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New constrained geometry catalysts-type yttrium, samarium and neodymium derivatives in olefin polymerization

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Abstract

A straightforward synthetic methodology to prepare *ansa*-monocyclopentadienyl-imino-pyridine dichloro metal derivatives of the type $MLCl_2(THF)$ {M = Y, Sm, Nd} has been developed. Here, we report the syntheses and characterizations of both the ligand and the complexes and the results of some catalytic tests towards olefin polymerization. The most astonishing data come from the influence of both the metal fragments and the co-catalysts used towards the selectivity in butadiene polymerization: in fact, changing these parameters it is possible to range from >99% 1,4 *cis*-polybutadiene to >99% 1,4 *trans*-polybutadiene.

Keywords: Yttrium; Samarium; Neodymium; Constrained geometry catalysts; Polybutadiene

1. Introduction

Cationic complexes of group 4 metals, e.g. alkyl zirconocenes or titanocenes, are highly active catalysts in homogeneous ethylene polymerization [1–3]. Polyethylene can be also obtained in the presence of neutral scandocene alkyl compounds, as well as in the presence of a number of cationic alkyl complexes of the rare-earth metals, stabilized by anionic ancillary non-cyclopentadienyl ligands, such as amido functionalized triazacyclononanes, β-diketiminates or benzoamidinate [4–10].

The synthesis of monocyclopentadienyl derivatives of rare-earth metals usually is not easy, therefore cationic half-metallocenes group 3 metals are not very widespread, although the expected electrophilicity, and consequently the predictable catalytic ability in the olefins polymerization, makes them attractive [11]. In past years, we developed the synthesis and characterization of monocyclopentadienyl-based zirconium and yttrium complexes [12,13]. Herein, we report a straightforward synthetic approach to prepare cyclopentadienyl-imino-pyridine dichloro complexes of yttrium, samarium and neodimium (see Chart 1).

The Y (**5**), Sm (**6**) and Nd (**7**) complexes, activated by a suitable co-catalyst, showed some activity in the polymerization of ethylene and butadiene. Both the activity and the selectivity strongly depend upon the metal ion and the co-catalyst used.

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 glove-box. All reaction and NMR solvents were thoroughly deoxygenated and dehydrated under argon by refluxing over suitable drying agents. The salts YCl_3, $SmCl_3$ and $NdCl_3$ (Strem) were used as received, like 2,6-dihydroxymethylpyridine (Aldrich). 2,6-Diisopropyl-aniline (Aldrich) was distilled at reduced pressure over KOH and kept in the dark, while dicyclopentadiene (Aldrich) was distilled immediately before use. Microanalyses were performed at the Istituto di

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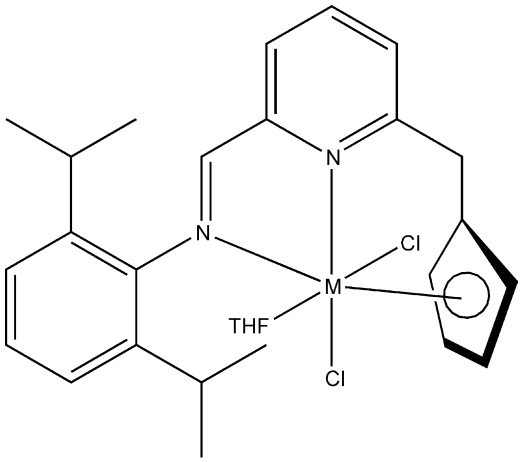


M = Y(**5**), Sm(**6**), Nd(**7**)

Chart 1. Y (**5**), Sm (**6**) and Nd (**7**) monocyclopentadienyl-imino-pyridine dichloro derivatives.

Chimica Inorganica e delle Superfici, CNR, Padova. IR spectra (KBr disks) were recorded from 4000 to 450 cm^{-1} on a Perkin-Elmer Spectrum One. ^1H NMR, $^{13}C\{^1H\}$ NMR, COSY, NOESY, APT, HMQC spectra were obtained as $CDCl_3$ or CD_2Cl_2 solutions on a Bruker Avance 300 spectrometer operating at 300 and 75 MHz, respectively. Mass spectra (E.I., 70 eV) were recorded on a Finnigan Trace GC–MS equipped with a probe controller for the sample direct inlet.

All the polymerization operations were performed under nitrogen atmosphere by using conventional Schlenk-line techniques. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. Methylaluminoxane (10% in toluene, Witco) was used as a solid after distillation of solvent. Ethylene (>98%), 1,3-butadiene (>99%), $Mg(Bu)_2$, $Al(i\text{-}Bu)_3$, BuLi and $AlH(i\text{-}Bu)_2$, were purchased from Aldrich, $B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$ were purchased from Boulder. ^{13}C NMR spectra of the polymers were recorded on an AX 400 Bruker spectrometer operating at 100 MHz at 298 K. The samples were prepared by dissolving 20 mg of polymer in 0.5 mL of $CDCl_3$. TMS was used as internal chemical shift reference. The structures of the polymers were determined by NMR analysis comparing the chemical shifts of the resonances observed in the spectra with the data reported in the literature [14,15]. Melting points were measured by using a Du Pont 9900 DSC calorimeter with a heating rate of 10 K/min, on previously melted and re-crystallized samples.

