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New (Anilidomethyl)pyridine Titanium(IV) and Zirconium(IV) Catalyst Precursors for the Highly Chemo- and Stereoselective *cis*-1,4-Polymerization of 1,3-Butadiene

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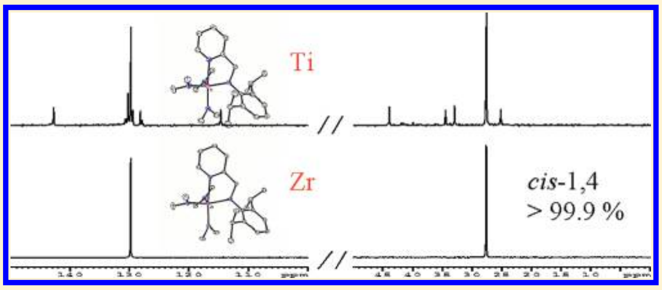
S *Supporting Information*

ABSTRACT: Group 4 metals complexes bearing anilidomethylpyridine ligands have been synthesized and characterized by nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis. All complexes, after activation by using Al^iBu_2H and methylalumoxane (MAO) were tested in 1,3-butadiene and α-olefins polymerization. The zirconium complexes showed higher activity with respect to the titanium homologous. Polymerization of ethylene resulted, in all cases in the production of high molecular weight linear polyethylene. Propylene polymerization tests provided substantially atactic polypropylene. 1,3-Butadiene polymerizations produced *cis*-1,4 polybutadiene, and in the case of zirconium complexes polymers with a content of *cis*-1,4 units higher a 99.9% were provided. Activity and stereoselectivity of the catalysts were related to the steric features of the complexes.



INTRODUCTION

The stereoselective polymerization of conjugated dienes promoted by transition metal complexes is an extensively studied topic and a challenging field in both academic and industrial environments for the relevance of these materials as synthetic rubbers.[1] In particular, the polybutadiene finds many and diverse applications. Its properties are highly dependent upon the microstructure of the polymer backbone which can range from highly *cis*-1,4 (soft, rubbery) to highly *trans*-1,4 (hard) through to *cis* or *trans* structures that contain a significant portion of pendant vinyl groups (*vinyl*-1,2).[2]

A large research interest about polymerization of 1,3-butadiene has been concentrated on the search of new catalytic systems able to simultaneously control both polymer microstructure, especially a *cis*-1,4-structure, and molecular weight distribution (M_w/M_n, MWD), which will improve mechanical and thermal properties such as toughness, impact strength, clarity, and haze of the resulting polymers.[2−8] In this framework, it is worth remarking that just a slight increase in the *cis*-1,4 regularity of the polymers can lead to a great improvement in the elastic properties. In the latest decades, catalysts based on titanium, cobalt, and nickel complexes were successfully utilized for this purpose.[1,9−16] For example, the catalytic systems $Ni(acac)_2$/MAO (acac = acetylacetonate) and $CpTiCl_3$/MAO (Cp = η^5- cyclopentadienyl) were able to produce polybutadiene with a content of cis-1,4 units higher than 80%.[17−19] Uranium allyl compounds have been used for the production of polybutadienes with a high content of cis-1,4 units yielding a product with improved physical properties.[20] Recently, homogeneous lanthanide based systems were shown to produce polybutadienes with more than 95% cis-1,4-structure and a relative narrow MWD (<2.0).[3−8] Moreover, it was also reported that titanium based half-metallocenes with various types of alkyl substituents on the cyclopentadienyl ring, activated by methylalumoxane (MAO), are able to promote living polymerization of 1,3-butadiene to afford polymers presenting a narrow MWD.[21]

In recent years, several nitrogen-based polydentate ligands emerged as an important alternative to the cyclopentadienyl fragment as ancillary ligand for homogeneous olefin polymerization catalyst.[22,23] Significant examples are amidinates,[24,25] pyrrolide-imines,[26−28] 2,6-bis(*N*-aryliminomethyl)pyridines,[29,30] α-diimines[31] and 2-aminopyridines,[32−34] that have been the object of several studies. In this framework, some of us have recently reported zirconium(IV) complexes bearing dianionic tridentate $[^-NNN^-]$ anilidomethylpyrrolidepyridine ligands, which produced catalysts affording ultrahigh molecular weight linear polyethylene and highly isotactic polypropylene[35,36] and bis(amidomethylpyridine) zirconium(IV) complexes which afforded moderately active catalysts in the polymerization of olefins.[37,38]

As an extension of these studies, in this paper we report the synthesis of some new anilidomethylpyridine ligands and of their group 4 metals complexes (see Scheme 1).

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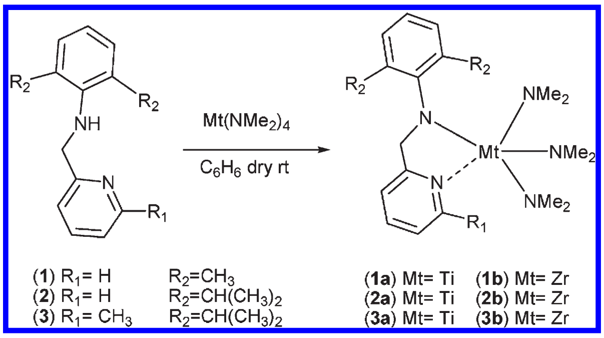
Scheme 1



These complexes were tested in the polymerization of ethylene, propylene, and 1,3-butadiene. The influence of the metal nature as well as of the ligand steric hindrance on the microstructure of the obtained polymers is also discussed. To the best of our knowledge, these compounds are the first example of group 4 metals complexes bearing NN ligands active as catalysts in the polymerization of conjugated dienes.

