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Scandium complexes with [N,N,Cp] and [N,N,O] donor-set ancillary ligands as catalysts in olefin polymerization

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ABSTRACT

New Sc(III) chloro-complexes [$ScCl_2$(NNCp)(THF)] (**1**), [$ScCl_2$(NNO)(THF)] (**2**) and [$ScCl_2$(NNHO)(THF)] (**3**) {NNCp = 6-cyclopentadienylmethyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine; NNO = 2-*tert*-butyl-6-((quinolin-8-ylimino)methyl)phenolate); NNHO = 2-*tert*-butyl-6-((quinolin-8-ylamino)methyl)phenolate} have been synthesized and characterized by NMR and mass spectrometry. The comparative results of the catalytic behavior of these scandium complexes towards ethylene and butadiene polymerization are reported and explained on the basis of the electronic and steric properties of the ancillary ligands.

1. Introduction

Group 4 metal complexes such as titanocenes and zirconocenes are highly active catalysts in homogeneous olefin polymerization [1]. However, it has been observed that the use of *ansa*-dicyclopentadienyl ligands can sometimes lead to a reduction of the electrophilicity of the metal centers and to create steric hindrance in the polymerization of higher α-olefins. In the last few years, to reduce both steric and electronic problems, research has been directed also toward the synthesis of new mono-cyclopentadienyl (CGC) and cyclopentadienyl-free derivatives. Phenoxyimine Group 4 metal complexes, developed by Fujita et al., have shown ethylene polymerization activities comparable or higher than those of metallocenes and in some cases α-olefin stereospecific polymerization [2].

Polyolefins can be also obtained in the presence of a number of neutral and cationic alkyl complexes of the rare-earth metals, stabilized by both cyclopentadienyl- and non-cyclopentadienyl ancillary ligands [3] and the expected electrophilicity of Group 3 metals makes them attractive as homogeneous catalysts for Ziegler–Natta polymerization.

Our recent research interest in the field of olefin polymerization has mainly been devoted to Group 3 and Lanthanides Constrained Geometry Catalysts [4] and Group 4 complexes with tridentate [N,N,O]-donor-set ancillary ligands [5]. In this paper we report the synthesis of three new Sc(III) chloro-complexes with anionic *ansa*-monocyclopentadienyl-imino-pyridine (**1**), quinolinephenoxyimine (**2**) and quinolinephenoxyamine (**3**) ancillary ligands, together with the results of a comparative catalytic behavior of these new species towards olefin polymerization.

2. Experimental

2.1. Materials and methods

All inorganic manipulations were carried out under oxygen- and moisture-free atmosphere in a Braun MB 200 G-II glovebox. All reaction solvents were thoroughly deoxygenated and dehydrated under argon by refluxing over suitable drying agents, while NMR solvents were kept in the dark over molecular sieves. The salt $ScCl_3$ (Strem) was used as received, like 2,6-dihydroxymethyl-pyridine, 8-aminoquinoline and 3-*tert*-butyl-2-hydroxybenzaldehyde (Aldrich). Cyclopentadiene was obtained by cracking of dicyclopentadiene (Aldrich). Potassium cyclopentadienide was obtained by reacting freshly distilled cyclopentadiene with a stoichiometric amount of potassium *tert*-butoxide (Aldrich) in hexane. 2,6-Diisopropylaniline (Aldrich) was purified by reaction with a stoichiometic amount of methanesulphonic acid (Aldrich) in *n*-hexane. The white precipitate formed was collected, washed with *n*-hexane and dried *in vacuo*. Subsequently, the methanesulphonate salt was allowed to react with $NaHCO_3$