2.2. Synthesis of 2-hydroxymethyl-6-chloromethyl-pyridine[10] (*1*) (C_7H_8ONCl, M_w = 157.60)

To a solution of 2,6-dihydroxymethyl-pyridine (3.00 g, 21.6 mmol) in liquid SO_2 (75 mL) cooled at −70 °C a slight excess of thionyl chloride (1.8 mL, 24.7 mmol) dissolved in CH_2Cl_2 (10 mL) was slowly added under vigorous magnetic stirring. Once the addition was ended the temperature was left to slowly (8 h) increase to room temperature, then the reaction mixture was left to react overnight. After removal of the solvent, water (20 mL) was added and the by-product 2,6-dichloromethyl-pyridine was removed by extraction with diethylether (2 mL × 30 mL). The pK_a of the aqueous solution was adjusted to about 7 by addition of aqueous NH_3 and the 2-hydroxymethyl-6-chloromethylpyridine was extracted with diethylether (3 mL × 20 mL). The resulting organic solution was dried with $MgSO_4$ and the product was isolated by *in vacuo* removal of the solvent, giving 1.84 g of white solid (55% yield).

Elemental analysis, found (%): C 53.25, H 5.20, N 8.75, Cl 22.60.

Calcd for C_7H_8ONCl (%): C 53.35, H 5.12, N 8.89, Cl 22.50.

^1H NMR ($CDCl_3$, 298 K): 7.67 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *H4*); 7.32 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *H3*); 7.23 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *H5*); 4.71 (s, 2H, *CH2OH*); 4.60 (s, 2H, *CH2Cl*); 4.45 (s, br, 1H, *OH*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 159.3 *C6*, 155.3 *C2*, 137.7 *C4*, 121.2 *C3*, 119.9 *C5*, 64.0 *CH2OH*, 46.2 *CH2Cl*.

2.3. Synthesis of 6-chloromethyl-pyridine-2-carbaldehyde (*2*) (C_7H_6ClNO, M_w = 155.58)

To a solution of oxalyl chloride (1.7 mL, 19.5 mmol) in CH_2Cl_2 (25 mL) cooled to −60 °C dimethylsulphoxide (2.9 mL, 40.8 mmol) was added dropwise [12]. After 5 min, a solution of 2-hydroxymethyl-6-chloromethylpyridine (3.00 g, 19.0 mmol) in CH_2Cl_2 (20 mL) was slowly added. The resulting solution was stirred at −60 °C until the formation of a milky suspension (about 15–20 min), then triethylamine (12 mL, 86.1 mmol) was added dropwise by maintaining the temperature under −50 °C. The colour of the reaction mixture turned to red, then the reactor was allowed to warm to room temperature and the reaction mixture was quenched with cold water (about 50 mL). The product was extracted with dichloromethane (3 mL × 50 mL) and the resulting organic fraction was dried over Na_2SO_4. The solvent and volatiles were removed under vacuum and the resulting red oil was purified by filtration on a silica gel column, using a 1:1 mixture of hexane–ethyl acetate as eluent. After the evaporation of the solvents, pentane (5 mL) was added to the resulting oil. After 2 h of vigorous stirring, the product was collected as a very pale yellow solid (2.571 g, 87% yield).

Elemental analysis: found (%): C 54.15, H 3.85, N 9.15, Cl 22.50.

Calcd per C_7H_6ClNO (%): C 54.04, H 3.89, N 9.00, Cl 22.79.

IR (KBr disk) (cm^{-1}): 1713 ν_{CO}.

^1H NMR ($CDCl_3$, 298 K): 10.03 (s, 1H, *CHO*); 7.95–7.65 (m, 3H, *H3*, *H4*, *H5*), 4.75 (s, 2H, *CH2*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 192.8 CHO, 157.4 *C6*, 152.2 *C2*, 138.1 *C4*, 126.0 *C5*, 120.8 *C3*, 46.0 *CH2*.

Mass data (E.I., 70 eV. T_{probe}: 100 °C, *m/z*): 155.1$[M]^{\bullet+}$, 127 $[M^{\bullet+}-CHO]^+$, 91.1 $[M^{\bullet+}-Cl-CHO]^+$.

2.4. Synthesis of (6-chloromethyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine (*3*) ($C_{19}H_{23}N_2Cl$, M_w = 314.85)

To a solution of the aldehyde (**2**) (1.18 g, 7.6 mmol) in anhydrous CH_2Cl_2 (50 mL), in the presence of molecular sieves 4 Å

(10 g) and anhydrous $MgSO_4$ or Na_2SO_4 (10 g), freshly distilled 2,6-diisopropylaniline (1.43 mL, 7.6 mmol) in anhydrous CH_2Cl_2 (30 mL) at room temperature and under magnetic stirring was added. The reaction mixture was left to react overnight. Then molecular sieves and the salt were filtered off and the solvent eliminated under vacuum to give an analytically pure yellow solid (2.338 g, 98% yield).

Elemental analysis: found (%): C 72.65, H 7.10, N 9.05, Cl 11.15.

Calcd for $C_{19}H_{23}N_2Cl$ (%): C 72.48, H 7.36, N 8.90, Cl 11.26.