RESULTS AND DISCUSSION

Synthesis and Characterization of the (Anilidomethyl)-pyridine Titanium(IV) and Zirconium(IV) Complexes. The ligands **1**−**3** were prepared by condensation reaction between *ortho*-substituted aniline and the appropriate pyridinecarbaldehyde, followed by reduction using $NaBH_3CN$ and then hydrolysis.[39] Ligands **1**−**3** were reacted with tetrakis(dimethylamido)-titanium or tetrakis(dimethylamido)zirconium to give complexes **1a**−**3a** and **1b**−**3b** as light yellow or orange powders in high yields (70−95%; Scheme 1). Complexes were characterized by NMR spectroscopy (^1H, ^{13}C NMR), elemental analysis and, for complexes **1a**, **2a**, and **2b**, also by single-crystal X-ray diffraction analysis.

In the ^1H NMR spectra of the titanium complexes **1a**−**3a**, the presence of one singlet for the two methylenic hydrogen atoms on the ligand framework ($PyCH_2NAr$) indicated the existence of a symmetric structure in solution. Moreover, two singlet, accounting for 6 and 12 H respectively, were observed for the NMe_2 groups, indicating that two of three NMe_2 groups have the same environment (e.g., both occupy either equatorial or trans apical positions) while the third one has a different position.

The ^1H NMR spectra for the zirconium complexes **1b** and **2b** were similar to the corresponding titanium complexes but, in both cases, only one broad singlet (δ ∼2.9 ppm;18 H) for the methyls of the dimethylamido groups was observed, probably as a consequence of a rapid positional equilibrium of the NMe_2 on the NMR time scale. On the contrary for the zirconium complex **3b**, bearing the bulkier ligand **3**, (as well as for the titanium compounds **1a**-**3a** described above) this process may be slower, and two singlets for the NMe_2 groups were observed.

Suitable crystals for X-ray diffraction analysis were obtained from hexane at −20 °C for compounds **1a**, **2a**, and **2b.** The molecular structures of **1a**, **2a**, and **2b** are shown respectively in Figures 1, 2 and 3, selected bond distances and angles are listed in the Supporting Information.

The five coordinate complexes adopt a distorted trigonal bipyramidal (tbp) geometry: the pyridine nitrogen atom N(1) and one of the three NMe_2 groups N(3) occupy the trans apical positions and the chelate ligand amide nitrogen atom N(2) and

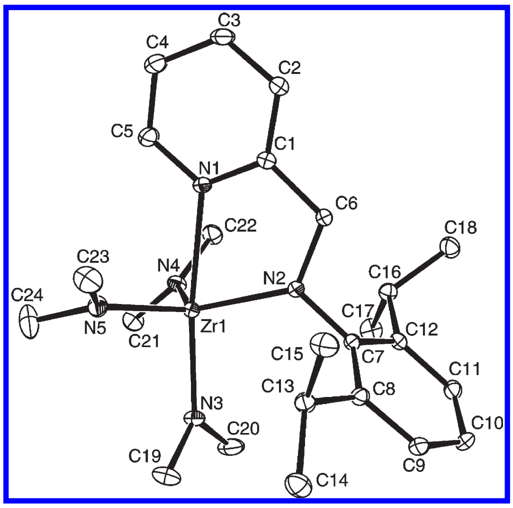


Figure 1. Ortep drawing of compound **1a**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 30% probability level.

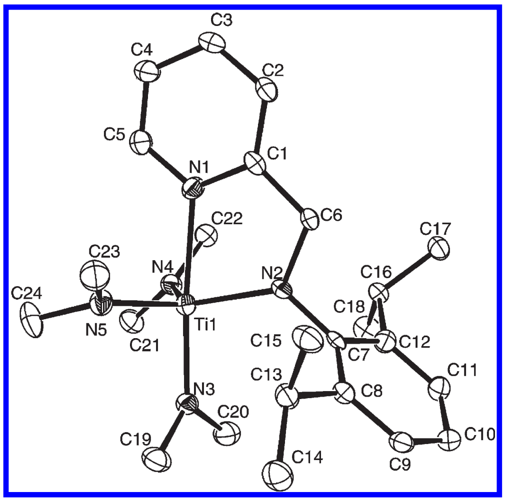


Figure 2. Ortep drawing of compound **2a**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 30% probability level.

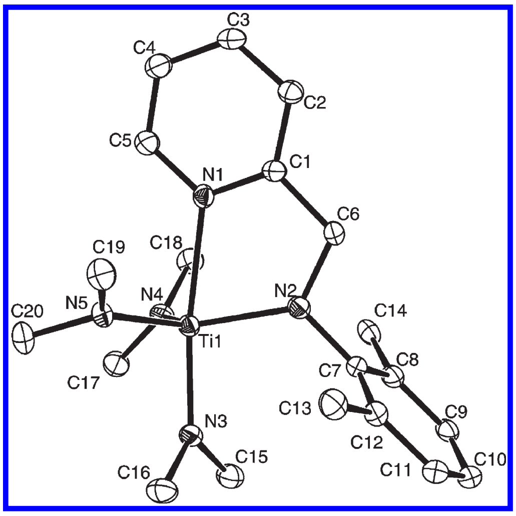


Figure 3. Ortep drawing of compound **2b**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 30% probability level.

the other two NMe_2 groups N(4) and N(5) atoms lie in the equatorial plane. The ratio $\tau = (\beta - \alpha)/60°$, where β and α are respectively the two angles N(1) —Mt—N(3) and N(2) —Mt —N(4), represents the percentage of distortion from the square pyramidal (sp) toward a trigonal bipyramidal (tbp) geometry. A value of zero applies to a compound with a sp geometry and a value of 1 to a tbp geometry; in this case τ values result to be 0.87, 0.91, and 0.90, respectively for **1a, 2a**, and **2b** compounds. Overall, the molecular structures of the three compounds resulted similar to analogous Hf compounds reported by Erker.[39]

In all cases (see Table 1S in the Supporting Information) the three Mt−NMe_2 bond distances are shorter than the Mt−N(1) and Mt−N(2) bond distances. This was an easily predictable feature for the Mt−N(1) distances, which are related to coordination bonds, but also for the Mt−N(2) distances, since the N(2) atoms belong to chelating ligands.

