ORGANOMETALLICS

Titanium Bis(amidinates) Bearing Electron Donating Pendant Arms as Catalysts for Stereospecific Polymerization of Propylene

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S Supporting Information

ABSTRACT: A series of titanium bis(amidinate) complexes containing pendant arms as one of the amidinate N substituents have been prepared and studied in the polymerization of propylene after their activation with MAO and other cocatalysts. The type of pendant arm greatly influences the reactivity and stereospecificity of the resulting polymers. The effect of the cocatalyst nature, its amount, and the time of the reaction have a dramatic effect on the reactivity of a titanium bis(amidinate) bis(dimethylamido) precatalyst containing a furyl group at the pendant arm.

T he use of amidinates and benzamidinates as ancillary ligands for group 4 complexes has been studied extensively over the past few years.^{1,2} These ligands are considered to be sterically equivalent to cyclopentadienyl ligands; however, the amidinates donate only four electrons to the metal in comparison to the six electrons donated by the cyclopentadienyl moiety and are thereby expected to increase the Lewis acidity of the metal in the resulting complex.³ In addition, amidinates have exhibited an attractive alternative to cyclopentadienyl ligands due to their synthetic accessibility, allowing facile tuning of their steric and electronic properties.⁴⁻⁶

Much of our current research has focused on the investigation of group 4 bis(amidinate) complexes as catalytic precursors for the polymerization of ethylene and propylene. For propylene, it was found that when titanium bis(amidinate) and bis-(benzamidinate) complexes were activated with methylalumoxane (MAO), the resulting catalytic mixture yielded a blend of stereospecific and elastomeric polypropylenes.⁷ Thorough examination of the mechanism revealed that each substituent of the amidinate ligand plays an important role in the formation of the resulting polymer. We have observed that, during the activation of bis(arylamidinate) group 4 precursors, one of the amidinate ligands migrates from the group 4 metal center to an aluminum in MAO. The remaining ligand of the resulting mono(arylamidinate) complex rearranges and reattaches to the metal center through the aromatic ring, creating a κ^6 coordination in addition to one nitrogen of the amidine moiety. The catalytic activity of the resulting complex was found to be very sensitive to the substitution on the aryl ring. Large steric hindrance of the substituent at the para position of the aromatic moiety, in comparison to hydrogen, decreases the activity of the resulting complex and induces an increase of the molecular weight of the obtained polymers.⁸

In addition, group 4 bis(benzamidinate) complexes bearing electron-withdrawing groups at the aromatic N substituents



induce higher polymerization activity,⁹ as opposed to the reduced activity observed when electron-donating groups were utilized.¹⁰ This electronic tailoring of the ligand has been found to lead to the formation of high-molecular-weight atactic polypropylene due to the complete loss of the symmetry of the active site involved in the monomer insertion.^{7a,9,11} Attempts to restrict this dynamic behavior have been unsuccessful, and as a result, we have consistently obtained mixtures of elastomeric and stereospecific polymers.

In light of these observations, more elaborate ligand systems were studied to limit ligand lability and migration. Among the candidate ligands, amidines with pendant pyridine^{12,13} and dimethylamine¹³ moieties have been used to stabilize various metals such as vanadium,¹⁴ titanium,¹⁵ and palladium¹² as mono(amidinate) complexes and zirconium¹³ as bis(amidinate) complexes. Hence, here we report the synthesis of titanium bis(benzamidinates) containing pyridine, dimethylamine, and furyl pendant moieties. These complexes were found to be active in the polymerization of propylene, producing highly isotactic polypropylenes. The stereoregularity of the polymers was found to be strongly dependent on the nature of the pendant arm moiety of the amidinate ligands and on the cocatalyst used. Unexpectedly, the stereochemistry of the polymer indicates that the stereoregularity of the resulting polymer was induced via a chain-end control mechanism.

The syntheses of ligands 1, 2, and 4 (eq 1) and of ligand 3 (eq 2) were performed according to previously published methodologies.^{12,13}

The titanium bis(benzamidinates) were prepared by protonolysis using 2 equiv of the amidine with $Ti(NMe_2)_4$ or $Ti(NMe_2)_2Cl_2$ at room temperature (eq 3).