^{1}H NMR ($CDCl_3$, 298 K): 8.30 (s, 1H, *CH = N*); 8.24 (d, 1H, $^3J_{HH}$ = 6.0 Hz, *H3*); 7.90 (t, 1H, $^3J_{HH}$ = 6.0 Hz, *H4*); 7.64 (d, 1H, $^3J_{HH}$ = 6.0 Hz, *H5*); A_2B spin system (3H, δ_A = 7.19 ppm, δ_B = 7.15 ppm, $^3J_{HH}$ = 7.9 Hz, *phenyl*); 4.77 (s, 2H, *CH2Cl*); 2.97 (sept, 2H, $^3J_{HH}$ = 6.0 Hz, *CH*); 1.19 (d, 12H, $^3J_{HH}$ = 6.0 Hz, *CH3*).

^{13}C {^{1}H} NMR ($CDCl_3$, 298 K): 162.6 *CH = N*, 156.7 *C6*, 154.0 *C2*, 148.2 *phenyl-C1*, 137.7 *C4*, 137.1 *phenyl-C2*, 124.5, 124.4 *C5*, *phenyl-C4*, 123.0 *phenyl-C3*, 120.5 *C3*, 46.4 *CH2Cl*, 27.9 *CH*, 23.4 *CH3*.

Mass data (E.I., 70 eV. T_{probe}: 120 °C, *m/z*): 314.4 $[M]^{\bullet+}$, 299.3 $[M^{\bullet+}-CH_3]^+$.

2.5. Synthesis of (6-cyclopentadiendemethyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine, sodium salt (**4**) ($C_{24}H_{27}N_2Na$, M_w = 366.47)

To a solution of (**3**) (0.500 g, 1.6 mmol) in anhydrous THF (25 mL) at −80 °C a THF solution of sodium cyclopentadienide NaCp (0.87 M, 3.65 mL, 3.2 mmol) was slowly added. The reaction mixture was allowed to gradually reach room temperature and then left to react overnight. The NaCl was eliminated by centrifugation and the solution was evaporated under vacuum to dryness, affording a red solid (0.565 g, 96% yield).

Elemental analysis: found (%): C 78.45, H 7.55, N 7.80.

Calcd for $C_{24}H_{27}N_2Na$ (%): C 78.66, H 7.43, N 7.64.

^{1}H NMR (d^5-pyridine, 298 K): 8.51 (s, 1H, *CH = N*); ABC spin system (3H, δ_A = 7.87 ppm, δ_B = 7.68 ppm, δ_C = 7.57 ppm, $J_{AB} = J_{BC}$ = 7.6 Hz, J_{AC} = 0.0 Hz, pyridine ring); 7.20–7.06 (m, 3H, *phenyl*); 6.48, 6.30 (A_2B_2 spin system, J_{AB} = 2.5 Hz, *Cp ring*); 4.59 (s, 2H, *CH2*); 2.91 (sept, 2H, $^3J_{HH}$ = 7.0 Hz, *CH*); 0.98 (d, 12H, $^3J_{HH}$ = 7.0 Hz, *CH3*).

2.6. Synthesis of (6-cyclopenta-1,3-dienylmethyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine and (6-cyclopenta-1,4-dienylmethyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine (**4^H**) ($C_{24}H_{28}N_2$, M_w = 344.49)

To a solution of the Schiff base (**3**) (2.31 g, 7.3 mmol) in anhydrous THF (20 mL) at −80 °C a solution of sodium cyclopentadienide (19.00 mL, 0.86 M, 16.3 mmol) in anhydrous THF (50 mL) was added under vigorous agitation. Once the addition was completed the reaction mixture was allowed to gradually warm to room temperature, then the resulting solution was left overnight under stirring. Subsequently, the reaction mixture was quenched with cold water (30 mL) and the crude product was extracted with dichloromethane (3 mL × 50 mL). The resulting organic fraction was dried over Na_2SO_4, the solvent was removed by evaporation under reduced pressure and the resulting yellow oil was purified by flash cromatography on silica gel, using a 9:1 mixture of hexane–ethyl acetate as eluent. The product was isolated as yellow oil by *in vacuo* removal of the solvent (1.51 g, 60% yield).

Elemental analysis: found (%): C 83.50, H 8.05, N 8.25.

Calcd (%) for $C_{24}H_{28}N_2$: C 83.68, H 8.19, N 8.13.

^{1}H NMR ($CDCl_3$, 298 K): 8.33 (s, 2H, *CH = N*); ABC spin system (6H, δ_A = 8.15 ppm, δ_B = 7.77 ppm, δ_C = 7.31 ppm, $J_{AB} = J_{BC}$ = 7.6 Hz, J_{AC} = 0.0 Hz, *pyridine rings*); 7.25–7.15 (m, 6H, *phenyl rings*); 6.56–6.15 (m, 6H, *vinilyc Cp protons*); 4.04 (s, 2H, *CH2*); 4.01 (s, 2H, *CH2*); 3.51 (sept, 4H, $^3J_{HH}$ = 7.0 Hz, *CH*); 3.05–3.00 (m, 4H, *aliphatic Cp protons*); 1.21 (d, 24H, $^3J_{HH}$ = 7.0 Hz, *CH3*).