The bite angle of the chelate ligand N(2)−Mt−N(1) results to be markedly smaller for the Zr compound **2b** 69.94(9)°, than for the two Ti compounds. Values of 73.04(12)° and 73.92(14)° are observed respectively for **1a** and **2a**, as expected considering the smaller radius of the metal center. The same angle was 70.6(1)° in an analogous Hf compound.[39]

The pyridine and the 2,6-dialkylphenyl aromatic rings are almost perpendicular to each other with angles of 88.05(12)° for **1a**, 77.68(14)° for **2a**, and 77.84(10)° for **2b**. For the latter compounds the dihedral angle display a more pronounced deviation because of the bulkier isopropyl groups; a similar value, 75.7(5)°, is observed also in the analogous Hf compound.[39]

Polymerization of Olefins. All complexes were tested as precatalysts for the polymerization of ethylene and propylene under 6 atm of monomer pressure after activation with Al^iBu_2H/MAO. In this respect, it is worth underlining that, theAl^iBu_2H/MAO cocatalyst system was significantly more efficient activator than MAO alone. This effect was previously observed for other dimethylamido zirconium catalysts, which reasonably require the presence of Al^iBu_2H to generate the Zr−H or Zr−alkyl bonds where the polymerization may start.[37,38,40,41] Polymers were characterized by NMR spectroscopy, DSC and GPC analyses. Activities, melting temperatures, and molecular weight data are collected in Tables 1 and 2 for ethylene and propylene polymerizations, respectively.

Polymerization of ethylene resulted in all cases in the production of linear polyethylene (mp =131−135 °C). Analysis of polymer samples by GPC revealed high or ultrahigh molecular weights with monomodal molecular weight distributions (MWD = 1.8−2.5). Overall, the zirconium complexes resulted much more active than the titanium complexes, with a trend of activities **1b** < **2b** < **3b** (runs 4−6, Table 3) parallel to the increasing bulkiness of the ligands. E. g.. the best performing system **3b**/Al^iBu_2H/MAO showed a productivity higher than 2.5 tons PE/(mol of Mt × h × atm)$^{-1}$ producing ultrahigh molecular weight linear polyethylene (M_w > 2 million dalton) with narrow molecular weight distribution (M_w/M_n 1,8).

In the propylene polymerization, the zirconium complexes **1b**−**3b** were observed to be more active than the corresponding titanium complexes. In any case, polypropylenes produced were substantially stereoirregular and regioirregular, although the Ti complexes **2a** and **3a** produced a much more regioregular

Table 1. Ethylene Polymerization Results

run[a]	precatalyst	activity[b]	T_m [°C]	M_w [$\times 10^4$]	M_w/M_n
1	**1a**	57	134	219	2.2
2	**2a**	45	134	160	2.5
3	**3a**	15	131	99	2.3
4	**1b**	770	135	107	2.4
5	**2b**	1820	134	172	2.1
6	**3b**	2560	135	224	1.8

[a] Conditions: precatalyst =10 μmol; cocatalyst = Al^iBu_2H/MAO; Al^iBu_2H/Mt = 30; $Al_{(MAO)}$/Mt = 1000; ethylene pressure = 6 atm; toluene = 90 mL; temperature = 25 °C. [b] Activity = kg of polymer × (mol of Mt × h × atm)$^{-1}$.

Table 2. Propylene Polymerization Results

run[a]	complex	activity[b]	[*mm*] %	[*mr*] %	[*rr*] %	vicinal CH_3 [%]	M_w [$\times 10^4$]	M_w/M_n
1	**1a**	22	42	34	24	8.0	539	2.9
2	**2a**	15	55	28	17	<1	332	3.1
3	**3a**	8	45	31	24	<1	257	3.3
4	**1b**	202	31	39	30	15.7	96	3.1
5	**2b**	353	18	43	39	20.5	14	2.6
6	**3b**	654	35	37	28	22.4	140	2.3

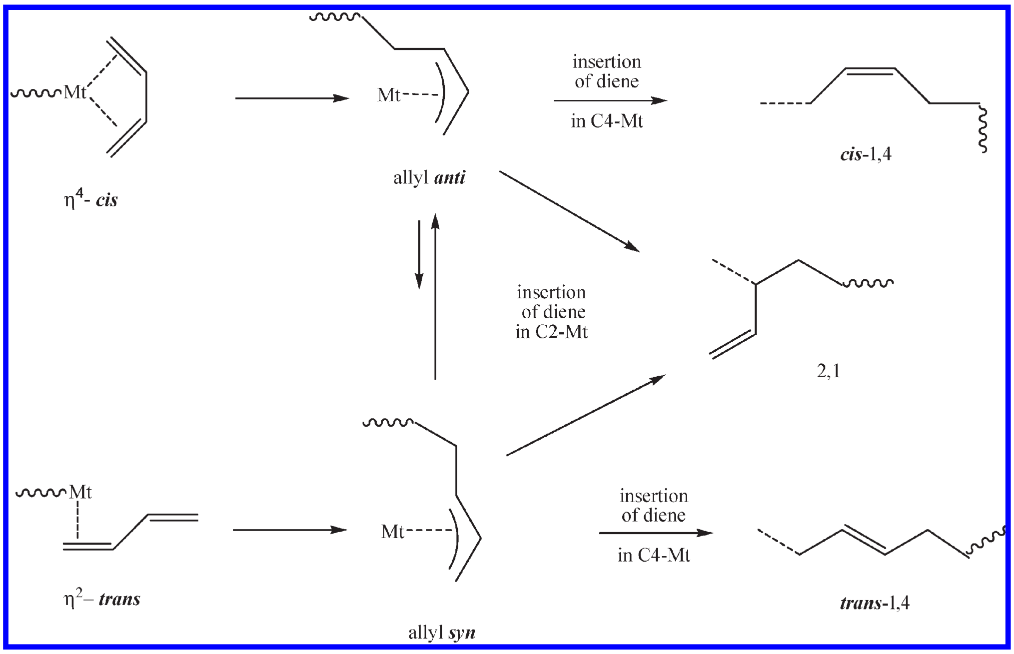
[a] Conditions: precatalyst = 10 μmol; cocatalyst = Al^iBu_2H/MAO; Al^iBu_2H/Mt = 30; $Al_{(MAO)}$/ Mt = 1000; propylene pressure = 6 atm; toluene = 90 mL; time = 60 min; Temperature = 25 °C. [b] Activity = kg of polymer × (mol of Mt × h × atm)$^{-1}$.

