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Amidinate Group 4 Complexes in the Polymerization of Olefins

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This perspective will present the use of amidinate group 4 complexes in α-olefin polymerizations. We will present the structural studies of the complexes bearing various numbers of amidinates as spectator ligands, with special emphasis on the bis(amidinate) group 4 systems. The mechanistic studies elucidate the influence of the various reaction conditions on the behaviour of the reactive species. Additionally, the study of the active species by techniques such as EPR spectroscopy and MALDI-TOF spectrometry are presented. We will also demonstrate how, based on such techniques, the highly sterospecific bis(amidinate) titanium complexes may be designed and applied in the polymerization of propylene.

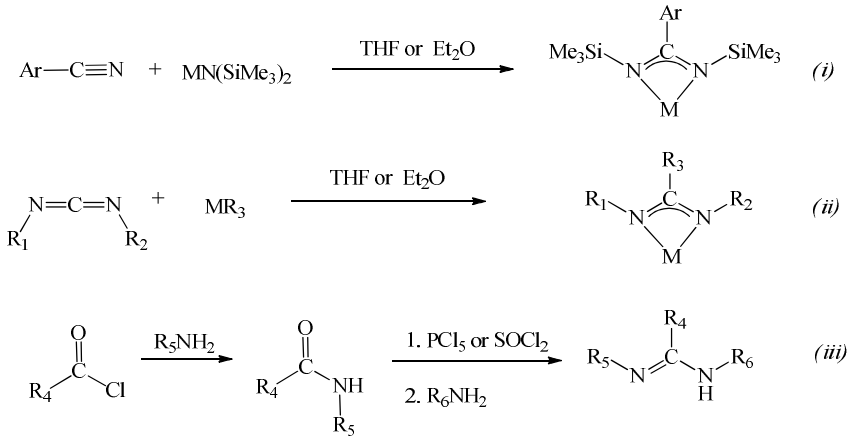
The discovery of olefin polymerization mediated by heterogeneous catalytic systems by Ziegler[1] and Natta[2] made polyolefins one of the most important commodity synthetic polymers, represented mostly by polyethylene and polypropylene with a global production of more than 100 million tons per year.[3,4] The development of homogeneous system analogues followed shortly thereafter, introducing metallocenes as precursors for olefin polymerization activated by alkylaluminium compounds.[5,6] The metallocene systems performed in a single site catalysis nature, generating uniform polymeric materials in low yields. It was not until 1977 that methylaluminoxane (MAO) was introduced as a co-catalyst, capable of generating catalytic mixtures with outstanding activities[7-9]

Since their first application as olefin polymerization catalysts, group 4 metallocenes have received considerable attention from the scientific community. Various metallocene systems contributed valuable information regarding the key steps of the polymerization mechanism. For example, the empirical relationship between the pre-catalyst symmetry and the polymer structure was established.[10] However, the search for more elaborate, easily accessible systems capable of producing polymers with various predicted stereo structures and precise molecular weights lead to the development of a different class of compounds during recent decades. Numerous post-metallocene catalysts have been designed possessing ancillary ligands containing donor motifs decorated by N, O and S atoms. For example, among the ligands containing nitrogen donors which have emerged, catalysts containing the amidinate ligands and their derivatives, such as guanidinates and aminopyridinates, have attracted considerable interest over the last 30 years.

The first neutral amidines were reported in 1868 in the pioneering work of Gerhardt,[11] who obtained them as a product of heating aniline with benzonitrile. However, the field of amidine chemistry remained dormant for over a century until Sanger reported the synthesis of $PhC(=NSiMe_3)(N(SiMe_3)_2)$.[12,13] Since then, amidinates have attracted the attention of numerous researchers and proved to be versatile ligands for the stabilization of various elements across the periodic table, and the application of these complexes has been demonstrated in the breadth of various chemical transformations.[14-18]

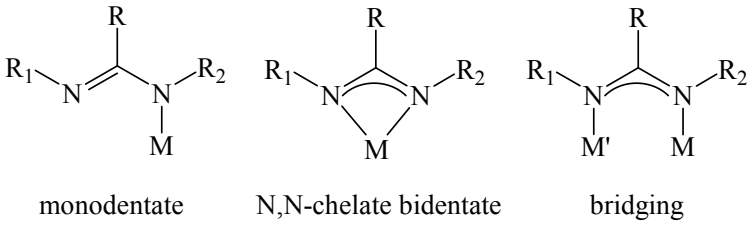
Anionic amidinates have emerged as an alternative to the cyclopentadienyl (Cp) ligands, primarily due to their steric similarity.[19,20] The main advantages of amidinates over the Cp analogues are their ease of modification, allowing for fine tuning of the electronic and steric properties of the ligand, and tailoring of the specific properties of the resulting complexes, leading to facile access to a large library of compounds. Similar to the carboxylate ligands, amidinates donate 4 electrons, allowing the resulting metal complexes to exhibit increased electrophilicity as compared to the metallocene equivalents. Amidines are most often synthesized

following three major routes: *i*. a sigmatropic rearrangement during the reaction between nitrile and silyl amides[12,21-23] (Scheme 1, (a)), *ii.* via an insertion of a carbodiimide into a metal-carbon bond,[24,25] (Scheme 1, (b)), and *iii*. through the condensation reaction between amines and acyl or imidoyl chlorides[26-29] (Scheme 1, (c)).



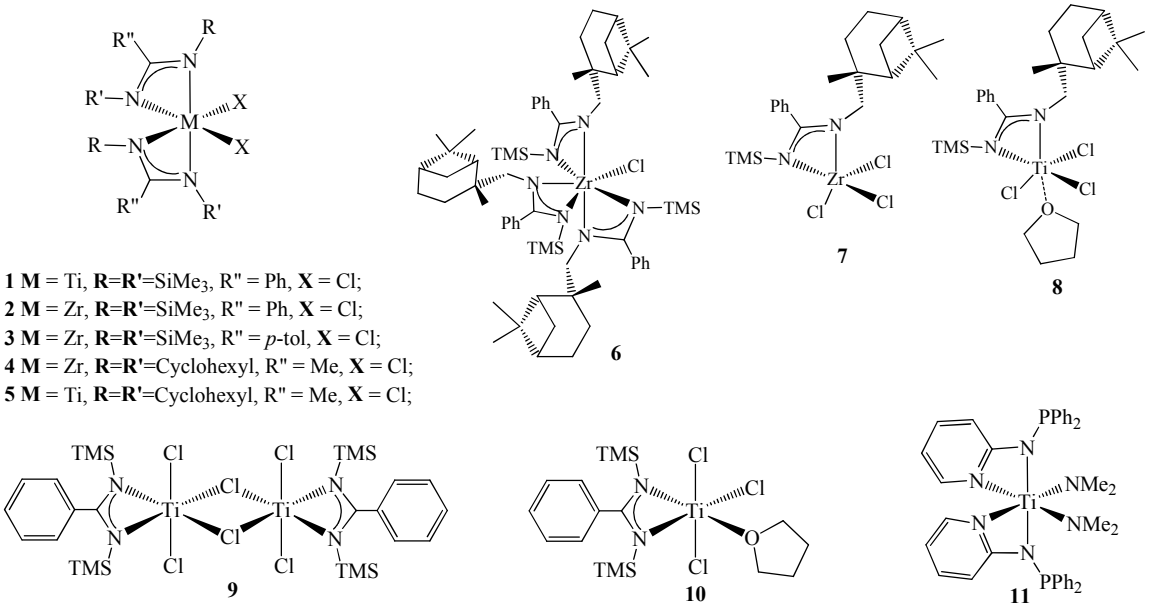
Scheme 1. Synthetic routes for the synthesis of amidines and amidinates.

In addition to the variety of easily modified electronic and steric properties, the different connectivity modes of amidinates revealed a remarkable ability of this class of ligands to stabilize the central metal (Scheme 2), adding to the diversity and versatility of the amidinates as ancillary ligands.



Scheme 2. Connectivity modes of amidinate ligands with metal centers.

