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Octahedral Complexes in the Polymerization of α-Olefins

*Sinai Aharonovich, Victoria Volkis, Moris S. Eisen**

Summary: A series of dimethyl titanium benzamidinate complexes has been prepared containing various functional groups at the aromatic ring. These functional groups were selected to study their electronic or steric effects at the cationic metal center in the polymerization of propylene. Quantitative structure activity relationship (QSAR) studies showed that a linear relationship is observed only for the Taft Parameter (Es). Mono- and bis-benzamidinate complexes were found to produce similar polymers indicating that alike active species are obtained regardless of the starting complex. Deuterium labeled 2-D-propene showed that a new epimerization mechanism for this type of complexes is operative.

Keywords: deuterium labeled polypropylene; elastomeric polypropylene; octahedral benzamidinate complexes; taft relationship

Introduction

Metallocenes have been play a crucial role for studying the polymerization of α-olefins.[1] The ability to transfer the different roles of the ligands and metal centers for s designed polymer is reaching a high level of sophistication,[2] and has open the search of the non-metallocene systems as alternatives catalysts for this polymerization process.[3] Among the various organometallic compounds synthesized during the last decade, the complexes of early transition metals with the bidentate *N,N′-bis*(trimethylsilyl) benzamidinate ligations $[\eta\text{-RC(NR}')_2]^-$ (where $R = C_6H_5$ or substituted phenyls, $R' =$ alkyl, aryl or $SiMe_3$) have been widely described as capable substitutes to the metallocene complexes.[4] The (bis)benzamidinate complexes are octahedral and hence are obtained as mixtures of racemic C_2-symmetry structures.

Compared to the cyclopentadienyl ligands, the benzamidinates differ from them with unique electronic properties. As a 4-electron donor, the anionic moiety $[RC(NSiMe_3)_2]^-$ polarizes the M-N bonds promoting greater electrophilicity of the metal center, as compared to the 6 electrons of the cyclopentadienyl ligands. The possibility to simply modify the steric and electronic properties of the benzamidinate-based ligands, through the changes in either the organic substituents at the nitrogen atom and/or different functional groups at the aromatic ring, makes these ligands very attractive for the synthesis of various organometallic complexes as potential catalytic precursors for the polymerization and α-olefins.[5] Interestingly, we have recently found that there is no linear relationship between an electronic parameter of the different functional groups at the aromatic rings (in the *para* position) and the termination rate of the cationic complexes. Herein we show, the effect of the number of ligands at the metal center and the use of labeled propylene introducing a new epimerization mechanism competing with the stereoregular polymerization.

Results and Discussions

A number of lithium benzamidinate ligands have been synthesized by the reaction of

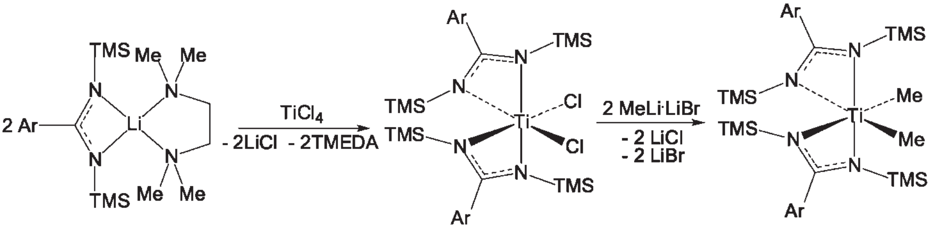
Schulich Faculty of Chemistry and Institute of Catalysis Science and Technology, Kyriat Hatechnion, Haifa, 32000, Israel
Fax: (+972) 4829-5703;
E-mail: chmoris@tx.technion.ac.il

Table 1.
Data for the polymerization of dichloride titanium (bis)benzamidinate complexes with different substituents at the *para* position of the aromatic ring activated by MAO.

