, with some catalysts herein, some of the initial product of 1,2 insertion can rearrange by migration of the coordinated metal atom to the end of the last inserted monomer before insertion of additional monomer occurs. This results in omega,2- enchainment and the formation of a methyl branch.

25



It is also known that with certain other catalysts, some of the initial product of 2,1 insertion can rearrange in a similar manner by migration of the coordinated metal atom to the end of the last inserted monomer. This results in omega,1-enchainment and no branch is formed.



10

Of the four types of alpha-olefin enchainment, omega,1-enchainment is unique in that it does not generate a branch. In a polymer made from an alpha-olefin of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_a\text{H}$, the total number of branches per 1000 methylene groups (B) can be expressed as:

$$B = (1000)(1-X_{\omega,1}) / [(1-X_{\omega,1})a + X_{\omega,1}(a+2)]$$

where $X_{\omega,1}$ is the fraction of omega,1-enchainment

20

Solving this expression for $X_{\omega,1}$ gives:

$$X_{\omega,1} = (1000 - aB) / (1000 + 2B)$$

This equation provides a means of calculating the fraction of omega,1-enchainment in a polymer of a linear alpha-olefin from the total branching B. Total branching can be measured by ^1H NMR or ^{13}C NMR. Similar equations can be written for branched alpha-

olefins. For example, the equation for 4-methyl-1-pentene is:

$$X_{\omega,1} = (2000 - 2B)/(1000 + 2B)$$

Most polymers of alpha-olefins made by other coordination polymerization methods have less than 5% omega,1-enchainment. Some of the alpha-olefin polymers described herein have unusually large amounts (say >5%) of omega,1-enchainment. In essence this is similar to stating that a polymer made from an α -olefin has much less than the "expected" amount of branching. Although many of the polymerizations described herein give substantial amounts of $\omega,1$ - and other unusual forms of enchainment of olefinic monomers, it has surprisingly been found that "unsymmetrical" α -diimine ligands of formula (VIII) give especially high amounts of $\omega,1$ -enchainment. In particular when R^2 and R^5 are phenyl, and one or both of these is substituted in such a way as different sized groups are present in the 2 and 6 position of the phenyl ring(s), $\omega,1$ -enchainment is enhanced. For instance, if one or both of R^2 and R^5 are 2-t-butylphenyl, this enchainment is enhanced. In this context when R^2 and/or R^5 are "substituted" phenyl the substitution may be not only in the 2 and/or 6 positions, but on any other position in the phenyl ring. For instance, 2,5-di-t-butylphenyl, and 2-t-butyl-4,6-dichlorophenyl would be included in substituted phenyl.

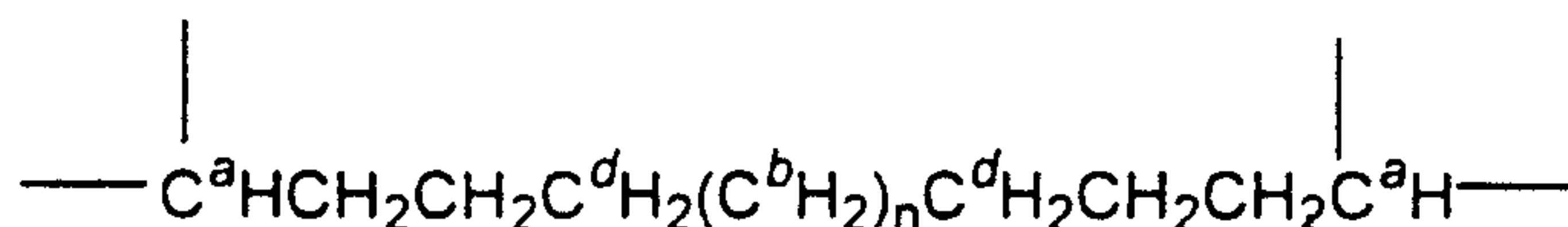
The steric effect of various groupings has been quantified by a parameter called E_s , see R. W. Taft, Jr., J. Am. Chem. Soc., vol. 74, p. 3120-3128, and M.S. Newman, Steric Effects in Organic Chemistry, John Wiley & Sons, New York, 1956, p. 598-603. For the purposes herein, the E_s values are those for o-substituted benzoates described in these publications. If the value for E_s for any particular group is not known, it can be determined by methods described in these publications. For the purposes herein, the value of hydrogen is defined to be the same as for methyl. It

is preferred that difference in E_s , when $R^{1,2}$ and preferably also R^5 is phenyl, between the groups substituted in the 2 and 6 positions of the phenyl ring is at least 0.15, more preferably at least about 0.20, and especially preferably about 0.6 or more. These phenyl groups may be unsubstituted or substituted in any other manner in the 3, 4 or 5 positions.

These differences in E_s are preferred in a diimine such as (VIII), and in any of the polymerization processes herein wherein a metal complex containing an α -diimine ligand is used or formed. The synthesis and use of such α -diimines is illustrated in Examples 454-463.

Because of the relatively large amounts of $\omega,1$ -enchainment that may be obtained using some of the polymerization catalysts reported herein novel polymers can be made. Among these homopolypropylene (PP). In some of the PP's made herein the structure

20



(XXXX)

may be found. In this structure each C^a is a methine carbon atom that is a branch point, while each C^b is a methylene group that is more than 3 carbon atoms removed from any branch point (C^a). Herein methylene groups of the type $-C^b H_2-$ are termed $\delta+$ (or delta+) methylene groups. Methylene groups of the type $-C^d H_2-$, which are exactly the third carbon atom from a branch point, are termed γ (gamma) methylene groups. The NMR signal for the $\delta+$ methylene groups occurs at about 29.75 ppm, while the NMR signal for the γ methylene groups appears at about 30.15 ppm. Ratios of these types of methylene groups to each other and the total number of methylene groups in the PP is done by the usual NMR integration techniques.

It is preferred that PP's made herein have about 25 to about 300 δ^+ methylene groups per 1000 methylene groups (total) in the PP.

It is also preferred that the ratio of $\delta^+:\gamma$ methylene groups in the PP be 0.7 to about 2.0.

The above ratios involving δ^+ and γ methylene groups in PP are of course due to the fact that high relatively high $\omega,1$ enchainment can be obtained. It is preferred that about 30 to 60 mole percent of the monomer units in PP be enchainment in an $\omega,1$ fashion. Using the above equation, the percent $\omega,1$ enchainment for polypropylene can be calculated as:

$$\% \omega,1 = (100)(1000-B)/(1000+2B)$$

wherein B is the total branching (number of methyl groups) per 1000 methylene groups in the polymer.

Homo- or copolymers of one or more linear α -olefins containing 3 to 8 carbon atoms may also have δ^+ carbon atoms in them, preferably at least about 1 or more δ^+ carbon atoms per 1000 methylene groups.

The above polymerization processes can of course be used to make relatively random copolymers (except for certain CO copolymers) of various possible monomers. However, some of them can also be used to make block polymers. A block polymer is conventionally defined as a polymer comprising molecules in which there is a linear arrangement of blocks, a block being a portion of a polymer molecule which the monomeric units have at least one constitutional or configurational feature absent from adjacent portions (definition from H. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, Vol. 2, John Wiley & Sons, New York, 1985, p. 324). Herein in a block copolymer, the constitutional difference is a difference in monomer units used to make that block, while in a block homopolymer the same monomer(s) are used but the repeat units making up different blocks are different structure and/or ratios of types of structures.

Since it is believed that many of the polymerization processes herein have characteristics that often resemble those of living polymerizations, making block polymers may be relatively easy. One method is to simply allow monomer(s) that are being polymerized to be depleted to a low level, and then adding different monomer(s) or the same combination of monomers in different ratios. This process may be repeated to obtain polymers with many blocks.

Lower temperatures, say about less than 0°C, preferably about -10° to about -30°, tends to enhance the livingness of the polymerizations. Under these conditions narrow molecular weight distribution polymers may be obtained (see Examples 367-369 and 371), and block copolymers may also be made (Example 370).

As pointed out above, certain polymerization conditions, such as pressure, affect the microstructure of many polymers. The microstructure in turn affects many polymer properties, such as crystallization. Thus, by changing polymerization conditions, such as the pressure, one can change the microstructure of the part of the polymer made under those conditions. This of course leads to a block polymer, a polymer have defined portions having structures different from other defined portions. This may be done with more than one monomer to obtain a block copolymer, or may be done with a single monomer or single mixture of monomers to obtain a block homopolymer. For instance, in the polymerization of ethylene, high pressure sometimes leads to crystalline polymers, while lower pressures give amorphous polymers. Changing the pressure repeatedly could lead to an ethylene homopolymer containing blocks of amorphous polyethylene and blocks of crystalline polyethylene. If the blocks were of the correct size, and there were enough of them, a thermoplastic elastomeric homopolyethylene could be

produced. Similar polymers could possibly be made from other monomer(s), such as propylene.

Homopolymers of α -olefins such as propylene, that is polymers which were made from a monomer that
5 consisted essentially of a single monomer such as propylene, which are made herein, sometimes exhibit unusual properties compared to their "normal" homopolymers. For instance, such a homopolypropylene usually would have about 1000 methyl groups per 1000
10 methylene groups. Polypropylenes made herein typically have about half that many methyl groups, and in addition have some longer chain branches. Other α -olefins often give polymers whose microstructure is analogous to these polypropylenes when the above
15 catalysts are used for the polymerization.

These polypropylenes often exhibit exceptionally low glass transition temperatures (Tg's). "Normal" polypropylene has a Tg of about -17°C , but the polypropylenes herein have a Tg of -30°C or less,
20 preferably about -35°C or less, and more preferably about -40°C or less. These Tg's are measured by Differential Scanning Calorimetry at a heating rate of $10^{\circ}\text{C}/\text{min}$, and the Tg is taken as the midpoint of the transition. These polypropylenes preferably have at
25 least 50 branches (methyl groups) per 1000 carbon atoms, more preferably at least about 100 branches per 1000 methylene groups.

Previously, when cyclopentene was coordination polymerized to higher molecular weights, the resulting
30 polymer was essentially intractable because of its very high melting point, greatly above 300°C . Using the catalysts here to homopolymerize cyclopentene results in a polymer that is tractable, i.e., may be reformed, as by melt forming. Such polymers have an end of
35 melting point of about 320°C or less, preferably about 300°C or less, or a melting point of about 275°C or less, preferably about 250°C or less. The melting point is determined by Differential Scanning

Calorimetry at a heating rate of 15°C/min, and taking the maximum of the melting endotherm as the melting point. However these polymers tend to have relatively diffuse melting points, so it is preferred to measure the "melting point" by the end of melting point. The method is the same, except the end of melting is taken as the end (high temperature end) of the melting endotherm which is taken as the point at which the DSC signal returns to the original (extrapolated) baseline. Such polymers have an average degree of polymerization (average number of cyclopentene repeat units per polymer chain) of about 10 or more, preferably about 30 or more, and more preferably about 50 or more.

In these polymers, enchainment of the cyclopentene repeat units is usually as cis-1,3-pentylene units, in contrast to many prior art cyclopentenenes which were enchainned as 1,2-cyclopentylene units. It is preferred that about 90 mole percent or more, more preferably about 95 mole percent or more of the enchainned cyclopentene units be enchainned as 1,3-cyclopentylene units, which are preferably cis-1,3-cyclopentylene units.

The X-ray powder diffraction pattern of the instant poly(cyclopentenenes) is also unique. To produce cyclopentene polymer samples of uniform thickness for X-ray measurements, powder samples were compressed into disks approximately 1 mm thick and 32 mm in diameter. X-ray powder diffraction patterns of the samples were collected over the range 10-50° 2θ. The diffraction data were collected using an automated Philips θ-θ diffractometer (Philips X'pert System) operating in the symmetrical transmission mode (Ni-filtered CuKα radiation, equipped with a diffracted beam collimator (Philips Thin Film Collimator system), Xe filled proportional detector, fixed step mode (0.05°/step), 12.5 sec./step, 1/4° divergence slit). Reflection positions were identified using the peak finding routine in the APD suite of programs provided with the

X'pert System. The X-ray powder diffraction pattern had reflections at approximately 17.3° , 19.3° , 24.2° , and 40.7° 2θ , which correspond to d-spacings of approximately 0.512, 0.460, 0.368 and 0.222 nm, respectively. These polymers have a monoclinic unit cell of the approximate dimensions: $a=0.561$ nm; $b=0.607$ nm; $c=7.37$ nm; and $\beta=123.2^\circ$.

Copolymers of cyclopentene and various other olefins may also be made. For instance a copolymer of ethylene and cyclopentene may also be made. In such a copolymer it is preferred that at least 50 mole percent, more preferably at least about 70 mole percent, of the repeat units are derived from cyclopentene. As also noted above, many of the polymerization systems described herein produce polyethylenes that have considerable branching in them. Likewise the ethylene units which are copolymerized with the cyclopentene herein may also be branched, so it is preferred that there be at least 20 branches per 1000 methylene carbon atoms in such copolymers. In this instance, the "methylene carbon atoms" referred to in the previous sentence do not include methylene groups in the cyclopentene rings. Rather it includes methylene groups only derived from ethylene or other olefin, but not cyclopentene.

Another copolymer that may be prepared is one from cyclopentene and an α -olefin, more preferably a linear α -olefin. It is preferred in such copolymers that repeat units derived from cyclopentene are 50 mole percent or more of the repeat units. As mentioned above, α -olefins may be enchainned in a 1, ω fashion, and it is preferred that at least 10 mole percent of the repeat units derived from the α -olefin be enchainned in such a fashion. Ethylene may also be copolymerized with the cyclopentene and α -olefin.

Poly(cyclopentene) and copolymers of cyclopentene, especially those that are (semi)crystalline, may be used as molding and extrusion resins. They may contain

various materials normally found in resins, such as fillers, reinforcing agents, antioxidants, antiozonants, pigments, tougheners, compatibilizers, dyes, flame retardant, and the like. These polymers
5 may also be drawn or melt spun into fibers. Suitable tougheners and compatibilizers include polycyclopentene resin which has been grafted with maleic anhydride, an grafted EPDM rubber, a grafted EP rubber, a functionalized styrene/butadiene rubber, or other
10 rubber which has been modified to selectively bond to components of the two phases.

In all of the above homo- and copolymers of cyclopentene, where appropriate, any of the preferred state may be combined any other preferred state(s).

15 The homo- and copolymers of cyclopentene described above may used or made into certain forms as described below:

1. The cyclopentene polymers described above may be part of a polymer blend. That is they may be
20 mixed in any proportion with one or more other polymers which may be thermoplastics and/or elastomers. Suitable polymers for blends are listed below in the listing for blends of other polymers described herein. One preferred type of polymer which may be blended is a
25 toughening agent or compatibilizer, which is often elastomeric and/or contains functional groups which may help compatibilize the mixture, such as epoxy or carboxyl.

2. The polycyclopentenenes described herein are
30 useful in a nonwoven fabric comprising fibrillated three-dimensional network fibers prepared by using of a polycyclopentene resin as the principal component. It can be made by flash-spinning a homogeneous solution containing a polycyclopentene. The resultant nonwoven
35 fabric is excellent in heat resistance, dimensional stability and solvent resistance.

3. A shaped part of any of the cyclopentene containing resins. This part may be formed by

injection molding, extrusion, and thermoforming.

Exemplary uses include molded part for automotive use, medical treatment container, microwave-range container, food package container such as hot packing container, oven container, retort container, etc., and heat-resisting transparent container such as heat-resisting bottle.

4. A sheet or film of any of the cyclopentene containing resins. This sheet or film may be clear and may be used for optical purposes (i.e. breakage resistant glazing). The sheet or film may be oriented or unoriented. Orientation may be carried out by any of the known methods such as uniaxial or biaxial drawing. The sheet or film may be stampable or thermoformable.

5. The polycyclopentene resins are useful in nonwoven fabrics or microfibers which are produced by melt-blowing a material containing as a main component a polycyclopentene. A melt-blowing process for producing a fabric or fiber comprises supplying a polycyclopentene in a molten form from at least one orifice of a nozzle into a gas stream which attenuates the molten polymer into microfibers. The nonwoven fabrics are excellent in heat-resistant and chemical resistant characteristics, and are suitable for use as medical fabrics, industrial filters, battery separators and so forth. The microfibers are particularly useful in the field of high temperature filtration, coalescing and insulation.

6. A laminate in which one or more of the layers comprises a cyclopentene resin. The laminate may also contain adhesives, and other polymers in some or all of the layers, or other materials such as paper, metal foil, etc. Some or all of the layers, may be oriented in the same or different directions. The laminate as a whole may also be oriented. Such materials are useful for containers, or other uses where barrier properties are required.

7. A fiber of a cyclopentene polymer. This fiber may be undrawn or drawn to further orient it. It is useful for apparel and in industrial application where heat resistance and/or chemical resistance are
5 important.

8. A foam or foamed object of a cyclopentene polymer. The foam may be formed in any conventional manner such as by using blowing agents.

9. The cyclopentene resins may be microporous
10 membranes. They may be used in process wherein semi-permeable membranes are normally used.

In addition, the cyclopentene resins may be treated or mixed with other materials to improve certain properties, as follows:

15 1. They may further be irradiated with electron rays. This often improves heat resistance and/or chemical resistance, and is relatively inexpensive. Thus the molding is useful as a material required to have high heat resistance, such as a structural
20 material, a food container material, a food wrapping material or an electric or electronic part material, particularly as an electric or electronic part material, because it is excellent in soldering resistance.

25 2. Parts with a crystallinity of at least 20% may be obtained by subjecting cyclopentene polymers having an end of melting point between 240 and 300°C to heat treatment (annealing) at a temperature of 120°C to just below the melting point of the polymer. Preferred
30 conditions are a temperature of 150 to 280°C. for a period of time of 20 seconds to 90 minutes, preferably to give a cyclopentene polymer which has a heat deformation temperature of from 200 to 260°C. These parts have good physical properties such as heat
35 resistance and chemical resistance, and thus are useful for, for example, general construction materials, electric or electronic devices, and car parts.

3. Cyclopentene resins may be nucleated to promote crystallization during processing. An example would be a polycyclopentene resin composition containing as main components (A) 100 parts by weight of a polycyclopentene and (B) 0.01 to 25 parts by weight of one or more nucleating agents selected from the group consisting of (1) metal salts of organic acids, (2) inorganic compounds, (3) organophosphorus compounds, and/or (4) metal salts of ionic hydrocarbon copolymer. Suitable nucleating agents may be sodium methylenebis(2,4-di-tertbutylphenyl) acid phosphate, sodium bis(4-tert-butylphenyl) phosphate, aluminum p-(tert-butyl) benzoate, talc, mica, or related species. These could be used in a process for producing polycyclopentene resin moldings by molding the above polycyclopentene resin composition at a temperature above their melting point.

4. Flame retardants and flame retardant combinations may be added to a cyclopentene polymer. Suitable flame retardants include a halogen-based or phosphorus-based flame retardant, antimony trioxide, antimony pentoxide, sodium antimonate, metallic antimony, antimony trichloride, antimony pentachloride, antimony trisulfide, antimony pentasulfide, zinc borate, barium metaborate or zirconium oxide. They may be used in conventional amounts.

5. Antioxidants may be used in conventional amounts to improve the stability of the cyclopentene polymers. For instance 0.005 to 30 parts by weight, per 100 parts by weight of the cyclopentene polymer, of an antioxidant selected from the group consisting of a phosphorous containing antioxidant, a phenolic antioxidant or a combination thereof. The phosphorous containing antioxidant may be a monophosphite or diphosphite or mixture thereof and the phenolic antioxidant may be a dialkyl phenol, trialkyl phenol, diphenylmonoalkoxyphenol, a tetraalkyl phenol, or a mixture thereof. A sulfur-containing antioxidant may

also be used alone or in combination with ~~other~~ antioxidants.

6. Various fillers or reinforcers, such as particulate or fibrous materials, may be added to
5 improve various physical properties.

7. "Special" physical properties can be obtained by the use of specific types of materials. Electrically conductive materials such as fine metallic wires or graphite may be used to render the polymer
10 electrically conductive. The temperature coefficient of expansion may be regulated by the use of appropriate fillers, and it may be possible to even obtain materials with positive coefficients of expansion. Such materials are particularly useful in electrical
15 and electronic parts.

8. The polymer may be crosslinked by irradiation or chemically as by using peroxides, optionally in the presence of suitable coagents. Suitable peroxides include benzoyl peroxide, lauroyl
20 peroxide, dicumyl peroxide, tert-butyl peroxide, tert-butylperoxybenzoate, tert-butylcumyl peroxide, tert-butylhydroperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3,1,1-bis(tert-
25 butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(tert-butylperoxy)valerate, 2,2-bis(tert-butylperoxy)butane and tert-butylperoxybenzene.

When polymerizing cyclopentene, it has been found
30 that some of the impurities that may be found in cyclopentene poison or otherwise interfere with the polymerizations described herein. Compounds such as 1,3-pentadiene (which can be removed by passage through 5A molecular sieves), cyclopentadiene (which can be
35 removed by distillation from Na), and methylenecyclobutane (which can be removed by distillation from polyphosphoric acid), may interfere

with the polymerization, and their level should be kept as low as practically possible.

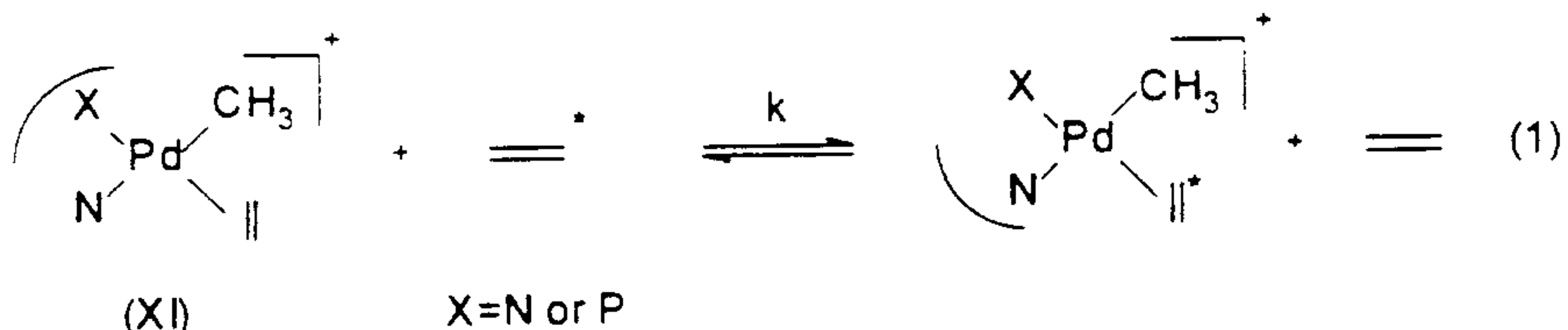
The above polymers (in general) are useful in many applications. Crystalline high molecular weight polymers are useful as molding resins, and for films for use in packaging. Amorphous resins are useful as elastomers, and may be crosslinked by known methods, such as by using free radicals. When such amorphous resins contain repeat units derived from polar monomers they are oil resistant. Lower molecular weight polymers are useful as oils, such as in polymer processing aids. When they contain polar groups, particularly carboxyl groups, they are useful in adhesives.

In many of the above polymerizations, the transition metal compounds employed as (part of the) catalysts contain(s) (a) metal atom(s) in a positive oxidation state. In addition, these complexes may have a square planar configuration about the metal, and the metal, particularly nickel or palladium, may have a d^8 electronic configuration. Thus some of these catalysts may be said to have a metal atom which is cationic and has a d^8 -square planar configuration.

In addition these catalysts may have a bidentate ligand wherein coordination to the transition metal is through two different nitrogen atoms or through a nitrogen atom and a phosphorus atom, these nitrogen and phosphorus atoms being part of the bidentate ligand. It is believed that some of these compounds herein are effective polymerization catalysts at least partly because the bidentate ligands have sufficient steric bulk on both sides of the coordination plane (of the square planar complex). Some of the Examples herein with the various catalysts of this type illustrate the degree of steric bulk which may be needed for such catalysts. If such a complex contains a bidentate ligand which has the appropriate steric bulk, it is

believed that it produces polyethylene with a degree of polymerization of at least about 10 or more.

It is also believed that the polymerization catalysts herein are effective because unpolymerized
5 olefinic monomer can only slowly displace from the complex a coordinated olefin which may be formed by β -hydride elimination from the growing polymer chain which is attached to the transition metal. The displacement can occur by associative exchange.
10 Increasing the steric bulk of the ligand slows the rate of associative exchange and allows polymer chain growth. A quantitative measure of the steric bulk of the bidentate ligand can be obtained by measuring at -85°C the rate of exchange of free ethylene with
15 complexed ethylene in a complex of formula (XI) as shown in equation 1 using standard ^1H NMR techniques, which is called herein the Ethylene Exchange Rate (EER). The neutral bidentate ligand is represented by YN where Y is either N or P. The EER is measured in
20 this system. In this measurement system the metal is always Pd, the results being applicable to other metals as noted below. Herein it is preferred for catalysts to contain bidentate ligands for which the second order rate constant for Ethylene Exchange Rate is about
25 20,000 $\text{L-mol}^{-1}\text{s}^{-1}$ or less when the metal used in the polymerization catalyst is palladium, more preferably about 10,000 $\text{L-mol}^{-1}\text{s}^{-1}$ or less, and more preferably about 5,000 $\text{L-mol}^{-1}\text{s}^{-1}$ or less. When the metal in the polymerization catalyst is nickel, the second order
30 rate constant (for the ligand in EER measurement) is about 50,000 $\text{L-mol}^{-1}\text{s}^{-1}$, more preferably about 25,000 $\text{L-mol}^{-1}\text{s}^{-1}$ or less, and especially preferably about 10,000 $\text{L-mol}^{-1}\text{s}^{-1}$ or less. Herein the EER is measured using the compound (XI) in a procedure (including temperature)
35 described in Examples 21-23.



In these polymerizations it is preferred if the bidentate ligand is an α -diimine. It is also preferred if the olefin has the formula $\text{R}^{17}\text{CH}=\text{CH}_2$, wherein R^{17} is hydrogen or n-alkyl.

In general for the polymers described herein, blends may be prepared with other polymers, and such other polymers may be elastomers, thermoplastics or thermosets. By elastomers are generally meant polymers whose T_g (glass transition temperature) and T_m (melting point), if present, are below ambient temperature, usually considered to be about 20°C . Thermoplastics are those polymers whose T_g and/or T_m are at or above ambient temperature. Blends can be made by any of the common techniques known to the artisan, such as solution blending, or melt blending in a suitable apparatus such as a single or twin-screw extruder. Specific uses for the polymers of this application in the blends or as blends are listed below.

Blends may be made with almost any kind of elastomer, such as EP, EPDM, SBR, natural rubber, polyisoprene, polybutadiene, neoprene, butyl rubber, styrene-butadiene block copolymers, segmented polyester-polyether copolymers, elastomeric polyurethanes, chlorinated or chlorosulfonated polyethylene, (per)fluorinated elastomers such as copolymers of vinylidene fluoride, hexafluoropropylene and optionally tetrafluoroethylene, copolymers of tetrafluoroethylene and perfluoro(methyl vinyl ether), and copolymers of tetrafluoroethylene and propylene.

Suitable thermoplastics which are useful for blending with the polymers described herein include: polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), and poly(ethylene

adipate); polyamides such as nylon-6, nylon-6,6, nylon-12, nylon-12,12, nylon-11, and a copolymer of hexamethylene diamine, adipic acid and terephthalic acid; fluorinated polymers such as copolymers of ethylene and vinylidene fluoride, copolymers of tetrafluoroethylene and hexafluoropropylene, copolymers of tetrafluoroethylene and a perfluoro(alkyl vinyl ether) such as perfluoro(propyl vinyl ether), and poly(vinyl fluoride); other halogenated polymers such as poly(vinyl chloride) and poly(vinylidene chloride) and its copolymers; polyolefins such as polyethylene, polypropylene and polystyrene, and copolymers thereof; (meth)acrylic polymers such as poly(methyl methacrylate) and copolymers thereof; copolymers of olefins such as ethylene with various (meth) acrylic monomers such as alkyl acrylates, (meth)acrylic acid and ionomers thereof, and glycidyl (meth)acrylate); aromatic polyesters such as the copolymer of Bisphenol A and terephthalic and/or isophthalic acid; and liquid crystalline polymers such as aromatic polyesters or aromatic poly(ester-amides).

Suitable thermosets for blending with the polymers described herein include epoxy resins, phenol-formaldehyde resins, melamine resins, and unsaturated polyester resins (sometimes called thermoset polyesters). Blending with thermoset polymers will often be done before the thermoset is crosslinked, using standard techniques.

The polymers described herein may also be blended with uncrosslinked polymers which are not usually considered thermoplastics for various reasons, for instance their viscosity is too high and/or their melting point is so high the polymer decomposes below the melting temperature. Such polymers include poly(tetrafluoroethylene), aramids such as poly(p-phenylene terephthalate) and poly(m-phenylene isophthalate), liquid crystalline polymer such as

poly(benzoxazoles), and non-melt processible polyimides which are often aromatic polyimides.

All of the polymers disclosed herein may be mixed with various additives normally added to elastomers and thermoplastics [see EPSE (below), vol. 14, p. 327-410]. For instance reinforcing, non-reinforcing and conductive fillers, such as carbon black, glass fiber, minerals such as clay, mica and talc, glass spheres, barium sulfate, zinc oxide, carbon fiber, and aramid fiber or fibrids, may be used. Antioxidants, antiozonants, pigments, dyes, delusterants, compounds to promote crosslinking may be added. Plasticizers such as various hydrocarbon oils may also be used.

The following listing is of some uses for polyolefins, which are made from linear olefins and do not include polar monomers such as acrylates, which are disclosed herein. In some cases a reference is given which discusses such uses for polymers in general. All of these references may be referred to.

For the references, "U" refers to W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed. VCH Verlagsgesellschaft mBH, Weinheim, for which the volume and page number are given, "ECT3" refers to the H. F. Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, "ECT4" refers to the J. I. Kroschwitz, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPST" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Technology, 1st Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPSE" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley & Sons, New York, for which volume and page numbers are given, and "PM" refers to J. A. Brydson, ed., Plastics Materials, 5 Ed., Butterworth-Heinemann, Oxford, UK, 1989, and the page is given. In

these uses, a polyethylene, polypropylene and a copolymer of ethylene and propylene are preferred.

1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers.

5 Elastomeric and/or relatively low molecular weight polymers are preferred.

2. An oil additive for smoke suppression in single-stroke gasoline engines is another use. Elastomeric polymers are preferred.

10 3. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a
15 carpet installation adhesive.

4. Lubricating oil additives as Viscosity Index Improvers for multigrade engine oil (ECT3, Vol 14, p. 495-496) are another use. Branched polymers are preferred. Ethylene copolymer with acrylates or other
20 polar monomers will also function as Viscosity Index Improvers for multigrade engine oil with the additional advantage of providing some dispersancy. 5. Polymer for coatings and/or penetrants for the protection of various porous items such as lumber and masonry,
25 particularly out-of-doors. The polymer may be in a suspension or emulsion, or may be dissolved in a solvent.

6. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower
30 molecular weight polymers are often used.

7. The polymers may be grafted with various compounds particularly those that result in functional groups such as epoxy, carboxylic anhydride (for instance as with a free radically polymerized reaction
35 with maleic anhydride) or carboxylic acid (EPSE, vol. 12, p. 445). Such functionalized polymers are particularly useful as tougheners for various thermoplastics and thermosets when blended. When the

polymers are elastomers, the functional groups which are grafted onto them may be used as curesites to crosslink the polymers. Maleic anhydride-grafted randomly-branched polyolefins are useful as tougheners for a wide range of materials (nylon, PPO, PPO/styrene alloys, PET, PBT, POM, etc.); as tie layers in multilayer constructs such as packaging barrier films; as hot melt, moisture-curable, and coextrudable adhesives; or as polymeric plasticizers. The maleic andhydride-grafted materials may be post reacted with, for example; amines, to form other functional materials. Reaction with aminopropyl trimethoxysilane would allow for moisture-curable materials. Reactions with di- and tri-amines would allow for viscosity modifications.

8. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical properties of the asphalt and/or extend the life of asphalt paving.

9. The polymers may be used as base resins for chlorination or chlorosulfonation for making the corresponding chlorinated or chlorosulfonated elastomers. The unchlorinated polymers need not be elastomers themselves.

10. Wire insulation and jacketing may be made from any of the polyolefins (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

11. The polymers, particularly the elastomers, may be used as tougheners for other polyolefins such as polypropylene and polyethylene.

12. The base for synthetic lubricants (motor oils) may be the highly branched polyolefins described herein (ECT3, vol. 14, p. 496-501).

13. The branched polyolefins herein can be used as drip suppressants when added to other polymers.

14. The branched polyolefins herein are especially useful in blown film applications because of their particular rheological properties (EPSE, vol. 7, p. 88-106). It is preferred that these polymers have
5 some crystallinity.

15. The polymer described herein can be used to blend with wax for candles, where they would provide smoke suppression and/or drip control.

16. The polymers, especially the branched
10 polymers, are useful as base resins for carpet backing, especially for automobile carpeting.

17. The polymers, especially those which are relatively flexible, are useful as capliner resins for carbonated and noncarbonated beverages.

18. The polymers, especially those having a relatively low melting point, are useful as thermal transfer imaging resins (for instance for imaging tee-shirts or signs).
15

19. The polymers may be used for extrusion or
20 coextrusion coatings onto plastics, metals, textiles or paper webs.

20. The polymers may be used as a laminating adhesive for glass.

21. The polymers are useful as for blown or
25 cast films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For packaging the films may be stretch-wrap,
30 shrink-wrap or cling wrap. The films are useful form many applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.

22. The polymers may be used to form flexible
35 or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the polymers have some

crystallinity. The polymer of the foams may be crosslinked.

23. In powdered form the polymers may be used to coat objects by using plasma, flame spray or
5 fluidized bed techniques.

24. Extruded films may be formed from these polymers, and these films may be treated, for example drawn. Such extruded films are useful for packaging of various sorts.

10 25. The polymers, especially those that are elastomeric, may be used in various types of hoses, such as automotive heater hose.

26. The polymers, especially those that are branched, are useful as pour point depressants for
15 fuels and oils.

27. These polymers may be flash spun to nonwoven fabrics, particularly if they are crystalline (see EPSE vol. 10, p. 202-253) They may also be used to form spunbonded polyolefins (EPSE, vol. 6, p. 756-
20 760). These fabrics are suitable as house wrap and geotextiles.

28. The highly branched, low viscosity polyolefins would be good as base resins for master-batching of pigments, fillers, flame-retardants, and
25 related additives for polyolefins. 29. The polymers may be grafted with a compound containing ethylenic unsaturation and a functional group such as a carboxyl group or a derivative of a carboxyl group, such as ester, carboxylic anhydride or carboxylate salt. A
30 minimum grafting level of about 0.01 weight percent of grafting agent based on the weight of the grafted polymer is preferred. The grafted polymers are useful as compatibilizers and/or tougheners. Suitable
grafting agents include maleic, acrylic, methacrylic,
35 itaconic, crotonic, alpha-methyl crotonic and cinnamic acids, anhydrides, esters and their metal salts and fumaric acid and their esters, anhydrides (when appropriate) and metal salts.

Copolymers of linear olefins with 4-vinylcyclohexene and other dienes may generally be used for all of the applications for which the linear olefins polymers (listed above) may be used. In addition they may be sulfur cured, so they generally can be used for any use for which EPDM polymers are used, assuming the olefin/4-vinylcyclohexene polymer is elastomeric.

Also described herein are novel copolymers of linear olefins with various polar monomers such as acrylic acid and acrylic esters. Uses for these polymers are given below. Abbreviations for references describing these uses in general with polymers are the same as listed above for polymers made from linear olefins.

1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers. Elastomeric and/or relatively low molecular weight polymers are preferred.

2. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a carpet installation adhesive.

3. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower molecular weight polymers are often used.

4. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical properties of the asphalt and/or extend the life of asphalt paving, see U.S. patent 3,980,598.

5. Wire insulation and jacketing may be made from any of the polymers (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

6. The polymers, especially the branched polymers, are useful as base resins for carpet backing, especially for automobile carpeting.

7. The polymers may be used for extrusion or
5 coextrusion coatings onto plastics, metals, textiles or paper webs.

8. The polymers may be used as a laminating adhesive for glass.

9. The polymers are useful as for blown or cast
10 films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For
15 packaging the films may be stretch-wrap, shrink-wrap or cling wrap. The films are useful form many applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.

10. The polymers may be used to form flexible
20 or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the polymers have some crystallinity. The polymer of the foams may be
25 crosslinked.

11. In powdered form the polymers may be used to coat objects by using plasma, flame spray or fluidized bed techniques.

12. Extruded films may be formed from these
30 polymers, and these films may be treated, for example drawn. Such extruded films are useful for packaging of various sorts.

13. The polymers, especially those that are elastomeric, may be used in various types of hoses,
35 such as automotive heater hose.

14. The polymers may be used as reactive diluents in automotive finishes, and for this purpose

it is preferred that they have a relatively low molecular weight and/or have some crystallinity.

15 15. The polymers can be converted to ionomers, which when they possess crystallinity can be used as molding resins. Exemplary uses for these ionomeric molding resins are golf ball covers, perfume caps, sporting goods, film packaging applications, as tougheners in other polymers, and usually extruded) detonator cords.

10 16. The functional groups on the polymers can be used to initiate the polymerization of other types of monomers or to copolymerize with other types of monomers. If the polymers are elastomeric, they can act as toughening agents.

15 17. The polymers can act as compatibilizing agents between various other polymers.

18. The polymers can act as tougheners for various other polymers, such as thermoplastics and thermosets, particularly if the olefin/polar monomer
20 polymers are elastomeric.

19. The polymers may act as internal plasticizers for other polymers in blends. A polymer which may be plasticized is poly(vinyl chloride).

25 20. The polymers can serve as adhesives between other polymers.

21. With the appropriate functional groups, the polymers may serve as curing agents for other polymers with complimentary functional groups (i.e., the functional groups of the two polymers react with each
30 other).

22. The polymers, especially those that are branched, are useful as pour point depressants for fuels and oils.

23. Lubricating oil additives as Viscosity
35 Index Improvers for multigrade engine oil (ECT3, Vol 14, p. 495-496) are another use. Branched polymers are preferred. Ethylene copolymer with acrylates or other polar monomers will also function as Viscosity Index

Improvers for multigrade engine oil with the additional advantage of providing some dispersancy.

24. The polymers may be used for roofing
5 membranes.

25. The polymers may be used as additives to various molding resins such as the so-called thermoplastic olefins to improve paint adhesion, as in automotive uses.

10 Polymers with or without polar monomers present are useful in the following uses. Preferred polymers with or without polar monomers are those listed above in the uses for each "type".

1. A flexible pouch made from a single layer or
15 multilayer film (as described above) which may be used for packaging various liquid products such as milk, or powder such as hot chocolate mix. The pouch may be heat sealed. It may also have a barrier layer, such as a metal foil layer.

20 2. A wrap packaging film having differential cling is provided by a film laminate, comprising at least two layers; an outer reverse which is a polymer (or a blend thereof) described herein, which contains a tackifier in sufficient amount to impart cling
25 properties; and an outer obverse which has a density of at least about 0.916 g/mL which has little or no cling, provided that a density of the outer reverse layer is at least 0.008 g/mL less than that of the density of the outer obverse layer. It is preferred that the
30 outer obverse layer is linear low density polyethylene, and the polymer of the outer obverse layer have a density of less than 0.90 g/mL. All densities are measured at 25°C.

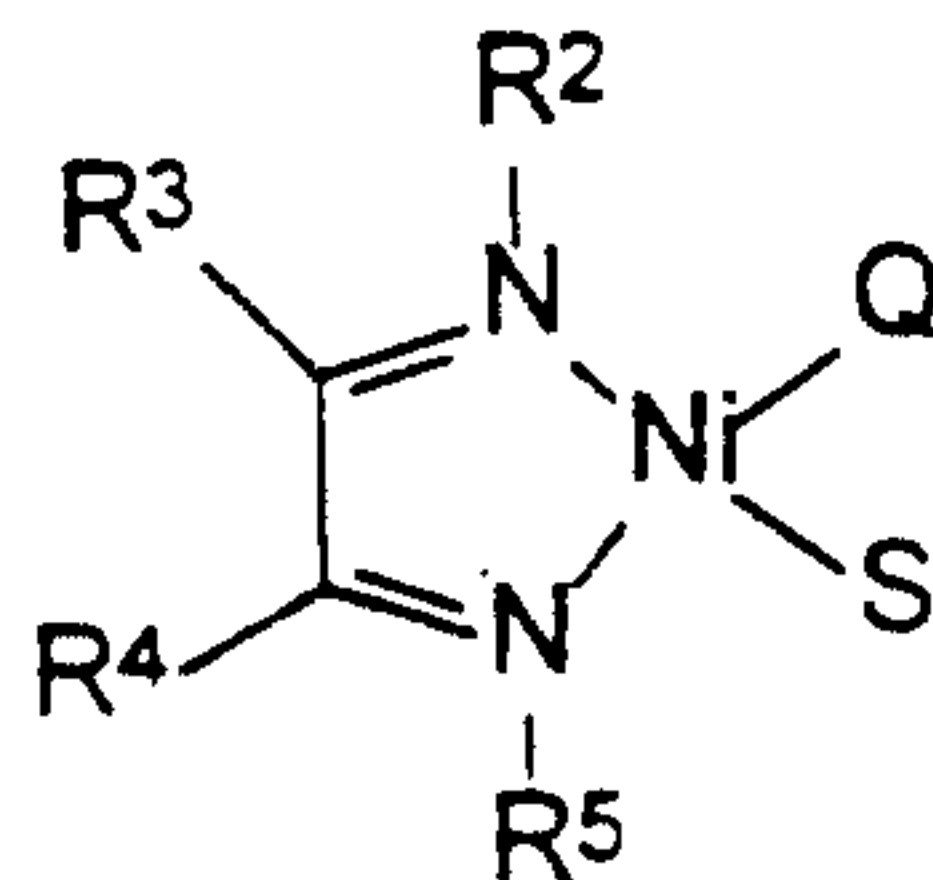
3. Fine denier fibers and/or multifilaments.
35 These may be melt spun. They may be in the form of a filament bundle, a non-woven web, a woven fabric, a knitted fabric or staple fiber.

4. A composition comprising a mixture of the polymers herein and an antifogging agent. This composition is especially useful in film or sheet form because of its antifogging properties.

5 5. Elastic, randomly-branched olefin polymers are disclosed which have very good processability, including processing indices (PI's) less than or equal to 70 percent of those of a comparative linear olefin polymer and a critical shear rate at onset of surface
10 melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a traditional linear olefin polymer at about the same I2 and Mw/Mn. The novel polymers may have higher low/zero shear viscosity and lower high
15 shear viscosity than comparative linear olefin polymers made by other means. These polymers may be characterized as having: a) a melt flow ratio, I_{10}/I_2 , ≥ 5.63 , b) a molecular weight distribution, Mw/Mn, defined by the equation: $Mw/Mn \leq (I_{10}/I_2) - 4.63$, and c)
20 a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn. Some blends of these polymer are characterized as
25 having: a) a melt flow ratio, I_{10}/I_2 , ≥ 5.63 , b) a molecular weight distribution, Mw/Mn, defined by the equation: $Mw/Mn \leq (I_{10}/I_2) - 4.63$, and c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate
30 at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn and (b) at least one other natural or synthetic polymer chosen from the polymer of claims 1, 3, 4, 6, 332, or 343, a conventional high density polyethylene, low
35 density polyethylene or linear low density polyethylene polymer. The polymers may be further characterized as having a melt flow ratio, I_{10}/I_2 , ≥ 5.63 , a molecular weight distribution, Mw/Mn, defined by the equation:

Mw/Mn $\leq$ (I10/I2)-4.63, and a critical shear stress at onset of gross melt fracture of greater than about 400 kPa (4×10^6 dyne/cm²) and their method of manufacture are disclosed. The randomly-branched olefin polymers preferably have a molecular weight distribution from about 1.5 to about 2.5. The polymers described herein often have improved processability over conventional olefin polymers and are useful in producing fabricated articles such as fibers, films, and molded parts. For this paragraph, the value I2 is measured in accordance with ASTM D-1238-190/2.16 and I10 is measured in accordance with ASTM D-1238-190/10; critical shear rate at onset of surface melt fracture and processing index (PI) are defined in U.S. Patent 5,278,272, which may be referred to.

In another process described herein, the product of the process described herein is an α -olefin. It is preferred that in the process a linear α -olefin is produced. It is also preferred that the α -olefin contain 4 to 32, preferably 8 to 20, carbon atoms.



(XXXI)

When (XXXI) is used as a catalyst, a neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion is also present as part of the catalyst system (sometimes called a "first compound" in the claims). By a "neutral Lewis acid" is meant a compound which is a Lewis acid capable for abstracting X⁻ from (I) to form a weakly coordinating anion. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF₅, Ar₃B (wherein Ar is

aryl), and BF_3 . By a cationic Lewis acid is meant a cation with a positive charge such as Ag^+ , H^+ , and Na^+ .

A preferred neutral Lewis acid is an alkyl aluminum compound, such as $\text{R}^{\text{f}}_3\text{Al}$, $\text{R}^{\text{f}}_2\text{AlCl}$, $\text{R}^{\text{f}}\text{AlCl}_2$, and
 5 "R^fAlO" (alkylaluminumoxane), wherein R^f is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminumoxane, $(\text{C}_2\text{H}_5)_2\text{AlCl}$, $\text{C}_2\text{H}_5\text{AlCl}_2$, and $[(\text{CH}_3)_2\text{CHCH}_2]_3\text{Al}$.

10 Relatively noncoordinating anions are known in the art, and the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p.
 15 927-942 (1993), both of which may be referred to.

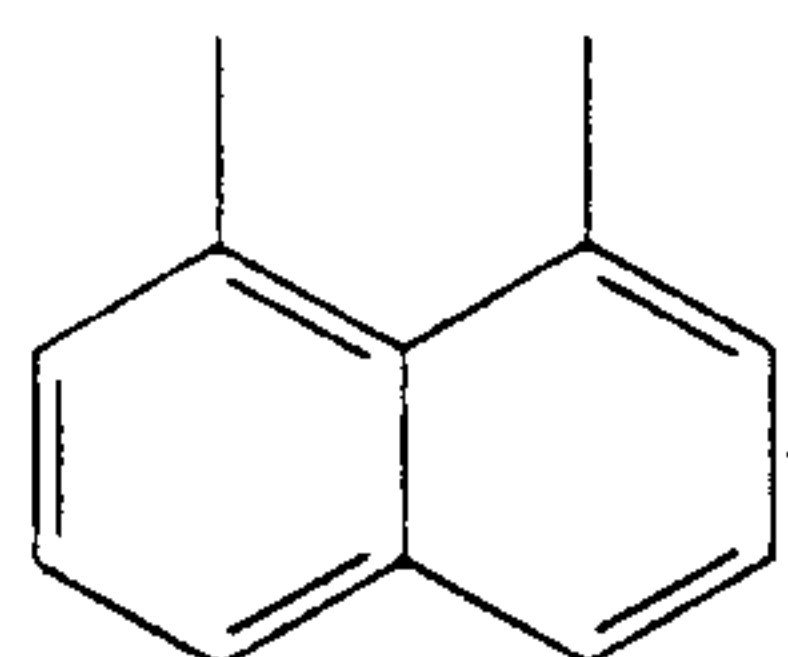
Among such anions are those formed from the aluminum compounds in the immediately preceding paragraph and X^- , including $\text{R}^{\text{f}}_3\text{AlX}^-$, $\text{R}^{\text{f}}_2\text{AlClX}^-$, $\text{R}^{\text{f}}\text{AlCl}_2\text{X}^-$, and "R^fAlOX⁻". Other useful noncoordinating anions
 20 include BAF^- {BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, SbF_6^- , PF_6^- , and BF_4^- , trifluoromethanesulfonate, p-toluenesulfonate, $(\text{R}_f\text{SO}_2)_2\text{N}^-$, and $(\text{C}_6\text{F}_5)_4\text{B}^-$.