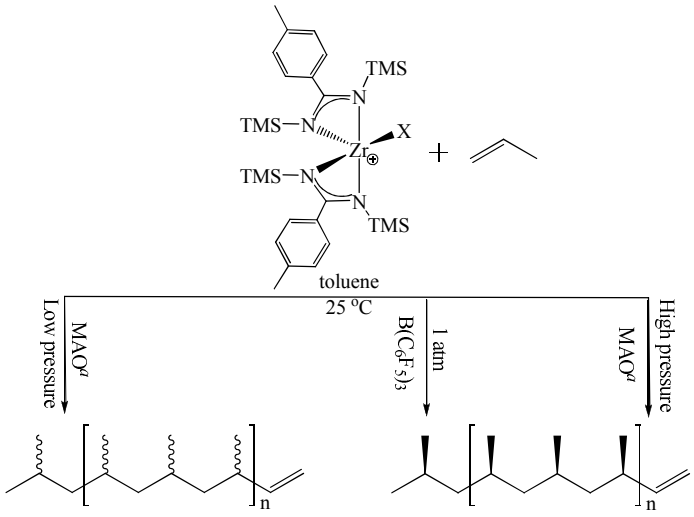
Group 4 amidinates appeared in literature for the first time in 1988[30] when $PhC(N(SiMe_3))_2TiCl_2$ (**1**) was prepared,[31] shortly followed by the synthesis of the zirconium analogue **2**;[32] the interest in amidinate ligands as ancillary ligands for achieving the homogeneous post-metallocene olefin polymerization began to attract attention in 1995 when $[PhC(NTMS)_2]ZrCl_2$ (**2**) and [*p*-Me-$C_6H_4C(NTMS)_2]ZrCl_2$ (**3**) complexes were used as precursors for the polymerization of ethylene after their activation with an excess of methylaluminoxane (MAO).[33] The results revealed that the (bis)benzamidinate zirconium dichloride complex was more active than the corresponding mono(benzamidinate)cyclopentadienyl zirconium dichloride complex, (26 kg $mol^{-1}atm^{-1}h^{-1}$ for **2** and 16 kg $mol^{-1}atm^{-1}h^{-1}$ for **3**), due to the increased electrophilic nature of the resulting complexes.[33] However, the reactivity of the bis(benzamidinates) remained lower than that of the zirconium bis-metallocenes. Changing both of the the *N*-amidinate substituent from $SiMe_3$ to cyclohexyl (Cy) led to similar reactivity of 16 kg $mol^{-1}atm^{-1}h^{-1}$ for complex **4** (Scheme 3) under the same experimental conditions.[34] Using the $(PhC(NCy)_2)_2TiCl_2$ (**5**) resulted in a lower activity (7 kg $mol^{-1}atm^{-1}h^{-1}$) as compared to the analogous zirconium complex **4**. As extensive studies on the polymerization of ethylene with group 4 amidinates and guanidinates has been previously reviewed,[35] this perspective will concentrate on the application of group 4 amidinate complexes in the polymerization of propylene.



Scheme 3. Complexes bearing various benzamidinates (**1-10**) and aminopyridinates (**11**) as ancillary ligands.

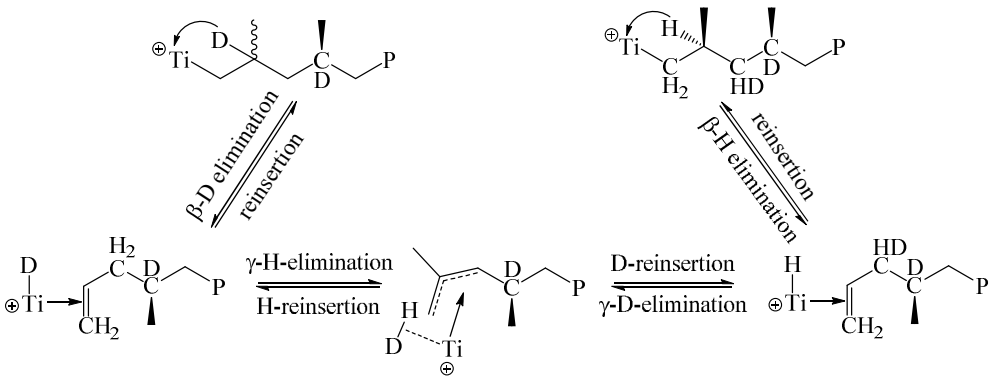
After the activity of the bis(benzamidinate) group 4 complexes was established in the polymerization of ethylene, an immediate interest in their application for the stereoregular polymerization of propylene emerged. First, it has been found that the pressure of propylene in the reaction plays an important role in the stereochemistry of the resulting polymer, yielding an atactic elastomeric polypropylene or an isotactic solid material when the reaction proceeded at atmospheric or high pressure of monomer, respectively (Scheme 4). These results triggered particular interest since the atactic polymer was formed despite the C_2 symmetry of the pre-catalyst, which was expected to produce isospecific stereoselectivity.[10,36] The deviation from Ewen empirical symmetry rules called for an investigation of the active species involved in the reaction.[37]

The formation of the elastomeric material has been proposed to originate due to a competing intermolecular epimerization of the last inserted monomer that exhibits higher reaction rates at low monomer concentration.[38,39] Additionally, the proposed mechanism has been corroborated by the isomerization of higher olefins, such as 1-octene, in the presence of the catalytically active mixture.[40,41]



Scheme 4. Reaction conditions affecting the stereoregularity of the polymers in the polymerization of propylene. [a] different MAO ratio allows the production of the isotactic material either as the major fraction or as a mixture with an elastomeric material.

In order to elucidate the origin of the formation of the elastomeric material from the C_2 symmetric precursors, deuterium labelled propylene was prepared and the formation of stereoerrors followed.[42] Using 2-D-propylene as a substrate revealed that the epimerization mechanism initially proposed by Busico[43-45] and Resconi[46,47] was not operative for these types of complexes, and a new type of intramolecular epimerization was revealed in which the β-D elimination is followed by γ–H elimination, then rapid reinsertion, resulting in formation of CDH groups in the polymer (Scheme 5). The result has also been supported by the observation that the higher pressure of the reaction resulted in the formation of the stereoregular polypropylene, since at higher monomer concentration, the rate of the stereospecific monomer insertion becomes faster than that of the epimerization rate.[48]



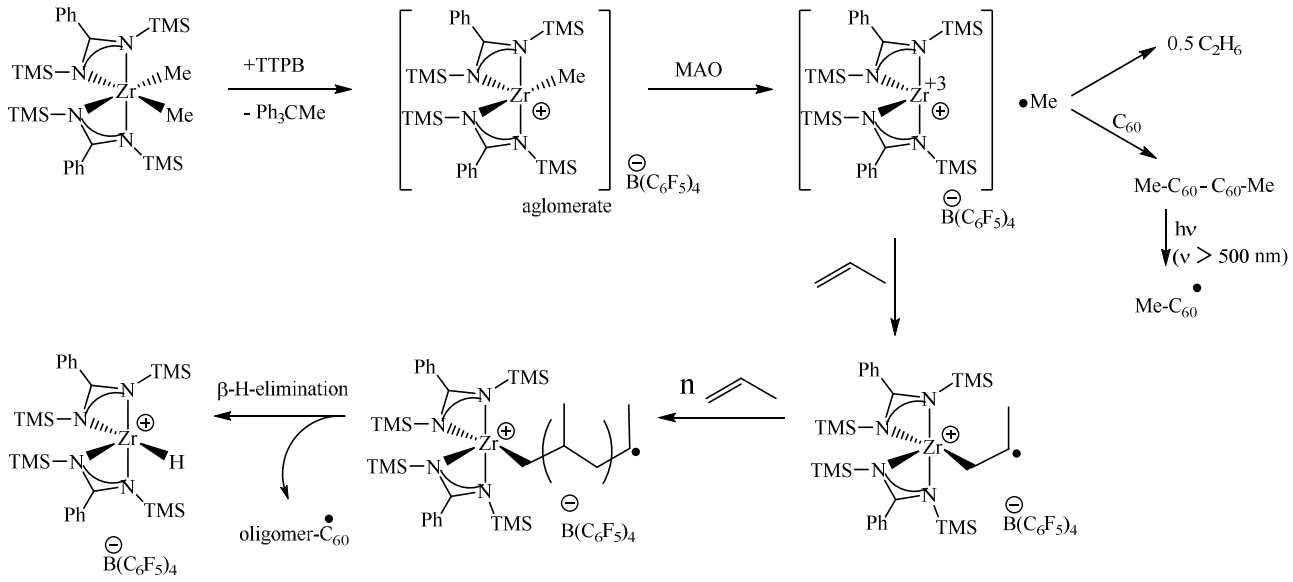
Scheme 5. Mechanistic labelling studies in the stereo-error formation in polypropylene during the reaction catalyzed by bis(amidinate) complexes.