Substituent	H	*p*-Me	*p*-Et	*p*-^{n}Bu	*p*-^{t}Bu	*p*-OMe
Activity$^{a)}$	24.7	15.8	10.2	9.93	24.0	9.82
mmmm [%]	12.5	19.0	17.4	15.3	10.2	10.7

$^{a)}$ g Polymer/mmoles catalyst · hr.

the corresponding substituted benzonitriles with $Li(N(TMS)_2)$. The reaction of two equivalents of the lithium ligands with $TiCl_4$ induces the synthesis of dichloride complexes and the concomitant reaction with MeLi produces the dimethyl titanium (bis)benzamidinate complexes (Eq. 1). The catalytic properties of several group 4 (bis)benzamidinate complexes in the polymerization of α-olefins have been previously investigated.[6] When activated with methylalumoxane (MAO) or other co-catalysts, these complexes demonstrated high catalytic activity for the polymerization of ethylene, propylene and styrene.[7] It was shown that the stereoregularity of the obtained polymers depends on the composition of the early-transition metal benzamidinate complexes and the conditions at which the polymerization reactions were performed. Thus, for example, we have found that for some benzamidinate zirconium complexes the change of the monomer concentration during the process allowed the formation of various types of polypropylene (atactic, isotactic or elastomeric).[7]



Ar = C_6H_5 (1), *p*-Me C_6H_4 (2), *p*-Et C_6H_4 (3), *p*-^{n}Bu C_6H_4 (4), *p*-^{t}Bu C_6H_4 (5), *p*-OMe C_6H_4 (6)

(1)

Since the putative cationic complexes were expected to be responsible for the activity of the complexes, it was anticipated that different electronic groups at the *para* position of the aromatic rings will induce a large effect in the activity of the catalysts, if the metal charge density can be allocated into the aromatic ring. We found that the activity and steroregularity of the resultant polypropylene were affected by the substituents (Table 1), and also that it is composed of a major elastomeric hexane soluble fraction and a minor solid insoluble fraction (Table 2). In contrast to our expectations, we have found no evidence of influence of the substituents on the propylene insertion, misinsertion or termination rates by electronic effects (i.e, Hammet).[8] However, surprisingly we have been able only to obtain a quantitative linear free energy relationship between the termination rate associated with the elastomeric fraction and the steric Taft parameter (Es).[8]

The steric linear relationship exhibited by these complexes indicates that the benzamidinate ligands are labile, affecting the rotation of the polymeric chain towards the position for β-H-elimination (rate determining step). Hence, the larger the substituent group at the aromatic rings of the complex, the slower the elimination.

The effect of the numbers of ligands at the metal center was studied by comparing the reactivity of the monomeric titanium (bis)benzamidinate

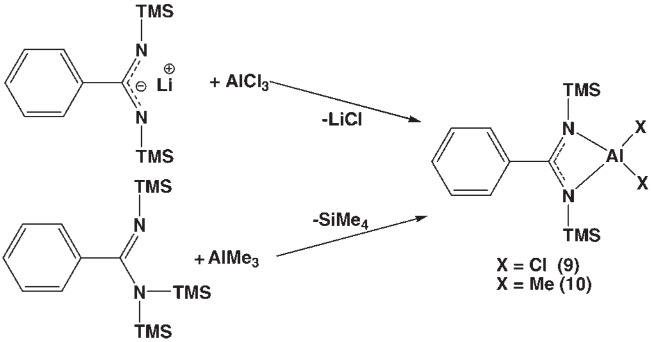
Table 2.
Fractionation data for the polymers obtained by the different dichloride titanium (bis)benzamidinate complexes activated by MAO.

Substituent	Hexane Soluble Fraction				Hexane Insoluble Fraction			
	m [g]	mmmm	$Mw \times 10^{-3}$	MWD	m [mg]	mmmm	$Mw \times 10^{-3}$	MWD
H	1.056	11.2	23	2.87	91	79.3	103	2.96
p-Me	0.445	15.5	122	2.90	68	73.4	59	3.24
p-Et	0.457	12.7	149	3.77	61	74.5	66	3.18
p-nBu	0.385	11.2	188	3.63	76	76.4	58	2.91
p-tBu	1.025	8.9	22	5.08	91	73.4	55	2.87
p-OMe	0.414	8.5	26	2.77	42	75.2	93	2.88

$[\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]_2TiCl_2$ (**1**)[6] and the dimeric titanium (mono)benzamidinate $\{[\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]\,TiCl_3\}_2$ (**7**)[6d,9] complexes. This latter complex reacts with THF producing a red crystalline solid of the monomeric complex $[\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]$ $TiCl_3THF$ (**8**).