Table 3. 1,3-Butadiene Polymerization Results

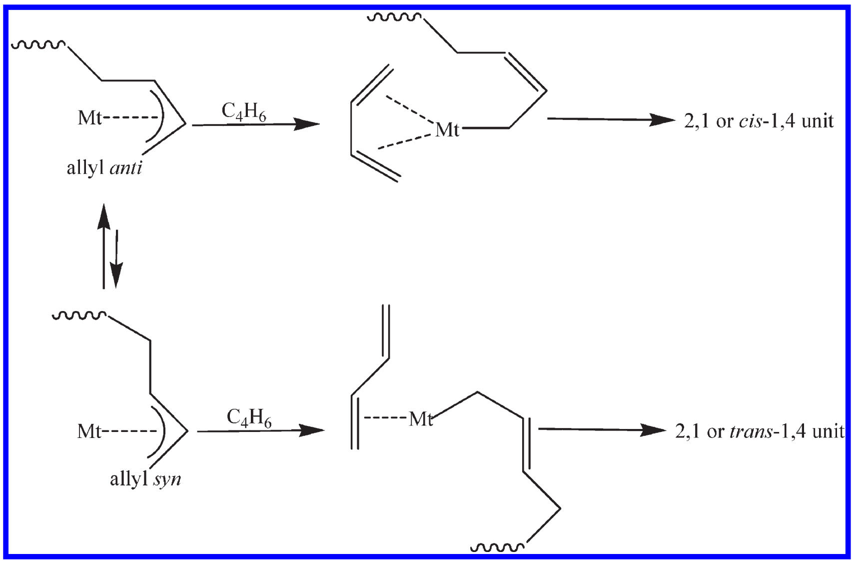
run[a]	complex	activity[b]	*cis*-1,4 units [%]	*trans*-1,4 units [%]	2,1 units [%]	T_m [°C]	Δ*H* [J/g]	M_w [$\times 10^3$]	M_w/M_n
I	**1a**	49	89.3	4.2	6.5	*n.d.*	*n.d.*	503	3.8
II	**2a**	265	83.0	5.5	11.5	*n.d.*	*n.d.*	864	3.2
III	**3a**	337	73.6	9.8	16.6	*n.d.*	*n.d.*	163	2.6
IV	**1b**	378	>99.9	-	-	−8.5	33.3	4299	2.0
V	**2b**	438	>99.9	-	-	−7.3	44.9	2630	2.0
VI	**3b**	773	>99.9	-	-	−8.5	39.5	3535	2.0

[a] Conditions: precatalyst = 10 μmol; cocatalyst = Al^iBu_2H/MAO; Al^iBu_2H/Mt = 30; $Al_{(MAO)}$/ Mt = 2000; temperature = 25 °C; toluene = 53 mL; time = 80 min. [b] Activity = kg polymer (mol of 1,3-butadiene mol of Mt h)$^{-1}$.

Scheme 2



Scheme 3



polymers, with less than 1% of vicinal CH_3 (see Table 2). In any case, the atactic structure of produced polypropylene was not unexpected on the basis of the precatalyst structure, involving only one bidentate monoanionic ancillary ligand and three potentially mobile monodentate ligands.[42]

Polymerization of 1,3-Butadiene. All complexes, after activation by Al^iBu_2H/MAO were also tested as catalysts for the polymerization of 1,3-butadiene. As in the case of α-olefins, the Al^iBu_2H/MAO cocatalyst system that showed good performance as activator for polymerization was also used. Polymers were characterized by NMR spectroscopy, DSC and GPC analyses. Activities, melting temperatures, and molecular weight as well as molecular microstructure data are collected in Table 3.

All catalysts were observed to be active in 1,3-butadiene polymerization, and as in the case of α-olefins, zirconium complexes showed the best performances. Moreover, for both classes of catalysts (titanium or zirconium), activities resulted to be slightly affected by the substituents (R1 and R2) of the ligand. In particular, increasing the steric bulk of the ligand, a gradual increase of activity was observed. This trend could be justified taking in account the ascertained 1,3-butadiene polymerization mechanism (see Scheme 2).[1,43] In fact, dealing with conjugated diolefins, it is worth recalling that the arrangement of a given monomer unit can be considered irreversible only after the insertion of the next one, since the growing chain end is likely η^3-bonded to the metal of the active catalytic species.