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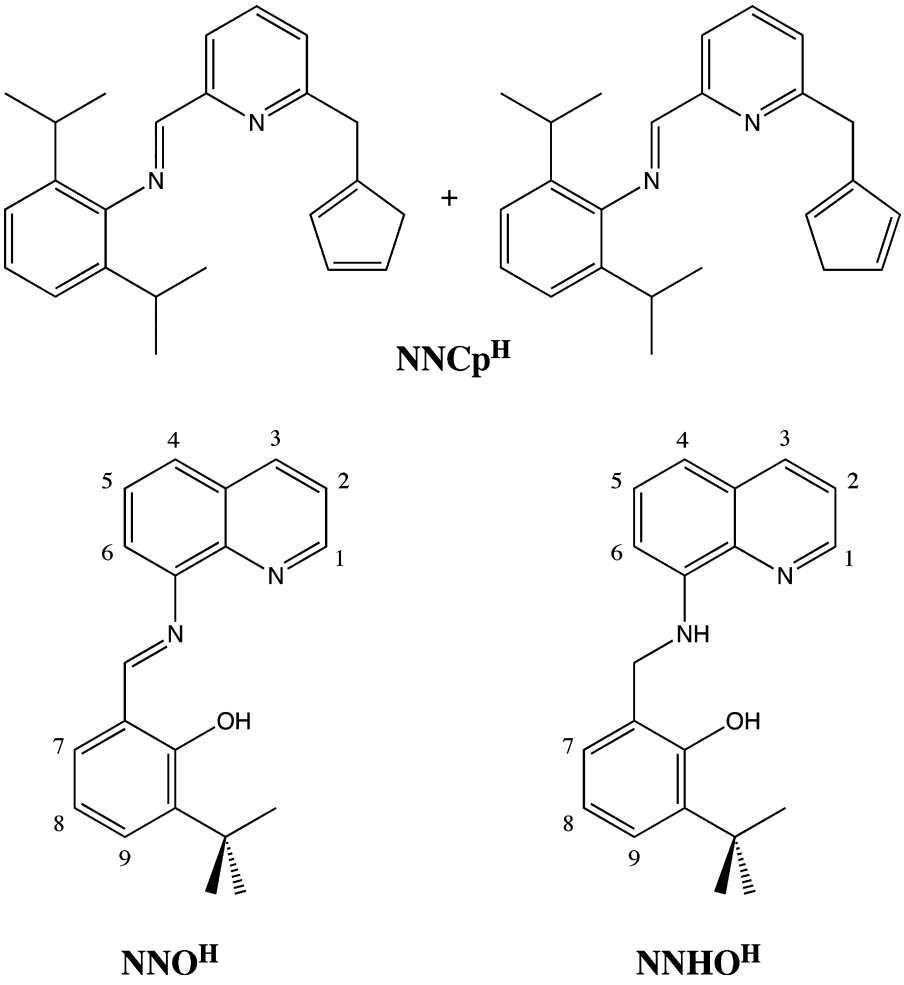


Scheme 1. $NNCp^H$, NNO^H and $NNHO^H$ compounds.

in water. 2,6-Diisopropylaniline was recovered by extraction with diethylether and, once dried the organic solution over anhydrous $MgSO_4$, the solvent was eliminated under reduced pressure to afford the pure aniline, which was stored in the dark.

The neutral ligand $NNCp^H$, which is a tautomeric mixture of (6-cyclopenta-1,3-dienylmethyl-pyridin-2-ylmethylene)-(2,6-di-isopropyl-phenyl)-amine and (6-ciclopenta-1,4-dienylmethyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine, was prepared following a reported procedure [4]. Also the synthesis of the ligand NNO^H, 2-*tert*-butyl-6-[(quinolin-8-ylimino)methyl] phenol, has been recently published [5]. These ligands are depicted in Scheme 1. The organometallic precursor $Sc(CH_2SiMe_3)_3{\cdot}2THF$ was synthesized following the literature method [6].

All the polymerization operations were performed under nitrogen atmosphere by using conventional Schlenk-line techniques. Methylaluminoxane (10% in toluene, Witco) was used as a solid after distillation of solvent. Ethylene (>98%), 1,3-butadiene (>99%), $Mg(Bu)_2$ were purchased from Aldrich, $B(C_6F_5)_3$ was purchased from Boulder.

2.2. Ligands and complexes characterization

Microanalyses were performed at the Istituto di Chimica Inorganica e delle Superfici, CNR, Padova. ^1H NMR, ^{13}C $\{^1H\}$ NMR, COSY, NOESY and ^{13}C APT were recorded at 298 K on a Bruker Avance 300 spectrometer operating at 300 MHz (^1H) and 75 MHz (^{13}C) and referred to internal tetramethylsilane. NMR deuterated solvents ($CDCl_3$, CD_2Cl_2, THF-d_8) were purchased from Eurisotop. Mass spectra (E.I., 70 eV) were recorded on a Finnigan Trace GC–MS equipped with a probe controller for the sample direct inlet.

2.3. Polymers analysis

The samples of polyethylenes for ^{13}C NMR analysis were prepared by dissolving 40 mg of polymer into tetrachloro-dideutero-ethane (0.5 mL). The spectra were recorded at 100 °C using hexamethyldisiloxane (HMDS) as internal chemical shift reference. Samples of polybutadienes for ^{13}C NMR spectra were prepared by dissolving polymer (20 mg) into $CDCl_3$ (0.5 mL). The spectra were recorded at room temperature using tetramethylsilane (TMS) as internal chemical shift reference. The gel permeation chromatography (GPC) analyses of the samples were performed at 135 °C by Waters instrument GPCV 2000 equipped with refractive index and viscosimeter detectors, using four PSS columns set consisting of 10^5, 10^4, 10^3, 10^2 Å (pore size) – 10 μm (particle size). *o*-Dichlorobenzene was the carrier solvent used with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards. Differential scanning calorimetry analyses have been carried out on a DSC 2920 apparatus manufactured by TA Instruments, calibrated

against an indium standard (T_m = 156.6 °C), with heating scans from −10 to 200 °C, at a 10 °C/min heating rate, under a flowing nitrogen atmosphere. Specimens were sealed in aluminum pans.