Hence, the (mono)benzamidinate titanium complexes (**7** or **8**) activated by MAO were found to be active for the polymerization of styrene, whereas the (bis)benzamidinate titanium dichloride complex (**1**) was completely inactive in this process under similar reaction conditions.[6d] Furthermore, none of the (mono)benzamidinate complexes were found to be active for the polymerization of propylene at a monomer pressure of 1 atm.[6d,7b] This result is similar with our findings, in which the bis(benzamidinate) titanium dichloride and dimethyl complexes activated with MAO also do not polymerize propylene at atmospheric pressure.[7b] However, when the complexes were used in the polymerization of propylene at higher concentrations (liquid propylene ~9.2 atm), in all cases similar activities were obtained. In spite of the different structural features of the used pre- catalysts, the amount of polymer and the molecular weights of the fractionized polymers created under the same conditions, and the stereoregularity of the fractions *were unexpectedly found to be alike*.[10] These results induce us to consider that possible *similar active species* are operative in the polymerization process regardless of the starting materials.

To explain these unexpected similarities, it was conceivable that during the polymerization process, the different complexes undergo rearrangements, forming equal number of species, similar in their structure, which are active for the polymerization reaction. To corroborate that hypothesis, one of such active species was postulated to be the corresponding aluminum benzamidinate complex that can be formed as a result of the interaction of the studied titanium benzamidinates with methylalumoxane. To confirm



(2)

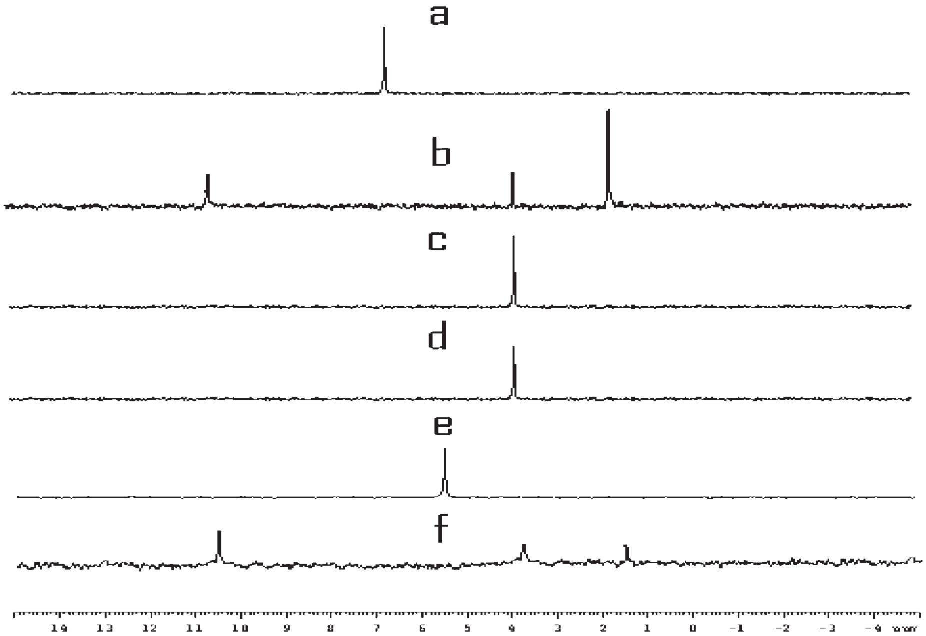
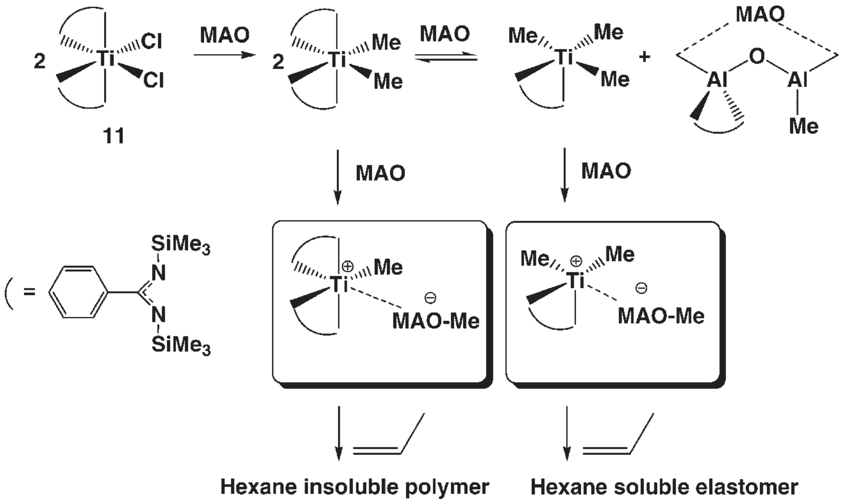


