

Reactivity of group 4 benzamidinate complexes towards mono- and bis-substituted silanes and 1,5-hexadiene

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Abstract

Zirconium and titanium bis(benzamidinate) dimethyl complexes were found to be active catalytic precursors for the oligomerization of mono- and bis-substituted silanes. The activation of such complexes, by an excess of MAO or by an equimolar amount of $B(C_6F_5)_3$, increases the catalytic activity of the complexes and the molecular weight of the obtained oligosilanes. The maximum polymerization index that was accomplished ($n = 90$) is by far the largest obtained with other organometallic complexes. In addition, the activated benzamidinate catalysts were also found to be active for the polymerization of 1,5-hexadiene producing poly(methyl-1,3-cyclopentane). For the latter, the results obtained with C_2 -symmetry bis(benzamidinate) dimethyl complexes were compared with a chiral complex bearing a myrtanyl group at the benzamidinate ligand.

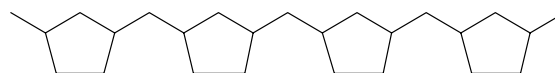
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Keywords: Benzamidinate complexes; Polysilanes; Dehydrogenative coupling of silanes; Polysilanes; Polymethylcyclopentane; Chiral complexes

1. Introduction

In the last three decades, the use of cyclopentadienyl containing complexes [1] and other related carbon- [2], oxygen- [3], and nitrogen-based ligands [4], such as chelating diamido [5], salicylaldiminato [6], acetylacetonate [7], amidinates [8] and some others, have been used as ancillary ligands in the synthesis of potential Ziegler–Natta types of catalysts for the oligomerization and polymerization of olefins [9], and for several other catalytic reactions [10].

Since the early report of Marvel and Stille [11] regarding the polymerization of 1,5-hexadiene to poly(methyl-1,3-cyclopentane) (PMCP) by metallocene complexes, the catalytic polymerization of non-conjugated dienes resulting in polycyclic polymer has been under detailed investigation [12,13]. One important feature of these reactions is the potential ability of the catalysts to co-polymerize 1,5-hexadiene with α -olefins, producing polymers with cyclopentane units and crosslinked moieties [14]. In addition, methyl-, methoxy- and phenyl-substituted hexa- and heptadienes can be polymerized producing functionalized polymers [15].



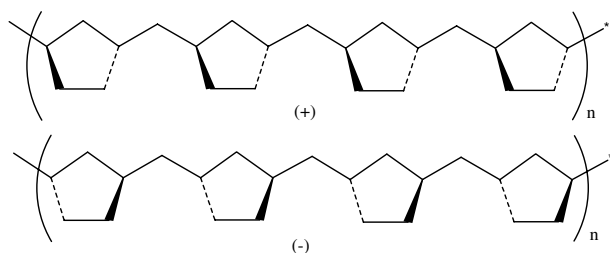
PMCP

The homogeneous metallocene complexes, Cp_2ZrCl_2 and Cp_2ZrMe_2 , were the first examples of organometallic pre-catalysts to promote such polymerizations [13]. The pre-catalysts were usually activated by an excess of MAO, boron compounds [16] or diethyl aluminium chloride co-catalysts [17]. The mechanism for the cyclic polymerization was proposed first by Marvel et al. [11,18]. This mechanism entails the insertion of the double bond into the M–Me bond of the catalyst followed by a cyclization resulting from the insertion of the second double bond

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of the substrate into the metal–carbon (from the growing polymer chain). Chain termination usually takes place via β -H elimination, although some examples of aluminium transfer termination mechanisms have been also described [19]. Due to the great importance of chiral polymers, the catalytic properties of some chiral pre-catalysts in the polymerization of 1,5-hexadiene have been also studied [20]. It was found that only the *trans*-isotactic polymer shows chiral properties.