2.4. Synthesis of 2-tert-butyl-6-[(quinolin-8-ylamino)methyl]phenol ($NNHO^H$)

A solution of NNO^H (2.1 g, 6.9 mmol) in anhydrous THF (50 mL) was cooled to −70 °C, then a 1 M solution of $LiAlH_4$ in THF (6.9 mL) was added drop-by-drop, keeping the temperature as constant as possible. The resulting solution was allowed to slowly reach room temperature (about 2 h) and then maintained under stirring for further 4 h. The reaction mixture was quenched with cold water (40 mL) and THF was quite completely removed by evaporation under reduced pressure. The crude product was extracted with diethylether (3× 50 mL) and the resulting organic fraction was dried over $MgSO_4$. The solvent was then removed under reduced pressure and the resulting white solid was dissolved under stirring in a small amount of pentane (5 mL). A white powder slowly started to separate and, after cooling overnight at −25 °C, the white product was collected by filtration and washed with cold pentane (1.86 g, 88% yield).

Elemental analysis—found (%): C 78.1, H 7.20, N 9.10. Calcd. for $C_{20}H_{22}N_2O$, M_W = 306.40 (%): C 78.40, H 7.24, N 9.14.

^{1}H NMR ($CDCl_3$, 298 K; refer to Scheme 1 for the numbering of aromatic H atoms): 8.78 (dd, 1H, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 1.6 Hz, H_1); 8.67 (s br, 1H, *OH*); 8.14 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.6 Hz, H_3); 7.45 (t, 1H, $^3J_{HH}$ = 7.6 Hz, H_5); 7.44 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 4.2 Hz, H_2); 7.33 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, H_9); 7.31 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, H_4); 7.15 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, H_7); 7.09 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, H_6); 6.91 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H_8); 6.51 (s br, 1H, *NH*); 4.62 (s, 1H, CH_2); 1.48 (s, 9H) *t-Bu*.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 147.7, 136.2, 127.3, 126.9, 126.5, 121.6, 119.3, 117.8, 109.9 CH *aromatic carbons*; 155.9, 144.4, 139.2, 137.2, 128.4, 124.5 *quaternary aromatic carbons*; 48.8 CH_2; 34.7 *quaternary* ^{t}*Bu*; 29.6 ^{t}*Bu*.

Mass data (E.I., 70 eV, *m*/*z*): 306 $[M]^{\bullet+}$, 291 $[M^{\bullet+}-CH_3]^+$.

2.5. Synthesis of $[ScCl_2(NNCp)(THF)]$ (**1**)

To a solution of the ligand $NNCp^H$ (0.379 g, 1.1 mmol) in THF (15 mL) a stoichiometric amount of potassium *tert*-butoxide (0.123 g, 1.1 mmol) was slowly added at room temperature. After 15 min under magnetic stirring, solid $ScCl_3$ (0.166 g, 1.1 mmol) was added and the resulting mixture was allowed to react at room temperature for 12 h. After elimination by centrifugation of the KCl by-product, the resulting yellow-brown solution was concentrated to ca. 5 mL under reduced pressure and by slow addition of *n*-hexane (25 mL) a dark yellowish powder separated out, which was filtered, washed with *n*-hexane and dried in vacuum (0.409 g, 70% yield).

Elemental analysis—found (%): C 63.1, H 6.60, N 5.30, Cl 13.4. Calcd for $C_{28}H_{35}Cl_2N_2OSc$, M_W = 531.45 (%): C 63.28, H 6.64, N 5.27, Cl 13.34.

^{1}H NMR (CD_2Cl_2, 298 K): 8.26 (s, 1H, *CH*=*N*); ABC spin system (3H, δ_A = 8.12 ppm, δ_B = 7.79 ppm, δ_C = 7.67 ppm, J_{AB} = 7.6 Hz, J_{BC} = 0.0 Hz, *pyridine ring*); 7.45–7.07 (m, 3H, *phenyl*); A_2B_2 spin system (4H, δ_A = 6.53 ppm, δ_B = 6.32 ppm, J_{AB} = 2.7 Hz, *Cp ring*); 4.55 (s, 2H, CH_2); 4.31 (m, br, 4H, *THF*); 3.62 (m, br, 1H, *CH*); 2.79 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, *CH*); 1.97 (m, br, 4H, *THF*); 1.28 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH_3); 1.10 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH_3).

Mass data (E.I., 70 eV, *m*/*z*): 458 $[M^{\bullet+}-THF]^{\bullet+}$, 423 $[M^{\bullet+}-THF-Cl]^+$.

