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(54) **Title:** NEW TRIDENTATE LIGAND COMPOUNDS WITH IMINO FURAN UNITS, METHOD FOR MANUFACTURING SAID COMPOUNDS, AND THEIR USE IN THE PREPARATION OF CATALYSTS FOR THE HOMOPOLYMERISATION AND COPOLYMERISATION OF ETHYLENE AND ALPHA-OLEFINS.

(57) **Abstract:** The present invention relates to new tridentate ligand compounds with imino furan units, to a method for manufacturing said compounds and to their use in the preparation of catalysts for the homopolymerisation or copolymerisation of ethylene and alpha-olefins.

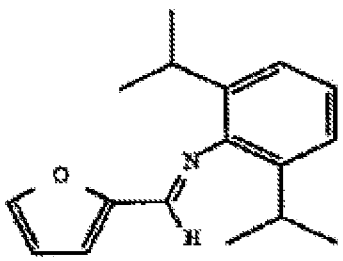
NEW TRIDENTATE LIGAND COMPOUNDS WITH IMINO FURAN UNITS, METHOD FOR MANUFACTURING SAID COMPOUNDS, AND THEIR USE IN THE PREPARATION OF CATALYSTS FOR THE HOMOPOLYMERISATION AND COPOLYMERISATION OF ETHYLENE AND ALPHA-OLEFINS

The present invention relates to new tridentate ligand compounds with imino furan units, to a method for manufacturing said compounds and to their use in the preparation of catalysts for the homopolymerisation and copolymerisation of ethylene and alpha-olefins.

More precisely, the present invention relates to the use of such new ligand compounds for preparing metallic complexes useful as catalysts for the homopolymerisation and copolymerisation of ethylene and α-olefins, to the catalytic systems including such metallic complexes and to a method for homopolymerising or copolymerising ethylene and α-olefins using such catalytic systems.

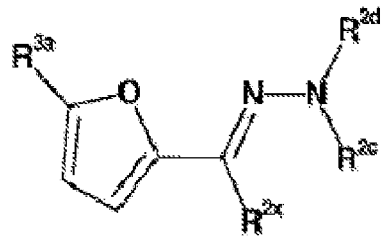
Different neutral bidentate ligands with imino furan units are mentioned :

In US patent 5,714,556 (ligand 78, column 36) :



; and

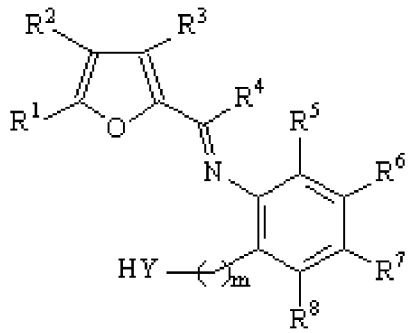
in WO 00/50470 (ligand a18, p 28) or corresponding US patent 6,545,108 B1



wherein R^{3a}, R^{2d}, R^{2c} and R^{2x} have different meanings.

The Applicant searched for other ligands in order to produce new catalysts for the polymerisation of ethylene and of α-olefins, and discovered the new tridentate anionic ligands with imino furane units, which are the subject-matter of the present invention. The homopolymers of ethylene obtained with such new catalysts are linear and have a monomodal distribution of polydispersity of 3 to 9 with very small tail ends.

A first subject-matter of the present invention relates to a compound of formula (I) :



(I)

wherein :

- R^1 to R^8 each represent independently hydrogen, halogen, a substituted or unsubstituted C_1-C_{20} hydrocarbyl group, an inert functional group, wherein each of the radicals R^1 to R^8 can be linked to a neighbouring radical in order to form a cycle with carbon atoms to which said radicals are attached ;
- Y represents O or NR^*, R^* being a C_1-C_{12} alkyl group or a C_6-C_{12} aryl group ;
- m is 0, 1 or 2.

The hydrocarbyl groups encompass methyl, tert-butyl and phenyl groups. The hydrocarbyl groups can include a heteroatom such as oxygen or nitrogen atoms in their chains.

The possible substituents of hydrocarbyl groups can be selected among CF_3, NO_2, OMe and halogen such as Cl.

The inert functional groups can be selected among CF_3, NO_2, OMe and halogen.

R^1 to R^3 are each preferably selected independently from the group consisting of hydrogen and aryl groups. Aryl groups can be selected among phenyl, naphthyl, and substituted phenyl groups.

R^4 is preferably selected in the group consisting of hydrogen and methyl group.

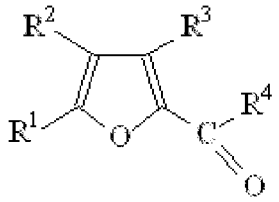
R^5 to R^8 are preferably independently selected in the group consisting of hydrogen, alkyl, aryl, methoxy, halogen, nitro and cyano.

Y is preferably O. m is preferably 0 or 1.

Specific compounds of formula (I) are the following ones :

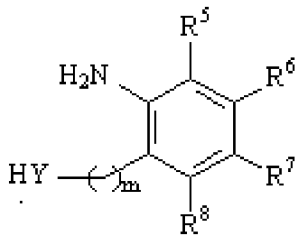
- 2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 4-methyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 4-tert-butyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-l]methyleneamino}phenol
- 3-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}biphenyl-4-ol
- 4-chloro-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(3-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 4-nitro-2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(3-nitrophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(3-chlorophenyl)furan-2-yl)]methyleneamino}phenol
- 2-{[5-(2-chlorophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(4-chlorophenyl)furan-2-yl]methyleneamino}phenol

Another subject-matter of the present invention relates to a method for manufacturing a compound of formula (I) as defined above, characterised in that a compound of formula (II) :



(II)

wherein R^1 to R^4 are as defined above
is reacted with a compound of formula (III) :



(III)

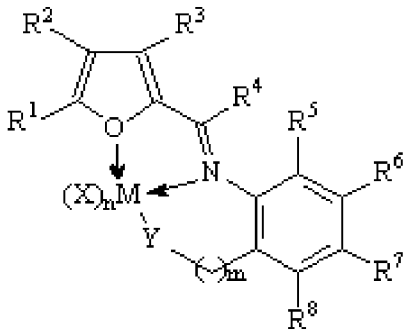
wherein m is 0, 1 or 2 and R^5 to R^8 are as defined above.

The general conditions of such a reaction are as follows :

- Reacting compound (III) with compound (II) in an alcohol such as methanol or ethanol, in the presence of a catalytic amount of a protic acid such as acetic acid, at room temperature.
- Removing the solvent by evaporation under reduced pressure to recover compound (I).
- Recrystallising or washing the product in an alcane such as pentane or hexane.

A further subject-matter of the present invention relates to the use of a compound as defined above or prepared by the method as defined above as a ligand of a metallic complex.