The discovery that the bis(benzamidinate) complexes operate under a different catalytic mechanism from the metallocenes motivated the investigation of complexes with various symmetries bearing the benzamidinate ligand (complexes **1-10**, Scheme 3). Complexes containing one, two, and three amidinates were prepared and tested for their catalytic activity in the polymerization of α-olefins. The chiral tris(amidinate) zirconium complex **6** and the bis(amidinate) zirconium complex **2** (C_3 and C_2 symmetry, respectively) generated highly isotactic material under high pressure of propylene (> 92 % *mmmm*) as a mixture with an elastomeric material, while the mono(amidinate) zirconium complex **7**, as well as the titanium mono(benzamidinate) analogue **8**, generated atactic polypropylene. The similarity of the stereoregularity of the resulting polymers when the C_3 and C_2 catalysts were used suggested a similar active species. The dynamic behaviour of the benzamidinate ligand at the metal center caused the formation of a "C_2 like" active site when the C_3 symmetric precatalyst was used, leading to the formation of isotactic polypropylene. Similar ligand dynamics were found to be operative when C_2 symmetric precatalysts were applied, resulting in the formation of a "C_1 like" active site and yielding atactic polymer.[34]

The bis(benzamidinate) titanium dichloride complex **1** and the mono(benzamidinate) complexes (**9** and **10**) were tested in the polymerization of propylene.[49,50] While the bis(benzamidinate) titanium dichloride was prepared straightforward from the reaction of 2 equivalents of the lithiated ligand and 1 equivalent of $TiCl_4$ in toluene, adjusting the ligand equivalents for the synthesis of the mono(amidinate) titanium trichloride resulted in the formation of the dimeric complex **9**. The mononuclear complex **10** may be easily generated by adding a coordinating solvent, such as tetrahydrofuran to the binuclear complex **9**.[51] When activated with MAO and reacted with propylene, all three complexes yielded the same elastomeric polymers and similar kinetic behaviour, despite the difference in the symmetry of the pre-catalysts, suggesting that a similar active species is operative in the process.[49] Interestingly, and in contrast to these findings, some titanium mono(amidinates) have demonstrated the ability to polymerize propylene with a predominantly syndiospecific stereochemistry at low temperatures (–60 °C, ~ 53 *rrrr* %). The elevation of the reaction temperature to 25 °C resulted, in some cases, in the formation of predominantly isotactic polypropylenes.[52]

To study the effect of the counter ion in the polymerization, the bis(benzamidinate) zirconium dichlorides were converted to the dimethyl analogues by reacting one equivalent of **2** and **3** with 2 equivalents of MeLi. The alkylated compounds were then activated with MAO or $B(C_6F_5)_3$, and the nature of the co-catalyst was found to influence the stereoselectivity of the polymerization. When MAO was used as the cocatalyst activator, the resulting polymer was an atactic polymer, however, when the $B(C_6F_5)_3$ was utilized, a solid isotactic polypropylene was formed (Scheme 4).[53] The reactivity of the active species generated by the different co-catalysts has shown the influence not only on the stereoselectivity, but also on the reactivity of the species, demonstrating lower activity when $B(C_6F_5)_3$ was used as an activator, establishing the importance of the counter ion near the cationic active species.

Surprisingly, when a mixture of both co-catalysts MAO and TTPB (trityl tetrakispentafluorophenylborate) (50:1, respectively) were used to activate the complex $[PhC(NTMS)_2]_2ZrCl_2$ (**2**) or its dimethylated analogue, an extraordinary increase in the catalytic activity was observed (433 kg $mol^{-1}h^{-1}$ as compared to the trace amounts of polypropylene obtained when activated with only 50 equiv of MAO), yielding an elastomeric material. It was noteworthy that TTPB was found to react with the $[PhC(NTMS)_2]_2ZrMe_2$ complex, however the formed species was inactive in the polymerization of propylene. The methyl group is abstracted by the trityl cation (Ph_3C^+), and the borate moiety ($B(C_6F_5)_4^-$) of the TTPB serves as the counter ion. EPR experiments revealed that MAO is able to reduce, at this stage, the Zr(IV) to a Zr(III) species. The EPR signal corresponding to the reduced species disappears after addition of propylene to the reaction mixture, indicating the oxidation of the metal to Zr(IV).[54] C_{60} radical trapping indicated that a radical methyl moiety is abstracted from the metal center when reduced by MAO. Trapping of higher oligomeric chains was not observed by MALDI-TOF, however, when the Ti complex **1** was used, hexyl radicals were observed (see Scheme 6 for the proposed mechanism).

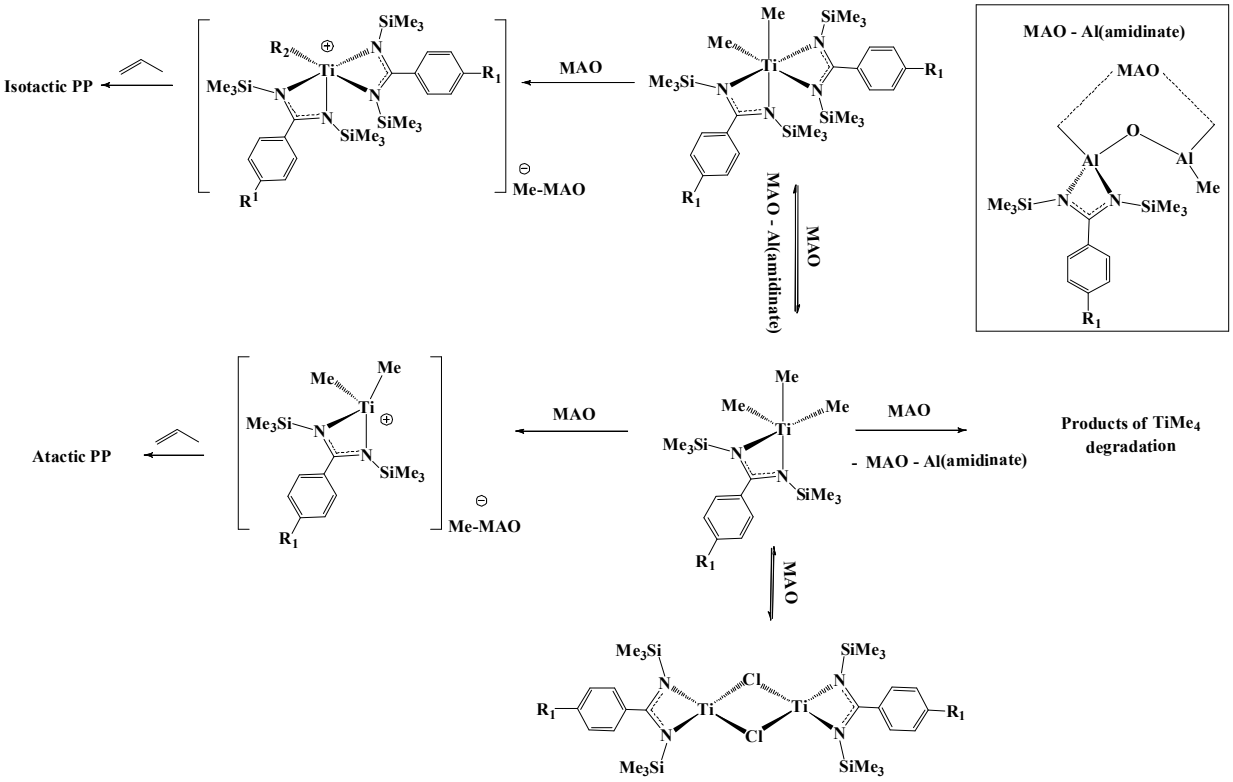


Scheme 6. Proposed mechanism for the activation of $[PhC(NTMS)_2]_2ZrMe_2$ by a mixture of MAO and TTPB.

