Abstract:

Title: IMPROVED CATALYSTS FOR ALPHA-OLEFIN MANUFACTURE

For two-letter codes and other abbreviations, refer to the “Guidance Notes on Codes and Abbreviations” appearing at the beginning of each regular issue of the PCT Gazette.
IMPROVED CATALYSTS FOR α-OLEFIN MANUFACTURE

FIELD OF THE INVENTION

Iron, cobalt, chromium or vanadium complexes of certain 2,6-pyridinecarboxaldehydediimines and 2,6-diacylpyridinediimines in which phenyl groups bound to imino nitrogen atoms are substituted in the meta position with aryl group(s) have longer catalytic lives, and other advantages, when used as catalysts to produce α-olefins by oligomerization of ethylene.

TECHNICAL BACKGROUND

α-Olefins are important items of commerce, hundreds of millions of kilograms being manufactured yearly. They are useful as monomers for (co)polymerizations and as chemical intermediates for the manufacture of many other materials, for example detergents and surfactants. α-Olefins are most commonly made by the oligomerization of ethylene. Many types of catalysts for this reaction are known, among them certain transition metal complexes of diimines of 2,6-pyridinecarboxaldehydes and 2,6-diacylpyridines and related compounds, see for instance US6103946, US6534691, US6555723, US6683187 and US 6710006, and WO04/026795, all of which are also incorporated by reference.

As with any catalyst system one is normally concerned about the length of time the catalyst remains active and/or retains a good percentage of its activity over a prolonged period. The diimine complex catalysts mentioned above often have good activity but this diminishes as the temperatures of the process is raised, particularly above about 80-100°C. Therefore such catalysts with improved and/or prolonged activities, especially at higher temperatures, are desired. Another important attribute of such catalysts are the ability to yield a linear Schulz-Flory distribution of products, even when the ortho positions of the phenyl rings attached to the imino nitrogen's are symmetrical with respect to one another. Such symmetrical diimines are more easily synthesized from their respective
anilines than such unsymmetrical diimines, the synthesis generally requiring at least one less step. Also often only one aniline need be used, as opposed to two different anilines being required for the unsymmetrical compounds.

The use of unsymmetrically ortho substituted ligands to obtain linear Schulz-Flory distributions is described in US 6710006.

**SUMMARY OF THE INVENTION**

This invention concerns a process for the oligomerization of ethylene to linear $\alpha$-olefins (LAOs), comprising contacting, at a temperature of $-20^\circ\text{C}$ to $200^\circ\text{C}$, ethylene and a Fe, Co, Cr or V complex of a ligand of the formula

![Formula](image)

wherein:

- $R^1$, $R^2$ and $R^3$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of $R^1$, $R^2$ and $R^3$ vicinal to one another taken together may form a ring;

- $R^4$ and $R^5$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group provided that $R^1$ and $R^4$ and/or $R^3$ and $R^5$ taken together may form a ring;

- $R^6$ and $R^7$ are each independently phenyl or substituted phenyl having a first ring atom bound to the imino nitrogen, provided that at least one of $R^6$ and $R^7$ is substituted in at least one meta position with an aryl or substituted aryl group.

This invention also includes the ligands (I), and their Fe, Co, Cr or V complexes.
BRIEF DESCRIPTION OF THE FIGURE

Figure 1 shows the Schulz-Flory distributions of α-olefins obtained from iron complexes 1 and 22.

DETAILS OF THE INVENTION

Herein certain terms are used, and many of them are defined below.

A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. As examples of hydrocarbyls may be mentioned unsubstituted alkyls, cycloalkyls and aryls. If not otherwise stated, it is preferred that hydrocarbyl groups (and alkyl groups) herein contain 1 to about 30 carbon atoms.

By "substituted hydrocarbyl" herein is meant a hydrocarbyl group that contains one or more substituent groups that are inert under the process conditions to which the compound containing these groups is subjected (e.g., an inert functional group, see below). The substituent groups also do not substantially detrimentally interfere with the polymerization process or operation of the polymerization catalyst system. 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 rings containing one or more heteroatoms, such as nitrogen, oxygen and/or sulfur, and the free valence of the substituted hydrocarbyl may be to the heteroatom. In a substituted hydrocarbyl, all of the hydrogens may be substituted, as in trifluoromethyl.

By "(inert) functional group" herein is meant a group, other than hydrocarbyl or substituted hydrocarbyl, which is inert under the process conditions to which the compound containing the group is subjected. The functional groups also do not substantially deleteriously interfere with any process described herein that the compound in which they are present may take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), and ether such as -OR wherein R is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional
The functional group alone should not coordinate to the metal atom more strongly than the groups in those compounds that are shown as coordinating to the metal atom, which is they should not displace the desired coordinating group.

By a "cocatalyst" or a "catalyst activator" is meant one or more compounds that react with a transition metal compound to form an activated catalyst species. One such catalyst activator is an "alkylaluminum compound" which, herein, means a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as, for example, alkoxide, hydride, an oxygen atom bridging two aluminum atoms and halogen may also be bound to aluminum atoms in the compound.

By a "linear \( \alpha \)-olefin (LAO) product" is meant a composition predominantly comprising a compound or mixture of compounds of the formula \( \text{H(CH}_2\text{CH}_2\text{)}_q\text{CH=CH}_2 \) wherein \( q \) is an integer of 1 to about 18. In most cases, the LAO product of the present process will be a mixture of compounds having differing values of \( q \) of from 1 to 18, with a minor amount of compounds having \( q \) values of more than 18. Preferably less than 50 weight percent, and more preferably less than 20 weight percent, of the product will have \( q \) values over 18. The product may further contain small amounts (preferably less than 30 weight percent, more preferably less than 10 weight percent, and especially preferably less than 2 weight percent) of other types of compounds such as alkanes, branched alkenes, dienes and/or internal olefins.

By a "primary carbon group" herein is meant a group of the formula \(-\text{CH}_2\-\), wherein the free valence — is to any other atom, and the bond represented by the solid line is to a ring atom of a substituted aryl to which the primary carbon group is attached. Thus the free valence — may be bonded to a hydrogen atom, a halogen atom, a carbon atom, an oxygen atom, a sulfur atom, etc. In other words, the free valence — may be to hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group.
Examples of primary carbon groups include \(-\text{CH}_3\), \(-\text{CH}_2\text{CH(}\text{CH}_3)_2\), \(-\text{CH}_2\text{Cl}\), \(-\text{CH}_2\text{C}_6\text{H}_5\), \(-\text{OCH}_3\) and \(-\text{CH}_2\text{OCH}_3\).