Received: December 1, 2013



Crystal structures of the complexes **5**, 7, and **9** are presented in Figures 1–3, respectively. For the metal complexes, in all cases,



Figure 1. Mercury representation of complex **5** (thermal ellipsoids with 25% probability). Hydrogen atoms are omitted for clarity. Representative bond lengths (Å) and angles (deg): Ti(1)-N(4) = 1.882(5), Ti(1)-N(2) = 2.224(4), Ti(1)-N(1) = 2.090(4), N(1)-C(7) = 1.304(5), N(2)-C(7) = 1.344(5); N(4)-Ti(1)-N(1) = 99.58(19), N(4)-Ti(1)-N(2) = 159.2(2), $N(4)-Ti(1)-N(2)^* = 95.0(2)$.



Figure 2. Mercury representation of complex 7 (thermal ellipsoids with 25% probability). Hydrogen atoms are omitted for clarity. Representative bond lengths (Å) and angles (deg): Ti(1)-N(3) = 2.258(5), Ti(1)-N(6) = 1.915(5), Ti(1)-N(1) = 2.151(4), Ti(1)-N(2) = 2.240(6), Ti(1)-N(5) = 1.893(5), Ti(1)-N(4) = 2.069(4), N(1)-C(1) = 1.364(7), N(2)-C(1) = 1.299(7), N(4)-C(22) = 1.352(7), N(3)-C(22) = 1.328(7); N(5)-Ti(1)-N(6) = 99.3(3), N(5)-Ti(1)-N(4) = 102.2(2), N(5)-Ti(1)-N(2) = 156.6(2), N(6)-Ti(1)-N(1) = 104.5(2), N(6)-Ti(1)-N(3) = 158.7(2).

the titanium is positioned between six nitrogen atoms: four from two amidinate moieties and two from the dimethylamido groups. The Ti–N bonds are within the range of those for previously reported titanium bis(amidinate) complexes.¹⁶ Interestingly, out



Figure 3. Mercury representation of complex **9** (thermal ellipsoids with 25% probability). Hydrogen atoms are omitted for clarity. Representative bond lengths (Å) and angles (deg): Ti(1)-N(5) = 1.901(4), Ti(1)-N(6) = 1.908(4), Ti(1)-N(2) = 2.090(3), Ti(1)-N(4) = 2.095(3), Ti(1)-N(1) = 2.225(3), Ti(1 - N(3) = 2.228(3), N(4)-C(2) = 1.324(5), N(3)-C(2) = 1.332(5), N(1)-C(1) = 1.336(5), N(2)-C(1) = 1.311(5); N(5)-Ti(1)-N(6) = 96.88(16), N(6)-Ti(1)-N(1) = 161.65(14), N(6)-Ti(1)-N(4) = 103.11(16), N(6)-Ti(1)-N(2) = 101.98(15), N(5)-Ti(1)-N(3) = 161.44(14), N(5)-Ti(1)-N(2) = 103.94(16), N(5)-Ti(1)-N(4) = 101.84(14).

of the five possibilities of arranging the four ligands around the metal center, complexes 5, 7, and 9 possess a close C_2 symmetry, with the amidinate nitrogen atoms bearing the pendant arm disposed opposite to each other (trans), similarly to the complexes containing four-electron-donor asymmetric ligands previously reported in the literature.¹⁷ As expected, due to the trans influence, the bonds between the nitrogens with the pendant arms and the titanium are shorter than the bonds between the titane nitrogens that are disposed trans to the dimethylamido moieties. The solid-state structures revealed that in the neutral complexes 5, 7, and 9 the pendant arm is not interacting with the metal center. It is important to point out that the structures of the complexes in the solid state correlate with the structures observed by NMR in solution, at room temperature.

Complexes 5-9 were reacted with MAO at the appropriate ratio to generate the active catalytic mixture for the polymerization of propylene (see Table 1). The mixtures of catalysts 5-9 with MAO are ESR silent, indicating that under the reaction conditions there is no Ti(III), and we did not observe any ligand migration to the MAO. The nature of the pendant arm plays an important role in the yield and in the stereospecificity of the resulting polypropylenes. We have observed that the activity of the complexes increases as the nucleophilicity of the arm moiety decreases. Hence, the lowest reactivity was observed for complex 5, with the NMe $_2$ motif and the most nucleophilic group, while the highest reactivity was exhibited by complex 9, bearing the least nucleophilic furyl moiety.¹⁸ We attribute this behavior to the interaction of the pendant arm with the metal center; however, we cannot rule out any interaction with the recently reported intermediate AlMe₂⁺ formed when using MAO.¹⁹

The isotacticities of the obtained polymers were found to follow the trend opposite to the reactivity of the complexes, in which the polymer with the highest stereoregularity was obtained by complex **5**.