The temperature at which the process is carried
 25 out is about -100°C to about $+200^\circ\text{C}$, preferably about 0°C to about 150°C , more preferably about 25°C to about 100°C . It is believed that at higher temperatures, lower molecular weight α -olefins are produced, all other factors being equal. The pressure at which the
 30 polymerization is carried out is not critical, atmospheric pressure to about 275 MPa being a suitable range. It is also believed that increasing the pressure increases the relative amount of α -olefin (as opposed to internal olefin) produced.

35 The process to make α -olefins may be run in a solvent (liquid), and that is preferred. The solvent may in fact be the α -olefin produced. Such a process may be started by using a deliberately added solvent

which is gradually displaced as the reaction proceeds. By solvent it is not necessarily meant that any or all of the starting materials and/or products are soluble in the (liquid) solvent.

- 5 In (I) it is preferred that R^3 and R^4 are both hydrogen or methyl or R^3 and R^4 taken together are



(An)

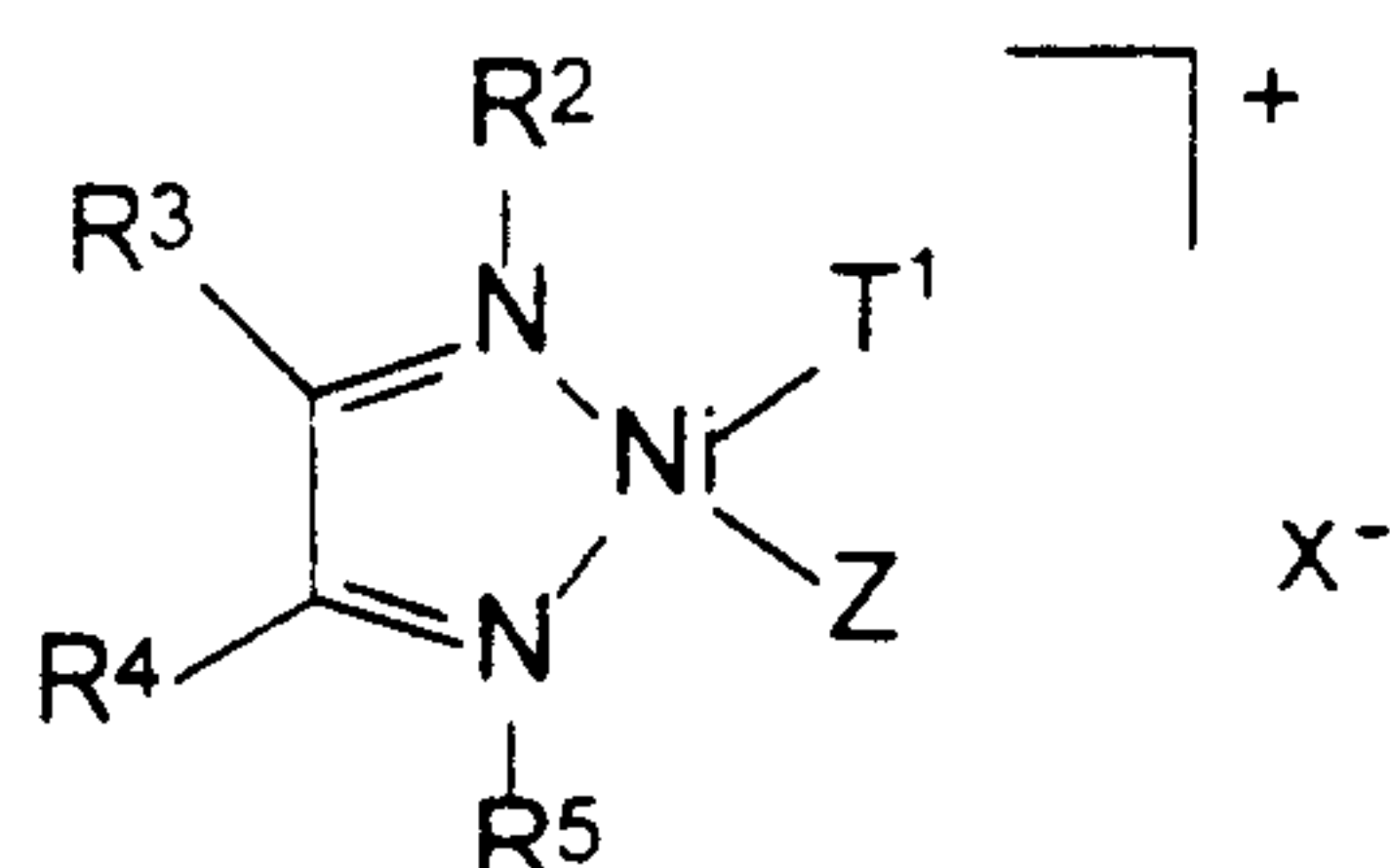
- 10 It is also preferred that each of Q and S is independently chlorine or bromine, and it is more preferred that both of Q and S in (XXXI) are chlorine or bromine.

- In (XXXI) R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl. What these groups are greatly determines whether the α -olefins of this process are made, or whether higher polymeric materials, i.e., materials containing over 25 ethylene units, are coproduced or produced almost exclusively. If R^2 and R^5 are highly sterically hindered about the nickel atom, the tendency is to produce higher polymeric material. For instance, when R^2 and R^5 are both 2,6-diisopropylphenyl mostly higher polymeric material is produced. However, when R^2 and R^5 are both phenyl, mostly the α -olefins of this process are produced. Of course this will also be influenced by other reaction conditions such as temperature and pressure, as noted above. Useful groups for R^2 and R^5 are phenyl, and p-methylphenyl.

- As is understood by the artisan, in oligomerization reactions of ethylene to produce α -olefins, usually a mixture of such α -olefins is obtained containing a series of such α -olefins differing from one another by two carbon atoms (an ethylene unit). The process for preparing α -olefins described herein produces products with a high

percentage of terminal olefinic groups (as opposed to internal olefinic groups). The product mixture also contains a relatively high percentage of molecules which are linear. Finally relatively high catalyst
 5 efficiencies can be obtained.

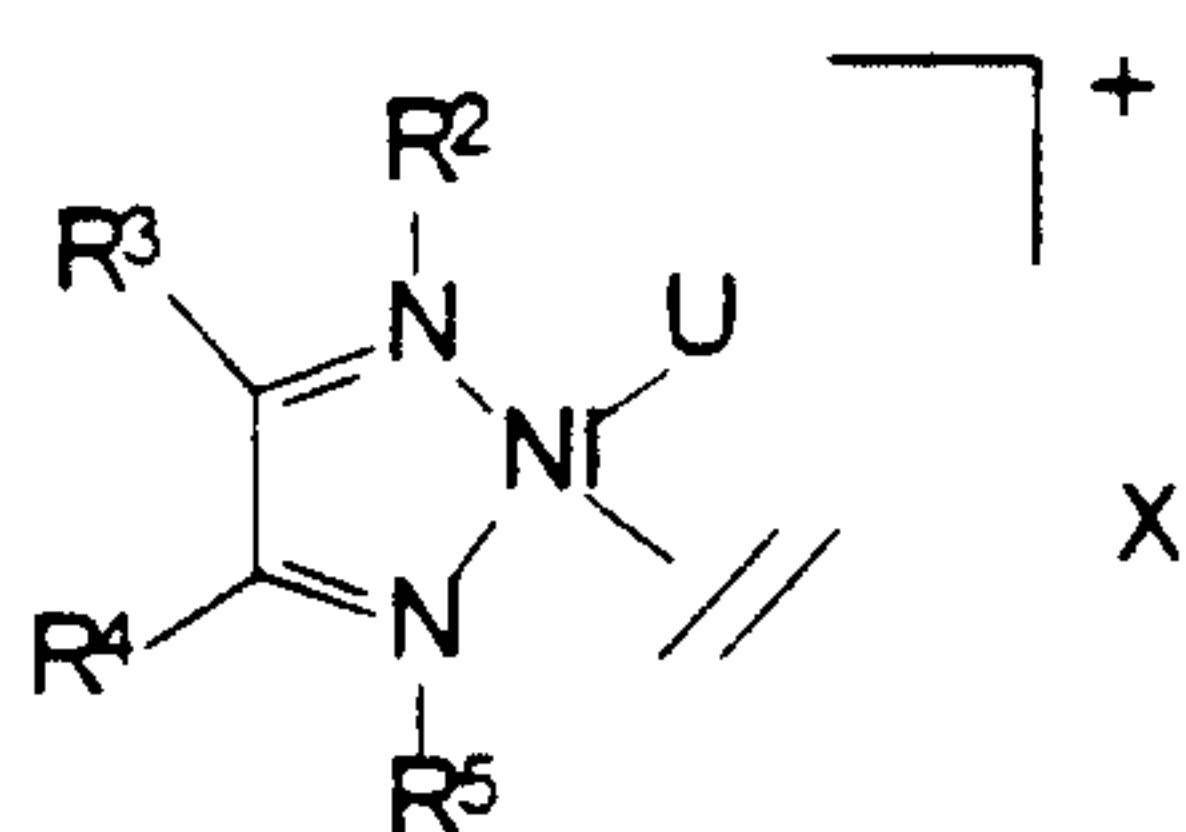
The α -olefins described as being made herein may also be made by contacting ethylene with one of the compounds



10

(III)

or



(XXXIV)

15

wherein R^2 , R^3 , R^4 , and R^5 are as defined (and preferred) as described above (for the preparation of α -olefins), and T^1 is hydrogen or n-alkyl containing up to 38 carbon atoms, Z is a neutral Lewis base wherein
 20 the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, U is n-alkyl containing up to 38 carbon atoms, and X is a noncoordinating anion
 25 (see above). The process conditions for making α -olefins using (III) or (XXXIV) are the same as for using (XXXI) to make these compounds except a Lewis or Bronsted acid need not be present. Note that the double line in (XXXIV) represents a coordinated

ethylene molecule. (XXXIV) may be made from (II) by reaction of (III) with ethylene. In other words, (XXXIV) may be considered an active intermediate in the formation of α -olefin from (III). Suitable groups for
5 Z include dialkyl ethers such as diethyl ether, and alkyl nitriles such as acetonitrile.

In general, α -olefins can be made by this process using as a catalyst a Ni[II] complex of an α -diimine of formula (VIII), wherein the Ni[II] complex is made by
10 any of the methods which are described above, using Ni[0], Ni[I] or Ni[II] precursors. All of the process conditions, and preferred groups on (VIII), are the same as described above in the process for making α -olefins.

15

EXAMPLES

In the Examples, the following convention is used for naming α -diimine complexes of metals, and the α -diimine itself. The α -diimine is indicated by the
20 letters "DAB". To the left of the "DAB" are the two groups attached to the nitrogen atoms, herein usually called R^2 and R^5 . To the right of the "DAB" are the groups on the two carbon atoms of the α -diimine group, herein usually termed R^3 and R^4 . To the right of all
25 this appears the metal, ligands attached to the metal (such as Q, S and T), and finally any anions (X), which when "free" anions are designated by a superscript minus sign (i.e., X^-). Of course if there is a "free" anion present, the metal containing moiety is cationic.
30 Abbreviations for these groups are as described in the Specification in the Note after Table 1. Analogous abbreviations are used for α -diimines, etc.

In the Examples, the following abbreviations are used:

35 ΔH_f - heat of fusion
acac - acetylacetonate
Bu - butyl
t-BuA - t-butyl acrylate

DMA - Dynamic Mechanical Analysis
DME - 1,2-dimethoxyethane
DSC - Differential Scanning Calorimetry
E - ethylene
5 EOC - end of chain
Et - ethyl
FC-75 - perfluoro(n-butyltetrahydrofuran)
FOA - fluorinated octyl acrylate
GPC - gel permeation chromatography
10 MA - methyl acrylate
MAO - methylaluminoxane
Me - methyl
MeOH - methanol
MMAO - a modified methylaluminoxane in which
15 about 25 mole percent of the methyl groups have been
replaced by isobutyl groups
M-MAO - see MMAO
MMAO-3A - see MMAO
Mn - number average molecular weight
20 MVK - methyl vinyl ketone
Mw - weight average molecular weight
Mz - viscosity average molecular weight
PD or P/D - polydispersity, M_w/M_n
Ph - phenyl
25 PMAO - see MAO
PMMA - poly(methyl methacrylate)
Pr - propyl
PTFE - polytetrafluoroethylene
RI - refractive index
30 RT (or rt) - room temperature
TCE - 1,1,2,2-tetrachloroethane
Tc - temperature of crystallization
Td - temperature of decomposition
Tg - glass transition temperature
35 TGA - Thermogravimetric Analysis
THF - tetrahydrofuran
Tm - melting temperature

TO - turnovers, the number of moles of monomer polymerized per g-atom of metal in the catalyst used

UV - ultraviolet

Unless otherwise noted, all pressures are gauge pressures.

In the Examples, the following procedure was used to quantitatively determine branching, and the distribution of branch sizes in the polymers (but not necessarily the simple number of branches as measured by total number of methyl groups per 1000 methylene groups). 100 MHz ^{13}C NMR spectra were obtained on a Varian Unity 400 MHz spectrometer using a 10 mm probe on typically 15-20 wt% solutions of the polymers and 0.05 M Cr(acetylacetonate) $_3$ in 1,2,4-trichlorobenzene (TCB) unlocked at 120-140°C using a 90 degree pulse of 12.5 to 18.5 μsec , a spectral width of 26 to 35 kHz, a relaxation delay of 5-9 s, an acquisition time of 0.64 sec and gated decoupling. Samples were preheated for at least 15 min before acquiring data. Data acquisition time was typically 12 hr. per sample. The T_1 values of the carbons were measured under these conditions to be all less than 0.9 s. The longest T_1 measured was for the Bu^+ , end of chain resonance at 14 ppm, which was 0.84 s. Occasionally about 16 vol. % benzene- d_6 was added to the TCB and the sample was run locked. Some samples were run in chloroform- d_1 , CDCl_3 - d_1 , (locked) at 30°C under similar acquisition parameters. T_1 's were also measured in CDCl_3 at ambient temperature on a typical sample with 0.05 M Cr(acetylacetonate) $_3$ to be all less than 0.68 s. In rare cases when Cr(acetylacetonate) $_3$ was not used, a 30-40 s recycle delay was used to insure quantitation. The glycidyl acrylate copolymer was run at 100°C with Cr(acetylacetonate) $_3$. Spectra are referenced to the solvent - either the TCB highfield resonance at 127.8 ppm or the chloroform- d_1 triplet at 77 ppm. A DEPT 135 spectrum was done on most samples to distinguish methyls and methines from methylenes. Methyls were

distinguished from methines by chemical shift. EOC is end-of-chain. Assignments reference to following naming scheme:

1. xBy: By is a branch of length y carbons; x is the carbon being discussed, the methyl at the end of the branch is numbered 1. Thus the second carbon from the end of a butyl branch is 2B4. Branches of length y or greater are designated as y⁺.
2. xEBy: EB is an ester ended branch containing y methylenes. x is the carbon being discussed, the first methylene adjacent to the ester carbonyl is labeled 1. Thus the second methylene from the end of a 5 methylene ester terminated branch would be 2EB5. ¹³C NMR of model compounds for EBy type branches for y=0 and y=5⁺ confirm the peak positions and assignments of these branches. In addition, a model compound for an EB1 branch is consistent with 2 dimensional NMR data using the well know 2D NMR techniques of hsqc, hmbc, and hsqc-tocsy; the 2D data confirms the presence of the EB5⁺, EB0, EB1 and other intermediate length EB branches

3. The methylenes in the backbone are denoted with Greek letters which determine how far from a branch point methine each methylene is. Thus ββ (beta beta) B denotes the central methylene in the following PCHRCH₂CH₂CH₂CHRP. Methylenes that are three or more carbons from a branch point are designated as γ⁺ (gamma⁺).

4. When x in xBy or xEBy is replaced by a M, the methine carbon of that branch is denoted.

Integrals of unique carbons in each branch were measured and were reported as number of branches per 1000 methylenes (including methylenes in the backbone and branches). These integrals are accurate to +/- 5% relative for abundant branches and +/- 10 or 20% relative for branches present at less than 10 per 1000 methylenes.

Such types of analyses are generally known, see for instance "A Quantitative Analysis of Low Density (Branched) Polyethylenes by Carbon-13 Fourier Transform Nuclear Magnetic Resonance at 67.9 MHz", D. E. Axelson, et al., Macromolecules 12 (1979) pp. 41-52; "Fine Branching Structure in High-Pressure, Low Density Polyethylenes by 50.10-MHz ^{13}C NMR Analysis", T. Usami et al., Macromolecules 17 (1984) pp. 1757-1761; and "Quantification of Branching in Polyethylene by ^{13}C NMR Using Paramagnetic Relaxation Agents", J. V. Prasad, et al., Eur. Polym. J. 27 (1991) pp. 251-254 (Note that this latter paper is believed to have some significant typographical errors in it).

It is believed that in many of the polymers described herein which have unusual branching, i.e., they have more or fewer branches than would be expected for "normal" coordination polymerizations, or the distribution of sizes of the branches is different from that expected, that "branches on branches" are also present. By this is meant that a branch from the main chain on the polymer may itself contain one or more branches. It is also noted that the concept of a "main chain" may be a somewhat semantic argument if there are sufficient branches on branches in any particular polymer.

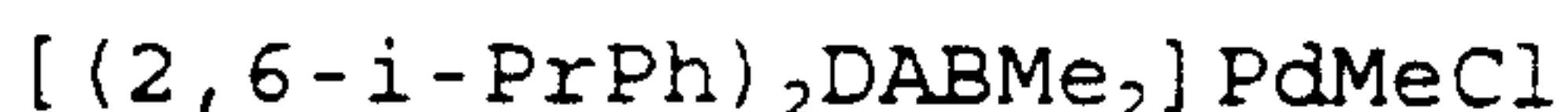
By a polymer hydrocarbyl branch is meant a methyl group to a methine or quaternary carbon atom or a group of consecutive methylenes terminated at one end by a methyl group and connected at the other end to a methine or quaternary carbon atom. The length of the branch is defined as the number of carbons from and including the methyl group to the nearest methine or quaternary carbon atom, but not including the methine or quaternary carbon atom. If the number of consecutive methylene groups is "n" then the branch contains (or the branch length is) n+1. Thus the structure (which represents part of a polymer) -

$\text{CH}_2\text{CH}_2\text{CH}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3]\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ contains 2 branches, a methyl and an ethyl branch.

For ester ended branches a similar definition is used. An ester branch refers to a group of consecutive methylene groups terminated at one end by an ester - COOR group, and connected at the other end to a methine or quaternary carbon atom. The length of the branch is defined as the number of consecutive methylene groups from the ester group to the nearest methine or quaternary carbon atom, but not including the methine or quaternary carbon atom. If the number of methylene groups is "n", then the length of the branch is n. Thus $-\text{CH}_2\text{CH}_2\text{CH}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOR}]\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ contains 2 branches, a methyl and an n=1 ester branch.

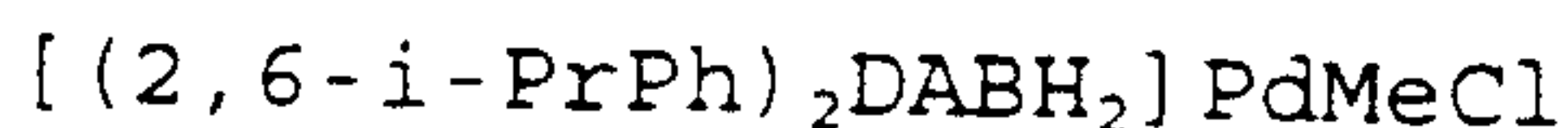
The ^{13}C NMR peaks for copolymers of cyclopentene and ethylene are described based on the labeling scheme and assignments of A. Jerschow et al, *Macromolecules* 1995, 28, 7095-7099. The triads and pentads are described as 1-cme, 1,3-ccmcc, 1,3-cmc, 2-cme, 2-cmc, 1,3-eme, 3-cme, and 4,5-cmc, where e = ethylene, c = cyclopentene, and m = meta cyclopentene (i.e. 1,3 enchainment). The same labeling is used for cyclopentene/1-pentene copolymer substituting p = pentene for e. The synthesis of diimines is reported in the literature (Tom Dieck, H.; Svoboda, M.; Grieser, T. Z. *Naturforsch* 1981, 36b, 823-832. Kliegman, J. M.; Barnes, R. K. *J. Org. Chem.* 1970, 35, 3140-3143.)

Example 1



Et_2O (75 mL) was added to a Schlenk flask containing CODPdMeCl (COD = 1,5-cyclooctadiene) (3.53 g, 13.3 mmol) and a slight excess of (2,6-i-PrPh) $_2$ DABMe $_2$ (5.43 g, 13.4 mmol, 1.01 equiv). An orange precipitate began to form immediately upon mixing. The reaction mixture was stirred overnight and the Et_2O and free COD were then removed via filtration. The product was washed with an additional 25 mL of Et_2O and then dried overnight in vacuo. A pale orange

powder (7.18 g, 95.8%) was isolated: ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.4 - 7.2 (m, 6, H_{aryl}), 3.06 (septet, 2, $J = 6.81$, CHMe_2), 3.01 (septet, 2, $J = 6.89$, $\text{C}'\text{HMe}_2$), 2.04 and 2.03 ($\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$), 1.40 (d, 6, $J = 6.79$, $\text{C}'\text{HMeMe}'$), 1.36 (d, 6, $J = 6.76$, CHMeMe'), 1.19 (d, 6, $J = 6.83$, CHMeMe'), 1.18 (d, 6, $J = 6.87$, $\text{C}'\text{HMeMe}'$), 0.36 (s, 3, PdMe); ^{13}C NMR (CD_2Cl_2 , 400 MHz) δ 175.0 and 170.3 ($\text{N}=\text{C}-\text{C}'=\text{N}$), 142.3 and 142.1 (Ar , Ar' : C_{ipso}), 138.9 and 138.4 (Ar , Ar' : C_o), 128.0 and 127.1 (Ar , Ar' : C_p), 124.3 and 123.5 (Ar , Ar' : C_m), 29.3 (CHMe_2), 28.8 ($\text{C}'\text{HMe}_2$), 23.9, 23.8, 23.5 and 23.3 (CHMeMe' , $\text{C}'\text{HMeMe}'$), 21.5 and 20.1 ($\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$), 5.0 ($J_{\text{CH}} = 135.0$, PdMe).

Example 2

Following the procedure of Example 1, an orange powder was isolated in 97.1% yield: ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.31 and 8.15 (s, 1 each, $N=C(H)-C'(H)=N$), 7.3 - 7.1 (m, 6, H_{aryl}), 3.22 (septet, 2, $J = 6.80$, $CHMe_2$), 3.21 (septet, 2, $J = 6.86$, $C'HMe_2$), 1.362, 1.356, 1.183 and 1.178 (d, 6 each, $J = 7.75 - 6.90$; $CHMeMe'$, $C'HMeMe'$), 0.67 (s, 3, $PdMe$); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 164.5 ($J_{CH} = 179.0$, $N=C(H)$), 160.6 ($J_{CH} = 178.0$, $N=C'(H)$), 144.8 and 143.8 (Ar, Ar': C_{ipso}), 140.0 and 139.2 (Ar, Ar': C_o), 128.6 and 127.7 (Ar, Ar': C_p), 124.0 and 123.4 (Ar, Ar': C_m), 29.1 ($CHMe_2$), 28.6 ($C'HMe_2$), 24.7, 24.1, 23.1 and 22.7 ($CHMeMe'$, $C'HMeMe'$), 3.0 ($J_{CH} = 134.0$, $PdMe$). Anal. Calcd for $(C_{27}H_{39}ClN_2Pd)$: C, 60.79; H, 7.37; N, 5.25. Found: C, 60.63; H, 7.24; N, 5.25.

Example 3

Following the procedure of Example 1, a yellow powder was isolated in 90.6% yield: ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.3 - 6.9 (m, 6, H_{aryl}), 2.22 (s, 6, Ar, Ar': Me), 2.00 and 1.97 ($N=C(Me)-C'(Me)=N$), 0.25 (s, 3, $PdMe$).

Example 4

Following the procedure of Example 1, an orange powder was isolated in 99.0% yield: ^1H NMR (CD_2Cl_2 , 400 MHz, 41 °C) δ 8.29 and 8.14 ($N=C(H)-C'(H)=N$), 7.2 - 7.1 (m, 6, H_{aryl}), 2.33 and 2.30 (s, 6 each, Ar, Ar': Me), 0.61 (s, 3, $PdMe$); ^{13}C NMR (CD_2Cl_2 , 100 MHz, 41 °C) δ 165.1 ($J_{CH} = 179.2$, $N=C(H)$), 161.0 ($J_{CH} = 177.8$, $N=C'(H)$), 147.3 and 146.6 (Ar, Ar': C_{ipso}), 129.5 and 128.8 (Ar, Ar': C_o), 128.8 and 128.5 (Ar, Ar': C_m), 127.9 and 127.3 (Ar, Ar': C_p), 18.7 and 18.2 (Ar, Ar': Me), 2.07 ($J_{CH} = 136.4$, $PdMe$).

Example 5

Following the procedure of Example 1, a yellow powder was isolated in 92.1% yield: ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.29 (d, 2, $J = 8.55$, Ar: H_m), 7.26 (d, 2, $J = 7.83$, Ar': H_m), 6.90 (d, 2, $J = 8.24$, Ar': H_o), 6.83 (d, 2, $J = 8.34$, Ar: H_o), 2.39 (s, 6, Ar, Ar': Me), 2.15 and 2.05 (s, 3 each, $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$), 0.44 (s, 3, PdMe); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 176.0 and 169.9 (N=C-C'=N), 144.9 and 143.7 (Ar, Ar': C_{ipso}), 137.0 and 136.9 (Ar, Ar': C_p), 130.0 and 129.3 (Ar, Ar': C_m), 122.0 and 121.5 (Ar, Ar': C_o), 21.2 (N=C(Me)), 20.1 (Ar, Ar': Me), 19.8 (N=C'(Me)), 2.21 ($J_{\text{CH}} = 135.3$, PdMe). Anal. Calcd for ($\text{C}_{19}\text{H}_{23}\text{ClN}_2\text{Pd}$): C, 54.17; H, 5.50; N, 6.65. Found: C, 54.41; H, 5.37; N, 6.69.

Example 6

Following the procedure of Example 1, a burnt orange powder was isolated in 90.5% yield: Anal. Calcd for ($\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{Pd}$): C, 51.93; H, 4.87; N, 7.12. Found: C, 51.36; H, 4.80; N, 6.82.

Example 7

Et_2O (25 mL) was added to a mixture of $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$ (0.81 g, 1.45 mmol) and 0.5 equiv of NaBAF (0.64 g, 0.73 mmol) at room temperature. A golden yellow solution and NaCl precipitate formed immediately upon mixing. The reaction mixture was stirred overnight and then filtered. After the Et_2O was removed in vacuo, the product was washed with 25 mL of hexane. The yellow powder was then dissolved in 25 mL of CH_2Cl_2 and the resulting solution was filtered in order to removed traces of unreacted NaBAF. Removal of CH_2Cl_2 in vacuo yielded a golden yellow powder (1.25 g, 88.2%): ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.73 (s, 8, BAF: H_o), 7.57 (s, 4, BAF: H_p), 7.33 (t, 2, $J = 7.57$, Ar: H_p), 7.27 (d, 4, $J = 7.69$, Ar: H_o), 7.18 (t, 2, $J = 7.64$, Ar: H_p), 7.10 (d, 4, $J = 7.44$, Ar': H_o), 2.88

(septet, 4, $J = 6.80$, CHMe_2), 2.75 (septet, 4, $J = 6.82$, $\text{C}'\text{HMe}_2$), 2.05 and 2.00 (s, 6 each, $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$), 1.22, 1.13, 1.08 and 1.01 (d, 12 each, $J = 6.61-6.99$, CHMeMe' , $\text{C}'\text{HMeMe}'$), 0.41 (s, 6, PdMe); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 177.1 and 171.2 ($\text{N}=\text{C}-\text{C}'=\text{N}$), 162.2 (q, $J_{\text{BC}} = 49.8$, BAF: C_{ipso}), 141.4 and 141.0 (Ar, Ar': C_{ipso}), 138.8 and 138.1 (Ar, Ar': C_o), 135.2 (BAF: C_p), 129.3 (q, $J_{\text{CF}} = 31.6$, BAF: C_m), 128.6 and 127.8 (Ar, Ar': C_p), 125.0 (q, $J_{\text{CF}} = 272.5$, BAF: CF_3), 124.5 and 123.8 (Ar, Ar': C_m), 117.9 (BAF: C_p), 29.3 (CHMe_2), 29.0 ($\text{C}'\text{HMe}_2$), 23.8, 23.7, 23.6 and 23.0 (CHMeMe' , $\text{C}'\text{HMeMe}'$), 21.5 and 20.0 ($\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$), 9.8 ($J_{\text{CH}} = 136.0$, PdMe). Anal. Calcd for $(\text{C}_{90}\text{H}_{98}\text{BClF}_{24}\text{N}_4\text{Pd}_2)$: C, 55.41; H, 5.06; N, 2.87. Found: C, 55.83; H, 5.09; N, 2.63.

Example 8



The procedure of Example 7 was followed with one exception, the removal of CH_2Cl_2 in vacuo yielded a product that was partially an oil. Dissolving the compound in Et_2O and then removing the Et_2O in vacuo yielded a microcrystalline red solid (85.5%): ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.20 and 8.09 (s, 2 each, $\text{N}=\text{C}(\text{H})-\text{C}'(\text{H})=\text{N}$), 7.73 (s, 8, BAF: H_o), 7.57 (s, 4, BAF: H_p), 7.37 (t, 2, $J = 7.73$, Ar: H_p), 7.28 (d, 4, $J = 7.44$, Ar: H_m), 7.24 (t, 2, Ar': H_p), 7.16 (d, 4, $J = 7.19$, Ar': H_m), 3.04 (septet, 4, $J = 6.80$, CHMe_2), 2.93 (septet, 4, $J = 6.80$, $\text{C}'\text{HMe}_2$), 1.26 (d, 12, $J = 6.79$, CHMeMe'), 1.14 (d, 12, $J = 6.83$, CHMeMe'), 1.11 (d, 12, $J = 6.80$, $\text{C}'\text{HMeMe}'$), 1.06 (d, 12, $J = 6.79$, $\text{C}'\text{HMeMe}'$), 0.74 (s, 6, PdMe); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 166.0 ($J_{\text{CH}} = 180.4$, $\text{N}=\text{C}(\text{H})$), 161.9 (q, $J_{\text{BC}} = 49.6$, BAF: C_{ipso}), 160.8 ($J_{\text{CH}} = 179.9$, $\text{N}=\text{C}'(\text{H})$), 143.5 and 143.0 (Ar, Ar': C_{ipso}), 139.8 and 138.9 (Ar, Ar': C_o), 135.2 (BAF: C_o), 129.3 (q, $J_{\text{CF}} = 31.4$, BAF: C_m), 129.3 and 128.5 (Ar, Ar': C_p), 125.0 (q, $J_{\text{CF}} = 272.4$, BAF: CF_3), 124.3 and 123.7 (Ar, Ar': C_m), 117.9 (BAF: C_p), 29.2 and 28.9 (CHMe_2 , $\text{C}'\text{HMe}_2$), 24.5, 24.1, 23.0, and 22.5

(CHMeMe', C'HMeMe'), 10.3 (PdMe). Anal. Calcd for (C₈₆H₉₀BClF₂₄N₄Pd₂): C, 54.52; H, 4.97; N, 2.96. Found: C, 54.97; H, 4.72; N, 2.71.

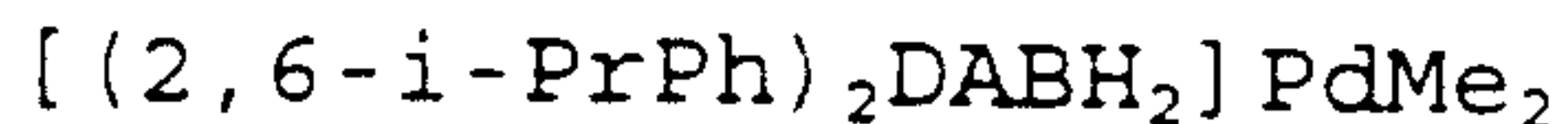
Example 9

- 5 Alternatively, the products of Examples 7 and 8 have been synthesized by stirring a 1:1 mixture of the appropriate PdMeCl compound and NaBAF in Et₂O for ~1 h. Removal of solvent yields the dimer + 0.5 equiv of Na⁺(OEt₂)₂BAF⁻. Washing the product mixture with
- 10 hexane yields ether-free NaBAF, which is insoluble in CH₂Cl₂. Addition of CH₂Cl₂ to the product mixture and filtration of the solution yields salt-free dimer: ¹H NMR spectral data are identical with that reported above.
- 15 For a synthesis of CODPdMe₂, see: Rudler-Chauvin, M., and Rudler, H. J. *Organomet. Chem.* 1977, 134, 115-119.

Example 10

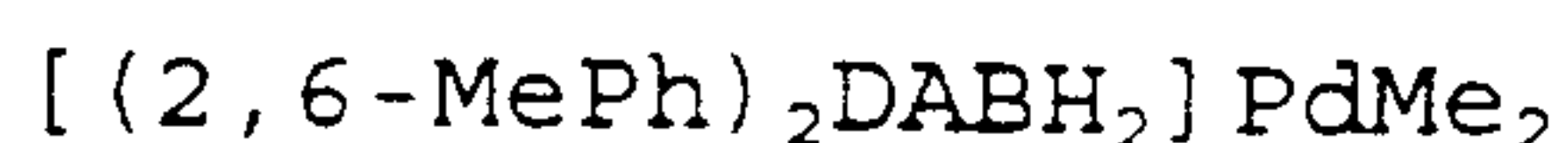
[(2,6-i-PrPh)₂DABMe₂]PdMe₂

- 20 A Schlenk flask containing a mixture of [(2,6-i-PrPh)₂DABMe₂]PdMeCl (2.00 g, 3.57 mmol) and 0.5 equiv of Me₂Mg (97.2 mg, 1.79 mmol) was cooled to -78 °C, and the reaction mixture was then suspended in 165 mL of Et₂O. The reaction mixture was allowed to warm to room
- 25 temperature and then stirred for 2 h, and the resulting brown solution was then filtered twice. Cooling the solution to -30 °C yielded brown single crystals (474.9 mg, 24.6%, 2 crops): ¹H NMR (C₆D₆, 400 MHz) δ 7.2-7.1 (m, 6, H_{aryl}), 3.17 (septet, 4, J = 6.92, CHMe₂), 1.39
- 30 (d, 12, J = 6.74, CHMeMe'), 1.20 (N=C(Me)-C(Me)=N), 1.03 (d, 12, J = 6.89, CHMeMe'), 0.51 (s, 6, PdMe); ¹³C NMR (C₆D₆, 100 MHz) δ 168.4 (N=C-C=N), 143.4 (Ar: C_{ipso}), 138.0 (Ar: C_o), 126.5 (Ar: C_p), 123.6 (Ar: C_m), 28.8 (CHMe₂), 23.6 and 23.5 (CHMeMe'), 19.5 (N=C(Me)-
- 35 C(Me)=N), -4.9 (J_{CH} = 127.9, PdMe). Anal. Calcd for (C₃₀H₄₆N₂Pd): C, 66.59; H, 8.57; N, 5.18. Found: C, 66.77; H, 8.62; N, 4.91.

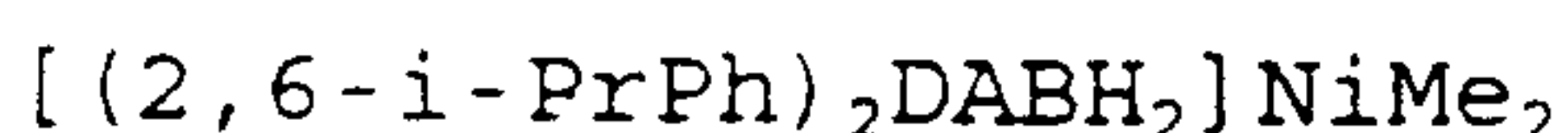
Example 11

The synthesis of this compound in a manner analogous to Example 10, using 3.77 mmol of $ArN=C(H)-$
5 $C(H)=NAr$ and 1.93 mmol of Me_2Mg yielded 722.2 mg (37.4%) of a deep brown microcrystalline powder upon recrystallization of the product from a hexane/toluene solvent mixture.

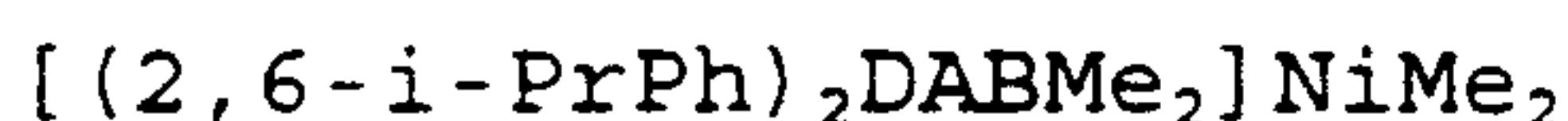
This compound was also synthesized by the
10 following method: A mixture of $Pd(acac)_2$ (2.66 g, 8.72 mmol) and corresponding diimine (3.35 g, 8.90 mmol) was suspended in 100 mL of Et_2O , stirred for 0.5 h at room temperature, and then cooled to $-78^\circ C$. A solution of
15 Me_2Mg (0.499 g, 9.18 mmol) in 50 mL of Et_2O was then added via cannula to the cold reaction mixture. After stirring for 10 min at $-78^\circ C$, the yellow suspension was allowed to warm to room temperature and stirred for an additional hour. A second equivalent of the diimine
20 was then added to the reaction mixture and stirring was continued for ~4 days. The brown Et_2O solution was then filtered and the solvent was removed in vacuo to yield a yellow-brown foam. The product was then extracted with 75 mL of hexane, and the resulting
25 solution was filtered twice, concentrated, and cooled to $-30^\circ C$ overnight to yield 1.43 g (32.0%) of brown powder: ^1H NMR (C_6D_6 , 400 MHz) δ 7.40 (s, 2, $N=C(H)-C(H)=N$), 7.12 (s, 6, H_{aryl}), 3.39 (septet, 4, $J = 6.86$, $CHMe_2$), 1.30 (d, 12, $J = 6.81$, $CHMeMe'$), 1.07 (d, 12, $J = 6.91$, $CHMeMe'$), 0.77 (s, 6, $PdMe$); ^{13}C NMR (C_6D_6 , 100
30 MHz) δ 159.9 ($J_{CH} = 174.5$, $N=C(H)-C(H)=N$), 145.7 (Ar: C_{ipso}), 138.9 (Ar: C_o), 127.2 (Ar: C_p), 123.4 (Ar: C_m), 28.5 ($CHMe_2$), 24.4 and 22.8 ($CHMeMe'$), -5.1 ($J_{CH} = 128.3$, $PdMe$). Anal. Calcd for $(C_{28}H_{42}N_2Pd)$: C, 65.55, H, 8.25; N, 5.46. Found: C, 65.14; H, 8.12; N, 5.14.

Example 12

This compound was synthesized in a manner similar to the second procedure of Example 11 (stirred for 5 h at rt) using 5.13 mmol of the corresponding diimine and 2.57 mmol of Me_2Mg . After the reaction mixture was filtered, removal of Et_2O in vacuo yielded 1.29 g (62.2%) of a deep brown microcrystalline solid: ^1H NMR (C_6D_6 , 100 MHz, 12°C) δ 6.98 (s, 2, $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$), 6.95 (s, 6, H_{aryl}), 2.13 (s, 12, Ar: Me), 0.77 (s, 6, PdMe); ^{13}C NMR (C_6D_6 , 400 MHz, 12°C) δ 160.8 (J_{CH} = 174.6, $\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}$), 147.8 (Ar: C_{ipso}), 128.2 (Ar: C_m), 128.15 (Ar: C_o), 126.3 (Ar: C_p), 18.2 (Ar: Me), -5.5 (J_{CH} = 127.6, Pd-Me).

Example 13

The synthesis of this compound has been reported (Svoboda, M.; tom Dieck, H. *J. Organomet. Chem.* 1980, 191, 321-328) and was modified as follows: A mixture of $\text{Ni}(\text{acac})_2$ (1.89 g, 7.35 mmol) and the corresponding diimine (2.83 g, 7.51 mmol) was suspended in 75 mL of Et_2O and the suspension was stirred for 1 h at room temperature. After cooling the reaction mixture to -78°C , a solution of Me_2Mg (401 mg, 7.37 mmol) in 25 mL of Et_2O was added via cannula. The reaction mixture was stirred for 1 h at -78°C and then for 2 h at 0°C to give a blue-green solution. After the solution was filtered, the Et_2O was removed in vacuo to give a blue-green brittle foam. The product was then dissolved in hexane and the resulting solution was filtered twice, concentrated, and then cooled to -30°C to give 1.23 g (35.9% , one crop) of small turquoise crystals.

Example 14

The synthesis of this compound has been reported (Svoboda, M.; tom Dieck, H. *J. Organomet. Chem.* 1980, 191, 321-328) and was synthesized according to the above modified procedure (Example 13) using $\text{Ni}(\text{acac})_2$

(3.02 g, 11.75 mmol), the corresponding diimine (4.80 g, 11.85 mmol) and Me_2Mg (640 mg, 11.77 mmol). A turquoise powder was isolated (620 mg, 10.7%).

Example 15

5 $\{[(2,6\text{-MePh})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{BAF}^-$

To a mixture of $[(2,6\text{-MePh})_2\text{DABMe}_2]\text{PdMeCl}$ (109.5 mg, 0.244 mmol) and NaBAF (216.0 mg, 0.244 mmol) were added 20 mL each of Et_2O and CH_2Cl_2 and 1 mL of CH_3CN . The reaction mixture was then stirred for 1.5 h and then the NaCl was removed via filtration. Removal of the solvent in vacuo yielded a yellow powder, which was washed with 50 mL of hexane. The product (269.6 mg, 83.8%) was then dried in vacuo: ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.73 (s, 8, BAF: H_O), 7.57 (s, 4, BAF: H_P), 7.22-7.16 (m, 6, H_{aryl}), 2.23 (s, 6, Ar: Me), 2.17 (s, 6, Ar': Me), 2.16, 2.14, and 1.79 (s, 3 each, $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$, NCMe), 0.38 (s, 3, PdMe); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 180.1 and 172.2 ($\text{N}=\text{C}-\text{C}'=\text{N}$), 162.1 (q, $J_{\text{BC}} = 49.9$, BAF: C_{ipso}), 142.9 (Ar, Ar': C_O), 135.2 (BAF: C_O), 129.3 (Ar: C_m), 129.2 (q, $J_{\text{CF}} = 30.6$, BAF: C_m), 129.0 (Ar': C_m), 128.4 (Ar: C_p), 128.2 (Ar: C_O), 127.7 (Ar': C_p), 127.4 (Ar': C_O), 125.0 (q, $J_{\text{CF}} = 272.4$, BAF: CF_3), 121.8 (NCMe), 117.9 (BAF: C_p), 20.2 and 19.2 ($\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$), 18.0 (Ar: Me), 17.9 (Ar': Me), 5.1 and 2.3 (NCMe, PdMe). Anal. Calcd for $(\text{C}_{55}\text{H}_{42}\text{BF}_{24}\text{N}_3\text{Pd})$: C, 50.12; H, 3.21; N, 3.19. Found: C, 50.13; H, 3.13, N, 2.99.

Example 16

$\{[(4\text{-MePh})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{BAF}^-$

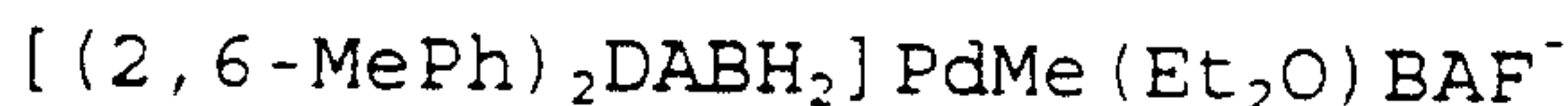
30 Following the procedure of Example 15, a yellow powder was isolated in 85% yield: ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.81 (s, 8, BAF: H_O), 7.73 (s, 4, BAF: H_P), 7.30 (d, 4, $J = 8.41$, Ar, Ar': H_m), 6.89 (d, 2, $J = 8.26$, Ar: H_O), 6.77 (d, 2, $J = 8.19$, Ar': H_O), 2.39 (s, 6, Ar, Ar': Me), 2.24, 2.17 and 1.93 (s, 3 each, $\text{N}=\text{C}(\text{Me})-\text{C}'(\text{Me})=\text{N}$, NCMe)Pd-Me; ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 180.7 and 171.6 ($\text{N}=\text{C}-\text{C}'=\text{N}$), 162.1 (q, $J_{\text{BC}} = 49.8$, BAF: C_{ipso}), 143.4 and 142.9 (Ar, Ar': C_{ipso}), 138.6 and 138.5 (Ar,

Ar': C_p), 135.2 (BAF: C_o), 130.6 and 130.4 (Ar, Ar': C_m), 129.3 (q, J_{CF} = 31.6, BAF: C_m), 125.0 (q, J_{CF} = 272.5, BAF: CF₃), 122.1 (NCMe), 121.0 and 120.9 (Ar, Ar': C_o), 117.9 (BAF: C_p), 21.5 (ArN=C(Me)), 21.1 (Ar, Ar': Me), 19.7 (ArN=C'(Me)), 6.2 and 3.0 (NCMe, PdMe).
 5 Anal. Calcd for (C₅₃H₃₈BF₂₄N₃Pd): C, 49.34; H, 2.97; N, 3.26. Found: C, 49.55; H, 2.93; N, 3.10.

Example 17

[(2,6-MePh)₂DABMe₂]PdMe(Et₂O)BAF⁻

10 A Schlenk flask containing a mixture of [(2,6-i-PrPh)₂DABMe₂]PdMe₂ (501 mg, 0.926 mmol) and H⁺(OEt₂)₂BAF⁻ (938 mg, 0.926 mmol) was cooled to -78°C. Following the addition of 50 mL of Et₂O, the solution was allowed to warm and stirred briefly (~15 min) at
 15 room temperature. The solution was then filtered and the solvent was removed in vacuo to give a pale orange powder (1.28 g, 94.5%), which was stored at -30°C under an inert atmosphere: ¹H NMR (CD₂Cl₂, 400 MHz, -60°C) δ 7.71 (s, 8, BAF: H_o), 7.58 (s, 4, BAF: H_p), 7.4 - 7.0
 20 (m, 6, H_{aryl}), 3.18 (q, 4, J = 7.10, O(CH₂CH₃)₂), 2.86 (septet, 2, J = 6.65, CHMe₂), 2.80 (septet, 2, J = 6.55, C'HMe₂), 2.18 and 2.15 (N=C(Me)-C'(Me)=N), 1.34, 1.29, 1.14 and 1.13 (d, 6 each, J = 6.4-6.7, CHMeMe', C'HMeMe'), 1.06 (t, J = 6.9, O(CH₂CH₃)₂), 0.33 (s, 3, PdMe); ¹³C NMR (CD₂Cl₂, 100 MHz, -60°C) δ 179.0 and
 25 172.1 (N=C-C'=N), 161.4 (q, J_{BC} = 49.7, BAF: C_{ipso}), 140.21 and 140.15 (Ar, Ar': C_{ipso}), 137.7 and 137.4 (Ar, Ar': C_o), 134.4 (BAF: C_p), 128.3 (q, J_{CF} = 31.3, BAF: C_m), 128.5 and 128.2 (Ar, Ar': C_p), 124.2 (q, J_{CF}
 30 = 272.4, BAF: CF₃), 117.3 (BAF: C_p), 71.5 (O(CH₂CH₃)₂), 28.7 (CHMe₂), 28.4 (C'HMe₂), 23.7, 23.6, 23.1 and 22.6 (CHMeMe', C'HMeMe'), 21.5 and 20.7 (N=C(Me)-C'(Me)=N), 14.2 (O(CH₂CH₃)₂)₂, 8.6 (PdMe). Anal. Calcd for
 35 (C₆₅H₆₅BF₂₄N₂OPd): C, 53.35; H, 4.48; N, 1.91. Found: C, 53.01; H, 4.35; N, 1.68.