By a "secondary carbon group" is meant the group

\[ \text{CH} \]

wherein the bond represented by the solid line is to a ring atom to which the secondary carbon group is attached, and both free bonds represented by the dashed lines are to an atom or atoms other than hydrogen and fluorine. These atoms or groups may be the same or different. In other words the free valences represented by the dashed lines may be hydrocarbyl, substituted hydrocarbyl or inert functional groups. Examples of secondary carbon groups include \(-\text{CH(}\text{CH}_3)_2\), \(-\text{CHCl}_2\), \(-\text{CH(}\text{C}_6\text{H}_5)_2\), cyclohexyl, \(-\text{CH(}\text{CH}_3)_2\text{OCH}_3\), and \(-\text{CH=CHCH}_3\).

By a "tertiary carbon group" is meant a group of the formula

\[ \text{C} \]

wherein the bond represented by the solid line is to a ring atom of a substituted aryl to which the tertiary carbon group is attached, and the three free bonds represented by the dashed lines are to an atom or atoms other than hydrogen and fluorine. In other words, the bonds represented by the dashed lines are to hydrocarbyl, substituted hydrocarbyl or inert functional groups. Examples of tertiary carbon groups include \(-\text{C(}\text{CH}_3)_3\), \(-\text{C(}\text{C}_6\text{H}_5)_3\), \(-\text{CCl}_3\), \(-\text{C(}\text{CHs})_2\text{OCH}_3\), \(-\text{C}=\text{CH}\), \(-\text{C(}\text{CH}_3)_2\text{CH=CH}_2\), aryl and substituted aryl such as phenyl, and 1-adamantyl.

By relatively noncoordinating (or weakly coordinating) anions are meant those anions as are generally referred to in the art in this manner, 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. Stares, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. Among
such anions are those formed from the aluminum compounds in the immediately preceding paragraph and X" including $R^9_{\text{AI}}X^\text{--}$, $R^9_{\text{AI}}C_2X^\text{--}$, $R^9_{\text{AI}}C_2I_2X^\text{--}$, and "$R^9_{\text{AI}}OX^\text{--}" wherein $R^9$ is alkyl. Other useful noncoordinating anions include BAF" (BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), SbF$_6^\text{--}$, PF$_6^\text{--}$, and BF$_4^\text{--}$, trifluoromethanesulfonate.

By a "monoanionic ligand" is meant a ligand with one negative charge.

By a "neutral ligand" is meant a ligand that is not charged.

"Alkyl group" and "substituted alkyl group" have their usual meaning (see above for substituted under substituted hydrocarbyl). Unless otherwise stated, alkyl groups and substituted alkyl groups preferably have 1 to about 30 carbon atoms.

By "aryl" is meant a monovalent aromatic group in which the free valence is to the carbon atom of an aromatic ring. An aryl may have one or more aromatic rings, which may be fused, connected by single bonds or other groups.

By "substituted aryl (phenyl)" is meant a monovalent aromatic (phenyl) group substituted as set forth in the above definition of "substituted hydrocarbyl", and also includes heteroaromatic rings as substituted aryl groups. Similar to an aryl, a substituted aryl may have one or more aromatic rings, which may be fused, connected by single bonds or other groups; however, when the substituted aryl has a heteroatom in the ring, the free valence in the substituted aryl group can be to the heteroatom (such as nitrogen) of the heteroaromatic ring instead of a carbon.

By "oligomerization conditions" herein is meant conditions for causing ethylene oligomerization with the catalysts described herein. Such conditions may include temperature, pressure, oligomerization method such as liquid phase, continuous, batch, and the like. Also included may be cocatalysts that are needed and/or desirable.
By a meta position is meant the usual meaning, meta to the first ring atom, i.e.

![Diagram of a molecule with a nitrogen atom in the meta position relative to the first ring atom.]

wherein, as noted above, the nitrogen atom is connected to the first ring atom.

In (I) and its Fe, Co, Cr or V complexes the structures of R<sup>6</sup> and R<sup>7</sup> are particularly important in determining the Schulz-Flory constant of the mixtures of LAOs produced. This is a measure of the molecular weights of the olefins obtained, usually denoted as factor K, from the Schulz-Flory theory (see for instance B. Elvers, et al., Ed. Ullmann's Encyclopedia of Industrial Chemistry, Vol. Al 3, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 243-247 and 275-276). This is defined as:

\[ K = \frac{n(C_{n+2} \text{olefin})}{n(C_n \text{olefin})} \]

wherein \(n(C_n \text{olefin})\) is the number of moles of olefin containing \(n\) carbon atoms, and \(n(C_{n+2} \text{olefin})\) is the number of moles of olefin containing \(n+2\) carbon atoms, or in other words the next higher oligomer of \(C_n\) olefin. From this can be determined the weight (mass) fractions of the various olefins in the resulting oligomeric reaction product mixture. The K factor is usually preferred to be in the range of about 0.6 to about 0.8 to make the \(\alpha\)-olefins of the most commercial interest. It is also important to be able to vary this factor, so as to produce those olefins that are in demand at the moment.

In R<sup>6</sup> and R<sup>7</sup> it is further preferred that:

- in R<sup>6</sup>, a second ring atom adjacent to said first ring atom (ortho position) is bound to a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and further provided that

- in R<sup>6</sup>, when said second ring atom is bound to a halogen or a primary carbon group, none, one or two of the other ring atoms in R<sup>6</sup> and
R\textsuperscript{7} adjacent to said first ring atom are bound to a halogen or a primary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R\textsuperscript{6}, when said second ring atom is bound to a secondary carbon group, none, one or two of the other ring atoms in R\textsuperscript{6} and R\textsuperscript{7} adjacent to said first ring atom are bound to a halogen, a primary carbon group or a secondary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R\textsuperscript{6}, when said second ring atom is bound to a tertiary carbon group, none or one of the other ring atoms in R\textsuperscript{6} and R\textsuperscript{7} adjacent to said first ring atom are bound to a tertiary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom.

In addition to the substitution patterns described immediately above for the second ring atoms, at least one of the four meta positions in R\textsuperscript{6} and R\textsuperscript{7} combined must be substituted by an aryl or substituted aryl group.

In one preferred form R\textsuperscript{6} is

\[ (II) \]

and R\textsuperscript{7} is

\[ (III) \]

wherein these groups are substituted as described above.

(II) and (III) may be identical (so that substitution on the imino nitrogen atoms is "symmetric") or they may be different, including different in the (second) ortho positions and/or the meta positions (so that the}
substitution on the imino nitrogen atoms is "asymmetric"). Also (II) and (III) may be symmetric with respect to their ortho positions and unsymmetric with respect to their meta positions, and vice versa.