Surprisingly, the analysis of the resulting isotactic polymers revealed that the stereochemistry of the polymerization was induced through a chain-end control mechanism (only the *mmmr* and *mmrm* pentads are present, and the *mrrm* pentad at δ 19.7–20.0 is not observed). The chain-end control has been achieved at low temperatures for various catalytic systems, producing isotactic polymers²⁰ and in some instances leading to

cat.	cat.:MAO:TTPB	time (h)	activity ^b	isotactic fraction $(\%)^c$	$mmmm^{d}$ (%)	M_{w}^{d}	PDI^d	$mp (^{\circ}C)^d$
5	1:1000:0	3	2.6	100	96	269500	2.3	152.3
5	1:1000:0	12	6.1	87	94	2280000	1.1	151.9
6	1:1000:0	3	13.7	56	77	24000	2.6	148.2
7	1:1000:0	3	4.3	57	76	80000	3.0	147.3
8	1:1000:0	3	20.9	59	77	91000	2.5	147.5
9	1:1000:0	3	30.0	0^e	10^e	34700 ^e	3.0 ^e	g
9	1:50:0	2	traces	n.d.	n.d.	n.d.	n.d.	n.d.
9	1:50:1	2	5.4	0^e	12^e	629000 ^e	1.5 ^e	g
9	1:100:0	2	5.0	100	f	100500	2.2	156.2
9	1:100:1	2	230.0	traces	9 ^e	18000 ^e	2.3 ^e	g
9	1:400:0	3	48.3	83	f	f	f	158.6

Table 1. Data for the Polyn	merization of Propy	lene with Comp	lexes 5–9 Activated b	y Various Cocatalysts"
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"Reaction conditions: 10 mg of complex, 6 mL of toluene, 30 mL of propylene, T = 298 K, P = 10 bar. Abbreviations: n.d., not determined; mp, melting point. ^bIn units of kg of polymer (mol of catalyst)⁻¹ h⁻¹ for all fractions. ^cPercentage by weight of the isotactic fraction from the total amount of obtained polymer. The complementary fraction is the atactic polymer. ^dThe values presented are for the heptane-insoluble stereoregular fraction of the polymer blend. ^eData for the elastomer formed. ^fThe percent *mmmm* of the resulting polymer could not be measured due to the extremely low solubility of the polymers. ^gThe melting point was not measured due to the low stereoregularity of the polymer.

syndiotactic polypropylene.²¹ To the best of our knowledge, this is the first case in which an isotactic polypropylene is obtained via chain-end control at room temperature. The same stereocontrol has been observed for all the stereoregular fractions generated by the complexes presented in this paper (see Figure 4 and the



Figure 4. ¹³C NMR of polypropylene obtained with a catalytic mixture of **5** and MAO (1:1000): (a) full spectrum; (b) enlarged methyl region.

Supporting Information). In order to estimate the influence of the reaction time on the reactivity and stereospecificity, complex **5** was mixed with MAO in a 1:1000 ratio and the polymerization was allowed to run for 12 h.

Increasing the time of the reaction led to larger amounts of polypropylene with a much higher molecular weight ($M_w = 2280000$, PDI = 1.1 for 12 h, after fractionalization, as compared to the single fraction obtained with $M_w = 269500$, PDI = 2.3 for 3 h) together with about ~12% of an atactic polypropylene ($M_w = 12600$, PDI = 2.0). The longer reaction time for complexes **6** (activity 11.3 kg of polymer (mol of catalyst)⁻¹ h⁻¹ after 8 h, 41% isotactic fraction; *mmmm* 76%) and **8** (activity 18.6 kg of polymer (mol of catalyst)⁻¹ h⁻¹ after 10 h, 46% isotactic fraction; *mmmm* 77%) led to similar activities and fraction distributions among the elastomeric and isotactic components. This result indicates that the active complexes are long lived, and it seems that there are no major additional intermediates as a function of time influencing the polymerization.