A further subject-matter of the present invention relates to a metallic complex of the formula (IV):



(IV)

wherein :

- R^1 to R^8, Y and m are as defined above ;
- M is a metal belonging to groups 3 to 8 of the Periodic Classification ;
- X represents an halogen, a substituted or unsubstituted C_1-C_{20} hydrocarbyl group, an amino group, an aryloxy group or an alkoxy group ; and
- n is a numeral value determined by the oxidation state of the metal minus one.

The preferred definitions for R^1 to R^8, Y and m are as mentioned above for the compound of formula (I).

M is preferably selected from the metals belonging to groups 3 to 8 of the Periodic Classification, being in particular Ti, Cr, Fe, Zr, Hf, V, Mn, a rare-earth metal, being preferably Ti, Cr, Fe and Zr.

X preferably represents halogen, alkyl such as benzyl, amino such as dimethylamino, alkoxy such as isopropoxy, aryloxy such as phenoxy, preferably halogen such as chlorine.

A further subject-matter of the present invention relates to a method for manufacturing a metallic complex as defined above, wherein a metallic compound of formula (V) :

$$MX_{n+1} \qquad (V)$$

wherein M, X and n are as defined above

is reacted with a ligand of the formula (I) as defined above.

The general conditions of such a reaction are as follows :

- Optionally reacting compound (I) with an equimolar amount of a deprotonating agent such as sodium hydride or butyl lithium, in tetrahydrofuran or diethyl ether at low temperature, under inert atmosphere.
- Adding the resulting mixture or a solution of compound (I) in tetrahydrofuran or diethyl ether to compound (V) and stirring at room temperature.
- Removing the solvent by evaporation under reduced pressure.
- Optionally dissolving the residue in an other solvent such as toluene or dichloromethane, filtering this solution to eliminate the sodium or the lithium salt and evaporating the filtrate to recover compound (IV).

A further subject-matter of the present invention relates to the use of the metallic complex as defined above or prepared by the process as defined above as a catalyst in the homopolymerisation and the copolymerisation of ethylene and α-olefins.

Exemplary α-olefins are the ones having from 3 to 8 carbon atoms, preferably propylene.

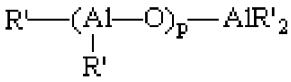
A further subject-matter of the present invention relates to a catalytic system comprising :

- the metallic complex as defined above ;
- an activating agent selected in particular from the aluminum alkyls, the aluminoxanes and the boron-based activators ; and
- optionally, a carrier of the said metallic complex.

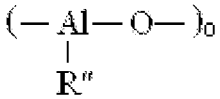
- The aluminum alkyls are represented by the formula AlR_x, wherein R are all identical or different, and are

selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminum alkyls are dialkylaluminum chloride, the most preferred being diethylaluminum chloride (Et_2AlCl).

- The preferred aluminoxanes comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by the formula :



for oligomeric, linear aluminoxanes, and



for oligomeric, cyclic aluminoxanes,

wherein :

- p is 1-40, preferably 10-20 ;
- o is 3-40, preferably 3-20 ; and
- R' or R" is a C_1-C_8 alkyl group, being preferably methyl. Methylaluminoxane is preferably used.

- Suitable boron-based activating agents that can be used comprise a triphenyl carbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium $[C(Ph_3)^+ B (C_6H_5)^-_4]$ as described in EP-A-0,427,696, or those of the general formula $[L\text{-}H']^+ [BAr_1Ar_2X_3X_4]^-$ as described in EP-A-0 277 004 (page 6, line 30 to page 7, line 7).

The support, if present, can be a porous mineral oxide. It is advantageously selected from silica, alumina and mixtures thereof. Preferably, it is silica.

The activating agent is preferably an alkyl aluminum or an aluminoxane, the molar ratio Al/M being approximately 500 to 2000, preferably about 1000.

Still a further subject-matter of the present invention relates to a method for homopolymerising or copolymerising ethylene and α-olefins, comprising the steps of :

(a) injecting into the reactor the catalytic system as defined above, a solvent and optionally a scavenger ;
(b) injecting the monomer and optional comonomer(s) into the reactor either before or after or simultaneously with step (a) ;
(c) maintaining under polymerisation conditions ;
(d) optionally adding an acidic solution of an alcohol to precipitate and filtrate the polymer ;
(e) retrieving the polymer under the form of a powder.

The scavenger may be selected from aluminium alkyls or diethyl zinc.

The monomers that can be used in the present invention are selected among ethylene and α-olefins having from 3 to 8 carbon atoms, being preferably ethylene and propylene.

The conditions of temperature and pressure for the polymerisation process are not particularly limited.

The pressure in the reactor can vary from 0.5 to 50 bars, preferably from 15 to 29 bars.

The polymerisation temperature can range from 10 to 100°C, preferably from 40 to 90°C.

The solvent is typically selected from alcanes or toluene, being preferably toluene, heptane or isobutane.

The reaction is usually carried out for a period of time of from 15 minutes to 24 hours.

The polymer obtained according to the present invention is typically obtained as a powder. The homopolyethylene that can be obtained have a Mn of 25 to 75 kDa, preferably of 30-60 kDa, a Mw of 150-400 kDa, preferably of 175-350 kDa, and a Mw/Mn of about 3 to 9.

The following Examples are intended to illustrate the present invention without limiting its scope.

In these Examples, the following abbreviation have been used :

MAO : Methylaluminoxane

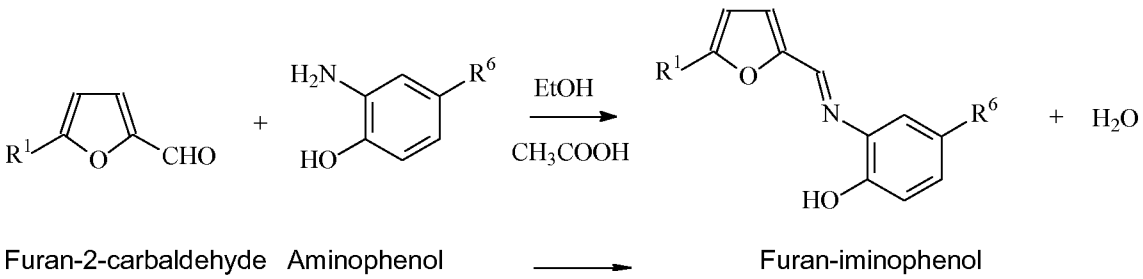
Me : Methyl

Ph : Phenyl

tBu : tert-Butyl

TiBAl : Triisobutylaluminium

Examples 1 to 12 : Synthesis of furan-iminophenol ligands



Furan-2-carbaldehyde Aminophenol ⟶ Furan-iminophenol

General procedure

The aminophenol (12 mmol) was added to a solution of furan-2-carbaldehyde (12 mmol) and acid acetic (0.4 ml) in ethanol (30 ml). The mixture was stirred at room temperature for 18 hours. Then the solvent was removed by evaporation under reduced pressure at 50°C.