In groups (II) and (III), with respect to the ortho positions, it is particularly preferred that

if \( R^8 \) is a primary carbon group or halogen, \( R^{13} \) is a primary carbon group or halogen, and \( R^{12} \) and \( R^{17} \) are hydrogen; or

if \( R^8 \) is a secondary carbon group, \( R^{13} \) is a primary carbon group, halogen or a secondary carbon group, more preferably a secondary carbon group, and \( R^{12} \) and \( R^{17} \) are hydrogen; or

if \( R^8 \) is a tertiary carbon group (more preferably a trihalo tertiary carbon group such as a trihalomethyl), and \( R^{12} \), \( R^{13} \) and \( R^{17} \) are hydrogen; or

if \( R^8 \) is a primary carbon group or halogen, \( R^{12} \) is a primary carbon group or halogen, and \( R^{13} \) and \( R^{17} \) are hydrogen; or

if \( R^8 \) is a secondary carbon group, \( R^{12} \) is a primary carbon group, halogen or a secondary carbon group, more preferably a secondary carbon group, and \( R^{13} \) and \( R^{17} \) are hydrogen.

In groups (II) and (II), with respect to the meta positions, it is particularly preferred that:

\( R^9 \) is aryl or substituted aryl and \( R^{11} \), \( R^{14} \) and \( R^{16} \) are hydrogen; or
\( R^{14} \) is aryl or substituted aryl and \( R^9 \), \( R^{11} \) and \( R^{16} \) are hydrogen; or
\( R^9 \) and \( R^{14} \) are each independently aryl or substituted aryl and \( R^{11} \) and \( R^{16} \) are hydrogen; or

\( R^9 \), \( R^{11} \), and \( R^{14} \) are each independently aryl or substituted aryl and \( R^{16} \) is hydrogen; or
\( R^9 \), \( R^{14} \), and \( R^{16} \) are each independently aryl or substituted aryl and \( R^{11} \) is hydrogen; or
\( R^9 \), \( R^{11} \), \( R^{14} \) and \( R^{16} \) are each independently aryl or substituted aryl.
In another preferred form of (II) and (III) with respect to the meta positions all of the aryl or substituted aryl groups are preferably the same.

In all preferred forms of (II) and (III), when they are not substituted as listed immediately above, it is preferred that those groups, R₈ through R₁₇, are hydrogen. It is also preferred that R¹, R² and R³ are hydrogen. It is preferred also that R⁴ and R⁵ are hydrogen or methyl, especially methyl.

It is to be understood that any preferred form of (II) and (III) with respect to the ortho positions, the meta positions, or any other positions in the ligand(l), may be combined to create a more preferred from of (I).

Preferred aryl and substituted aryl groups are phenyl and substituted phenyl, and specific preferred groups are phenyl, tolyl (o-, m- or p-methyl), 3,5-bis(trifluoromethyl)phenyl, 5-methyl-2-thiophenyl, and p-fluorophenyl.

In the present complexes and their use as oligomerization catalysts, a preferred transition metal is iron. Preferably the oxidation state of the iron atom is +2.

Generally speaking the present complexes are effective oligomerization catalysts from about -20°C to about 200°C, preferably about 0°C to about 150°C, and more preferably about 80°C to about 150°C. The pressure (if one or more monomers such as ethylene are gaseous) is not critical, atmospheric pressure to 70 MPa being a useful range. Any combination of temperature and pressure may be used. The particular combination of temperature and pressure chosen will reflect many factors, including oligomer yield, type of oligomerization process being used, the relative economics of various conditions, etc. A cocatalyst is often added which is an alkylating or hydriding agent. A preferred type of cocatalyst is an alkylaluminum compound, and preferred alkylaluminum compounds are methylaluminoxane, trimethylaluminum, and other trialkylaluminum compounds. Especially preferred alkylaluminum compounds are methylaluminoxane, trimethylaluminum.
Useful forms of complexes of (II) include those of the following formulas (written as iron complexes, but analogous structures may be written for Co, Cr and V):

\[ \text{wherein:} \]

\[ R^1, R^2, R^3, R^4, R^5, R^6, \text{ and } R^7 \text{ are as defined above;} \]

\[ \text{each } X \text{ is independently a monoanion;} \]

\[ A \text{ is a } \pi\text{-allyl or } \pi\text{-benzyl group;} \]
L\textsuperscript{1} is a neutral monodentate ligand which may be displaced by said olefin or an open coordination site, and L\textsuperscript{2} is a monoanionic monodentate ligand which preferably can add to an olefin, or L\textsuperscript{1} and L\textsuperscript{2} taken together are a monoanionic bidentate ligand, provided that said monoanionic monodentate ligand or said monoanionic bidentate ligand may add to said olefin; and

Q is a relatively noncoordinating anion.

Preferably each X is independently halide or carboxylate, more preferably both of X are chloride or bromide.

When A is present, in effect L\textsuperscript{1} and L\textsuperscript{2} taken together are A. (X) may be used as a starting material for forming an active polymerization complex. For example (X) may be reacted with:

(a) a first compound W, which is a neutral Lewis acid capable of abstracting X\textsuperscript{-} and alkyl group or a hydride group from M to form WX\textsuperscript{-}, (WR\textsuperscript{40})\textsuperscript{-} or WH\textsuperscript{+}, wherein R\textsuperscript{40} is alkyl, and which is also capable of transferring an alkyl group or a hydride to M, provided that WX\textsuperscript{-} is a weakly coordinating anion; or

(b) a combination of second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X\textsuperscript{-}, a hydride or an alkyl group from M to form a weakly coordinating anion.

Thus W may be an alkylaluminum compound, while the second compound may be a dialkylzinc compound and the third compound may be a borane such as tris(pentafluorophenyl)borane. Such combinations and compounds for W are well known in the art, see for instance U.S. Patents 5,955,555 and 5,866,663, both of which are hereby included by reference.

In many instances compounds (XI) or (XII), if added directly to an oligomerization process, may be active catalysts without the addition of any cocatalysts, or just the addition of a Lewis acid which may form a relatively noncoordinating anion by abstraction of A\textsuperscript{-} or L\textsuperscript{2}\textsuperscript{-} from the complex. In (XI) L\textsuperscript{2} may be an alkyl group, which is in fact an oligomer of
the ethylene being oligomerized, while \( L' \) may be an open coordination site or \( L^1 \) is one of the olefins being polymerized. For example if ethylene is being oligomerized, \( L^2 \) may be \(-(CH_2CH_2)_zD\) wherein \( z \) is a positive integer and \( D \) is an anion (which originally was \( L^2 \)) between which ethylene could insert between \( L^2 \) and the Fe atom. The chemistry of such types of compounds is known; see for instance U.S. Patents 5,866,663 and 5,955,555, both of which are hereby included by reference.

The oligomerization process may be a batch, semibatch or continuous process, and a continuous process is preferred. Typically the process is carried out as a solution process, either with a separate solvent or using the LAOs as produced as the solvent. These types of processes are well known in the art. For example a solution process may be carried out in one or more continuous stirred tank reactors (CSTR), or a pipeline reactor. Such processes and conditions for the oligomerization are described in US6103946, US6534691, US6555723, US6683187 and US6710006, and WO04/026795, all of which were previously incorporated by reference.