2.6. Synthesis of $[ScCl_2(NNO)(THF)]$ (**2**)

To a solution of the ligand NNO^H (0.335 g, 1.1 mmol) in THF (20 mL) a stoichiometric amount of potassium *tert*-butoxide (0.123 g, 1.1 mmol) was slowly added at room temperature. After 15 min under magnetic stirring, solid $ScCl_3$ (0.166 g, 1.1 mmol) was added and the resulting mixture was allowed to react at room temperature for 12 h. THF was removed by evaporation under reduced pressure and the solid residue was extracted with CH_2Cl_2 (5× 20 mL). The resulting bright yellow solution was concentrated under reduced pressure to 5 mL. By slow addition of diethylether (20 mL) a yellow microcrystalline product precipitated which was filtered, washed with diethylether and dried under vacuum (0.492 g, 92% yield).

Elemental analysis—found (%): C 58.5, H 5.50, N 5.65, Cl 14.5. Calcd for $C_{24}H_{27}Cl_2N_2O_2Sc$, M_W = 491.35 (%): C 58.67, H 5.54, N 5.70, Cl 14.43.

^{1}H NMR (CD_2Cl_2, 298 K; refer to Scheme 1 for the numeration of aromatic H atoms): 9.53 (dd, 1H, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.7 Hz, H_1); 9.01 (s, 1H, *CH*=*N*); 8.53 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.7 Hz, H_3); 8.02 (d, 1H, $^3J_{HH}$ = 7.3 Hz, H_6); 7.91 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H_4); 7.76 (dd, 1H, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 8.0 Hz, H_5); 7.73 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.9 Hz, H_2); 7.55 (dd, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.8 Hz, H_9); 7.42 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.8 Hz, H_7); 6.80 (dd, 1H, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 8.0 Hz, H_8); 3.56 (m, 4H, *THF*); 1.86 (m, 4H, *THF*); 1.51 (s, 9H, ^{t}*Bu*).

Mass data (E.I., 70 eV, *m*/*z*): 418 $[M^{\bullet+}-THF]^{\bullet+}$, 403 $[M^{\bullet+}-THF-CH_3]^+$, 383 $[M^{\bullet+}-THF-Cl]^+$.

2.7. Synthesis of $[ScCl_2(NNHO)(THF)]$ (**3**)

To a solution of the ligand $NNHO^H$ (0.460 g, 1.5 mmol) in THF (25 mL) a stoichiometric amount of solid potassium *tert*-butoxide (0.168 g, 1.5 mmol) was slowly added at room temperature. After 15 min under magnetic stirring the resulting solution was added drop by drop to a suspension of $ScCl_3$ (0.226 g, 1.5 mmol) in 10 mL of THF. The reaction mixture was allowed to react overnight at room temperature. After elimination by filtration of the KCl formed, the solution was concentrated to ca. 2 mL under reduced pressure. By addition of diethylether (25 mL) a yellow-pink precipitate slowly separated out, which was filtered, washed with diethylether and dried under vacuum (0.629 g, 85% yield).

Elemental analysis—found (%): C 58.2, H 5.95, N 5.70, Cl 14.4. Calcd for $C_{24}H_{29}Cl_2N_2O_2Sc$, M_W = 493.36 (%): C 58.43, H 5.92, N 5.68, Cl 14.37.

^{1}H NMR (THF-d_8, 298 K; refer to Scheme 1 for the numeration of aromatic H atoms): 9.64 (dd, 1H, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.6 Hz, H_1); 8.53 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, H_3); 8.12 (d, 1H, $^3J_{HH}$ = 7.7 Hz, H_6); 7.93 (d, 1H, $^3J_{HH}$ = 7.7 Hz, H_4); 7.78 (t, 1H, $^3J_{HH}$ = 7.7 Hz, H_5); 7.71 (dd, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 8.0 Hz, H_3); 6.89 (d, 1H, $^3J_{HH}$ = 7.5 Hz, H_9); 6.63 (d, 1H, $^3J_{HH}$ = 7.5 Hz, H_7); 6.49 (s, slightly br, 1H, *NH*); 6.22 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H_8); 5.05, 4.31 (AB spin system, slightly br, $^2J_{HH}$ = 12.0 Hz, CH_2); 1.42 (s, 9H, ^{t}*Bu*). The presence of one molecule of coordinated THF was detected by recording the ^{1}H NMR spectrum in CD_2Cl_2 at 298 K: 3.72 (m, 4H, *THF*); 1.87 (m, 4H, *THF*).

Mass data (E.I., 70 eV, *m*/*z*): 420 $[M^{\bullet+}-THF]^{\bullet+}$, 404 $[M^{\bullet+}-THF-H-CH_3]^{\bullet+}$.

2.8. Synthesis of [Sc(CH_2SiMe_3)$_2$(NNCp)] (**1^R**)

To a solution of the ligand NNCp^H (6.9 mg, 2.0×10^{-5} mol) in 90 mL of toluene was added drop by drop a stoichiometric amount of a solution of Sc[($CH_2Si(CH_3)_3$)$_3$]·2THF (8.5 mg, 2.0×10^{-5} mol) in 10 mL of toluene. The reaction mixture was allowed to react 15 min at −20 °C, and used in the polymerization reactions. The reaction product is not stable at room temperature.