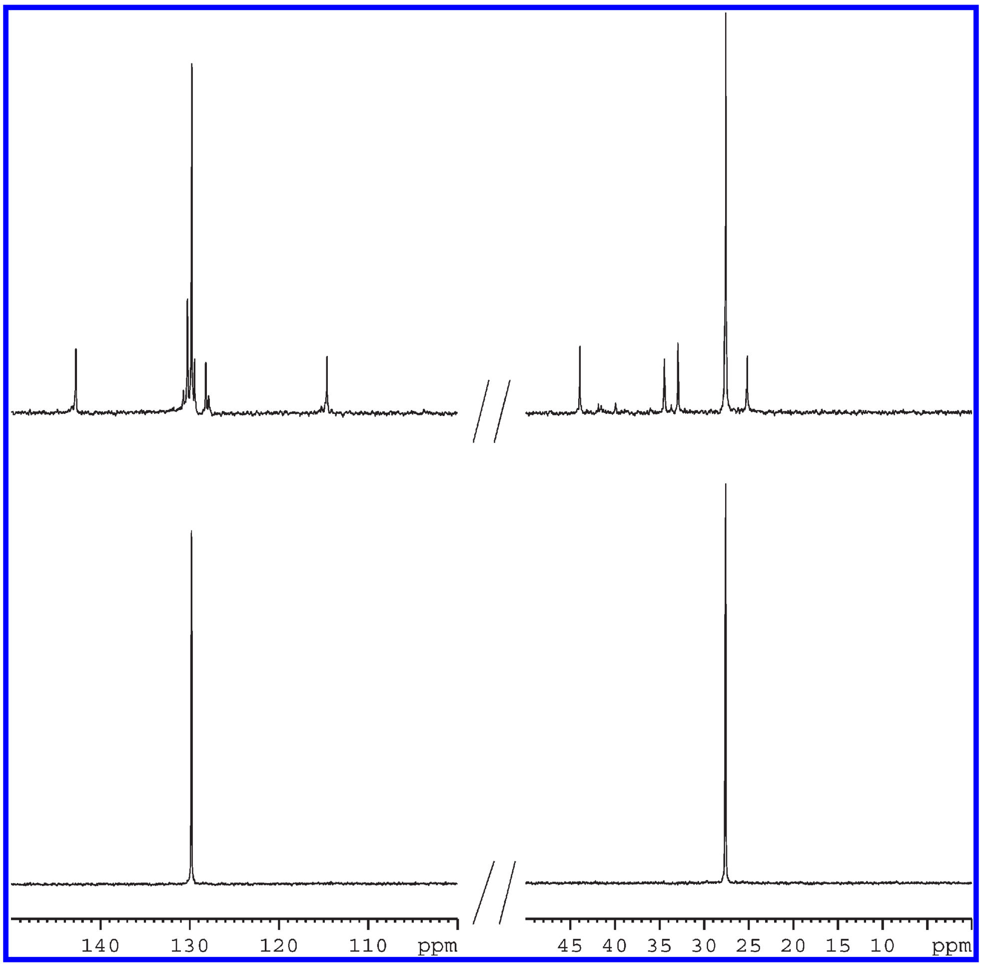


Figure 4. ^{13}C NMR of samples II (up) and V (down) of Table 3. (tetramethylsilane scale, $CDCl_3$, room temperature).

Possibly, the bulkier ligands of catalysts **2a**, **2b**, **3a**, and **3b**, with respect to **1a**, and **1b** induce a positive effect on the polymerization activity owing to a destabilization of the dormant η^3-allyl species, generating an η^1-bonded growing-chain that allows the coordination and the facile insertion of a new monomer unit (see Scheme 3).

Catalysts **1a**, **1b**, which have ancillary ligands with lower steric hindrance, are less active because they likely produce stable complexes with incoming monomer units, as well as with the μ^3-allyl-coordinated growing chain.

Regarding the microstructure of the obtained polybutadienes it can be observed that while titanium based catalysts produce polymers with a content of *cis* 1,4-units between 74 and 89%, zirconium-based catalysts exclusively afford highly *cis* 1,4-polybutadiene (>99.9%, see Table 3 and also Figure 4). This behavior could be related to the ionic radius of the two metals (titanium or zirconium). As expected by simple steric considerations, the larger ionic radius of zirconium complexes could promote the η^4-*cis* coordination of a monomer unit with a consequent *cis* 1,4-butadiene insertion.

As matter of fact, single-crystal X-ray diffraction analysis disclosed a smaller bite angle of the chelate ligand (see X-ray diffraction analysis section and Supporting Information) for the zirconium complexes vs the titanium ones. On the contrary, the smaller ionic radius of titanium could also allow the η^2-*trans* coordination of a monomer unit and the formation of a *trans* 1,4- or a 2,1-butadiene unit.

Zirconium-based catalysts also produce higher molecular weight polybutadiene with lower polydispersity indexes with respect to the titanium homologues (see Table 3).

Also this feature could be explained taking in account that titanium catalysts could allow not only the η^4-*cis*, but also the η^2-*trans* coordination of 1,3-butadiene: the latter two butadiene coordination modes could lead to the formation of more stable intermediate species that inhibit monomer insertion, resulting in more frequent termination reactions.

CONCLUSIONS

Group 4 metals complexes bearing anilidomethylpyridine ligands have been synthesized and characterized. These catalytic precursors, after activation by using Al^iBu_2H and MAO were tested in both α-olefins and 1,3-butadiene polymerization. Polymerization of ethylene resulted, in all cases in the production of linear polyethylene. Analysis of polymer samples by GPC revealed high or ultrahigh molecular weights (M_w > 2 million dalton) with monomodal molecular weight distributions (M_w/M_n 1,8).

Propylene polymerization provided substantially stereoirregular and regioirregular products.

All catalysts resulted active in 1,3-butadiene polymerization, and, as in the case of α-olefins, zirconium complexes showed the best performances. Regarding the microstructure of the obtained polybutadienes it was observed that while titanium based catalysts produce polymers with a content of *cis* 1,4-units between 74 and 89 for %, zirconium based catalysts exclusively afford highly *cis* 1,4-polybutadiene (>99.9%). This behavior could be related to the ionic radius of the two metals (titanium or zirconium). As expected by simple steric considerations, the larger ionic radius of zirconium complexes could favor the η^4-*cis* coordination of a monomer unit with a consequent *cis* 1,4-butadiene insertion. On the contrary, the smaller ionic radius of titanium could also allow the η^2-*trans* coordination of a monomer unit and the formation of a *trans* 1,4- or a 2,1-butadiene unit.

