

# Synthesis and Spectroscopic Characterization of Titanium Pyridylanilido Complexes as Catalysts for the Polymerization of 1,3-Butadiene and Isoprene

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## Abstract

A series of titanium(IV) complexes of general formula  $TiCl_3[N,N\text{-(pyridin-2-ylalkyl)anilido}]$ ,  $TiCl_3L$ , **8-13**, were prepared by reactions of  $TiCl_4$  with substituted (pyridin-2-ylalkyl)anilines,  $L_H$ , and characterized by analytical and spectroscopic methods. Compound **10** was obtained by using  $TiI_4$  as

titanium precursor. In the case of  $L_H = 2,6$ -diisopropyl(pyridin-2-ylmethyl)aniline, **1**, and 2,6-diisopropyl(pyridin-2-ylethyl)aniline, **2**, the intermediate formation of  $TiCl_4L_H$ , **6-7**, was detected, undergoing HCl elimination on heating to finally give **8** and **9**. The products are not stable in coordinating solvents (thf,  $CH_3CN$ ). Ligand dissociation was observed from  $TiCl_3(N,N$ -2,6-diisopropyl(pyridin-2-ylmethyl)anilido, **8**, resulting in the formation of  $Ti_2OCl_6(CH_3CN)_4$  and 2-(2,6-diisopropyl-phenylaminomethyl)pyridinium hexachlorotitanate. By reaction of  $TiCl_3(thf)_3$  or  $TiI_3$  with **1** and **2** at ca 100 °C, the air sensitive derivatives  $TiCl_2L$ , **14**, and  $TiI_2L$ , **15**, were afforded.

All titanium complexes were evaluated as catalysts for the polymerization of 1,3-butadiene and isoprene, in association with methylaluminoxane (MAO). The results indicate that the catalytic activity is strictly dependent on the nature of the ligands and the oxidation state of the metal, while the nature of the titanium complex has negligible influence on the selectivity.

Keywords: titanium, coordination complexes, catalyst, polymerization, 1,3-butadiene, isoprene

## 1. Introduction

The stereospecific polymerization of conjugated dienes with catalytic systems based on transition metals began in 1954, straight after the first results obtained in the polymerization of propylene [1].

The first catalytic systems were obtained by combining  $TiCl_4$  or  $TiCl_3$ , previously used for the polymerization of ethylene or propylene, with aluminum alkyls [1].

The first synthesized stereoregular diene polymer was a polyisoprene having a structure very similar to that of natural rubber (i.e. *cis*-1,4 structure) [2], immediately followed by the polyisoprene with the same structure as that of gutta-percha (i.e. *trans*-1,4-structure) [3]. The  $TiCl_4/AlR_3$  catalytic system, R = methyl, ethyl, *iso*-butyl, cyclohexyl, was the first catalyst employed for the polymerization of 1,3-butadiene [1, 2]. According to the Al/Ti molar ratio, polybutadienes can be obtained with prevalently *cis*-1,4 structure (i.e. content of *cis*-1,4 units equal to 65%-70%), or with a mixed *cis*-1,4

/ *trans*-1,4 structure.

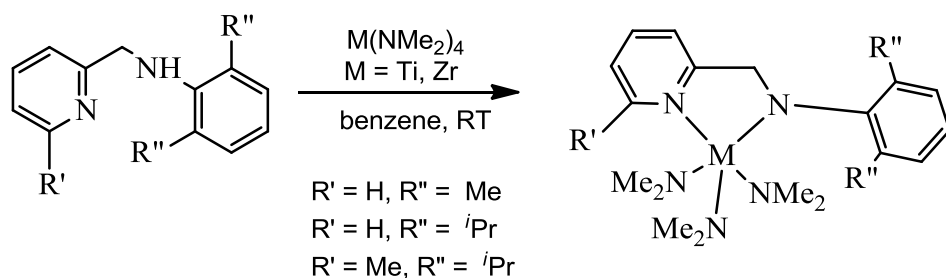
Polybutadienes having a higher content of *cis*-1,4 units, i.e. about 92-95%, have been prepared by combining various types of aluminum alkyl compounds (e.g., Al<sup>i</sup>Bu<sub>3</sub>) with titanium-based catalysts containing iodine [e.g., TiI<sub>4</sub>, TiCl<sub>2</sub>I<sub>2</sub>, TiCl<sub>3</sub>I] [1, 4], or using catalytic systems based on TiCl<sub>4</sub>, AlI<sub>3</sub> and aluminum hydrides [5]. These systems represented the starting points for the development of the industrial processes adopted both in Europe and in USA.

Over recent years, a new generation of catalysts has been introduced, based on transition metals (e.g., Cr, Fe, Co, V) and lanthanides (e.g., Nd, Pr) complexes with N-, O- and P-donor ligands, such as bis-imines, iminopyridines, ketoimines, mono- and bi-dentate phosphines. These coordination complexes, in combination with methylaluminoxane (MAO), afford catalytic systems particularly active in the formation of diene polymers with a controlled microstructure (i.e. *cis*-1,4/1,2 mixed structure, *cis*-1,4/1,2 with a variable content of 1,2 units) [6]. They also produce stereoregular diene polymers from different monomers such as isoprene, 1,3-pentadiene, 1,3-hexadiene, 3-methyl-1,3-pentadiene, 1,3-heptadiene, 1,3-octadiene and 5-methyl-1,3-hexadiene [7], enabling to establish a relationship between the structure of the catalyst, the structure of the monomer and the microstructure of the polymer [6, 8].

In recent years, an increasing number of (pyridin-2-ylalkyl)anilido metal complexes have been studied, due to the established catalytic polymerization activity of this class of compounds and novel structural features presented by the metal complexes of such ligands [9].

As far as group 4 metals are concerned, examples of coordination compounds containing substituted (pyridin-2-ylalkyl)anilido are known [9g-m 10], and many of them have resulted effective in the polymerization of ethylene and/or propylene [9b, h-m].

In 2011, Pellecchia and coworkers prepared a series of derivatives of titanium and zirconium (Scheme 1) which showed a good activity in the stereospecific polymerization of 1,3-butadiene, after activation by Al(<sup>i</sup>Bu)<sub>2</sub>H/MAO [11].

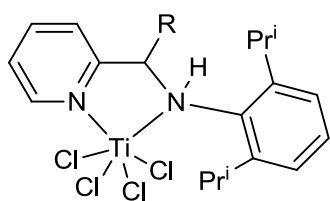


Scheme 1. Synthesis of 2,6-dialkyl-*N,N*-(pyridin-2-ylmethyl)anilido derivatives of titanium and zirconium

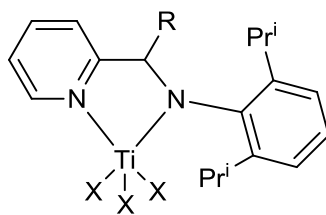
It is noteworthy that most of the compounds reported in the literature are prepared from  $M(NMe_2)_4$  or from  $M(CH_2Ph)_4$ , while only a few preparations use the easily available tetrahalides [9m, 12].