2.9. Polymerization

Run 1–8. Polymerizations of ethylene were performed in a 250 mL glass-autoclave introducing the amount of catalyst and cocatalyst dissolved in 125 mL of toluene, as reported in Table 1. The mixtures were fed with the monomer and kept under magnetic stirring over the runs. The polymerization mixtures were poured in acidified ethanol after venting the autoclave, then the polymers were recovered by filtration, washed with fresh ethanol and dried *in vacuo* at 60 °C.

Run 9. Polymerization of ethylene was performed in a 250 mL glass-autoclave thermostatted at −20 °C, introducing, in 25 mL of cold toluene, the solution of **1^R**. The mixture was fed with ethylene and kept under magnetic stirring over the run. The autoclave was vented and the polymerization mixture was poured in acidified ethanol. We did not obtain polymer.

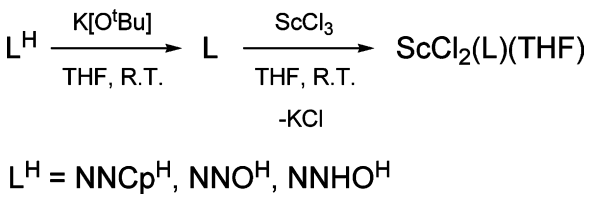
Run 10. Polymerization of ethylene was performed in a 250 mL glass-autoclave thermostatted at −20 °C, introducing the solution of **1^R** and then 2.0×10^{-2} mol of MAO dissolved in 25 mL of cold toluene. The mixture was fed with ethylene and kept under magnetic stirring over the run. The autoclave was vented and the polymer was recovered as usual.

Runs 11–14. Polymerizations of 1,3-butadiene were performed by introducing 19 mL of dry toluene and the cocatalysts into 100 mL glass flasks equipped with magnetic stirrer. The flasks were cooled with liquid nitrogen and the inert gas was evacuated. 1.5 g of 1,3-butadiene were condensed into the flasks, then the reactors were quickly thermostatted at the reaction temperature and polymerizations were started by injecting 1 mL of toluene solution of scandium compounds. Introduction of a few amount of ethanol stopped the polymerizations, then the polymers were coagulated in an excess of acidified ethanol, washed several times with fresh ethanol and dried *in vacuo* at room temperature.

3. Results and discussion

3.1. Synthesis of NNHO^H

The compound NNO^H has been also used as starting material for the synthesis of the new ligand NNHO^H, 2-*tert*-butyl-6-((quinolin-8-ylamino)methyl)phenol, in order to compare catalytic behavior of scandium complexes having two isoelectronic ligands with different basicity, the scandium derivatives with the ligand NNO^H and the corresponding form without the imine double bond. The neutral ligand was obtained in good yield by reducing at low temperature in THF the imine group of NNO^H, as depicted in Scheme 2. Elemental analysis (C, H, N) agrees with the proposed formulation. ^{1}H COSY and NOESY experiments allowed the assignment of all the proton resonances of the ^{1}H NMR spectrum. The ^{13}C APT (attached-proton-test) NMR allowed to separate CH and quaternary aromatic carbons and to assign the CH_2 and ^{t}Bu groups. Finally, the most meaningful signals of the mass spectrum corresponded to the molecular ion and the molecular ion after the loss of a methyl fragment from the *tert*-butyl group.



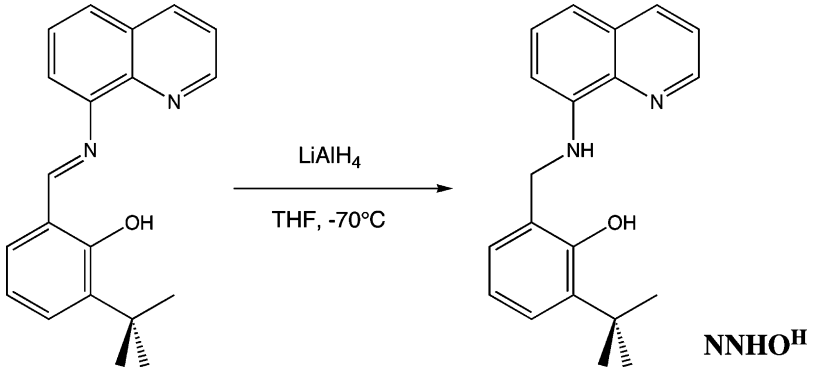
Scheme 3. Synthesis of scandium complexes **1**, **2** and **3**.

3.2. Synthesis of the complexes

Scandium complexes **1**, **2** and **3** were prepared following the same synthetic strategy, *i.e.* the deprotonation of the neutral ligands NNCp^H, NNO^H or NNHO^H with a stoichiometric amount of potassium *tert*-butoxide, followed by the reaction of the anionic ancillary ligand obtained with $ScCl_3$, as depicted in Scheme 3.