The residue was recrystallised in pentane at a temperature of -20°C (Examples 1 to 6). Alternatively, the residue was stirred with 250 ml of pentane, filtered and dried under vacuum (Examples 7 to 12).

Example 1 : Preparation of 2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol (R^1 = 2-CF_3-C_6H_4 ; R^6 = H)

Using 2-aminophenol and 5-(2-(trifluoromethyl)phenyl)furan-2-carbaldehyde, 3.53 g of 2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 89%).

RMN^1 H (CD_2Cl_2, 500 MHz) : ppm 8.57 (s, 1H, HC=N), 7.92 (d, 1H, CF_3-C_6H_4), 7.86 (d, 1H, CF_3-C_6H_4), 7.69 (t, 1H, CF_3-C_6H_4), 7.57 (t, 1H, CF_3-C_6H_4), 7.50 (s, 1H, OH), 7.35 (dd, 1H, C_6H_4OH), 7.23 (td, 1H, C_6H_4OH), 7.18 (d, 1H, C_4H_2O), 7.02 (dd, 1H, C_6H_4OH), 6.95 (td, 1H, C_6H_4OH), 6.94 (d, 1H, C_4H_2O).

Example 2 : Preparation of 4-methyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol (R^1 = 2-CF_3-C_6H_4 ; R^6 = Me)

Using 2-amino-4-methylphenol and 5-(2-(trifluoromethyl)phenyl)furan-2-carbaldehyde, 3.82 g of 4-methyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 92 %).

RMN ^{1}H (CD_2Cl_2, 500 MHz) : ppm 8.53 (s, 1H, HC=N), 7.90 (d, 1H, CF_3-C_6H_4), 7.85 (d, 1H, CF_3-C_6H_4), 7.68 (t, 1H, CF_3-C_6H_4), 7.56 (t, 1H, CF_3-C_6H_4), 7.36 (s, 1H, OH), 7.15 (m, 2H, C_6H_3OH and C_4H_2O), 7.05 (dq, 1H, C_6H_3OH), 6.92 (m, 2H, C_6H_3OH and C_4H_2O), 2.35 (s, 3H, CH_3).

Example 3 : Preparation of 4-tert-butyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol (R^1 = 2-CF_3-C_6H_4 ; R^6 = tBu)

Using 2-amino-4-tert-butylphenol and 5-(2-(trifluoromethyl)phenyl)furan-2-carbaldehyde, 4.25 g of 4-tert-butyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 91 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.57 (s, 1H, HC=N), 7.91 (d, 1H, CF_3-C_6H_4), 7.85 (d, 1H, CF_3-C_6H_4), 7.67 (t, 1H, CF_3-C_6H_4), 7.56 (t, 1H, CF_3-C_6H_4), 7.39 (s, 1H, OH), 7.35 (d, 1H, C_6H_3OH), 7.28 (dd, 1H, C_6H_3OH), 7.16 (d, 1H, C_4H_2O), 6.94 (m, 2H, C_6H_3OH and C_4H_2O), 1.37 (s, 9H, tBu).

Example 4 : Preparation of 3-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}biphenyl-4-ol (R^1=2-CF_3-C_6H_4; R^6=Ph)

Using 3-aminobiphenyl-4-ol and 5-(2-(trifluoromethyl)phenyl)furan-2-carbaldehyde, 1.64 g of 3-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}biphenyl-4-ol was obtained as an orange powder (yield 34 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.62 (s, 1H, HC=N), 7.91 (d, 1H, CF_3-C_6H_4), 7.85 (d, 1H, CF_3-C_6H_4), 7.67 (t, 1H, CF_3-C_6H_4), 7.63 (m, 3H, Ph), 7.56 (m, 2H, OH and CF_3-C_6H_4), 7, 49 (m, 3H, C_6H_3OH and Ph), 7.37 (tt, 1H, C_6H_3OH), 7.19 (d, 1H, C_4H_2O), 7.11 (d, 1H, C_6H_3OH), 6.95 (d, 1H, C_4H_2O).

Example 5 : Preparation of 4-chloro-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol (R^1 = 2-CF_3-C_6H_4 ; R^6 = Cl)

Using 2-amino-4-chlorophenol and 5-(2-(trifluoromethyl)phenyl)furan-2-carbaldehyde, 3.76 g of 4-chloro-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 86 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.52 (s, 1H, HC=N), 7.91 (d, 1H, CF_3-C_6H_4), 7.86 (d, 1H, CF_3-C_6H_4), 7.71 (t, 1H, CF_3-C_6H_4), 7.59 (t, 1H, CF_3-C_6H_4), 7.38 (s, 1H, OH), 7.34 (d, 1H, C_6H_3OH), 7.22 (d, 1H, C_4H_2O), 7.19 (dd, 1H, C_6H_3OH), 6.97 (d, 1H, C_6H_3OH), 6.95 (d, 1H, C_4H_2O).

Example 6 : Preparation of 2-{[5-(3-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol (R^1 = 3-CF_3-C_6H_4 ; R^6 = H)

Using 2-aminophenol and 5-(3-(trifluoromethyl)phenyl)furan-2-carbaldehyde, 3.44 g of 2-{[5-(3-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 86 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.59 (s, 1H, HC=N), 8.10 (m, 1H, CF_3-C_6H_4), 8.05 (dm, 1H, CF_3-C_6H_4), 7.64 (m, 2H, CF_3-C_6H_4), 7.44 (s, 1H, OH), 7.36 (dd, 1H, C_6H_4OH), 7.24 (ddd, 1H, C_6H_4OH), 7.20 (d, 1H, C_4H_2O), 7.03 (dd, 1H, C_6H_4OH), 7.01 (d, 1H, C_4H_2O), 6.96 (ddd, 1H, C_6H_4OH).

Example 7 : Preparation of 4-nitro-2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol (R^1 = 4-NO_2-C_6H_4 ; R^6 = NO_2)

Using 2-amino-4-nitrophenol and 5-(4-nitrophenyl)furan-2-carbaldehyde, 4.10 g of 4-nitro-2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 97 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.72 (s, 1H, HC=N), 8.36 (m, 2H, NO_2-C_6H_4), 8.31 (d, 1H, C_6H_3OH), 8.2 (dd, 1H, C_6H_3OH), 8.04 (m, 2H, NO_2-C_6H_4), 7.34 (d, 1H, C_6H_3OH), 7.16 (m, 2H, C_4H_2O).