^{13}C {^{1}H} NMR ($CDCl_3$, 298 K): 163.8 *CH = N*, 137.7, 125.0, 119.3 *pyridine primary carbons*, 137.5, 134.7, 132.8, 132.4, 129.5, 129.1 *Cp primary carbons*, 124.8, 123.4 *phenyl primary carbons*, 44.0, 42.0 *Cp secondary carbons*, 40.3, 39.4 *CH2*, 28.4 *CH*, 23.8 *CH3*.

Mass data (E.I., 70 eV. T_{probe}: 120 °C, *m/z*): 344 $[M]^{\bullet+}$, 329.4 $[M^{\bullet+}-CH_3]^+$.

2.7. Synthesis of $YLCl_2(THF)$(**5**) ($C_{28}H_{35}Cl_2N_2OY$, M_w = 575.40)

2.7.1.1. Method 1

To a suspension of YCl_3 (0.215 g, 1.1 mmol) in anhydrous THF (50 mL) a THF solution (20 mL) of **4** (0.403 g, 1.1 mmol) at room temperature and under magnetic stirring was dropwise added. At the end of the addition the yellow-gold suspension obtained was left to react overnight. After elimination of NaCl by centrifugation, the yellow solution was concentrated to 10 mL under vacuum and by addition of *n*-hexane (20 mL) afforded yellow microcrystals (0.415 g, 66% yield).

2.7.1.2. Method 2

To a solution of **4^H** (0.379 g, 1.1 mmol) in THF a stoichiometric amount of potassium *tert*-butoxide (0.123 g, 1.1 mmol) was slowly added at room temperature. After 15 min under stirring, solid YCl_3 (0.215 g, 1.1 mmol) was added and the resulting mixture was allowed to react for 12 h. After elimination of the KCl by centrifugation, the yellow solution was concentrated to 10 mL under vacuum and by addition of *n*-hexane (20 mL) afforded yellow microcrystals (0.432 g, 68% yield).

Elemental analysis: found (%): C 58.15, H 6.20, N 4.80, Cl 12.40.

Calcd for $C_{28}H_{35}Cl_2N_2OY$ (%): C 58.45, H 6.13, N 4.87, Cl 12.32.

^{1}H NMR (CD_2Cl_2, 298 K): 8.15 (s, 1H, *CH = N*); ABC spin system (3H, δ_A = 8.07 ppm, δ_B = 7.70 ppm, δ_C = 7.59 ppm, $J_{AB} = J_{AC}$ = 8.2 Hz, J_{BC} = 0.0 Hz, *pyridine ring*); 7.42–7.05 (m, 3H, *phenyl*); 6.43, 6.18 (A_2B_2 spin system, 4H, J_{AB} = 2.0 Hz, *Cp ring*); 4.51 (s, 2H, *CH2*); 3.84 (m, br, 4H, *THF*); 3.51 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, *CH*); 2.96 (m, br, 1H, *CH*); 1.85 (m, br, 4H, *THF*);

Table 1
Polymerization of ethylene in the presence of (**5**), (**6**) and (**7**) based catalytic systems

Run[a]	Catalyst	Co-catalyst[a]	Activity[b]	m.p. (°C)
1[c]	**5**	BuLi/AlH(*i*-Bu)$_2$	150	132
2[d]	**5**	MAO	1400	135
3[e]	**5**	Mg(Bu)$_2$/B(C$_6$F$_5$)$_3$	310	–[f]
4[g]	**5**	[C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$]/Al(*i*-Bu)$_3$	90	132
5[d]	**6**	MAO	60	133
6[d]	**7**	MAO	250	132

[a] All the run were performed by dissolving, in 125 mL of toluene, 2.0×10^{-5} mol of catalyst, the proper amount of co-catalyst, under pressure of 6 bar of ethene for 20 h.
[b] Activity in g of polymer/(mol of catalyst)(h)(mol L^{-1} of ethylene).
[c] (**1**)/BuLi/HAl(*i*-Bu)$_2$ = 1/10/10; temperature = 20 °C [ethene] = 1.34 mol L^{-1}.
[d] (catalyst)/MAO = 1/1000 (based on Al); temperature = 50 °C [ethene] = 0.87 mol L^{-1}.
[e] (**1**)/Mg(Bu)$_2$ /B(C$_6$F$_5$)$_3$ = 1/10/10; temperature = 50 °C [ethene] = 0.87 mol L^{-1}.
[f] oligomers.
[g] (**1**)/Al(*i*-Bu)$_3$ /(C$_6$H$_5$)$_3$C B(C$_6$F$_5$)$_4$, = 1/5/1; temperature = 50 °C [ethene] = 0.87 mol L^{-1}.

1.27 (d, 6H, $^3J_{HH}$ = 6.7 Hz, *CH$_3$*); 1.01 (d, 6H, $^3J_{HH}$ = 6.7 Hz, *CH$_3$*).

^{13}C {^{1}H} NMR (CD$_2$Cl$_2$, 298 K): 166.7 *CH=N*, 140.5, 127.8, 127.4, 127.3, 124.1 *phenyl and pyridine primary aromatic carbons*; 116.4, 114.0 *cyclopentadienil primary carbons*, 67.7 THF; 37.6 *CH$_2$*, 28.6 *CH*, 25.7 *THF*, 23.6 *CH*, 26.7, 23.3 *CH$_3$*.