Example 18

Following the procedure of Example 17, an orange powder was synthesized in 94.3% yield and stored at -30°C: ¹H NMR (CD₂Cl₂, 400 MHz, -60°C) δ 8.23 and 8.20 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H_O), 7.54 (s, 4, BAF: H_P), 7.40 - 7.27 (m, 6, H_{aryl}), 3.32 (q, 4, J = 6.90, O(CH₂CH₃)₂), 3.04 and 3.01 (septets, 2 each, J = 6.9 - 7.1, CHMe₂ and C'HMe₂), 1.32, 1.318, 1.14 and 1.10 (d, 6 each, J = 6.5 - 6.8, CHMeMe' and C'HMeMe'), 1.21 (t, 6, J = 6.93, O(CH₂CH₃)₂), 0.70 (s, 3, PdMe); ¹³C NMR (CD₂Cl₂, 100 MHz, -60°C) δ 166.9 (J_{CH} = 182.6, N=C(H)), 161.5 (J_{BC} = 49.7, BAF: C_{ipso}), 161.3 (J_{CH} = 181.6, N=C'(H)), 143.0 and 141.8 (Ar, Ar': C_{ipso}), 138.7 and 137.8 (Ar, Ar': C_O), 134.4 (BAF: C_O), 129.1 and 128.8 (Ar, Ar': C_P), 128.3 (J_{CF} = 31.3, BAF: C_m), 124.0 and 123.9 (Ar, Ar': C_m), 117.3 (BAF: C_P), 72.0 (O(CH₂CH₃)₂), 28.5 and 28.4 (CHMe₂, C'HMe₂), 25.2, 24.1, 21.9 and 21.7 (CHMeMe', C'HMeMe'), 15.2 (O(CH₂CH₃)₂), 11.4 (J_{CH} = 137.8, PdMe). Anal. Calcd for (C₆₃H₆₁BF₂₄N₂OPd): C, 52.72; H, 4.28; N, 1.95. Found: C, 52.72; H, 4.26; N, 1.86.

Example 19

Following the procedure of Example 17, a magenta powder was isolated and stored at -30°C: ¹H NMR (CD₂Cl₂, 400 MHz, -60°C; A H₂O adduct and free Et₂O were observed.) δ 7.73 (s, 8, BAF: H_O), 7.55 (s, 4, BAF: H_P), 7.4 - 7.2 (m, 6, H_{aryl}), 3.42 (s, 2, OH₂), 3.22 (q, 4, O(CH₂CH₃)₂), 3.14 and 3.11 (septets, 2 each, J = 7.1, CHMe₂, C'HMe₂), 1.95 and 1.78 (s, 3 each, N=C(Me)-C'(Me)=N), 1.42, 1.39, 1.18 and 1.11 (d, 6 each, J = 6.6 - 6.9, CHMeMe' and C'HMeMe'), 0.93 (t, J = 7.5, O(CH₂CH₃)₂), -0.26 (s, 3, NiMe); ¹³C NMR (CD₂Cl₂ 100 MHz, -58°C) δ 175.2 and 170.7 (N=C-C'=N), 161.6 (q, J_{BC} = 49.7, BAF: C_{ipso}), 141.2 (Ar: C_{ipso}), 139.16 and 138.68 (Ar, Ar': C_O), 136.8 (Ar': C_{ipso}), 134.5 (BAF: C_O), 129.1 and 128.4 (Ar, Ar': C_P), 128.5

(q, $J_{CF} = 32.4$, BAF: C_m), 125.0 and 124.2 (Ar, Ar': C_m), 124.3 (q, $J_{CF} = 272.5$, BAF: CF_3), 117.4 (BAF: C_p), 66.0 ($O(CH_2CH_3)_2$), 29.1 ($CHMe_2$), 28.9 ($C'HMe_2$), 23.51, 23.45, 23.03, and 22.95 ($CHMeMe'$, $C'HMeMe'$), 21.0 and 19.2 ($N=C(Me)-C'(Me)=N$), 14.2 (OCH_2CH_3)₂, -0.86 ($J_{CH} = 131.8$, NiMe). Anal. Calcd for $(C_{65}H_{65}BF_{24}N_2NiO)$: C, 55.15; H, 4.63; N, 1.98. Found: C, 54.74; H, 4.53; N, 2.05.

Example 20

10 $[-(2,6-MePh)_2DABH_2]NiMe(Et_2O)BAF^-$

Following the procedure of Example 17, a purple powder was obtained and stored at $-30^\circ C$: ^1H NMR (CD_2Cl_2 , 400 MHz, $-80^\circ C$; H_2O and Et_2O adducts were observed in an 80:20 ratio, respectively.) δ 8.31 and 8.13 (s, 0.8 each, $N=C(H)-C'(H)=N$; H_2O Adduct), 8.18 and 8.00 (s, 0.2 each, $N=C(H)-C'(H)=N$; Et_2O Adduct), 7.71 (s, 8 BAF: C_o), 7.53 (s, 4, BAF: C_p), 7.5 - 7.0 (m, 6, H_{aryl}), 4.21 (s, 1.6, OH_2), 3.5 - 3.1 (m, 8, $O(CH_2CH_3)_2$, $CHMe_2$, $C'HMe_2$), 1.38, 1.37, 1.16 and 1.08 (d, 4.8 each, $CHMeMe'$, $C'HMeMe'$; H_2O Adduct; These peaks overlap with and obscure the $CHMe_2$ doublets of the Et_2O adduct.), 0.27 (s, 2.4, $PdMe$; H_2O Adduct), 0.12 (s, 0.6, $PdMe$: Et_2O Adduct).

Examples 21-23

25 The rate of exchange of free and bound ethylene was determined by ^1H NMR line broadening experiments at $-85^\circ C$ for complex (XI), see the Table below. The NMR instrument was a 400 MHz Varian® NMR spectrometer. Samples were prepared according to the following procedure: The palladium ether adducts $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(OEt_2)\}BAF$, $\{[(2,6-i-PrPh)_2An]PdMe(OEt_2)\}BAF$, and $\{[(2,6-i-PrPh)_2DABH_2]PdMe(OEt_2)\}BAF$ were used as precursors to (XI), and were weighed (~15 mg) in a tared 5 mm dia. NMR tube in a nitrogen-filled drybox. The tube was then capped with a septum and Parafilm® and cooled to $-80^\circ C$. Dry, degassed CD_2Cl_2 (700 μL) was then added to the palladium complex via gastight syringe, and the

tube was shaken and warmed briefly to give a homogeneous solution. After acquiring a -85°C NMR spectrum, ethylene was added to the solution via gastight syringe and a second NMR spectrum was acquired at -85°C . The molarity of the BAF counterion was calculated according to the moles of the ether adduct placed in the NMR tube. The molarity of (XI) and free ethylene were calculated using the BAF peaks as an internal standard. Line-widths (W) were measured at half-height in units of Hz for the complexed ethylene signal (usually at 5 to 4 ppm) and were corrected for line widths (W_0) in the absence of exchange.

For (XI) the exchange rate was determined from the standard equation for the slow exchange approximation:

$$k = (W - W_0)\pi/[=],$$

where [=] is the molar concentration of ethylene. These experiments were repeated twice and an average value is reported below.

Rate Constants for Ethylene Exchange^a

Ex.	(XI)	k ($\text{L}\cdot\text{M}^{-1}\text{s}^{-1}$)
21	$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(=)\}\text{BAF}$	45
22	$\{[(2,6\text{-}i\text{-PrPh})_2\text{An}]\text{PdMe}(=)\}\text{BAF}$	520
23	$\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMe}(=)\}\text{BAF}$	8100

^aThe T_1 of free ethylene is 15 sec. A pulse delay of 60 sec and a 30° pulse width were used.

Example 24

Anhydrous FeCl_2 (228 mg, 1.8 mmol) and (2,6-*i*-PrPh)₂DABAn (1.0 g, 2.0 mmol) were combined as solids and dissolved in 40 ml of CH_2Cl_2 . The mixture was stirred at 25°C for 4 hr. The resulting green solution was removed from the unreacted FeCl_2 via filter cannula. The solvent was removed under reduced

pressure resulting in a green solid (0.95 g, 84% yield).

A portion of the green solid (40 mg) was immediately transferred to another Schlenk flask and dissolved in 50 ml of toluene under 1 atm of ethylene. The solution was cooled to 0°C, and 6 ml of a 10% MAO solution in toluene was added. The resulting purple solution was warmed to 25°C and stirred for 11 hr. The polymerization was quenched and the polymer precipitated by acetone. The resulting polymer was washed with 6M HCl, water and acetone. Subsequent drying of the polymer resulted in 60 mg of white polyethylene. ¹H NMR (CDCl₃, 200 MHz) δ 1.25 (CH₂, CH) δ 0.85 (m, CH₃).

Example 25

(2-t-BuPh)₂DABMe₂

A Schlenk tube was charged with 2-t-butylaniline (5.00 mL, 32.1 mmol) and 2,3-butanedione (1.35 mL, 15.4 mmol). Methanol (10 mL) and formic acid (1 mL) were added and a yellow precipitate began to form almost immediately upon stirring. The reaction mixture was allowed to stir overnight. The resulting yellow solid was collected via filtration and dried under vacuum. The solid was dissolved in ether and dried over Na₂SO₄ for 2-3 h. The ether solution was filtered, condensed and placed into the freezer (-30°C). Yellow crystals were isolated via filtration and dried under vacuum overnight (4.60 g, 85.7%): ¹H NMR (CDCl₃, 250 MHz) δ 7.41 (dd, 2H, J = 7.7, 1.5 Hz, H_m), 7.19 (td, 2H, J = 7.5, 1.5 Hz, H_m or H_p), 7.07 (td, 2H, J = 7.6, 1.6 Hz, H_m or H_p), 6.50 (dd, 2H, J = 7.7, 1.8 Hz, H_o), 2.19 (s, 6H, N=C(Me)-C(Me)=N), 1.34 (s, 18H, C(CH₃)₃).

Examples 26 and 27

General Polymerization Procedure for Examples 26 and 27: In the drybox, a glass insert was loaded with [(η³-C₃H₅)Pd(μ-Cl)]₂ (11 mg, 0.03 mmol), NaBAF (53 mg, 0.06 mmol), and an α-diimine ligand (0.06 mmol). The insert was cooled to -35°C in the drybox freezer, 5 mL

of C_6D_6 was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a ^1H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum

Example 26

α -Diimine was $(2,6-i-PrPh)_2DABMe_2$. Polyethylene (50 mg) was isolated as a solid. ^1H NMR spectrum (C_6D_6) is consistent with the production of 1- and 2-butenes and branched polyethylene.

Example 27

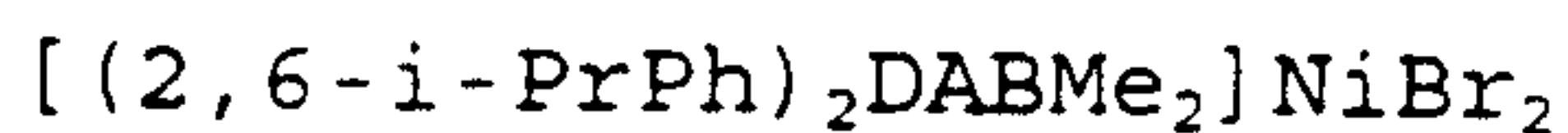
α -Diimine was $(2,6-i-PrPh)_2DABAn$. Polyethylene (17 mg) was isolated as a solid. ^1H NMR spectrum (C_6D_6) is consistent with the production of branched polyethylene.

Example 28

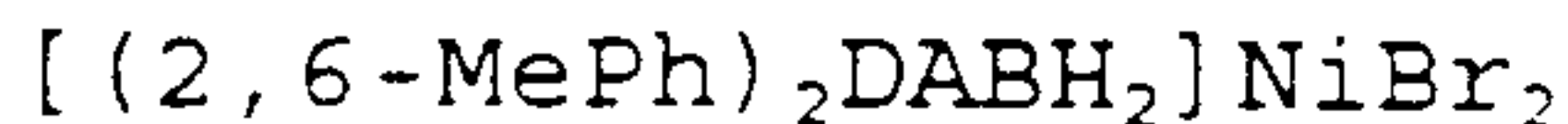
$[(2,6-i-PrPh)_2DABH_2]NiBr_2$

The corresponding diimine (980 mg, 2.61 mmol) was dissolved in 10 mL of CH_2Cl_2 in a Schlenk tube under a N_2 atmosphere. This solution was added via cannula to a suspension of $(DME)NiBr_2$ (DME = 1,2-dimethoxyethane) (787 mg, 2.55 mmol) in CH_2Cl_2 (20 mL). The resulting red/brown mixture was stirred for 20 hours. The solvent was evaporated under reduced pressure resulting in a red/brown solid. The product was washed with 3 x 10 mL of hexane and dried in vacuo. The product was isolated as a red/brown powder (1.25 g, 82% yield).

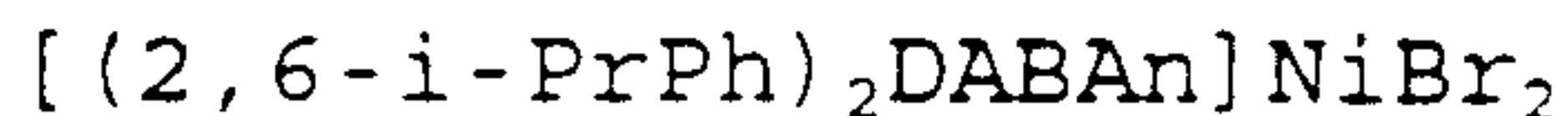
Example 29



Using a procedure similar to that of Example 28, 500 mg (1.62 mmol) $(DME)NiBr_2$ and 687 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as an orange/brown powder (670 mg, 67% yield).

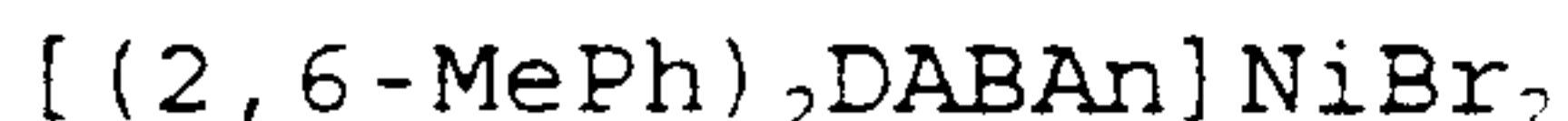
Example 30

Using a procedure similar to that of Example 28,
500 mg (1.62 mmol) (DME)NiBr₂ and 448 mg (1.70 mmol) of
5 the corresponding diimine were combined. The product
was isolated as a brown powder (622 mg, 80% yield).

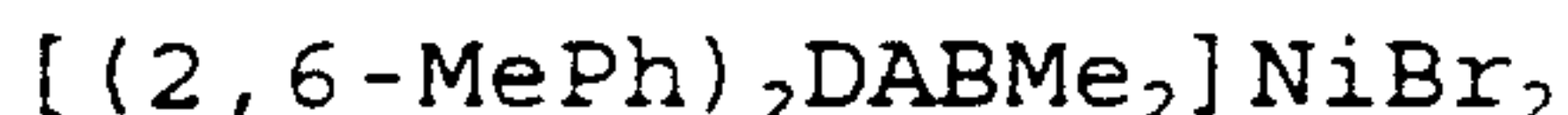
Example 31

Using a procedure similar to that of Example 28,
10 500 mg (1.62 mmol) (DME)NiBr₂ and 850 mg (1.70 mmol) of
the corresponding diimine were combined. The product
was isolated as a red powder (998 mg, 86% yield).
Anal. Calcd. for C₃₆H₄₀N₂Br₂Ni: C, 60.12; H, 5.61; N,
3.89. Found C, 59.88; H, 5.20; N, 3.52.

15

Example 32

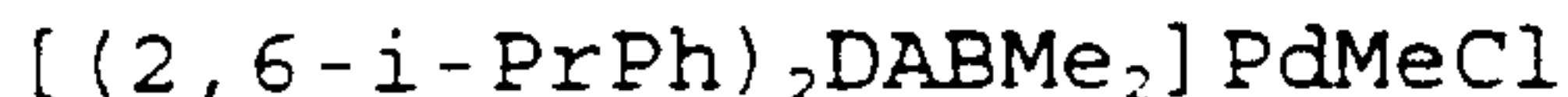
The corresponding diimine (1.92 g, 4.95 mmol) and
(DME)NiBr₂ (1.5 g, 4.86 mmol) were combined as solids
in a flame dried Schlenk under an argon atmosphere. To
20 this mixture 30 mL of CH₂Cl₂ was added giving an orange
solution. The mixture was stirred for 18 hours
resulting in a red/brown suspension. The CH₂Cl₂ was
removed via filter cannula leaving a red/brown solid.
The product was washed with 2 x 10 mL of CH₂Cl₂ and
25 dried under vacuum. The product was obtained as a
red/brown powder (2.5 g, 83% yield).

Example 33

Using a procedure similar to that of Example 32,
30 the title compound was made from 1.5 g (4.86 mmol)
(DME)NiBr₂ and 1.45 g (4.95 mmol) of the corresponding
diimine. The product was obtained as a brown powder
(2.05 g, 81% yield).

Example 34

35



(COD)PdMeCl (9.04 g, 34.1 mmol) was dissolved in
200 ml of methylene chloride. To this solution was
added the corresponding diimine (13.79 g, 34.1 mmol).

The resulting solution rapidly changed color from yellow to orange-red. After stirring at room temperature for several hours it was concentrated to form a saturated solution of the desired product, and
 5 cooled to -40°C overnight. An orange solid crystallized from the solution, and was isolated by filtration, washed with petroleum ether, and dried to afford 12.54 g of the title compound as an orange powder. Second and third crops of crystals obtained
 10 from the mother liquor afforded an additional 3.22 g of product. Total yield = 87%.

Examples 35-39

The following compounds were made by a method similar to that used in Example 34.

15

Example	Compound
35	$[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdMeCl}$
36	$[(2,6\text{-}i\text{-PrPh})_2\text{DABAn}]\text{PdMeCl}$
37	$[(\text{Ph})_2\text{DABMe}_2]\text{PdMeCl}$
20 38	$[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMeCl}$
39	$[(2,4,6\text{-MePh})_2\text{DABMe}_2]\text{PdMeCl}$

Note: The diethyl ether complexes described in Examples 41-46 are unstable in non-coordinating
 25 solvents such as methylene chloride and chloroform. They are characterized by ^1H NMR spectra recorded in CD_3CN ; under these conditions the acetonitrile adduct of the Pd methyl cation is formed. Typically, less than a whole equivalent of free diethylether is
 30 observed by ^1H NMR when $[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\text{X}$ is dissolved in CD_3CN . Therefore, it is believed the complexes designated as " $\{[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\}\text{X}$ " below are likely mixtures of
 35 $\{[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\}\text{X}$ and $[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMeX}$, and in the latter complexes the X ligand (SbF_6 , BF_4 , or PF_6) is weakly coordinated to palladium. A formula of the type " $\{[(\text{R})_2\text{DAB}(\text{R}')_2]\text{PdMe}(\text{OEt}_2)\}\text{X}$ " is a "formal" way of conveying the approximate overall composition of

this compound, but may not accurately depict the exact coordination to the metal atom.

Listed below are the ^{13}C NMR data for Example 36.

5

 ^{13}C NMR data

TCB, 120C, 0.05M CrAcAc

<u>freq ppm</u>	<u>intensity</u>	
46.5568	24.6005	1 cmp and/or 1,3 ccmcc
44.9321	3.42517	1,3 cmc
40.8118	55.4341	2 pmp
40.3658	145.916	1,3 pmp
39.5693	18.458	methylenes from 2 cmp and/or 2 cmc
38.7782	4.16118	
38.6295	5.84037	
38.2844	8.43098	
38.1198	8.29802	
37.8384	3.83966	
37.5198	13.4977	
37.2384	23.4819	
37.1163	16.8339	
36.7446	114.983	
36.0012	6.19217	
35.7198	5.17495	
34.2278	4.83958	
32.9216	20.2781	3B_6^+ , 3EOC
32.619	3.6086	
32.4172	2.98497	
32.1995	10.637	
31.9765	42.2547	
31.8809	143.871	
30.4686	27.9974	
30.3199	47.1951	
30.0225	36.1409	
29.7411	102.51	
29.311	4.83244	
28.7111	117.354	
28.2597	9.05515	
27.1659	22.5725	
27.0067	5.81855	
26.1146	13.5772	
24.5642	2.59695	$\beta\beta\text{B}$
22.6368	12.726	2B_5^+ , 2EOC
20.1413	3.7815	2B_3
19.7271	20.0959	1B_1
17.5236	7.01554	end group
14.2528	3.03535	1B_3
13.8812	12.3635	1B_4^+ , 1EOC

Example 40

A procedure analogous to that used in Example 54, using (4-Me₂NPh)₂DABMe₂ in place of (2-C₆H₄-^tBu)₂DABMe₂, afforded {[(4-NMe₂Ph)₂DABMe₂]PdMe(MeCN)}SbF₆·MeCN as a purple solid (product was not recrystallized in this instance). ¹H NMR (CD₂Cl₂) δ 6.96 (d, 2H, H_{aryl}), 6.75 (mult, 6H, H_{aryl}), 3.01 (s, 6H, NMe₂), 2.98 (s, 6H, NMe'₂), 2.30, 2.18, 2.03, 1.96 (s's, 3H each, N=CMe, N=CMe', and free and coordinated N≡CMe), 0.49 (s, 3H, Pd-Me).

10

Example 41

{[(2,6-*i*-PrPh)₂DABMe₂]PdMe(Et₂O)_n}SbF₆⁻
[(2,6-*i*-PrPh)₂DABMe₂]PdMeCl (0.84 g, 1.49 mmol) was suspended in 50 mL of diethylether and the mixture cooled to -40°C. To this was added AgSbF₆ (0.52 g, 1.50 mmol). The reaction mixture was allowed to warm to room temperature, and stirred at room temperature for 90 min. The reaction mixture was then filtered, giving a pale yellow filtrate and a bright yellow precipitate. The yellow precipitate was extracted with 4 x 20 mL 50/50 methylene chloride/diethyl ether. The filtrate and extracts were then combined with an additional 30 mL diethyl ether. The resulting solution was then concentrated to half its original volume and 100 mL of petroleum ether added. The resulting precipitate was filtered off and dried, affording 1.04 g of the title compound as a yellow-orange powder (83% yield). ¹H NMR (CD₃CN) δ 7.30 (mult, 6H, H_{aryl}), 3.37 [q, free O(CH₂CH₃)₂], 3.05-2.90 (overlapping sept's, 4H, CHMe₂), 2.20 (s, 3H, N=CMe), 2.19 (s, 3H, N=CMe'), 1.35-1.14 (overlapping d's, 24H, CHMe₂), 1.08 (t, free O(CH₂CH₃)₂), 0.28 (s, 3H, Pd-Me). This material contained 0.4 equiv of Et₂O per Pd, as determined by ¹H NMR integration.

35

Example 42

A procedure analogous to that used in Example 41, using AgBF₄ in place of AgSbF₆, afforded the title compound as a mustard yellow powder in 61% yield. This

material contained 0.3 equiv of Et₂O per Pd, as determined by ¹H NMR integration. ¹H NMR in CD₃CN was otherwise identical to that of the compound made in Example 41.

5

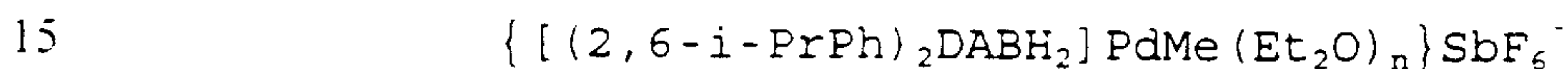
Example 43



A procedure analogous to that used in Example 41, using AgPF₆ in place of AgSbF₆, afforded the title compound as a yellow-orange powder in 72% yield. This material contained 0.4 equiv of Et₂O per Pd, as determined by ¹H NMR integration. ¹H NMR in CD₃CN was identical to that of the compound of Example 41.

10

Example 44



A procedure analogous to that used in Example 41, using [(2,6-*i*-PrPh)₂DABH₂]₂PdMeCl in place of [(2,6-*i*-PrPh)₂DABMe₂]₂PdMeCl, afforded the title compound in 71% yield. ¹H NMR (CD₃CN) δ 8.30 (s, 2H, N=CH and N=CH'), 7.30 (s, 6H, H_{aryl}), 3.37 [q, free O(CH₂CH₃)₂], 3.15 (br, 4H, CHMe₂), 1.40-1.10 (br, 24H, CHMe₂), 1.08 (t, free O(CH₂CH₃)₂), 0.55 (s, 3H, Pd-Me). This material contained 0.5 equiv of Et₂O per Pd, as determined by ¹H NMR integration.

20

25

Example 45



[(2,4,6-MePh)₂DABMe₂]₂PdMeCl (0.50 g, 1.05 mmol) was partially dissolved in 40 mL 50/50 methylene chloride/diethylether. To this mixture at room temperature was added AgSbF₆ (0.36 g, 1.05 mmol). The resulting reaction mixture was stirred at room temperature for 45 min. It was then filtered, and the filtrate concentrated in vacuo to afford an oily solid. The latter was washed with diethyl ether and dried to afford the title compound as a beige powder. ¹H NMR (CD₃CN) δ 6.99 (s, 4H, H_{aryl}), 3.38 [q, free O(CH₂CH₃)₂], 2.30-2.00 (overlapping s's, 24H, N=CMe, N=CMe' and aryl Me's), 1.08 (t, free O(CH₂CH₃)₂), 0.15

30

35

s, 3H, Pd-Me). This material contained 0.7 equiv of Et₂O per Pd, as determined by ¹H MR integration.

Example 46



5 A procedure analogous to that used in Example 41, using [(2,6-*i*-PrPh)₂DABAn]PdMeCl in place of [(2,6-*i*-PrPh)₂DABMe₂]PdMeCl, afforded the title compound in 92% yield. ¹H NMR (CD₃CN) δ 8.22 (br t, 2H, H_{aryl}), 7.60-7.42 (br mult, 8H, H_{aryl}), 6.93 (br d, 1H, H_{aryl}), 6.53
10 (br d, 1H, H_{aryl}), 3.38 [q, free O(CH₂CH₃)₂], 3.30 (br mult, 4H, CHMe₂), 1.36 (br d, 6H, CHMe₂), 1.32 (br d, 6H, CHMe₂), 1.08 (t, free O(CH₂CH₃)₂), 1.02 (br d, 6H, CHMe₂), 0.92 (br d, 6H, CHMe₂), 0.68 (s, 3H, Pd-Me). The amount of ether contained in the product could not
15 be determined precisely by ¹H NMR integration, due to overlapping resonances.

Example 47



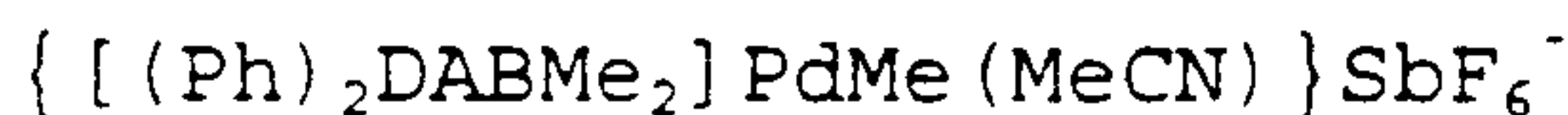
A procedure analogous to that used in Example 41, using AgOSO₂CF₃ in place of AgSbF₆, afforded the title
20 compound as a yellow-orange powder. ¹H NMR in CD₃CN was identical to that of the title compound of Example 41, but without free ether resonances.

Example 48

25 $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{SbF}_6^-$
[(2,6-*i*-PrPh)₂DABMe₂]PdMeCl (0.40 g, 0.71 mmol) was dissolved in 15 mL acetonitrile to give an orange solution. To this was added AgSbF₆ (0.25 g, 0.71 mmol) at room temperature. AgCl immediately precipitated
30 from the resulting bright yellow reaction mixture. The mixture was stirred at room temperature for 3 h. It was then filtered and the AgCl precipitate extracted with 5 mL of acetonitrile. The combined filtrate and extract were concentrated to dryness affording a yellow
35 solid. This was recrystallized from methylene chloride/petroleum ether affording 0.43 g of the title compound as a bright yellow powder (Yield = 75%). ¹H NMR (CDCl₃) δ 7.35-7.24 (mult, 6H, H_{aryl}), 2.91 (mult,

4H, CHMe₂), 2.29 (s, 3H, N=CMe), 2.28 (s, 3H, N=CMe'), 1.81 (s, 3H, N≡CMe), 1.37-1.19 (overlapping d's, 24H, CHMe's), 0.40 (s, 3H, Pd-Me). This compound can also be prepared by addition of acetonitrile to {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆⁻.

Example 49



A procedure analogous to that used in Example 48, using [(Ph)₂DABMe₂]PdMeCl in place of [(2,6-i-PrPh)₂DABMe₂]PdMeCl, afforded the title compound as a yellow microcrystalline solid upon recrystallization from methylene chloride / petroleum ether. This complex crystallizes as the acetonitrile solvate from acetonitrile solution at -40°C. ¹H NMR of material recrystallized from methylene chloride/petroleum ether: (CDCl₃) δ 7.46 (mult, 4H, H_{aryl}), 7.30 (t, 2H, H_{aryl}), 7.12 (d, 2H, H_{aryl}), 7.00 (d, 2H, H_{aryl}), 2.31 (s, 3H, N=CMe), 2.25 (s, 3H, N=CMe'), 1.93 (s, 3H, N≡CMe), 0.43 (s, 3H, Pd-Me).

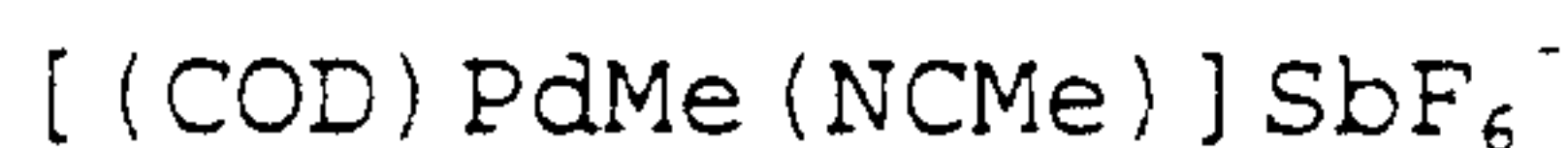
Example 50



[(2,6-EtPh)₂DABMe₂]PdMeCl (0.200 g, 0.396 mmol) was dissolved in 10 mL of acetonitrile to give an orange solution. To this was added NaBAF (0.350 g, 0.396 mmol). The reaction mixture turned bright yellow and NaCl precipitated. The reaction mixture was stirred at room temperature for 30 min and then filtered through a Celite[®] pad. The Celite[®] pad was extracted with 5 mL of acetonitrile. The combined filtrate and extract was concentrated in vacuo to afford an orange solid, recrystallization of which from methylene chloride / petroleum ether at -40°C afforded 0.403 g of the title compound as orange crystals (Yield = 74%). ¹H NMR (CDCl₃) δ 7.68 (s, 8H, H_{ortho} of anion), 7.51 (s, 4H, H_{para} of anion), 7.33-7.19 (mult, 6H, H_{aryl} of cation), 2.56-2.33 (mult, 8H, CH₂CH₃), 2.11 (s, 3H, N=CMe), 2.09 (s, 3H, N=CMe'), 1.71 (s, 3H, N≡CMe), 1.27-1.22 (mult, 12H, CH₂CH₃), 0.41 (s, 3H, Pd-Me).

Example 51

A procedure analogous to that used in Example 50, using AgSbF_6 in place of NaBAF , afforded the title
5 compound as yellow crystals in 99% yield after recrystallization from methylene chloride/petroleum ether at -40°C .

Example 52

10 To $(\text{COD})\text{PdMeCl}$ (1.25 g, 4.70 mmol) was added a solution of acetonitrile (1.93 g, 47.0 mmol) in 20 mL methylene chloride. To this clear solution was added AgSbF_6 (1.62 g, 4.70 mmol). A white solid immediately precipitated. The reaction mixture was stirred at room
15 temperature for 45 min, and then filtered. The yellow filtrate was concentrated to dryness, affording a yellow solid. This was washed with ether and dried, affording 2.27 g of $[(\text{COD})\text{PdMe}(\text{NCMe})]\text{SbF}_6^-$ as a light yellow powder (yield = 95%). ^1H NMR (CD_2Cl_2) δ 5.84
20 (mult, 2H, $\text{CH}=\text{CH}$), 5.42 (mult, 2H, $\text{CH}'=\text{CH}'$), 2.65 (mult, 4H, CHH'), 2.51 (mult, 4H, CHH'), 2.37 (s, 3H, NCMe), 1.18 (s, 3H, Pd-Me).

Example 53

25 A procedure analogous to that used in Example 52, using NaBAF in place of AgSbF_6 , afforded the title compound as a light beige powder in 96% yield.

Example 54

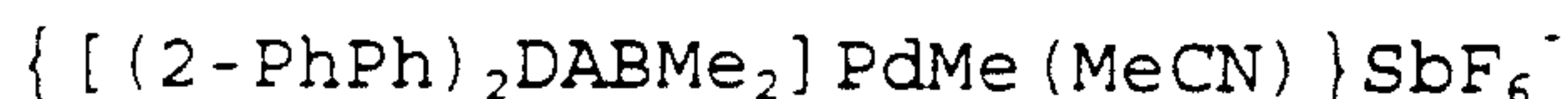
To a suspension of (2-t-BuPh)₂DABMe₂ (0.138 g, 0.395 mmol) in 10 mL of acetonitrile was added
5 [(COD)PdMe(NCMe)]SbF₆ (0.200 g, 0.395 mmol). The resulting yellow solution was stirred at room temperature for 5 min. It was then extracted with 3 x 10 mL of petroleum ether. The yellow acetonitrile phase was concentrated to dryness, affording a bright
10 yellow powder. Recrystallization from methylene chloride/petroleum ether at -40 °C afforded 180 mg of the title product as a bright yellow powder (yield = 61%). ¹H NMR (CD₂Cl₂) δ 7.57 (dd, 2H, H_{aryl}), 7.32 (mult, 4H, H_{aryl}), 6.88 (dd, 2H, H_{aryl}), 6.78 (dd, 2H,
15 H_{aryl}), 2.28 (s, 3H, N=CMe), 2.22 (s, 3H, N=CMe'), 1.78 (s, 3H, N≡CMe), 1.48 (s, 18H, ^tBu), 0.52 (s, 3H, Pd-Me).

Example 55

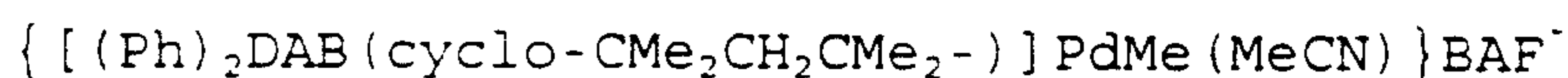
20 A procedure analogous to that used in Example 54, using (Np)₂DABMe₂ in place of (2-t-BuPh)₂DABMe₂, afforded the title compound as an orange powder in 52% yield after two recrystallizations from methylene chloride/petroleum ether. ¹H NMR (CD₂Cl₂) δ 8.20-7.19
25 (mult, 14 H, H_{aromatic}), 2.36 (d, J = 4.3 Hz, 3H, N=CMe), 2.22 (d, J = 1.4 Hz, 3H, N=CMe'), 1.32 (s, 3H, NCMe), 0.22 (s, 3H, Pd-Me).

Example 56

30 A procedure analogous to that used in Example 54, using (Ph₂CH)₂DABH₂ in place of (2-t-BuPh)₂DABMe₂, afforded the title compound as a yellow microcrystalline solid. ¹H NMR (CDCl₃) δ 7.69 (s, 1H, N=CH), 7.65 (s, 1H, N=CH'), 7.44-7.08 (mult, 20H,
35 H_{aryl}), 6.35 (2, 2H, CHPh₂), 1.89 (s, 3H, NCMe), 0.78 (s, 3H, Pd-Me).

Example 57

A procedure analogous to that used in Example 54, using (2-PhPh)₂DABMe₂ in place of (2-t-BuPh)₂DABMe₂,
5 afforded the title compound as a yellow-orange powder in 90% yield. Two isomers, due to *cis* or *trans* orientations of the two ortho phenyl groups on either side of the square plane, were observed by ¹H NMR. ¹H NMR (CD₂Cl₂) δ 7.80-6.82 (mult, 18H, H_{aryl}), 1.98, 1.96,
10 1.90, 1.83, 1.77, 1.73 (singlets, 9H, N=CMe, N=CMe', NCMe for *cis* and *trans* isomers), 0.63, 0.61 (singlets, 3H, Pd-Me for *cis* and *trans* isomers).

Example 58

15 To a solution of [(COD)PdMe(NCMe)]BAF⁻ (0.305 g, 0.269 mmol) dissolved in 15 mL of acetonitrile was added N,N'-diphenyl-2,2',4,4'-tetramethyl-cyclopentylidiazine (0.082 g, 0.269 mmol). A gold colored solution formed rapidly and was stirred at room
20 temperature for 20 min. The solution was then extracted with 4 x 5 mL petroleum ether, and the acetonitrile phase concentrated to dryness to afford a yellow powder. This was recrystallized from methylene chloride/petroleum ether at -40°C to afford 0.323 g
25 (90%) of the title compound as a yellow-orange, crystalline solid. ¹H NMR (CDCl₃) δ 7.71 (s, 8H, H_{ortho} of anion), 7.54 (s, 4H, H_{para} of anion), 7.45-6.95 (mult, 10H, H_{aryl} of cation), 1.99 (s, 2H, CH₂), 1.73 (s, 3H, NCMe), 1.15 (s, 6H, Me₂), 1.09 (s, 6H, Me'₂),
30 0.48 (s, 3H, Pd-Me).

Example 59

Under a nitrogen atmosphere {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆⁻ (3.60 g, 4.30 mmol) was
35 weighed into a round bottom flask containing a magnetic stirbar. To this was added a -40°C solution of methyl acrylate (1.85 g, 21.5 mmol) dissolved in 100 ml of methylene chloride. The resulting orange solution was

stirred for 10 min, while being allowed to warm to room temperature. The reaction mixture was then concentrated to dryness, affording a yellow-brown solid. The crude product was extracted with methylene chloride, and the orange-red extract concentrated, layered with an equal volume of petroleum ether, and cooled to -40°C . This afforded 1.92 g of the title compound as yellow-orange crystals. An additional 1.39 g was obtained as a second crop from the mother liquor; total yield = 91%. ^1H NMR (CD_2Cl_2) δ 7.39-7.27 (mult, 6H, H_{aryl}), 3.02 (s, 3H, OMe), 2.97 (sept, 4H, CHMe_2), 2.40 (mult, 2H, CH_2), 2.24 (s, 3H, $\text{N}=\text{CMe}$), 2.22 (s, 3H, $\text{N}=\text{CMe}'$), 1.40-1.20 (mult, 26H, CHMe_2 and CH_2'), 0.64 (mult, 2H, CH_2'').

15

Example 60

$\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\}\text{SbF}_6^-$
 AgSbF_6 (0.168 g, 0.489 mmol) was added to a -40°C solution of $\{[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{PdMeCl}$ (0.260 g, 0.487 mmol) and methyl acrylate (0.210 g, 2.44 mmol) in 10 mL methylene chloride. The reaction mixture was stirred for 1 h while warming to room temperature, and then filtered. The filtrate was concentrated *in vacuo* to give a saturated solution of the title compound, which was then layered with an equal volume of petroleum ether and cooled to -40°C . Red-orange crystals precipitated from the solution. These were separated by filtration and dried, affording 0.271 g of the title compound (68% yield). ^1H NMR (CD_2Cl_2) δ 8.38 (s, 1H, $\text{N}=\text{CH}$), 8.31 (s, 1H, $\text{N}=\text{CH}'$), 7.41-7.24 (mult, 6H, H_{aryl}), 3.16 (mult, 7H, OMe and CHMe_2), 2.48 (mult, 2H, CH_2), 1.65 (t, 2H, CH_2'), 1.40-1.20 (mult, 24H, CHMe_2), 0.72 (mult, 2H, CH_2'').

35

Example 61

$\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\}[\text{B}(\text{C}_6\text{F}_5)_3\text{Cl}]$
 $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$ (0.038 g, 0.067 mmol) and methyl acrylate (0.028 g, 0.33 mmol) were dissolved in CD_2Cl_2 . To this solution was added $\text{B}(\text{C}_6\text{F}_5)_3$ (0.036

g, 0.070 mmol). ^1H NMR of the resulting reaction mixture showed formation of the title compound.

Example 62

A 100 mL autoclave was charged with chloroform (50 mL), $\{[(2\text{-t-BuPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.090 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred at 25°C and 2.1 MPa ethylene for 3 h. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 2.695 g of branched polyethylene. The number average molecular weight (M_n), calculated by ^1H NMR integration of aliphatic vs. olefinic resonances, was 1600. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 59; for a linear polymer this would result in 18 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 154. Therefore, it may be concluded that this material was branched polyethylene. ^1H NMR (CDCl_3) δ 5.38 (mult, vinyl H's), 1.95 (mult, allylic methylenes), 1.62 (mult, allylic methyls), 1.24 (mult, non-allylic methylenes and methines), 0.85 (mult, non-allylic methyls).

Example 63

A suspension of $\{[(2\text{-t-BuPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.015 g, 0.02 mmol) in 5 mL FC-75 was agitated under 2.8 MPa of ethylene for 30 min. The pressure was then increased to 4.1 MPa and maintained at this pressure for 3 h. During this time the reaction temperature varied between 25 and 40°C . A viscous oil was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. The number average molecular weight (M_n), calculated by ^1H NMR integration of aliphatic vs. olefinic resonances, was 2600. DP for this material was calculated on the basis of the ^1H NMR spectrum to be 95; for a linear polymer this would result in 11 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR

spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 177.

Example 64

A 100 mL autoclave was charged with chloroform (55 mL), $\{[(2\text{-PhPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.094 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred at 25°C and 2.1 MPa ethylene for 3 h. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 2.27 g of a pale yellow oil. Mn was calculated on the basis of ^1H NMR integration of aliphatic vs. olefinic resonances to be 200. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 7.2; for a linear polymer this would result in 200 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 283.

Example 65

A suspension of $[(2\text{-PhPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.016 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h 40 min. During this time the reaction temperature varied between 23 and 41°C. A viscous oil (329 mg) was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. Mn was calculated on the basis of ^1H NMR integration of aliphatic vs. olefinic resonances to be 700. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 24.1; for a linear polymer this would result in 45 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 173.

Example 66

A 100 mL autoclave was charged with FC-75 (50 mL), $\{(\text{Ph}_2\text{DABMe}_2)\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.076 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at 24°C for 1.5 h. The ethylene pressure was then vented, and the FC-75 mixture removed from the reactor.

A small amount of insoluble oil was isolated from the mixture by decanting off the FC-75. The reactor was washed out with 2 x 50 mL CHCl_3 , and the washings added to the oil. Volatiles removed from the resulting solution in vacuo to afford 144 mg of an oily solid. Mn was calculated on the basis of ^1H NMR integration of aliphatic vs. olefinic resonances to be 400. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 13.8; for a linear polymer this would result in 83 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 288.

Example 67

A 100 mL autoclave was charged with chloroform (50 mL), $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{BAF}^-$ (0.165 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred under 2.1 MPa of ethylene for 60 min; during this time the temperature inside the reactor increased from 22 to 48°C. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 15.95 g of a viscous oil. ^1H NMR of this material showed it to be branched polyethylene with 135 methyl-ended branches per 1000 methylenes. GPC analysis in trichlorobenzene (vs. a linear polyethylene standard) gave $M_n = 10,400$, $M_w = 22,100$.

Example 68

This was run identically to Example 67, but with $\{[(2,6\text{-EtPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.090 g, 0.12 mmol) in place of the corresponding BAF salt. The temperature of the reaction increased from 23 to 30°C during the course of the reaction. 5.25 g of a viscous oil was isolated, ^1H NMR of which showed it to be branched polyethylene with 119 methyl-ended branches per 1000 methylenes.

Example 69

A suspension of $\{[(\text{Np})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.027 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h; during this time the temperature inside the reactor varied between 25 and 40°C. Two FC-75 insoluble fractions were isolated from the reaction mixture. One fraction, a non-viscous oil floating on top of the FC-75, was removed by pipette and shown by ^1H NMR to be branched ethylene oligomers for which $M_n = 150$ and with 504 methyl-ended branches per 1000 methylenes. The other fraction was a viscous oil isolated by removing FC-75 by pipette; it was shown by ^1H NMR to be polyethylene for which $M_n = 650$ and with 240 methyl-ended branches per 1000 methylenes.

Example 70

A suspension of $\{[(\text{Ph}_2\text{CH})_2\text{DABH}_2]\text{PdMe}(\text{NCMe})\}\text{SbF}_6^-$ (0.016 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h 40 min. During this time the reaction temperature varied between 23 and 41°C. A viscous oil (43 mg) was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. M_n was calculated on the basis of ^1H NMR integration of aliphatic vs. olefinic resonances to be approximately 2000. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 73; for a linear polymer this would result in 14 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 377.

Example 71

A 100 mL autoclave was charged with FC-75 (50 mL), $\{(\text{Ph}_2\text{DAB}(\text{cyclo} - \text{CMe}_2\text{CH}_2\text{CMe}_2 -))\text{PdMe}(\text{MeCN})\}\text{BAF}^-$ (0.160 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at 24-25°C for 3.5 h. The ethylene pressure was then vented, and the cloudy FC-75 mixture removed from the reactor. The FC-75 mixture was extracted with chloroform, and the chloroform extract concentrated to dryness affording 0.98 g of an oil. M_n

was calculated on the basis of ^1H NMR integration of aliphatic vs. olefinic resonances to be 500. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 19.5; for a linear polymer this would result in 57 methyl-ended branches per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 452.

Example 72

10 A 100 mL autoclave was charged with FC-75 (50 mL), $\{[(4\text{-NMe}_2\text{Ph})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{SbF}_6^-$ (MeCN) (0.091 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at 24°C for 1.5 h. The ethylene pressure was then vented, and the cloudy FC-75 mixture removed from the reactor. The FC-75 was extracted with 15 3 x 25 mL of chloroform. The reactor was washed out with 3 x 40 mL CHCl_3 , and the washings added to the extracts. Volatiles removed from the resulting solution in vacuo to afford 556 mg of an oil. Mn was 20 calculated on the basis of ^1H NMR integration of aliphatic vs. olefinic resonances to be 200. The degree of polymerization, DP, was calculated on the basis of the ^1H NMR spectrum to be 8.4; for a linear polymer this would result in 154 methyl-ended branches 25 per 1000 methylenes. However, based on the ^1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 261.

Example 73

Under nitrogen, a 250 mL Schlenk flask was charged 30 with 10.0 g of the monomer $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_n\text{CF}_3$ (avg $n = 9$), 40 mL of methylene chloride, and a magnetic stirbar. To the rapidly stirred solution was added $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{SbF}_6^-$ (0.075 g, 0.089 mmol) in small portions. The resulting yellow-orange 35 solution was stirred under 1 atm of ethylene for 18 h. The reaction mixture was then concentrated, and the viscous product extracted with ~ 300 mL of petroleum ether. The yellow filtrate was concentrated to

dryness, and extracted a second time with ~ 150 mL petroleum ether. ~ 500 mL of methanol was added to the filtrate; the copolymer precipitated as an oil which adhered to the sides of the flask, and was isolated by
5 decanting off the petroleum ether/ methanol mixture. The copolymer was dried, affording 1.33 g of a slightly viscous oil. Upon standing for several hours, an additional 0.70 g of copolymer precipitated from the petroleum ether/ methanol mixture. By ^1H NMR
10 integration, it was determined that the acrylate content of this material was 4.2 mole%, and that it contained 26 ester and 87 methyl-ended branches per 1000 methylenes. GPC analysis in tetrahydrofuran (vs. a PMMA standard) gave $M_n = 30,400$, $M_w = 40,200$. ^1H NMR
15 (CDCl_3) δ 4.36 (t, $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$), 2.45 (mult, $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$), 2.31 (t, $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$), 1.62 (mult, $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{R}_f$), 1.23 (mult, other methylenes and methines), 0.85 (mult, methyls). ^{13}C NMR gave branching per 1000 CH_2 : Total methyls (91.3), Methyl
20 (32.8), Ethyl (20), Propyl (2.2), Butyl (7.7), Amyl (2.2), $\geq\text{Hex}$ and end of chains (22.1). GPC analysis in THF gave $M_n = 30,400$, $M_w = 40,200$ vs. PMMA.