Aiming to develop novel catalytic systems starting from less expensive and easy to handle precursors [tetrabenzyl- and tetra(alkylamido) species are very sensitive to moisture and may ignite in air], we started a research on the reactivity of titanium tetra- and trihalides with (pyridin-2-ylalkyl)aniline. In this paper, we report on the preparation of novel alkyl-*N*-(pyridin-2-ylalkyl)aniline and -anilido complexes of titanium(IV) and titanium(III) (Chart 1). The complexes, in combination with MAO, afford polybutadienes and polyisoprenes with a predominant *cis*-1,4 and mixed *cis*-1,4/3,4 structure, respectively.

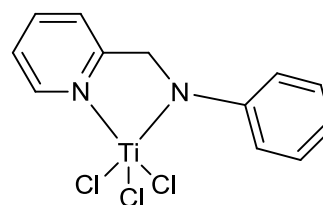
**Chart 1.** Structures of titanium complexes



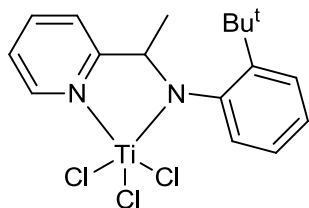
R = H, **6**, Me, **7**



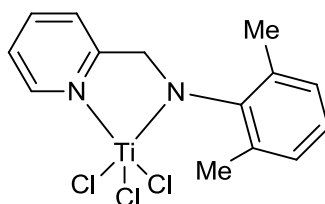
R = H, X = Cl, **8**  
 R = Me, X = Cl, **9**  
 R = Me, X = I, **10**



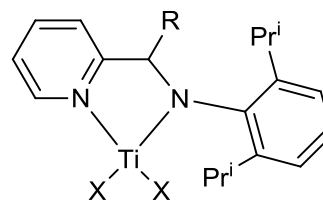
**11**



**12**



**13**



R = H, X = Cl, **14**  
 R = Me, X = I, **15**

## 2. Experimental

**2.1. General procedures and materials.** Unless otherwise stated, manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Nitrogen was purified by passage over columns of CaCl<sub>2</sub>, molecular sieves and BTS catalysts or by passage over the columns Alphagaz Purifiers O<sub>2</sub>-Free and H<sub>2</sub>O-Free (Air Liquide). THF (Aldrich, ≥99.9%) was refluxed over Na/benzophenone for 8 h and then distilled. Toluene (Aldrich, >99.5%) was refluxed over Na for 8 h and then distilled and stored over molecular sieves. Aniline (Aldrich, 99%) was distilled at reduced pressure and stored in an inert atmosphere, 1,3-Butadiene (Air Liquide, >99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to -20 °C. Isoprene (Fluka, ≥99.5%) was refluxed over calcium hydride for 3 h, then distilled trap-to-trap and stored under dry nitrogen. TiCl<sub>4</sub> (Aldrich, 99.9 %) was

distilled under inert atmosphere prior to use. MAO (Aldrich, 10 wt% solution in toluene), tetrachloroethane-d<sub>2</sub> (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) (Aldrich, >99.5% atom D), 2-pyridinecarboxaldehyde (Aldrich), 2-acetylpyridine (Aldrich), 2,6-di-*iso*-propylaniline (Aldrich), 2-*tert*-butylaniline (Aldrich), 2,6-dimethylaniline (Aldrich), *n*-butyl lithium (Aldrich) were used as received.

TiCl<sub>3</sub>(THF)<sub>3</sub> [13], 2,6-diisopropyl(pyridin-2-ylmethyl)aniline, **1**, 2,6-diisopropyl(pyridin-2-ylethyl)aniline, **2**, (pyridin-2-ylmethyl)aniline, **3**, 2,6-dimethyl(pyridin-2-ylmethyl)aniline, **5**, were prepared according to the literature procedure [14].

Elemental Analysis were performed with a Perkin Elmer CHN Analyzer 2400 Series.

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded using a nuclear magnetic resonance spectrometer mod. Bruker Avance 400, using deuterated tetrachloroethane (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) at 103°C, and hexamethyldisiloxane (HDMS) as internal standard, or deuterated chloroform (CDCl<sub>3</sub>) or dichloromethane-d<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>), at 25°C, and tetramethylsilane (TMS) as internal standard. Polymer solutions were used with concentrations equal to 10% in weight with respect to the total weight of the polymer solution. The microstructure of polymers [i.e. *cis*-1,4 unit content (%) in polybutadiene; *cis*-1,4 unit content (%) and 3,4 unit content (%) in polyisoprene] was determined through the analysis of the spectra based on literature [15].

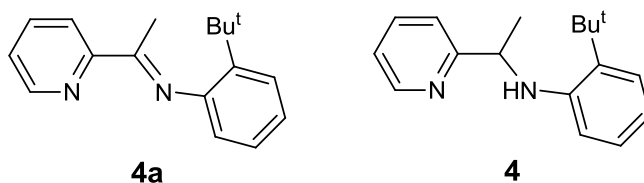
The FTIR-ATR spectra of ligands and complexes were recorded using a Bruker IFS 48 or a Perkin Elmer Spectrum One spectrophotometers equipped with a Thermo Spectra-Tech horizontal ATR connection. The FT-IR spectra of the polymers were obtained from polymeric films on potassium bromide (KBr) tablets. Films were obtained through the evaporation of the solvent from a solution in hot 1,2-dichlorobenzene. The concentration of the polymeric solutions analyzed was equal to 10% in weight with respect to the total weight of the polymeric solution.

The determination of the molecular weight (MW) of the polymers was performed through GPC (Gel Permeation Chromatography) operating under the following conditions: Agilent 1100 pump; Agilent 1100 I.R. detector; PL Mixed-A columns; solvent/eluent: tetrahydrofuran (THF); flow rate: 1 ml/min;

temperature: 25°C; molecular mass calculation: Universal Calibration method. The weight-average molecular weight ( $M_w$ ) and the Polydispersion Index (PDI) are reported, corresponding to the ratio  $M_w/M_n$  ( $M_n$  = number-average molecular weight).