All air-sensitive compounds were prepared and handled under a \( \text{N}_2\text{ZAr} \) atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. Anhydrous iron(II) chloride, 1-(6-acetyl-pyridin-2-yl)-ethanone, 3-bromo-2-methylphenylamine, 3,5-dibromo-4-methylphenylamine, 5-bromo-2-methylphenylamine, 4-fluorophenylboronic acid, 3,5-bis-trifluorornethylphenylboronic acid, 5-methyl-2-thiophene boronic acid, tris(dibenzylideneacetone) dipalladium (0), cesium carbonate, di-f-butylchlorophosphine, 2.0 \( M \) solution of benzylmagnesium chloride in THF, MMAO and n-butanol were purchased from Aldrich. Complex 1 was prepared according to US 5955555. In the Examples, THF is tetrahydrofuran.
EXAMPLE 1

2,6-Bisd -(2-methyl-3-bromophenylimino)ethyl)p yricline (15)

![Chemical Structure of 2,6-Bisd -(2-methyl-3-bromophenylimino)ethyl)p yricline (15)]

1-(6-Acetylpyridin-2-yl)ethanone [18.87 g (0.116 mol)], 45.3 g (0.243 mol) of 3-bromo-2-methylphenylamine, 300 ml of the toluene and a few crystals of para-toluene sulfonic acid were refluxed under a flow of nitrogen with a Dean-Stark trap for 3 d until the calculated amount of water was separated (4.16 ml). The solvent was removed by a rotary evaporator and the resultant reaction mixture was recrystallized from 50 ml of ethanol. The yield of 15 was 47.9 g (83%) as a pale yellow solid. ¹H NMR (500 MHz, THF-D₈, TMS): δ 2.15 (s, 6 H, Me), 2.33 (s, 6 H, Me), 6.67 (m, 2H, Arom-H), 7.35 (m, 4H, Arom-H), 7.90 (t, 3JHH=7.8 Hz, 1H, Py-H), 8.50 (d, 3JHH=7.8 Hz, 2H, Py-H). ¹³C NMR (500 MHz, THF-D₈, (selected signals)): δ 168.0 (C=N). Anal. Calculated for C₂₃H₂₁Br₂N₃ (Mol. Wt.: 499.24): C, 55.33; H, 4.24; N, 8.42. Found: C, 55.40; H, 4.42; N, 8.46.

EXAMPLE 2

2,6-Bisd -(2-methyl-3-(4-fluorophenyl)phenylimino)ethylp yridine (18)

![Chemical Structure of 2,6-Bisd -(2-methyl-3-(4-fluorophenyl)phenylimino)ethylp yridine (18)]

4-Fluorophenylboronic acid [4.71 g (0.0337 mol)], 5.60 g (0.0112 mol) of 15, 10.97 g (0.0337 mol) of cesium carbonate, 0.77 g (0.00084 mol) of tris(dibenzylideneacetone) dipalladium (0), 0.35 g (0.0016 mol) of di-f-butyl(2,2-dimethylpropyl)phosphane and 50 ml of dioxane were stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting mixture was purified by recrystallization from 20 ml of ethanol. Yield of 18 was 3.74 g (63%) as
a light yellow solid. \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\), TMS): \(\delta 1.95\) (s, 6 H, Me), 2.40 (s, 6 H, Me), 6.63 (m, 2H, Arom-H), 7.40 (m, 14H, Arom-H), 7.91 (t, \(^3\)J\(_{HH}\)=7.8 Hz, 1H, Py-H), 8.40 (d, \(^3\)J\(_{HH}\)=7.8 Hz, 2H, Py-H). \(^{13}\)C NMR (500 MHz, CD\(_2\)Cl\(_2\), (selected signals)): \(\delta 168.1\) (C=N).

\(^{19}\)F NMR (CD\(_2\)Cl\(_2\)): \(-63.54\) (s, 12F).


**EXAMPLE 3**

2,5-Bis(1-(2-methy!-3-(3,5-bis(trifluoromethyl)phenyl)phenyliminothethyQpyridine (19)

3.5~Bis(trifluoromethyl)phenylboronic acid, 16, [7.44 g (0.0289 mol)], 4.80 g (0.0096 mol) of 15, 9.40 g (0.0289 mol) of cesium carbonate, 0.66 g (0.00072 mol) of tris(dibenzylideneacetone) dipalladium (0), 0.38 g (0.0018 mol) of di-f-butyl(2,2-dimethylpropyl)phosphane and 50 ml of dioxane were stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting mixture was purified by recrystallization from 20 ml of ethanol. Yield of 19 was 5.14 g (76%) as a slight yellow solid. \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\), TMS): \(\delta 2.05\) (s, 6 H, Me), 2.41 (s, 6 H, Me), 6.68 (m, 2H, Arom-H), 7.05 (m, 2H, Arom-H), 7.30 (m, 2H, Arom-H), 7.95 (m, 7H, Arom-H and Py-H), 8.45 (d, \(^3\)J\(_{HH}\)=7.8 Hz, 2H, Py-H). \(^{13}\)C NMR (500 MHz, CD\(_2\)Cl\(_2\), (selected signals)): \(\delta 167.7\) (C=N). \(^{19}\)F NMR (CD\(_2\)Cl\(_2\)): \(-63.54\) (s, 12F). Anal. Calcd. for C\(_{35}\)H\(_{27}\)F\(_2\)N\(_3\) (Mol. Wt: 765.63): C, 61.18; H, 3.55; N, 5.49. Found: C, 61.36; H, 3.70; N, 5.52. The structure was proven by X-ray analysis.
EXAMPLE 4

2,6-Bis(1-(2-methyl-3-(3-methylthiophene-2-yl)-phenyl)phenylimino)ethyl)pyridine (20)

5-Methyl-2-thiophene boronic acid [10.0 g (0.0704 mol)], 8.79 g (0.0176 mol) of cesium carbonate, 1.62 g (0.00177 mol) of tris(dibenzylideneacetone) dipalladium (0), 0.91 g (0.0042 mol) of di-f-butyl(2,2-dimethylpropyl)phosphane and 50 ml of dioxane were stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting mixture was purified by recrystallization from 20 ml of ethanol. The yield of 20 was 3.26 g (35%) as a light yellow solid. $^1$H NMR (500 MHz, C$_6$D$_6$, TMS): $\delta$ 2.12 (s, 6 H, Me), 2.32 (s, 6 H, Me), 2.39 (s, 6 H, Me), 6.50 (s, 2H, Arom-H), 6.70 (m, 2H, Arom-H), 7.20 (m, 7H, Arom-H), 8.49 (d, $^{3}$J$_{HH}$=7.8 Hz, 2H, Py-H). $^{13}$C NMR (500 MHz, C$_6$D$_6$, (selected signals)): $\delta$ 166.6 (C=N). Anal. Calcd. for C$_{33}$H$_{31}$N$_3$S$_2$ (Mol. Wt: 533.75): C, 74.26; H, 5.85; N, 7.87. Found: C, 74.29; H, 5.91; N, 7.95.