The importance of the solvent was investigated when using complex **1**, revealing that an increase in the solvent polarity leads to a decrease in the molecular weight of the polymers, however, the stereoregularity of the resulting polymer remained around 8-12 *mmmm* %, regardless of the solvent.[55] Complex **11**, containing a slightly different aminopyridine ligand framework, was also studied in order to compare to the amidine analogues.[55,56] Additional aminopyridinate ligands have also been extensively investigated in parallel to the amidinate scaffolds, and comprehensive reviews summarizing the results has been previously published.[57-65] However, when discussing the catalytic activity of such frameworks, the complexes were tested mostly in ethylene polymerization and the co-polymerization of ethylene with propylene.

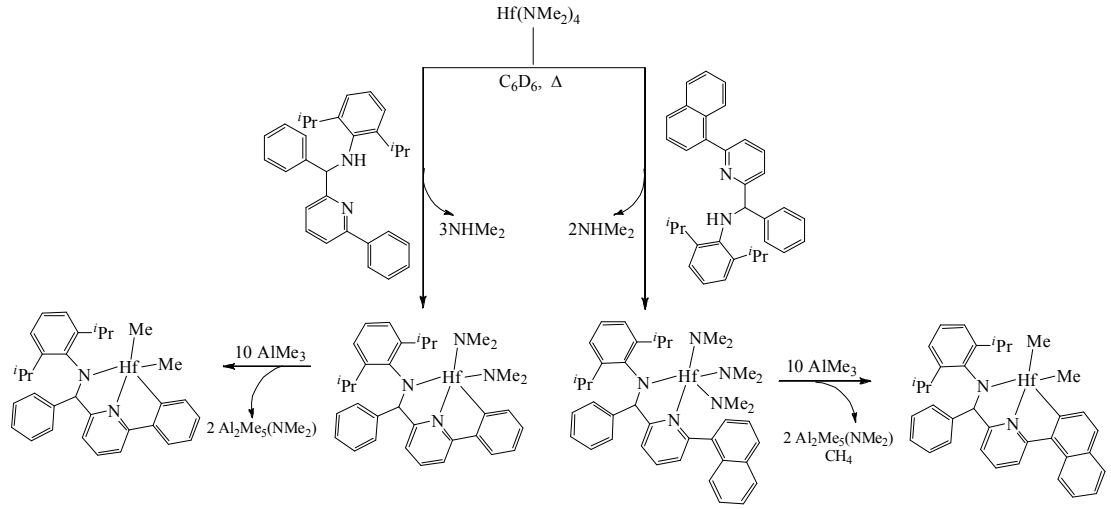
When complex **11** (Scheme 3) was used as a pre-catalyst for the polymerization of propylene, lower activities as compared to the corresponding amidinate systems were observed, similar to the behaviour seen in the previously published results.[66] Interestingly, complex **11** followed the same trends in catalytic behaviour as its amidinate group 4 analogues.[48]

The presumed formation of a similar active species during the activation of the benzamidinate complexes (**1**, **9**, **10)** called for a deeper mechanistic investigation. The lack of the stereospecificity during the polymerization with C_2 precursors and similar behaviour to the C_1 precursors led to the conclusion that one of the amidinates dissociates from the metal center and migrates to the aluminium in the MAO (Scheme 7). The assumption was corroborated by NMR analysis of the reaction mixture of **1** with MAO by a systematic comparison to the mono(amidinate) group 4 complexes and respective mono(amidinate) aluminium dimethyl complex.[50,67]



Scheme 7. Generation of active species upon the activation of titanium bis(benzamidinates) with MAO, leading to the formation of two polymeric fractions.

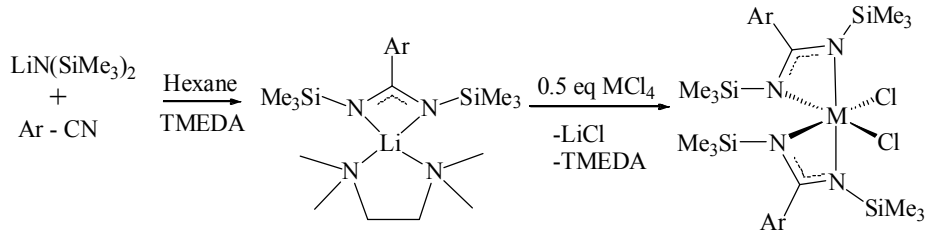
When the resulting polymer was fractionated with hot diethyl ether or hexane, two polymeric materials were obtained: a major, soluble atactic elastomer with similar structure to the elastomers described by Resconi,[68] and a minor, insoluble isotactic fraction. These results revealed that the cationic bis(benzamidinate)titanium methyl complex is responsible for the formation of the isotactic fraction, whereas the corresponding cationic mono(benzamidinate) titanium species produces the elastomeric material.[50]
Contrary to the mono(amidinate) systems, some complexes bearing only one ancillary ligand demonstrated stereospecific behaviour towards propylene polymerization. High throughput screening methods have led to the discovery of the hafnium complexes, bearing pyridyl-amido ligands.[69] The neutral ligands were reacted with the metal precursor, generating the mono substituted hafnium complex, however a peculiar behaviour of the ligands has been observed during the reaction of the tris(dimethylamido) complexes to the methylated analogue by the reaction with $AlMe_3$; instead of the formation of the trimethyl derivative, the metallation of the aryl ring of the ligand was observed. (Scheme 8).



Scheme 8. Formation of the mono substituted hafnium pyridyl-amido complexes.

The resulting mono pyridyl-amido complexes have shown the ability to generate isotactic polypropylene when activated by TTPB or with a combination of $[Me_2PhNH][B(C_6F_5)_4]$ with $Al(iBu)_2H$.[70] The pyridyl-amido ligands are known to be prone to *ortho*-metallation of the aryl ring, and have been modified to allow the synthesis of the numerous catalysts capable of producing the isotactic polypropylene, ranging between 56 and 94% *mmmm*.[70,71]

Based on the mechanistic data available for benzamidinate complexes, various ligands were studied to find a correlation between ligand structure and catalyst reactivity, as well as polymer properties. The first approach was to change the substituent on the *ipso*-carbon of the amidinate. The ligands were prepared following a sigmatropic rearrangement (*vide supra* Scheme 1a), and the lithiated ligands were reacted with $TiCl_4$ to generate complexes **12-21**, and with $ZrCl_4$ under the same reaction conditions to generate complexes **22-27** (Scheme 9).



M = Ti:

12: Ar = *p*OMeC$_6$H$_4$; **13:** Ar = *p*MeC$_6$H$_4$; **14:** Ar = *p*EtC$_6$H$_4$; **15:** Ar = *p*^{n}BuC$_6$H$_4$;
16: Ar = *p*^{t}BuC$_6$H$_4$; **17:** Ar = *p*CF$_3$C$_6$H$_4$; **18:** Ar = *o*OMeC$_6$H$_4$; **19:** Ar = 2-furyl;
20: Ar = 2-pyridyl; 2**1:** Ar = 2-thiophene;

M = Zr:

22: Ar = *p*OMeC$_6$H$_4$; **23:** Ar = *p*EtC$_6$H$_4$; **24:** Ar = *p*^{n}BuC$_6$H$_4$; **25:** Ar = *o*OMeC$_6$H$_4$;
26: Ar = *m*OMeC$_6$H$_4$; **27:** Ar =3-furyl;

Scheme 9. Synthesis of substituted bis(benzamidinate) titanium and zirconium dichloride complexes.