Example 8 : Preparation of 2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol (R^1 = 4-NO_2-C_6H_4 ; R^6 = H)

Using 2-aminophenol and 5-(4-nitrophenyl)furan-2-carbaldehyde, 3.62 g of 2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 98%).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.59 (s, 1H, HC=N), 8.33 (m, 2H, NO_2-C_6H_4), 7.99 (m, 2H, NO_2-C_6H_4), 7.49 (s, 1H, OH), 7.37 (dd, 1H, C_6H_4OH), 7.25 (td, 1H, C_6H_4OH), 7.21 (d, 1H, C_4H_2O), 7.12 (d, 1H, C_4H_2O), 7.04 (dd, 1H, C_6H_4OH), 6.97 (td, 1H, C_6H_4OH).

Example 9 : Preparation of 2-{[5-(3-nitrophenyl)furan-2-yl]methyleneamino}phenol (R^1 = 3-NO_2-C_6H_4 ; R^6 = H)

Using 2-aminophenol and 5-(3-nitrophenyl)furan-2-carbaldehyde, 3.51 g of 2-{[5-(3-nitrophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 95 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.62 (t, 1H, NO_2-C_6H_4), 8.55 (s, 1H, HC=N), 8.24 (dm, 1H, NO_2-C_6H_4), 8.13 (dm, 1H, NO_2-C_6H_4), 7.65 (t, 1H, NO_2-C_6H_4), 7.34 (dd, 1H, C_6H_4OH), 7.24 (td, 1H, C_6H_4OH), 7.18 (d, 1H, C_4H_2O), 7.05 (d, 1H, C_4H_2), 7.04 (dd, 1H, C_6H_4OH), 6.96 (td, 1H, C_6H_4OH).

Example 10 : Preparation of 2-{[5-(3-chlorophenyl)furan-2-yl)]methyleneamino}phenol (R^1 = 3-Cl-C_6H_4 ; R^6 = H)

Using 2-aminophenol and 5-(3-chlorophenyl)furan-2-carbaldehyde, 2.94 g of 2-{[5-(3-chlorophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 82 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.43 (s, 1H, HC=N), 7.9 (s, 1H, OH), 7.78 (m, 1H, Cl-C_6H_4), 7.64 (dt, 1H, Cl-C_6H_4), 7.35 (m, 2H, Cl-C_6H_4 and C_6H_4OH), 7.27 (m, 2H, Cl-C_6H_4 and C_6H_4OH), 7.06 (m, 2H, C_6H_4OH and C_4H_2O), 6.95 (td, 1H, C_6H_4OH), 6.88 (d, 1H, C_4H_2O).

Example 11 : Preparation of 2-{[5-(2-chlorophenyl)furan-2-yl]methyleneamino}phenol (R^1 = 2-Cl-C_6H_4 ; R^6 = H)

Using 2-aminophenol and 5-(2-chlorophenyl)furan-2-carbaldehyde, 2.69 g of 2-{[5-(2-chlorophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 75 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.59 (s, 1H, HC=N), 8.08 (dd, 1H, Cl-C_6H_4), 7.54 (dd, 1H, Cl-C_6H_4), 7.44 (td, 2H, Cl-C_6H_4 and OH), 7.36 (m, 3H, Cl-C_6H_4 and C_6H_4OH and C_4H_2O), 7.23 (td, 1H, C_6H_4OH), 7.21 (d, 1H, C_4H_2O), 7.02 (dd, 1H, C_6H_4OH), 6.96 (td, 1H, C_6H_4OH).

Example 12 : Preparation of 2-{[5-(4-chlorophenyl)furan-2-yl]methyleneamino}phenol (R^1 = 4-Cl-C_6H_4, R^6=H)

Using 2-aminophenol and 5-(4-chlorophenyl)furan-2-carbaldehyde, 3.18 g of 2-{[5-(4-chlorophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 89 %).

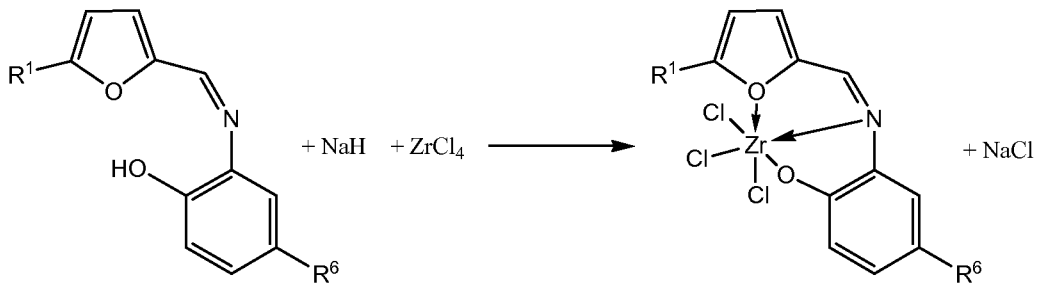
RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.55 (s, 1H, HC=N), 7.81 (dm, 2H, Cl-C_6H_4), 7.47 (dm, 2H, Cl-C_6H_4), 7.35 (dd, 1H, C_6H_4OH), 7.23 (td, 1H, C_6H_4OH), 7.22 (d, 1H, C_4H_2O), 7.03 (dd, 1H, C_6H_4OH), 6.96 (dt, 1H, C_6H_4OH), 6.92 (d, 1H, C_4H_2O).

Example 13 : Preparation of 4-chloro-2-{[5-(4-chlorophenyl)furan-2-yl]methyleneamino}phenol (R^1 = 4-Cl-C_6H_4, R^6=H)

Using 2-amino-4-chlorophenol and 5-(4-chlorophenyl)furan-2-carbaldehyde, 3.18 g of 4-chloro-2-{[5-(4-chlorophenyl)furan-2-yl]methyleneamino}phenol were obtained as a yellow powder (yield 95 %).

RMN ^1H (CD_2Cl_2, 500 MHz) : ppm 8.45 (s, 1H, HC=N), 7.76 (dm, 2H, Cl-C_6H_4), 7.44 (dm, 2H, Cl-C_6H_4), 7.38 (bs, 1H, OH), 7.29 (d, 1H, C_6H_3OH), 7.16 (m, 2H, C_6H_3OH), 6.95 (d, 1H, C_4H_2O), 6.89 (d, 1H, C_4H_2O).

Examples 14 to 25 : Synthesis of furan-iminophenoxyzirconium trichloride complexes



General procedure

The synthesis was done under inert atmosphere with dried solvents. Sodium hydride (2.5 mmol, 0.06 g) was added to a solution of a ligand (2.5 mmol as prepared in Examples 1 to 12, respectively) in THF (15 ml) at -20°C.