A second important process that has attained a large industrial and academic interest regards the formation of linear polysilanes. Being potential precursors for ceramics, non-linear optics, deep-UV photo resists, conductive and photoconductive polymers [21], and nanoparticle polycarbosilanes [22], linear polysilanes became a target for many synthetic approaches. The simplest and most industrially used synthetic method for silane polymerization is via the Wurst reaction [23], which can be thermal [24], sonic [25] or electrochemical [26]. Along with such important advantages as high activity, commodity and high molecular weight of the resulting polymers, this synthetic method has strong limitations in polymer linearity, and the ability to control the process. In addition, chain cyclization side-reactions on the early steps of polymerization, and a wide molecular weight distribution strongly limit the fields of use for such polymers. Therefore, development of an alternative organometallic approach in the polymerization of silanes has been of intense research [27]. Among new synthetic approaches, hydrosilylation, transition metal-catalyzed dehydrocoupling of organic silanes, electrochemical routes to organosilicon polymers, and other metal complex-catalyzed syntheses of organosilicon polymers, have been investigated [21b,23].

For example, metallocene-type difluoro-, diphenoxy- and diamino- catalysts were found to be active in the dehydrogenative coupling of mono-substituted silanes towards oligomers, which are produced with high conversion (80–90%), with molecular weights up to 4400 Da and the ratios between linear and cyclic polymer are from 1:2 to 1:30 [28]. Interestingly, hafnium complexes provides the greatest amount of the linear products, whereas titanium metallocene complexes react about ten times faster than the corresponding Zr and Hf complexes [29]. The mechanism of the polymerization of silanes by metallocene complexes has

been investigated in detail, and intermediates have been isolated [29].

One of the most active complexes for the polymerization of mono-substituted silanes was obtained by Corey by the reaction *in situ* between dichlorozirconocene, *n*-BuLi and phenylsilane [30]. Oligomers with molecular weights between 700 and 3000 Da were obtained and with 60–99% conversion. Other similar complexes usually produced mixtures of the low molecular weight oligomers, which contain 12–20 silicon atoms (according to the GPC results) [29]. Regarding late transition metals, a nickel indenyl complex (1-MeInd)Ni(PPh₃)Cl that was activated by either MAO or LiAlH₄ was found to be active in the oligomerization of phenylsilane giving linear products with 90% conversion [31].

Zirconocene and titanocene alkyne complexes are able to oligomerize di-substituted silanes as methylphenylsilane, giving a mixture of dimers, trimers and tetramers; whereas for diphenylsilane, only dimers with low conversion have been obtained [32]. Hence, it is indeed challenging to research for new complexes that will polymerize bulky di-substituted silanes.

Fascinatingly, the structure and molecular weight of some polysilanes can be controlled by the structure of the organometallic catalyst [29]. Some metallocene-type catalysts are able to regulate the stereochemistry of the propagated chain, producing syndiotactic [33] or isotactic [34] polymers.

Recently, we have investigated the polymerization of ethylene and propylene promoted by racemic mixtures of bis (benzamidinate) zirconium and titanium *cis*-octahedral complexes [35]. Moreover, chiral benzamidinate complexes have been also synthesized and utilized for the stereoregular polymerization of propylene and styrene and for the isomerization of α -olefins [36].

It has been only shown regarding the use of benzamidinate complexes for the cyclic polymerization of 1,5-hexadiene, that the tris-trimethylsilyl benzamidinate zirconium monochloride complex can selectively polymerize 1,5-hexadiene producing short oligomers ($M_w = 800$, conversion 60–90%) [37].

In this paper we present the results of polymerization of 1,5-hexadiene with titanium and zirconium bis-benzamidinate complexes and with a chiral zirconium tris-benzamidinate complex. The polymerization conditions, the nature of catalysts and ligands and their influence on the properties of the resulted PMCP will be discussed. The NMR study of the polymer structure is shown as well. In addition, we also disclose here studies for the polymerization of mono- and bis-substituted silanes initiated by the benzamidinate complexes of titanium and zirconium. The effect of the polymerization conditions, the nature of catalysts and different co-catalysts on the polymerization reaction and on the properties of the obtained polysilanes is presented. These processes were studied conceptually to expand the scope of reactivity of the benzamidinate neutral and cationic complexes.