Mass data (E.I., 70 eV. T$_{probe}$: 120 °C, *m/z*): 503 [M$^{\bullet+}$−THF]$^+$.

2.8. Synthesis of $SmLCl_2(THF)$ (**6**) ($C_{28}H_{35}Cl_2N_2OSm$, PM = 636.86)

To a solution of SmCl$_3$ (0.282 g, 1.1 mmol) in anhydrous THF (25 mL) at −20 °C and under vigorous stirring a THF solution (30 mL) of **4** (0403 g, 1.1 mmol) was dropwise added. At the end of the addition, the yellow-gold suspension obtained was left to reach room temperature and to react overnight. After elimination of NaCl by centrifugation, the yellow solution was concentrated to 10 mL under vacuum and by addition of *n*-hexane (20 mL) afforded yellow microcrystals (0.470 g, 67% yield).

Elemental analysis: found (%): C 52.90, H 5.50, N 4.45, Cl 11.20.

Calcd for C$_{28}$H$_{35}$Cl$_2$N$_2$OSm (%): C 52.81, H 5.54, N 4.40, Cl 11.13.

Mass data (E.I., 70 eV. T$_{probe}$: 110 °C, *m/z*): 564 [M$^{\bullet+}$−THF]$^+$, 529 [M$^{\bullet+}$−THF−Cl]$^+$.

2.9. Synthesis of $NdLCl_2(THF)$ (**7**) ($C_{28}H_{35}Cl_2N_2NdO$, M_w = 630.74)

To a suspension of NdCl$_3$ (0.276 g, 1.1 mmol) in anhydrous THF (50 mL) at −20 °C and under vigorous stirring a THF solution (30 mL) of **4** (0403 g, 1.1 mmol) was dropwise added during a period of half one hour. Once ended the addition, the green suspension obtained was left to reach room temperature and left to react overnight. After elimination of NaCl by centrifugation, the light green solution was concentrated to 10 mL under vacuum and by addition of *n*-hexane (20 mL) afforded light green microcrystals (0.522 g, 75% yield).

Elemental analysis: found (%): C 53.20, H 5.50, N 4.50, Cl 11.35.

Calcd for C$_{28}$H$_{35}$Cl$_2$N$_2$NdO (%): C 53.32, H 5.59, N 4.44, Cl 11.24.

Mass data (E.I., 70 eV. T$_{probe}$: 120 °C, *m/z*): 558 [M$^{\bullet+}$−THF]$^+$, 523 [M$^{\bullet+}$−THF−Cl]$^+$.

2.10. Polymerization

2.10.1. Run **1–6**

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

2.10.2. Runs **7–12**

Polymerizations of 1,3-butadiene were performed by introducing 19 mL of dry toluene and the co-catalysts into 100 mL glass flasks equipped with magnetic stirrer. The flasks were cooled with liquid nitrogen and the inert gas was evacuated. 1,3-Butadiene (the amount are reported in Table 2) was condensed into the flasks, then the reactors were quickly thermostated at the reaction temperature and polymerizations were started by

Table 2
Polymerization of butadiene in the presence of (**5**), (**6**) and (**7**) based catalytic systems

Run[a]	Catalyst (mol)	Co-catalyst[b]	[Butadiene] (mol/L)	Activity[c]	Microstructure
7	**5** (5.96×10^{-6})	MAO	0.31	320	>99% 1,4 *cis*
8	**5** (3.97×10^{-5})	Mg(Bu)$_2$/B(C$_6$F$_5$)$_3$	1.79	8	20% 1,4 *cis*; 80% 1,4 *trans*
9	**6** (8.95×10^{-6})	MAO	2.3	17	76% 1,4 *cis*; 17% 1,4 *trans*, 7% 1,2
10	**6** (8.95×10^{-6})	Mg(Bu)$_2$/B(C$_6$F$_5$)$_3$	1.79	0.4	30% 1,4 *cis*; 70% 1,4*trans*
11	**7** (8.85×10^{-6})	MAO	1.2	22	65% 1,4 *cis*; 35% 1,4 *trans*
12	**7** (3.54×10^{-5})	Mg(Bu)$_2$/B(C$_6$F$_5$)$_3$	1.79	0.5	>99% 1,4 *trans*

[a] All the run were performed by dissolving, in 20 mL of toluene, the butadiene, the catalyst, the co-catalyst. Temperature 25 °C.
[b] (Catalyst)/MAO = 1/1000 (based on Al); (catalyst/Mg(Bu)$_2$/B(C$_6$F$_5$)$_3$ = 1/5/1.
[c] Activity in g of polymer/(mol of catalyst)(h)(mol L^{-1} of butadiene).

injecting 1 mL of a toluene solution of **5**,**6** or **7**. Polymerizations were stopped by introducing a few amount of ethanol. 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