Gas chromatography-mass spectrometry (GC-MS) was performed using a Thermo ISQ single quadrupole mass spectrometer. Samples of the ligands were dissolved in methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) at a concentration of 0.1 mg/ml and were analyzed using said spectrometer operating under the following conditions: ionization method: electronic ionization (EI); GC ramp: 50°C for 2 minutes, heating at a speed of 10°C/min to 300°C; injector temperature: 300°C; injection volume: 1  $\mu\text{l}$ ; transfer line temperature: 280°C; temperature of the ionic source: 250°C; quadrupole scan parameters: 35 amu - 500 amu with scan time of 0.2 sec.

## 2.2. Synthesis of 2-tert-Butyl(pyridin-2-ylmethyl)aniline, **4**



In a 500 ml flask, 2-acetylpyridine (12.9 g, 106.5 mmol) was added to a solution of 2-tert-butylaniline (15.89 g, 106.5 mmol) in methanol (300 ml). The mixture obtained was stirred at room temperature, for 48 hours. The solvent was removed by evaporation at reduced pressure and the residue was crystallized from methanol obtaining 20 g (75% yield) of **4a** as a yellow crystalline solid. Anal. Found (calculated for  $\text{C}_{17}\text{H}_{20}\text{N}_2$ ): C: 81.17 (80.91); H: 8.14 (7.99); N: 10.91 (11.10) %.

Compound **4a** (28 g, 111 mmol) and 800 ml of anhydrous methanol were loaded into a 2 liter reactor, equipped with a stirrer. After cooling at 0°C, sodium borohydride (38 g, 1004 mmol) was added in small portions. The mixture obtained was stirred overnight at room temperature, then switched off with brine and extracted with ethyl acetate. The solvent was then removed by distillation at reduced

pressure and the residue was purified through elution on a silica gel chromatography column [eluent: hexane/ethyl acetate 9/1 (v/v)], and subsequently treated with cold ethyl ether, obtaining 11 g (39% yield) of **4** as a crystalline colorless solid. Anal. Found (calculated for  $C_{17}H_{22}N_2$ ): C: 80.00 (80.27); H: 9.12 (8.72); N: 11.31 (11.01) %. GC-MS:  $M^+ = m/z$  254;  $[M-CH_3]^+ = m/z$  239;  $[M-C_4H_9]^+ = m/z$  197;  $m/z = 183$ ;  $m/z$  132  $C_7H_{10}N_2$ ;  $[M-C_{10}H_{14}N]^+ = m/z$  106;  $[M-C_{12}H_{18}N]^+ = m/z$  78.  $^1H$ -NMR ( $CDCl_3$ ,  $\delta$  ppm): 8.64 (d, 1H, Py), 7.70 (dt, 1H, Py), 7.36 (d, 1H, Py), 7.25 (dd, 1H, Py), 7.18-6.55 (m, 4H, Ar), 5.0 (broad s, 1H, NH), 4.7 (q, 1H, NCH( $CH_3$ )), 1.57 (d, 3H, -NCH( $CH_3$ )), 1.5 (s, 9H, -C( $CH_3$ )<sub>3</sub>).

### 2.3. Synthesis and characterization of $TiCl_4L_H$ , $L_H = 2,6$ -diisopropyl-*N*-(pyridin-2-ylmethyl)aniline, **6**; $2,6$ -diisopropyl-*N*-(pyridin-2-ylethyl)aniline, **7**.

Only the preparation of **7** is described in detail, the other being performed in a very similar way. A 0.5 M  $TiCl_4$  solution in heptane (3.6 ml, 1.8 mmol) was added dropwise to a solution of 0.5 g of  $2,6$ -diisopropyl-*N*-(pyridin-2-ylethyl)aniline (1.8 mmol) in heptane (15 ml). An orange solid formed on addition. After 4 h stirring at room temperature, the solid was recovered by filtration, washed with hexane (2 x 2 ml) and dried at reduced pressure, at ambient temperature, obtaining 0.76 g (89 % yield) of **7** as moisture very sensitive orange microcrystalline solid. Anal. Found (calculated for  $C_{19}H_{26}Cl_4N_2Ti$ ): C: 48.00 (48.34); H: 5.48 (5.55); N: 5.75 (5.93); Ti: 9.64 (10.14); Cl: 29.01 (30.04) %. IR (solid state): 3230m-s, 3064w, 2965s, 2928m, 2868w, 1604s, 1568w, 1483s, 1459s, 1441s, 1382m, 1363m, 1132m-s, 1062m, 1004vs, 808vs, 798vs, 767vs, 755vs  $cm^{-1}$ .  $^1H$ -NMR ( $CDCl_3$ ,  $\delta$  ppm): 9.23 (d, 1H, o-H, Py), 8.17-6.93 (6H, aromatics), 5.37 (m, 1H, CH( $CH_3$ )), 4.30 (br, 1H, NH), 3.30 (m, 2H, CH( $CH_3$ )<sub>2</sub>), 1.57 (d, 3H, -NCH( $CH_3$ )), 1.41 (d, 6H, -CH( $CH_3$ )<sub>2</sub>), 1.24 (d, 6H, -CH( $CH_3$ )<sub>2</sub>).

$TiCl_4L_H$ ,  $L_H = 2,6$ -diisopropyl-*N*-(pyridin-2-ylmethyl)aniline, **6**. (87 % yield) moisture very sensitive, orange microcrystalline solid. Anal. Found (calculated for  $C_{18}H_{24}Cl_4N_2Ti$ ): C: 47.12



(47.20); H: 5.15 (5.28); N: 5.97 (6.12); Ti: 9.84 (10.45); Cl: 29.76 (30.96) %. IR (solid state): 3248m, 3057w, 2964m, 2870w, 1607m, 1569w, 1445m, 1383w, 1297w, 1211w, 1087m, 1024m, 856w, 806m-s, 766vs  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 9.19 (d, 1H, o-H, Py), 7.99-7.06 (6H, aromatics), 5.05 (m, 1H,  $\text{CH}_2$ ), 4.35 (br, 1H, NH), 3.45 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.32 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

**2.4. Synthesis and characterization of  $\text{TiX}_3\text{L}$ , X = Cl, L = *N,N*-2,6-diisopropyl(pyridin-2-ylmethyl)anilido, **8**; X = Cl, L = *N,N*-2,6-diisopropyl(pyridin-2-ylethyl)anilido, **9**; X = I, L = *N,N*-2,6-diisopropyl(pyridin-2-ylethyl)anilido, **10**; X = Cl, L = *N,N*-(pyridin-2-ylmethyl)anilido, **11**; X = Cl, L = *N,N*-2-*tert*-butyl(pyridin-2-ylethyl)anilido, **12**; X = Cl, L = *N,N*-2,6-dimethyl(pyridin-2-ylmethyl)anilido, **13**.**