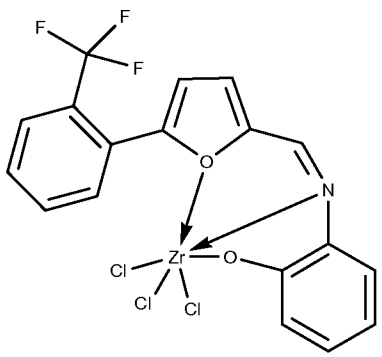
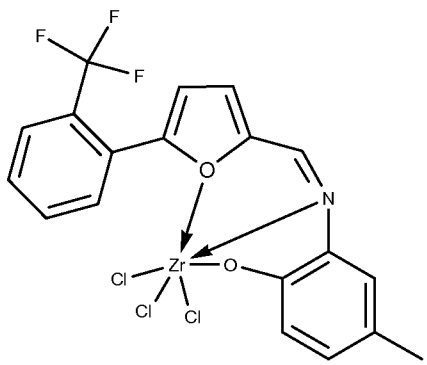
After 2 hours, this red solution was added dropwise to $ZrCl_4$ (2.5 mmol, 0.583 g) and the mixture was stirred overnight at room temperature. Then the solvent was removed by evaporation under reduced pressure and the residue was dissolved in 30 ml of dichloromethane. The solution was filtered through a pad of celite and the filtrate was dried under vacuum. The residue was washed with pentane and dried under vacuum to result in a final product under the form of a red or orange powder.

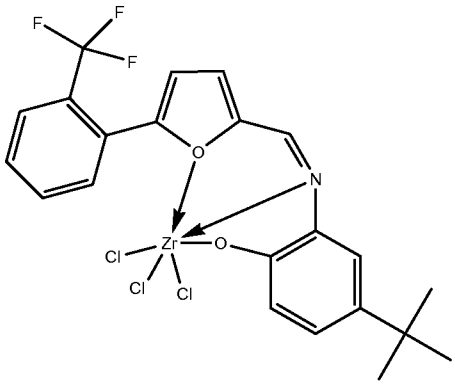
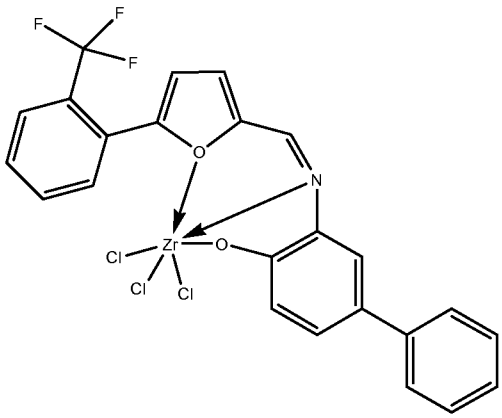
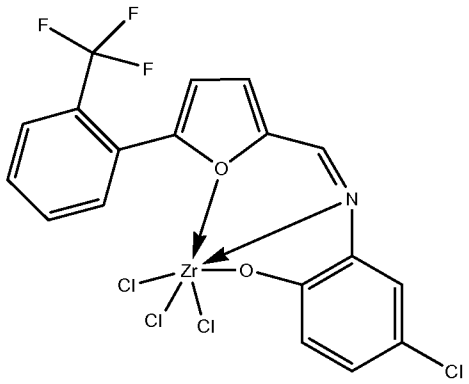
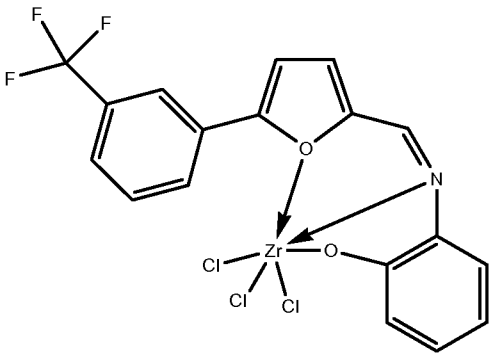
In Table 1 thereafter are listed the complexes obtained thereby as well as for each of them the amount obtained and the yield.

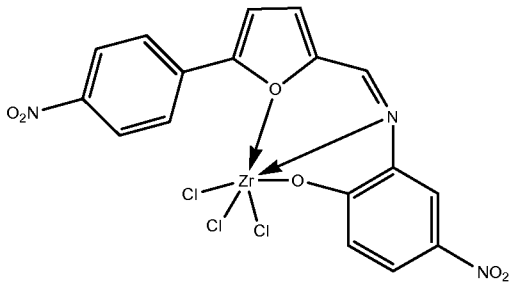
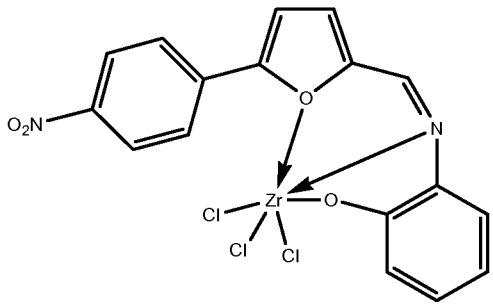
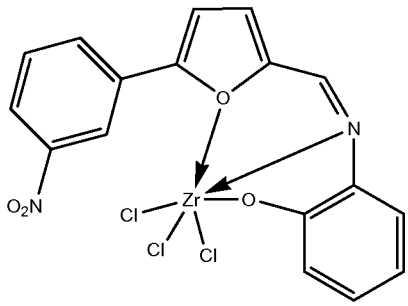
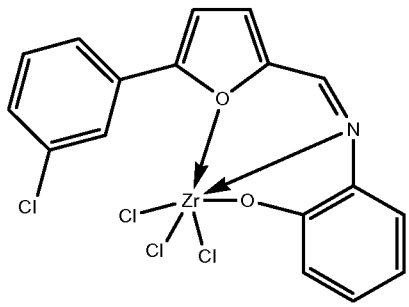
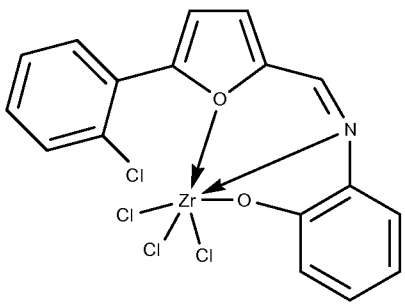
The yield is defined as follows:

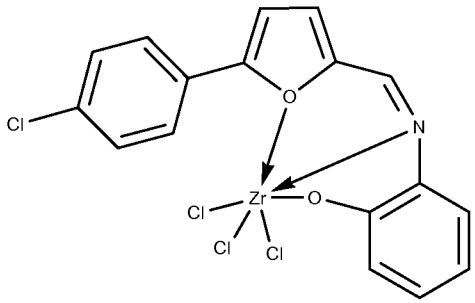
mass of complex obtained/mass of complex expected for 2.5 mmol