EXAMPLE 5

2,6-Bisd-(2-methyl-3-(4-fluorophenyl)phenylimino)ethyl)pyridine iron (II) chloride (21)

Anhydrous iron(II) chloride [0.43 g (0.0034 mol)] was dissolved in 40 ml warm n-butanol. Then, 2.0 g (0.0038 mol) of 18 was added in one portion in the reaction mixture. The mixture was kept at 40°C for 1 h and then was cooled to ambient temperature. The resultant blue precipitate
was filtered off and washed twice by 20 ml of pentane and dried at 133 Pa pressure. Yield of 21 was 3.83 g (87%). Anal. Calculated for C\textsubscript{35}H\textsubscript{29}Cl\textsubscript{2}F\textsubscript{2}FeN\textsubscript{3} (Mol. Wt: 656.37): C, 64.05; H, 4.45; N, 6.40. Found: C, 64.23; H, 4.61; N, 6.48. Direct probe MSr Exact Mass for C\textsubscript{35}H\textsubscript{29}Cl\textsubscript{2}F\textsubscript{2}FeN\textsubscript{3}: 655.11. Found: 655.11.

**EXAMPLE 6**

2,6-Bisf 1-(2-methyl-3-(3,5-bis(trifluoromethyl)phenyl)phenylimino)ethyl)pyridine iron (II) chloride (22)

Anhydrous iron(II) chloride [0.50 g (0.0039 mol)] was dissolved in 40 ml warm n-butanol. Then, 3.0 g of 19 was added in one portion into the solution. The mixture was kept at 40°C for 1 h and then was cooled to ambient temperature. The resultant blue precipitate was filtered off and washed twice by 20 ml of pentane and dried at 133 Pa pressure. Yield of 22 was 3.83 g (87%). Anal. Calculated for C\textsubscript{39}H\textsubscript{27}Cl\textsubscript{2}F\textsubscript{2}FeN\textsubscript{3} (Mol. Wt: 892.38): C, 52.49; H, 3.05; N, 4.71. Found: C, 52.57; H, 3.21; N, 4.96. The structure was proven by X-ray analysis.

**EXAMPLE 7**

2,6-Bis(1-(2-methyl-3-(3-methylthiophene-2-yl)-phenyl)phenylimino)ethyl)pyridine iron (II) chloride (23)

[Diagram]

20 [0.5 g (0.00094 mol)] was dissolved in 30 ml of THF, and then 0.11 g (0.00087 mol) of iron(II) chloride was added in one portion. The resultant blue precipitate was filtered after 12 h of stirring, washed twice with 20 ml of pentane, and dried at 133 Pa pressure. Yield of 23 was 1.34

EXAMPLE 8
2.6-Bisf 1-(2-methyl-3-(3,5-bis(trifluoromethyl)phenyl)phenylimino)ethyl)pyridine iron (III) chloride (24)

EXAMPLE 9
2.6-Bis(1-(2-methyl-5-bromo-phenylimino)ethyl)pyridine (26)

19 (1.0 g (0.0013 mol)) was dissolved in 50 ml THF, and then 0.20 g (0.0012 mol) of anhydrous iron(III) chloride was added in one portion. The mixture was stirred for 20 min at ambient temperature. The resultant orange precipitate was filtered of and washed twice with 20 ml of pentane and dried at 1 Pa pressure. Note - it is believed that this compound is slowly converted to the iron(II) compound in THF by hydrogen abstraction. Yield of 24 was 0.88 g (73%). Anal. Calculated for C₃₉H₂₇Cl₁₂F₁₂FeN₃ (Mol. Wt: 927.84): C, 50.48; H, 2.93; N, 4.53. Found: C, 50.59; H, 3.20; N, 4.57. Direct probe MS: Exact Mass for C₃₉H₂₇Cl₁₂F₁₂FeN₃: 926.04. Found: 926.04.

EXAMPLE 9
2.6-Bis(1-(2-methyl-5-bromo-phenylimino)ethyl)pyridine (26)

1-(6-Acetyl-pyridin-2-yl)ethanone [8.33 g (0.051 mol)], 20.0 g (0.107 mol) of 5-bromo-2-methyl-phenylamine and 200 ml of dry toluene with a few crystals of para-toluenesulfonic acid were refluxed under the flow of the nitrogen using a Dean-Stark trap for 3 d until the calculated
amount of the water was separated (1.84 ml). The solvent was removed in a rotary evaporator and the resultant reaction mixture was recrystallized from 50 ml of ethanol. The yield of 26 was 19.88 g (78%) as a pale yellow solid. \(^1\)H NMR (500 MHz, \(\text{C}_6\text{D}_6\), TMS): \(\delta\) 1.90 (s, 6 H, Me), 2.12 (s, 6 H, Me), 6.50 (m, 2H, Arom-H), 7.20 (m, 4H, Arom-H), 7.30 (t, \(\text{J}_{\text{H-H}}=7.8\) Hz, 1H, Py-H), 8.40 (d, \(\text{J}_{\text{H-H}}=7.8\) Hz, 2H, Py-H). \(^13\)C NMR (500 MHz, \(\text{C}_6\text{D}_6\), (selected signals)): \(\delta\) 167.4 (C=N). Anal. Calculated for \(\text{C}_{23}\text{H}_2\text{IBr}_2\text{N}_3\) (Mol. Wi: 499.24): C, 55.33; H, 4.24; N, 8.42. Found: C, 55.48; H, 4.45; N, 8.53.

EXAMPLE 10

**Benzyl-di-f-butylphosphane (28)**

Di-f-butylchlorophosphine [75.0 g (0.415 mol) and 0.5 mole of a 2.0 \(M\) solution of benzylimagnesium chloride in THF (200 ml) were refluxed under argon for 2 days. The reaction mixture was allowed to cool off to RT and an aqueous solution of ammonium chloride was added slowly. The organic phase was separated, and dried with magnesium sulfate. After removal of the solvent, the product was purified by distillation in vacuum. The yield of 28 was 94.3 g (96%) with b.p. 56-59°C/13 Pa. \(^31\)P NMR (CDCl\(_3\)) + 36.63 ppm. \(^1\)H NMR (CDCl\(_3\)) 1.18 (s, 9H, Me\(_3\)C), 2.90 (d, \(\text{J}_{\text{P-H}}=2.92\) Hz, P-CH\(_2\)-Ph), 7.1- 7.6 (m, 5H, aromatic protons). Anal. Calcd. for \(\text{C}_{15}\text{H}_{25}\text{P}\) (Mol. Wt: 236.33): C, 76.23; H, 10.66; P, 13.1 1. Found: C, 76.15; H, 10.58; P, 12.87.