Only the preparation of **12** is described in detail, the other being performed in a very similar way. A 0.8 M  $\text{TiCl}_4$  solution in heptane (1.1 ml, 0.88 mmol) was added dropwise to a solution of 0.2 g of 2-*tert*-butyl-*N*-(pyridin-2-ylethyl)aniline (0.8 mmol) in heptane (20 ml). An orange solid formed on addition. After 30' stirring at room temperature, the mixture was refluxed for 3h. After cooling at room temperature, the solid was recovered by filtration, washed with hexane (2 x 3 ml) and dried at reduced pressure, at ambient temperature, obtaining 0.18 g (56 % yield) of **12** as a moisture very sensitive, orange microcrystalline solid. Anal. Found (calculated for  $\text{C}_{17}\text{H}_{21}\text{Cl}_3\text{N}_2\text{Ti}$ ): C: 49.91 (50.10); H: 5.00 (5.19); N: 6.66 (6.87); Ti: 10.95 (11.74); Cl: 25.21 (26.09) %. IR (solid state): 3062w, 2964m, 1606m-s, 1570m, 1447m-s, 1295m-w, 1163m-w, 1098m, 1056m, 1026m, 986w, 746vs, 726vs, 716vs  $\text{cm}^{-1}$ . ( $\text{CDCl}_3$ ,  $\delta$  ppm): 9.22 (d, 1H, o-H, Py), 8.31-7.00 (7H, aromatics), 5.31 (m, 1H,  $\text{CH}(\text{CH}_3)$ ), 1.60 (d, 3H,  $\text{NCH}(\text{CH}_3)$ ), 1.49 (d, 9H,  $\text{C}(\text{CH}_3)_3$ ).

**$\text{TiCl}_3\text{L}$ , L = *N,N*-2,6-diisopropyl(pyridin-2-ylmethyl)anilido, **8**.** (83 % yield), moisture very sensitive, yellow microcrystalline solid. Anal. Found (calculated for  $\text{C}_{18}\text{H}_{23}\text{Cl}_3\text{N}_2\text{Ti}$ ): C: 51.12 (51.28); H: 5.35 (5.50); N: 6.40 (6.64); Ti: 10.84 (11.35); Cl: 24.12 (25.23) %. IR (solid state): 3067w,

2963m, 1608m, 1556m-s, 1444m-s, 1383m-w, 1363m-w, 1179m, 1054m, 1023m, 806s, 765vs, 757s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 9.25 (d, 1H, o-H, Py), 8.10-7.20 (6H, aromatics), 5.05 (m, 1H,  $\text{CH}_2$ ), 3.56 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.45 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.35 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 152-117 (aromatics), 56.8 (N- $\text{CH}_2$ ), 29.3 ( $\text{CH}(\text{CH}_3)_2$ ), 25.6 ( $\text{CH}(\text{CH}_3)_2$ ), 24.7 ( $\text{CH}(\text{CH}_3)_2$ ).

**$\text{TiCl}_3\text{L}$ , L = *N,N*-2,6-diisopropyl(pyridin-2-ylethyl)anilido, 9.** (80 % yield), moisture very sensitive, yellow microcrystalline solid. Anal. Found (calculated for  $\text{C}_{19}\text{H}_{25}\text{Cl}_3\text{N}_2\text{Ti}$ ): C: 52.12 (52.38); H: 5.35 (5.78); N: 6.30 (6.43); Ti: 10.65 (10.99); Cl: 24.18 (24.41) %. IR (solid state): 3065w, 2965m, 1610m, 1554m-s, 1442m-s, 1383m-w, 1359m-w, 1181m, 1045m, 1023m, 810s, 763vs, 758s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 9.17 (d, 1H, o-H, Py), 8.25-7.05 (6H, aromatics), 5.27 (m, 1H,  $\text{CH}(\text{CH}_3)$ ), 3.27 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.48 (d, 3H, NCH( $\text{CH}_3$ )), 1.30 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.20 (d, 6H, - $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$  ppm): 163-121 (aromatics), 61.0 (N- $\text{CH}(\text{CH}_3)$ ), 29.3 ( $\text{CH}(\text{CH}_3)_2$ ), 25.8 ( $\text{CH}(\text{CH}_3)_2$ ), 24.1 ( $\text{CH}(\text{CH}_3)_2$ ), 19.6 (N- $\text{CH}(\text{CH}_3)$ ).

**$\text{TiI}_3\text{L}$ , L = *N,N*-2,6-diisopropyl(pyridin-2-ylethyl)anilido, 10.** (57 % yield starting from  $\text{TiI}_4$ ), moisture very sensitive dark brown microcrystalline solid. Anal. Found (calculated for  $\text{C}_{19}\text{H}_{25}\text{I}_3\text{N}_2\text{Ti}$ ): C: 32.01 (32.14); H: 3.71 (3.55); N: 3.99 (3.94); Ti: 6.82 (6.74); I: 53.25 (53.62) %. IR (solid state): 3051w, 2965s, 2870m, 1613s, 1547w, 1462s, 1438s, 1388m, 1336m, 1065m, 1016vs, 805vs, 765vs  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 9.01 (d, 1H, o-H, Py), 8.32-7.10 (6H, aromatics), 5.05 (m, 1H,  $\text{CH}(\text{CH}_3)$ ), 3.31 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.49 (d, 3H, NCH( $\text{CH}_3$ )), 1.32 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.25 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ).

**$\text{TiCl}_3\text{L}$ , L = *N,N*-(pyridin-2-ylmethyl)anilido, 11.** (48 % yield), moisture very sensitive light brown microcrystalline solid. Anal. Found (calculated for  $\text{C}_{12}\text{H}_{11}\text{Cl}_3\text{N}_2\text{Ti}$ ): C: 42.73 (42.71); H: 3.32 (3.29); N: 8.27 (8.30); Ti: 13.52 (14.18); Cl: 30.97 (31.52) %. IR (solid state): 3208m, 3055m, 1611m-s, 1486s, 1430w, 1203m, 1094m, 1025m-s, 864w, 767vs, 758vs, 688vs  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 9.20 (d, 1H, o-H, Py), 8.50-6.70 (8H, aromatics), 4.95 (m, 2H,  $\text{CH}_2$ ).

**TiCl<sub>3</sub>L**, **L** = *N,N*-2,6-dimethyl(pyridin-2-ylmethyl)anilido, **13**. (94 % yield), moisture very sensitive, brown microcrystalline solid. Anal. Found (calculated for C<sub>14</sub>H<sub>15</sub>Cl<sub>3</sub>N<sub>2</sub>Ti): C: 45.33 (46.00); H: 3.90 (4.14); N: 7.45 (7.66); Ti: 12.45 (13.10); Cl: 28.32 (29.10) %. IR (solid state): 3064w, 2962m-w, 1607m, 1523w, 1464m, 1295m, 1260m, 1177mw, 1098m-s, 1056m-s, 950w, 744vs cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ ppm): 9.00 (d, 1H, o-H, Py), 8.00-6.90 (6H, aromatics), 4.63 (m, 2H, CH<sub>2</sub>), 2.30 (m, 6H, CH<sub>3</sub>).