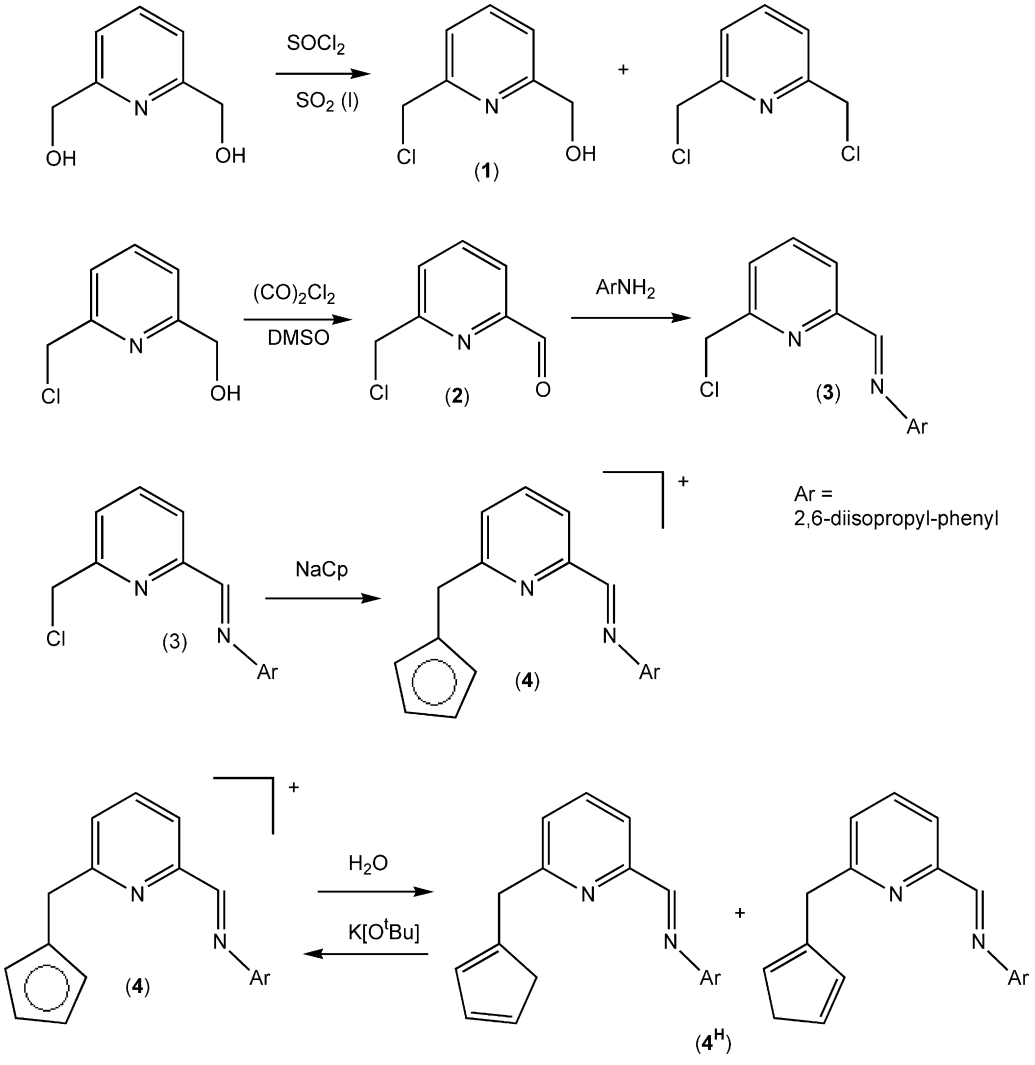
3.1. Ligand syntheses

The *ansa*-imino-cyclopentadienyl-pyridine ligand (**4**) was synthesized according to the following successive reactions (see Scheme 1):

(1) monochloruration of 2,6-dihydroxymethyl-pyridine;
(2) oxidation of the alcoholic group of (**1**) to aldehyde;
(3) condensation of the aldehyde group of (**2**) with 2,6-diisopropyl-aniline;
(4) nucleophilic substitution of the Cl atom of (**3**) with cyclopentadienide ion.

The reaction 1 was carried out by using $SOCl_2$ in liquid SO_2. The use of liquid SO_2 as solvent increases the yield of (**1**) by solubilizing the pyridinium salt of the starting material due to the presence of HCl formed during the reaction: in fact the high solvating power of the liquid SO_2 allows the complete solubilization of all the species in the reaction mixture. The reaction was carried out with the stoichiometric ratio diol/thionyl chloride 1:1.2 at low temperature. All the products of the reaction, i.e. the 2,6-dichloromethyl-pyridine, the 2-hydroxymethyl-6-chloromethylpyridine (**1**) and the unreacted 2,6-dihydroxymethyl-pyridine can be easily isolated by successive selective extractions. The first extraction by diethylether from the acid aqueous solution allowed the isolation of the 2,6-dichloromethyl-pyridine, while after the neutralization by diluted ammonia solution the 2-hydroxymethyl-6-chloromethylpyridine (**1**) is isolated by successive extractions with diethylether. The small amount of unreacted 2,6-dihydroxymethyl-pyridine can be recovered from the aqueous fraction.