In this framework, it is worth pointing out that, to our knowledge, these group 4 complexes bearing NN ligands are the first example of catalysts active in the *cis* 1,4-butadiene polymerization.

■ EXPERIMENTAL SECTION

General Procedure. Manipulation of sensitive materials was carried out under nitrogen using Schlenk or glovebox techniques. Hexane, benzene, and toluene were refluxed over sodium and then methylene chloride over calcium hydride and then distilled under nitrogen prior to use. $CDCl_3$, CD_2Cl_2, and C_6D_6 were dried over calcium hydride, distilled prior to use, and stored on molecular sevies. The 1,1,2,2-tetrachloroethane-d_2 was used as received for polymer samples analysis. Methylaluminoxane (MAO), 10 wt % in toluene solution, was purchased from Sigma-Aldrich; the residual $AlMe_3$ contained in it was removed by distilling the volatile under reduced pressure, washing the resulting solid with dry hexane and drying the obtained white powder in vacuo. Ethylene and propene were purchased from SON and used without further purification; 1-hexene was distilled over calcium hydride prior to use. All other chemicals were commercially available (Aldrich) and used as received.

NMR spectra were recorded on a Bruker Advance 400, 300, and 250 MHz spectrometers. ^{13}C NMR polyethene and polypropene spectra were recorded on an AM Bruker 62.5 MHz spectrometrer in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 100 °C and reported vs hexamethyldisiloxane (HDMS). ^{13}C NMR polybutadiene spectra were recorded on an AM Bruker 75 MHz spectrometrer in chloroform-d_1 ($CDCl_3$) at 25 °C and reported vs tetramethylsylane (TMS). Elemental analysis were measured on a Thermo Finnigan Flash EA 1112 series C, H, N, S analyzer. Molecular weights (M_n and M_w) and polydispersities (MWD) of polyethylene and polypropylene samples were determined by high-temperature gel permeation chromatography (GPC) using PL-GPC210 with PL-Gel Mixed A columns, a RALLS detector (Precison Detector, PD2040 at 800 nm), a H502 viscometer (Viscotek,), a refractive detector, and a DM400 data manager. The measurements were recorded at 150° using 1,2,4-trichlorobenzene as solvent and narrow molecular weight distribution polystyrene standards as reference. Molecular weights (M_n and M_w) and polydispersities (MWD) of polybutadiene were determined at 35 °C using tetrahydrofuran (THF) as solvent and narrow molecular weight polystyrene standards as reference. Some GPC measurements were performed on Waters GPC-V200 RI detector at 135 °C using 1,2-dichlorobenzene as solvent and Styragel columns (range 10^7−10^3). Every value was the average of two independent measurements. Polymer melting points (T_m) were measured by differential scanning calorimetry (DSC) using a DSC 2920 TA Instruments in nitrogen flow with a heating and cooling rate of 10 °C min^{-1}. Melting temperatures were reported for the second heating cycle.

*Synthesis of 2,6-Dimethyl-N-((pyridin-2-yl)methyl)benzenamine (**1**).* To a solution of 2-pyridinecarboxaldehyde (3.37 g, 31.5 mmol) and 2,6-dimethylaniline (3.82 g, 31.6 mmol) in methanol (100 mL) were added a few drops of formic acid (88%) at room temperature. The resulting solution was stirred at room temperature for 20 h. The orange solution was dried over Na_2SO_4; after filtration, the solvent was distilled off by rotary evaporation. The crude product was washed twice with cold methanol obtaining an orange solid (yield: 5.95 g, 90%). Reduction of the imine function was carried out by using $NaBH_3CN$ in methanol, following a previously reported procedure,[39] yielding a light orange powder.

δ_H (250 MHz, $CDCl_3$, 293 K, Me_4Si): 2.32 (6H, s, CH_3), 4.28 (2H, s, −CH_2), 6.83 (1H, d, J = 7.3 Hz, ArH), 6.99 (2H, d, J = 7.3 Hz, ArH), 7.19−728 (2H, m, ArH), 7.63 (1H, t, J = 7.5 Hz, ArH), 8.61 (1H, d, J = 5.5 Hz, *o*-PyH). δ_C (62.5 MHz, $CDCl_3$, 293 K, Me_4Si): 18.86 (CH_3), 53.85 (CH_2), 122.19, 122.30, 128.99, 129.70, 136.64, 146.32, 149.46, 159.32 (Ar−C).

Anal. Found: C, 79.12; H, 7.23; N, 13.17. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20.

*Synthesis of 2,6-Diisopropyl-N-((pyridin-2-yl)methyl)benzenamine (**2**).* The imine ligand was obtained as above, reacting 2-pyridinecarboxaldehyde (2.14 g, 20 mmol) and 2,6-diisopropylaniline (3.72 g, 21 mmol) (yield: 4.84 g, 91%). The subsequent reduction reaction with $NaBH_3CN$ gave amino ligand as light brown powder (yield: 4.68 g, 96%).

δ_H (400 MHz, $CDCl_3$, 293 K, Me_4Si): 1.42 (12H, d, J = 6.8 Hz, −$CH(CH_3)_2$), 3.47 (2H, m, −$CH(CH_3)_2$), 4.20 (1H, br s, NH), 4.59 (2H, s, −CH_2), 7.04−7.12 (3H, m, ArH), 7.22 (1H, dd, ArH), 7.30 (1H, d, J = 7.7 Hz, ArH), 7.67 (1H, t, J = 7.3 Hz, ArH), 8.62 (1H, d, J = 5.3 Hz, *o*-PyH). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si): 24.44 (CH_3), 27.86 (CH), 56.97 (CH_2), 122.18, 123.74, 124.05, 136.63, 142.86, 143.23, 149.51, 159.17 (Ar−C).