When all the complexes were activated with MAO and reacted with propylene, two polymeric fractions were always generated, albeit in different ratios. For the quantitative comparison between the various complexes, the following equations for the rate of the monomer insertion (Ri) (Eq 1) and rate of the chain termination (Rt) (Eq 2) were utilized for each complex an all fractions.[67]

$$Monomer\ insertion\ rate\ (Ri) = \frac{m(polymer)[g]}{Mw(monomer)[g\ mol^{-1}] \times time\ [h]} \quad (1)$$

$$Chain\ termination\ rate\ (Rt) = \frac{m(polymer)[g]}{Mn(monomer)[g\ mol^{-1}] \times time\ [h]} \quad (2)$$

Interestingly, a linear relationship between the Rt of the elastomeric fraction and the steric parameter, Taft (Es), of the aryl substituent (Figure 1a) at the *para*-position was revealed.[67] These results indicated that the larger *para*-substituent induced a slower Rt and generates polymers with higher molecular weights. Mechanistic studies indicate that the benzamidinate ligand opens, rotates around the N-C amidinate bond, and disposes the aryl ring closer to the metal center, forming a CGC-type complex and placing the *para* aryl substituent in close proximity to the metal centre, impeding the chain β-H elimination and allowing for additional growth of the polymer chain. NOE experiments performed with complex **12** shows that the *p*-OMe substituent of the aromatic ring is located in close proximity to the TMS and the methyl group of MAO (distance of less than 5 Å), corroborating the proposed opening and rearrangement of the ligand (E-*syn*, Scheme 10).[67,72]

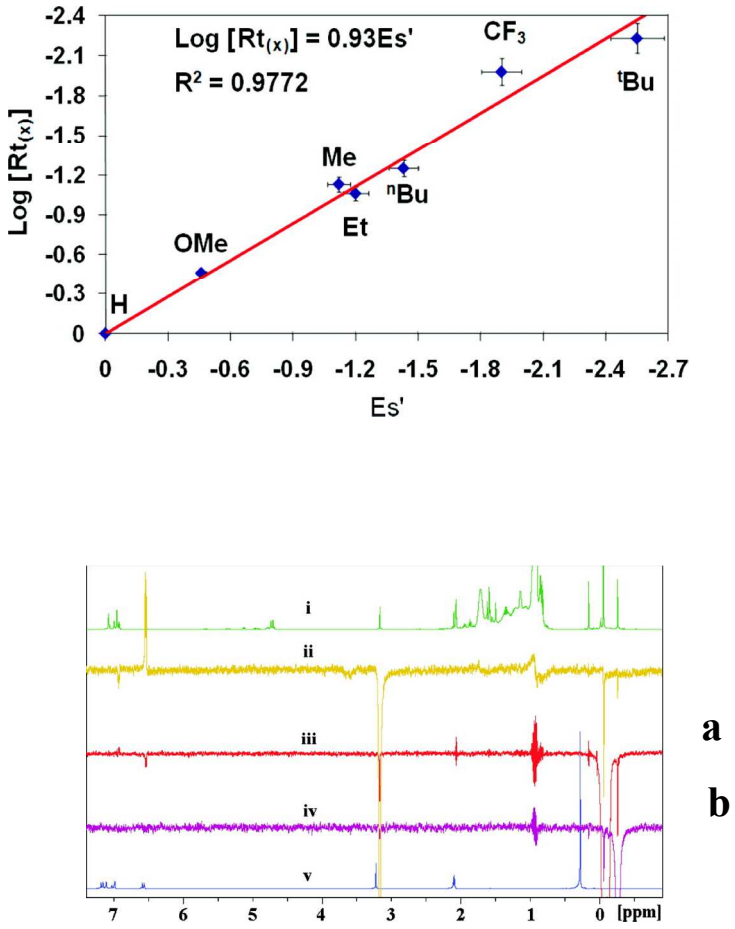
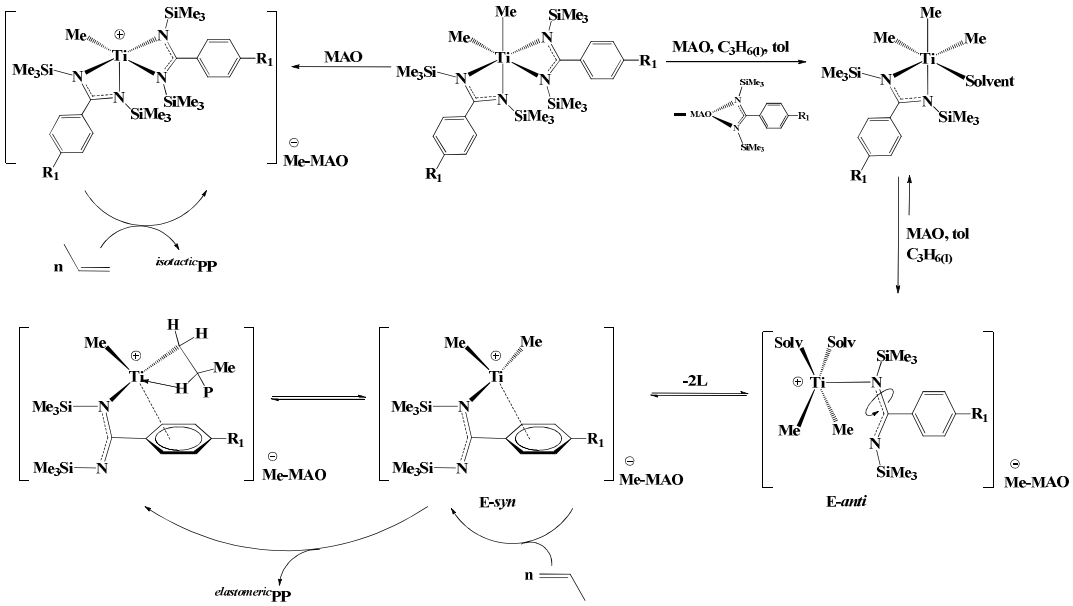
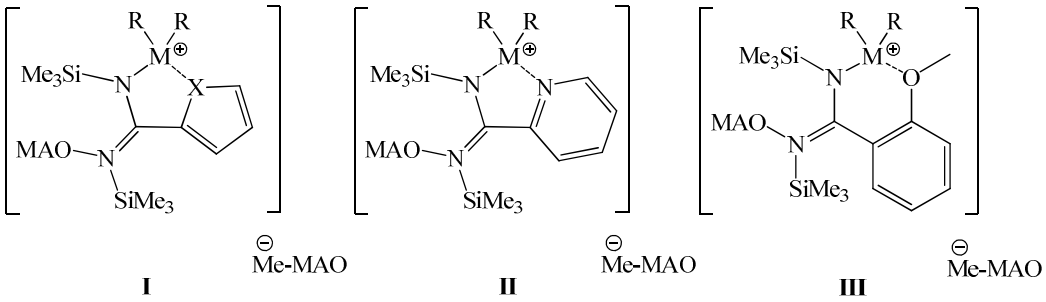


Figure 1. Mechanistic studies of the catalytically active species generated from the bis(benzamidinate) titanium dichloride complex **12**: (**a**) Linear Free Energy Relationship (LFER) between the *para* substituent of the aryl of the benzamidinate ligand and the rate of the growing chain termination (log (Rt)); (**b**) ^{1}H NMR monitoring of the catalytic mixture of complex **12** in C_7D_8: (i) ^{1}H NMR spectrum; (ii−iv) ^{1}H NMR spectra showing the NOE after irradiation of the OMe (3.19 ppm), TMS (0.04 ppm), and MAO (−0.24 ppm) Me signals, respectively; (v) ^{1}H NMR spectrum of complex. "Reprinted with permission from S. Aharonovich, M. Botoshansky, Y. S. Balazs and M. S. Eisen, *Organometallics*, 2012, **31**, 3435-3438. Copyright (2012) American Chemical Society."

An unusual effect was observed when either a heterocyclic or an *ortho*-methoxy substituted amidinate was used. The opening and rearrangement of the amidinate induces the coordination of the heteroatom to the metal, allowing the formation of larger metallacycles (5-6 membered rings) found to be highly active in the polymerization of propylene (complexes **I, II, III**).[73, 74]



Scheme 10. Generation of active species during the polymerization of propylene with bis(benzamidinate) titanium complexes.



Scheme 11. Plausible species formed as a result of the rearrangement of the remaining amidinate ligand in complexes **18-21** and **25**.

The results of the selected propylene polymerizations with bis(amidinate) group 4 complexes after the activation with 1000 equivalents of MAO are presented in Table 1.