Table 1

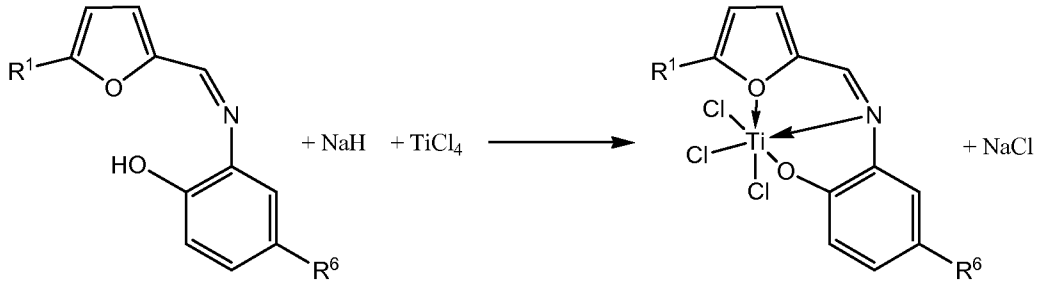
Example	Ligand of Example	Complex	Mass (g)	Yield (%)
14	1		1.31	99
15	2		1.34	99

16	3		1.38	95
17	4		1.50	99
18	5		1.12	80
19	6		1.16	88

20	7		1.34	97
21	8		1.29	100
22	9		1.29	100
23	10		1.44	100
24	11		1.41	100

25	12		1.42	100

Examples 26 to 31 : Synthesis of furan-iminophenoxytitanium trichloride complexes



General procedure

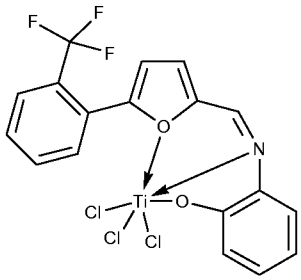
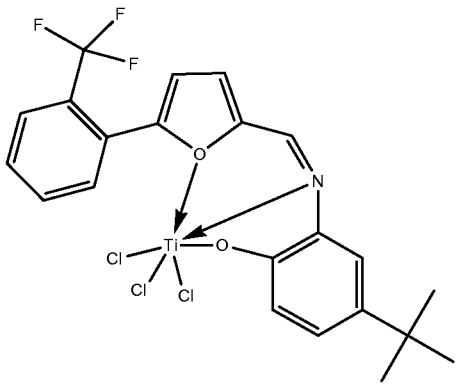
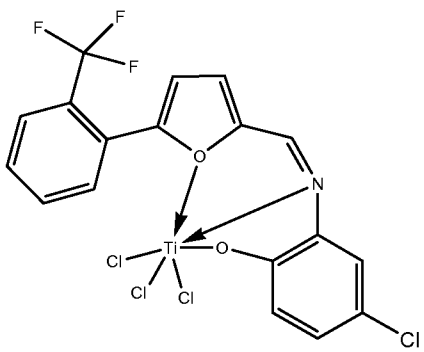
The synthesis was done under inert atmosphere with dried solvents. Sodium hydride (2.5 mmol, 0.06 g) was added to a solution of a ligand (2.5 mmol as prepared in Examples 1 to 13) in THF (15 ml) at -20°C. Then, $TiCl_4$ (2.5 mmol, 0.110 ml) was added dropwise to this red solution and the mixture was stirred overnight at room temperature. Then the solvent was removed by evaporation under reduced pressure and the residue was dissolved in 70 ml of dichloromethane. The solution was filtered through a pad of celite and the filtrate was dried under vacuum. The residue was washed with pentane and dried under vacuum to result in a final product under the form of a red or orange powder.

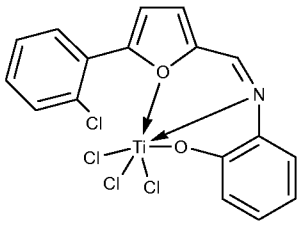
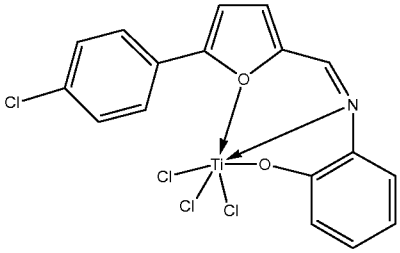
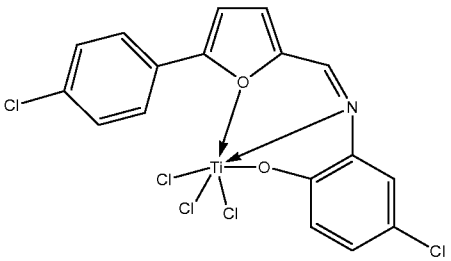
In Table 2 thereafter are listed the complexes obtained thereby as well as for each of them the amount obtained and the yield.

The yield is defined as follows:

mass of complex obtained/mass of complex expected for 2.5 mmol

Table 2

Example	Ligand of Example	Complex	Mass (g)	Yield (%)
26	1		0.74	45
27	3		0.61	61
28	5		0.86	66

29	11		0.58	52
30	12		0.55	49
31	13		0.09	14

Examples 32 to 56 : Polymerisation of ethylene

General procedure

Polymerisation reactions were realised on a 24 parallel reactor unit containing 50 ml glass inserts with magnetic stirrers. In a glove box, 1 mg of complex (as prepared in Examples 14 to 31) was introduced into a vial. Then, 0,8 ml of MAO (30 wt % in toluene) and 24 ml of toluene were added. The vials were crimped with a septum and installed into the reactor unit heated at 60°C. The septa of the vials were pierced by the needles of the reactor unit. The stirring was started and regulated at 1000 rpm. Ethylene was then injected and the pressure was regulated at 22 bar, while the temperature was increased to 80°C. These conditions were maintained during 30 min., then the reactors were depressurised and cooled down. The vials were opened and an acidic alcoholic solution was added. The polymers were filtered, washed and dried. GPC curves are illustrated in figure 1.