Found C, 80.37; H, 8.95; N, 10.17. Calc. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44%

*Synthesis of 2,6-Diisopropyl-N-((6-methylpyridin-2-yl)methyl)benzenamine (**3**).* The imine ligand was obtained as above, reacting 6-methyl-2-pyridinecarboxaldehyde (2.30 g, 18 mmol) and 2,6-diisopropylaniline (3.36 g, 19 mmol) (yield: 4.34 g, 86%). The subsequent reduction reaction with $NaBH_3CN$ gave amino ligand as light brown powder (yield: 4.25 g, 98%).

δ_H (400 MHz, $CDCl_3$, 293 K, Me_4Si): 1.23 (12H, d, J = 6.8 Hz, −$CH(CH_3)_2$), 2.59 (3H, s, −CH_3), 3.39 (2H, m, −$CH(CH_3)_2$), 4.17 (2H, s, −CH_2), 4.20 (1H, br s, NH), 7.04−7.13 (5H, m, ArH), 7.53 (1H, t, J = 7.8 Hz, ArH). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si): 24.43, 24.65 (CH_3), 27.93 (CH), 56.65 (CH_2), 119.08, 121.83,122.98, 123.74, 123.86, 137.0, 142.72, 143.6, 158.28 (Ar−C).

Anal. Found: C, 80.67; H, 9.25; N, 9.97. Calcd for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92.

*Synthesis of **1a**.* A 0.245 g sample of ligand **1** (1.1 mmol) were dissolved in 10 mL of benzene. To a this solution was added dropwise a solution of tetrakis(dimethylamido)titanium (0.267 mL, 1.1 mmol) in 5 mL. The resulting solution was stirred for 2 h at room temperature. The solvent was then distilled off in vacuo and the resulting powder was washed twice with hexane (2 × 5 mL). The complex was recrystallized from dichloromethane/hexane (yield: 0.403 g, 93%).

δ_H (400 MHz, C_6D_6, 293 K, Me_4Si): 2.38 (6H, s, CH_3), 2.87 (6H, br s, −$N(CH_3)_2$), 3.13 (12H, br s, −$N(CH_3)_2$), 4.49 (2H, s, −CH_2), 6.46 (1H, t, J = 6.7 Hz, ArH), 6.59 (1H, d, J = 7.6 Hz, ArH), 6.89 (1H, m, ArH), 6.97 (1H, m, ArH), 7.22 (2H, d, J = 7.8 Hz, ArH), 7.89 (1H, d, J = 5.0 Hz, *o*PyAr). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si): 18.58 (CH_3), 46.45, 46.98 ($N(CH_3)_2$), 64.16 (CH_2), 120.67, 121.66, 122.44, 127.75, 133.66, 136.60, 147.58, 154.52, 163.34 (Ar−C).

Anal. Found: C, 61.26; H,8.47; N, 17.91. Calcd for $C_{20}H_{33}N_5Ti$: C, 61.38; H, 8.50; N, 17.89.

*Synthesis of **1b**.* The reaction was performed as above, reacting 0.245 g of ligand **1** (1.1 mmol) and tetrakis(dimethylamido)zirconium (0.293 g, 1.1 mmol) in 15 mL of hexane (yield: 0.450 g, 94%).

δ_H (400 MHz, C_6D_6, 293 K, Me_4Si): 2.42 (6H, s, CH_3), 2.94 (18H, br s, −$N(CH_3)_2$), 4.45(2H, s, −CH_2), 6.46−7.24 (6H, m, ArH), 8.11(1H, d, $J = 5.5$ Hz, oPyAr). δ_C (100 MHz, C_6D_6, 293 K, Me_4Si): 18.7 (CH_3), 43.21 ($N(CH_3)_2$), 62.58 (CH_2), 120.95, 121.38, 123.18, 134.33, 136.78, 147.71, 152.58, 164.51 (Ar−C).

Anal. Found: C, 55.07; H,7.59; N, 16.12. Calcd for $C_{20}H_{33}N_5Zr$: C, 55.26; H, 7.65; N, 16.11.

*Synthesis of **2a**.* The reaction was performed as above, reacting 0.276 g of ligand **2** (1.0 mmol) and tetrakis(dimethylamido)titanium (0.243 mL, 1.0 mmol) in 15 mL of hexane (yield: 0.400 g, 89%).

δ_H (400 MHz, C_6D_6, 293 K, Me_4Si): 1.39 (6H, d, $J = 6.7$ Hz, $-CH(CH_3)_2$), 1.55 (6H, d, $J = 6.7$ Hz, $-CH(CH_3)_2$), 3.04 (6H, s, $-N(CH_3)_2$), 3.25 (12H, s, $-N(CH_3)_2$), 3.76 (2H, m, $CH(CH_3)_2$), 4.95 (2H, s, $-CH_2$), 6.58−7.35 (6H, m, ArH), 8.00 (1H, d, $J = 5.1$ Hz, *o*-PyAr). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si): 24.11, 27.36 (CH_3), 27.76 (CH), 46.30, 48.20 ($N(CH_3)_2$), 67.06 (CH_2), 120.46, 121.60, 122.92, 123.22, 136.62, 144.34, 147.51, 162.91 (Ar−C).

Anal. Found: C, 64.36; H,9.14; N, 15.58. Calcd for $C_{24}H_{41}N_5Ti$: C, 64.42; H, 9.24; N, 15.65.

*Synthesis of **2b**.* The reaction was performed as above, reacting 0.250 g of ligand **2** (0.9 mmol) and tetrakis(dimethylamido)zirconium (0.248 g, 0.9 mmol) in 15 mL of benzene (yield: 0.425 g, 96%).

δ_H (400 MHz, C_6D_6, 293 K, Me_4Si): 1.44 (6H, d, $J = 6.9$ Hz, $-CH(CH_3)_2$), 1.60 (6H, d, $J = 6.9$ Hz, $-CH(CH_3)_2$), 3.10 (18H, br s, $-N(CH_3)_2$), 3.77 (2H, m, $CH(CH_3)_2$), 4.85 (2H, s, $-CH_2$), 6.60 (2H, m, ArH), 6.94 (1H, t, $J = 7.7$ Hz, ArH), 7.28 −7.38 (3H, m, ArH), 8.25 (1H, d, $J = 5.5$ Hz, *o*-PyAr). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si) 24.03, 27.12 (CH_3), 27.62 (CH), 39.93, 43.44 ($N(CH_3)_2$), 65.43 (CH_2), 121.67, 122.37, 123.74, 125.24, 138.45, 147.93, 163.57 (Ar−C).