The oxidation of the 2-hydroxymethyl-6-chloromethyl-pyridine (**1**) was carried out with oxalyl chloride and



Scheme 1. Reaction pathway for the synthesis of (**4**).

dimethylsulphoxide [16] at low temperature (−60 °C) to give a reactive intermediate of the type [Me_2SCl]Cl, which reacts with the alcoholic group by oxydazing it to aldehyde. The crude product was purified by filtration on silica gel giving the product (**2**) in good yields (>80%).

The condensation reaction with 2,6-diisopropylaniline was carried out by adding to the reagents molecular sieves 4 Å and anhydrous $MgSO_4$ or Na_2SO_4 to shift the reaction equilibrium towards the imine product (**3**) in almost quantitative yields.

The introduction of the cyclopentadienyl group was made as the final step 4 as we have observed that, if the reaction 4 is made before the reaction 3, a mixture of hardly separable product was obtained, probably due to the reaction of the cyclopentadienyl ion with the aldehyde group. The reaction is carried out in THF at low temperature (−80 °C). By using a stoichiometry 1:2.2 in the final reaction the product **4** was obtained as the monosodium salt. Usually the purity of the sodium salt of **4** sometimes was satisfactory to be directly used in the syntheses of the complexes. Moreover, if necessary, a purification of the species **4** after protonation with water of its sodium salt could be done by flash chromatography ($\mathbf{4^H}$). The neutral tautomeric mixture can be quantitatively deprotonated with bases like potassium *tert*-butoxide. The whole reaction pathway is summarized in Scheme 1.

The presence of two tautomers for $\mathbf{4^H}$ is confirmed by NMR spectroscopy: in fact, even if the downfield and the aliphatic regions of the ^{1}H NMR spectrum does not give any information about the presence of the two species, two groups of signals are present both for the vinyl and allyl groups of the cyclopentadiene and for the methylenic group in the ^{1}H NMR and ^{13}C $\{^1H\}$ NMR spectra.

3.2. Syntheses of the Y (5), Sm (6) and Nd(7) chloro-complexes $MLCl_2(THF)$

The yttrium complex **5** was prepared by the very slow addition of the ligand sodium salt **4** to a suspension of YCl_3 in THF at room temperature. Many attempts to carry out the reaction at low temperatures afforded lower yields of the final product. Alternatively, the protonated ligand $\mathbf{4^H}$ was reacted with potassium *tert*-butoxide in THF at room temperature and subsequently solid YCl_3 was slowly added. In both cases the mixtures obtained were allowed to react for 12 h. After separation of NaCl or KCl the complex $YLCl_2(THF)$ (**5**) was obtained as yellow microcrystals and was fully characterized by NMR and Mass Spectrometry. Its ^{1}H NMR and ^{13}C $\{^1H\}$ NMR spectra showed, downfield, the signals of the imine group, the pyridine and phenyl rings. The Cp ring appears as a pseudo-A_2B_2 spin system. The aliphatic region showed the co-ordinated THF molecule, the methylenic and isopropylic groups: these last ones were non-equivalent, since the co-ordination to the metal fragment does not allow the free rotation of the phenyl ring around the C(phenyl)-N(imine) single bond. The MS spectrum of the complex showed the presence of the signal at 503 *m/z* assignable to the molecular ion after the loss of the co-ordinated THF molecule, which is immediately lost because of the relatively high temperature (about 300 °C) of the sample injection system.

Analogous complexes $LnLCl_2(THF)$ {Ln = Sm(III) (**6**), Nd(III) (**7**)} were prepared according to the synthetic method applied for the yttrium derivative. Due to the strong paramagnetism of the Nd(III) and Sm(III) the NMR spectra did not allow precise assignments. In addition to the elemental analyses, the complexes were characterized by mass spectrometry. In the case of the samarium complex (**6**) meaningful signals were observed at 564 *m/z*, assignable to the molecular ion without THF, and at 529 *m/z* assignable to the $[M^{\bullet+} - Cl - THF]^+$ fragment formed by the loss of a chlorine atom from the previous ion. Both the assignments were done by comparison between the theoretical and experimental isotopic clusters. Analogously, the mass spectrum of the neodymium complex (**7**) showed a signal at 558 *m/z* attributable to the molecular ion without THF and another at 523 *m/z* due to the $[M^{\bullet+}-Cl-THF]^+$ ion.