Changing the arm from NMe_2 to pyridine increases the reactivity of complex 6 but reduces the stereoselectivity of the

polymer. Only 56% of the resulting polypropylene is stereoregular (mmmm 77%). Elongation of the linker between the amidinate backbone and the pyridine moiety from -CH2-(complex 6) to $-CH_2CH_2-$ (complexes 7 and 8) does not influence the stereoregularity of the resulting polymers dramatically in terms of distribution of the fractions in the resulting blend and percent mmmm. On the basis of our previous observations we assumed that the C_6F_5 ring that has been introduced into the second nitrogen atom of the amidinate instead of C₆H₅ does not play a major role in the polymerization stereoregularity.⁹ Interestingly, the longer linker yields polymers with higher molecular weights (Table 1). Changing the metal ligand from dimethylamido (7) to chloride (8) results in a more active catalyst, similarly to the previously reported trend for the titanium bis(amidinate) complexes.¹⁰ In contrary to behavior described previously in the literature, both dimethylamido (7) and dichloride (8) complexes yield polymers with similar molecular weights and isotacticities, corroborating the suggestion that these complexes lead to the same cationic species with a minimum counterion effect.

Higher loadings of MAO (MAO:M = 2000 or 3000) did not lead to higher activities of the catalytic mixtures generated by complexes 5-9; however, decreasing the loading of MAO to 400 equiv resulted in complete loss of activity for complexes 5-8, and an unexpected peculiar behavior was observed for complex 9.

The reactivity of the catalytic mixture generated by complex 9 together with 400 mol equiv of MAO increased, yielding highly isotactic polypropylene (melting point 158.6 °C) as the major fraction of the resulting polypropylene blend (83%, Table 1). Increasing the reaction time did not improve the yield of the reaction. In order to further investigate the nature of the active species generated by complex 9, the precatalyst was reacted with 100 equiv of MAO, followed by the addition of 1 equiv of $[Ph_{3}C]^{+}[B(C_{6}F_{5})_{4}]^{-}$ (TTPB). The addition of TTPB resulted in a dramatic increase in the activity (Table 1); however, the stereoregularity of the polymerization was completely lost, yielding only an atactic elastomeric material. It is evident that, at the cationic complex, MAO serves as a counterion at low loadings (9:MAO 1:100), allowing the furyl pendant arm to interact with the metal center and inducing the formation of isotactic polypropylene. Increasing the amount of MAO reduces the ability of furyl to interact with the metal, hence leading toward an atactic polymer. It is plausible that, when the borate

counterion is introduced, its interaction with the metal induces the removal of the furyl from the metal to the MAO, again allowing the formation of an atactic polymer. Surprisingly, the addition of the cocatalyst TTPB to the catalytic mixtures generated by complexes **5**–**8** with MAO (M:MAO = 1:1000) did not influence the activity of the complexes or the stereoregularity of the resulting polypropylenes. Unfortunately, our attempts to isolate titanium complexes with two amidinates as ancillary ligands and alkyls as labile groups ($-CH_2Ph$, -Me), in order to further investigate the catalyst behavior, led to a rapid decomposition of the resulting complexes. Switching to the more stable metal precursor Ti(CH_2TMS)₄ yielded no reactions at room temperature, and higher reaction temperatures caused decomposition of the resulting species.

Titanium bis(amidinate) complexes bearing different electron-donating motifs as a pendant arm were prepared and demonstrated stereospecific behavior in the polymerization of propylene. The complexes showed a correlation among the nucleophilicity of the pendant arm, the activity of the formed catalyst, and the stereoregularity of the resulting polymers. The highest activity and lowest percent mmmm was obtained for the complex containing a furyl pendant arm (9), followed by pyridine (6-8), reaching the maximum stereospecificity and the lowest activity for the complex with the NMe₂ pendant arm (5). The mechanism responsible for the stereoregularity of the resulting polymers was chain-end control, leading to isotactic polypropylene at room temperature. Decreasing the ratio between complex 9 and MAO led to an increase of the complex activity, and the major fraction of the resulting polypropylene was obtained as a highly isotactic material. Addition of the TTPB cocatalyst to the active mixture of 9 and MAO results in a dramatic increase in catalyst reactivity, leading however to stereoirregular elastomeric polypropylene as a single product.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving details of the syntheses and characterization data for the ligands, complexes, and polymers and crystallographic data for the ligands and complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest. [§]Deceased on September 25, 2013.

ACKNOWLEDGMENTS

This research was supported by the USA-Israel Binational Science Foundation under Contract 2010109.

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