EXAMPLE 11

**2,6-Bis(1-(5-(3,5-bis(trifluoromethyl)benz-n-6-methylphenylimino)ethyl)pyridine (27)**

3,5-Bis-trifluoromethylphenylboronic acid [10.3 g (0.04 mol)], 5.0 g (0.01 mol) of 26, 12.64 g (0.0388 mol) of cesium carbonate, 0.71 g (0.00078 mol) of tris(dibenzylideneacetone) dipalladium (0), 0.55 g (0.00233 mol) of 28, and 50 ml of dioxane were stirred at room
temperature for 24 h. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting mixture was purified by recrystallization from 20 ml of ethanol. Yield of 27 was 4.45 g (58%) as a light yellow solid. \( ^1H \) NMR (500 MHz, \( \text{C}_6\text{D}_6 \), TMS): \( \delta 2.10 \) (s, 6 H, Me), \( \delta 2.32 \) (s, 6 H, Me), \( \delta 6.80 \) (s, 2H, Arom-H), \( \delta 6.85 \) (m, 2H, Arom-H), \( \delta 7.11 \) (m, 2H, Arom-H), \( \delta 7.30 \) (m, 2H, Arom-H), \( \delta 7.40 \) (t, \( J_{HH} = 7.8 \) Hz, 1H, Py-H), \( \delta 7.60 \) (s, 2H, Arom-H), \( \delta 8.50 \) (d, \( J_{HH} = 7.8 \) Hz, 2H, Py-H). \( ^{13}C \) NMR (500 MHz, \( \text{C}_6\text{D}_6 \), (selected signals)): \( \delta 167.3 \) (C=N). \( ^{19}F \) NMR (\( \text{C}_6\text{D}_6 \)) - 63.07 (s, 12F).

**EXAMPLE 12**

2.6-Bis(1-(5-(3,5-bis(trifluoromethyl)phenyl)-6-methylphenylimino)ethylopyridine iron (II) chloride (30)

![Structure](image)

27 [0.9 g (0.001 18 mol)] was dissolved in 30 ml of THF, and then 0.13 g (0.001 mol) of anhydrous iron(II) chloride was added in one portion. The resultant blue precipitate was filtered after 12 h of stirring, washed twice by 20 ml of pentane, and dried at 133 Pa pressure. Yield of 30 was 0.95 g (83%). Anal. Calculated for \( \text{C}_{39}\text{H}_{27}\text{Cl}_2\text{F}_{12}\text{FeN}_3 \) (Mol. Wt.: 892.38): C, 52.49; H, 3.05; N, 4.71. Found: C, 52.54; H, 3.14; N, 4.78. The structure was proven by X-ray analysis.
EXAMPLE 13

1-(6-ri-(4-Bromo-2,6-dirr!ethyl-phenylirnino)-ethyl-pyridin-2-yl)-ethanone

(31)

1-(6-Acetyl-pyridin-2-yl)-ethanone [22.5 g (0.138 mol), 25.0 g (0.125) o f 4-bromo-2,6-dimethylphenylamine and 300 ml of n-propanol with a few crystals of p-toulenesulfonic acid were stirred at room temperature for 36 h in a 500 ml flask under a flow of the nitrogen. The resultant yellow precipitate was filtered and washed with 20 ml of methanol. It was then dried at 133 Pa pressure overnight. The yield of 31 was 19.08 g (44%) as a yellow solid. 1H NMR (500 MHz, CD2Cl2, TMS): δ 1.95 (s, 6 H, Me), 2.22 (s, 3 H, Me), 2.30 (s, 3 H, Me), 6.80 (s, 2H, Arom-H), 7.95 (t, 3JHH=8.0 HZ, 1H, Py-H), 8.15 (d, 3JHH=8.0 HZ, 1H, Py-H), 8.40 (d, 3JHH=8.0 HZ, 1H, Py-H). 13C NMR (500 MHz, CD2Cl2, TMS (selected signals)): δ 168.4 (C=N), 199.5 (C=O). Anal. Calculated for C17H17BrN2O (Mol. Wt.: 345.23): C, 59.14; H, 4.96; N, 8.11. Found: C, 59.18; H, 5.07; N, 8.15.

EXAMPLE 14

4-Bromo-2,6-dimethyl-phenyl)(1-f6-f1-(3,5-dibromo-4-
methylphenylimino)ethy pyridin-2-yl)-ethylidene)amine (32)

31 [5.0 g (0.0145 mol)], 4.45 g (0.016 mol) of 3,5-dibromo-4-methylphenylamine, 100 g of fresh molecular sieves and 100 ml of toluene were
kept at 90°C for 3 d under a flow of nitrogen. The solvent was removed by a rotary evaporator and the residue was recrystallized from 10 ml of ethanol. The yield of 32 was 5.75 g (67%) as a yellow solid. \(^1\)H NMR (500 MHz, \(\text{CD}_2\text{Cl}_2\), TMS): \(\delta \) 1.60 (s, 6 H, Me), 2.10 (s, 3 H, Me), 2.15 (s, 3 H, Me), 2.45 (s, 3 H, Me), 6.97 (s, 2H, Arom-H), 7.15 (s, 2H, Arom-H), 7.40 (t, \(^3\)J\(_{HH}\)=8.0 Hz, 1H, Py-H), 8.20 (d, \(^3\)J\(_{HH}\)=8.0 Hz, 1H, Py-H), 8.40 (d, \(^3\)J\(_{HH}\)=8.0 Hz, 1H, Py-H). \(^{13}\)C NMR (500 MHz, \(\text{CD}_2\text{Cl}_2\), TMS (selected signals)): \(\delta \) 168.5 (C=N), 164.4 (C=N). Anal. Calculated for \(\text{C}_{24}\text{H}_{22}\text{Br}_3\text{N}_3\) (Mol. Wt: 592.16): C, 48.68; H, 3.74; N, 7.10. Found: C, 48.69; H, 3.82; N, 7.17.

**EXAMPLE 15**

4-(3,5-Bis-trifluoromethylphenyl)-2,6-dimethyl-phenyl \(\pi\)(1-{6-ri-(3,5-(3,5-bis(trifluoromethyl)phenyl)-4-methylphenylimino)ethvlpyridin-2-vl}ethvlidene)amine (33)