The ^{1}H NMR of [$ScCl_2$(NNCp)(THF)] (**1**) shows, downfield, the signals of the imine, the pyridine and the phenyl protons. The Cp protons appear as a pseudo-A_2B_2 spin system. The aliphatic region shows the coordinated THF molecule, the methylene and isopropyl protons: these last ones are non-equivalent, since the coordination to the metal fragment does not allow the free rotation of the phenyl ring around the C(phenyl)-N(imine) bond. The MS spectrum of the complex shows the presence of a signal at 458 *m*/*z* assignable to the molecular ion after the loss of the coordinated THF molecule and a signal at 423 *m*/*z* assignable to the fragment formed by the loss of a chlorine atom from the previous ion.

COSY and NOESY experiments allowed the complete assignment of all the protons of compound [$ScCl_2$(NNO)(THF)] (**2**). Besides the aromatic protons (in the region 9.53 – 6.80), the multiplets due to the coordinated THF (δ = 3.56 and 1.86 ppm) and the *tert*-butyl singlet (δ = 1.51 ppm), a characteristic signal for this type of



Scheme 2. NNHO^H synthesis.

Table 1
Polymerization of ethylene in the presence of **1** bases catalytic systems

Run[a]	Catalyst	Mao/Sc mole ratio	T (°C)	Time (h)	Yield (g)	M_w[b] ($\times 10^5$)	M_w/M_n	Relative activity[c]
1	**1**	1000	50	1	15.1	18.0	1.2	126
2	**1**	700	50	1	14.7	18.0	1.2	123
3	**1**	500	50	1	14.4	18.0	1.2	120
4	**1**	300	50	1	3.37	15.5	1.3	28
5	**1**	200	50	1	1.33	16.0	1.4	11
6	**1**	100	50	1	0.12	16.0	–	1

[a] All the runs were performed by dissolving, in 125 mL of toluene, 2.0×10^{-5} mol of catalyst, the proper amount of MAO (based on Al), under pressure of 6 bar of ethylene.
[b] Determined by GPC analysis (see Section 2). The calibration was made by polystyrene standard.
[c] The reactivity values are referred to that of run 6 arbitrarily defined equal 1.

Table 2
Polymerization of ethylene in the presence of **2** and **3** bases catalytic systems

Run[a]	Catalyst	Mao/Sc mole ratio	T (°C)	Time (h)	Yield (g)	M_w[b] ($\times 10^5$)	M_w/M_n
7	**2**	1000	50	19	0.14	6.3	1.9
8	**3**	1000	50	16	1.1	6.7	1.5

[a] All the runs were performed by dissolving, in 125 mL of toluene, 2.0×10^{-5} mol of catalyst, the proper amount of MAO (based on Al), under pressure of 6 bar of ethylene.
[b] Determined by GPC analysis (see Section 2). The calibration was made by polystyrene standard.

compounds is the downfield singlet at $\delta = 9.01$ ppm, corresponding to the imine proton –CH=N– [5]. The MS spectrum of complex **2** shows, besides the molecular fragment after the loss of the coordinated THF molecule at 418 m/z, two additional signals at 403 m/z and 383 m/z assignable to the ions formed after the loss of a methyl fragment or a chlorine atom from the $[M^{\bullet+}-THF]^{\bullet+}$ ion, respectively.

A complete assignment of all ^{1}H NMR signals was obtained also for compound **3**, [$ScCl_2$(NNHO)(THF)]. Besides the aromatic protons in the region 9.64–6.22, an interesting downfield signal is the slightly broad singlet at 6.49 ppm, assignable to the *NH* proton. The ^{1}H NMR shows also the THF signals ($\delta = 3.72$ and 1.87 ppm) and the *tert*-butyl singlet at $\delta = 1.42$ ppm. The –CH_2– group appears as an AB spin system at $\delta = 5.05$ ppm and $\delta = 4.31$ ppm, with a $^2J_{HH}$ coupling constant of 12.0 Hz which is typical of geminal coupling. The non-equivalence of the two methylene protons is diagnostic of the coordination of the amine nitrogen atom to the metal center, which makes the sp^3 N-atom of ancillary ligand chiral. The MS spectrum of complex **3** shows the molecular fragment after the loss of the coordinated THF molecule at 418 m/z. Moreover, a signal attributable to the loss of a –CH_3 and a –H fragment from $[M^{\bullet+}-THF]^{\bullet+}$ is present at 404 m/z; these two fragments probably derive from the ^{t}Bu and the –NH– groups of the NNHO ligand respectively.