### 2.5. Thermal treatment of **6** and **7**. Formation of **8** and **9**.

An orange suspension of **6** (0.279 g, 0.61 mmol) in heptane was heated at the reflux temperature for 3 h; the color of the suspension turned quickly to yellow. After cooling at room temperature, the solid was recovered by filtration, washed with hexane (2 x 3 ml) and dried at reduced pressure, at room temperature, obtaining 0.205 g (80 % yield) of **8**. Anal. Found (calculated for C<sub>18</sub>H<sub>23</sub>Cl<sub>3</sub>N<sub>2</sub>Ti): C: 51.10 (51.28); H: 5.35 (5.50); N: 6.40 (6.64) %.

The thermal conversion of **7** into **9** was performed in a very similar way.

**2.6. Dissolution of **8** with CH<sub>3</sub>CN**. Compound **8** (0.549 g, 1.30 mmol) was dissolved in acetonitrile (5 ml) obtaining an orange-brown solution. After ca 10 h at room temperature, a microcrystalline orange solid was present. The solid was recovered by filtration, washed with Et<sub>2</sub>O and pentane and dried shortly in vacuo at room temperature, affording 0.064 g (21 % yield based on titanium) of Ti<sub>2</sub>OCl<sub>6</sub>(CH<sub>3</sub>CN)<sub>4</sub>, **8a**, as a yellow solid [16]. Anal. Found (calculated for C<sub>8</sub>H<sub>12</sub>Cl<sub>6</sub>N<sub>4</sub>OTi<sub>2</sub>): C: 19.98 (19.66); H: 2.59 (2.48); N: 11.61 (11.47); Ti: 20.00 (19.59); Cl: 43.99 (43.53) %. IR (solid state)  $\tilde{\nu}_{CN}$ : 2308m, 2283m-s cm<sup>-1</sup>. The brown orange solution produced orange crystals after 24 h at room temperature. The crystals were collected by filtration, shortly dried in vacuo at room temperature affording **8b**\*CH<sub>3</sub>CN (0.110 g, 10 % yield) as orange crystals. Anal. Found (calculated for

C<sub>38</sub>H<sub>53</sub>Cl<sub>6</sub>N<sub>5</sub>Ti) C: 54.20 (54.30); H: 6.47 (6.36); N: 8.42 (8.33); Ti: 5.49 (5.69); Cl: 25.49 (25.31) %.

The orange crystals were used for the diffractometric study.

## **2.7. Synthesis and characterization of TiX<sub>2</sub>L, X = Cl, L = *N,N*-2,6-diisopropyl(pyridin-2-ylmethyl)anilido, **14**; X = I, L = *N,N*-2,6-diisopropyl(pyridin-2-ylethyl)anilido, **15****

Only the preparation of **14** is described in detail, the other being performed in a very similar way.

TiCl<sub>3</sub>(THF)<sub>3</sub> (0.31 g, 0.83 mmol) was added to a solution of 0.222 g (0.827 mmol) of 2,6-diisopropyl-*N*-(pyridin-2-ylmethyl)aniline in toluene (20 ml). The formation of a dark green suspension was immediately observed. After 3 h stirring at room temperature, the solid was recovered by filtration, washed with hexane (2 x 3 ml) and dried at reduced pressure, at ambient temperature, obtaining 0.19 g (59 % yield) of **14** as air sensitive brown microcrystalline solid. Anal. Found (calculated for C<sub>18</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>2</sub>Ti): C: 55.37 (55.98); H: 5.75 (6.00); N: 7.00 (7.25); Ti: 12.02 (12.40); Cl: 18.97 (18.36) %. IR (solid state): 3050w, 2968m, 2874w, 1603m, 1570w, 1450m, 1381w, 1214w, 1080m, 1021m, 860w, 766vs cm<sup>-1</sup>.

**TiI<sub>2</sub>L, L = *N,N*-2,6-diisopropyl(pyridin-2-ylethyl)anilido, **15**.** (96 % yield), moisture very sensitive, dark brown microcrystalline solid. Anal. Found (calculated for C<sub>18</sub>H<sub>23</sub>I<sub>2</sub>N<sub>2</sub>Ti): C: 36.45 (37.99); H: 4.07 (4.14); N: 4.66 (4.92); Ti: 7.98 (8.41); I: 43.80 (44.60) %. IR (solid state): 3057w, 2962m, 2865w, 1611m, 1559w, 1448m, 1380w, 1290w, 1210w, 1085m, 1027m, 808m-s, 763vs cm<sup>-1</sup>.

## **2.8. Polymerization Reactions. General Procedure**

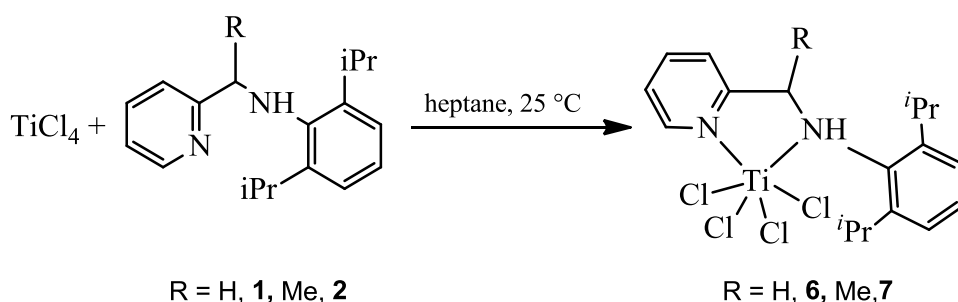
All operations were carried out under an atmosphere of dry dinitrogen. A standard procedure is reported in the case of 1,3-butadiene. The polymerizations with isoprene were carried out by the same procedure. 1,3-Butadiene was condensed into a 25 ml dried glass reactor kept at -20°C. Toluene was added and the solution so obtained was brought to the desired polymerization temperature. Methylaluminoxane (MAO) and the titanium compound were then added as toluene solutions. The

polymerization was terminated with methanol containing a small amount of hydrochloric acid, the polymer was coagulated and repeatedly washed with methanol, then dried in vacuum at room temperature to constant weight.