Example 74

A 100 mL autoclave was charged with
25 $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4](\text{BF}_4)_2$ (0.058 g, 0.12 mmol) and chloroform (40 mL). To this was added a solution of (2,6-i-PrPh) $_2$ DABMe $_2$ (0.070 g, 0.17 mmol) dissolved in 10 mL of chloroform under ethylene pressure (2.1 MPa). The pressure was maintained at 2.1 MPa for 1.5 h,
30 during which time the temperature inside the reactor increased from 22 to 35°C. The ethylene pressure was then vented and the reaction mixture removed from the reactor. The reactor was washed with 3 x 50 mL of chloroform, the washings added to the reaction mixture,
35 and volatiles removed from the resulting solution in vacuo to afford 9.77 g of a viscous oil. ^1H NMR of this material showed it to be branched polyethylene with 96 methyl-ended branches per 1000 methylenes.

Example 75

A 100 mL autoclave was charged with
[Pd(CH₃CN)₄](BF₄)₂ (0.053 g, 0.12 mmol) and chloroform
(50 mL). To this was added a solution of (2,6-i-
5 PrPh)₂DABMe₂ (0.070 g, 0.17 mmol) dissolved in 10 mL of
chloroform under ethylene pressure (2.1 MPa). The
pressure was maintained at 2.1 MPa for 3.0 h, during
which time the temperature inside the reactor increased
from 23 to 52°C. The ethylene pressure was then vented
10 and the reaction mixture removed from the reactor. The
reactor was washed with 3 x 50 mL of chloroform, the
washings added to the reaction mixture, and volatiles
removed from the resulting solution in vacuo to afford
25.98 g of a viscous oil. ¹H NMR of this material
15 showed it to be branched polyethylene with 103 methyl-
ended branches per 1000 methylenes. GPC analysis in
trichlorobenzene gave M_n = 10,800, M_w = 21,200 vs.
linear polyethylene.

Example 76

20 A mixture of 20 mg (0.034 mmol) of [(2,6-i-
PrPh)DABH₂]NiBr₂ and 60 mL dry, deaerated toluene was
magnetically-stirred under nitrogen in a 200-mL three-
necked flask with a gas inlet tube, a thermometer, and
a gas exit tube which vented through a mineral oil
25 bubbler. To this mixture, 0.75 mL (65 eq) of 3M
poly(methylalumoxane) (PMAO) in toluene was added via
syringe. The resulting deep blue-black catalyst
solution was stirred as ethylene was bubbled through at
about 5 ml and 1 atm for 2 hr. The temperature of the
30 mixture rose to 60°C in the first 15 min and then
dropped to room temperature over the course of the
reaction.

The product solution was worked up by blending
with methanol; the resulting white polymer was washed
35 with 2N HCl, water, and methanol to yield after drying
(50°C/vacuum/nitrogen purge) 5.69g (6000 catalyst
turnovers) of polyethylene which was easily-soluble in
hot chlorobenzene. Differential scanning calorimetry

exhibited a broad melting point at 107°C (67 J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):

- 5 $M_n=22,300$; $M_w=102,000$; $M_w/M_n=4.56$. ^{13}C NMR analysis: branching per 1000 CH_2 : total Methyls (60), Methyl (41), Ethyl (5.8), Propyl (2.5), Butyl (2.4), Amyl (1.2), $\geq$ Hexyl and end of chain (5); chemical shifts were referenced to the solvent: the high field carbon
10 of 1,2,4-trichlorobenzene (127.8 ppm). A film of polymer (pressed at 200°C) was strong and could be stretched and drawn without elastic recovery.

Example 77

- In a Parr[®] 600-mL stirred autoclave under
15 nitrogen was combined 23 mg (0.039 mmol) of [(2,6-i-PrPh)DABH₂]NiBr₂, 60 mL of dry toluene, and 0.75 mL of poly(methylalumoxane) at 28°C. The mixture was stirred, flushed with ethylene, and pressurized to 414 kPa with ethylene. The reaction was stirred at 414 kPa
20 for 1 hr; the internal temperature rose to 31°C over this time. After 1 hr, the ethylene was vented and 200 mL of methanol was added with stirring to the autoclave. The resulting polymer slurry was filtered; the polymer adhering to the autoclave walls and
25 impeller was scraped off and added to the filtered polymer. The product was washed with methanol and acetone and dried (80°C/vacuum/nitrogen purge) to yield 5.10g (4700 catalyst turnovers) of polyethylene. Differential scanning calorimetry exhibited a melting
30 point at 127°C (170 J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=49,300$; $M_w=123,000$; $M_w/M_n=2.51$. Intrinsic viscosity (trichlorobenzene,
35 135°C): 1.925 dL/g. Absolute molecular weight averages corrected for branching: $M_n=47,400$; $M_w=134,000$; $M_w/M_n=2.83$. ^{13}C NMR analysis; branching per 1000 CH_2 : total Methyls (10.5), Methyl (8.4), Ethyl (0.9), Propyl

(0), Butyl (0), $\geq$ Butyl and end of chain (1.1); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). A film of polymer (pressed at 200°C) was strong and stiff and could be stretched and drawn without elastic recovery. This polyethylene is much more crystalline and linear than the polymer of Example 76. This example shows that only a modest pressure increase from 1 atm to 414 kPa allows propagation to successfully compete with rearrangement and isomerization of the polymer chain by this catalyst, thus giving a less-branched, more-crystalline polyethylene.

Example 78

A mixture of 12 mg (0.020 mmol) of [(2,6-i-PrPh)DABH₂]NiBr₂ and 40 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 15°C in a 100-mL three-necked flask with an addition funnel, a thermometer, and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.5 mL of poly(methylalumoxane) in toluene was added via syringe; the resulting burgundy catalyst solution was stirred for 5 min and allowed to warm to room temperature. Into the addition funnel was condensed (via a Dry Ice condenser on the top of the funnel) 15 mL (about 10g) of cis-2-butene. The catalyst solution was stirred as the cis-2-butene was added as a liquid all at once, and the mixture was stirred for 16 hr. The product solution was treated with 1 mL of methanol and was filtered through diatomaceous earth; rotary evaporation yielded 0.35g (300 catalyst turnovers) of a light yellow grease, poly-2-butene. ¹³C NMR analysis; branching per 1000 CH₂: total Methyls (365), Methyl (285), Ethyl (72), $\geq$ Butyl and end of chain (8); chemical shifts were referenced to the solvent chloroform-d₁ (77 ppm).

Listed below are the ¹³C NMR data upon which the above analysis is based.

¹³C NMR Data

CDCl ₃ , RT, 0.05M CnAcAc	
Freq ppm	Intensity
41.6071	11.2954
41.1471	13.7193
38.6816	3.55568
37.1805	7.07882
36.8657	33.8859
36.7366	35.1101
36.6196	33.8905
36.2645	12.1006
35.9094	13.3271
35.8004	11.8845
35.5785	4.20104
34.7351	24.9682
34.4325	39.3436
34.3114	59.2878
34.1177	125.698
33.9886	121.887
33.8837	120.233
33.5326	49.8058
33.004	132.842
32.7377	51.2221
32.657	55.6128
32.3705	18.1589
31.5876	9.27643
31.3818	16.409
31.0066	15.1861
30.0946	41.098
29.9736	42.8009
29.7072	106.314
29.3602	60.0884
29.2512	35.0694
29.114	26.6437
28.9769	29.1226
27.9358	3.57351
27.7501	3.56527
27.0682	14.6121
26.7333	81.0769
26.3257	14.4591
26.015	11.8399
25.3008	8.17451
25.0627	5.98833
22.4801	3.60955
22.3308	10.4951
19.6192	90.3272
19.4618	154.354
19.3085	102.085
18.9937	34.7667
18.8525	38.7651
13.7721	11.2148
11.0484	54.8771
10.4552	10.8437
10.1283	11.0735
9.99921	9.36226

2B₄
2B₅+, EOC
1B₁
1B₁
1B₁
1B₁
1B₁
1B₄+, EOC, 1B₃
1B₂
1B₂
1B₂
1B₂

Example 79

A mixture of 10 mg (0.017 mmol) of [(2,6-i-PrPh)DABH₂]NiBr₂ and 40 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 5°C in a 100-mL three-necked flask with an addition funnel, a thermometer, and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.5 mL of 3M poly(methylalumoxane) in toluene was added via syringe; the resulting burgundy catalyst solution was stirred at 5°C for 40 min. Into the addition funnel was condensed (via a Dry Ice condenser on the top of the funnel) 20 mL (about 15 g) of 1-butene. The catalyst solution was stirred as the 1-butene was added as a liquid all at once. The reaction temperature rose to 50°C over 30 min and then dropped to room temperature as the mixture was stirred for 4 hr. The product solution was treated with 1 mL of methanol and was filtered through diatomaceous earth; rotary evaporation yielded 6.17 g (1640 catalyst turnovers) of clear, tacky poly-1-butene rubber. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=64,700$; $M_w=115,000$; $M_w/M_n=1.77$. ¹³C NMR analysis; branching per 1000 CH₂: total Methyls (399), Methyl (86), Ethyl (272), ≥Butyl and end of chain (41); chemical shifts were referenced to the solvent chloroform-d₁ (77 ppm). This example demonstrates the polymerization of an alpha-olefin and shows the differences in branching between a polymer derived from a 1-olefin (this example) and a polymer derived from a 2-olefin (Example 78). This difference shows that the internal olefin of Example 78 is not first isomerized to an alpha-olefin before polymerizing; thus this catalyst is truly able to polymerize internal olefins.

Listed below are the ¹³C NMR data upon which the above analysis is based.

¹³C NMR DataCDCl₃, RT, 0.05M CrAcAc

Freq ppm	Intensity	
43.8708	6.42901	
41.5304	11.1597	
41.0825	16.1036	
38.7623	103.647	
38.1247	50.3288	
37.3338	24.6017	
36.8173	30.0925	
35.756	55.378	
35.0337	22.3563	
34.1419	64.8431	
33.8514	55.3508	
33.4116	90.2438	
33.0645	154.939	
32.7094	51.3245	
32.431	23.0013	3B ₅
30.946	12.8866	3B ₆ +
30.1551	26.1216	
29.7516	54.6262	
29.4248	40.7879	
27.6008	8.64277	
27.2417	20.1564	
27.1207	21.9735	
26.7777	45.0824	
26.0755	66.0697	
25.6599	77.1097	
24.3807	8.9175	
23.4809	32.0249	2B ₄ , 2B ₅ +, 2EOC
22.8393	8.06774	
22.1372	16.4732	
19.4981	57.7003	1B ₁
19.3609	70.588	1B ₁
15.132	17.2402	1B ₄ +
13.8448	7.9343	1B ₄ +
12.2509	27.8653	
12.037	27.0118	
11.0766	6.61931	1B ₂
10.2938	98.0101	1B ₂
10.1364	104.811	1B ₂

Example 80

- 5 A 22-mg (0.037-mmol) sample of [(2,6-i-PrPh)DABH₂]NiBr₂ was introduced into a 600-mL stirred Parr® autoclave under nitrogen. The autoclave was sealed and 75 mL of dry, deaerated toluene was introduced into the autoclave via gas tight syringe
- 10 through a port on the autoclave head. Then 0.6 mL of 3M poly(methylalumoxane) was added via syringe and stirring was begun. The autoclave was pressurized with

180

propylene to 414 kPa and stirred with continuous propylene feed. There was no external cooling. The internal temperature quickly rose to 33°C upon initial propylene addition but gradually dropped back to 24°C
5 over the course of the polymerization. After about 7 min, the propylene feed was shut off and stirring was continued; over a total polymerization time of 1.1 hr, the pressure dropped from 448 kPa to 358 kPa. The propylene was vented and the product, a thin, honey-
10 colored solution, was rotary evaporated to yield 1.65g of a very thick, brown semi-solid. This was dissolved in chloroform and filtered through diatomaceous earth; concentration yielded 1.3 g (835 catalyst turnovers) of tacky, yellow polypropylene rubber. Gel permeation
15 chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polypropylene using universal calibration theory): $M_n=7,940$; $M_w=93,500$; $M_w/M_n=11.78$.

Example 81

20 A mixture of 34 mg (0.057 mmol) of [(2,6-i-PrPh)DABH₂]NiBr₂ and 20 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 5°C in a 100-mL three-necked flask with a thermometer and a nitrogen inlet tube which vented through a mineral oil bubbler.
25 To this mixture, 0.7 mL of 3M poly(methylalumoxane) in toluene was added via syringe and the resulting deep blue-black solution was stirred for 30 min at 5°C. To this catalyst solution was added 35 mL of dry, deaerated cyclopentene, and the mixture was stirred and
30 allowed to warm to room temperature over 23 hr. The blue-black mixture was filtered through alumina to remove dark blue-green solids (oxidized aluminum compounds from PMAO); the filtrate was rotary evaporated to yield 1.2 g (310 catalyst turnovers) of
35 clear liquid cyclopentene oligomers.

Example 82

A 20-mg (0.032 mmol) sample of [(2,6-i-PrPh)DABMe₂]NiBr₂ was placed in Parr® 600-mL stirred

autoclave under nitrogen. The autoclave was sealed and 100 mL of dry, deaerated toluene and 0.6 mL of 3M poly(methylalumoxane) were injected into the autoclave through the head port, and mixture was stirred under
5 nitrogen at 20°C for 50 min. The autoclave body was immersed in a flowing water bath and the autoclave was then pressurized with ethylene to 2.8 MPa with stirring as the internal temperature rose to 53°C. The autoclave was stirred at 2.8 MPa (continuous ethylene
10 feed) for 10 min as the temperature dropped to 29°C, and the ethylene was then vented. The mixture stood at 1 atm for 10 min; vacuum was applied to the autoclave for a few minutes and then the autoclave was opened.

The product was a stiff, swollen polymer mass
15 which was scraped out, cut up, and fed in portions to 500 mL methanol in a blender. The polymer was then boiled with a mixture of methanol (200 mL) and trifluoroacetic acid (10 mL), and finally dried under high vacuum overnight to yield 16.8g (18,700 catalyst
20 turnovers) of polyethylene. The polymer was somewhat heterogeneous with respect to crystallinity, as can be seen from the differential scanning calorimetry data below; amorphous and crystalline pieces of polymer could be picked out of the product. Crystalline
25 polyethylene was found in the interior of the polymer mass; amorphous polyethylene was on the outside. The crystalline polyethylene was formed initially when the ethylene had good access to the catalyst; as the polymer formed limited mass transfer, the catalyst
30 became ethylene-starved and began to make amorphous polymer. Differential scanning calorimetry:
(crystalline piece of polymer): mp: 130°C (150J/g);
(amorphous piece of polymer): -48°C (Tg); mp: 42°C (3J/g), 96°C (11J/g). Gel permeation chromatography
35 (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=163,000$; $M_w=534,000$;
 $M_w/M_n=3.27$. This example demonstrates the effect of

ethylene mass transfer on the polymerization and shows that the same catalyst can make both amorphous and crystalline polyethylene. The bulk of the polymer was crystalline: a film pressed at 200°C was tough and stiff.

Example 83

A 29-mg (0.047 mmol) sample of [(2,6-i-PrPh)DABMe₂]NiBr₂ was placed in Parr® 600-mL stirred autoclave under nitrogen. The autoclave was sealed and 100 mL of dry, deaerated toluene and 0.85 mL of 3M poly(methylalumoxane) were injected into the autoclave through the head port. The mixture was stirred under nitrogen at 23°C for 30 min. The autoclave body was immersed in a flowing water bath and the autoclave was pressurized with ethylene to 620 kPa with stirring. The internal temperature peaked at 38°C within 2 min. The autoclave was stirred at 620 kPa (continuous ethylene feed) for 5 min as the temperature dropped to 32°C. The ethylene was then vented, the regulator was readjusted, and the autoclave was pressurized to 34.5 kPa (gauge) and stirred for 20 min (continuous ethylene feed) as the internal temperature dropped to 22°C. In the middle of this 20 min period, the ethylene feed was temporarily shut off for 1 min, during which time the autoclave pressure dropped from 34.5 kPa (gauge) to 13.8 kPa; the pressure was then restored to 34.5 kPa. After stirring 20 min at 34.5 kPa, the autoclave was once again pressurized to 620 kPa for 5 min; the internal temperature rose from 22°C to 34°C. The ethylene feed was shut off for about 30 sec before venting; the autoclave pressure dropped to about 586 kPa.

The ethylene was vented; the product was a dark, thick liquid. Methanol (200 mL) was added to the autoclave and the mixture was stirred for 2 hr. The polymer, swollen with toluene, had balled up on the stirrer, and the walls and bottom of the autoclave were coated with white, fibrous rubbery polymer. The

polymer was scraped out, cut up, and blended with methanol in a blender and then stirred with fresh boiling methanol for 1 hr. The white rubber was dried under high vacuum for 3 days to yield 9.6 g (7270 catalyst turnovers) of rubbery polyethylene. ¹H NMR analysis (CDCl₃): 95 methyl carbons per 1000 methylene carbons.

Differential scanning calorimetry: -51°C (T_g); mp: 39.5°C (4J/g); mp: 76.4°C (7J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M_n=223,000; M_w=487,000; M_w/M_n=2.19.

The polyethylene of Example 83 could be cast from hot chlorobenzene or pressed at 200°C to give a strong, stretchy, hazy, transparent film with good recovery. It was not easily chloroform-soluble. This example demonstrates the use of the catalyst's ability (see Example 82) to make both amorphous and crystalline polymer, and to make both types of polymer within the same polymer chain due to the catalyst's low propensity to chain transfer. With crystalline blocks (due to higher ethylene pressure) on both ends and an amorphous region (due to lower- pressure, mass transfer-limited polymerization) in the center of each chain, this polymer is a thermoplastic elastomer.

Example 84

A Schlenk flask containing 147 mg (0.100 mmol) of {[(2,6-*i*-PrPh)DABMe₂]PdMe(OEt₂)}BAF⁻ was cooled to -78°C, evacuated, and placed under an ethylene atmosphere. Methylene chloride (100 ml) was added to the flask and the solution was then allowed to warm to room temperature and stirred. The reaction vessel was warm during the first several hours of mixing and the solution became viscous. After being stirred for 17.4 h, the reaction mixture was added to ~600 mL of MeOH in order to precipitate the polymer. Next, the MeOH was decanted off of the sticky polymer, which was then

dissolved in ~600 mL of petroleum ether. After being filtered through plugs of neutral alumina and silica gel, the solution appeared clear and almost colorless. The solvent was then removed and the viscous oil (45.31 g) was dried in vacuo for several days: ^1H NMR (CDCl_3 , 400 MHz) δ 1.24 (CH_2 , CH), 0.82 (m, CH_3); Branching: ~128 CH_3 per 1000 CH_2 ; DSC: $T_g = -67.7^\circ\text{C}$. GPC: $M_n = 29,000$; $M_w = 112,000$.

Example 85

Following the procedure of Example 84 $\{[(2,6\text{-i-PrPh})\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$ (164 mg, 0.112 mmol) catalyzed the polymerization of ethylene for 24 h in 50 mL of CH_2Cl_2 to give 30.16 g of polymer as a viscous oil. ^1H NMR (C_6D_6) δ 1.41 (CH_2 , CH), 0.94 (CH_3); Branching: ~115 CH_3 per 1000 CH_2 ; GPC Analysis (THF, PMMA standards, RI Detector): $M_w = 262,000$; $M_n = 121,000$; PDI = 2.2; DSC: $T_g = -66.8^\circ\text{C}$.

Example 86

The procedure of Example 84 was followed using 144 mg (0.100 mmol) of $\{[(2,6\text{-i-PrPh})\text{DABH}_2]\text{PdMe}(\text{OEt}_2)\}\text{BAF}^-$ in 50 mL of CH_2Cl_2 and a 24 h reaction time. Polymer (9.68 g) was obtained as a free-flowing oil. ^1H NMR (CDCl_3 , 400 MHz) δ 5.36 (m, $\text{RHC}=\text{CHR}'$), 5.08 (br s, $\text{RR}'\text{C}=\text{CHR}''$), 4.67 (br s, $\text{H}_2\text{C}=\text{CRR}'$), 1.98 (m, allylic H), 1.26 (CH_2 , CH), 0.83 (m, CH_3); Branching: ~149 CH_3 per 1000 CH_2 ; DSC: $T_g = -84.6^\circ\text{C}$.

Example 87

A 30-mg (0.042-mmol) sample of $[(2,6\text{-i-PrPh})\text{DABAn}]\text{NiBr}_2$ was placed in Parr® 600-mL stirred autoclave under nitrogen. The autoclave was sealed and 150 mL of dry toluene and 0.6 mL of 3M polymethylalumoxane were injected into the autoclave through the head port. The autoclave body was immersed in a flowing water bath and the mixture was stirred under nitrogen at 20°C for 1 hr. The autoclave was then pressurized with ethylene to 1.31 MPa with stirring for 5 min as the internal temperature peaked at 30°C . The ethylene was then vented to 41.4 kPa

(gauge) and the mixture was stirred and fed ethylene at 41.4 kPa for 1.5 hr as the internal temperature dropped to 19°C. At the end of this time, the autoclave was again pressurized to 1.34 MPa and stirred for 7 min as
5 the internal temperature rose to 35°C.

The ethylene was vented and the autoclave was briefly evacuated; the product was a stiff, solvent-swollen gel. The polymer was cut up, blended with 500 mL methanol in a blender, and then stirred overnight
10 with 500 mL methanol containing 10 mL of 6N HCl. The stirred suspension in methanol/HCl was then boiled for 4 hr, filtered, and dried under high vacuum overnight to yield 26.1 g (22,300 catalyst turnovers) of polyethylene. Differential scanning calorimetry: -49°C
15 (T_g); mp: 116°C (42J/g). The melting transition was very broad and appeared to begin around room temperature. Although the melting point temperature is higher in this Example than in Example 76, the area under the melting endotherm is less in this example,
20 implying that the polymer of this Example is less crystalline overall, but the crystallites that do exist are more ordered. This indicates that the desired block structure was obtained. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene
25 reference, results calculated as polyethylene using universal calibration theory): M_n=123,000; M_w=601,000; M_w/M_n=4.87. The polyethylene of this example could be pressed at 200°C to give a strong, tough, stretchy, hazy film with partial elastic recovery. When the
30 stretched film was plunged into boiling water, it completely relaxed to its original dimensions.

Example 88

A 6.7-mg (0.011-mmol) sample of [(2,6-i-PrPh)DABMe₂]NiBr₂ was magnetically-stirred under
35 nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene as 0.3 mL of 3M poly(methylalumoxane) was injected via syringe. The mixture was stirred at 23°C for 40 min to give a deep blue-green solution of

atalyst. Dry, deaerated cyclopentene (10 mL) was injected and the mixture was stirred for 5 min. The flask was then pressurized with ethylene at 20.7 MPa and stirred for 22 hr. The resulting viscous solution
5 was poured into a stirred mixture of 200 mL methanol and 10 mL 6N HCl. The methanol was decanted off and replaced with fresh methanol, and the polymer was stirred in boiling methanol for 3 hr. The tough, stretchy rubber was pressed between paper towels and
10 dried under vacuum to yield 1.0g of poly[ethylene/cyclopentene]. By ^1H NMR analysis(CDCl_3): 100 methyl carbons per 1000 methylene carbons. Comparison of the peaks attributable to cyclopentene (0.65 ppm and 1.75 ppm) with the standard
15 polyethylene peaks (0.9 ppm and 1.3 ppm) indicates about a 10 mol% cyclopentene incorporation. This polymer yield and composition represent about 2900 catalyst turnovers. Differential scanning calorimetry: -44°C (Tg). Gel permeation chromatography
20 (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=122,000$; $M_w=241,000$; $M_w/M_n=1.97$.

25 Listed below are the ^{13}C NMR data upon which the above analysis is based.

^{13}C NMR data		
TCB, 120C, 0.05M CrAcAc		
Freq ppm	Intensity	
50.9168	5.96663	
46.3865	3.27366	1 cme and/or 1,3 ccmcc
40.7527	40.5963	2 eme
40.567	41.9953	1,3 eme
40.3336	45.8477	1,3 eme
37.1985	60.1003	
36.6998	41.2041	
36.0579	11.2879	
35.607	25.169	
34.4771	19.0834	
34.0845	22.8886	
33.1243	20.1138	
32.8962	27.6778	
31.8406	75.2391	
30.0263	76.2755	

29.6921	170.41	
28.9494	18.8754	
28.647	25.8032	
27.4588	22.2397	
27.1086	48.0806	
24.3236	3.31441	
22.5783	4.64411	2B ₅ +, 2 EOC
19.6712	43.1867	1B ₁
17.5546	1.41279	end group
14.3399	1.74854	1B ₃
13.8518	5.88699	1B ₄ +, 1EOC
10.9182	2.17785	2B ₁

Example 89

A 7.5-mg (0.013-mmol) sample of [(2,6-t-BuPh)₂DABMe₂]NiBr₂ was magnetically stirred under
5 nitrogen in a 50-mL Schlenk flask with 40 mL of dry, deaerated toluene as 0.5 mL of 3M poly(methylalumoxane) was injected via syringe. The mixture was stirred at 23°C for 1 hr to give a deep blue-green solution of catalyst. The flask was pressurized with ethylene at
10 20.7 kPa (gauge) and stirred for 20 hr. The solution, which had become a reddish-brown suspension, was poured into a stirred mixture of 200 mL methanol and 10 mL 6N HCl and was stirred at reflux for 1 hr. The methanol was decanted off and replaced with fresh methanol, and
15 the white polymer was stirred in boiling methanol for 1 hr. The stiff, stretchy rubber was pressed between paper towels and then dried under vacuum to yield 1.25 g (3380 catalyst turnovers) of polyethylene. ¹H-1 NMR analysis (C₆D₆): 63 methyl carbons per 1000 methylene
20 carbons. Differential scanning calorimetry: -34°C (T_g); mp: 44°C (31J/g); mp: 101°C (23J/g).

Example 90

A 5.5 mg (0.0066 mmol) sample of {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆⁻ was allowed to stand at
25 room temperature in air for 24 hr. A 100-mL three-neck flask with a magnetic stirrer and a gas inlet dip tube was charged with 40 mL of reagent methylene chloride and ethylene gas was bubbled through with stirring to saturate the solvent with ethylene. The sample of
30 {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆⁻ was then rinsed

into the flask with 5 mL of methylene chloride and ethylene was bubbled through with stirring for 5 hr. The clear yellow solution was rotary evaporated to yield 0.20 g (1080 catalyst turnovers) of a thick yellow liquid polyethylene.

Example 91

A 600-mL stirred Parr® autoclave was sealed and flushed with nitrogen, and 100 mL of dry, deaerated toluene was introduced into the autoclave via gas tight syringe through a port on the autoclave head. The autoclave was purged with propylene gas to saturate the solvent with propylene. Then 45 mg (0.054 mmol) of $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ was introduced into the autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 45 mg of $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ under nitrogen in a glove box; then 1-2 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head port. This method avoids having the catalyst in solution with no stabilizing ligands.

The autoclave was pressurized with propylene to 41.4 MPa and stirred for 2.5 hr, starting with continuous propylene feed. The autoclave was cooled in a running tap water bath at 22°C. The internal temperature quickly rose to 30°C upon initial propylene addition but soon dropped back to 22°C. After 0.5 hr, the propylene feed was shut off and stirring was continued. Over 2 hr, the pressure dropped from 41.4 MPa to 38.6 MPa. The propylene was then vented. The product was a thin, honey-colored solution. Rotary evaporation yielded 2.3 g (1010 catalyst turnovers) of very thick, dark-brown liquid polypropylene which was almost elastomeric when cool. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polypropylene using universal calibration theory): $M_n=8,300$; $M_w=15,300$; $M_w/M_n=1.84$. ^{13}C NMR analysis; branching per 1000 CH_2 :

total Methyls (545), Propyl (1.3), $\geq$ Butyl and end of chain (9.2); chemical shifts. The polymer exhibited a glass transition temperature of -44°C by differential scanning calorimetry.

5 Listed below are the ^{13}C NMR data upon which the above analysis is based.

^{13}C NMR data		
CDCl_3 , RT, 0.05M CrAcAc		
Freq ppm	Intensity	
46.4978	13.2699	Methylenes
45.8683	11.9947	Methylenes
45.3639	10.959	Methylenes
45.1783	11.3339	Methylenes
44.5568	8.41708	Methylenes
44.4398	7.69019	Methylenes
44.3026	6.29108	Methylenes
44.1372	6.73541	Methylenes
43.5036	5.49837	Methylenes
42.4262	5.03113	Methylenes
41.6918	3.72552	Methylenes
39.1537	4.23147	Methines and Methylenes
38.7179	25.2596	Methines and Methylenes
37.8664	10.0979	Methines and Methylenes
37.6727	14.3755	Methines and Methylenes
37.0755	17.623	Methines and Methylenes
36.781	42.0719	Methines and Methylenes
36.559	10.0773	Methines and Methylenes
34.5495	5.34388	Methines and Methylenes
34.3195	7.48969	Methines and Methylenes
33.5488	12.6148	Methines and Methylenes
33.351	20.5271	Methines and Methylenes
32.7982	4.10612	Methines and Methylenes
32.4108	22.781	Methines and Methylenes
31.8701	5.90488	Methines and Methylenes
31.5957	10.6988	Methines and Methylenes
29.8364	44.4935	Methines and Methylenes
29.7072	103.844	Methines and Methylenes
29.3925	152.645	Methines and Methylenes
29.0293	6.71341	Methines and Methylenes
27.6089	38.7993	Methines and Methylenes
27.4193	10.3543	Methines and Methylenes
27.0763	66.8261	Methines and Methylenes
26.9552	92.859	Methines and Methylenes
26.7615	55.7233	Methines and Methylenes
26.3661	20.1674	Methines and Methylenes
24.8529	16.9056	Methine Carbon of XXVIII
23.1217	12.5439	Methine carbons of XXVIII and XXIX, 2B_4+ , EOC
22.6779	13.0147	Methine carbons of XXVIII and XXIX, 2B_4+ , EOC
22.5245	9.16236	Methine carbons of XXVIII and XXIX, 2B_4+ , EOC

22.3389	77.3342	Methine carbons of XXVIII and XXIX, 2B ₄ ⁺ , EOC
21.9757	9.85242	Methine carbons of XXVIII and XXIX, 2B ₄ ⁺ , EOC
21.1405	10.0445	Methyls
20.4182	8.49663	Methyls
19.9743	25.8085	Methyls
19.825	31.4787	Methyls
19.3811	44.9986	Methyls
19.1995	31.3058	Methyls
13.8569	6.37761	Methyls
13.8004	7.67242	Methyls
137.452	22.0529	Methyls
128.675	44.6993	Methyls
127.88	43.8939	Methyls
124.959	22.4025	Methyls
122.989	3.3312	Methyls

Example 92

A 600-mL stirred Parr[®] autoclave was sealed, flushed with nitrogen, and heated to 60°C in a water bath. Fifty mL (48 g; 0.56 mol) of dry, deaerated methyl acrylate was introduced into the autoclave via gas tight syringe through a port on the autoclave head and ethylene gas was passed through the autoclave at a low rate to saturate the solvent with ethylene before catalyst addition. Then 60 mg (0.07 mmol) of {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆⁻ was introduced into the autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 60 mg of {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆⁻ under nitrogen in a glove box; then 1 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head port. This method avoids having the catalyst in solution with no stabilizing ligands.

The autoclave was pressurized with ethylene to 689 kPa and continuously fed ethylene with stirring for 4.5 hr; the internal temperature was very steady at 60°C. The ethylene was vented and the product, a clear yellow solution, was rinsed out of the autoclave with chloroform, rotary evaporated, and held under high vacuum overnight to yield 1.56 g of thin light-brown liquid ethylene/methyl acrylate copolymer. The

infrared spectrum of the product exhibited a strong ester carbonyl stretch at 1740 cm^{-1} . ^1H -1 NMR analysis (CDCl_3): 61 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH_2COOMe ; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 16.6 mol% (37.9 wt%). This product yield and composition represent 480 ethylene turnovers and 96 methyl acrylate turnovers. ^{13}C NMR analysis; branching per 1000 CH_2 : total methyls (48.3), Methyl (20.8), Ethyl (10.5), Propyl (1), Butyl (8), $\geq$ Amyl and End of Chain (18.1), methyl acrylate (94.4); ester-bearing $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$ branches as a % of total ester: $n \geq 5$ (35.9), $n=4$ (14.3), $n=1,2,3$ (29.5), $n=0$ (20.3); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C , polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=3,370$; $M_w=5,450$; $M_w/M_n=1.62$.

Listed below are the ^{13}C NMR data upon which the above analysis is based.

¹³C NMR data

Freq ppm	Intensity	TCB 120C, 0.05M CrAcAc
53.7443	2.19635	CH ₂ Cl ₂ solvent impurity
50.9115	8.84408	
50.641	132.93	
45.5165	7.55996	MEB ₀ 43.8 ppm:2 adjacent MEB ₀
39.6917	2.71676	
39.2886	7.91933	
38.1639	13.843	
37.7926	26.6353	
37.1666	20.6759	
36.6733	8.65855	
34.6256	17.6899	
34.4612	16.7388	
34.1429	85.624	
33.9095	124.997	1EB ₄ +
33.676	40.0271	Contributions from EB
33.2888	11.4719	Contributions from EB
32.8644	14.4963	Contributions from EB
32.3498	17.5883	Contributions from EB
32.0475	9.83096	Contributions from EB
31.8459	30.9676	Contributions from EB
31.7079	12.7737	Contributions from EB
31.5912	13.8792	Contributions from EB
31.0873	19.6266	Contributions from EB
30.6258	10.5512	
30.1324	58.6101	
29.6497	169.398	
29.4322	48.5318	
29.1934	95.4948	
27.8619	8.70181	
27.4269	32.9529	
26.9283	78.0563	
26.5145	27.0608	
26.3554	14.0683	
25.4588	21.9081	2EB ₄ (tent)
25.3315	9.04646	2EB ₄ (tent)
24.9761	64.2333	2EB ₅ +
24.2069	10.771	BBB (beta-beta-B)
23.0451	9.50073	2B ₄
22.9337	6.90528	2B ₄
22.5518	30.0427	2B ₅ +, EOC
19.9842	1.87415	2B ₃
19.6288	17.125	1B ₁
19.1673	6.0427	1B ₁
16.7695	2.23642	
14.3	-	1B ₃
13.7882	34.0749	1B ₄ +, EOC
11.0774	4.50599	1B ₂
10.8705	10.8817	1B ₂
189.989	1.04646	EB ₀ Carbonyl
175.687	3.33867	EB ₀ Carbonyl
175.406	14.4124	EB ₀ Carbonyl
175.22	5.43832	EB ₀ Carbonyl
175.061	3.53125	EB ₀ Carbonyl

172.859	11.2356	EB ₁ + Carbonyl
172.605	102.342	EB ₁ + Carbonyl
172.09	7.83303	EB ₁ + Carbonyl
170.944	3.294	EB ₁ + Carbonyl

Example 93

A 45-mg (0.048-mmol) sample of $\{[(2,6-i-PrPh)_2DABAn]PdMe(Et_2O)\}SbF_6^-$ was placed in a 600-mL Parr
5 ® stirred autoclave under nitrogen. To this was added 50 mL of dry, deaerated methylene chloride, and the autoclave was pressurized to 414 kPa with ethylene. Ethylene was continuously fed at 414 kPa with stirring at 23-25°C for 3 hr; then the feed was shut off and the
10 reaction was stirred for 12 hr more. At the end of this time, the autoclave was under 89.6 kPa (absolute). The autoclave was repressurized to 345 kPa with ethylene and stirred for 2 hr more as the pressure dropped to 255 kPa, showing that the catalyst was still
15 active; the ethylene was then vented. The brown solution in the autoclave was rotary evaporated, taken up in chloroform, filtered through alumina to remove catalyst, and rotary evaporated and then held under high vacuum to yield 7.35 g of thick, yellow liquid
20 polyethylene. ¹H NMR analysis (CDCl₃): 131 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M_n=10,300; M_w=18,100;
25 M_w/M_n=1.76.

Example 94

A 79-mg (0.085-mmol) sample of $\{[(2,6-i-PrPh)_2DABAn]PdMe(Et_2O)\}SbF_6^-$ was placed in a 600-mL Parr
30 ® stirred autoclave under nitrogen. To this was added 50 mL of dry, deaerated methyl acrylate, and the autoclave was pressurized to 689 kPa with ethylene. The autoclave was warmed to 50°C and the reaction was stirred at 689 kPa for 70 hr; the ethylene was then vented. The clear yellow solution in the autoclave was
35 filtered through alumina to remove catalyst, rotary

5

Example 95

14

Example 96

30

yellow granular rubber; this was scraped out of the autoclave and held under high vacuum to yield 29.0 g (15,700 catalyst turnovers) of spongy, non-tacky, rubbery polyethylene which had good elastic recovery and was very strong; it was soluble in chloroform or chlorobenzene.

The polyethylene was amorphous at room temperature: it exhibited a glass transition temperature of -57°C and a melting endotherm of -16°C (35J/g) by differential scanning calorimetry. On cooling, there was a crystallization exotherm with a maximum at 1°C (35J/g). Upon remelting and recooling the melting endotherm and crystallization exotherm persisted, as did the glass transition. Dynamic mechanical analysis at 1Hz showed a $\tan \delta$ peak at -51°C and a peak in the loss modulus E'' at -65°C ; dielectric analysis at 1000 Hz showed a $\tan \delta$ peak at -35°C . ^1H NMR analysis (CDCl_3): 86 methyl carbons per 1000 methylene carbons. ^{13}C NMR analysis: branching per 1000 CH_2 : total Methyls (89.3), Methyl (37.2), Ethyl (14), Propyl (6.4), Butyl (6.9), $\geq\text{Am}$ and End Of Chain (23.8); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (trichlorobenzene, 135°C , polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=137,000$; $M_w=289,000$; $M_w/M_n=2.10$. Intrinsic viscosity (trichlorobenzene, 135°C): 2.565 dL/g. Absolute molecular weight averages corrected for branching: $M_n=196,000$; $M_w=425,000$; $M_w/M_n=2.17$. Density (determined at room temperature with a helium gas displacement pycnometer): $0.8546 \pm 0.0007 \text{ g/cc}$.

Example 97

A 49-mg (0.058 mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{SbF}_6^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 30 mL of dry, deaerated hexane. The autoclave was stirred and pressurized to 5.9 MPa with ethylene.

The internal temperature peaked briefly at 34°C; a cool water bath was placed around the autoclave body. The reaction was stirred for 16 hr at 23°C. At 14 hr, the ethylene feed was shut off; the autoclave pressure
5 dropped to 5.8 MPa over 2 hr; the ethylene was then vented. The autoclave contained a light yellow, gooey rubber swollen with hexane, which was scraped out of the autoclave and held under high vacuum to yield 28.2 g (17,200 catalyst turnovers) of spongy, non-tacky,
10 rubbery polyethylene which had good elastic recovery and which was very strong.

The polyethylene was amorphous at room temperature: it exhibited a glass transition temperature of -61°C and a melting endotherm of -12°C
15 (27J/g) by differential scanning calorimetry. Dynamic mechanical analysis at 1Hz showed a tan δ peak at -52°C and a peak in the loss modulus E'' at -70°C; dielectric analysis at 1000 Hz showed a tan δ peak at -37°C. ^1H NMR analysis (CDCl_3): 93 methyl carbons per 1000
20 methylene carbons. ^{13}C NMR analysis: branching per 1000 CH_2 : total Methyls (95.4), Methyl (33.3), Ethyl (17.2), Propyl (5.2), Butyl (10.8), Amyl (3.7), $\geq\text{Hex}$ and End Of Chain (27.4); chemical shifts were referenced to the solvent: the high field carbon of
25 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=149,000$; $M_w=347,000$; $M_w/M_n=2.33$. Density (determined at room temperature
30 with a helium gas displacement pycnometer): 0.8544 ± 0.0007 g/cc.

Example 98

Approximately 10-mesh silica granules were dried at 200°C and were impregnated with a methylene chloride
35 solution of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{SbF}_6^-$ to give a 10 wt% loading of the catalyst on silica.

A 0.53-g (0.063 mmol) sample of silica gel containing 10 wt% $\{[(2,6\text{-i-}$

$\text{PrPh})_2\text{DABMe}_2\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{SbF}_6^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 40 mL of dry, deaerated hexane. The autoclave was stirred and pressurized to 5.5 MPa with ethylene; the ethylene feed was then turned off. The internal temperature peaked briefly at 31°C. The reaction was stirred for 14 hr at 23°C as the pressure dropped to 5.3 MPa; the ethylene was then vented. The autoclave contained a clear, yellow, gooey rubber swollen with hexane. The product was dissolved in 200 mL chloroform, filtered through glass wool, rotary evaporated, and held under high vacuum to yield 7.95 g (4500 catalyst turnovers) of gummy, rubbery polyethylene. ^1H NMR analysis (CDCl_3): 96 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=6,900$; $M_w=118,000$; $M_w/M_n=17.08$.

20

Example 99

A 108-mg (0.073 mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{BAF}^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added via syringe 75 mL of deaerated reagent grade methyl acrylate containing 100 ppm hydroquinone monomethyl ether and 100 ppm of phenothiazine. The autoclave was pressurized to 5.5 MPa with ethylene and was stirred at 35°C as ethylene was continuously fed for 90 hr; the ethylene was then vented. The product consisted of a swollen clear foam wrapped around the impeller; 40 mL of unreacted methyl acrylate was poured off the polymer. The polymer was stripped off the impeller and was held under high vacuum to yield 38.2 g of clear, grayish, somewhat-tacky rubber. ^1H NMR analysis (CDCl_3): 99 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH_2COOMe ; 2.30ppm) peaks with the integrals of the carbon chain

methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 0.9 mol% (2.6 wt%). This product yield and composition represent 18,400 ethylene turnovers and 158 methyl acrylate
5 turnovers. ^{13}C NMR analysis: branching per 1000 CH_2 : total Methyls (105.7), Methyl (36.3), Ethyl (22), Propyl (4.9), Butyl (10.6), Amyl (4), $\geq\text{Hex}$ and End Of Chain (27.8), methyl acrylate (3.4); ester-bearing $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$ branches as a % of total ester: $n \geq 5$
10 (40.6), $n=1,2,3$ (2.7), $n=0$ (56.7); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as
15 polymethylmethacrylate using universal calibration theory): $M_n=151,000$; $M_w=272,000$; $M_w/M_n=1.81$.

Example 100

A 62-mg (0.074-mmol) sample of $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ was placed in a
20 600-mL Parr® stirred autoclave under nitrogen with 200 mL of deaerated aqueous 10% (v/v) n-butanol. The autoclave was pressurized to 2.8 MPa with ethylene and was stirred for 16 hr. The ethylene was vented and the polymer suspension was filtered. The product consisted
25 of a fine gray powdery polymer along with some larger particles of sticky black polymer; the polymer was washed with acetone and dried to yield 0.60 g (290 catalyst turnovers) of polyethylene. The gray polyethylene powder was insoluble in chloroform at RT;
30 it was soluble in hot tetrachloroethane, but formed a gel on cooling to RT. ^1H NMR analysis (tetrachloroethane- d_2 ; 100°C): 43 methyl carbons per 1000 methylene carbons. Differential scanning calorimetry exhibited a melting point at 89°C (78J/g)
35 with a shoulder at 70°C; there was no apparent glass transition.

Example 101

A 78-mg (0.053-mmol) sample of $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{BAF}^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 40 mL of dry, deaerated t-butyl acrylate
5 containing 100 ppm hydroquinone monomethyl ether. The autoclave was pressurized with ethylene to 2.8 MPa and was stirred and heated at 35°C as ethylene was continuously fed at 2.8 MPa for 24 hr; the ethylene was then vented. The product consisted of a yellow, gooey
10 polymer which was dried under high vacuum to yield 6.1 g of clear, yellow, rubbery ethylene/t-butyl acrylate copolymer which was quite tacky. ^1H NMR analysis (CDCl_3): 102 methyl carbons per 1000 methylene carbons. Comparison of the integral of the ester t-butoxy (1.44
15 ppm) peak with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a t-butyl acrylate content of 0.7 mol% (3.3 wt%). This yield and composition represent 3960 ethylene turnovers and 30 t-butyl acrylate turnovers.
20 Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=112,000$; $M_w=179,000$; $M_w/M_n=1.60$.

Example 102

25 A 19-mg (0.022-mmol) sample of $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}\text{SbF}_6^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. The autoclave was pressurized to 5.2 MPa with ethylene and was stirred for 2 hr; the ethylene feed was then shut
30 off. The autoclave was stirred for 16 hr more as the ethylene pressure dropped to 5.0 MPa; the ethylene was then vented. The autoclave contained a light yellow, granular sponge rubber growing all over the walls and head of the autoclave; this was scraped out to yield
35 13.4 g (21,800 catalyst turnovers) of spongy, non-tacky, rubbery polyethylene which was very strong and elastic. ^1H NMR analysis (CDCl_3): 90 methyl carbons per 1000 methylene carbons.

Differential scanning calorimetry exhibited a glass transition at -50°C . Gel permeation chromatography (trichlorobenzene, 135°C , polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=175,000$; $M_w=476,000$; $M_w/M_n=2.72$.

Example 103

A 70-mg (0.047-mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{BAF}^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 70 mL of deaerated reagent grade methyl acrylate containing 100 ppm each hydroquinone monomethyl ether and phenothiazine and 0.7 mL (1 wt%; 4.7 mol%) deaerated, deionized water. The autoclave was stirred at 35°C as ethylene was continuously fed at 4.8 MPa for 16 hr; the ethylene was then vented. The product consisted of a clear solution. Rotary evaporation yielded 1.46 g of ethylene/methyl acrylate copolymer as a clear oil. The infrared spectrum of the product exhibited a strong ester carbonyl stretch at 1740cm^{-1} . ^1H NMR analysis (CDCl_3): 118 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH_2COOMe ; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 0.7 mol% (2.2 wt%). This product yield and composition represent 1090 ethylene turnovers and 8 methyl acrylate turnovers. Gel permeation chromatography (trichlorobenzene, 135°C , polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=362$; $M_w=908$; $M_w/M_n=2.51$.

Example 104

A 53-mg (0.036-mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{BAF}^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 100 mL of dry, deaerated methylene chloride. The autoclave was immersed in a cool water bath and stirred

as it was pressurized to 4.8 MPa with ethylene. Ethylene was continuously fed with stirring at 4.8 MPa and 23°C for 23 hr; the ethylene then was vented. The product consisted of a clear rubber, slightly swollen with methylene chloride. The polymer was dried under high vacuum at room temperature to yield 34.5 g (34,100 catalyst turnovers) of clear rubbery polyethylene. ¹H NMR analysis (CDCl₃): 110 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=243,000$; $M_w=676,000$; $M_w/M_n=2.78$.

Example 104A

A 83-mg (0.056-mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{BAF}^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 70 mL of dry, deaerated, ethanol-free chloroform. The autoclave was immersed in a cool water bath and stirred as it was pressurized to 4.7 MPa with ethylene. Ethylene was continuously fed with stirring at 4.7 MPa and 23°C for 21 hr; the ethylene then was vented. The product consisted of a pink, rubbery, foamed polyethylene, slightly swollen with chloroform. The polymer was dried under vacuum at 40°C to yield 70.2 g (44,400 catalyst turnovers) of pink, rubbery polyethylene which was slightly tacky. ¹H NMR analysis (CDCl₃): 111 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=213,000$; $M_w=728,000$; $M_w/M_n=3.41$.

Example 105

A 44-mg (0.052-mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{SbF}_6^-$ was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 20 mL of dry, deaerated methylene chloride. To this was added 5 mL (5.25 g; 73 mmol) of freshly distilled

- acrylic acid (contains a few ppm of phenothiazine as a radical polymerization inhibitor) via syringe and the mixture was immediately pressurized with ethylene at 5.52 kPa and stirred for 40 hr. The dark yellow solution was rotary evaporated and the residue was stirred with 50 mL water for 15 min to extract any acrylic acid homopolymer. The water was drawn off with a pipette and rotary evaporated to yield 50 mg of dark residue. The polymer which had been water-extracted was heated under high vacuum to yield 1.30 g of ethylene/acrylic acid copolymer as a dark brown oil. The infrared spectrum showed strong COOH absorbances at 3400-2500 and at 1705cm⁻¹, as well as strong methylene absorbances at 3000-2900 and 1470cm⁻¹.
- A 0.2-g sample of the ethylene/acrylic acid copolymer was treated with diazomethane in ether to esterify the COOH groups and produce an ethylene/methyl acrylate copolymer. The infrared spectrum of the esterified copolymer showed a strong ester carbonyl absorbance at 1750cm⁻¹; the COOH absorbances were gone. ¹H NMR analysis (CDCl₃): 87 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH₂COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 5.3 mol% (14.7 wt% methyl acrylate => 12.3 wt% acrylic acid in the original copolymer). This product yield and composition represent 780 ethylene turnovers and 43 acrylic acid turnovers. Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): M_n=25,000; M_w=42,800; M_w/M_n=1.71.
- Listed below are the ¹³C NMR data upon which the above analysis is based.