\[
\begin{align*}
\text{3,5-Bis-trifluoromethylphenylboronic acid [9.92 g (0.0385 mol)]}, & \text{ 3.80 g (0.0096 mol) of 32, 12.54 g (0.0385 mol) of cesium carbonate, 0.88 g (0.00096 mol) of tris(dibenzylideneacetone) dipalladium (0), 0.50 g (0.0023 mol) of dHf-butyl(2,2~dimethylpropyl)phosphane and 50 ml of dioxane were stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting mixture was purified by recrystallization from 20 ml of ethanol. Yield of 33 was 5.14 g (76%) as a light yellow solid. } \\
\text{\(^1\)H NMR (500 MHz, \(\text{CD}_2\text{Cl}_2\), TMS ): \(\delta \) 1.55 (s, 3 H, Me), 1.90 (s, 6 H, Me), 2.30 (s, 3 H, Me), 2.49 (s, 3 H, Me), 6.40 (s, 2H, Arom-H), 6.97 (s, 2H, Arom-H), 7.15 (s, 2H, Arom-H), 7.40 (t, } \\
\text{\(^3\)J\(_{HH}\)=8.0 Hz, 1H, Py-H), 7.60 (s, 4H, Arom-H), 8.20 (d, \(^3\)J\(_{HH}\)=8.0 Hz, 1H, Py-H), 8.40 (d, \(^3\)J\(_{HH}\)=8.0 Hz, 1H, Py-H). } \\
\text{\(^{13}\)C NMR (500 MHz, \(\text{CD}_2\text{Cl}_2\), (selected signals)): \(\delta \) 168.0 (C=N), 167.2 (C=N). } \\
\text{\(^{19}\)F NMR (\(\text{CD}_2\text{Cl}_2\) \(\delta \) -} \\
\end{align*}
\]
62.96 (s, 12F), - 63.00 (s, 6F). Anal. Calcd. for C_{48}H_{31}F_{18}N_{3} (Mol. Wt.: 991.75): C, 58.13; H, 3.15; IST, 4.24. Found: C, 58.25; H, 3.18; N, 4.30.

**EXAMPLE 16**

4-(3,5-Bis(trifluoromethyl)phenyl)-2,6-dimethylphenyl)(1-(6-ri-(3,5-(3,5-bis-trifluoromethylphenyl)-4-methyl-phenylimino)ethynpyridin-2-

yl)ethylidene)amine iron (II) chloride (34)

![Chemical Structure](image)

33 [0.5 g (0.0005 mol)] was dissolved in 20 ml of THF, and then 0.064 g (0.0005 mol) of anhydrous iron(II) chloride was added in one portion. The resultant blue precipitate was filtered off after 12 h of stirring, washed twice with 20 ml of pentane, and dried at 133 Pa pressure. Yield of 34 was 0.95 g (83%). Anal. Calculated for C_{48}H_{31}Cl_{2}F_{18}FeN_{3} (Mol. Wt: 1118.50): C, 51.54; H, 2.79; N, 3.76. Found: C, 51.57; H, 3.02; N, 3.94. The structure was proven by X-ray analysis.

**EXAMPLES 17-30 and Comparative Example A**

Oligomerization of Ethylene to g-Olefins

In these Examples complex 1 is

![Chemical Structure](image)

**Oligomerization Procedure**

The oligomerizations were done in a 1-liter stainless steel Autoclave Engineering Zipperclave (Autoclave Engineers, Erie, PA 16509, USA). The iron complex and modified methylaluminoxane (modified methylalumoxane, 7 weight % solution in o-xylene, having some n-butyl groups in place of methyl groups, obtained from Akzo-Nobel Inc., Chicago,
IL 60606 USA) cocatalyst were charged separately using stainless steel injection tubes. The steps for a typical oligomerization follow.

The injectors were charged in a glove box. The cocatalyst was charged into the injector assembly along with a 10 ml chase of o-xylene. The complexes are prepared as suspensions in o-xylene (10mg/100 ml). A sample was withdrawn from a well-stirred suspension and was added to 10 ml of o-xylene. The injectors were attached to autoclave ports equipped with dip tubes. Nitrogen was sparged through the loose fittings at the attachment points prior to making them tight. The desired charge of o-xylene was then pressured into the autoclave. The agitator and heater were turned on, and when the desired temperature was reached, the cocatalyst was charged to the clave by blowing ethylene down through the cocatalyst injector. After a significant pressure rise was seen in the autoclave to indicate the cocatalyst and chase solvent have entered, the injector was isolated from the process using its valves. The pressure controller was then set to 34.5 kPa below the desired ethylene operating pressure and was put in the automatic mode to allow it to control the operation of the ethylene addition valve. When the pressure was 34.5 kPa below the desired operating pressure, the controller was put into manual mode and the valve was set to 0% output. When the batch temperature was stable and at the desired value, the catalyst was injected using enough nitrogen such that the pressure was boosted to the desired operating pressure. At the same time as the catalyst injection, the pressure controller was put in the automatic mode and the oligomerization started. The 34.5 kPa boost was obtained routinely by having a small reservoir between the nitrogen source and the catalyst injector. A valve was closed between the nitrogen source and the reservoir prior to injecting the catalyst so the same volume of nitrogen was used each time to inject the catalyst suspension. To stop the oligomerization, the pressure controller was put into manual, the ethylene valve was closed, and the reactor was cooled.
The amount of metal complex used in the examples depended on the activity of that catalyst. This was done to minimize the exotherm but still enough to make enough α-olefins for analysis.

Conditions and some results for the oligomerizations are shown in Table 1.

<table>
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<th>Ex.</th>
<th>Complex(μmoles)</th>
<th>MMAO,μmoles</th>
<th>Temperature, °C</th>
<th>K value</th>
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<td>21 (0.152)</td>
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<td>120</td>
<td>0.65</td>
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<td>21 (0.107)</td>
<td>1.13</td>
<td>100</td>
<td>0.68</td>
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<tr>
<td>20</td>
<td>22 (0.457)</td>
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<td>130</td>
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<td>120</td>
<td>0.58</td>
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</table>

- **TABLE 1**

  a) Conditions: solvent: o-xylene; pressure: 4.83 MPa(gauge); b) Determined from GC, using extrapolated values for C-10 and C-12 olefins.

Figure 1 shows the Schulz-Flory distributions of α-olefins for oligomerization using 1 (comparative Example A) and 22 (Example 21) as the complexes. It is surprising that 22, which is symmetrical with respect to ortho substitution of the phenyl rings attached to the imino nitrogen atoms, gives such a linear Schulz-Flory distribution, since it was previously believed the such symmetrical ligands led to nonlinear distributions as exemplified by 1, see US 6710006. In Figure 1 the diamonds and upper line (on the left) represent the distribution obtained from 1, while the triangles and lower line (on the left) represent the distribution obtained from 22. The horizontal axis is the degree of polymerization (number of ethylene repeat units) minus 2, while the vertical axis is the natural logarithm of (the weight fraction of a certain degree of polymerization divided by that degree of polymerization).
Table 2 gives ethylene flows (in L/min) with time (min) for selected runs at 120°C, and is a measure of the activity and longevity of the catalyst (Note maximum measurable low rate is 12 L/min).

### TABLE 2

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</table>
PCT CLAIMS

1. A process for the oligomerization of ethylene to linear \( \alpha \)-olefins, comprising contacting, at a temperature of \(-20^\circ C\) to \(200^\circ C\), ethylene and an Fe, Co, Cr or V complex of a ligand of the formula

\[
\text{(I)}
\]

wherein:

- \( R^1, R^2 \) and \( R^3 \) are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of \( R^1, R^2 \) and \( R^3 \) vicinal to one another taken together may form a ring;

- \( R^4 \) and \( R^5 \) are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group provided that \( R^1 \) and \( R^4 \) and/or \( R^3 \) and \( R^5 \) taken together may form a ring;

- \( R^6 \) and \( R^7 \) are each independently phenyl or substituted phenyl having a first ring atom bound to the imino nitrogen, provided that at least one of \( R^6 \) and \( R^7 \) is substituted in at least one meta position with an aryl or substituted aryl group.