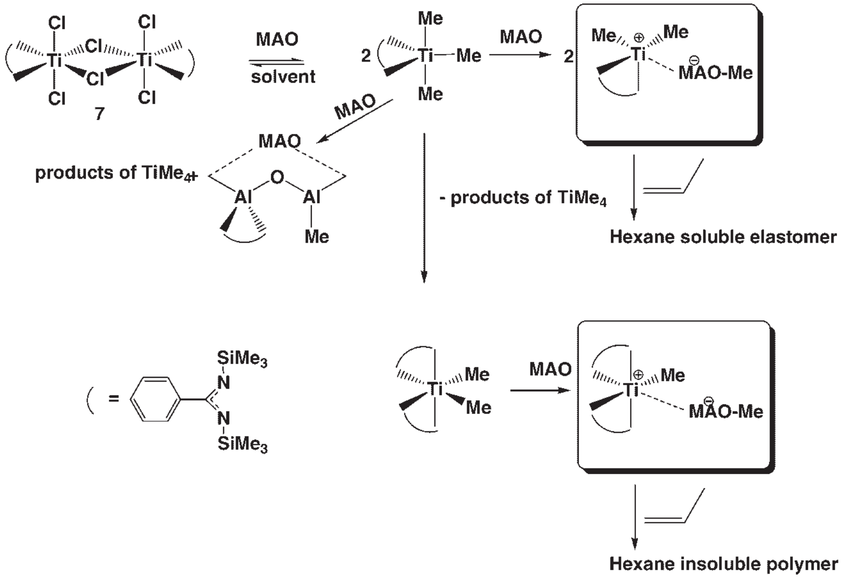
Figure 1.
^{29}Si NMR following up in the formation of new species from titanium benzamidinate complexes in toluene-d$_8$. **a** – pure complex **11**, **b** –complex **11** + MAO at a 1:20 respective ratio, **c** – pure complex **9**, **d** – pure complex **10**, **e** – pure dimer complex **7**, **f** – complex 7+ MAO at a respective 1:1 ratio.

experimentally such assumption, the aluminum benzamidinate dichloride (**9**) and dimethyl (**10**) complexes were synthesized (Eq. 2).

The features of activation of the benzamidinate complexes with methylalumoxane were followed by ^{29}Si NMR to allow us to discriminate the various species formed at



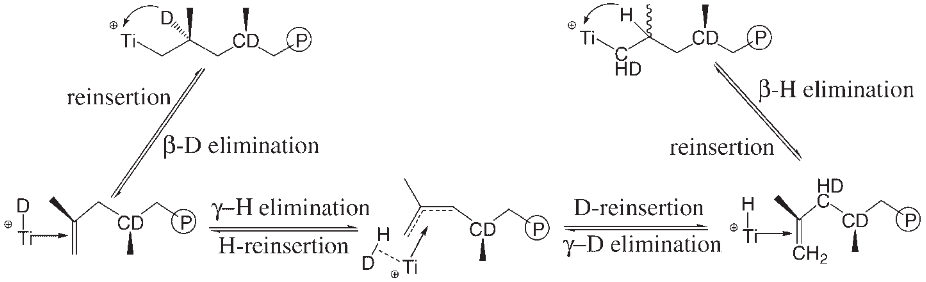
Scheme 1.
Plausible rearrangement of complex **11**.