The reaction of a stoichiometric amount of $Sc(CH_2SiMe_3)_3{\cdot}2THF$ and NNCp^H at low temperature should afford the alkylated analogous of chloro-compound **1**, [$Sc(CH_2SiMe_3)_2$(NNCp)] (**1^R**), by protonolysis of a Sc–C bond of the scandium precursor and coordination of the deprotonated ancillary ligand. Since the reaction product is unstable at room temperature, the reaction mixture was freshly prepared before the polymerization runs and kept at −20 °C. The synthesis of this compound offers, however, the possibility to verify the eventual catalytic activity of a neutral scandium alkyl complex towards olefin polymerization.

3.3. Polymerization

Cationic alkyl complex of Group 4 metals are the most common single-site olefin polymerization catalysts. Isoelectronic neutral alkyl complexes of Group 3 metals generally show much lower polymerization activity. One approach to increase the polymerization activity involves the generation of cationic alkyl species obtained by alkyl abstraction from neutral dialkyl or chloride complex by suitable activator. Thus, all synthesized compounds were tested in the polymerization of ethylene with methylaluminoxane (MAO) or $Mg(Bu)_2/B(C_6F_5)_3$ as cocatalysts.

Scandium complexes **1**, **1^R**, **2** and **3** activated by MAO give linear polyethylene having high melting point (135 °C), high molecular weight and narrow polydispersity, whereas activation of complexes by $Mg(Bu)_2/B(C_6F_5)_3$ do not produce a catalytically active species.

Observing Tables 1–3, polyethylenes obtained by scandium complex **1** and **1^R** have $M_w > 1 \times 10^6$, whereas complexes **2** and **3** produce polymers having $M_w > 6 \times 10^5$. Probably, the high steric hindrance of NNCp, as well as NNO and NNHO anionic ligands could prevent the β hydrogen elimination, which represents, generally, the most relevant chain termination process. The narrow polydispersity is indicative of single site catalytic species. It is worth noting that high M_w were frequently obtained performing ethylene polymerization by scandium complexes having bulky ligands [7].

Examining the polymerization results reported in Tables 1–3, it is possible to note that the catalyst based on scandium complex **1** is the most active. In fact, polymer yields are two hundred times higher than **3** and two thousand times higher than **2**, in spite of the really longer reaction times used for **2**- and **3**-based catalytic systems, necessary to obtain easily analyzable quantities of polyethylene. This fact could be explained on considering the different electronic environments of the metal center due to different ligands. In fact, the electronic contribution of NNCp ligand is 10 electrons, whereas NNO and NNHO ligands contribute to stabilize the catalytic species only by six electrons. It is worth recalling that the polymerization reactions consist in the coordination of olefin to the metal followed by its insertion in the metal-polymeril σ-bond. The electronic remarkable unsaturation of scandium complexes with ligands NNO and NNHO, with respect to NNCp ligand, could on the one hand support the olefin coordination to the metal, whereas, on the other hand, generate a strong metal olefin π-bond and consequently a less reactive species in the insertion step.

This hypothesis is able also to rationalize the different reactivity of catalysts based on complexes **2** and **3**, respectively. In fact, the metal is bonded, in both cases, to pyridine nitrogen and alkoxide oxygen, and it is further bonded to imine nitrogen in the

Table 3
Polymerization of ethylene in the presence of **1^R** bases catalytic systems

Run[a]	Catalyst	Mao/Sc mole ratio	T (°C)	Time (h)	Yield (g)	M_w[b] ($\times 10^5$)	M_w/M_n
9	**1^R**	–	−20	80	–	–	–
10	**1^R**	1000	−20	63	2.0	16.0	1.3

[a] All the runs were performed by dissolving, in 125 mL of toluene, 2.0×10^{-5} mol of catalyst, the proper amount of MAO (based on Al), under pressure of 6 bar of ethylene.
[b] Determined by GPC analysis (see Section 2). The calibration was made by polystyrene standard.

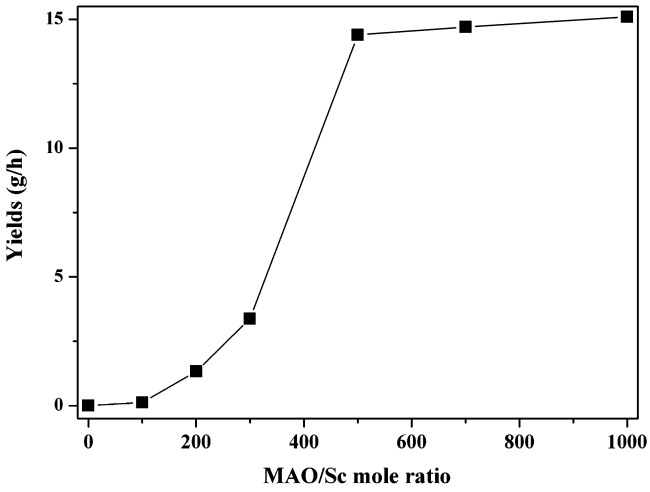


Fig. 1. Experimental plots of yields of polyethylene in g/h versus mole ratio MAO (based on Al)/Sc for complex **1**.