2. The process as recited in claim 1 wherein \( R^6 \) is

\[
\text{(II)}
\]

and \( R^7 \) is
wherein:

if $R_8$ is a primary carbon group or halogen, $R_{13}$ is a primary carbon group or halogen, and $R_{12}$ and $R_{17}$ are hydrogen; or

if $R_8$ is a secondary carbon group, $R_{13}$ is a primary carbon group, halogen or a secondary carbon group, more preferably a secondary carbon group, and $R_{12}$ and $R_{17}$ are hydrogen; or

if $R_8$ is a tertiary carbon group (more preferably a trihalo tertiary carbon group such as a trihalomethyl), and $R_{12}$, $R_{13}$ and $R_{17}$ are hydrogen; or

if $R_8$ is a primary carbon group or halogen, $R_{12}$ is a primary carbon group or halogen, and $R_{13}$ and $R_{17}$ are hydrogen; or

if $R_8$ is a secondary carbon group, $R_{12}$ is a primary carbon group, halogen or a secondary carbon group, more preferably a secondary carbon group, and $R_{13}$ and $R_{17}$ are hydrogen.

3. The process as recited in any one of the preceding claims wherein $R_6$ is

and $R_7$ is

$R_9$ is aryl or substituted aryl and $R_9$, $R_{11}$ and $R_{16}$ are hydrogen; or

$R_{14}$ is aryl or substituted aryl and $R_9$, $R_{11}$ and $R_{16}$ are hydrogen; or
R\(^9\) and R\(^{11}\) are each independently aryl or substituted aryl and R\(^{16}\) are hydrogen; or

R\(^9\), R\(^{11}\), and R\(^{14}\) are each independently aryl or substituted aryl and R\(^{16}\) is hydrogen; or

R\(^9\), R\(^{14}\), and R\(^{16}\) are each independently aryl or substituted aryl and R\(^{11}\) is hydrogen; or

R\(^9\), R\(^{11}\), R\(^{14}\) and R\(^{16}\) are each independently aryl or substituted aryl.

4. The process as recited in any one of the preceding claims wherein said temperature is about 80\(^\circ\)C to about 150\(^\circ\)C.

5. The process as recited in claim 1 which is batch, semi-batch or continuous.

6. A compound of the formula

\[
\begin{align*}
\text{R}^1, \text{R}^2 \text{ and } \text{R}^3 & \text{ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of } \text{R}^1, \text{R}^2, \text{ and } \text{R}^3 \text{ vicinal to one another taken together may form a ring;} \hfill \\
\text{R}^4 \text{ and } \text{R}^5 & \text{ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group provided that } \text{R}^1 \text{ and } \text{R}^4 \text{ and/or } \text{R}^3 \text{ and } \text{R}^5 \text{ taken together may form a ring;} \hfill \\
\text{R}^6 \text{ and } \text{R}^7 & \text{ are each independently phenyl or substituted phenyl having a first ring atom bound to the imino nitrogen, provided that at least one of } \text{R}^6 \text{ and } \text{R}^7 \text{ is substituted in at least one meta position with an aryl or substituted aryl group.}
\end{align*}
\]

7. A compound which is a Fe, Co, Cr or V complex of a ligand of the formula
wherein:

- \( R_1, R_2 \) and \( R_3 \) are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of \( R_1, R_2 \) and \( R_3 \) vicinal to one another taken together may form a ring;
- \( R_4 \) and \( R_5 \) are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group provided that \( R_1 \) and \( R_4 \) and/or \( R_3 \) and \( R_5 \) taken together may form a ring;
- \( R_6 \) and \( R_7 \) are each independently phenyl or substituted phenyl having a first ring atom bound to the imino nitrogen, provided that at least one of \( R_6 \) and \( R_7 \) is substituted in at least one meta position with an aryl or substituted aryl group.

8. The compound as recited in claim 6 or 7 wherein \( R_8 \) is

![Diagram II](image-url)

and \( R_7 \) is

![Diagram III](image-url)

wherein:

- if \( R_8 \) is a primary carbon group or halogen, \( R_13 \) is a primary carbon group or halogen, and \( R_12 \) and \( R_17 \) are hydrogen; or

---
it K” is a secondary carbon group, R^{13} is a primary carbon group, halogen or a secondary carbon group, more preferably a secondary carbon group, and R^{12} and R^{17} are hydrogen; or

if R^8 is a tertiary carbon group (more preferably a trihalo tertiary carbon group such as a trihalomethyl), and R^{12}, R^{13} and R^{17} are hydrogen; or

if R^8 is a primary carbon group or halogen, R^{12} is a primary carbon group or halogen, and R^{13} and R^{17} are hydrogen; or

if R^8 is a secondary carbon group, R^{12} is a primary carbon group, halogen or a secondary carbon group, more preferentially a secondary carbon group, and R^{13} and R^{17} are hydrogen.

9. The compound as recited in claim 6, 7 or 8 wherein R^6 is

\[ \text{Diagram} \]

and R^7 is

\[ \text{Diagram} \]

R^9 is aryl or substituted aryl and R^{11}, R^{14} and R^{16} are hydrogen; or

R^{14} is aryl or substituted aryl and R^9, R^{11} and R^{16} are hydrogen; or

R^9 and R^{14} are each independently aryl or substituted aryl and R^{11} and R^{16} are hydrogen; or

R^9, R^{11}, and R^{14} are each independently aryl or substituted aryl and R^{16} is hydrogen; or

R^9, R^{14}, and R^{16} are each independently aryl or substituted aryl and R^{11} is hydrogen; or

R^9, R^{11}, R^{14} and R^{16} are each independently aryl or substituted aryl.
INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/043946

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C2/32 C07D213/53 C07F15/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C C07D C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No

F.X IONKIN, ALEX S. ET AL: "High-Temperature Catalysts for the Production of .alpha.-Olefin Based on Iron(II) and Iron(III) Tridentate Bis(imino)pyridine Complexes with Double Pattern of Substitution: Ortho-Methyl plus meta-Aryl" ORGANOMETALLICS, 25(12), 2978-2992 CODEN: ORGN7; ISSN: 0276-7333, 2006, XP002426869 the whole document 1-9


X WO 2004/026795 A (DU PONT [US]) 1 April 2004 (2004-04-01) cited in the application the whole document

D Further documents are listed in the continuation of Box C

X See patent family annex

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Date of the actual completion of the international search
27 March 2007

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## INTERNATIONAL SEARCH REPORT

**Information on patent family members**

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