Table 1. Data for the polymerization of propylene with titanium and zirconium bis(amidinates) of type $[R^1\text{-}C(NR^2NR^3)]_2MX_2$

Complex					activity kg(PP) mol(M) h	hexane soluble fraction				hexane non-soluble fraction			
M	R^1	R^2	R^3	X		weight%	Mw x10^3	PD	*mmmm*%	weight%	Mw x10^3	PD	*mmmm*%
Ti[67]	Ph	$SiMe_3$		Cl	24.7	92.1	23	2.8	11.2	7.9	103	2.9	79.3
Ti[67]	*p*Me-C_6H_4	$SiMe_3$		Cl	15.8	86.7	122	2.9	15.5	13.3	59	3.2	73.4
Ti[67]	*p*Et-C_6H_4	$SiMe_3$		Cl	10.2	88.2	149	3.7	12.7	11.8	66	3.2	74.5
Ti[67]	*p*^{n}Bu-C_6H_4	$SiMe_3$		Cl	9.9	83.5	188	3.6	11.2	16.5	58	2.9	76.4
Ti[67]	*p*^{t}Bu-C_6H_4	$SiMe_3$		Cl	24.0	91.8	22	5.1	8.9	8.2	55	2.9	73.4
Ti[67]	*p*OMe-C_6H_4	$SiMe_3$		Cl	9.8	90.8	26	2.8	8.5	9.2	93	2.9	75.2
Ti[72]	*p*CF_3-C_6H_4	$SiMe_3$		Cl	6.0	62.0	867	2.3	9.6	38.0	560	3.2	58.6
Ti[72]	*o*OMe-C_6H_4	$SiMe_3$		Cl	12.2	100	64	2.7	5.6	traces	-	-	-
Ti[72]	*p*Et-C_6H_4	$SiMe_3$		Cl	2.6	91.6	95	2.5	10.0	8.4	48	2.0	73.3
Zr[73]	Ph	$SiMe_3$		Cl	3.4	44.1	47	6.8	19.5	55.9	75	6.2	63.5*(I)*[a] 48.4*(S)*[a]
Zr[73]	*p*OMe-C_6H_4	$SiMe_3$		Cl	9.0	52.2	15	3.0	7.9	47.8	55	2.4	61.4*(I)*[a] 53.8*(S)*[a]
Zr[73]	*p*Et-C_6H_4	$SiMe_3$		Cl	2.6	53.8	16	2.7	15.7	46.2	108	7.7	62.0*(I)*[a] 35.9*(S)*[a]
Zr[73]	*p*^{t}Bu-C_6H_4	$SiMe_3$		Cl	2.4	50.0	82	9.2	15.9	50.0	125	13.9	67.2*(I)*[a] 49.2*(S)*[a]
Zr[73]	*o*OMe-C_6H_4	$SiMe_3$		Cl	5.7	63.2	3,793	2.3	15.9	36.8	117	14.7	71.0*(I)*[a] 48.7*(S)*[a]
Zr[73]	*m*OMe-C_6H_4	$SiMe_3$		Cl	18	76.1	15	2.6	12.6	23.9	17	2.5	66.1*(I)*[a] 40.0*(S)*[a]
Zr[73]	3-furyl	$SiMe_3$		Cl	12.8	72.6	51	5.12	21.6	27.4	91	8.2	84.2*(I)*[a] 42.8*(S)*[a]
Ti[74]	2-furyl	$SiMe_3$		Cl	35.6	90.5	42	2.1	11.9	9.5	93.8	2.8	60.3
Ti[75]	2-thiophene	$SiMe_3$		Cl	32.8	80.0	303	19.4	10.2	20.0	784	2.4	61.0
Ti[74]	2-pyridyl	$SiMe_3$		Cl	230	96.6	226	2.6	7.7	3.4	71	3.1	55.8
Ti[76]	H	Cyclohexyl	Cyclohexyl	NMe_2	25.3	80.4	32	2.5	10.0	19.6	196		40.0
Ti[76]	H	*o*-OMe-C_6H_4	*o*-OMe-C_6H_4	NMe_2	9.0	-	-	-	-	100	821		27.0
Ti[76]	Me	*o*-OMe-C_6H_4	*o*-OMe-C_6H_4	NMe_2	13.3	75.4	16	2.4	11.0	24.6	225		54.0
Ti[76]	Et	*o*-OMe-C_6H_4	*o*-OMe-C_6H_4	NMe_2	7.9	70.7	24	2.7	15.0	29.3	270		40.0
Ti[77]	Ph		$CH_2CH_2N(Me_2)_2$	NMe_2	2.6	nr[b]	nr[b]	nr[b]	nr[b]	100.0	269	2.3	96.0
Ti[77]	Ph		-CH_2(2-pyridin)	NMe_2	13.7	nr[b]	nr[b]	nr[b]	nr[b]	56.0	24	2.6	77.0
Ti[77]	Ph		-CH_2(2-furyl)	NMe_2	30.0	nr[b]	nr[b]	nr[b]	nr[b]	0.0	35	3.0	10.0
Ti[77]	Ph	C_6F_5	-CH_2CH_2(2-pyridin)	NMe_2	4.3	nr[b]	nr[b]	nr[b]	nr[b]	57	80	3.0	76.0
Ti[78]	*i*Pr	C_6F_5		NMe_2	97.0	100.0	251	8.3	-	-	-	-	-
Ti[78]	*i*Pr	C_6H_5		NMe_2	33.5	100.0	55	3.9	-	-	-	-	-
Zr[78]	*i*Pr	C_6F_5		NMe_2	113.0[c]	100.0	4.5	4.5	-	-	-	-	-

Typical reaction conditions: 1000 equiv of MAO, 6 mL of toluene, 30 mL of liquid propylene, room temperature; [a]*(I)mmmm* pentad by ^{13}C-NMR, *(S) rrrr* pentad by ^{13}C-NMR, [b]not reported; [c]active only at 60 °C

Similar to the titanium complexes, a dynamic behaviour of the amidinate ligands has also been observed for the zirconium benzamidinate complexes. In general, the zirconium bis(amidinates) are less reactive, but generate polymers with higher

isotacticities as compared to the corresponding titanium analogues. The distribution between the elastomeric and stereospecific fractions for the generated polypropylenes by the zirconium complexes is also found to vary slightly, with increased mass percentages of the stereoregular fraction in the mixture. Surprisingly, analysis of the resulting polymer components have shown that the diethyl ether soluble fraction consisted of the expected atactic material, however the insoluble fraction contained two products, an isotacic polypropylene formed by the site-control mechanism, and another moderately syndiotactic material formed by a chain control mechanism (Figure 2).[73]

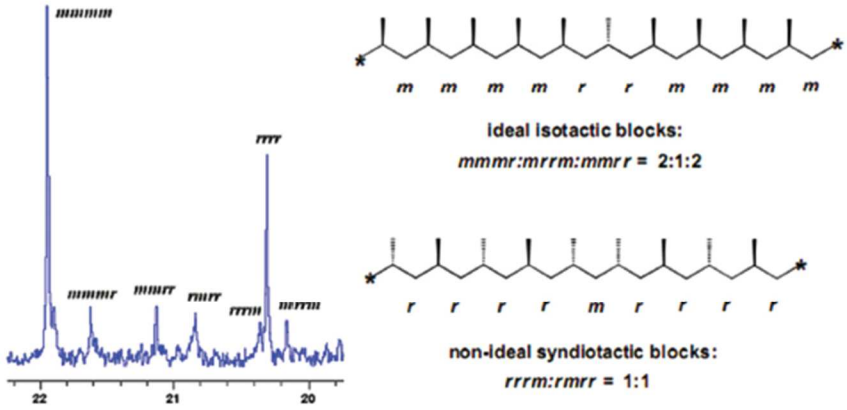
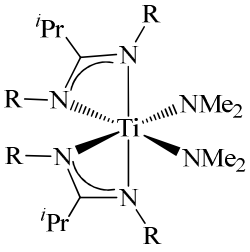
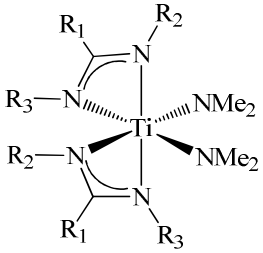


Figure 2.[13]C NMR spectrum of the methyl region of the hexane insoluble fraction of polypropylenes obtained by zirconium bis(amidinates). "Reproduced from Ref. 73 with permission from The Royal Society of Chemistry."

Attempts to restrain the ligand around the metal center as a chelate were unsuccessful and resulted in polymeric material as mixtures of the major elastomer and minor (between 10-15 %w/w) stereoregular isotactic fraction. In order to eliminate the possibility of rearrangement into the CGC-type species, an aliphatic moiety (^{i}Pr) was introduced into the amidine *ipso*-carbon. Previous work by Fujita *et. al*. with fluorinated FI-catalysts was shown to induce the living polymerization of ethylene, as well as the syndiospecific polymerization of propylene.[79-81] These findings inspired the investigation into the use of fluorinated amidinates; these were prepared and introduced as ancillary ligands for group 4 olefin polymerization pre-catalysts. The ligands have been prepared through the condensation between isobutyric acid and the appropriate anilines, using (polyphosphoric trimethylsilyl ester) PPSE[82] as the condensation agent. The ligands were added to $Ti(NMe_2)_4$ to generate the corresponding bis(amidinate) titanium bis(dimethylamido) complexes used as polymerization precatalysts in combination with MAO as co-catalysts without any further chemical modifications.