### 3. Results and discussion

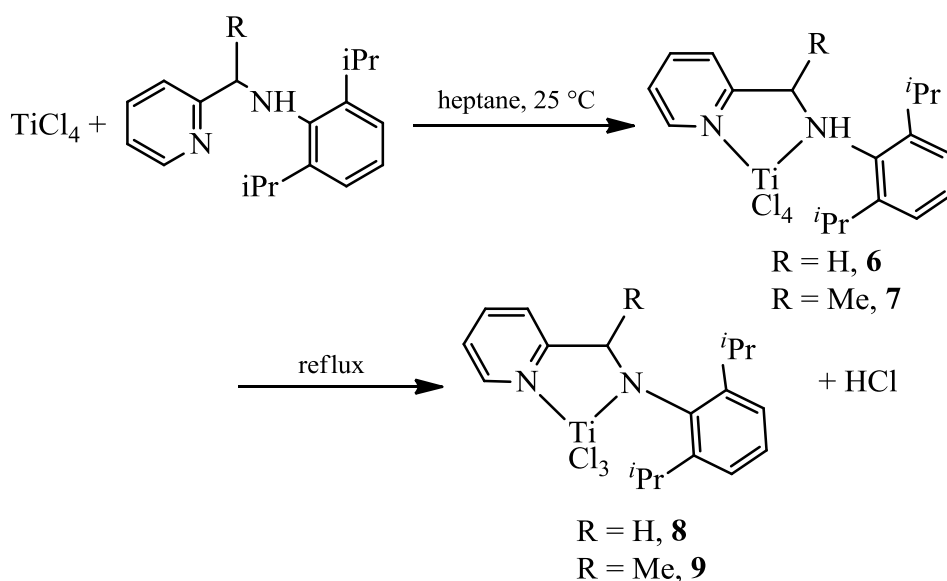
$\alpha$ -Anilinopyridines were prepared via condensation with equimolar amine and 2-acetyl-pyridine or 2-pyridine-carboxylaldehyde followed by reduction of the iminopyridine by sodium borohydride as described in the literature. Compound **4** has not been reported in the literature, thus a detailed preparation and characterization is given. Analytical and spectral data of known [14] **1**, **3** and **5** are given as Supplementary Material (Section S1).

The reaction of **1** and **2** with  $\text{TiCl}_4$  is fast in heptane at room temperature affording **6** and **7** (Scheme 2) as very moisture sensitive, orange microcrystalline solids, which were characterized by elemental analytical and by IR and  $^1\text{H-NMR}$  spectra. The formation of the adduct of  $\text{TiCl}_4$  (*i.e.*, without evolution of  $\text{HCl}$ , *vide infra*) is confirmed by the  $\text{Cl/Ti}$  molar ratio = 4 and by the presence of strong absorptions at 3230 and 3248  $\text{cm}^{-1}$  in the IR spectra of **6** and **7**, respectively, assigned to the NH stretching vibration of the coordinated ligands (the  $\tilde{\nu}_{\text{NH}}$  is observed at 3308 and 3333  $\text{cm}^{-1}$  in the uncoordinated ligands). Moreover, resonances at 9.19 and 9.23 ppm, assigned to the *ortho*-H of the pyridine ring, are observed in the  $^1\text{H-NMR}$  spectra (the resonances of the same protons occur at 8.61 and 8.64 ppm in **1** and **2**, respectively). These evidences suggest that **1** and **2** behave as bidentate ligands with both the pyridine- and the aniline nitrogen atoms involved in the coordination to titanium.



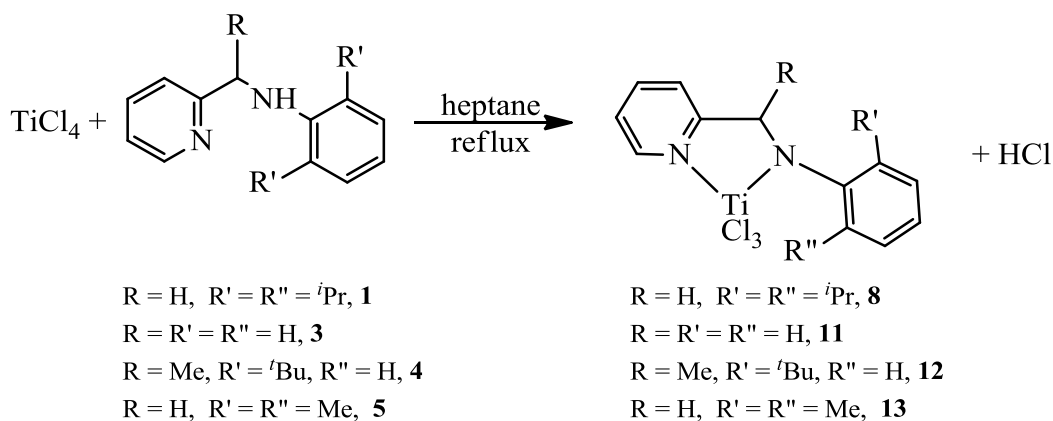
Scheme 2. Synthesis of **6** and **7**.

Compounds **6** and **7** are slightly soluble in chlorinated hydrocarbons, react with basic solvents such as Et<sub>2</sub>O or thf and are almost insoluble in hydrocarbons. They are not thermally stable and, if boiled in heptane, readily evolve HCl with formation of 2,6-diisopropyl(pyridin-2-ylalkyl)anilido derivatives, as it has been experimentally demonstrated in the case of the conversion of **6/7** into **8/9** (Scheme 3).



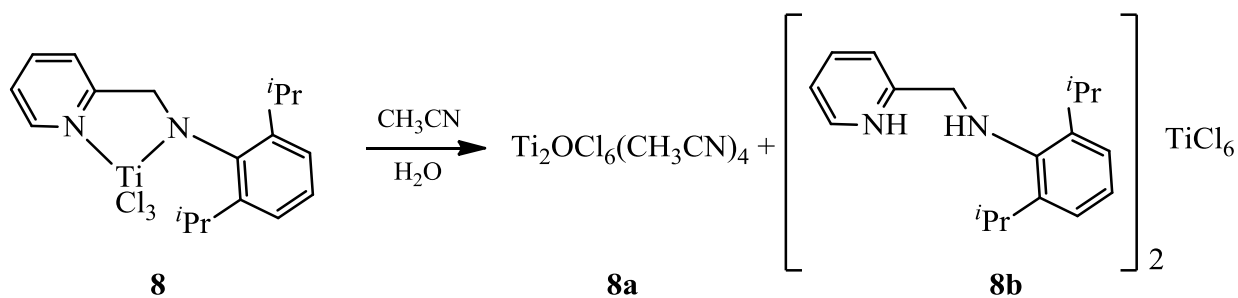
Scheme 3. Thermal conversion of **6/7** into **8/9**.