$$LScX_2 + MAO \rightleftharpoons [LSc\text{-}Me]^+[MAOX_2]^-$$

$$LScX_2 + Mg(Bu)_2 \rightleftharpoons LScBu_2 + MgX_2$$

$$LScBu_2 + B(C_6F_5)_3 \rightleftharpoons [LSc\text{-}Bu]^+[B(Bu)(C_6F_5)_3]^-$$

L = NNCp, NNO, NNHO
X = Cl, CH_2SiMe_3

Scheme 4. Cationization reaction of scandium compounds by MAO and $Mg(Bu)_2/B(C_6F_5)_3$.

complex **2** and to amine nitrogen in the complex **3**. Evidently lower basicity of imine group, with respect to amine group, produces a catalytic species having higher electrophilicity and consequently, a stronger metal olefin π-bond. Therefore, accordingly, kinetic of insertion step for a **2**-based catalytic system could be less favored.

Moreover, catalyst based on scandium complex **1** is much more active than analogous catalysts based on yttrium, samarium and neodymium [4]. This suggests that the catalytic activity of the cationic alkyl species in ethylene polymerization is strongly depended on the metal ion size.

In Table 1 the polymerization results in the presence of **1** activated by different MAO/Sc mole ratios are reported. It is possible to observe that the amount of cocatalyst is a crucial factor for the catalyst activity. In fact, it increases with the increase of Al/Sc mole ratio. In Fig. 1 the data of runs performed in the presence of **1**/MAO catalytic system are plotted and as one can see, the yield reaches a maximum for a mole ratio Al/Sc ≈ 500 and subsequently it is almost constant.

Table 3 reports the results obtained using $[Sc(CH_2SiMe_3)_2(NNCp)]$ ($\mathbf{1^R}$) as catalyst, that represents the alkylated form of complex **1**. Run 9 and 10 were carried out at −20 °C, because the alkyl derivative is instable at room temperature. Run 9 was performed without MAO, in order to estimate the catalytic activity of the neutral species. In these conditions scandium complex $\mathbf{1^R}$ does not give polymer. In the same condition, but after activation with MAO (run 10), it instead yields linear polyethylene.

This fact prove that the cationization of scandium complexes $LScX_2$ effected by MAO to form $[LSc\text{-}CH_3]^+[MAOX_2]^-$ ion pairs is necessary in order to obtain an active catalytic species (see Scheme 4).

Scandium compounds **1**–**3** were also tested in the polymerization of butadiene (see Table 4). They produce polybutadiene prevailingly with 1,4–*cis* microstructure, but with low activity.

Table 4
Polymerization of butadiene in the presence of **1**, **2**, **3**, $\mathbf{1^R}$ based catalytic systems

Run[a]	Catalyst	T (°C)	Time (h)	Yield (mg)	microstructure
11	**1**	25	24	25	77% 1,4-*cis*; 23% 1,4-*trans*
12	**2**	25	93	100	86% 1,4-*cis*; 10% 1,4-*trans* 4% 1,2
13	**3**	25	16	70	55% 1,4-*cis*; 45% 1,4-*trans*
14	$\mathbf{1^R}$	-20	720	140	78% 1,4-*cis*; 22% 1,4-*trans*

[a] All the runs were performed by dissolving, in 20 mL of toluene, 1.5 g of butadiene, 1.0×10^{-5} mol of catalyst and 1.0×10^{-3} mol of MAO (based on Al).

Activation of complexes **1**–**3** was also carried out in the presence of $Mg(Bu)_2$ and $B(C_6F_5)_3$ but polymerizations of butadiene, as well as of ethylene, did not produce polymers.

The different behavior of scandium complexes, in the presence of MAO or $Mg(Bu)_2$ and $B(C_6F_5)_3$ cocatalysts, depend on species generated by the activation reactions. In particular, the anion $[MAOX_2]^-$ generated could be less coordinating than $[B(Bu)(C_6F_5)_3]^-$ produced when the cocatalyst is the system $Mg(Bu)_2/B(C_6F_5)_3$ (see Scheme 4). A non-coordinating anion makes easier the coordination of the monomer on the cationic active species, thus allowing the polymerization reaction.

4. Conclusion

In this paper the synthesis of three new scandium chlorocomplexes with different donor sets has been reported and, on the basis of catalytic tests towards ethylene polymerization, the correlation between electron-donor ability of the ancillary ligands and catalytic activity of the corresponding complexes has been highlighted. It was concluded that the active catalytic species should be cationic alkyl derivatives formed by *in situ* reaction between precursors and cocatalysts and that the final activity in the experimental conditions described is strongly dependent upon the coordinating ability of the counter-anion formed. Finally, it was observed a low activity of the considered systems towards butadiene polymerization, even if in some cases a relatively good selectivity towards 1,4-*cis*-polybutadiene was achieved.

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