¹³C NMR Data
CDCl₃, 0.05M CrAcAc, 30C

Freq ppm	Intensity
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51.0145	24.9141	
45.434	1.11477	MEB ₀
38.8925	2.29147	
38.5156	6.51271	
37.3899	10.7484	
37.0713	17.3903	
36.7634	17.6341	
36.4182	3.57537	
36.2961	6.0822	
34.459	2.158	
34.0289	9.49713	
33.7369	34.4456	
33.3705	49.2646	
32.8926	18.2918	
32.3935	10.5014	
32.0271	3.5697	3B ₅
31.5705	30.6837	3B ₆ +, 3EOC
31.1723	1.54526	
29.813	46.4503	
29.3511	117.987	
29.1387	21.034	
28.9953	30.603	
28.613	7.18386	
27.2007	8.02265	
26.744	23.8731	
26.3777	46.8498	
26.006	5.42389	
25.5547	8.13592	
25.0609	5.46013	2 EB ₄ (tentative)
24.9175	2.30355	2 EB ₄ (tentative)
24.6042	15.7434	2 EB ₅ +
23.7547	2.78914	
23.3777	5.63727	
22.7936	8.07071	2B ₄
22.6768	3.78032	2B ₄
22.3211	33.1603	2B ₅ +, 2EOC
19.3477	15.4369	1B ₁
18.8645	5.97477	1B ₁
14.1814	1.99297	1B ₃
13.7407	38.5361	1B ₄ +, 1EOC
11.0274	6.19758	1B ₂
10.5124	10.4707	1B ₂
176.567	9.61122	EB ₀ carbonyl
174.05	9.03673	EB ₁ + carbonyl
173.779	85.021	EB ₁ + carbonyl

Example 106

A 25-mg (0.029-mmol) sample of $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(O)CH_3\}SbF_6^-$ was magnetically stirred under 55.2 kPa of ethylene in a 50-mL Schlenk flask with 20 mL of dry methylene chloride and 5 mL (4.5 g; 39 mmol) of methyl 4-pentenoate for 40 hr at room temperature. The yellow solution was rotary

evaporated to yield 3.41 g of ethylene/methyl 4-pentenoate copolymer as a yellow oil. The infrared spectrum of the copolymer showed a strong ester carbonyl absorbance at 1750cm^{-1} . ^1H NMR analysis (CDCl₃): 84 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH₂COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl 4-pentenoate content of 6 mol% (20 wt%). This yield and composition represent about 3400 ethylene turnovers and 200 methyl 4-pentenoate turnovers. ^{13}C NMR quantitative analysis: branching per 1000 CH₂: total Methyls (93.3), Methyl (37.7), Ethyl (18.7), Propyl (2), Butyl (8.6), $\geq\text{Am}$ and end of chains (26.6), $\geq\text{Bu}$ and end of chains (34.8); ester-bearing branches -CH(CH₂)_nCO₂CH₃ as a % of total ester: $n\geq 5$ (38.9), $n=4$ (8.3), $n=1,2,3$ (46.8), $n=0$ (6); chemical shifts were referenced to the solvent: chloroform-d₁ (77 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=32,400$; $M_w=52,500$; $M_w/M_n=1.62$.

Example 107

A 21-mg (0.025-mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{C(O)CH}_3\}\text{SbF}_6^-$ was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 5 mL of dry methylene chloride and 5 mL (4.5 g; 39 mmol) of methyl 4-pentenoate for 74 hr. The yellow solution was rotary evaporated to yield 0.09 g of a yellow oil, poly[methyl 4-pentenoate]. The infrared spectrum showed a strong ester carbonyl absorbance at 1750cm^{-1} . The ^1H NMR (CDCl₃) spectrum showed olefinic protons at 5.4-5.5ppm; comparing the olefin integral with the integral of the ester methoxy at 3.67ppm indicates an average degree of polymerization of 4 to 5. This example demonstrates the ability of this catalyst to

homopolymerize alpha olefins bearing polar functional groups not conjugated to the carbon-carbon double bond.

Example 108

A 53-mg (0.063-mmol) sample of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}] \text{PdCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\} \text{SbF}_6^-$ was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 25 mL of dry, deaerated toluene and 25 mL (26 g; 0.36 mol) of freshly distilled acrylic acid containing about 100 ppm phenothiazine. The autoclave was pressurized to 2.1 MPa with ethylene and was stirred for 68 hr at 23°C; the ethylene was then vented. The autoclave contained a colorless, hazy solution. The solution was rotary evaporated and the concentrate was taken up in 50 mL of chloroform, filtered through diatomaceous earth, rotary evaporated, and then held under high vacuum to yield 2.23 g of light brown, very viscous liquid ethylene/acrylic acid copolymer. The infrared spectrum showed strong COOH absorbances at 3400-2500 and at 1705cm^{-1} , as well as strong methylene absorbances at 3000-2900 and 1470cm^{-1} .

A 0.3-g sample of the ethylene/acrylic acid copolymer was treated with diazomethane in ether to esterify the COOH groups and produce an ethylene/methyl acrylate copolymer. The infrared spectrum showed a strong ester carbonyl absorbance at 1750cm^{-1} ; the COOH absorbances were gone. ^1H NMR analysis (CDCl_3): 96 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH_2COOMe ; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 1.8 mol% (5.4 wt% methyl acrylate => 4.5 wt% acrylic acid in the original copolymer). This product yield and composition represent 1200 ethylene turnovers and 22 acrylic acid turnovers. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using

universal calibration theory): $M_n=5,330$; $M_w=15,000$;
 $M_w/M_n=2.82$.

Example 109

5 A 600-mL stirred Parr® autoclave was sealed and
flushed with nitrogen. Fifty mL (48 g; 0.56 mol) of
dry, deaerated methyl acrylate was introduced into the
autoclave via gas tight syringe through a port on the
autoclave head. Then 60 mg (0.07 mmol) of $\{[(2,6-i-$
10 $\text{PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{BAF}^-$ was introduced into the
autoclave in the following manner: a 2.5-mL gas tight
syringe with a syringe valve was loaded with 60 mg of
 $\{[(2,6-i-\text{PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{BAF}^-$ under nitrogen in
a glove box; then 1 mL of dry, deaerated methylene
15 chloride was drawn up into the syringe and the contents
were quickly injected into the autoclave through a head
port. This method avoids having the catalyst in
solution with no stabilizing ligands.

The autoclave body was immersed in a running tap
water bath; the internal temperature was very steady at
20 22°C. The autoclave was pressurized with ethylene to
2.8 MPa and continuously fed ethylene with stirring for
4.5 hr. The ethylene was then vented and the product,
a mixture of methyl acrylate and yellow gooey polymer,
was rinsed out of the autoclave with chloroform, rotary
25 evaporated, and held under high vacuum overnight to
yield 4.2 g of thick, light-brown liquid
ethylene/methyl acrylate copolymer. The infrared
spectrum of the product exhibited a strong ester
carbonyl stretch at 1740cm^{-1} . ^1H NMR analysis (CDCl_3):
30 82 methyl carbons per 1000 methylene carbons.
Comparison of the integrals of the ester methoxy
(3.67ppm) and ester methylene (CH_2COOMe ; 2.30ppm) peaks
with the integrals of the carbon chain methyls (0.8-
0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl
35 acrylate content of 1.5 mol% (4.4 wt%). This product
yield and composition represent 2000 ethylene turnovers
and 31 methyl acrylate turnovers. ^{13}C NMR analysis:
branching per 1000 CH_2 : total Methyls (84.6), Methyl

(28.7), Ethyl (15.5), Propyl (3.3), Butyl (8.2), 2Hex -
and End Of Chain (23.9), methyl acrylate (13.9). Ester-
bearing $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$ branches as a % of total ester:
n $\geq$ 5 (34.4), n=4 (6.2), n=1,2,3 (13), n=0 (46.4). Mole%:
5 ethylene (97.6), methyl acrylate (2.4); chemical shifts
were referenced to the solvent: the high field carbon
of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation
chromatography (tetrahydrofuran, 30°C,
polymethylmethacrylate reference, results calculated as
10 polymethylmethacrylate using universal calibration
theory): $M_n=22,000$; $M_w=45,500$; $M_w/M_n=2.07$.

A mixture of 1.45 g of this ethylene/methyl
acrylate copolymer, 20 mL dioxane, 2 mL water, and 1
mL of 50% aqueous NaOH was magnetically stirred at
15 reflux under nitrogen for 4.5 hr. The liquid was then
decanted away from the swollen polymer and the polymer
was stirred several hours with three changes of boiling
water. The polymer was filtered, washed with water and
methanol, and dried under vacuum (80°C/nitrogen purge)
20 to yield 1.2 g soft of ionomer rubber, insoluble in hot
chloroform. The FTIR-ATR spectrum of a pressed film
(pressed at 125°C/6.9 MPa) showed a strong ionomer peak
at 1570cm^{-1} and virtually no ester carbonyl at 1750cm^{-1} .
The pressed film was a soft, slightly tacky rubber
25 with about a 50% elongation to break. This example
demonstrates the preparation of an ionomer from this
ethylene/methyl acrylate polymer.

Example 110

The complex $[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMeCl}$ (0.020 g,
30 0.036 mmol) was weighed into a vial and dissolved in 6
ml CH_2Cl_2 . NaBAF (0.032g, 0.036 mmol) was rinsed into
the stirring mixture with 4 ml of CH_2Cl_2 . There was an
immediate color change from orange to yellow. The
solution was stirred under 6.2 MPa ethylene in a Fisher
35 Porter tube with temperature control at 19°C. The
internal temperature rose to 22°C during the first 15
minutes. The temperature controller was raised to
30°C. After 35 minutes, the reaction was consuming

ethylene slowly. After a total reaction time of about 20 h, there was no longer detectable ethylene consumption, but the liquid level in the tube was noticeably higher. Workup by addition to excess MeOH gave a viscous liquid precipitate. The precipitate was redissolved in CH_2Cl_2 , filtered through a 0.5 micron PTFE filter and reprecipitated by addition to excess MeOH to give 7.208 g dark brown viscous oil (7180 equivalents of ethylene per Pd). ^1H NMR (CDCl_3) 0.8-1.0 (m, CH_3); 1.0-1.5 (m, CH and CH_2). Integration allows calculation of branching: 118 methyl carbons per 1000 methylene carbons. GPC in THF vs. PMMA standard: $M_n=12,700$, $M_w=28,800$, $M_w/M_n=2.26$.

Example 111

The solid complex $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ (0.080 g, 0.096 mmol) was placed in a Schlenk flask which was evacuated and refilled with ethylene twice. Under one atm of ethylene, black spots formed in the center of the solid complex and grew outward as ethylene was polymerized in the solid state and the resulting exotherm destroyed the complex. Solid continued to form on the solid catalyst that had not been destroyed by the exotherm, and the next day the flask contained considerable solid and the reaction was still slowly consuming ethylene. The ethylene was disconnected and 1.808 g of light gray elastic solid was removed from the flask (644 equivalents ethylene per Pd). The ^1H NMR in CDCl_3 was similar to example 110 with 101 methyl carbons per 1000 methylene carbons. Differential Scanning Calorimetry (DSC): first heat 25 to 150°C , $15^\circ\text{C}/\text{min}$, no events; second heat -150 to 150°C , $T_g = -53^\circ\text{C}$ with an endothermic peak centered at -20°C ; third heat -150 to 275°C , $T_g = -51^\circ\text{C}$ with an endothermic peak centered at -20°C . GPC (trichlorobenzene, 135°C , polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=13,000$, $M_w=313,000$, $M_w/M_n=24$.

Example 11

The complex $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox followed by 40 ml of dry dioxane. The septum-capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene. The light orange mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. There was rapid uptake of ethylene. A room temperature water bath was used to control the temperature of the reaction. After 20 h, the reaction was worked up by removing the solvent in vacuo to give 10.9 g of a highly viscous fluid (3870 equivalents of ethylene per Pd). Dioxane is a solvent for the Pd complex and a non-solvent for the polymer product. ^1H NMR (CDCl_3) 0.8-1.0 (m, CH_3); 1.0-1.5 (m, CH and CH_2). Integration allows calculation of branching: 100 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): Partially resolved trimodal distribution with $M_n=16300$, $M_w=151000$, $M_w/M_n=9.25$. DSC (second heat, -150°C to 150°C, 15°C/min) $T_g=-63^\circ\text{C}$, endothermic peak centered at 30°C.

Example 113

Polymerization of ethylene was carried out according to example 112, using pentane as solvent. Pentane is a non-solvent for the Pd complex and a solvent for the polymer product. The reaction gave 7.47 g of dark highly viscous fluid (2664 equivalents of ethylene per Pd). ^1H NMR analysis (CDCl_3): 126 methyl carbons per 1000 methylene carbons. ^{13}C NMR analysis, branching per 1000 CH_2 : Total methyls (128.8), Methyl (37.8), Ethyl (27.2), Propyl (3.5), Butyl (14.5), Amyl (2.5), $\geq\text{Hexyl}$ and end of chain (44.7), average number of carbon atoms for $\geq\text{Hexyl}$ branches = 16.6 (calculated from intrinsic viscosity

and GPC molecular weight data). Quantitation of the -
CH₂CH(CH₃)CH₂CH₃ structure per 1000 CH₂'s: 8.3. These
side chains are counted as a Methyl branch and an Ethyl
branch in the quantitative branching analysis. GPC
5 (trichlorobenzene, 135°C, polystyrene reference,
results calculated as linear polyethylene using
universal calibration theory): $M_n=9,800$, $M_w=16,100$,
 $M_w/M_n=1.64$. Intrinsic viscosity (trichlorobenzene,
135°C) = 0.125 g/dL. Absolute molecular weights
10 calculated by GPC (trichlorobenzene, 135°C, polystyrene
reference, corrected for branching using measured
intrinsic viscosity): $M_n=34,900$, $M_w=58,800$, $M_w/M_n=1.68$.
DSC (second heat, -150°C to 150°C, 15°C/min) $T_g = -$
71°C, endothermic peak centered at -43 °C.

15 Example 114

Polymerization of ethylene was carried out
according to example 112, using distilled degassed
water as the medium. Water is a non-solvent for both
the Pd complex and the polymer product. The mixture
20 was worked up by decanting the water from the product
which was then dried in vacuo to give 0.427 g of dark
sticky solid (152 equivalents of ethylene per Pd). ¹H
NMR analysis (CDCl₃): 97 methyl carbons per 1000
methylene carbons. GPC (trichlorobenzene, 135°C,
25 polystyrene reference, results calculated as linear
polyethylene using universal calibration theory):
 $M_n=25,100$, $M_w=208,000$, $M_w/M_n=8.31$.

Example 115

Polymerization of ethylene was carried out
30 according to example 112, using 2-ethylhexanol as the
solvent. The Pd complex is sparingly soluble in this
solvent and the polymer product is insoluble. The
polymer product formed small dark particles of high
viscosity liquid suspended in the 2-ethylhexanol. The
35 solvent was decanted and the polymer was dissolved in
CHCl₃ and reprecipitated by addition of excess MeOH.
The solvent was decanted, and the reprecipitated
polymer was dried in vacuo to give 1.66 g of a dark

highly viscous fluid (591 equivalents of ethylene per Pd). ^1H NMR analysis (CDCl_3): 122 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene, 135°C , polystyrene reference, results calculated as linear polyethylene using universal calibration theory):
5 $M_n=7,890$, $M_w=21,600$, $M_w/M_n=2.74$.

Example 116

The solid complex $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ (0.084 g, 0.100 mmol) was
10 loaded into a Schlenk flask in the drybox. The flask was connected to a Schlenk line under 1 atm of ethylene, and cooled to -78°C . Solvent, (CH_2Cl_2 , 40 ml) was added by syringe and after equilibrating at -78°C under ethylene, the mixture was warmed to room
15 temperature under ethylene. The mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. There was rapid uptake of ethylene. A room temperature water bath was used to control the temperature of the reaction. After 24 h,
20 the reaction was worked up by removing the solvent in vacuo to give 24.5 g of a highly viscous fluid (8730 equivalents of ethylene per Pd). CH_2Cl_2 is a good solvent for both the Pd complex and the polymer product. The polymer was dissolved in CH_2Cl_2 , and
25 reprecipitated by addition to excess MeOH in a tared flask. The solvent was decanted, and the reprecipitated polymer was dried in vacuo to give 21.3 g of a dark highly viscous fluid. ^1H NMR analysis (CDCl_3): 105 methyl carbons per 1000 methylene carbons.
30 C-13 NMR analysis, branching per 1000 CH_2 : Total methyls (118.6), Methyl (36.2), Ethyl (25.9), Propyl (2.9), Butyl (11.9), Amyl (1.7), $\geq\text{Hexyl}$ and end of chains (34.4), average number of carbon atoms for $\geq$ Hexyl branches = 22.5 (calculated from intrinsic
35 viscosity and GPC molecular weight data). Quantitation of the $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ structure per 1000 CH_2 's: 8.1. These side chains also counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis.

- GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=25,800$, $M_w=45,900$, $M_w/M_n=1.78$. Intrinsic viscosity (trichlorobenzene, 135°C) = 0.24 g/dL. Absolute molecular weights calculated by GPC (trichlorobenzene, 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity): $M_n=104,000$, $M_w=188,000$, $M_w/M_n=1.81$.
- 10 Listed below are the ^{13}C NMR data upon which the above analysis is based.

¹³C NMR Data
TCB, 120C, 0.06M CrAcAc

Freq ppm	Intensity	
39.7233	5.12305	
39.318	17.6892	MB ₂
38.2022	17.9361	MB ₃ +
37.8369	32.3419	MB ₃ +
37.2469	43.1136	αB ₁ , 3B ₃
36.8335	10.1653	αB ₁ , 3B ₃
36.7452	14.674	αB ₁ , 3B ₃
34.9592	10.3554	αγ+B, (4B ₄ , 5B ₅ , etc.)
34.6702	24.015	αγ+B, (4B ₄ , 5B ₅ , etc.)
34.5257	39.9342	αγ+B, (4B ₄ , 5B ₅ , etc.)
34.2006	109.158	αγ+B, (4B ₄ , 5B ₅ , etc.)
33.723	36.1658	αγ+B, (4B ₄ , 5B ₅ , etc.)
33.3136	12.0398	MB ₁
32.9323	20.7242	MB ₁
32.4266	6.47794	3B ₅
31.9409	96.9874	3B ₆ +, 3EOC
31.359	15.2429	γ+γ+B, 3B ₄
31.0981	19.2981	γ+γ+B, 3B ₄
30.6606	15.8689	γ+γ+B, 3B ₄
30.2271	96.7986	γ+γ+B, 3B ₄
30.1188	54.949	γ+γ+B, 3B ₄
29.7455	307.576	γ+γ+B, 3B ₄
29.5809	36.2391	γ+γ+B, 3B ₄
29.3361	79.3542	γ+γ+B, 3B ₄
29.2157	23.0783	γ+γ+B, 3B ₄
27.6424	24.2024	βγ+B, 2B ₂ , (4B ₅ , etc.)
27.526	29.8995	βγ+B, 2B ₂ , (4B ₅ , etc.)
27.3534	23.1626	βγ+B, 2B ₂ , (4B ₅ , etc.)
27.1607	70.8066	βγ+B, 2B ₂ , (4B ₅ , etc.)
27.0042	109.892	βγ+B, 2B ₂ , (4B ₅ , etc.)
26.5908	7.13232	βγ+B, 2B ₂ , (4B ₅ , etc.)
26.3941	23.945	βγ+B, 2B ₂ , (4B ₅ , etc.)
25.9446	4.45077	βγ+B, 2B ₂ , (4B ₅ , etc.)
24.4034	9.52585	ββB
24.2428	11.1161	ββB
23.1391	21.2608	2B ₄
23.0227	11.2909	2B ₄
22.6494	103.069	2B ₅ +, 2EOC
20.0526	5.13224	2B ₃
19.7355	37.8832	1B ₁
19.2017	14.8043	1B ₁ , Structure XXVII
14.4175	4.50604	1B ₃
13.9118	116.163	1B ₄ +, 1EOC
11.1986	18.5867	1B ₂ , Structure XXVII
10.9617	32.3855	1B ₂

Example 117

Polymerization of ethylene was carried out according to example 116, at a reaction temperature of 0°C and reaction time of several hours. The polymer product formed a separate fluid phase on the top of the mixture. The reaction was quenched by adding 2 ml acrylonitrile. The product was moderately viscous fluid, 4.5 g (1600 equivalents of ethylene per Pd). ¹H NMR analysis (CDCl₃): 108 methyl carbons per 1000 methylene carbons. ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (115.7), Methyl (35.7), Ethyl (24.7), Propyl (2.6), Butyl (11.2), Amyl (3.2), ≥Hexyl and end of chain (37.1). Quantitation of the -CH₂CH(CH₃)CH₂CH₃ structure per 1000 CH₂'s: 7.0. These side chains are counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory: M_n=15,200, M_w=23,700, M_w/M_n=1.56.

Example 118

The Pd complex {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆⁻ (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox, and 40 ml of FC-75 was added. The septum-capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. The mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. Both the Pd initiator and the polymer are insoluble in FC-75. After 15 days, the reaction flask contained a large amount of gray elastic solid. The FC-75 was decanted, and the solid polymer was then dissolved in CHCl₃ and precipitated by addition of the solution to excess MeOH. The polymer was dried in vacuo, and then dissolved in o-dichlorobenzene at 100°C. The hot solution was filtered through a 10 μm PTFE filter. The filtered polymer solution was shaken

In a separatory funnel with concentrated sulfuric acid, followed by distilled water, followed by 5% NaHCO₃ solution, followed by two water washes. The polymer appeared to be a milky suspension in the organic layer during this treatment. After washing, the polymer was precipitated by addition to excess MeOH in a blender and dried at room temperature in vacuo to give 19.6 g light gray elastic polymer fluff (6980 equivalents of ethylene per Pd). ¹H NMR analysis (CDCl₃): 112 methyl carbons per 1000 methylene carbons. ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (114.2), Methyl (42.1), Ethyl (24.8), Propyl (5.1), Butyl (10.2), Amyl (4), ≥Hexyl and end of chain (30.3), average number of carbon atoms for ≥Hexyl branches = 14.4 (calculated from intrinsic viscosity and GPC molecular weight data). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory: M_n=110,000, M_w=265,000, M_w/M_n=2.40. Intrinsic viscosity (trichlorobenzene, 135°C) = 1.75 g/dL. Absolute molecular weights calculated by GPC (trichlorobenzene, 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity): M_n=214,000, M_w=535,000, M_w/M_n=2.51.

25

Example 119

Polymerization of ethylene was carried out according to example 112, using the complex {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆⁻ (0.084 g, 0.100 mmol) as the initiator and CHCl₃ as the solvent. The reaction gave 28.4 g of dark viscous fluid (10,140 equivalents of ethylene per Pd). ¹H NMR analysis (CDCl₃): 108 methyl carbons per 1000 methylene carbons. ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (119.5), Methyl (36.9), Ethyl (25.9), Propyl (2.1), Butyl (11), Amyl (1.9), ≥Hexyl and end of chain (38.9). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene

35

using universal calibration theory): $M_n=10,800$,
 $M_w=26,800$, $M_w/M_n=2.47$.

Example 120

Polymerization of ethylene was carried out
5 according to example 112, using the complex $[(2,6-i-PrPh)_2DABMe_2]PdMe(OSO_2CF_3)$ (0.068g, 0.10 mmol) as the
initiator and $CHCl_3$ as the solvent. The reaction gave
5.98 g of low viscosity fluid (2130 equivalents of
ethylene per Pd). ^1H NMR ($CDCl_3$) 0.8-1.0 (m, CH_3);
10 1.0-1.5 (m, CH and CH_2); 1.5-1.7 (m, $CH_3CH=CH-$); 1.9-
2.1 (broad, $-CH_2CH=CHCH_2-$); 5.3-5.5 (m, $-CH=CH-$).
Integration of the olefin end groups assuming one
olefin per chain gives $M_n = 630$ (DP = 24). A linear
polymer with this molecular weight and methyl groups at
15 both ends should have 46 methyl carbons per 1000
methylene carbons. The value measured by integration
is 161, thus this polymer is highly branched.

Example 121

Polymerization of ethylene was carried out
20 according to example 112, using the complex $\{[(2,6-i-PrPh)_2DABH_2]PdCH_2CH_2CH_2C(O)OCH_3\}SbF_6^-$ (0.082 g, 0.10 mmol)
as the initiator and $CHCl_3$ as the solvent. The
reaction gave 4.47 g of low viscosity fluid (1600
equivalents of ethylene per Pd). ^1H NMR ($CDCl_3$) is
25 similar to example 120. Integration of the olefin end
groups assuming one olefin per chain gives $M_n = 880$ (DP
= 31). A linear polymer with this molecular weight and
methyl groups at both ends should have 34 methyl
carbons per 1000 methylene carbons. The value measured
30 by integration is 156, thus this polymer is highly
branched.

Example 122

Polymerization of ethylene was carried out
according to example 112, using the complex $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}BCl(C_6F_5)_3^-$
35 (0.116 g, 0.10 mmol) as the initiator and $CHCl_3$ as the solvent.
The reaction gave 0.278 g of low viscosity fluid, after
correcting for the catalyst residue this is 0.160 g (57

equivalents of ethylene per Pd). M_n estimated by integration of olefin end groups is 300.

Example 123

The complex $[(2,6-i-PrPh)_2DABMe_2]PdMeCl$ (0.056 g, 0.10 mmol) was loaded into a Schlenk flask in the drybox followed by 40 ml of dry toluene. A solution of ethyl aluminum dichloride (1.37 ml of 0.08 M solution in o-dichlorobenzene) was added while stirring. Polymerization of ethylene was carried out using this solution according to example 112. The reaction gave 0.255 g of low viscosity fluid, after correcting for the catalyst residue this is 0.200 g (71 equivalents of ethylene per Pd). M_n estimated by integration of olefin end groups is 1300.

Example 124

Methyl acrylate was sparged with argon, dried over activated 4A sieves, passed through activity 1 alumina B in the drybox, and inhibited by addition of 20 ppm phenothiazine. The solid complex $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}SbF_6^-$ (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox. The flask was connected to a Schlenk line under 1 atm of ethylene, and cooled to $-78^\circ C$. Forty ml of CH_2Cl_2 was added by syringe and after equilibrating at $-78^\circ C$ under ethylene, 5 ml of methyl acrylate was added by syringe and the mixture was warmed to room temperature under ethylene. After 40 h, the reaction was worked up by removing the solvent in vacuo to give 3.90 g of moderately viscous fluid. Integration of the ^1H NMR spectrum showed that this copolymer contained 6.9 mole % methyl acrylate. No poly(methyl acrylate) homopolymer could be detected in this sample by ^1H NMR. ^1H NMR shows that a significant fraction of the ester groups are located at the ends of hydrocarbon branches: 3.65(s, $-CO_2CH_3$, area=4.5), 2.3(t, $-CH_2CO_2CH_3$, ester ended branches, area=3), 1.6(m, $-CH_2CH_2CO_2CH_3$, ester ended branches, area=3), 0.95-1.55(m, CH and other CH_2 , area=73), 0.8-0.95(m, CH_3 , ends of branches or ends of

chains, area=9.5) This is confirmed by the ^{13}C NMR quantitative analysis: Mole%: ethylene (93.1), methyl acrylate (6.9), Branching per 1000 CH_2 : Total methyls (80.2), Methyl (30.1), Ethyl (16.8), Propyl (1.6),
5 Butyl (6.8), Amyl (1.3), $\geq$ Hexyl and end of chain (20.1), methyl acrylate (41.3), Ester branches $\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$ as a % of total ester: $n \geq 5$ (47.8), $n=4$ (17.4), $n=1,2,3$ (26.8), $n=0$ (8).

GPC of this sample was done in THF vs. PMMA
10 standards using a dual UV/RI detector. The outputs of the two detectors were very similar. Since the UV detector is only sensitive to the ester functionality, and the RI detector is a relatively nonselective mass detector, the matching of the two detector outputs
15 shows that the ester functionality of the methyl acrylate is distributed throughout the entire molecular weight range of the polymer, consistent with a true copolymer of methyl acrylate and ethylene.

A 0.503 g sample of the copolymer was fractionated
20 by dissolving in benzene and precipitating partially by slow addition of MeOH. This type of fractionation experiment is a particularly sensitive method for detecting a low molecular weight methyl acrylate rich component since it should be the most soluble material
25 under the precipitation conditions.

The precipitate 0.349 g, (69%) contained 6.9 mole % methyl acrylate by ^1H NMR integration, GPC (THF, PMMA standard, RI detector): $M_n=19,600$, $M_w=29,500$, $M_w/M_n=1.51$. The soluble fraction 0.180g (36%)
30 contained 8.3 mole % methyl acrylate by ^1H NMR integration, GPC (THF, PMMA standard, RI detector): $M_n=11,700$, $M_w=19,800$, $M_w/M_n=1.70$. The characterization of the two fractions shows that the acrylate content is only slightly higher at lower
35 molecular weights. These results are also consistent with a true copolymer of the methyl acrylate with ethylene.

Example 125

Methyl acrylate was sparged with argon, dried over activated 4A sieves, passed through activity 1 alumina B in the drybox, and inhibited by addition of 20 ppm phenothiazine. The complex [(2,6-i-PrPh)₂DABMe₂]PdMe(OSO₂CF₃) (0.068 g, 0.10 mmol) was loaded into a Schlenk flask in the drybox, and 40 ml of CHCl₃ was added followed by 5 ml of methyl acrylate. The septum capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. The light orange mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. After 20 h, the reaction was worked up by removing the solvent and unreacted methyl acrylate in vacuo to give 1.75 g of a low viscosity copolymer.

¹³C NMR quantitative analysis: Mole%: ethylene (93), methyl acrylate (7), Branching per 1000 CH₂: Total methyls (100.9), Methyl (33.8), Ethyl (19.8), Propyl (1.9), Butyl (10.1), Amyl (7.3), ≥Hexyl and end of chains (28.4), methyl acrylate (41.8). This sample is low molecular weight - total methyls does not include end of chain methyls. Ester branches - CH(CH₂)_nCO₂CH₃ as a % of total ester: n≥5 (51.3), n=4 (18.4), n=1,2,3 (24), n=0 (6.3).

Example 126

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}BAF⁻ (0.136 g, 0.10 mmol) in CH₂Cl₂ solvent with a reaction time of 72 hours to give 4.93 g of copolymer.

Example 127

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆⁻ (0.084 g, 0.10 mmol) with a reaction time of 72 hours to give 8.19 g of copolymer.

Example 128

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.082 g, 0.10 mmol) to give 1.97 g of copolymer.

Example 129

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{CH}_3\text{CN})\}\text{SbF}_6^-$ (0.080 g, 0.10 mmol) to give 3.42 g of copolymer. The ^1H NMR shows primarily copolymer, but there is also a small amount of poly(methyl acrylate) homopolymer.

Example 130

Ethylene and methyl acrylate (20 ml) were copolymerized in 20 ml of CHCl_3 according to example 125 using catalyst $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.339 g, 0.40 mmol) to give 2.17 g of copolymer after a reaction time of 72 hours. ^{13}C NMR quantitative analysis: Mole%: ethylene (76.3), methyl acrylate (23.7). Branching per 1000 CH_2 : Total methyls (28.7), Methyl (20.5), Ethyl (3.8), Propyl (0), Butyl (11), $\geq$ Amyl and end of chains (13.6), methyl acrylate (138.1). Ester branches - $\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$ as a % of total ester: $n \geq 5$ (38.8), $n=4$ (20), $n=1,2,3$ (15.7), $n=0$ (25.4).

Example 131

Ethylene and methyl acrylate (20 ml) were copolymerized in 20 ml of CHCl_3 at 50°C for 20 hours according to example 125 using catalyst $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.339 g, 0.40 mmol) to give 0.795 g of copolymer. DSC (two heats, -150 to $+150^\circ\text{C}$, $15^\circ\text{C}/\text{min}$) shows $T_g = -48^\circ\text{C}$.

Example 132

A solution of the ligand $(2,6\text{-}i\text{-PrPh})_2\text{DAB}(\text{Me}_2)$ (0.045 g, 0.11 mmol) dissolved in 2 ml of CHCl_3 was added to a solution of the complex $[\text{PdMe}(\text{CH}_3\text{CN})(1,5\text{-cyclooctadiene})]^+\text{SbF}_6^-$ (0.051 g, 0.10 mmol) in 2 ml of CHCl_3 . This mixture was combined with 35 ml of

additional CHCl_3 and 5 ml of methyl acrylate in a Schlenk flask in a drybox, and then a copolymerization with ethylene was carried out according to example 125 to give 1.94 g of copolymer.

5

Example 133

Methyl acrylate (5 ml) was added to the solid catalyst $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{BF}_4^-$ (0.069g, 0.10 mmol) followed by 40 ml of CHCl_3 . The addition of methyl acrylate before the CHCl_3 is often important to avoid deactivation of the catalyst. A copolymerization with ethylene was carried out according to example 125 to give 2.87 g of copolymer.

10

Characterization of poly(ethylene-co-methyl acrylate)
by ^1H NMR

15

NMR spectra in CDCl_3 were integrated and the polymer compositions and branching ratios were calculated. See example 124 for chemical shifts and assignments.

20

Example	Yield(g)	methyl acrylate (mole %)	CH_3 per 1000 CH_2	CO_2CH_3 per 1000 CH_2
124	3.9	6.9	80	42
125	1.75	7.1	104	45
126	4.93	5.6	87	34
127	8.19	6.1	87	37
128	1.97	7.3	159	50
129	3.42	9.5	86	59
130	2.17	22.8	29	137
131	0.795	41	14	262
132	1.94	6.1	80	36
133	2.87	8.2	70	49

Molecular Weight Characterization

GPC was done in THF using PMMA standards and an RI detector except for example 133 which was done in trichlorobenzene at 135°C vs. polystyrene reference

25

with results calculated as linear polyethylene using universal calibration theory. When polymer end groups could be detected by ^1H NMR (5.4 ppm, multiplet, -CH=CH-, internal double bond), M_n was calculated assuming two olefinic protons per chain.

Example	M_n	M_w	M_w/M_n	M_n (^1H NMR)
124	15,500	26,400	1.70	
125	1,540	2,190	1.42	850
126	32,500	49,900	1.54	
127	12,300	22,500	1.83	
128	555	595	1.07	360
129	16,100	24,900	1.55	
130	800	3,180	3.98	1,800
131				1,100
132	15,200	26,000	1.71	
133	5,010	8,740	1.75	

Example 134

Ethylene and t-butyl acrylate (20 ml) were copolymerized according to example 130 to give 2.039 g of viscous fluid. ^1H NMR of the crude product showed the desired copolymer along with residual unreacted t-butyl acrylate. The weight of polymer corrected for monomer was 1.84 g. The sample was reprecipitated to remove residual monomer by slow addition of excess MeOH to a CHCl_3 solution. The reprecipitated polymer was dried in vacuo. ^1H NMR (CDCl_3): 2.2 (t, $-\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$, ester ended branches), 1.6 (m, $-\text{CH}_2\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$, ester ended branches), 1.45 (s, $-\text{C}(\text{CH}_3)_3$), 0.95-1.45 (m, CH and other CH_2), 0.75-0.95 (m, CH_3 , ends of hydrocarbon branches or ends of chains). This spectrum shows that the esters are primarily located at the ends of hydrocarbon branches; integration gave 6.7 mole % t-butyl acrylate. ^{13}C NMR quantitative analysis, branching per 1000 CH_2 : Total methyls (74.8), Methyl (27.7), Ethyl (15.3), Propyl (1.5), Butyl (8.6), $\geq$ Amyl

and end of chains (30.8), $-\text{CO}_2\text{C}(\text{CH}_3)_3$ ester (43.2).
 Ester branches $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{C}(\text{CH}_3)_3$ as a % of total
 ester: $n \geq 5$ (44.3), $n=1,2,3,4$ (37.2), $n=0$ (18.5). GPC
 (THF, PMMA standard): $M_n=6000$ $M_w=8310$ $M_w/M_n = 1.39$.

5

Example 135

Glycidyl acrylate was vacuum distilled and
 inhibited with 50 ppm phenothiazine. Ethylene and
 glycidyl acrylate (5 ml) were copolymerized according
 to Example 125 using catalyst $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.084 g, 0.10
 10 mmol). The reaction mixture was filtered through a
 fritted glass filter to remove chloroform insolubles,
 and the chloroform was removed in vacuo to give 14.1 g
 viscous yellow oil which still contained residual
 15 unreacted glycidyl acrylate. The sample was
 reprecipitated to remove residual monomer by slow
 addition of excess acetone to a CHCl_3 solution. The
 reprecipitated polymer was dried in vacuo to give 9.92
 g of copolymer containing 1.8 mole % glycidyl acrylate.
 20 ^1H NMR (CDCl_3): 4.4, 3.9, 3.2, 2.85,
 2.65 (multiplets, 1H each $-\text{CH}_2\text{CHCH}_2\text{O}$) 2.35 (t,
 $-\text{CH}_2\text{CO}_2\text{CH}_2\text{CHCH}_2\text{O}$, ester ended branches), 1.65(m,
 $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CHCH}_2\text{O}$, ester ended branches), 0.95-1.5(m, CH
 and other CH_2), 0.75-0.95(m, CH_3 , ends of hydrocarbon
 25 branches or ends of chains). This spectrum shows that
 the epoxide ring is intact, and that the glycidyl ester
 groups are primarily located at the ends of hydrocarbon
 branches. GPC (THF, PMMA standard): $M_n=63,100$
 $M_w=179,000$ $M_w/M_n = 2.85$.
 30 ^{13}C NMR quantitative analysis, branching per 1000
 CH_2 : Total methyls (101.7), Methyl (32.5), Ethyl
 (21.3), Propyl (2.4), Butyl (9.5), Amyl (1.4), $\geq$ Hexyl
 and end of chains (29.3), Ester branches $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}$
 as a % of total ester: $n \geq 5$ (39.7), $n=4$ (small amount),
 35 $n=1,2,3$ (50.7), $n=0$ (9.6).

A 3.24-g sample of the copolymer was dissolved in 50 mL of refluxing methylene chloride. A solution of 0.18 g oxalic acid dihydrate in 5 mL of 1:1 chloroform-acetone was added to the solution of copolymer and the solvent was evaporated off on a hot plate. The thick liquid was allowed to stand in an aluminum pan at room temperature overnight; the pan was then placed in an oven at 70°C for 1.5 hr followed by 110°C/vacuum for 5 hr. The cured polymer was a dark, non-tacky soft rubber which tore easily (it had a very short elongation to break despite its rubberiness).

Example 136

1-Pentene (20 ml) and methyl acrylate (5 ml) were copolymerized in 20 ml chloroform for 96 hours using catalyst $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.084 g, 0.10 mmol). The solvent and unreacted monomers were removed *in vacuo* to give 0.303 g copolymer (0.219 g after correcting for catalyst residue). The ^1H NMR spectrum was similar to the ethylene/methyl acrylate copolymer of example 124 suggesting that many of the ester groups are located at the ends of hydrocarbon branches. Integration shows that the product contains 21 mole % methyl acrylate. There are 65 acrylates and 96 methylys per 1000 methylene carbons. GPC (THF, PMMA standard): $M_n=6400$ $M_w=11200$ $M_w/M_n = 1.76$.

Example 137

Benzyl acrylate was passed through activity 1 alumina B, inhibited with 50 ppm phenothiazine, and stored over activated 4A molecular sieves. Ethylene and benzyl acrylate (5 ml) were copolymerized according to example 135 to give 11.32 g of viscous fluid. ^1H NMR of the crude product showed a mixture of copolymer and unreacted benzyl acrylate (35 wt %). The residual benzyl acrylate was removed by two reprecipitations, the first by addition of excess MeOH to a chloroform solution, and the second by addition of excess acetone to a chloroform solution. ^1H NMR (CDCl_3): 7.35 (broad

5.1 (s, $-\text{CH}_2\text{C}_6\text{H}_5$), 2.35 (t, $-\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$, ester ended branches), 1.6 (m, $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$, ester ended branches), 0.95-1.5 (m, CH and other CH_2), 0.75-0.95 (m, CH_3 , ends of hydrocarbon branches or ends of chains). Integration shows that the product contains 3.7 mole % benzyl acrylate. There are 21 acrylates and 93 methylys per 1000 methylene carbons. GPC (THF, PMMA standard): $M_n=46,200$ $M_w=73,600$ $M_w/M_n = 1.59$.

^{13}C NMR quantitative analysis, Branching per 1000 CH_2 : Total methylys (97.2), Methyl (32.9), Ethyl (20.3), Propyl (2.4), Butyl (9.7), Amyl (2.9), $\geq$ Hexyl and end of chains (35.2), benzyl acrylate (17.9), Ester branches $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{R}$ as a % of total ester: $n \geq 5$ (44.5), $n=4$ (7.2), $n=1,2,3$ (42.3), $n=0$ (6)

15 Example 138

1-Pentene (10 ml) and ethylene (1 atm) were copolymerized in 30 ml chloroform according to example 125 using catalyst $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.084 g, 0.10 mmol) to give 9.11 g highly viscous yellow oil. The ^1H NMR spectrum was similar to the poly(ethylene) of example 110 with 113 methyl carbons per 1000 methylene carbons. ^{13}C NMR quantitative analysis, branching per 1000 CH_2 : Total methylys (119.5), Methyl (54.7), Ethyl (16.9), Propyl (8.4), Butyl (7.7), Amyl (7.2), $\geq$ Hexyl and end of chains (30.9). GPC (trichlorobenzene, 135°C , polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=25,000$, $M_w=44,900$, $M_w/M_n=1.79$.

30 Listed below are the ^{13}C NMR data upon which the above analysis is based.

^{13}C NMR Data		
TCB, 120°C , 0.05M CrAcAc		
Freq ppm	Intensity	
39.6012	5.53532	
39.4313	6.33425	MB_2
38.3004	8.71403	MB_3+
37.9446	17.7325	MB_3+
37.2809	36.416	αB_1 , 3B_3
36.7659	5.10586	αB_1 , 3B_3

34.3181	56.1758	$\alpha\gamma+B$
33.8243	15.6271	$\alpha\gamma+B$
33.3942	8.09189	MB_1
32.9854	20.3523	MB_1
32.6721	4.35239	MB_1
32.327	4.06305	$3B_5$
31.9394	27.137	$3B_6+, 3 EOC$
31.4031	9.62823	$\gamma+\gamma+B, 3B_4$
30.235	52.8404	$\gamma+\gamma+B, 3B_4$
29.7518	162.791	$\gamma+\gamma+B, 3B_4$
29.3164	26.506	$\gamma+\gamma+B, 3B_4$
27.5695	15.4471	$B\gamma+B, 2B_2$
27.1341	59.1216	$B\gamma+B, 2B_2$
26.4811	8.58222	$B\gamma+B, 2B_2$
24.4475	5.93996	$\beta\beta B$
23.12	5.05181	$2B_4$
22.6369	29.7047	$2B_5+, 2 EOC$
20.1626	6.29481	$2B_3$
19.7378	31.9342	$1B_1$
19.2068	3.93019	$1B_1$
14.2582	5.59441	$1B_3$
13.8706	36.3938	$1B_4+, 1 EOC$
10.9768	9.89028	$1B_2$

Example 139

1-Pentene (20 ml) was polymerized in 20 ml chloroform according to example 138 to give 2.59 g of viscous fluid (369 equivalents 1-pentene per Pd). Integration of the ^1H NMR spectrum showed 118 methyl carbons per 1000 methylene carbons. DSC (two heats, -150 to +150°C, 15°C/min) shows $T_g = -58^\circ C$ and a low temperature melting endotherm from -50°C to 30°C (32 J/g).

^{13}C NMR quantitative analysis, branching per 1000 CH₂: Total methyls (118), Methyl (85.3), Ethyl (none detected), Propyl (15.6), Butyl (non detected), $\geq$ Amyl and end of chains (17.1). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n = 22,500$, $M_w = 43,800$, $M_w/M_n = 1.94$.

Listed below are the ^{13}C NMR data upon which the above analysis is based.

¹³C NMR data

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
42.6277	4.69744	αα for Me & Et ⁺
39.5428	9.5323	3 rd carbon of a 6 ⁺ carbon side chain that has a methyl branch at the 4 position
38.1357	3.59535	
37.8384	13.9563	MB ₃ ⁺
37.5888	28.4579	
37.2224	54.6811	αB ₁ , 3B ₃
35.5287	6.51708	
35.2419	3.55603	
34.6366	7.35366	
34.2437	22.3787	
32.911	45.2064	MB ₁
32.5977	10.5375	
32.38	4.02878	
31.8809	14.1607	3B ₆ ⁺ , 3EOC
30.6916	8.44427	γ ⁺ γ ⁺ B
30.0703	63.1613	γ ⁺ γ ⁺ B
29.6987	248	γ ⁺ γ ⁺ B
29.2633	17.9013	γ ⁺ γ ⁺ B
28.8916	3.60422	
27.1182	66.2971	βγ ⁺ B, (4B ₅ , etc.)
24.5324	16.8854	
22.5784	16.0395	2B ₅ ⁺ , 2EOC
20.1041	13.2742	
19.6952	54.3903	1B ₁ , 2B ₃
14.2104	12.2831	
13.8281	16.8199	1B ₄ ⁺ , EOC, 1B ₃

Integration of the CH₂ peaks due to the structure
 5 -CH(R)CH₂CH(R')- , where R is an alkyl group, and R' is
 an alkyl group with two or more carbons showed that in
 69% of these structures, R = Me. The region integrated
 for the structure where both R and R' are ≥Ethyl was
 39.7 ppm to 41.9 ppm to avoid including an interference
 10 from another type of methylene carbon on a side chain.

Example 140

[(2,6-i-PrPh)₂DABMe₂]PdMeCl (0.020 g, 0.036 mmol)
 was dissolved in 4 ml CH₂Cl₂ and methyl acrylate
 15 (0.162 g, 0.38 mmol, inhibited with 50 ppm
 phenothiazine) was added while stirring. This solution
 was added to a stirred suspension of NaBAF (0.033 g,
 0.038 mmol) in 4 ml of CH₂Cl₂. After stirring for 1

four, the mixture was filtered through a 0.5 μ m PTFE membrane filter to remove a flocculant gray precipitate. The solvent was removed from the filtrate in vacuo to give a solid which was recrystallized from a CH₂Cl₂/pentane mixture at -40°C to give 0.39 g (75% yield) of orange crystalline $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}BAF^-$. ¹H NMR (CDCl₃): 0.65(m, CH₂, 2H); 1.15-1.45(four sets of doublets for -CH(CH₃)₂ and multiplet at 1.4 for a CH₂, total area = 26H); 2.19,2.21 (s,s, CH₃ of ligand backbone, 6H); 2.40(m, CH₂, 2H); 2.90 (m, -CH(CH₃)₂, 4H); 3.05(s, -CO₂CH₃, 3H); 7.25-7.75(m, aromatic H of ligand and counterion, 19H).

All GPC data reported for examples 141-170, 177, and 204-212 were run in trichlorobenzene vs. polyethylene standards unless otherwise indicated. All DSC data reported for examples 141-170, 177, and 204-212 (second heat, -150°C to 150°, 10 or 15°C/min).