Compounds **8**, **11-13** have been obtained by thermal treatment of TiCl<sub>4</sub>/ substituted pyridylaniline in heptane (Scheme 4). Formation of HCl has been confirmed by venting the reaction mixture with nitrogen and testing the gases with a pH indicator before and after the addition of the ligand. The iodide **10** has been obtained starting from TiI<sub>4</sub> and limiting the heating time to 30 min. In this case, it was not possible to isolate the TiI<sub>4</sub>L<sub>H</sub> derivative due to formation of HI even at room temperature.



Scheme 4. Synthesis of compounds **8**, **11-13**.

Compounds were characterized by analytical (Cl/Ti molar ratio = 3) and spectroscopic data. The absence of the  $\tilde{\nu}_{\text{NH}}$  stretching vibration and the shift from 8.66 ppm (av.) to 9.12 ppm (av.) of the ortho proton of the pyridine ring on coordination, suggest bidentate coordination of the ligand as an anionic species. All adducts are poorly soluble in hydrocarbons (including aromatic hydrocarbons), slightly soluble in chlorinated hydrocarbons and very soluble in acetone, thf, with probable reaction on standing. All compounds are very sensitive to moisture both in solution and in the solid state. As a matter of fact, during an attempt of recrystallization of **8** from  $\text{CH}_3\text{CN}$ , the known  $\text{Ti}_2\text{OCl}_6(\text{CH}_3\text{CN})_4$ , **8a** [16], and bis(2-(2,6-diisopropylphenylaminomethyl)pyridinium) hexachlorotitanate, **8b**, were isolated in low yields, Scheme 5. The nature of the products suggests the presence of adventitious water in the system. Due to the oxophilicity of titanium(IV), a partial hydrolysis of the  $\text{TiCl}_3$  moiety occurred in acetonitrile with formation of **8a**. The release of HCl as a consequence of the hydrolysis, may rationalize the formation of **8b** via protonation of the pyridine ring of **4**.



Scheme 5. Decomposition of **8** with acetonitrile in the presence of water

Compound **8a** was identified by elemental analysis and IR spectroscopy. The IR spectrum shows absorptions due to the acetonitrile at 2308 and 2283  $\text{cm}^{-1}$ , shifted to higher wavenumbers with respect to the uncoordinated species due to coordination [17]. Crystals of **8b** were characterized by elemental analysis and X-ray diffraction as the bis(2-(2,6-diisopropylphenylaminomethyl) pyridinium) hexachlorotitanate, acetonitrile solvate. The structure of **8b**· $\text{CH}_3\text{CN}$  consists of two N-pyridine protonated 2-(2,6-diisopropylphenylaminomethyl) pyridinium cations and a  $[\text{TiCl}_6]^{2-}$  anion (Figure 1). Details of the structure are given as Supplementary Material, and include a selection of bond distances and angles (Table S1) and a discussion of the H-bonds present in the structure (Figure S1 and Table S2).

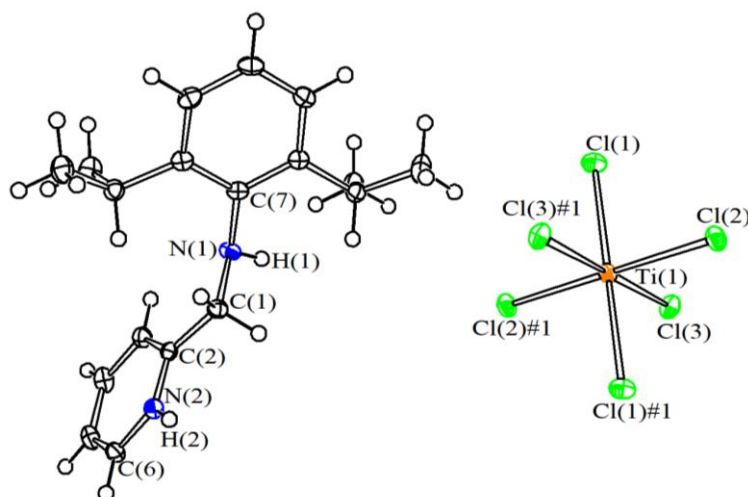
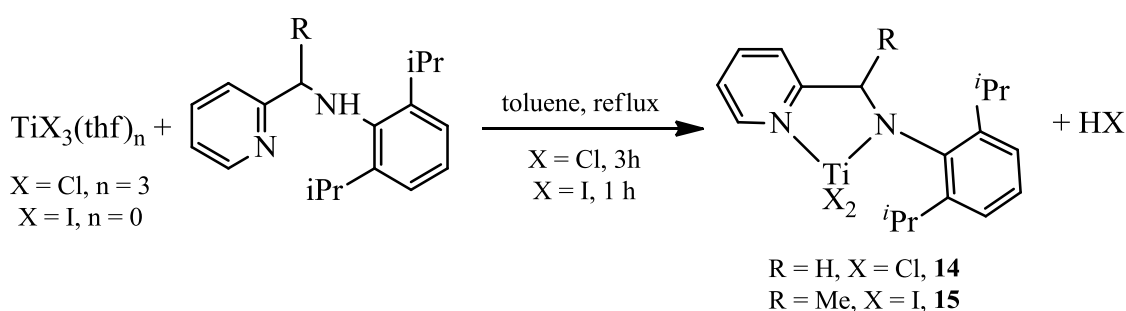


Figure 1. Structure of **8b**· $\text{CH}_3\text{CN}$ . Symmetry transformations used to generate equivalent atoms: #1  $-x+1/2, -y+1/2, -z+1$ .



In order to extend our knowledge to the behavior of Group 4 metal halides with this class of ligands, we studied the reaction of titanium(III) halides with 2,6-diisopropyl(pyridin-2-ylmethyl)aniline, **1**. Reactions were performed in toluene starting from  $\text{TiCl}_3(\text{thf})_3$  or  $\text{TiI}_3$  at ca 100 °C and afforded air sensitive brown, **14**, and dark brown, **15**, microcrystalline solids (scheme 6), which were characterized by analytical and spectral data. They show a very limited solubility in common organic solvents and react with Lewis bases such as  $\text{CH}_3\text{CN}$  or  $\text{thf}$  with formation of adducts which were not considered further.



Scheme 6. Synthesis of compounds **14** and **15**.

### 3.1. Polymerization reactions

The behavior of all the prepared titanium complexes in the polymerization of 1,3-butadiene and isoprene was examined (Table 1). Upon activation with methylaluminoxane (MAO), they exhibit a quite good activity and selectivity as regards the polymerization of butadiene, giving predominantly *cis*-1,4 polymers. Lower yields and less stereoregular polymers, with mixed *cis*-1,4/3,4 structure, were instead obtained from isoprene.