Results are summarised as follows:

Table 3

Example	Complex of Example	Mass of complex (mg)	µmol of Complex	Mass of PE (g)	Activity*		Tm** (°C)
					(g/g/h)	kg/mmol/h	
32	14	1.18	2.23	0.79	1344	0.71	n.d.
33	14	1.12	2.13	0.95	1692	0.89	132.8
34	15	1.20	2.22	0.91	1513	0.82	132.8
35	15	1.09	2.02	0.98	1792	0.97	132.8
36	16	1.04	1.78	0.99	1904	1.11	134.1
37	16	1.13	1.94	0.85	1499	0.88	n.d.
38	17	1.14	1.89	1.09	1512	1.15	132.8
39	17	1.28	2.12	1.03	1609	0.97	n.d.
40	18	1.04	1.84	0.90	1736	0.98	n.d.
41	18	1.08	1.93	1.32	2435	1.37	133.4
42	19	1.05	1.99	0.89	1695	0.89	n.d.
43	19	1.11	2.10	0.98	1769	0.93	134
44	20	1.08	1.96	0.91	1690	0.93	n.d.
45	20	1.20	2.18	0.85	1421	0.78	133.2
46	21	1.375	2.72	0.675	981.8	0.50	n.d.
47	22	1.067	2.11	0.833	1561	0.79	n.d.
48	23	0.955	1.93	1.124	2354	1.16	n.d.
49	24	0.993	2.01	1.05	2115	1.05	n.d.
50	25	1.029	2.08	1.293	2513	1.24	n.d.
51	26	0.5908	1.22	0.89	3013	1.46	n.d.
52	27	0.5575	1.03	0.88	3157	1.71	n.d.
53	28	0.539	1.04	0.92	3414	1.77	n.d.
54	29	0.4813	1.07	0.62	2576	1.16	n.d.
55	30	0.4725	1.05	1.01	4275	1.93	n.d.
56	31	0.5018	1.03	0.93	3707	1.80	n.d.

*Activity = Mass of PE (g)/Mass of complex (g)/0.5 h or Mass of PE (g)/µmol of complex/0.5 h

**Tm = measured by DSC method (Differential Scanning Calorimetry) at the second heating (Ramp of 50°C/min from -40°C to 180°C

n.d. = not determined

Examples 57 to 60 : Preparation of supported catalysts

General procedure

The support used was silica Sylopol® 952x1836 from Grace, modified with MAO to obtain a support with 60 wt% of MAO. The complex and the support were stirred in 50 ml of toluene at room temperature during 2 hours. Then the toluene was removed, the resulting catalyst was washed 3 times with pentane and dried under vacuum. The data are given in table 3.

Table 4

Example	Complex of example	Mass of support (g)	Mass of complex (g)	Al* (%)	Zr* (%)
57	16	5.003	0.113	13.85	0.26
58	17	5.262	0.116	13.45	0.28
59	18	5.154	0.119	13.5	0.29
60	19	5.057	0.12	13.60	0.35

*Elemental analysis measured by ICP-AES (Inductively Complet Plasma Atomic Emission Spectrometry)

Examples 61 to 68 : Polymerisation of ethylene with supported catalysts

General procedure

Ethylene polymerisation reactions were carried out in a 130 ml stainless steel autoclave equipped with mechanical

stirring and a stainless steel injection cylinder. In a typical reaction run, the reactor was first dried under nitrogen flow at 100°C during 10 min. Then it was cooled down to the reaction temperature (85°C) and 35 ml of isobutane were introduced into the reactor with a syringe pump, followed by the comonomer if required. The pressure was adjusted to the desired value (23.8 bar) with ethylene. In an argon-filled glove box, 100 mg of the supported catalyst of examples 57 to 60, the scavenger (0.3 ml of TiBAl 10 wt% in hexanes) and 0.4 ml of n-heptane were placed into the injection cylinder. The valve was closed and the cylinder was connected to the reactor under nitrogen flow. The active catalyst mixture was then introduced into the reactor with 40 ml of isobutane. After 1 hour, the reactor was cooled down to room temperature and slowly depressurised, and the polymer was recovered. The polymerisation results are displayed in table 4.

TABLE 5

Example	Catalyst of example	Mass of catalyst (mg)	Mass of PE(g)	Activity* (g/g/h)
61	57	99.7	1.30	13.04
62	57	99.9	1.48	14.81
63	58	100.1	1.50	14.99
64	58	100.4	1.16	11.56
65	59	101.1	1.89**	18.69
66	59	100.0	1.79	17.91
67	60	99.7	0.90	9.03
68	60	99.9	0.98	9.81

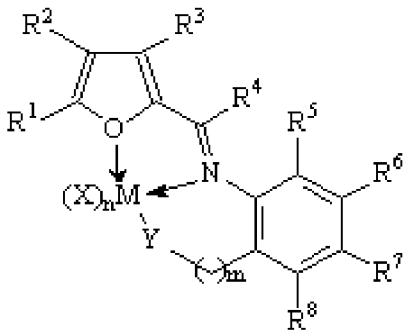
*Activity is expressed as g polyethylene per g catalyst per hour.

The melting temperature Tm of example 42 was of 132.3°C as measured by DSC.

5

CLAIMS

1. A metallic complex of formula (IV) :



(IV)

wherein :

- R^1 to R^8 each represent independently H, halogen, substituted or unsubstituted C_1-C_{20} hydrocarbyl, an inert functional group, wherein each of the radicals R^1 to R^8 can be linked to a neighbouring substituent in order to form a cycle with carbon atoms to which said radicals are attached;
- Y represents O or NR^*, R^* being C_1-C_{12} alkyl or C_6-C_{12} aryl;
- m is 0, 1 or 2;
- M is a metal belonging to the groups 4 to 7 of the Periodic Classification;
- X represents an halogen, a substituted or unsubstituted C_1-C_{20} hydrocarbyl group, an amino, an aryloxy group or an alkoxy group ; and
- n is a numeral value determined by the oxidation state of M minus one.

2. The metallic complex according to claim 1, wherein R^1 to R^3 are each selected independently from the group consisting of H, halogen, alkyl and aryl having up to 12 carbon atoms.

3. The metallic complex according to claim 1 or claim 2, wherein R^4 is selected in the group consisting of hydrogen and methyl.

4. The metallic complex according to any one of claims 1 to 3, wherein R^5 to R^8 are each independently selected from the group consisting of H, alkyl or aryl having up to 12 carbon atoms, halogen, methoxy, nitro and cyano.

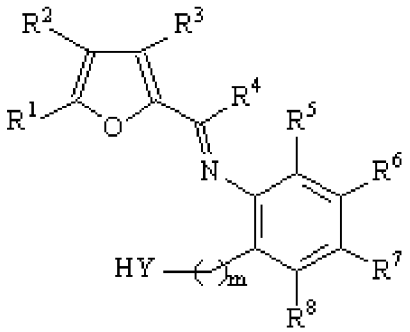
5. The metallic complex according to any one of the preceding claims, wherein Y is O.

6. The metallic complex according to any one of the preceding claims, wherein M is selected from Ti, Cr, Zr, Hf and V.

7. The metallic complex according to any one of the preceding claims, wherein X is halogen, amino, alkyl, alkoxy, aryloxy having up to 12 carbon atoms, preferably halogen.