Scheme 2.
Plausible mechanism for the disproportionation of complex **7**.

different steps of the activation (Figure 1). The spectra obtained for those complexes were compared to the spectra of the aluminum benzamidinates.

In Figure 1, the spectrum (**a**) exhibits the clean signal of the pure monomeric dimethyl titanium (bis)benzamidinate $[\eta\text{-}C_6H_5\text{-}C(NSiMe_3)_2]_2TiMe_2$ complex (**11**). This signal has no matches with the signals obtained in spectrum (**b**) of the same complex **11** activated with MAO. It is important to point out that the central signals in spectrum (**b**) matches the signal obtained in both spectrum (**c**) and (**d**) corresponding for the aluminum benzamidinate complexes **9** and **10**, respectively. Similarly, the spectrum (**e**) of the pure dimer complex **7** exhibits only one single signal, but after the addition of MAO (**f**) the same three signals as obtained with complex **11** (spectrum **b**) are observed. Hence, based on our previous results for cationic bis(benzamidinate) complexes,[6d,7b,10] we can substantiate that the



Scheme 3.
Epimerization mechanism for the formation of –CH- and –CHD groups in the deuterated polymers catalyzed by titanium benzamidinate complexes.

small signal at the lowest chemical shift in spectrum (**b**) belongs to the bis(benzamidinate) titanium methyl cationic complex, whereas the large signal at the highest magnetic field corresponds to the (mono)-benzamidinate alkyl cationic complex.[10] The formation of the aluminum complex involves the metathesis of the benzamidinate ligand from the titanium complexes to one of the aluminum centers at MAO.

The activities of aluminium complexes (**9** and **10)** were found to be an order of magnitude lower ($\sim 0.5 \times 10^4$ g PP $\times$ mol $Al^{-1} \times h^{-1}$) as compared to the corresponding titanium pre-catalysts. The molecular weight, polydispersity and tacticity of the elastomeric polymers produced by these aluminum complexes were also found to be closely related to the hexane soluble polymeric fractions obtained by the titanium complexes.

At the same time, the low activity of these complexes (**9** and **10)** activated by MAO, allowed us to conclude that the formation of the hexane soluble fraction (more than 90% of the whole polymers produced by the benzamidinate catalytic systems) that may be produced by these aluminium species, obtained by the partial migration of the benzamidinate ligand from Ti to Al, is insignificant. Hence, the formation of the polydisperse hexane soluble elastomeric polypropylenes mainly depends on the presence of one of the other two active intermediates.

The additional two signals on the ^{29}Si NMR spectra (Figure 1b and 1f) are representative of two different complexes each of which probably responsible for the formation of a different fractions. Assuming that a (bi)benzamidinate titanium methyl complex, with a C_2 symmetry, is responsible for the small isotactic hexane insoluble fraction, a second monomeric (mono)benzamidinate titanium cationic alkyl complex must be responsible for the formation of the elastomeric hexane soluble polymer. Hence, it is reasonable that complex **11** rearranges as equal to complex **7** forming the same active species. Plausible mechanisms for the rearrangement of complex **11** and **7** are described in Scheme 1 and 2, respectively.

The "atactic elastomeric polymer", obtained with MAO, was recently rationalized using deuterated labeled propylene (2-D-propene), via an intramolecular epimerization reaction of the growing polypropylene chain at the last-inserted monomeric unit (Scheme 3),[11] which is a totally different mechanism than those encounter for metallocene complexes.[12]

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