Example 141

A Schlenk flask containing $\{[(2,6-i-PrPh)_2DABH_2]NiMe(Et_2O)\}BAF^-$ (1.3 mg, 8.3×10^{-7} mol) under an argon atmosphere was cooled to -78°C. Upon cooling, the argon was evacuated and the flask backfilled with ethylene (1 atm). Toluene (75 mL) was added via syringe. The polymerization mixture was then warmed to 0°C. The solution was stirred for 30 minutes. Polymer began to precipitate from the solution within minutes. After 30 minutes, the polymerization was terminated upon exposing the catalyst to air. The polymer was precipitated from acetone, collected by filtration and washed with 6 M HCl, water, and acetone. The polymer was dried in vacuo. The polymerization yielded 1.53 g of polyethylene (1.3×10^5 TO). $M_n = 91,900$; $M_w = 279,000$; $M_w/M_n = 3.03$; $T_m = 129^\circ C$. ¹H NMR (C₆D₅Cl, 142°C) 0.6 methyls per 100 carbons.

Example 142

The reaction was done in the same way as in Example 141 using 1.3 mg of $\{[(2,6-i-$

$[(i\text{-PrPh})_2\text{DABMe}_2]\text{NiMe}(\text{Et}_2\text{O})\}\text{BAF}^-$ (8.3×10^{-7} mol). The polymer was isolated as a white solid (0.1 g).

Examples 143-148

General procedure for the polymerization of ethylene by the methylaluminoxane (MAO) activation of nickel complexes containing bidentate diimine ligands: Polymerization at 0°C: The bisimine nickel dihalide complex (1.7×10^{-5} mol) was combined with toluene (100 mL) in a flame dried Schlenk flask under 1 atmosphere ethylene pressure. The polymerization was cooled to 0°C in an ice-water bath. The mixture was stirred at 0°C for 15 minutes prior to activation with MAO. Subsequently, 1.5 mL of a 10% MAO (100 eq) solution in toluene was added onto the nickel dihalide suspension. The solution was stirred at 0°C for 10, 30, or 60 minutes. Within minutes increased viscosity and/or precipitation of polyethylene was observed. The polymerization was quenched and the polymer precipitated from acetone. The polymer was collected by suction filtration and dried under vacuum for 24 hours. See Table I for a detailed description of molecular weight and catalyst activity data.

Example No.	Catalyst
143	$[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
144	$[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{NiBr}_2$
145	$[(2,6\text{-MePh})_2\text{DABH}_2]\text{NiBr}_2$
146	$[(2,6\text{-}i\text{-PrPh})_2\text{DABAn}]\text{NiBr}_2$
147	$[(2,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$
148	$[(2,6\text{-MePh})_2\text{DABMe}_2]\text{NiBr}_2$

Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	M _n	M _w	M _w /M _n	Thermal Analysis (°C)
143	0°C. 30 m	5.3	22,700	80,900	231,000	2.85	119 (T _m)
144 ²	0°C. 30 m	3.8	16,300	403,000	795,000	1.97	115 (T _m)
145 ³	0°C. 30 m	3.4	14,300	42,900	107,000	2.49	131 (T _m)
146 ⁴	0°C. 30 m	7.0	29,900	168,000	389,000	2.31	107 (T _m)
147	0°C. 10 m	3.7	47,500	125,000	362,000	2.89	122 (T _m)
148	0°C. 10 m	5.1	65,400	171,000	440,000	2.58	115 (T _m)

¹ Polymerization reactions run at 1 atmosphere ethylene pressure.

² Branching Analysis by ¹³C NMR per 1000 CH₂:

Ex. 144: Total methyls (54.3), Methyl (43.4), Ethyl (3.3), Propyl (2), Butyl (1.3), ≥Butyl and end of chains (5.7).

Ex. 146: Total methyls (90.9), Methyl (65.3), Ethyl (7.2), Propyl (4.5), Butyl (3.5), Amyl (4.5), ≥Hexyl and end of chains (10.2).

³ Ex. 145: ¹H NMR (C₆D₅Cl), 142°C) 0.1 methyl per 100 carbon atoms.

Examples 149-154

Polymerization at Ambient Temperature

The general procedure described for the MAO activation of the diimine nickel dihalides was followed in the polymerizations detailed below, except all polymerizations were run between 25-30°C.

	<u>Example No.</u>	<u>Catalyst</u>
20	149	[(2,6- <i>i</i> -PrPh) ₂ DABH ₂]NiBr ₂
	150	[(2,6- <i>i</i> -PrPh) ₂ DABMe ₂]NiBr ₂
	151	[(2,6-MePh) ₂ DABH ₂]NiBr ₂
	152	[(2,6- <i>i</i> -PrPh) ₂ DABAn]NiBr ₂
	153	[(2,6-MePh) ₂ DABAn]NiBr ₂
25	154	[(2,6-MePh) ₂ DABMe ₂]NiBr ₂

Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	M _n	M _w	M _w /M _n	Thermal Analysis (°C)
149	30°C. 30 m	2.5	12,200	15,500	34,900	2.25	--
150 ⁴	25°C. 30 m	3.4	14,500	173,000	248,000	1.44	-51 (T _g)
151 ³	25°C. 30 m	7.2	30,800	13,900	39,900	2.88	90,112 (T _m)
152 ⁴	25°C. 30 m	4.2	18,000	82,300	175,000	2.80	39 (T _m)
153	25°C. 10 m	4.9	62,900	14,000	25,800	1.85	--
154	25°C. 10 m	3.7	47,500	20,000	36,000	1.83	--

¹ Polymerization reactions run at 1 atmosphere ethylene pressure.

² Branching Analysis by ¹³C NMR per 1000 CH₂:

Ex. 150: Total methyls (116.3), Methyl (93.5),
5 Ethyl (6.2), Propyl (3.2), Butyl (2.9), Am (6.6), ≥Hex
and end of chains (11.2).

Ex. 152: Total methyls (141.9), Methyl (98.1),
Ethyl (15.9), Propyl (5.6), Butyl (6.8), Amyl (4.1), ≥
Hex and end of chains (10.7). Quantitation of the -
10 CH₂CH(CH₃)CH₂CH₃ structure per 1000 CH₂'s: 8.

³ Ex. 151: ¹H NMR (C₆D₅Cl), 142°C) 3 methyl per 100
carbon atoms.

Example 155

A standard solution of [(2,6-i-PrPh)₂DABAN]NiBr₂
15 was prepared as follows: 1,2-difluorobenzene (10 mL)
was added to 6.0 mg of [(2,6-i-PrPh)₂DABAN]NiBr₂ (8.4 x
10⁻⁶ mol) in a 10 mL volumetric flask. The standard
solution was transferred to a Kontes flask and stored
under an argon atmosphere.

20 The standard catalyst solution (1.0 mL, 8.4 x
10⁻⁷ mol catalyst) was added to a Schlenk flask which
contained 100 mL toluene, and was under 1 atmosphere
ethylene pressure. The solution was cooled to 0°C, and
1.5 mL of a 10% solution of MAO (≥1000 eq) was added.
25 The solution was stirred for 30 minutes. Polymer began
to precipitate within minutes. The polymerization was
quenched and the polymer precipitated from acetone.
The resulting polymer was dried in vacuo (2.15 g, 1.84
x 10⁵ TO). M_n = 489,000; M_w = 1,200,000; M_w/M_n = 2.47

30 Example 156

The polymerization of ethylene at 25°C was
accomplished in an identical manner to that described
in Example 155. The polymerization yielded 1.8 g of
polyethylene (1.53 x 10⁵ TO). M_n = 190,000; M_w =
35 410,000; M_w/M_n = 2.16; ¹H NMR (C₆D₅Cl, 142°C) 7 methyls
per 100 carbons.

Example 157

A standard solution of $[(2,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$ was prepared in the same way as described for the complex in Example 155 using 5.0 mg of $[(2,6\text{-MePh})_2\text{DABAn}]\text{NiBr}_2$ (8.4×10^{-6} mol).

- 5 Toluene (100 mL) and 1.0 mL of the standard solution of complex 5 (8.3×10^{-7} mol catalyst) were combined in a Schlenk flask under 1 atmosphere ethylene pressure. The solution was cooled to 0°C , and 1.5 mL of a 10% solution of MAO (≥ 1000 eq) was added. The
10 polymerization mixture was stirred for 30 minutes. The polymerization was terminated and the polymer precipitated from acetone. The reaction yielded 1.60 g of polyethylene (1.4×10^5 TO). $M_n = 590,000$; $M_w = 1,350,000$; $M_w/M_n = 2.29$.

15 Example 158

- Toluene (200 mL) and 1.0 mL of a standard solution of $[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$ (8.3×10^{-7} mol catalyst) were combined in a Fisher-Porter pressure vessel. The resulting solution was cooled to 0°C , and 1.0 mL of a
20 10% MAO (≥ 1000 eq) solution in toluene was added to activate the polymerization. Subsequent to the MAO addition, the reactor was rapidly pressurized to 276 kPa. The solution was stirred for 30 minutes at 0°C . After 30 minutes, the reaction was quenched and polymer
25 precipitated from acetone. The resulting polymer was dried under reduced pressure. The polymerization yielded 2.13 g of white polyethylene (1.82×10^5 TO). $M_n = 611,000$; $M_w = 1,400,000$; $M_w/M_n = 2.29$; $T_m = 123^\circ\text{C}$; $^1\text{H NMR}$ ($\text{C}_6\text{D}_5\text{Cl}$, 142°C) 0.5 methyls per 100 carbons.

30 Examples 159-160

Polymerization of Propylene

- The diimine nickel dihalide complex (1.7×10^{-5} mol) was combined with toluene (100 mL) in a Schlenk flask under 1 atmosphere propylene pressure. The
35 polymerization was cooled to 0°C , and 1.5 mL of a 10% MAO (100 eq) solution in toluene was added. The solution was stirred for 2 hours. The polymerization

was quenched and the polymer precipitated from acetone. The polymer was dried under vacuum.

	Example No.	Catalyst
	159	$[(2,6\text{-}i\text{-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
5	160	$[(2,6\text{-}i\text{-PrPh})_2\text{DABAn}]\text{NiBr}_2$

Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	M _n	M _w	M _w /M _n	Thermal Analysis (°C)
159	0°C.2h	1.3	900	131,000 a	226,000	1.72	-20 (T _g)
160	0°C.2h	4.3	2,900	147,000	235,000	1.60	-78, -20 (T _g)

^aGPC (toluene, polystyrene standard)

Ex. 159: ¹H NMR (C₆D₅Cl), 142°C) 30 methyls per 100 carbon atoms.

10 Ex. 160: ¹H NMR (C₆D₅Cl), 142°C) 29 methyls per 100 carbon atoms. Quantitative ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (699). Based on the total methyls, the fraction of 1,3-enchainment is 13%. Analysis of backbone carbons (per 1000 CH₂): δ⁺ (53),
15 δ⁺/γ (0.98).

Listed below are the ¹³C NMR data upon which the above analysis is based.

20	¹³ C NMR Data	
	TCB, 140C, 0.05M CrAcAc	
	Freq ppm	Intensity
	47.3161	53.1767
	46.9816	89.3849
	46.4188	82.4488
	45.84	23.1784
	38.4702	12.8395
	38.0985	29.2643
	37.472	18.6544
	37.2915	24.8559
	35.3747	15.6971
	34.5623	14.6353
	33.3145	14.2876
	32.996	12.2454
	30.9464	24.2132
	30.6703	57.4826
	30.081	30.122 γ to single branch

29.6987	29.2186	δ^+ to branch
28.3659	298.691	
27.4792	33.2539	
27.1235	29.7384	
24.5324	9.45408	
21.1554	20.0541	
20.6244	110.077	
19.9926	135.356	
16.9342	8.67216	
16.4829	8.81404	
14.9962	8.38097	

Example 161

[(2,6-i-PrPh)₂DABH₂]NiBr₂ (10 mg, 1.7×10^{-5} mol) was combined with toluene (40 mL) under a N₂ atmosphere. A 10% solution of MAO (1.5 mL, 100 eq) was
5 added to the solution. After 30 minutes, the Schlenk flask was backfilled with propylene. The reaction was stirred at room temperature for 5.5 hours. The polymerization was quenched, and the resulting polymer dried under vacuum (670 mg, 213 TO/h). $M_n = 176,000$;
10 $M_w = 299,000$; $M_w/M_n = 1.70$. Quantitative ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (626), Methyl (501), Ethyl (1), ≥Butyl and end of chain (7). Based on the total methyls, the fraction of 1,3-
15 enchainment is 22%. Analysis of backbone carbons (per 1000 CH₂): δ^+ (31), δ^+/γ (0.76).

Examples 162-165

The diimine nickel dihalide catalyst precursor (1.7×10^{-5} mol) was combined with toluene (40 mL) and 1-hexene (10 mL) under a N₂ atmosphere. Polymerization
20 reactions of 1-hexene were run at both 0°C and room temperature. A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. Typically the polymerization reactions were stirred for 1-2 hours. The polymer was precipitated from acetone and collected by suction
25 filtration. The resulting polymer was dried under vacuum.

	Ex. No.	Catalyst
	162	$[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
	163	$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$
	164	$[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$
5	165	$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$

Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	M _n ^a	M _w	M _w /M _n	Thermal Analysis (°C)
162	25°C. 1 h	3.0	2100	173,000	318,000	1.84	-48 (T _g)
163	25°C. 1 h	1.2	860	314,000	642,000	2.05	-54 (T _g) -19 (T _m)
164	0°C. 2 h	3.0	1100	70,800	128,000	1.80	-45 (T _g)
165	0°C. 2 h	1.5	540	91,700	142,000	1.55	-49 (T _g)

^aGPC (toluene, polystyrene standards).

Branching Analysis Ex. 162: by ¹³C NMR per 1000

CH₂:

10 Total methyls (157.2), Methyl (47), Ethyl (1.9),
Propyl (4.5), Butyl (101.7), ≥Am and end of chain
(4.3).

¹³C NMR data (Example 162)

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
42.8364	7.99519	Methine
41.3129	27.5914	αα to two Eth ⁺ branches
40.5759	19.6201	αα to two Eth ⁺ branches
37.8831	14.7864	Methines and Methylenes
37.2984	93.6984	Methines and Methylenes
36.6684	6.99225	Methines and Methylenes
35.5773	36.067	Methines and Methylenes
34.655	55.825	Methines and Methylenes
34.3091	63.3862	Methines and Methylenes
33.8356	24.1992	Methines and Methylenes
33.428	53.7439	Methines and Methylenes
32.9957	51.1648	Methines and Methylenes
31.9169	17.4373	Methines and Methylenes
31.5546	14.008	Methines and Methylenes
31.1552	10.6667	Methines and Methylenes
30.5993	34.6931	Methines and Methylenes
30.274	56.8489	Methines and Methylenes
30.1258	42.1332	Methines and Methylenes
29.747	97.9715	Methines and Methylenes
29.1047	47.1924	Methines and Methylenes
28.8823	64.5807	Methines and Methylenes
28.1289	13.6645	Methines and Methylenes
27.5648	61.3977	Methines and Methylenes
27.1777	50.9087	Methines and Methylenes
27.0213	31.6159	Methines and Methylenes
26.9142	31.9306	Methines and Methylenes
26.4572	4.715666	Methines and Methylenes
23.2085	154.844	2B ₄
22.6074	12.0719	2B ₅ ⁺ , EOC
20.0669	8.41495	1B ₁
19.6963	57.6935	1B ₁
15.9494	17.7108	
14.3477	8.98123	
13.8742	248	1B ₄ ⁺ , EOC

Example 166

- 5 [(2,6-*i*-PrPh)₂DABMe₂]NiBr₂ (10.4 mg, 1.7 x 10⁻⁵ mol) was combined with toluene (15 mL) and 1-hexene (40 mL) under 1 atmosphere ethylene pressure. The solution was cooled to 0°C, and 1.5 mL of a 10% MAO (100 eq) solution in toluene was added. The reaction was
- 10 stirred at 0°C for 2.5 hours. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (1.4g). Mn = 299,000; Mw = 632,000; Mw/Mn = 2.12.

Branching Analysis by ^{13}C NMR per 1000 CH_2 : Total methyls (101.3), Methyl (36.3), Ethyl (1.3), Propyl (6.8), Butyl (47.7), $\geq$ Amyl and end of chains (11.5).

Example 167

5 $[(2,6\text{-i-PrPh})_2\text{DABH}_2]\text{NiBr}_2$ (10 mg, 1.7×10^{-5} mol) was added to a solution which contained toluene (30 mL) and 1-octene (20 mL) under 1 atm ethylene. A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. The resulting purple solution was allowed to stir for 4
10 hours at room temperature. Solution viscosity increased over the duration of the polymerization. The polymer was precipitated from acetone and dried under vacuum resulting in 5.3 g of copolymer. $M_n = 15,200$, $M_w = 29,100$, $M_n/M_w = 1.92$.

15 Example 168

$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$ (12 mg, 1.7×10^{-5} mol) was combined with toluene (75 mL) in a Schlenk flask under 1 atmosphere ethylene pressure. The mixture was cooled to 0°C , and 0.09 mL of a 1.8 M solution in toluene of
20 Et_2AlCl (10 eq) was added. The resulting purple solution was stirred for 30 minutes at 0°C . The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (6.6 g, 2.8×10^4 TO). M_n
25 = 105,000; $M_w = 232,000$; $M_w/M_n = 2.21$

Example 169

$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$ (12 mg, 1.7×10^{-5} mol) was combined with toluene (75 mL) under 1 atmosphere propylene pressure. The solution was cooled to 0°C and
30 0.1 mL of Et_2AlCl (≥ 10 eq) was added. The reaction was stirred at 0°C for 2 hours. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (3.97 g, 2800 TO).

35 Example 170

$[(2,6\text{-i-PrPh})_2\text{DABAn}]\text{NiBr}_2$ (12 mg, 1.7×10^{-5} mol) was combined with toluene (50 mL) and 1-hexene (25 mL) under a N_2 atmosphere. Et_2AlCl (0.01 mL, 10 eq) was

added to the polymerization mixture. The resulting purple solution was allowed to stir for 4 hours. After 4 hours the polymerization was quenched and the polymer precipitated from acetone. The polymerization yielded
5 1.95 g poly(1-hexene) (348 TO/h). $M_n = 373,000$; $M_w = 680,000$; $M_w/M_n = 1.81$.

Example 171

1-Tetradecene (20 ml) was polymerized in methylene chloride (10 ml) for 20 hr using catalyst $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}SbF_6^-$ (0.04 g, 0.05
10 mmol). The solvent and reacted monomer were removed in vacuo. The polymer was precipitated to remove unreacted monomer, by the addition of acetone to a chloroform solution. The precipitated polymer was
15 dried in vacuo to give a 10.2 g yield. ^{13}C NMR (trichlorobenzene, $120^\circ C$) integrated to give the following branching analysis per 1000 methylene carbons: Total methyls (69.9), methyl (24.5), ethyl (11.4), propyl (3.7), butyl (2.3) amyl (0.3), $\geq$ Hexyl
20 and end of chain (24.2). Thermal analysis showed $T_g = -42.7^\circ C$, and $T_m = 33.7^\circ C$ (15.2 J/g).

Listed below are the ^{13}C NMR data upon which the above analysis is based.

¹³C NMR Data

TCB, 120C, 0.05M CrAcAc		
Freq ppm	Intensity	
39.3416	7.78511	MB ₂
38.2329	5.03571	MB ₃ +
37.8616	9.01667	MB ₃ +
37.5857	3.33517	MB ₃ +
37.2462	31.8174	αB ₁ , 3B ₃
36.6415	2.92585	αB ₁ , 3B ₃
34.668	5.10337	αγ ⁺ B
34.2384	38.7927	αγ ⁺ B
33.7397	16.9614	3B ₅
33.3471	3.23743	3B ₆ +, 3EOC
32.9387	16.0951	γ ⁺ γ ⁺ B, 3B ₄
31.9148	27.6457	γ ⁺ γ ⁺ B, 3B ₄
31.1297	6.03301	γ ⁺ γ ⁺ B, 3B ₄
30.212	59.4286	γ ⁺ γ ⁺ B, 3B ₄
29.7398	317.201	γ ⁺ γ ⁺ B, 3B ₄
29.3101	32.1392	γ ⁺ γ ⁺ B, 3B ₄
27.1511	46.0554	βγ ⁺ B, 2B ₂
27.0185	53.103	βγ ⁺ B, 2B ₂
26.419	9.8189	βγ ⁺ B, 2B ₂
24.244	2.46963	ββB
22.6207	28.924	2B ₅ +, 2EOC
20.0479	3.22712	2B ₃
19.7084	18.5679	1B ₁
14.3929	3.44368	1B ₃
13.8677	30.6056	1B ₄ +, 1EOC
10.9448	9.43801	1B ₂

Example 172

- 5 4-Methyl-1-pentene (20 ml) was polymerized in methylene chloride (10 ml) for 19 hr using catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆⁻ (0.04 g, 0.05 mmol). The solvent and unreacted monomer were removed in vacuo. The polymer was precipitated to
- 10 remove residual monomer by addition of excess acetone to a chloroform solution. The precipitated polymer was dried in vacuo to give a 5.7 g yield. ¹³C NMR (trichlorobenzene, 120°C) integrated to give 518 methyls per 1000 methylene carbon atoms. Thermal
- 15 analysis showed Tg -30.3°C.

Listed below are the ¹³C NMR data upon which the above analysis is based.

¹³C NMR Data
TCB, 120C, 0.05M CrAcAc

Freq ppm	Intensity
47.8896	13.3323
47.4011	8.54293
45.7127	26.142
45.1392	17.4909
43.9658	13.9892
43.1375	12.7089
42.6171	11.5396
41.8207	9.00437
39.203	64.9357
37.9712	24.4318
37.3075	87.438
35.4862	16.3581
34.9553	24.5286
34.35	31.8827
33.3624	25.7696
33.0226	42.2982
31.4403	25.3221
30.6226	38.7083
28.504	26.8149
27.989	81.8147
27.7341	78.3801
27.5802	94.6195
27.458	75.8356
27.0864	35.5524
25.6103	97.0113
23.4333	59.6829
23.0563	41.5712
22.536	154.144
21.9944	5.33517
20.7307	16.294
20.4971	34.7892
20.2953	29.9359
19.7378	62.0082

Example 173

1-Eicosene (19.0 g) was polymerized in methylene chloride (15 ml) for 24 hr using catalyst {[(2,6-i-
5 PrPh)₂DABMe₂] PdCH₂CH₂CH₂C(O)OCH₃} SbF₆⁻ (0.047 g, 0.05 mmol). The solvent and unreacted monomer were removed in vacuo. The polymer was precipitated to remove residual monomer by addition of excess acetone to a chloroform solution of the polymer. The solution was
10 filtered to collect the polymer. The precipitated polymer was dried in vacuo to give a 5.0 g yield. ¹³C NMR quantitative analysis, branching per 1000 CH₂: Total methyls (27), Methyl (14.3), Ethyl (0), Propyl

(0.2), Butyl (0.6), Amyl (0.4), $\geq$ Hexyl and end of chains (12.4).

Integration of the CH₂ peaks due to the structure -CH(R)CH₂CH(R')-, where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 82% of these structures, R = Me.

Listed below are the ¹³C NMR data upon which the above analysis is based.

10

¹³C NMR data

TCB, 120C, 0.05M CrAcAc

<u>Freq ppm</u>	<u>Intensity</u>	
37.7853	13.978	MB ₂ ⁺
37.1428	52.1332	α B
34.1588	41.067	α B ₄ ⁺
32.826	26.6707	MB ₁
31.8066	24.9262	3B ₆ ⁺ , 3EOC
30.0703	96.4154	$\gamma^+\gamma^+$ B, 3B ₄
29.6243	1239.8	$\gamma^+\gamma^+$ B, 3B ₄
27.0013	78.7094	B γ^+ B, (4B ₅ , etc.)
22.5041	23.2209	2B ₅ ⁺ , 2EOC
19.605	30.1221	1B ₁
13.759	23.5115	1B ₄ ⁺ , EOC

Example 174

The complex [(2,6-i-PrPh)₂DABH₂]PdMeCl (0.010 g, 0.019 mmol) and norbornene (0.882 g, 9.37 mmol) were weighed into a vial and dissolved in 2 ml CH₂Cl₂. NaBAF (0.032g, 0.036 mmol) was rinsed into the stirring mixture with 2 ml of CH₂Cl₂. After stirring about 5 minutes, there was sudden formation of a solid precipitate. Four ml of o-dichlorobenzene was added and the solution became homogenous and slightly viscous. After stirring for 3 days, the homogeneous orange solution was moderately viscous. The polymer was precipitated by addition of the solution to excess MeOH, isolated by filtration, and dried in vacuo to give 0.285 g (160 equivalents norbornene per Pd) bright orange glassy solid. DSC (two heats, 15°C/min) showed no thermal events from -50 to 300°C. This is consistent with addition type poly(norbornene). Ring-opening polymerization of norbornene is known to

produce an amorphous polymer with a glass transition temperature of about 30-55°C.

Example 175

The solid complex $\{[(2,6-i-$
5 $\text{PrPh})_2\text{DABH}_2]\text{PdMe}(\text{Et}_2\text{O})\}\text{SbF}_6^-$ (0.080 g, 0.10 mmol) was added as a solid to a stirring solution of norbornene (1.865 g) in 20 ml of o-dichlorobenzene in the drybox. About 30 min after the start of the reaction, there was slight viscosity (foam on shaking) and the homogeneous
10 mixture was dark orange/red. After stirring for 20 h, the solvent and unreacted norbornene were removed in vacuo to give 0.508 g orange-red glassy solid (54 equivalents norbornene/Pd). ^1H NMR (CDCl_3): broad featureless peaks from 0.8-2.4 ppm, no peaks in the
15 olefinic region. This spectrum is consistent with addition type poly(norbornene). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=566$ $M_w=1640$ $M_w/M_n=2.90$.

20

Example 176

4-Methyl-1-pentene (10 ml) and ethylene (1 atm) were copolymerized in 30 ml of chloroform according to example 125 using catalyst $\{[(2,6-i-$
25 $\text{PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.084 g, 0.10 mmol) to give 23.29 g highly viscous yellow oil. The ^1H NMR spectrum was similar to the poly(ethylene) of example 110 with 117 methyl carbons per 1000 methylene carbons. ^{13}C NMR quantitative analysis, branching per 1000 CH_2 : Total methyls (117.1), Methyl (41.5), Ethyl
30 (22.7), Propyl (3.3), Butyl (13), Amyl (1.2), $\geq\text{Hexyl}$ and end of chains (33.1), $\geq\text{Amyl}$ and end of chains (42.3). By ^{13}C NMR this sample contains two identifiable branches at low levels attributable to 4-methyl-1-pentene. The Bu and $\geq\text{Amyl}$ peaks contain small
35 contributions from isopropyl ended branch structures.

Example 177

CoCl_2 (500 mg, 3.85 mmol) and (2,6-i-PrPh) $_2$ DABAn (2.0 g, 4.0 mmol) were combined as solids and dissolved

in 50 mL of THF. The brown solution was stirred for 4 hours at 25°C. The solvent was removed under reduced pressure resulting in a brown solid (1.97 g, 82% yield).

5 A portion of the brown solid (12 mg) was immediately transferred to another Schlenk flask and dissolved in 50 mL of toluene under 1 atmosphere of ethylene. The solution was cooled to 0°C, and 1.5 mL of a 10% MAO solution in toluene was added. The
10 resulting purple solution was warmed to 25°C and stirred for 12 hours. The polymerization was quenched and the polymer precipitated from acetone. The white polymer (200 mg) was collected by filtration and dried under reduced pressure. $M_n = 225,000$, $M_w = 519,000$,
15 $M_w/M_n = 2.31$, $T_g = -42^\circ$, $T_m = 52^\circ\text{C}$ and 99.7°C .

Example 178

Ethyl 10-undecenoate (10 ml) and ethylene (1 atm) were copolymerized in 30 ml of CH_2Cl_2 according to example 125 using catalyst $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}\text{SbF}_6^-$ (0.084 g, 0.10
20 mmol). The copolymer was precipitated by removing most of the CH_2Cl_2 in vacuo, followed by addition of excess acetone. The solution was decanted and the copolymer was dried in vacuo to give 1.35 g viscous fluid. ^1H
25 NMR (CDCl_3): 0.75-0.95(m, CH_3); 0.95-1.5(m, - $\text{C}(\text{O})\text{OCH}_2\text{CH}_3$, CH_2 , CH); 1.5-1.7(m, $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3$); 1.9-2.0(m, $-\text{CH}_2\text{CH}=\text{CH}-$); 2.3(t, $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3$); 4.15(q, $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3$); 5.40(m, $-\text{CH}=\text{CH}-$). The olefinic and allylic peaks are due to isomerized ethyl
30 10-undecenoate which has coprecipitated with the copolymer. Adjusting for this, the actual weight of copolymer in this sample is 1.18 g. The copolymer was reprecipitated by addition of excess acetone to a chloroform solution. ^1H NMR of the reprecipitated
35 polymer is similar except there are no peaks due to isomerized ethyl 10-undecenoate at 1.9-2.0 and 5.40 ppm. Based on integration, the reprecipitated copolymer contains 7.4 mole % ethyl 10-undecenoate, and

63 methyl carbons per 1000 methylene carbons. ^{13}C NMR
quantitative analysis, branching per 1000 CH_2 : Total
methylys (84.5), Methyl (31.7), Ethyl (16.9), Propyl
(1.5), Butyl (7.8), Amyl (4.4), $\geq$ Hexyl and end of
5 chains (22.3). GPC (THF, PMMA standard): $M_n=20,300$
 $M_w=26,300$ $M_w/M_n = 1.30$. ^{13}C NMR quantitative
analysis, branching per 1000 CH_2 : ethyl ester (37.8),
Ester branches $-\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{CH}_3$ as a % of total
ester: $n \geq 5$ (65.8), $n=4$ (6.5), $n=1,2,3$ (26.5), $n=0$
10 (1.2).

Listed below are the ^{13}C NMR data upon which the
above analysis is based.

¹³C NMR Data

Freq ppm	Intensity
59.5337	53.217
39.7234	2.57361
39.3145	7.80953
38.2207	11.9395
37.8437	20.3066
37.2225	29.7808
36.7181	5.22075
34.6792	17.6322
34.265	107.55
33.7181	21.9369
33.3093	8.22574
32.9164	15.0995
32.396	8.52655
32.0828	5.79098
31.9075	37.468
31.127	13.8003
30.6757	8.38026
30.2084	52.5908
29.9961	27.3761
29.72	151.164
29.5076	39.2815
29.2899	69.7714
28.727	6.50082
27.5164	20.4174
26.9908	64.4298
26.5713	9.18236
26.3749	11.8136
25.5519	4.52152
25.0528	43.7554
24.2457	7.9589
23.1094	10.0537
22.9926	4.71618
22.6156	37.2966
20.0245	2.4263
19.6847	25.9312
19.1643	5.33693
17.5183	2.20778
14.2954	66.1759
13.8653	43.8215
13.414	2.52882
11.1521	5.9183
10.9237	14.9294
174.945	3.27848
172.184	125.486
171.695	4.57235

Example 179

The solid complex $\{[(2,6-i-PrPh)_2DABH_2]PdMe(Et_2O)\}SbF_6^-$ (0.080 g, 0.10 mmol) was
5 added as a solid to a stirring solution of cyclopentene
(1.35 g, 20 mmol) in 20 ml of dichlorobenzene in the

drybox. After stirring 20 h, the slightly viscous solution was worked up by removing the solvent in vacuo to give 1.05 g sticky solid (156 equivalents of cyclopentene per Pd). ^1H NMR (CDCl_3): complex spectrum from 0.6-2.6 ppm with maxima at 0.75, 1.05, 1.20, 1.55, 1.65, 1.85, 2.10, 2.25, and 2.50. There is also a multiplet for internal olefin at 5.25-5.35. This is consistent with a trisubstituted cyclopentenyl end group with a single proton (W. M. Kelly et. al., Macromolecules 1994, 27, 4477-4485.) Integration assuming one olefinic proton per polymer chain gives DP=8.0 and Mn=540. IR (Thin film between NaCl plates, cm^{-1}): 3048 (vw, olefinic end group, CH stretch), 1646 (vw, olefinic end group, $\text{R}_2\text{C}=\text{CHR}$ trisubstituted double bond stretch), 1464 (vs), 1447 (vs), 1364 (m), 1332 (m), 1257 (w), 1035 (w), 946 (m), 895 (w), 882 (w), 803 (m, cyclopentenyl end group, $\text{R}_2\text{C}=\text{CHR}$ trisubstituted double bond, CH bend), 721 (vw, cyclopentenyl end group, $\text{RHC}=\text{CHR}$ disubstituted double bond, CH bend). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=138$ $M_w=246$ $M_w/M_n=1.79$.

Example 180

25 The solid complex $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdCH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_3\}\text{SbF}_6^-$ (0.084 g, 0.10 mmol) was added to a stirring solution of 10.0 ml cyclopentene in 10 ml CHCl_3 in the drybox. After stirring for 20 h, the mixture appeared to be separated into two phases. The solvent and unreacted monomer were removed in vacuo leaving 2.20 g off-white solid (323 equivalents cyclopentene per Pd). DSC (25 to 300°C, 15°C/min, first heat): $T_g = 107^\circ\text{C}$, T_m (onset) = 165 °C, T_m (end) = 260 °C, Heat of fusion = 29 J/g.

35 Similar results were obtained on the second heat. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using

DEMANDES OU BREVETS VOLUMINEUX

LA PRÉSENTE PARTIE DE CETTE DEMANDE OU CE BREVET
COMPREND PLUS D'UN TOME.

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JUMBO APPLICATIONS/PATENTS

THIS SECTION OF THE APPLICATION/PATENT CONTAINS MORE
THAN ONE VOLUME

THIS IS VOLUME 1 OF 2

NOTE: For additional volumes please contact the Canadian Patent Office

WHAT IS CLAIMED IS:

1. A process for the polymerization of one or more olefins, comprising the step of contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, said one or more olefins with
5 a catalyst composition adapted for the polymerization of said one or more olefins, the catalyst composition comprising a transition metal complex of a neutral bidentate ligand, wherein the transition metal and the neutral bidentate ligand are coordinated in a square planar configuration; the neutral
10 bidentate ligand and the transition metal are coordinated through two different nitrogen atoms, the nitrogen atoms being part of the neutral bidentate ligand; and the neutral bidentate ligand has sufficient steric bulk on both sides of the coordination plane to permit formation of a polymer of
15 said one or more olefins with a degree of polymerization of at least about 10 or more.

2. The process of claim 1, wherein the transition metal is in a positive oxidation state.

3. The process of claim 1, wherein the transition metal
20 has a d^8 electronic configuration.

4. The process of claim 1, wherein the transition metal is nickel, cobalt, iron or palladium.

5. The process of claim 1, wherein the transition metal is nickel or palladium.

25 6. The process of claim 5, wherein the transition metal is nickel.

7. The process of claim 1, wherein the transition metal has further bonded to it a group Q, a group S or both, in an amount equal to the oxidation state of the transition metal,
30 wherein Q and S are independently an alkyl, chloride, iodide or bromide.

8. The process of claim 1, wherein the transition metal has an oxidation state of 2.

9. The process of claim 7, wherein the catalyst composition further comprises a compound W, which is a neutral
5 Lewis acid capable of abstracting either Q^- or S^- to form WQ^- or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion.

10. The process of claim 9, wherein the compound W is
10 further capable of transferring a hydride or alkyl group to the transition metal.

11. The process of claim 1, wherein the catalyst composition further comprises an alkyl aluminum compound.

12. The process of claim 1, wherein the transition metal
15 has bonded to it another ligand that may be displaced by said olefin or add to said olefin, or both.

13. The process of claim 1, wherein the neutral bidentate ligand is an α -diimine.

14. The process of claim 1, wherein said one or more
20 olefins are selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, norbornene and a substituted norbornene, wherein each R^{17} is independently hydrocarbyl or substituted hydrocarbyl, provided that any olefinic bond in said olefin is
25 separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

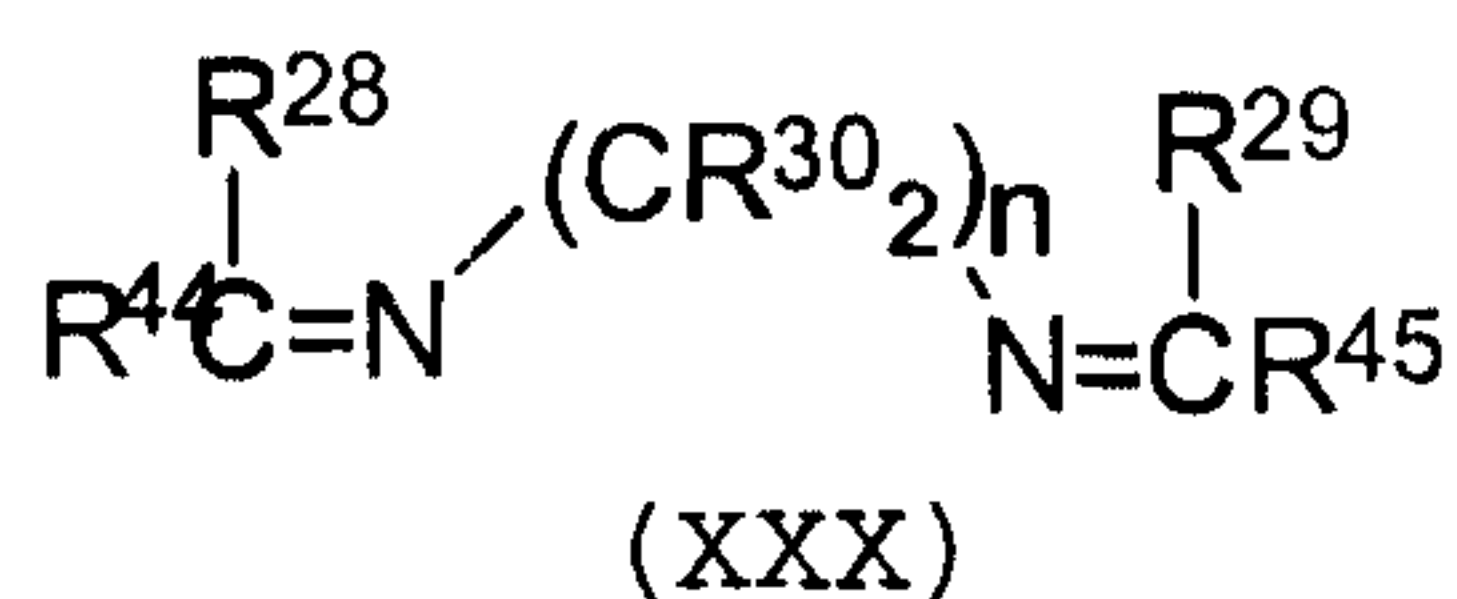
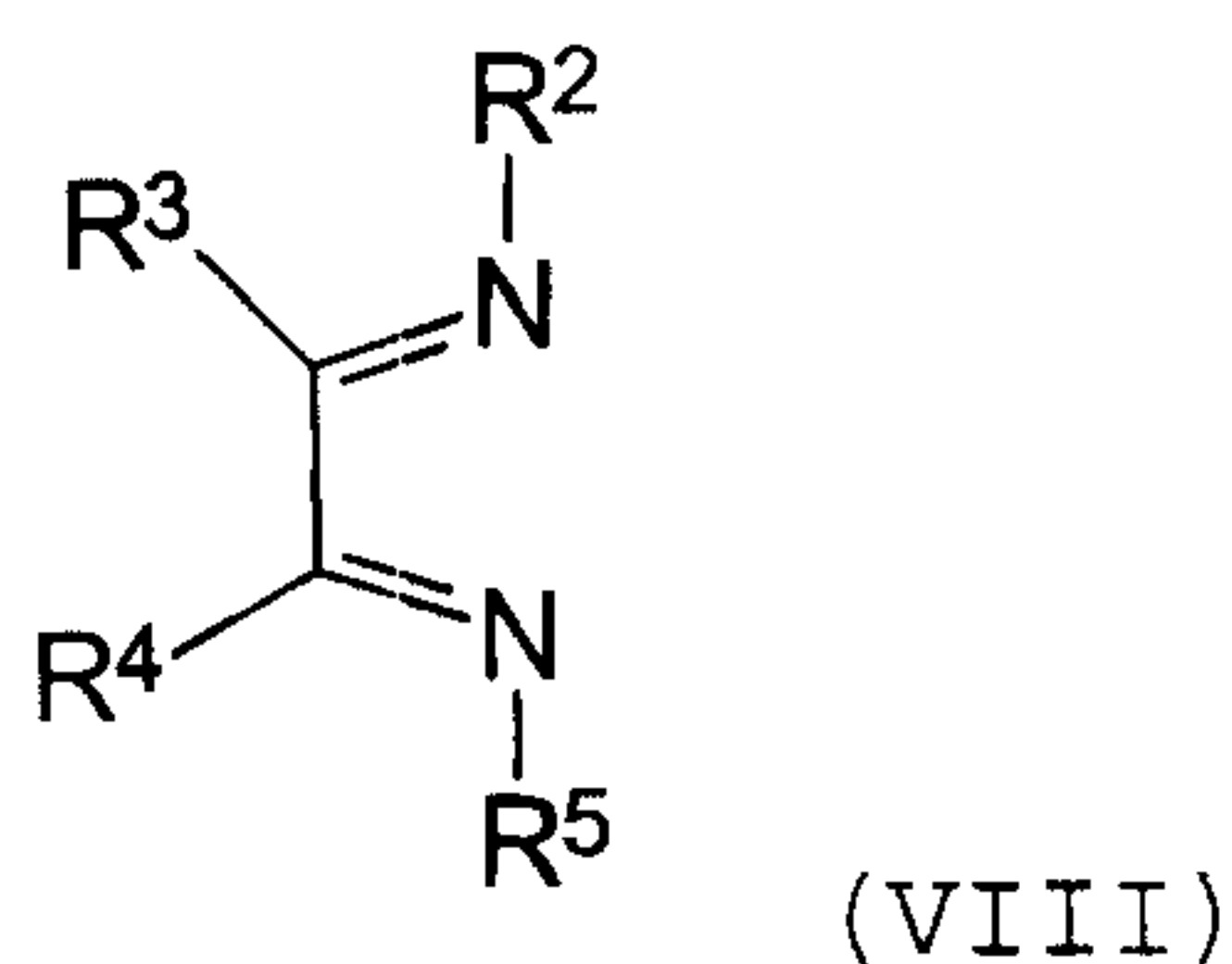
15. The process of claim 14, wherein said one or more olefins consist essentially of ethylene such that an ethylene homopolymer is produced.

16. The process of any one of claims 1, 3 and 7-15, wherein the transition metal is nickel or palladium in a positive oxidation state; and the bidentate ligand, has an Ethylene Exchange Rate of less than $20,000 \text{ L-mol}^{-1}\text{s}^{-1}$ when said catalyst contains a palladium atom, and less than $50,000 \text{ L-mol}^{-1}\text{s}^{-1}$ when said catalyst contains a nickel atom; and provided that when M is Pd a diene is not present.

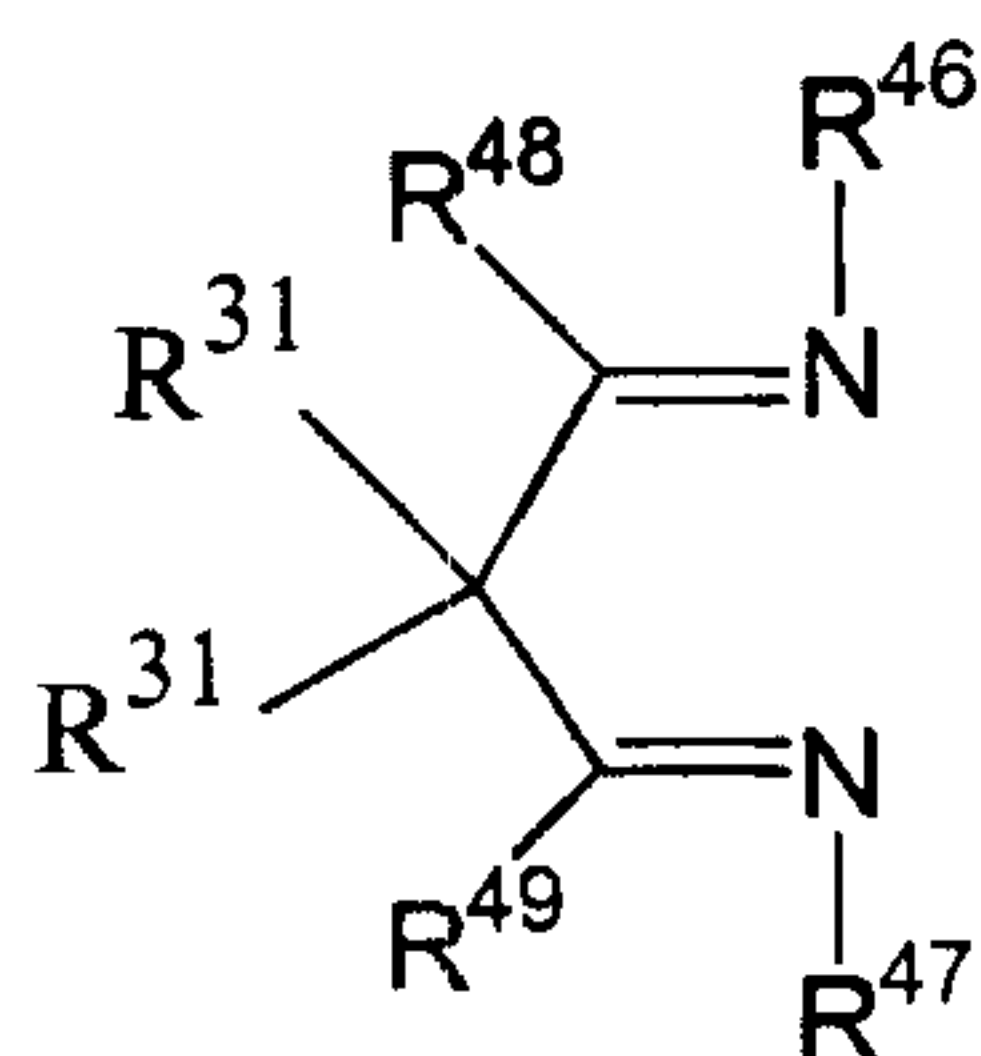
17. The process of claim 16, wherein said Ethylene Exchange Rate is less than $10,000 \text{ L-mol}^{-1}\text{s}^{-1}$ when said catalyst contains a palladium atom, and less than $25,000 \text{ L-mol}^{-1}\text{s}^{-1}$ when said catalyst contains a nickel atom.