2. Results and discussion

2.1. Synthesis of the catalysts

The bis-benzamidinate derivatives of titanium and zirconium were synthesized as described in literature [35k]. The lithium salt of the ligand was obtained by the reaction of benzonitrile and $\text{LiN}(\text{SiMe}_3)_2$ as described in a previous publication [38]. The reaction of the latter lithium ligand with ZrCl_4 or TiCl_4 resulted in the formation of the bis(benzamidinate)dichloride complexes. Finally, dimethyl complexes of zirconium (**1**) and titanium (**2**) were prepared by the methylation of the dichloride complexes with methyl lithium. The zirconium complex containing the chiral myrtanyl group attached to benzamidinate ligand (**3**) was synthesized also as described in literature [36]. All benzamidinate complexes were either used as neutral complexes or activated with either methylalumoxane (MAO) or tris(pentafluorophenyl)borane, as shown in Scheme 1.

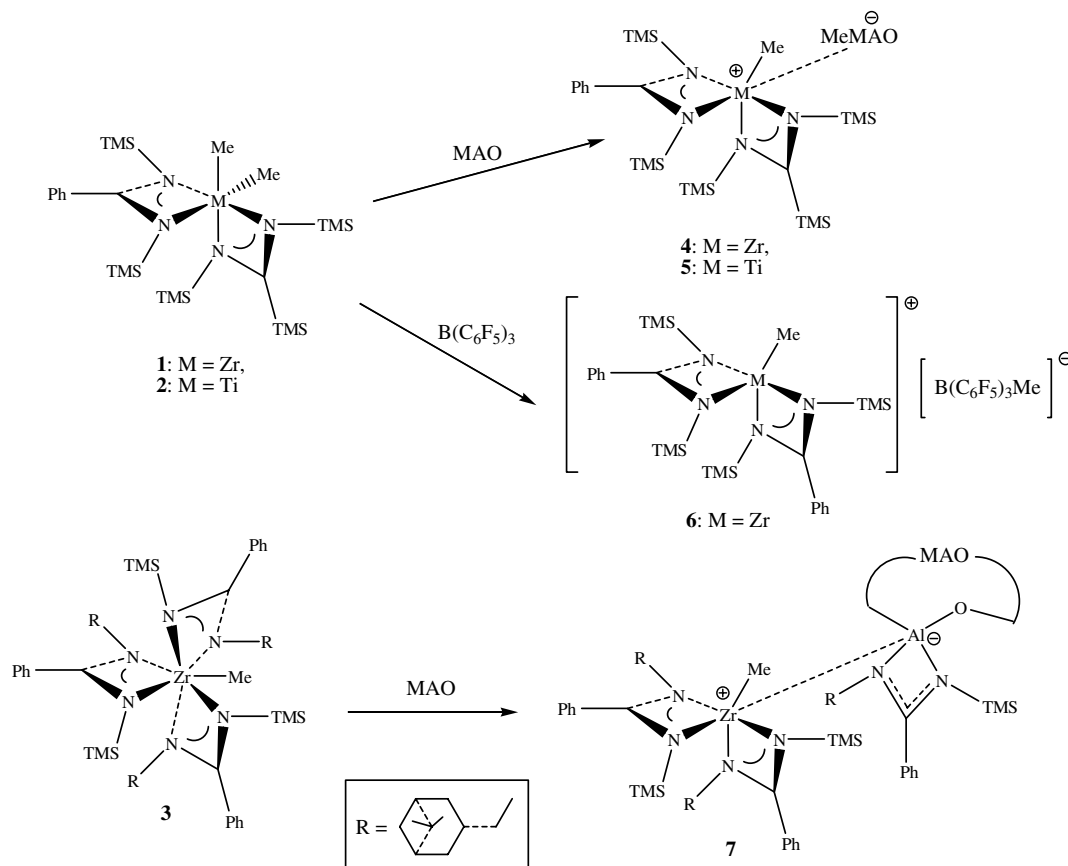
2.2. Polymerization of 1,5-hexadiene

The polymerization of 1,5-hexadiene was carried out using catalysts **1–3**. MAO was used as the co-catalyst to form the putative cationic active species **4**, **5**, and **7** (Scheme 1). The influence of the polymerization conditions

and the nature of complexes on the activity and the properties of the polymers were studied. In addition, we were interested to compare the polymerization results using complexes **1–2** which are obtained as racemic mixtures of octahedral complexes with the results using complex **3** containing chiral centers. The polymerization data are presented in Table 1.