27 **R** = C_6F_5,
28 **R** = C_6H_5,
29 **R** = ^{p}F-C_6H_4,
30 **R** = ^{m}F-C_6H_4,
31 **R** = 8-F-naphthalene;
32 **R** = C_6F_5 with Zr as metal center.

33 $\mathbf{R_2}$ = DiPP, $\mathbf{R_3}$ = Cyclohexyl, $\mathbf{R_1}$ = H;
34 $\mathbf{R_2}$ = DiPP, $\mathbf{R_3}$ = ^{i}Pr, $\mathbf{R_1}$ = H;
35 $\mathbf{R_2}$ = DiPP, $\mathbf{R_3}$ = Ph, $\mathbf{R_1}$ = H;
36 $\mathbf{R_2}$ = $\mathbf{R_3}$ = Cyclohexyl, $\mathbf{R_1}$ = H;
37 $\mathbf{R_2}$ = $\mathbf{R_3}$ = ^{o}anisyl, $\mathbf{R_1}$ = H;
38 $\mathbf{R_2}$ = $\mathbf{R_3}$ = ^{o}anisyl, $\mathbf{R_1}$ = Me;
39 $\mathbf{R_2}$ = $\mathbf{R_3}$ = ^{o}anisyl, $\mathbf{R_1}$ = Et;

Scheme 12. Group 4 amidinates containing electron-withdrawing fluorinated *N*-substituents, **27-32**, and electron-donating *N*-substituents, **33-39**.

The introduction of the electron-withdrawing fluorinated amidinates did not lead to similar trends as seen in the fluorinated FI catalysts (living polymerization of olefins,[83,84] or the induction of unexpected stereospecificity of the resulting polymer[84-86]). The fluorinated bis(amidinates), however, demonstrated a different activity towards propylene as compared to other bis(benzamidinates) titanium complexes. The resulting polymer consisted of only one atactic elastomer, suggesting the absence of "C_2 symmetry-like" species after the activation with MAO, however both amidinates remain coordinated to the metal centre. It was shown that in the presence of electron-withdrawing ligands, the fluorinated bis(amidinate)titanium bis(dimethylamido) complexes exhibited a dynamic behaviour even in their neutral form. The NMR studies revealed that the ligands rearrange from a κ^2 to κ^1 mode of coordination, leading to an open catalytic site, impeding the stereo control of the incoming monomer and resulting in the formation of a high molecular weight atactic elastomer. The positions of the fluorine atoms of the ligand were found to influence the R*i* and R*t* values as compared to the corresponding complex without fluorinated ligands (**28**). The ligand with only a *para*-F (complex **29**) induces a faster R*i* due to the increased electrophilicity of the metal center, whereas the complex containing a *meta*-F (complex **30**) suppresses the R*t* via its interaction with the metal center. Interestingly, the fluorinated zirconium complex **32** showed no reactivity toward propylene at room temperature, however at 60 ^{o}C, the complex exhibits an impressive activity of 113 kg mol^{-1} h^{-1} (Table 1), yielding an viscid, atactic, low molecular weight polymer.[78]

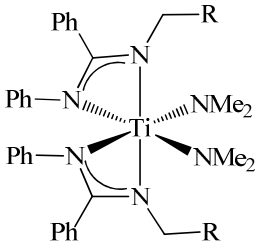
As the use of electron withdrawing groups (EWG) led to more active, but less stereoselective titanium and zirconium complexes as compared to the unsubstituted amidinates, the study of electron donating groups (EDG) in amidinate complexe represent the logical antithesis. It was expected that the introduction of EDGs into the amidinate framework would increase the electron density at the active site, decreasing ligand lability and inducing stereospecific polymerization. Cautious selection of the EDG was found prudent in order to minimally alter steric effects of these new amidinates. For example, the introduction of bulky substituents, such as diisopropylphenyl (DiPP), at both nitrogen positions of the amidinate leads to a lack of the reactivity of the ligands (RC(NDiPP)$_2^-$ = R = Ph, Me, Et, *i*Pr) with many titanium precursors at various ratios. The sterically demanding ligand PhC(NDiPP)$_2^-$ has been previously reported to react with zirconium tetrachloride, forming the corresponding bis(benzamidinate)zirconium dichloride, however the amidinates are unusually disposed in a *trans* fashion due to the steric influence.[87] Introduction of two ligands containing the DiPP moiety was possible only when an asymmetric substitution design was utilized, keeping DiPP as the substituent of one nitrogen atom, while using a smaller group (cyclohexyl (**33**), ^{i}Pr (**34**) or Ph (**35**)) at the second nitrogen.

The propylene polymerization activities of the asymmetric titanium complexes were found to be lower than those containing EWGs. In addition, similar trends in activity and polymer fractions were obtained as compared to the symmetric benzamidinates. Interestingly, the complexes bearing an *N*-alkyl substituent, such as isopropyl or cyclohexyl, were found to be more active than the corresponding N-aryl-substituted ligand.[76] These results encouraged the preparation of the symmetric complex (**33**) containing two cyclohexyl or *o*-anisyl groups. Complex **36** was found to be most active among the complexes containing EDGs, allowing the formation of a stereospecific polymer (~20%, 40% *mmmm*). When the *o*-anisyl moiety was introduced into the amidinate framework (complexes **37-39**), the polymerization behaviour was shown to also be influenced by the substituent at the *ipso*-carbon position, leading to isotactic polypropylene (up to 54% *mmmm*) and high molecular weight polymers (up to ~821,000 daltons) (Table 1). The remote location of the *ipso*-carbon substituent makes its impact on the catalytic behaviour an interesting mechanistic feature. It was shown for complex (**39**) that the anisyl group is unable to rotate freely, allowing the interaction of the methoxy moiety with the metal center, impeding the elimination of the growing chain and forming high molecular weight polymers.

As aforementioned, when bis(benzamidinate) group 4 complexes are activated with MAO, the metal center undergoes reduction to the M(III) species after the dissociation of a methyl radical which may be trapped by C_{60}. The reduced metal is oxidized back to the active M(IV) species upon the addition of propylene (Scheme 6). Surprisingly, only the bis(amidinate) complexes bearing fluorinated N-substituents (**27,** and **29-32**) were not reduced by MAO.

Since the immobilization of the ligand by the introduction of EDG was unsuccessful since the methoxy groups were not coordinated to the metal center, an alkyl moiety was introduced that is connected to an electron donating pendant arm.[88,89] The denticity of the ligands has been shown to vary as a function of the central metal atom size, increasing the coordination number as the size of the metal center increases.[90,91] A number of bis(benzamidinate)titanium bis(dimethylamido) complexes have been prepared containing variable pendant arms (**40-43**) by reacting two equivalents of the neutral amidines with one equivalent of Ti(NMe$_2$)$_4$. From the X-ray crystallographic analysis of the molecular structures, it was evident that the arm did not coordinate to the metal centre in the neutral form. However, a strong relationship was seen between the nucleophilicity of the arm and the activity of the complexes, and the stereospecificity of the resulting polymers. Complex **40** containing the most nucleophilic moiety NMe$_2$[92] promoted the formation of a highly isotactic polypropylene as a single fraction (Figure 3) with the lowest yield. Only minor effects are exhibited by the length of the linker of the pendant arm. Pentad analysis of the resulting polymer revealed that the isotacticity is a result of a chain-end mechanism, which has been previously unseen at room temperatures.[77] When complex **43** was activated by 100 equivalents of MAO, the resulting polymer consisted of an isotactic polypropylene (5 kg mol^{-1} h^{-1}), however when the ratio of MAO was increased, the activity of the mixture became much higher, reaching a maximum of 48.3 kg mol^{-1} h^{-1} at a cat:MAO ratio of 1:400, however, the product consisted of two fractions: a major isotactic fraction and a minor elastomeric

fraction. The use of 1000 equivalents of MAO slightly decreased the activity (**43**:MAO of 1:400 produced polypropylene with activity of 48.3 kg mol^{-1} h^{-1}, and **43**:MAO of 1:1000 resulted in formation of polymer with activity of 30.0 kg mol^{-1} h^{-1}), producing only an elastomeric material. The activation of complex **43** with MAO and TTPB (as shown above) resulted in an increased activity by an order of magnitude (230 kg mol^{-1} h^{-1}), however, the resulting polymer was an atactic elastomer, indicating the



40: R = -CH_2NMe_2, **41: R** = 2-pyridyl,

42: R = -CH_2-2-pyridyl, **43: R** = 2-furyl

importance of the counter-ion on the active site and its influence on the activity and stereoselectivity of the polymerization.