Anal. Found: C, 58.67; H,8.35; N, 14.08. Calcd for $C_{24}H_{41}N_5Zr$: C, 58.73; H, 8.42; N, 14.27.

*Synthesis of **3a**.* The reaction was performed as above, reacting 0.350 g of ligand **3** (1.76 mmol) and tetrakis(dimethylamido)titanium (0.427 mL, 1.76 mmol) in 20 mL of benzene (yield: 0.550 g, 68%).

δ_H (400 MHz, CD_2Cl_2, 293 K, Me_4Si): 1.14 (6H, d, $J = 6.8$ Hz, $-CH(CH_3)_2$), 1.1.27 (6H, d, $J = 6.8$ Hz, $-CH(CH_3)_2$), 2.35 (3H, s, $PyCH_3$), 2.61 (6H, s, $-N(CH_3)_2$), 3.04 (12H, s, -$N(CH_3)_2$), 3.41 (2H, m, $CH(CH_3)_2$), 4.79 (2H, s, -$PyCH_2$), 6.93−7.68 (6H, m, ArH). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si): 23.81, 24.68, 27.11 (CH_3), 27.89 (CH), 43.43, 44.03 ($N(CH_3)_2$), 56.70 (CH_2), 117.47, 117.83, 118.94, 123.77, 137.07, 142.67, 146.73, 153.36 (Ar−C).

Anal. Found: C, 64.98; H,9.25; N, 15.03. Calcd for $C_{25}H_{43}N_5Ti$: C, 65.06; H, 9.39; N, 15.17.

*Synthesis of (**3b**).* The reaction was performed as above, reacting 0.500 g of ligand **3** (1.7 mmol) and tetrakis(dimethylamido)zirconium (0.472 g, 1.7 mmol) in 20 mL of benzene (yield: 0.840 g, 97%).

δ_H (400 MHz, C_6D_6, 293 K, Me_4Si): 1.30 (6H, d, $J = 6.8$ Hz, $-CH(CH_3)_2$), 1.47 (6H, d, $J = 6.8$ Hz, $-CH(CH_3)_2$), 2.29 (3H, s, $PyCH_3$), 2.84 (6H, s, $-N(CH_3)_2$), 2.96 (12H, s, $-N(CH_3)_2$), 3.68 (2H, m, $CH(CH_3)_2$), 4.77 (2H, s, $-CH_2$), 6.42 (1H, d, $J = 7.7$ Hz, ArH), 6.49 (1H, d, $J = 7.6$ Hz, ArH), 6.83 (1H, t, $J = 7.6$ Hz, ArH), 7.1−7.27 (3H, m, ArH). δ_C (100 MHz, $CDCl_3$, 293 K, Me_4Si): 22.21, 24.11, 27.07 (CH_3), 28.12 (CH), 42.57, 44.38 ($N(CH_3)_2$), 65.66 (CH_2), 118.22, 122.49, 123.19, 123.50, 137.41, 145.28, 149.93, 15911, 163.77 (Ar−C).

Anal. Found: C, 59.39; H,8.55; N, 13.59. Calcd for $C_{25}H_{43}N_5Zr$: C, 59.47; H, 8.58; N, 13.87.

Polymerizations. *1,3-Butadiene Polymerization.* Polymerizations of 1,3-butadiene were performed by introducing toluene (50 mL) and MAO (580 mg, 1×10^{-2} mol) into 100-ml glass flasks equipped with magnetic stirrer. The inert gas was evacuated, the solutions were cooled with liquid nitrogen, and 1,3-butadiene (2,8 g, 0.052 mol) was assimilated into the flask. Then, the reactors were quickly thermostated at 25 °C, the nitrogen inert atmosphere was replaced and the precatalyst (10 μmol) in toluene (2 mL) preaged for 10 min with a toluene solution (1 mL, 0.28M) of $AliBu_2H$. was injected. After the required polymerization time (80 min), the mixture was poured into acidified ethanol. The polymers were washed with fresh ethanol, recovered by filtration, and dried at 40 °C in a vacuum oven.

α-Olefin Polymerization. Ethylene and propylene polymerizations were performed into a 500 mL Büchi glass autoclave. The reactor vessels were charged sequentially with MAO and a toluene solution of precatalyst in toluene (2 mL), preaged for 10 min with a solution of $AliBu_2H$ in toluene. The mixture was thermostated at the required temperature and the monomer gas feed was started. In all cases, after the required polymerization time the mixture was poured into acidified ethanol. The polymers were recovered by filtration, and dried at 40 °C in a vacuum oven.

X-ray Crystallography. Suitable crystals were selected and mounted on a cryoloop with paratone oil and measured at 100 K with a Rigaku AFC7S diffractometer equipped with a Mercury[2] CCD detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data reduction was performed with the crystallographic package CrystalClear.[44] Data have been corrected for Lorentz, polarization, and absorption. The structure was solved by direct methods using the program SIR2002[45] and refined by means of full matrix least-squares based on F^2 using the program SHELXL97.[46] For all compounds non-hydrogen atoms were refined anisotropically, hydrogen atoms were positioned geometrically and included in structure factors calculations but not refined. Crystal data and refinement details are reported in Table 2S of the Supporting Information. Crystal structures were drawn using ORTEP32.[47]

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic information files in CIF format, selected bond distances and bond angles, crystal data, and refinement details for compounds **1a**, **2a**, and **2b** and ^{13}C NMR data for samples II and V of Table 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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