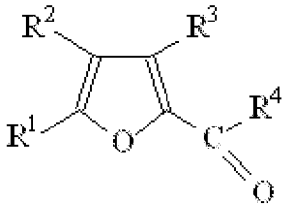
8. A method for manufacturing a metallic complex of formula IV as defined in any one of claims 1 to 7, that comprises the steps of:

a) preparing a compound of formula I



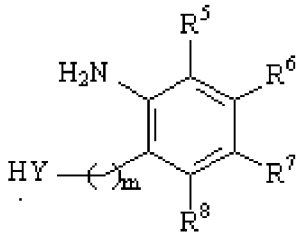
(I)

by reacting a compound of formula II



(II)

wherein R^1 to R^4 are as defined in claim 1
with a compound of formula III



(III)

wherein m, Y, and R^5 to R^8 are as defined in claim 1;

b) reacting compound of formula I with a metallic compound of formula V

$$MX_{n+1} \qquad (V)$$

wherein M, X and n are as defined in claim 1.

9. The method of claim 8 wherein the compound of formula I is selected from the group consisting of:

- 2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 4-methyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 4-tert-butyl-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-l]methyleneamino}phenol

- 3-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}biphenyl-4-ol
- 4-chloro-2-{[5-(2-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(3-(trifluoromethyl)phenyl)furan-2-yl]methyleneamino}phenol
- 4-nitro-2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(4-nitrophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(3-nitrophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(3-chlorophenyl)furan-2-yl)]methyleneamino}phenol
- 2-{[5-(2-chlorophenyl)furan-2-yl]methyleneamino}phenol
- 2-{[5-(4-chlorophenyl)furan-2-yl]methyleneamino}phenol

10. A catalytic system comprising :

- the metallic complex as defined in anyone of claims 1 to 7;
- an activating agent selected in particular among aluminium alkyls, aluminoxanes and boron-based activators, in particular aluminoxanes, preferably methylaluminoxane ; and
- optionally, a support of said metallic complex.

11. The catalytic system according to claim 10, wherein the activating agent is aluminium alkyl or aluminoxane, the molar ratio Al/M being approximately 500 to 2000, preferably 1000.

12. A method for homopolymerising or copolymerising ethylene and α-olefins, that comprises the steps of :

(a) injecting into the reactor the catalytic system as defined in claim 10 or 11 and a solvent and optionally a scavenger ;

(b) injecting the monomer and optional comonomer(s) into the reactor, either before or after or simultaneously with step (a) ;

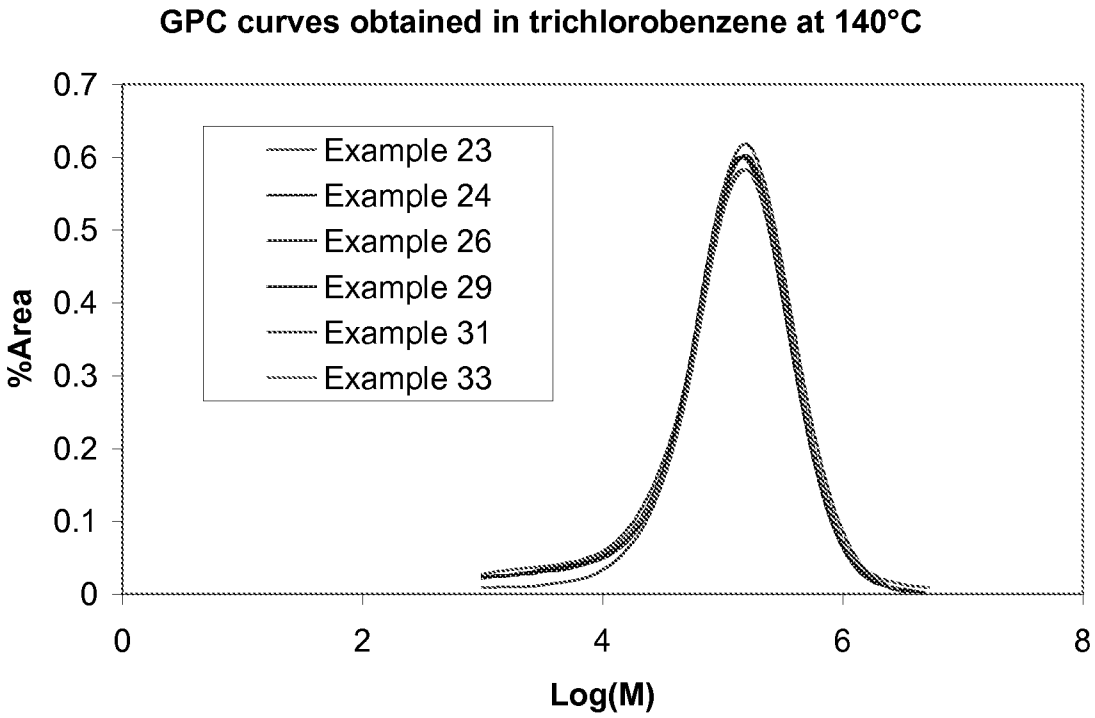
(c) maintaining under polymerisation conditions ;

(d) optionally adding an acidic solution of an alcohol to precipitate and filtrate the polymer ;

(e) retrieving the polymer under the form of a powder.

13. The method of claim 12 wherein the monomer is ethylene or propylene and the comonomer is propylene or 1-hexene.

Figure 1


GPC curves obtained in trichlorobenzene at 140°C
%Area
Log(M)
Example 23
Example 24
Example 26
Example 29
Example 31
Example 33
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/056692

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J21/00 C08F4/76 C08F2/00

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)
B01J C08F

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, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/107345 A1 (ITTEL STEVEN DALE [US] ET AL) 8 August 2002 (2002-08-08) compound (XIX) on page 6 page 1, column 1, paragraph 5	1-13
Y	EP 1 238 989 A (MITSUI CHEMICALS INC [JP]) 11 September 2002 (2002-09-11) examples on pages 37, 38, 74 and 75 claims 1-7	1-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
16 October 2008	22/10/2008

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/056692

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 5 714 556 A (JOHNSON LYNDA KAYE [US] ET AL) 3 February 1998 (1998-02-03) cited in the application compound 78 in column 36 abstract	1-13
Y	WO 2004/041796 A (BASF AG [DE]; PREISHUBER-PFLUEGL PETER [DE]; OKUDA JUN [DE]; REIMER VA) 21 May 2004 (2004-05-21) claims 1,7,17; examples 2-4	1-13
Y	BELAL A A M: "Complexes of Co(II), Ni(II), Cu(II), UO2(II), Fe(III), Y(III) and La(III) with Schiff bases derived from 2-furancarboxaldehyde and hydroxyanilines" ASW.SC.TEC.BULL., vol. 17, 1996, pages 2-11, XP009093256 first formula on page 7 FOA chelates in Table 1 page 3, paragraph 1	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/056692

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