18. The process of claim 16, wherein the transition metal is nickel.

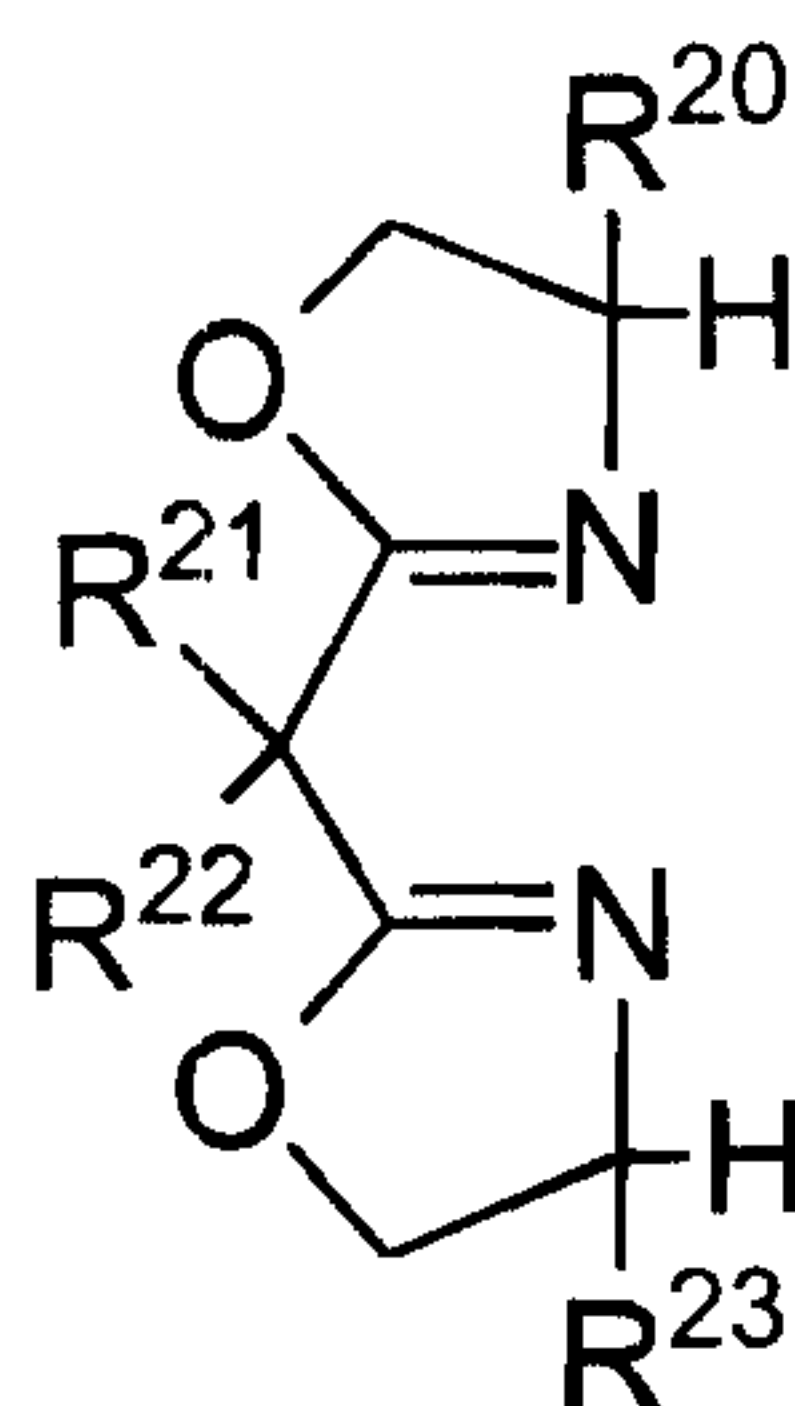
19. The process of claim 14, wherein the neutral bidentate ligand is selected from the group consisting of



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(XXIII)



(XXXII)

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

R⁴⁴ is hydrocarbyl or substituted hydrocarbyl, and R²⁸ is hydrogen, hydrocarbyl or substituted hydrocarbyl or R⁴⁴ and R²⁸ taken together form a ring;

R⁴⁵ is hydrocarbyl or substituted hydrocarbyl, and R²⁹ is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring;

R⁴⁶ and R⁴⁷ are each independently hydrocarbyl, or substituted hydrocarbyl, provided that the carbon atom bound

to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{48} and R^{49} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

5 each R^{31} is independently hydrocarbyl, substituted hydrocarbyl, or hydrogen;

 each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

10 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

R^{21} and R^{22} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

15 when said neutral bidentate ligand is (XXX) M is not Pd;
 when M is Pd a diene is not present; and

 when norbornene or substituted norbornene is used no other olefin is present.

20. The process of claim 19, wherein:

20 R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring;

25 each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other

olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R^{44} is hydrocarbyl, and R^{28} is hydrogen or hydrocarbyl, or R^{44} and R^{28} taken together form a ring;

5 R^{45} is hydrocarbyl, and R^{29} is hydrogen or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen or hydrocarbyl, or two of R^{30} taken together form a ring;

each R^{31} is independently hydrogen or hydrocarbyl;

10 R^{46} and R^{47} are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{48} and R^{49} are each independently hydrogen or hydrocarbyl;

R^{20} and R^{23} are independently hydrocarbyl; and

15 R^{21} and R^{22} are each independently hydrogen or hydrocarbyl.

21. The process of claim 19, wherein said transition metal also has bonded to it a ligand that may be displaced by said olefin or add to said olefin, or both.

20 22. The process of claim 19, wherein the transition metal is Co, Fe, Ni or Pd.

23. The process of claim 22, wherein the transition metal is Ni or Pd.

24. The process of claim 19, wherein:

25 the transition metal is Ni or Pd

the neutral bidentate ligand is of the formula (VIII);

said one or more olefins are a fluorinated olefin of the formula $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_a\text{R}_f\text{R}^{42}$, and an olefin is selected from the group consisting of ethylene and an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$;

5 a is an integer of 2 to 20;

R_f is perfluoroalkylene optionally containing one or more ether groups;

R^{42} is fluorine or a functional group; and

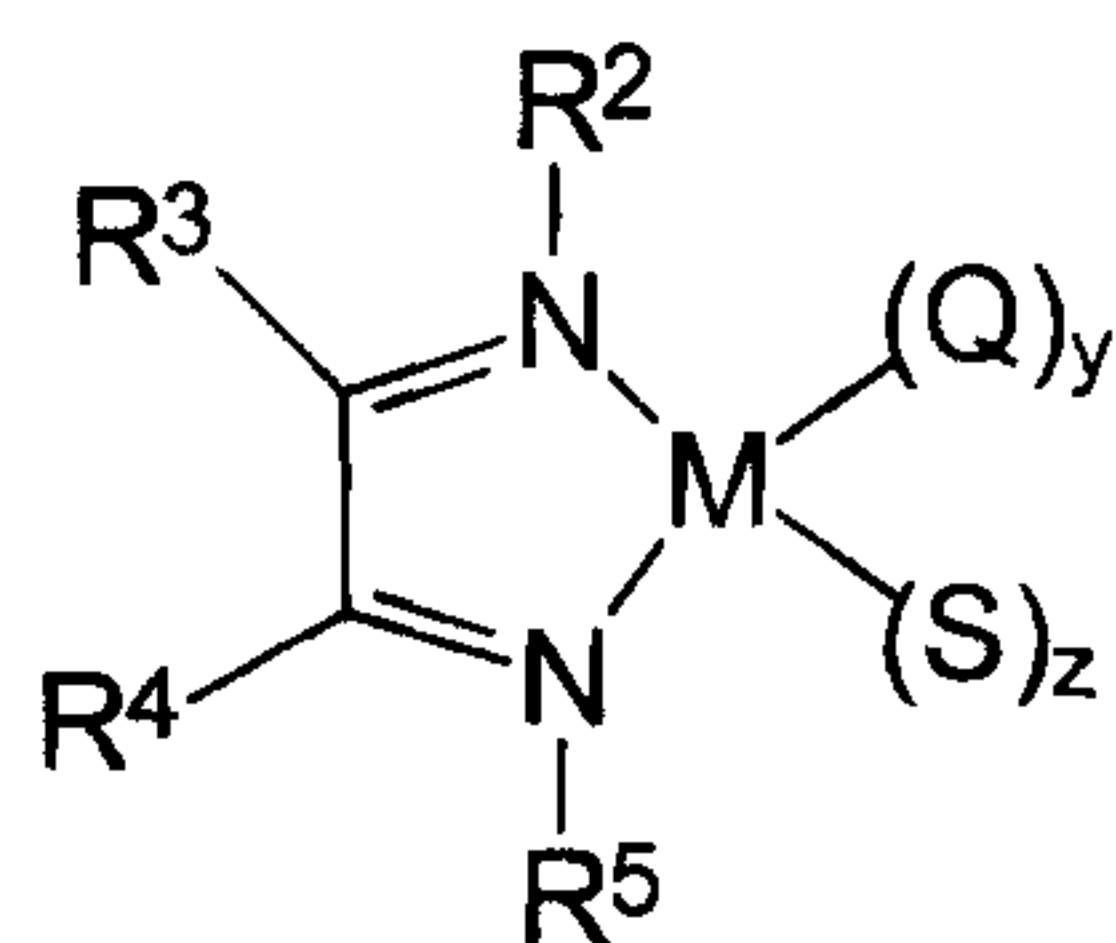
each R^{17} is independently saturated hydrocarbyl.

10 25. The process of claim 24, wherein:

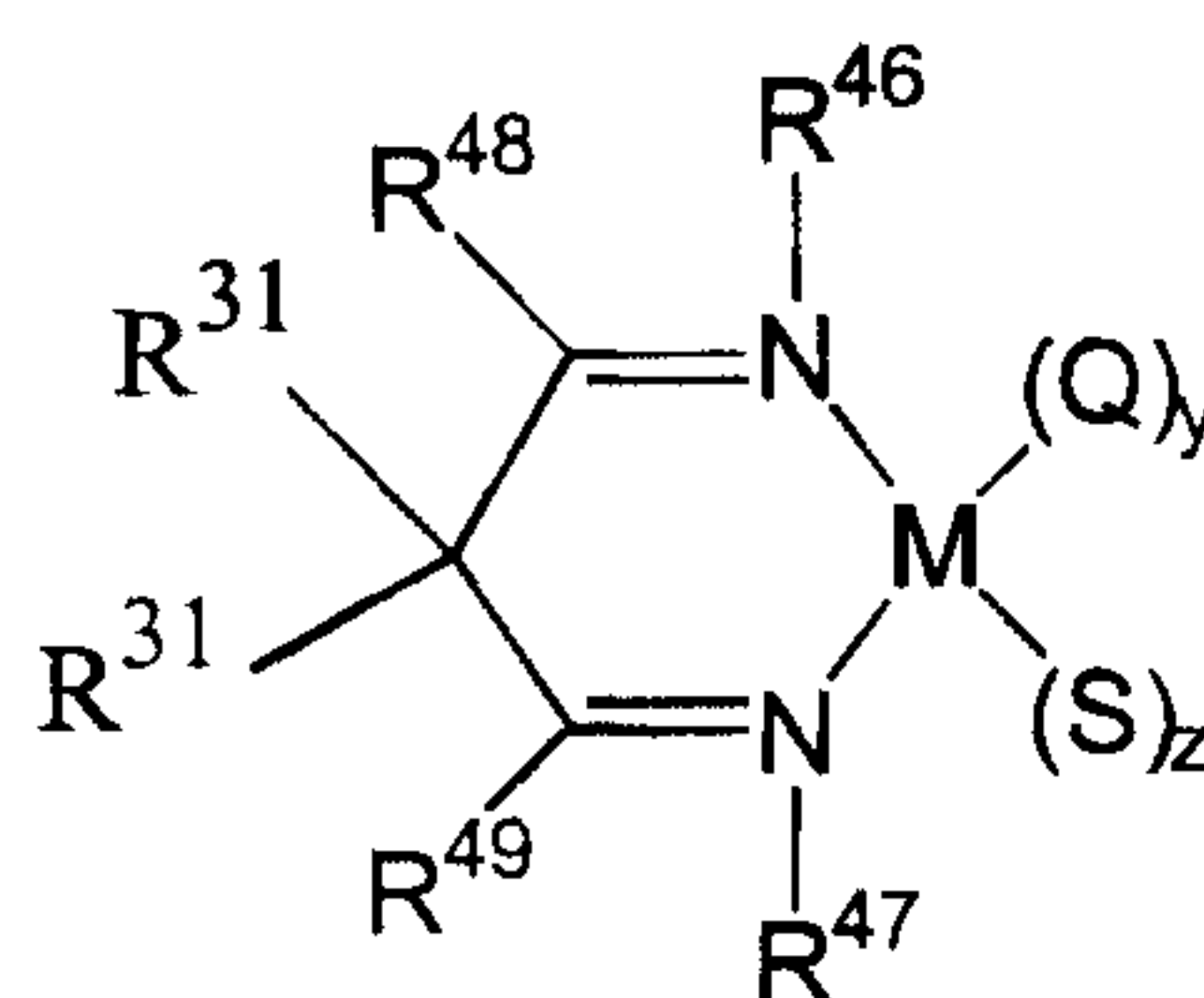
R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

15 R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

26. The process of claim 19, wherein the transition metal complex is of the formula (XI), (XV) or (XVII)

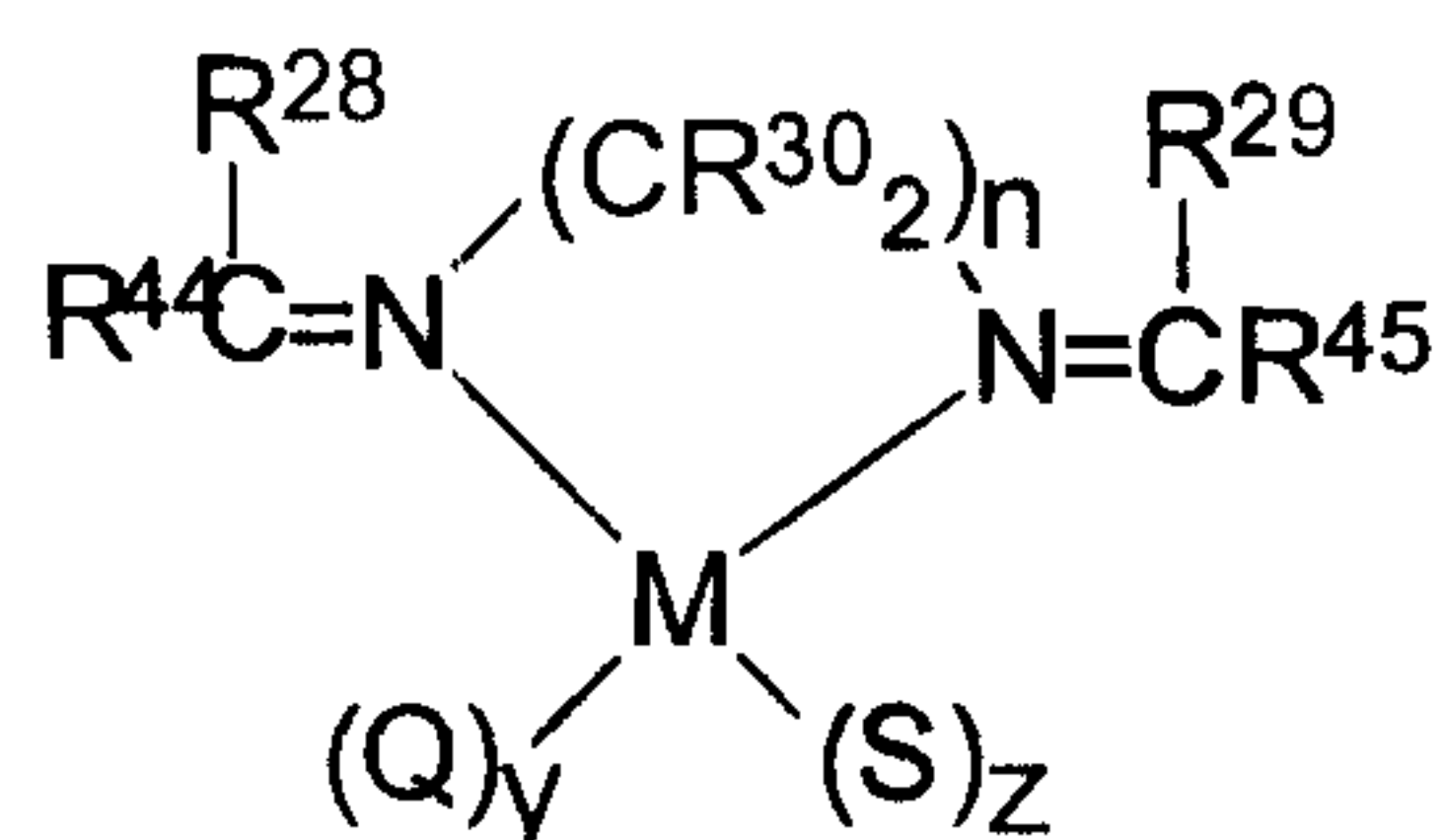


(XI)



(XV)

415



(XVII)

wherein:

M is Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd in an m oxidation state;

$$y + z = m$$

Q is alkyl, hydride, chloride, iodide, or bromide; and

S is alkyl, hydride, chloride, iodide, or bromide; and

the catalyst composition further comprises a compound W, which is a neutral Lewis acid capable of abstracting either Q⁻ or S⁻ to form WQ⁻ or WS⁻, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

provided that except when M is a rare earth metal, Ti, Zr, Sc, V, Cr, Fe, Co or Ni, then when both Q and S are each independently chloride, bromide or iodide, W is capable of transferring a hydride or alkyl group to M.

27. The process of claim 26, wherein:

R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

5 R^{44} is hydrocarbyl, and R^{28} is hydrogen or hydrocarbyl, or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl, and R^{29} is hydrogen or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

10 each R^{30} is independently hydrogen or hydrocarbyl, or two of R^{30} taken together form a ring;

each R^{31} is independently hydrogen or hydrocarbyl;

R^{46} and R^{47} are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

15 R^{48} and R^{49} are each independently hydrogen or hydrocarbyl.

28. The process of claim 26, wherein the compound W is R^9AlCl_2 , R^9_2AlCl , $R^9_3Al_2Cl_3$, or an alkylaluminumoxane in which the alkyl group has 1 to 4 carbon atoms, and wherein R^9 is alkyl containing 1 to 4 carbon atoms, and the molar ratio of
20 W:transition metal complex is about 5 to about 1000.

29. The process of claim 26, wherein:

M is Ti(IV), Q and S are chloride, and y and z are each both 2;

25 M is Zr(IV), Q and S are chloride, and y and z are each both 2;

M is Co(II), Q and S are bromide, and y and z are each both 1;

M is Fe(II), Q and S are chloride, and y and z are each both 1;

M is Sc(III), Q and S are chloride, y is 1 and z is 2;

5 M is Ni(II), Q and S are bromide or chloride, and y and z are each both 1;

M is Pd(II), Q and S are methyl, and y and z are each both 1;

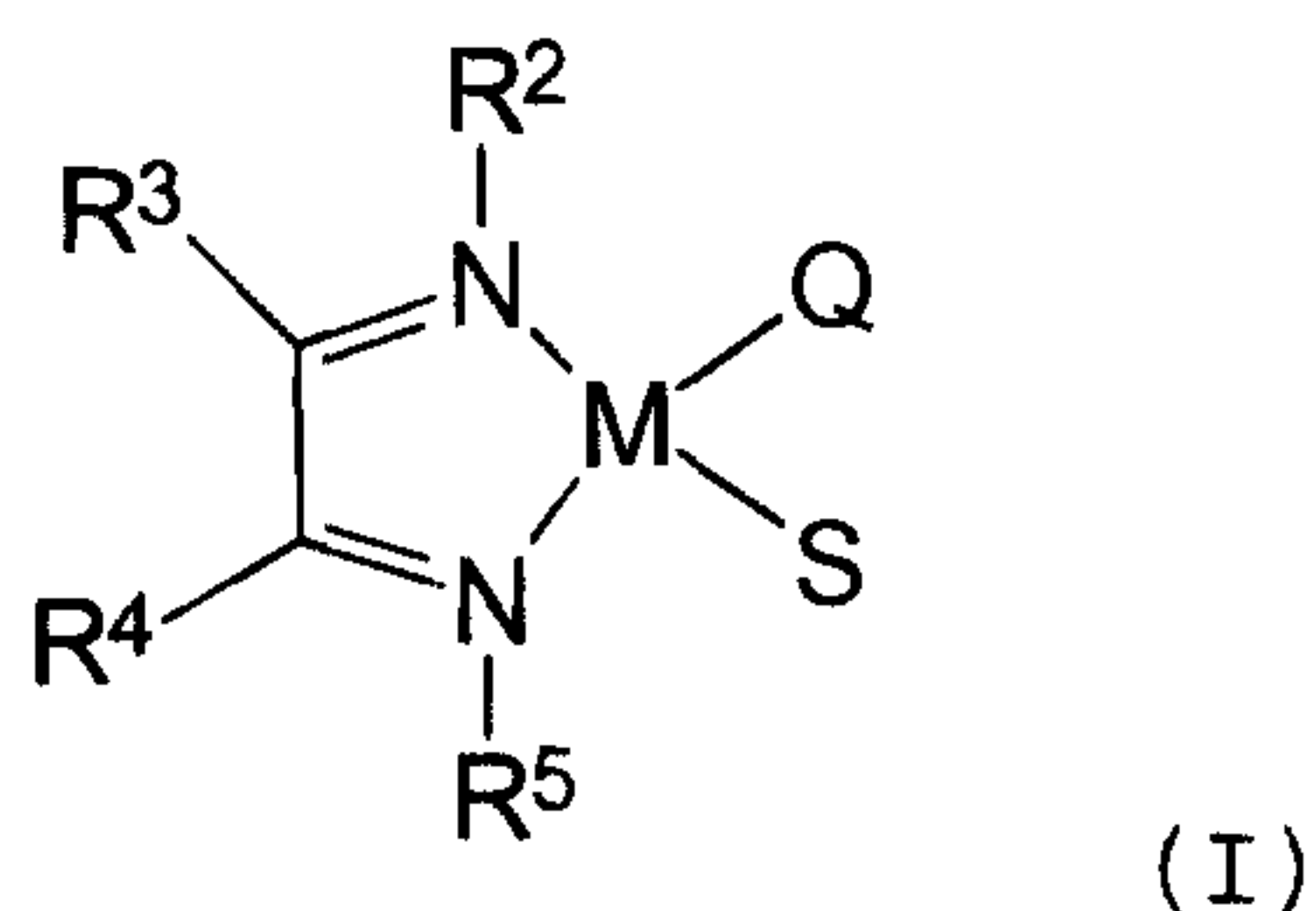
M is Pd(II), Q and S are chloride, and y and z are each both 1;

10 M is Ni(I), Q is methyl, chloride, bromide, iodide or acetylacetonate, y is 1, and z is 0;

M is Pd(II), Q is methyl and S is chloride, and y and z are each both 1; or

15 M is Ni(II), Q and S are methyl, and y and z are each both 1.

30. The process of claim 26, wherein the transition metal complex is of the formula (I)



wherein M is Ni(II), Co(II), Fe(II) or Pd(II).

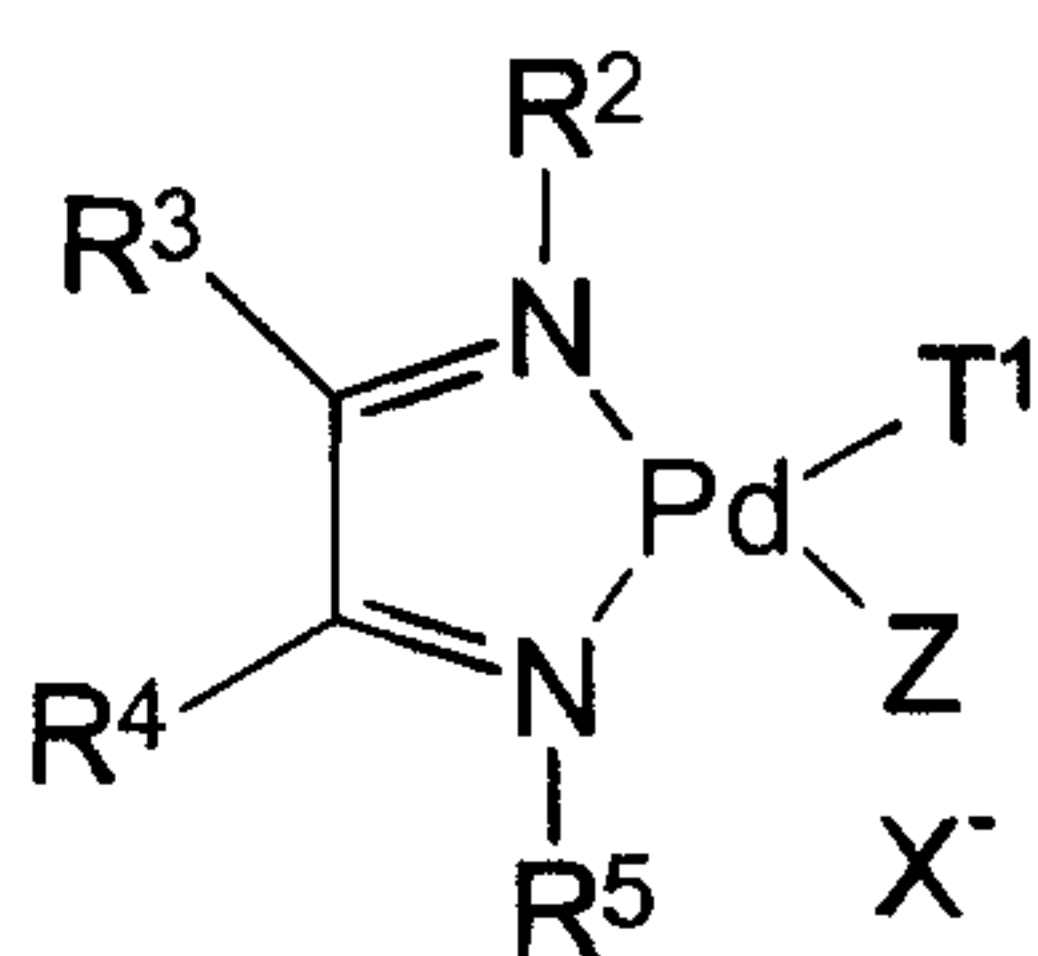
20 31. The process of claim 30, wherein:

R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

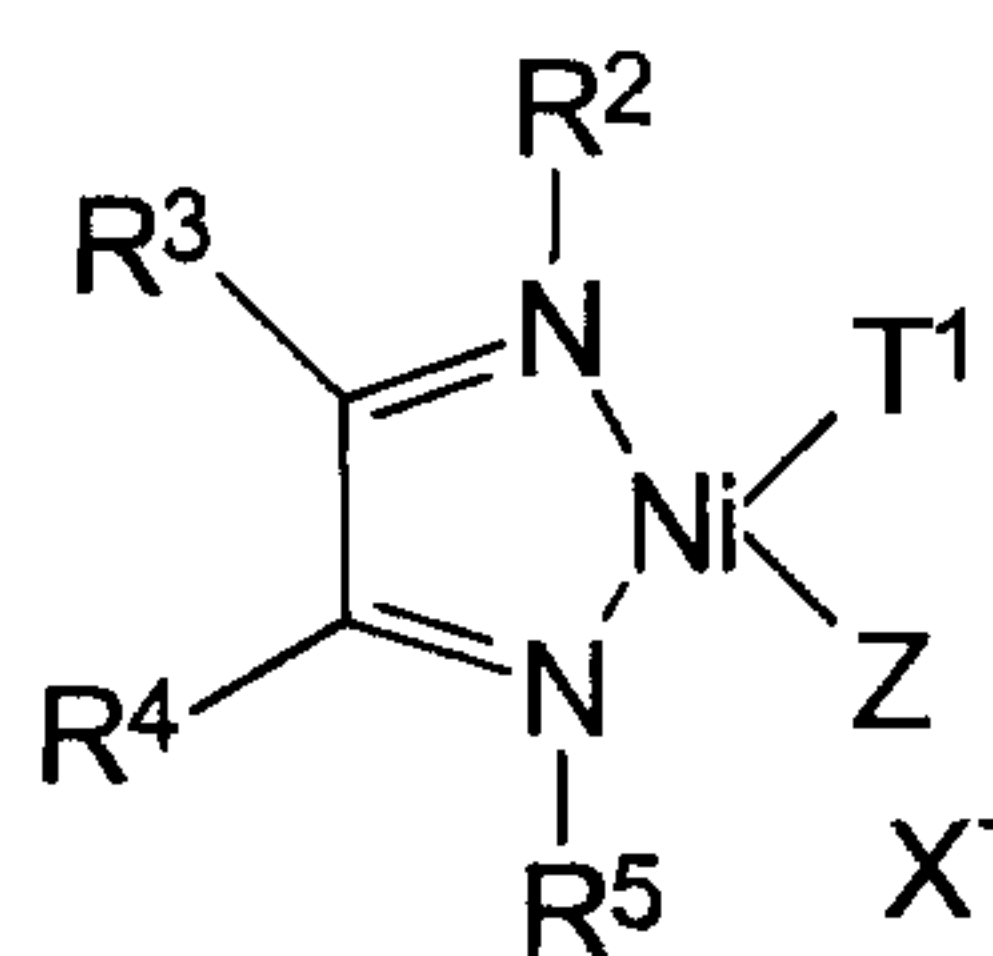
R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and

each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or
 5 at least two saturated carbon atoms.

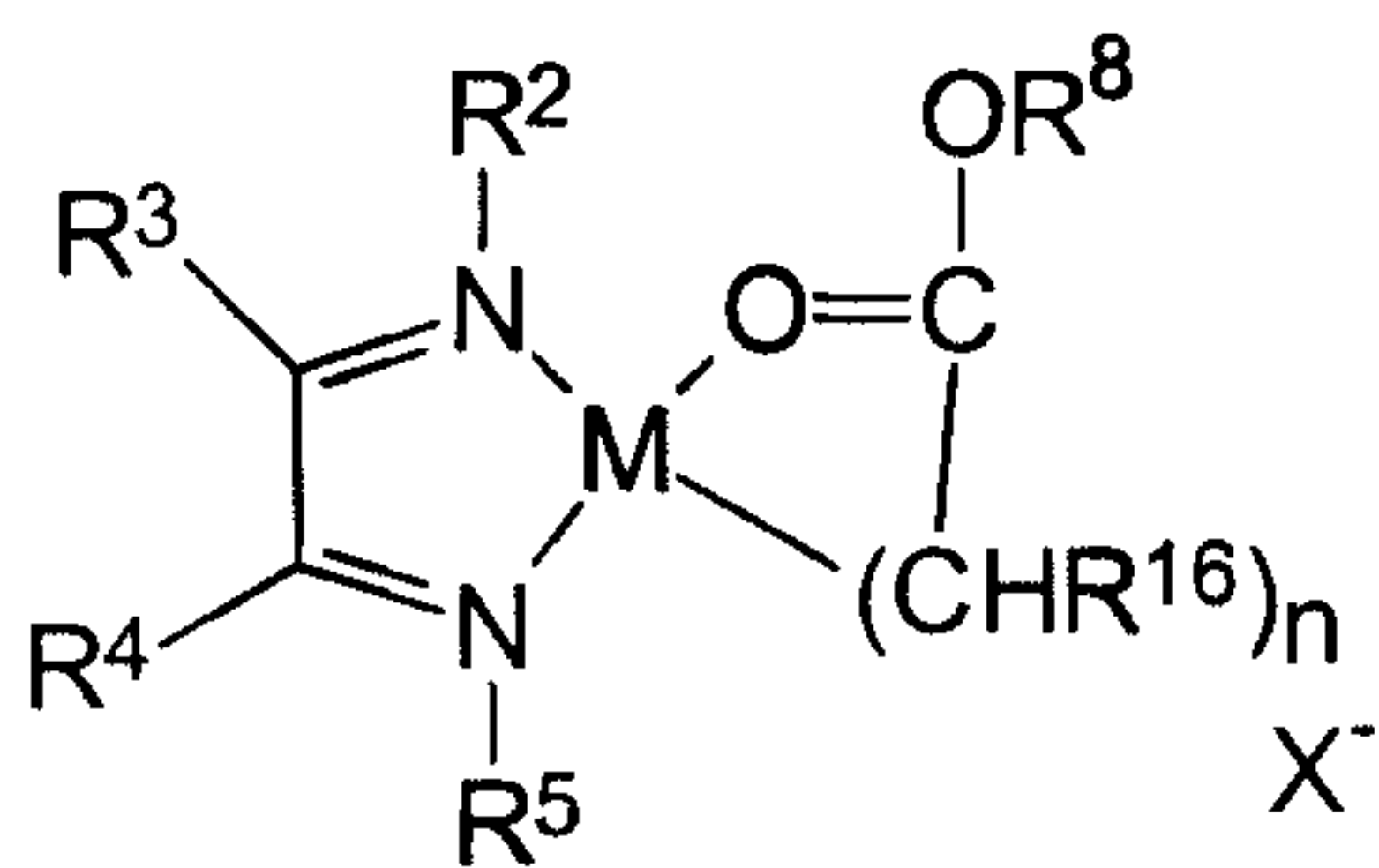
32. The process of claim 19, wherein the transition metal complex is of the formula (II), (III), (IV), (V) or (VII)



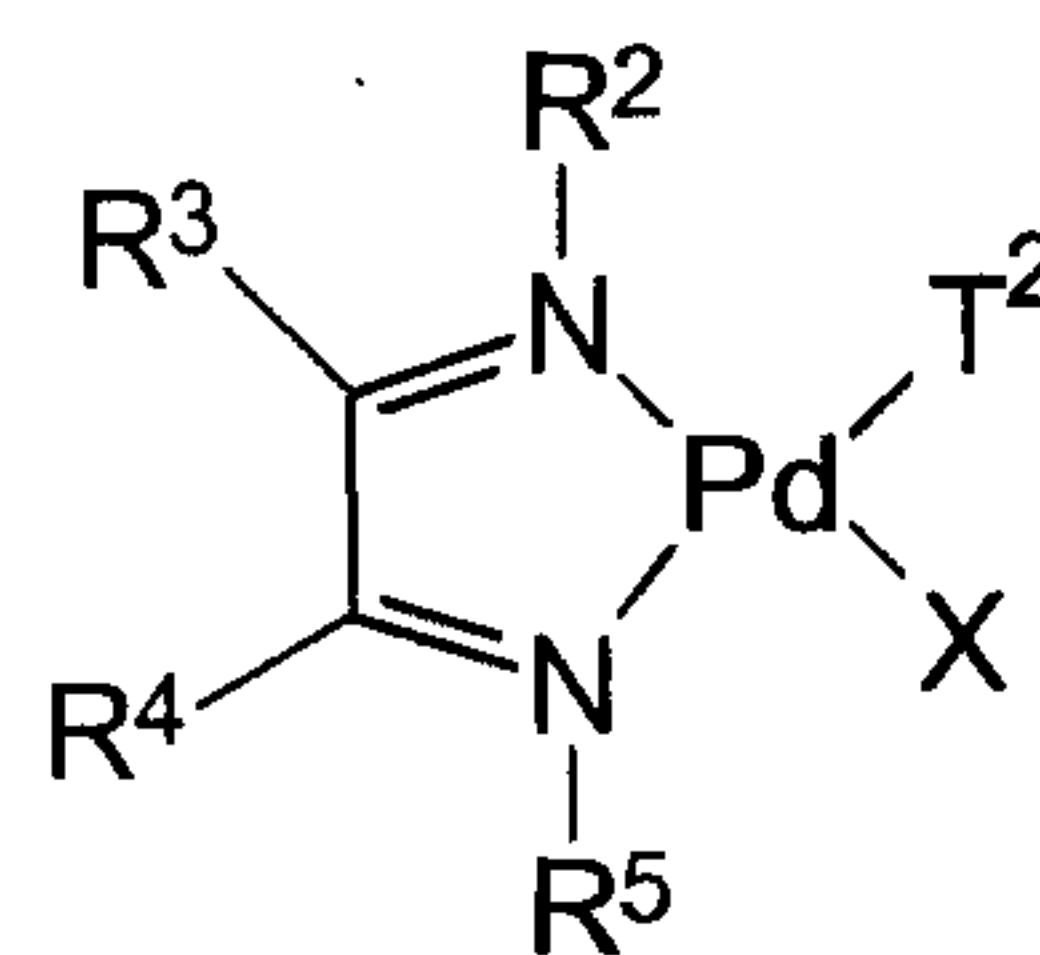
(II)



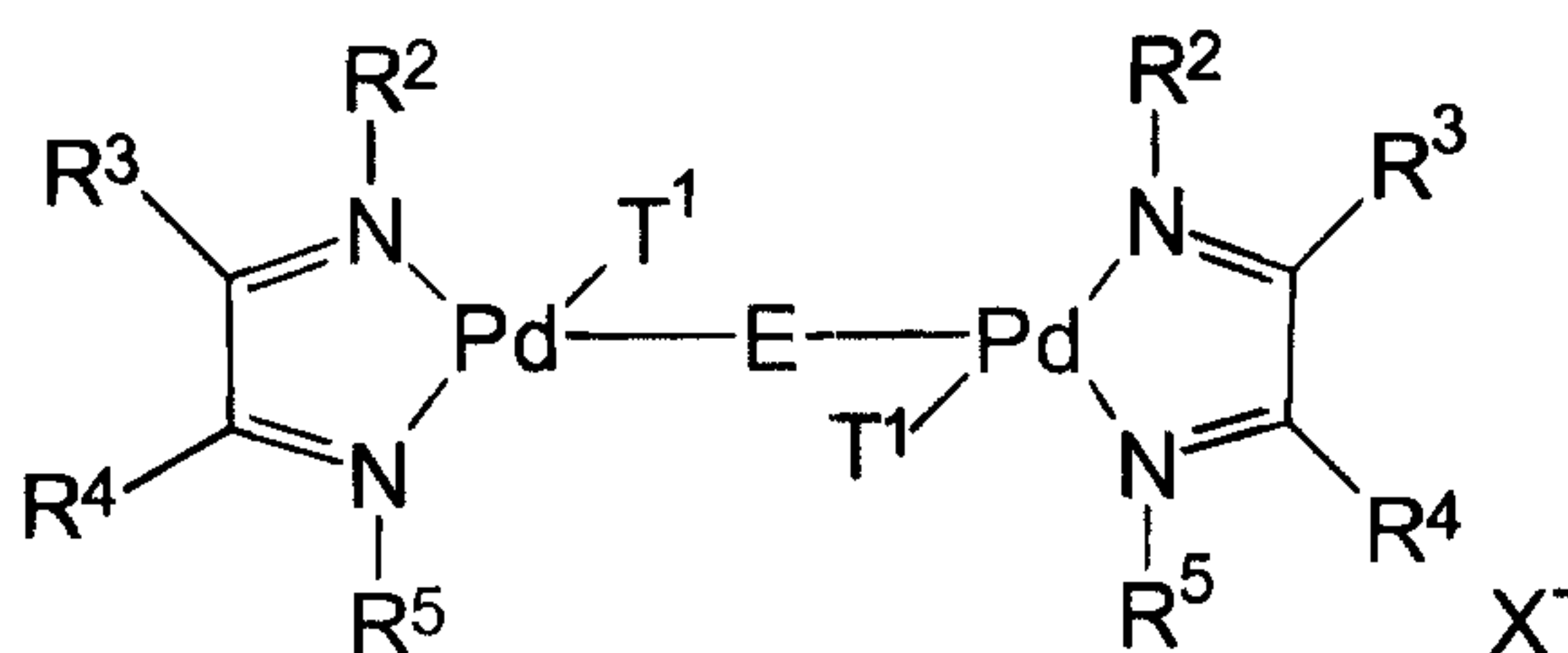
(III)



(IV)



(VII)



(V)

wherein:

T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

5 X is a weakly coordinating anion;

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

M is Ni(II) or Pd(II);

10 each R¹⁶ is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

E is halogen or -OR¹⁸;

R¹⁸ is hydrocarbyl not containing olefinic or acetylenic bonds;

15 R⁸ is hydrocarbyl; and

T² is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, R¹⁵C(=O)- or R¹⁵OC(=O)-.

20 33. The process of claim 32, wherein:

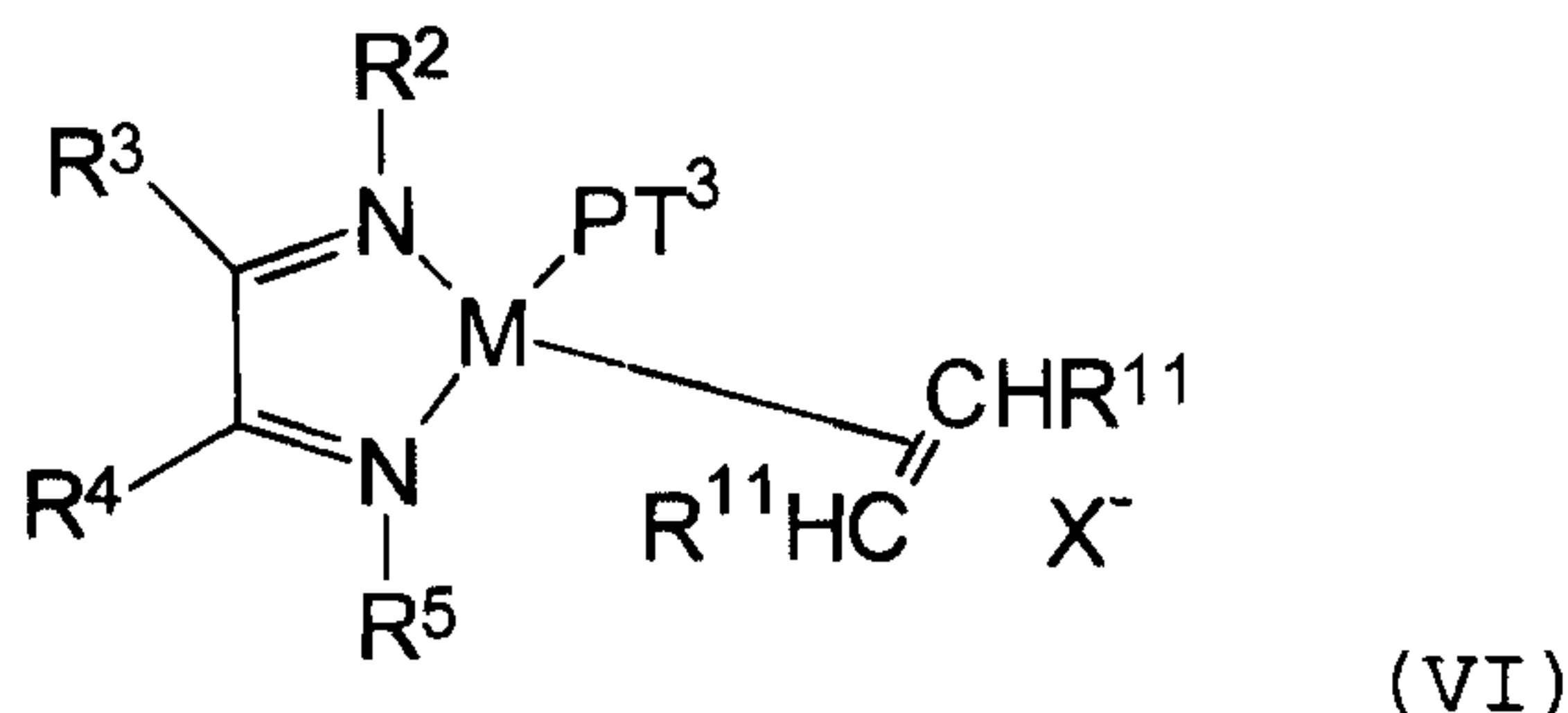
R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

25 R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring; and

each R¹⁷ is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other

olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

34. The process of claim 19, wherein the transition metal complex is of the formula (VI)



wherein:

M is Ni(II) or Pd(II);

each R^{11} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

10 T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-CH_2CH_2CH_2CO_2R^8$;

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, CO, or a vinyl ketone;

15

R^8 is hydrocarbyl;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

20

R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and

X is a weakly coordinating anion;

provided that when M is Ni(II), R^{11} is not $-\text{CO}_2R^8$.

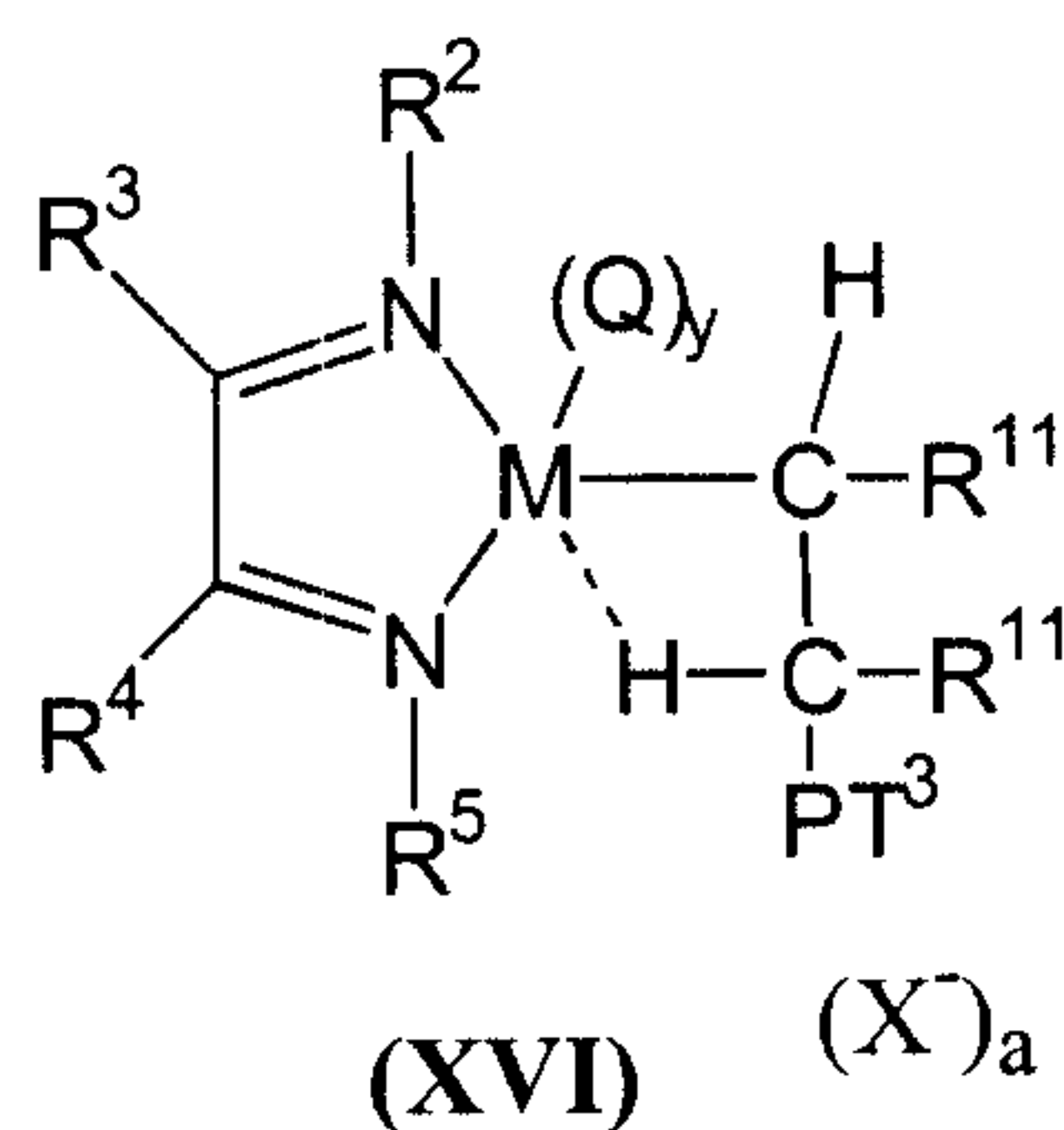
35. The process of claim 34, wherein:

5 R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and

10 each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

36. The process of claim 19, wherein the transition metal
15 complex is of the formula (XVI)



wherein:

M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

20 each R^{11} is independently hydrogen or alkyl, or both of R^{11} taken together are hydrocarbylene to form a carbocyclic ring;

T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^8$; Q is a monoanion;

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected
5 from the group consisting of ethylene, an olefin of the formula $\text{R}^{17}\text{CH}=\text{CH}_2$ or $\text{R}^{17}\text{CH}=\text{CHR}^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{CO}_2\text{R}^1$, CO, or a vinyl ketone;

10 R^8 is hydrocarbyl;

a is 1 or 2;

$y + a + 1 = m$;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is
15 separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and

20 X is a weakly coordinating anion;

provided that, when M is Ni(II), T^3 is not $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^8$.