3.3. Polymerization reactions

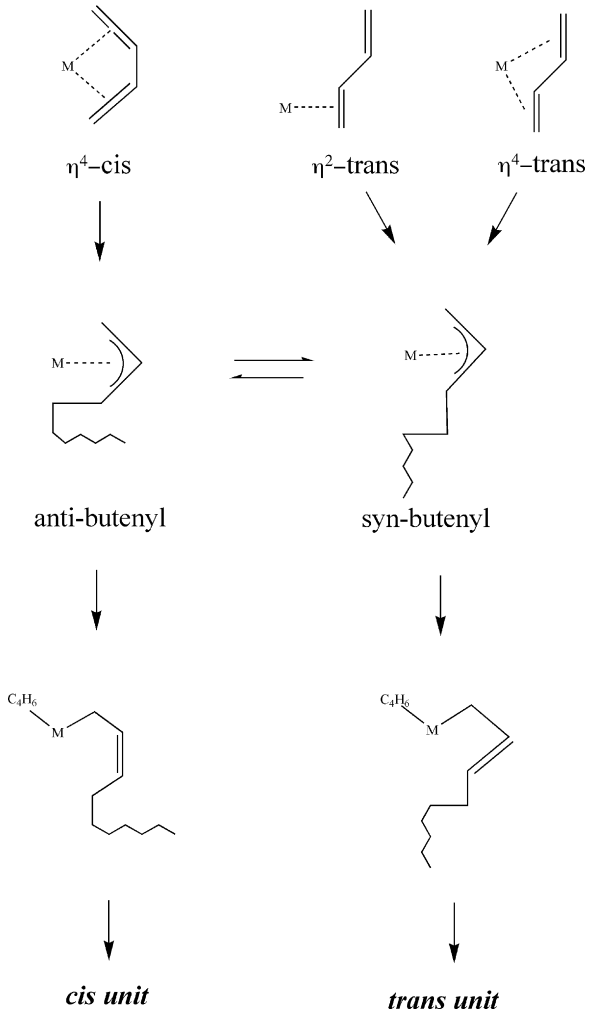
Yttrium compound (**5**) was tested in the polymerization of ethylene in the presence of several co-catalysts, i.e. BuLi/AlH(*i*-Bu)$_2$, MAO, Mg(Bu)$_2$/B(C_6F_5)$_3$ and [$C(C_6H_5)_3$][B(C_6F_5)$_4$]/Al(*i*-Bu)$_3$. The polymerization conditions and the corresponding results are summarized in Table 1. On inspection of the data the following can be observed:

(i) All the systems produce linear polyethylene, presenting a melting point of the polymers, always higher than 130 °C.
(ii) (**5**) Mixed with MAO affords the most active system.
(iii) Activation of (**5**) with Mg(Bu)$_2$ and B(C_6F_5)$_3$ only gives oligomerization of ethylene.

In Table 1, the polymerization data relative to samarium (**6**) and neodymium (**7**) based catalysts are also reported. Complex (**5**) always showed higher reactivity, although derivatives (**6**) and (**7**) were used in the same conditions.

Complexes (**5**), (**6**) and (**7**) activated with MAO or with Mg(Bu)$_2$ and B(C_6F_5)$_3$ were tested in the polymerization of butadiene. The catalysts showed very low activities affording polybutadiene with low molecular weight ($M_w = 10^3$–10^4 g/mol^{-1}) but with MWD unimodal and narrow ($M_w/M_n = 1.4$–2). However, unexpected results relative to polymer microstructure (showed in Table 2) were obtained. In fact, polymerization performed by using MAO as activator of group 3 metal compounds produced prevailingly a 1,4-*cis* polybutadiene (e.g. yttrium based catalyst give exclusively 1,4-*cis* units). Instead, by using as co-catalyst Mg(Bu)$_2$ and B(C_6F_5)$_3$, prevailingly 1,4-*trans* polybutadiene was obtained (e.g. samarium based catalyst give exclusively 1,4-*trans* units).

It is well known from the literature, that the formation of a 1,4-*cis* or a 1,4-*trans* unit arise from an π-allyl terminal growing chain *anti* or *syn*, respectively. *Anti*-allyl group is generated by a *s-cis* monomer coordination and insertion. *Syn*-allyl group can be both obtained by a *trans* monomer insertion and by isomerization of less thermodynamically stable *anti*-group [17,18]. The two mechanisms are depicted in Scheme 2. Generally, η^4-*cis* coordination of butadiene is possible when the catalytic site



Scheme 2. Mechanisms for the formation of *cis*- or *trans*-polybutadiene.

is slightly hindered, whereas η^2 or η^4-*trans* coordination are feasible on more hindered catalytic site.

Polymer microstructures obtained in the presence of different co-catalyst can be related to the different species generated during the activation. In particular, the catalytic intermediates whose formation is supposed are:

$$MLCl_2 + MAO \rightarrow [ML{-}CH_3]^+[MAOCl_2]^- \quad (1)$$

$$MLCl_2 + Mg(Bu)_2 + B(C_6F_5)_3 \rightarrow [ML{-}Bu]^+[B(Bu)(C_6F_5)_3]^- + MgCl_2 \quad (2)$$

The anion of the active species could influence the polymer microstructure determining the steric hindrance of the catalytic site. In particular, the $[ML{-}CH_3]^+[MAOCl_2]^-$ ion pair should have a less hindered catalytic site and therefore lead to a *s-cis* monomer coordination and insertion, whereas the more hindered site of $[LM{-}Bu]^+[B(Bu)(C_6F_5)_3]^-$ leads to a *s-trans* monomer coordination and insertion.

The stereoselectivity in the polymerization of butadiene in the presence of lanthanide based catalysts was already observed by Kaita et al. [19]. However, in all the reported cases, there were not ever so strong effects.

4. Conclusions

In conclusion, it is interesting to observe how both the nature of the metal ion and the co-catalyst play a fundamental role not only in catalytic activity, but also in selectivity of the $MLCl_2$(THF)-based systems. In fact, as discussed before, the change in selectivity can be really tremendous, ranging from >99% 1,4 *cis*-polybutadiene to >99% 1,4 *trans*-polybutadiene. Further studies will be carried out in order to improve the activity of the catalytic systems here presented.

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