**Table 1.** Polymerization of 1,3-butadiene (B) and isoprene (I) with catalytic systems based on titanium complexes<sup>a</sup>

	Ti complex	monomer	Time (min)	Yield (g)	Conv. (%)	$N^b$ ( $\text{min}^{-1}$ )	<i>cis</i> -1,4 <sup>c</sup> (%)	1,2 <sup>c,d</sup> (%)	$M_w$ ( $\text{g mol}^{-1}$ )	$M_w/M_n$
1	<b>6</b>	B	60	0,270	19,3	8	82,2	17,8	285700	2.1
2	<b>7</b>	B	600	traces						
3	<b>8</b>	B	7	0,601	42,9	159	82,5	17,5	314600	2.0
4	<b>10</b>	B	1200	0,172	12,3	$\ll 1$				
5	<b>11</b>	B	65	0,719	51,4	21	87,1	12,9	305400	2.0
6	<b>12</b>	B	135	0,562	40,1	8	81,2	18,8	535800	1.9
7	<b>13</b>	B	7	0,424	30,3	112	84,1	15,9	654800	1.8

8	<b>14</b>	B	5	1.400	100	519	84,4	15,6	745300	2.1
9	<b>15</b>	B	1200	traces						
10	<b>6</b>	I	300	0,289	21,3	1	57,1	42,9	248500	2,2
11	<b>7</b>	I	7200	—						
12	<b>8</b>	I	30	0,757	55,7	37	56,5	43,5	267600	2,1
13	<b>10</b>	I	7200	—						
14	<b>11</b>	I	100	0,214	15,7	3	55,2	44,8	453800	2,4
15	<b>12</b>	I	200	0,197	14,5	1	55,9	44,1	497100	2,0
16	<b>13</b>	I	150	0,811	59,6	8	31,5	68,5	351200	2,8
17	<b>14</b>	I	165	1,05	77,9	9	39,4	61,6	575650	2,0
18	<b>15</b>	I	7200	—						

<sup>a</sup> Polymerization conditions: monomer, 2 ml; toluene, total volume 16 ml; MAO,  $1 \times 10^{-2}$  moles; Ti,  $1 \times 10^{-5}$  moles; room temperature (22°C);

<sup>b</sup> moles of monomer polymerized/ mol of Ti  $\times$  min;

<sup>c</sup> determined by FT-IR and NMR analysis;

<sup>d</sup> 3,4-isomer in case of isoprene.

The results obtained can be summarized as follows:

- the nature of the ligand seems to have an almost negligible effect on the polymerization regioselectivity in case of butadiene: polybutadienes with a predominantly *cis*-1,4 structure (in the range 82-87%) were obtained, irrespective of the type of ligand bonded to the titanium atom. On the contrary, some effect is observed in the case of isoprene polymerization: polymers with a mixed *cis*-1,4/3,4 structure were obtained, the *cis* content varying in the range 31-57%. At the moment, however, it is difficult to attribute these differences to a particular structure of the catalyst; further work is ongoing to clarify this behavior. The fact that, under the same polymerization conditions (*i.e.*, solvent, polymerization temperature, nature of the titanium complex, type of cocatalyst and MAO/Ti molar ratio), predominantly *cis*-1,4 polymers are obtained from butadiene while polymers with a mixed *cis*-1,4/3,4 structure from isoprene, is clearly attributable to the different monomer structures. According to the well-known diene polymerization mechanism proposed several years ago by Porri and coworkers [1, 6, 8], the presence of a methyl group on the isoprene monomer coordinated to the titanium atom and on the allyl group through which the growing chain is bonded to the titanium atom, associated with the presence of a ligand on the titanium atom, likely make the insertion of the monomer at C1 or C3 of the allylic unit comparable, with consequent formation of a polymer with a mixed *cis*-1,4/3,4 structure. In case of butadiene, the lack of substituents on the monomer likely makes

the insertion of the monomer at C1 preferred, with consequent formation of a polymer with a predominant *cis*-1,4 structure.

- the nature of the ligand has a noticeable effect on the catalyst activity. Catalysts based on titanium complexes **6** and **7** with N-protonated ligands (pyridine-anilines) exhibit the lowest activity. Catalysts based on titanium complexes with pyridine-anilido ligands such as **8** and **13** (disubstituted phenyl ring and non-methylated pyridine-anilido bridge) showed the highest activity. The activity seems to increase with increasing the substitution on the phenyl ring on the anilido nitrogen (cf. runs 5-7-3). On the other hand, the presence of a methyl group on the pyridine-anilido bridge seems to have a negative effect on the catalyst activity (cf. runs 3-4, 12-13, 8-9, and 17-18). The negative effect of the methyl group is also supported by the results obtained in the polymerization of butadiene with **12**-based catalyst: the activity resulted rather low despite the presence of a substitution (*tert*-butyl group) on the phenyl ring that should lead to an increase in activity. Evidently, the negative impact of the methyl group (substitution on the bridge) on the catalytic activity is predominant with respect to the positive impact of the *tert*-butyl group (substitution on the phenyl ring).

- the oxidation state of titanium has a significant influence on the catalyst activity, being the highest activity observed with the **14**-based catalyst, in which the titanium atom is in the oxidation state (+3), which, as it is well known, is the common oxidation state of titanium in the stereospecific polymerization of 1,3-dienes [1-5].

### Concluding Remarks

Titanium(IV) and titanium(III) complexes derived from (pyridin-2-ylalkyl)aniline ( $L_H$ ) of general formula  $TiX_nL$  ( $n = 2, 3$ ) were synthesized and characterized by analytical and spectroscopic methods. The compounds are thermally robust and, in combination with MAO, provide rather active catalytic systems for the polymerization of 1,3-butadiene and isoprene. In particular the catalyst based on complex **13** exhibits a higher activity compared to that of various previously reported titanium

catalysts (e.g.,  $\text{Ti}(\text{O}^n\text{Bu})_4$ ,  $\text{TiCl}_3(\text{THF})_3$ ,  $\text{CpTiCl}_3$ ) [18]. The selectivity is not very high, particularly concerning the polymerization of isoprene, on considering that, from the application point of view, it would be desirable to have a  $\geq 97\%$  *cis* content. It is our intention to study possibilities to increase the *cis* relative content by working on the optimization of the polymerization conditions, but also on the nature of the ligand, even if at present this seems to have only a weak influence on the catalytic selectivity.

### Acknowledgements.

Thanks are due to the University of Pisa (*Fondi di Ateneo 2017*) and to Versalis S.p.A.

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