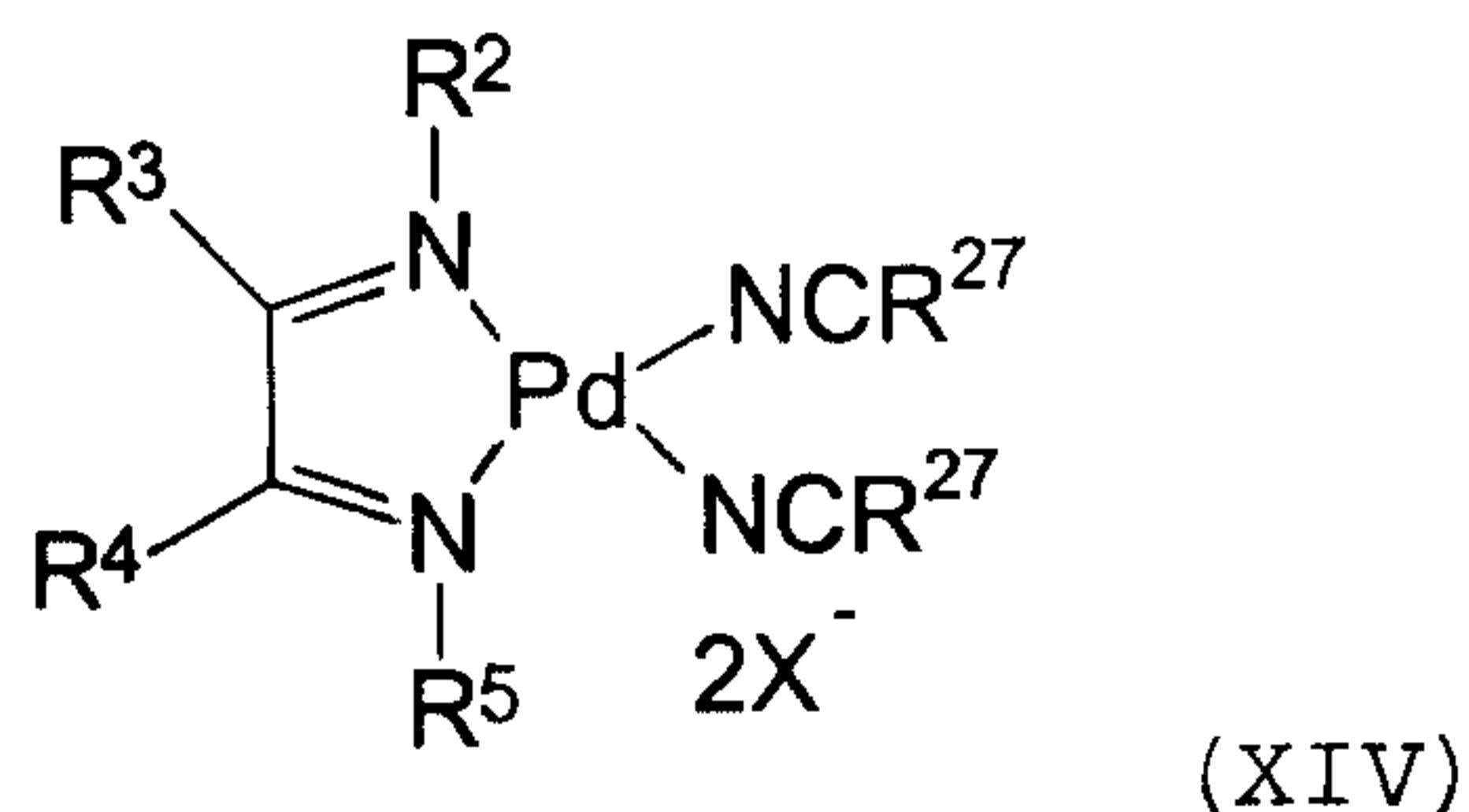
37. The process of claim 36, wherein:

R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at
25 least two carbon atoms bound to it; and

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring;

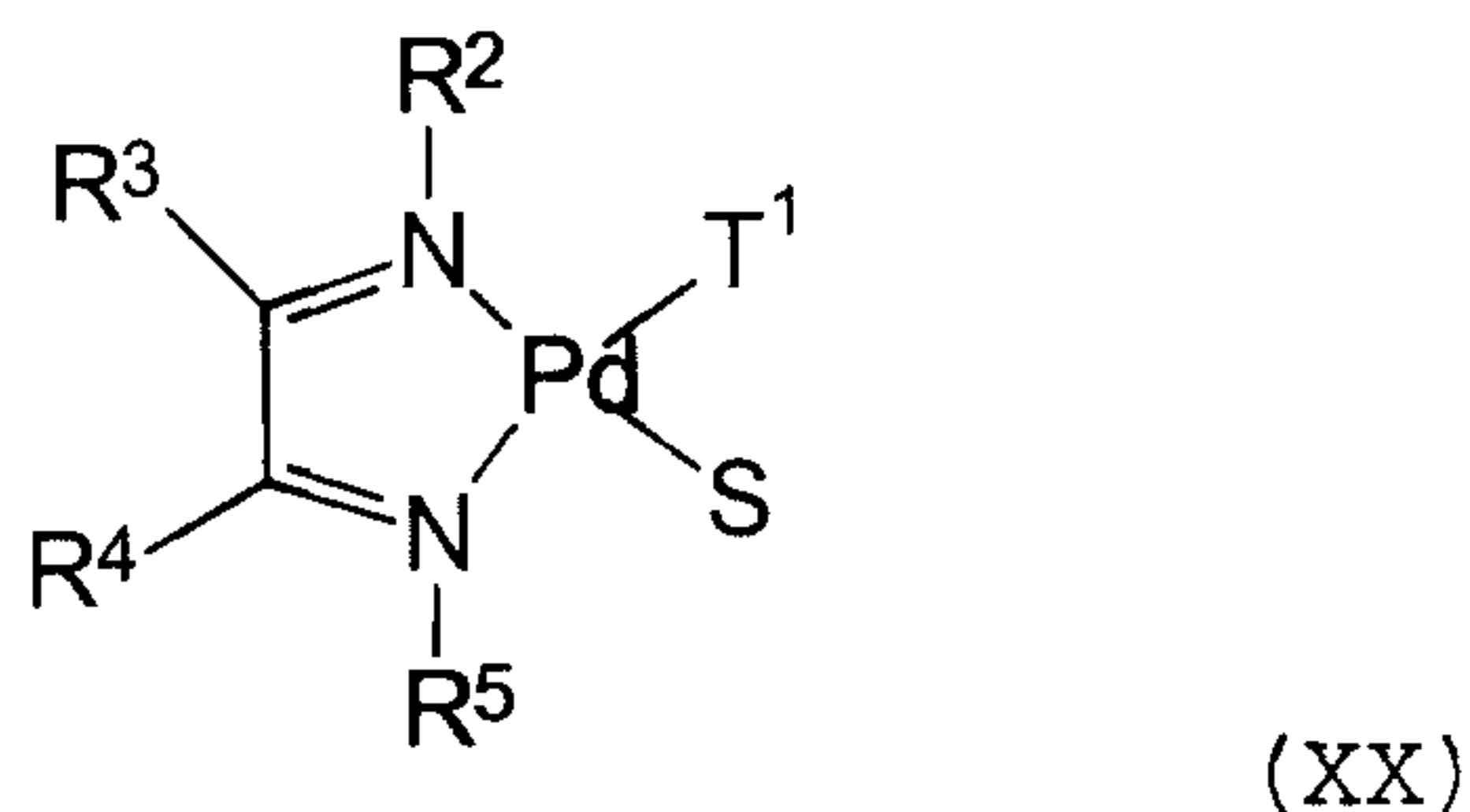
each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

- 5 38. The process of claim 19, wherein the transition metal complex is of the formula (XIV)



wherein each R^{27} is independently hydrocarbyl, and each X is a weakly coordinating anion.

- 10 39. The process of claim 19, wherein the transition metal complex is of the formula (XX)



wherein:

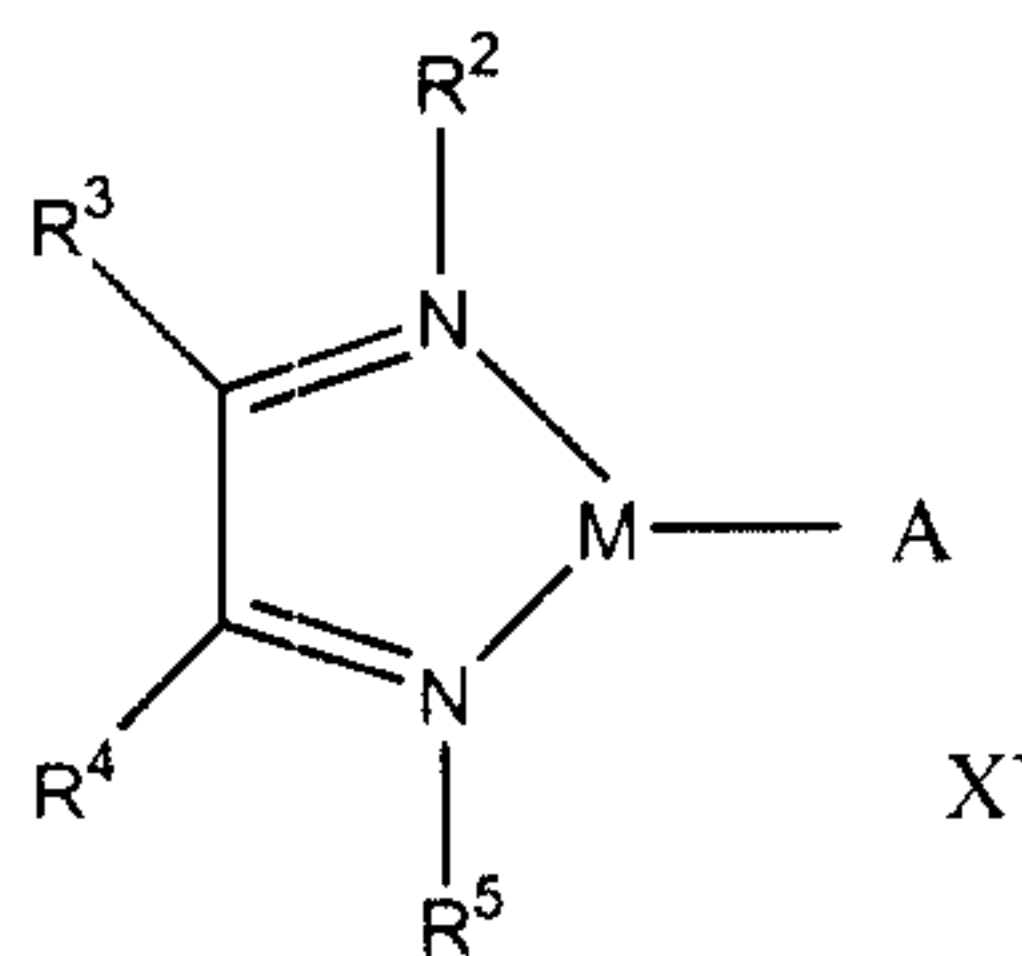
- 15 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=O)-$ or $R^{15}OC(=O)-$;

S is chloride, iodide, or bromide; and

the catalyst composition further comprises a compound which is a source of a relatively noncoordinating monoanion.

40. The process of claim 39, wherein said source is an alkali metal salt of said monoanion.

41. The process of claim 19, wherein the transition metal complex is of the formula (XXXVII)



XXXVII

wherein M is Ni(II) or Pd(II); A is a π -allyl or π -benzyl group; and X is a weakly coordinating anion.

42. The process of claim 41, wherein:

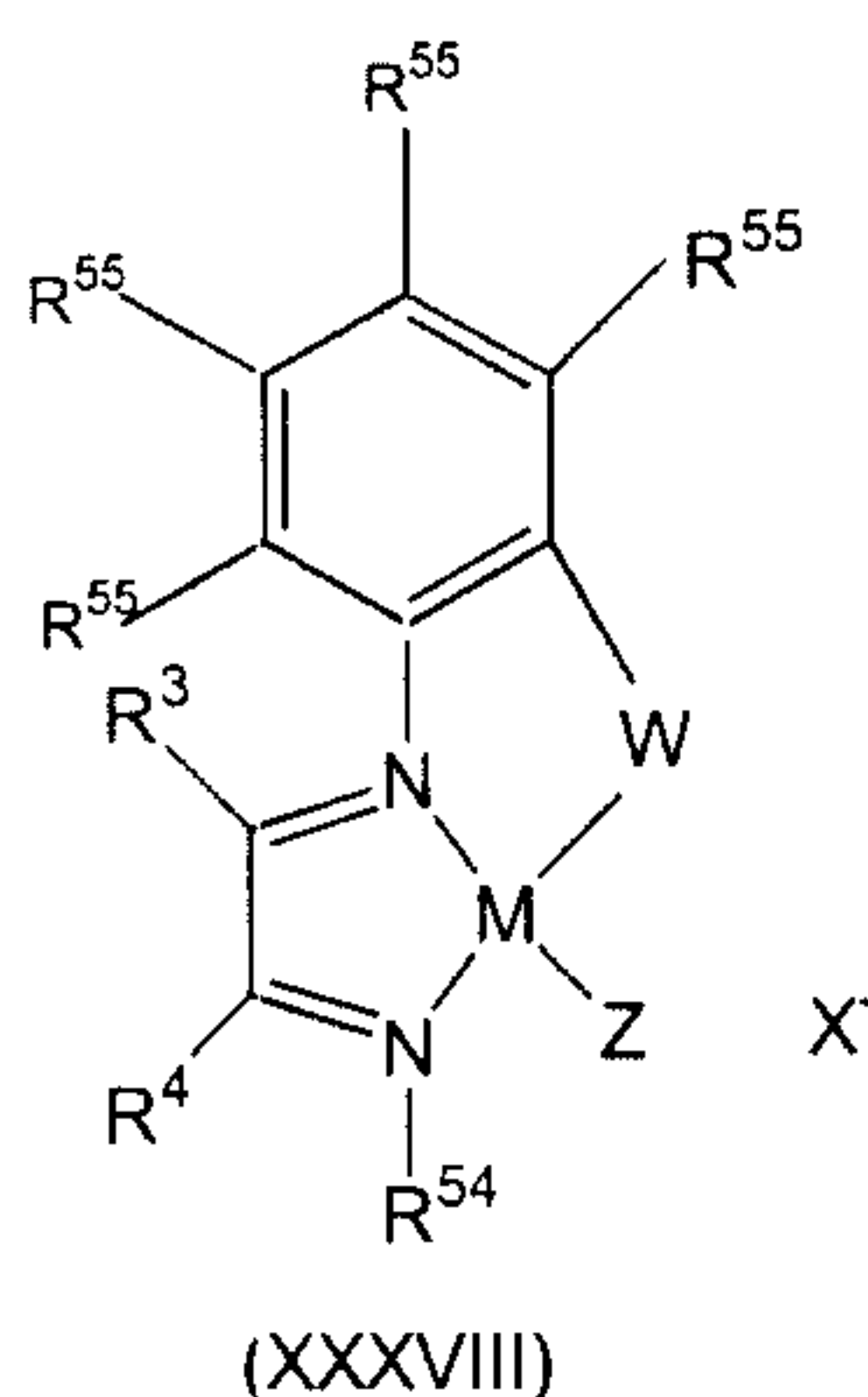
10 R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and

15 each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

43. The process of claim 19 wherein the transition metal compound is of the formula (XXXVIII)

425



wherein:

R^{54} is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom
5 has at least two carbon atoms bound to it;

each R^{55} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

10 Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of the compound having the formula (XXXVIII) is less than about 6, or an olefin of the formula $R^{17}CH=CHR^{17}$;

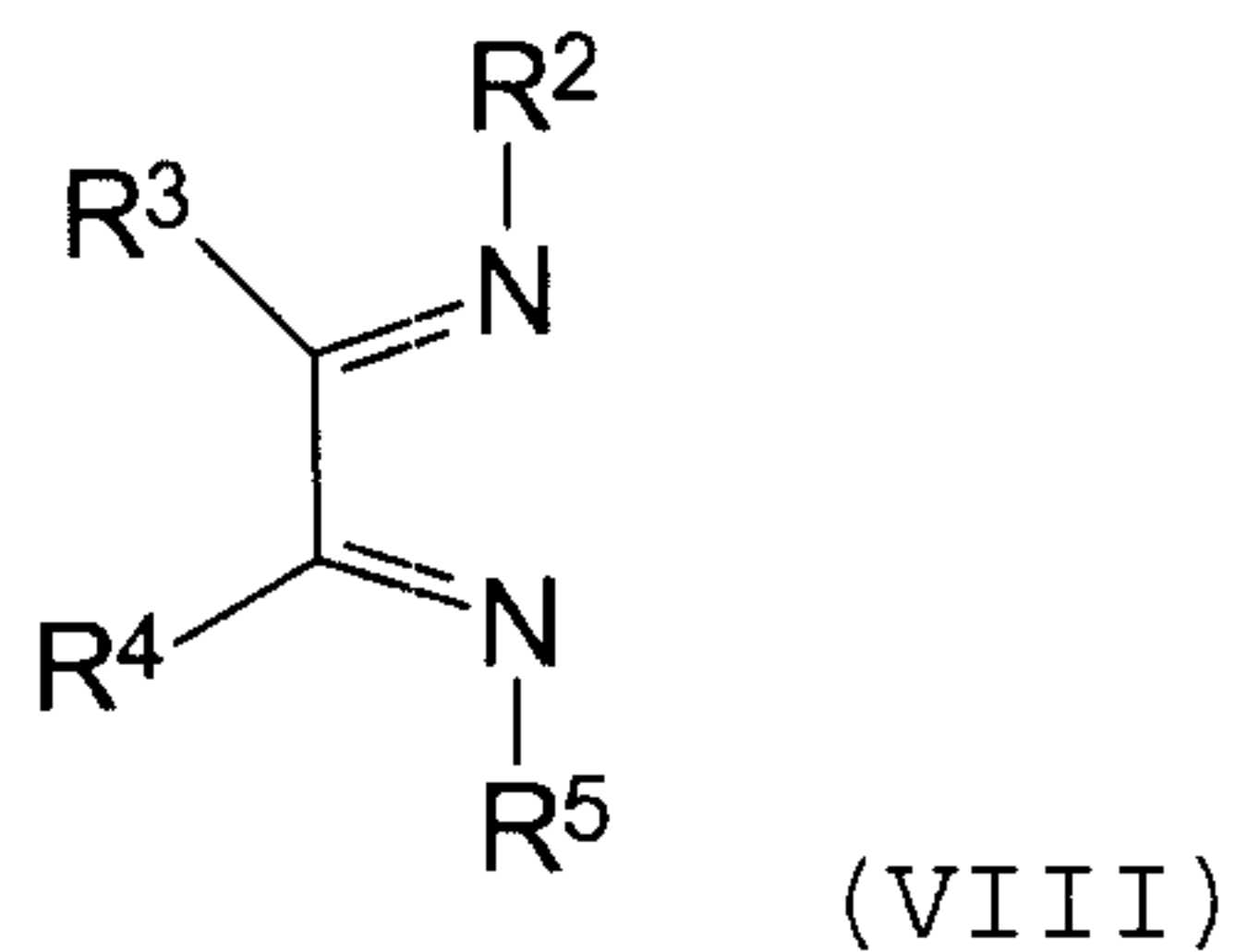
15 each R^{17} is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and

X is a weakly coordinating anion;

provided that when M is Ni, W is alkylene and each R^{17} is independently hydrogen or saturated hydrocarbyl.

20 44. The process of claim 19, wherein said neutral bidentate ligand is a compound of the formula (VIII)

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and a compound of the formula $[\text{Pd}(\text{R}^{13}\text{CN})_4]\text{X}_2$, or a combination of $\text{Pd}[\text{OC}(\text{O})\text{R}^{40}]_2$ and HX , wherein:

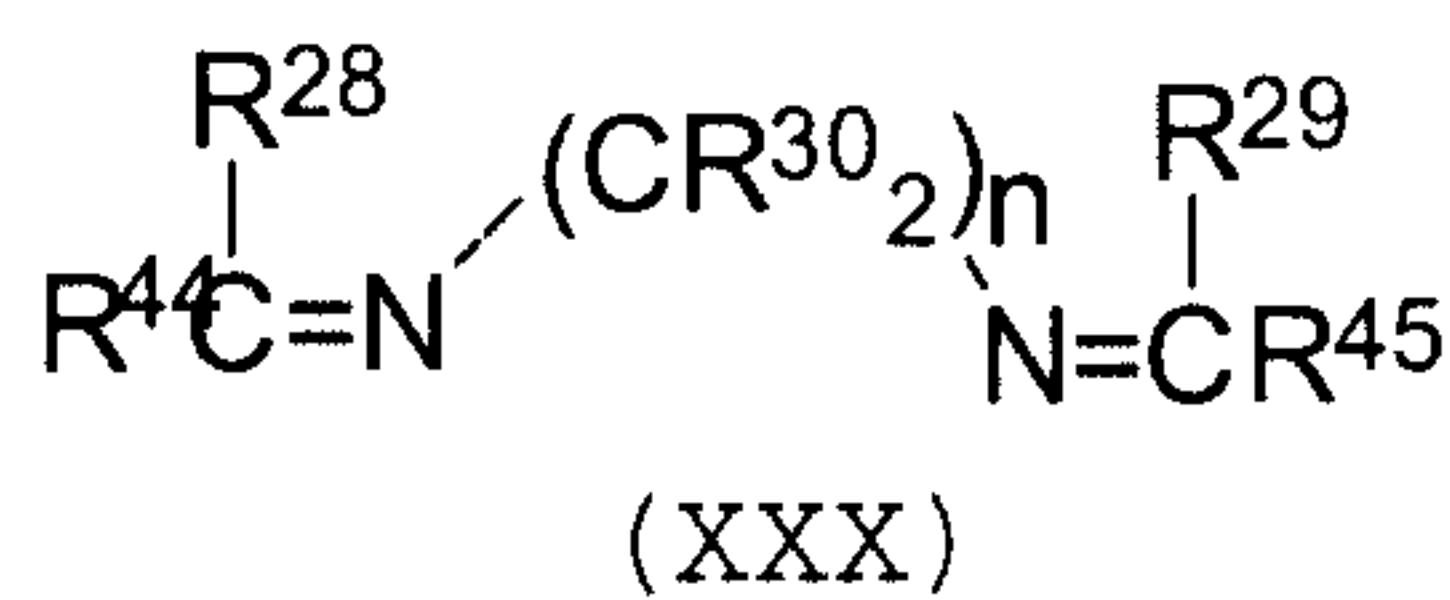
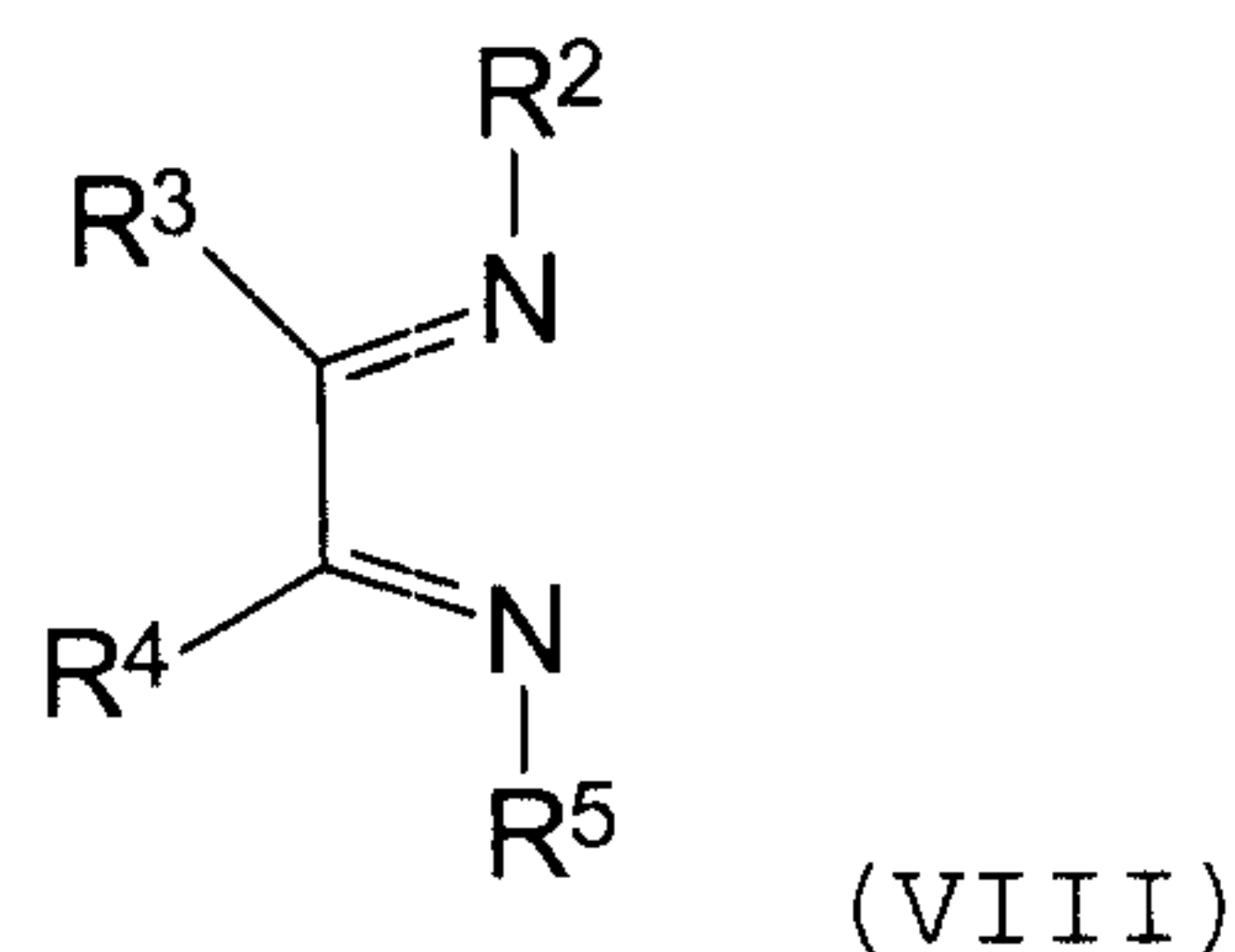
each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided R^{17} contains no olefinic bonds;

R^{13} is hydrocarbyl;

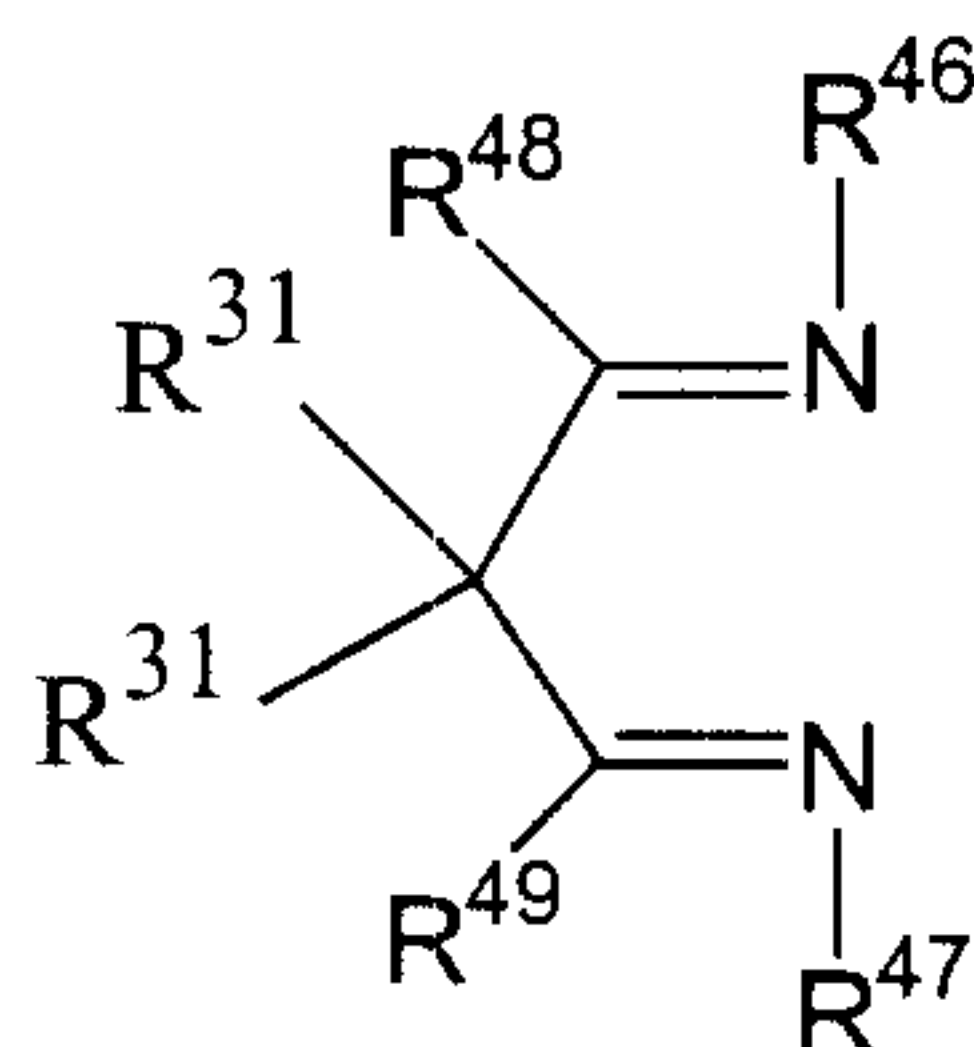
R^{40} is hydrocarbyl or substituted hydrocarbyl; and

X is a weakly coordinating anion.

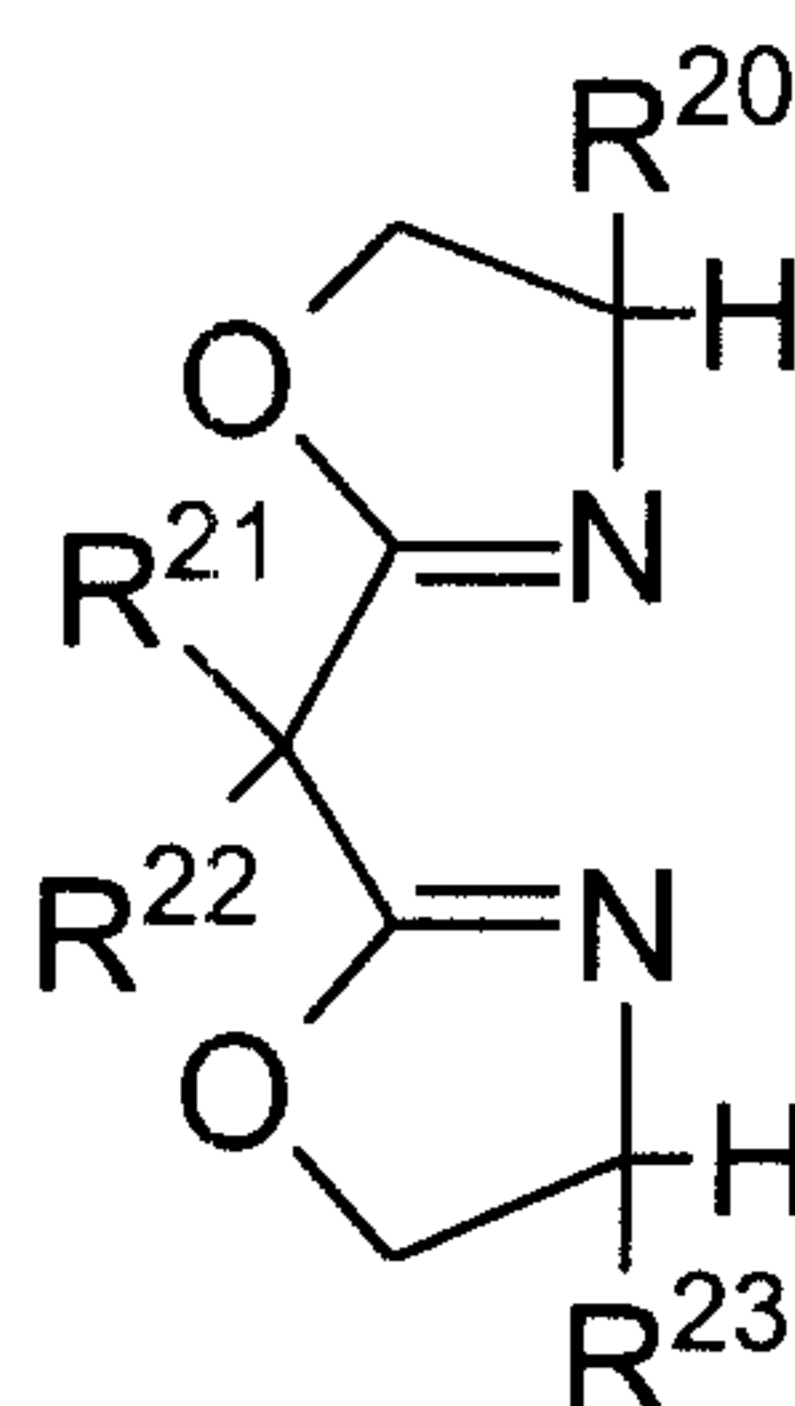
45. The process of claim 19, wherein said neutral bidentate ligand is a compound of the formula (VIII), (XXX), (XXXII) or (XXIII)



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(XXIII)



(XXXII)

a Ni[0], Pd[0] or Ni[I] compound containing a ligand
 which may be displaced by a ligand of the formula (VIII),
 5 (XXX), (XXXII) or (XXIII);

an oxidizing agent; and

a source of a relatively weakly coordinating anion.

46. The process of claim 45, wherein:

R^2 and R^5 are each independently hydrocarbyl, provided
 10 that the carbon atom bound to the imino nitrogen atom has at
 least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or
 R^3 and R^4 taken together are hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl provided that any
 15 olefinic bond in said olefin is separated from any other
 olefinic bond or aromatic ring by a quaternary carbon atom or
 at least two saturated carbon atoms;

R^{44} is hydrocarbyl, and R^{28} is hydrogen or hydrocarbyl, or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl, and R^{29} is hydrogen or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

5 each R^{30} is independently hydrogen or hydrocarbyl, or two of R^{30} taken together form a ring;

each R^{31} is independently hydrogen or hydrocarbyl;

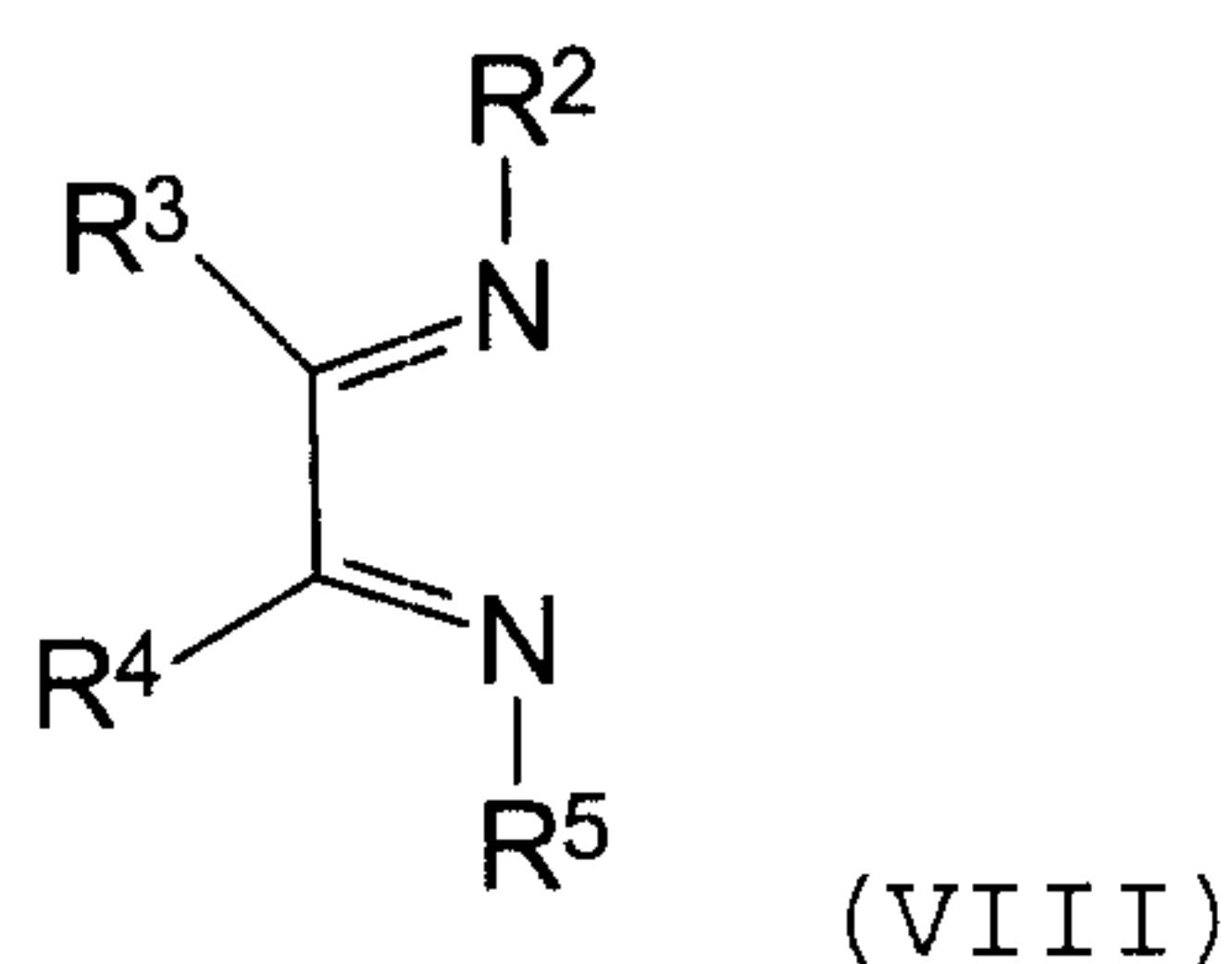
R^{46} and R^{47} are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at
10 least two carbon atoms bound to it;

R^{48} and R^{49} are each independently hydrogen or hydrocarbyl;

R^{20} and R^{23} are independently hydrocarbyl; and

R^{21} and R^{22} are each independently hydrogen or hydrocarbyl.

15 47. The process of claim 45, wherein said one or more olefins are contacted with a ligand of the formula (VIII)



a Ni[0] compound containing a ligand which may be displaced by a ligand of the formula (VIII);

20 oxygen; and

an alkyl aluminum compound.

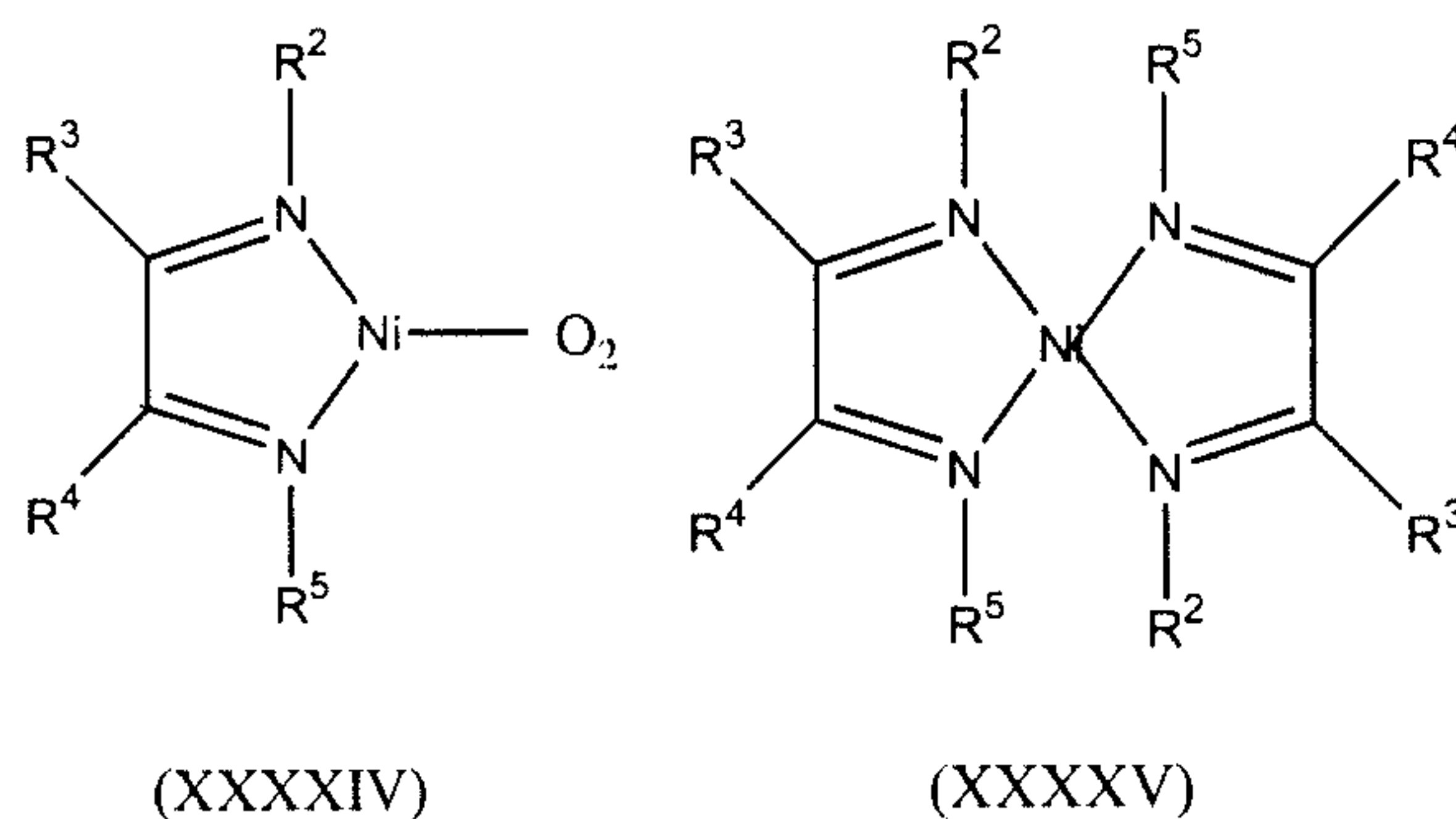
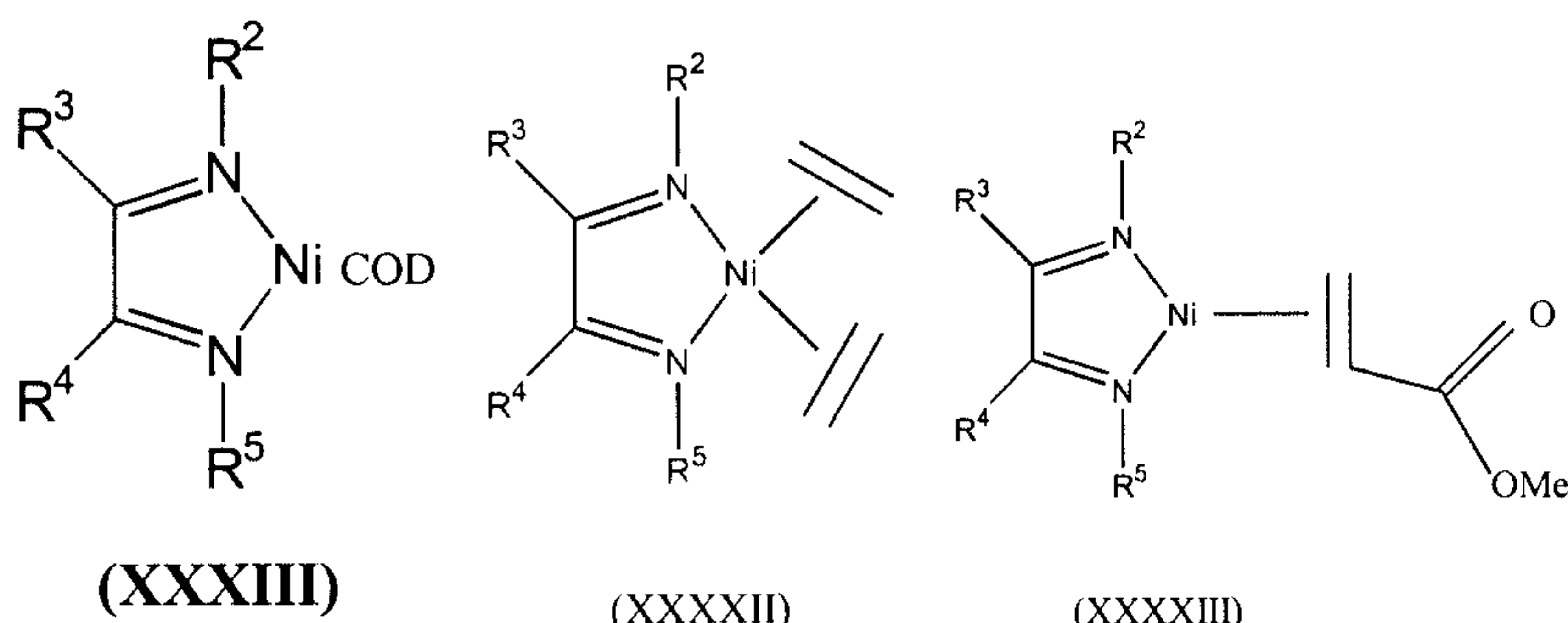
48. The process of claim 47, wherein:

R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or
5 R^3 and R^4 taken together are hydrocarbylene to form a ring; and

each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

10 49. The process of claim 19, wherein said one or more olefins are contacted with oxygen and an alkyl aluminum compound, or a compound of the formula HX, and a compound of the formula (XXXIII), (XXXXII), (XXXXIII), (XXXXIV) or (XXXXV)



wherein X is a weakly coordinating anion.

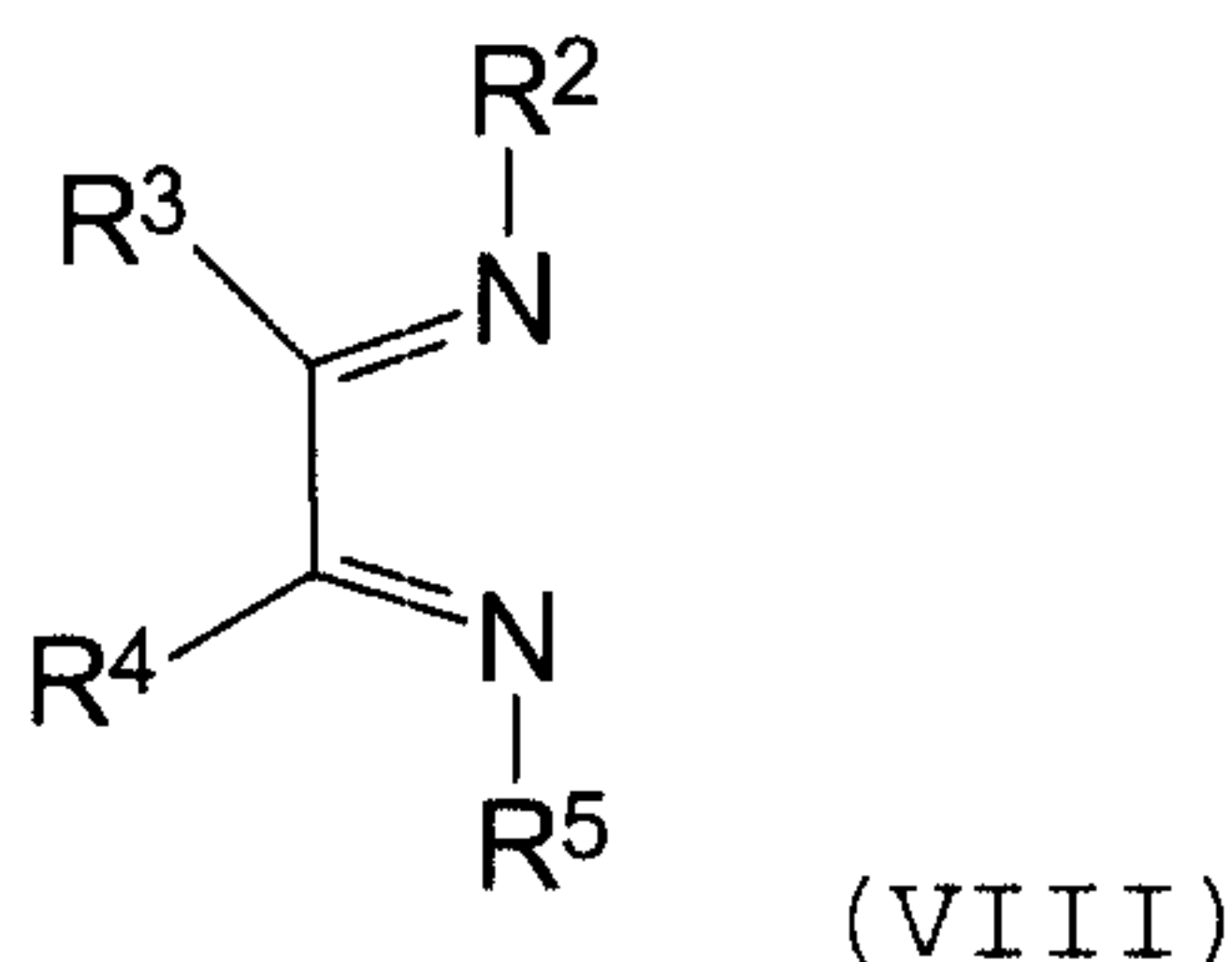
50. The process of claim 49, wherein:

R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or
5 R^3 and R^4 taken together are hydrocarbylene to form a ring; and

each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

10 51. The process of claim 19, wherein said one or more olefins are contacted with a ligand of the formula (VIII)



a Ni[0] compound containing a ligand which may be displaced by a ligand of the formula (VIII); and

15 HX or a Bronsted acidic solid;

wherein X is a weakly coordinating anion.

52. The process of claim 51, wherein:

R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at
20 least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and

each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.