Scheme 13. Bis(benzamidinate)titanium bis(dimethylamido) complexes containing electron donating pendant arms.

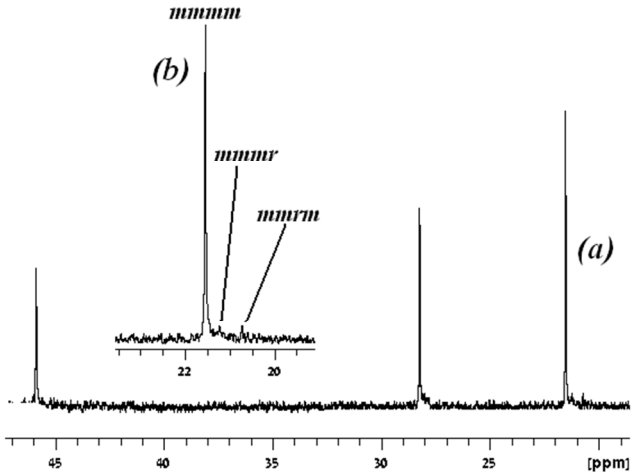
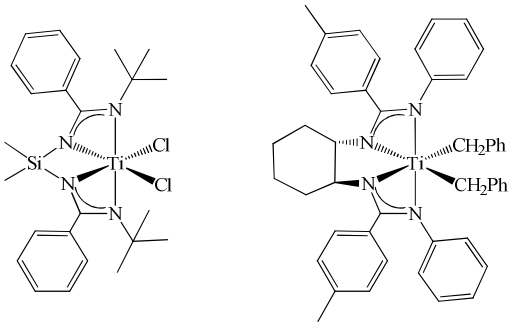


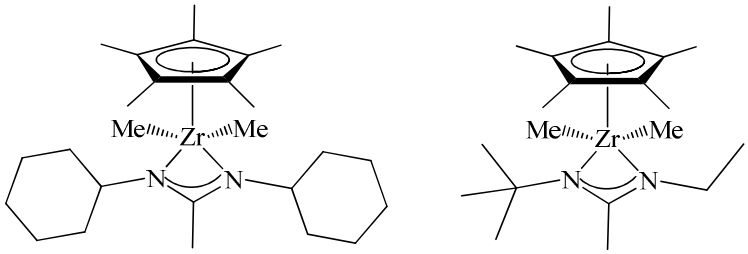
Figure 3. ^{13}C-NMR of polypropylene obtained from the catalytic mixture of **43**:MAO 1:1000 (a) full spectrum, (b) enlarged methyl region. "Reprinted with permission from T. Elkin, M. Botoshansky, R. M. Waymouth, M. S. Eisen *Organometallics*, **2014**, *33*, pp 840–843. Copyright (2014) American Chemical Society"

Another approach of increasing the chelate effect in bis(amidinate) systems has been developed by bridging between two amidinates, analogous to the *ansa*-metallocenes. Such bridged systems may be approached from two main synthetic methods, sigmatropic rearrangement leading to systems where amidinates are bridged with a silicon-containing chain, or an all carbon bridging chain formed by a condensation reaction. The first system has been shown to be synthetically challenging, limiting the scope of the resulting complexes, allowing for the formation of only one mononuclear complex incorporating a silyl-bridged ligand around the metal centre and two working ligands (Scheme 14).[93-98] Systems containing all carbon linkers have demonstrated more thermal and chemical robustness, and complexes may be prepared enantiomerically pure.[99,100] Catalytic studies with these new types of bridged complexes will be vital for the understanding of the structure and activity of the bis(amidinate) group 4 complexes as catalysts for olefin polymerization.



Scheme 14. Examples of mononuclear linked bis(amidinate) titanium complexes.

The versatility of the amidinate ligand has increased even more when combined with other ancillary ligands, among them being Cp ligands[101-105] and imino-enamido ligands.[106] These types of systems have been found to be useful in ethylene polymerization, as well as 1-hexene living polymerization[107-109] and co-polymer formation.[110] For example, complex **43** demonstrated rather low activity in the polymerization of 1-hexene. After a slight modification of the ligand, complex **44** was shown to form a catalytically active species capable of generating highly isospecific polypropylene. Additionally, the same catalytic mixture containing **44**:co-catalysts at 1:1 ratio bearing amidinates and Cp ligands serves as catalysts promoting living stereospecific polymerization of various monomers such as ethylene and 1-octene.



43 **44**

Scheme 15. Structure of the mono(amidinate) mono Cp* complexes **43** and **44**, promoting the living stereoselective polymerization of α-olefins and stereo-block polypropylene.

When the activation of the mixture was generated by reacting one equivalent of **44** with only 0.5 equivalents of the co-catalyst $[Me_2PhNH][B(C_6F_5)_4]$, the polymerization of the polymer resulted in the formation of atactic polypropylene under the conditions of the degenerative transfer mechanism. Due to this special feature, it became possible to produce isotactic-atactic stereo-block polymers with the controlled lengths of each block and of the whole polymer chain simply by the adding more **44** or co-catalyst to the mixture at different times.[111]

In summary, the group 4 bis(amidinate) complexes and their derivatives, in our opinion, will continue to develop into versatile catalysts with numerous applications. Additionally, the study of the amidinates will inspire and contribute to the development of new ligand frameworks for olefin polymerization, such as *N,N*-dialkylcarbamato complexes that have been recently applied to yield atactic polypropylene.[112]

Conclusions

Herein, we have presented recent advances in the application of amidinate group 4 complexes, revealing the effects of the ligands, metal centres, and various reaction conditions on the resulting polymerization. Simple amidinates demonstrate the ability to rearrange around the metal center and migrate to the aluminium, leading to a loss of the stereospecificity of the product. The aromatic substitution on the *ipso*-carbon leads to the formation of a CGC-type species, inducing steric effects from the *p*-aryl substituent leading to increased molecular weight of the obtained polymers and reduced activity of the complexes for the larger substituent. The introduction of electron deficient substituents on the nitrogen sites of the ligand results in higher activity as

compared to electron-donating moieties, however, the stereospecificity of the polymer for the former is completely lost. The immobility of the ligand was achieved when electron donating pendant arms were introduced into the ligand framework, resulting in the formation of isotactic polypropylene as a single product for the complexes bearing the most nucleophilc arm.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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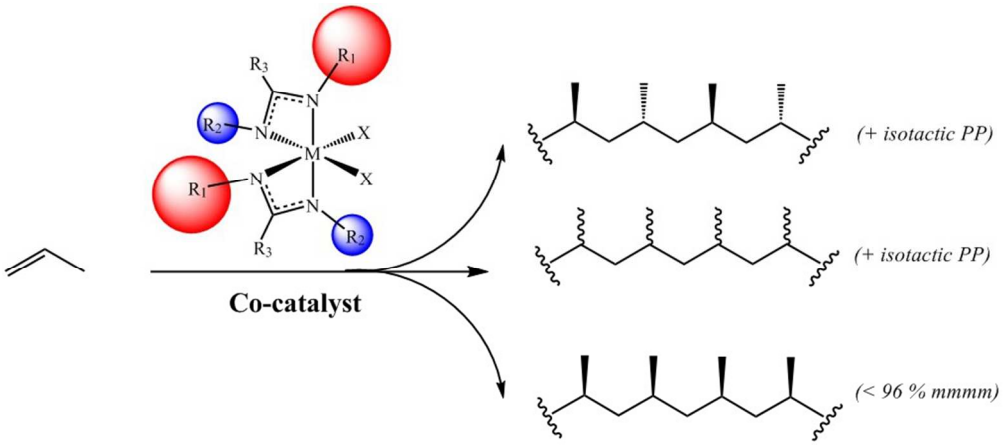

Graphical abstract
267x118mm (96 x 96 DPI)