As can be concluded from the polymerization data, all complexes were found to be active catalysts for the polymerization of 1,5-hexadiene, producing only polycyclic polymers with a similar activity as compared to the metallocene complexes. The PMCP obtained with the bis-benzamidinate complexes **4–5** demonstrated elastomeric properties, whereas the polymers obtained by the chiral complex **7** were obtained as solid polymers, both polymers were soluble in hot toluene. This fact indicates that no apparent crosslinking, which is also characteristic for polymers with high stereoregularity, occurred during the polymerization of this olefin [39].

The cationic complex **7** was found to be more active in the polymerization, as compared to complexes **4** and **5**, respectively. It was found that during the activation of complex **3**, MAO removes one of the chiral benzamidinate ligands making the resulted active species **7** [36]. Due to the presence of the myrtanyl group that is attached to the benzamidinate ancillary ligand via a methylene group, the effective



Scheme 1. Group IV neutral and putative cationic benzamidinate complexes.

Table 1

Data for the cyclic polymerization of 1,5-hexadiene promoted by the benzamidinate complexes **4**, **5** and **7**^a

Run	Catalyst	M:MAO	T (°C)	$A \times 10^{-3b}$	<i>cis:trans</i> (%) ^c	Type of polymer	mp ^d (°C)	M_n	M_w	MWD ^e
1	4	1:100	25	2.2	55:45	E ^f	–	5000	13,500	2.72
2	4	1:400	25	6.8	58:42	E	–	5200	13,500	2.62
3	5	1:100	25	2.4	52:48	E	–	23,000	31,000	1.35
4	5	1:400	25	4.1	54:46	E	–	13,900	21,100	1.52
5	7	1:100	25	27	41:59	S ^f	76	1560	2180	1.4
6	7	1:100	50	35	31:69	S	82	2460	3200	1.3
7	7	1:800	50	110	36:64	S	88	3120	4680	1.5

^a 6 mL toluene.^b g polm./(mol cat h).^c Calculated from the integration of 1,3-*cis*- and *trans*-carbons in ¹³C NMR.^d From DSC measurements from the second thermogram.^e M_w/M_n ; M_n , M_w and MWD were measured by GPC.^f E – elastomer, S – solid.

coordinative unsaturation of complex **7** is more open than in complexes **4** and **5**, and as a result, the entrance of the monomer becomes less crowded and easier. The activity of complex **7** increases with rising temperature, as well as a Zr:Al ratio. Concerning the properties of the resulted polymer, one can indicate two important effects: molecular weight of oligomers grows with the increasing of the temperature (entries 5 and 6) and the ratio between MAO and the catalyst (entries 6 and 7).

2.3. NMR determination of the microstructure of PMCP

The typical ¹³C NMR spectrum (in toluene *d*₈) at 45 °C for PMCP produced by the benzamidinate complex **7** in toluene is presented in Fig. 1. The signals in the region of

30–45 ppm are related to the PMCP carbons and those labeled by asterisks, characterize the chain end. The signals obtained in Fig. 1 are in good agreement with the literature data for a polymer that is obtained via a β-H elimination mechanism [40,43]. The same spectrum was observed for polymers produced by complexes **4** and **5**.

Two factors influence the stereochemistry in the cyclic polymerization of the non-conjugated dienes: the orientations between the rings in the polymer chain, and the ring closing orientation. Hence, four kinds of different stereoregular orientations can be found in the cyclic polymer [11,15]: *cis*-isotactic (or *meso*-diisotactic), *cis*-syndiotactic (or *meso*-disyndiotactic), *trans*-syndiotactic (or *racemo*-disyndiotactic) and *trans*-isotactic (or *racemo*-diisotactic):

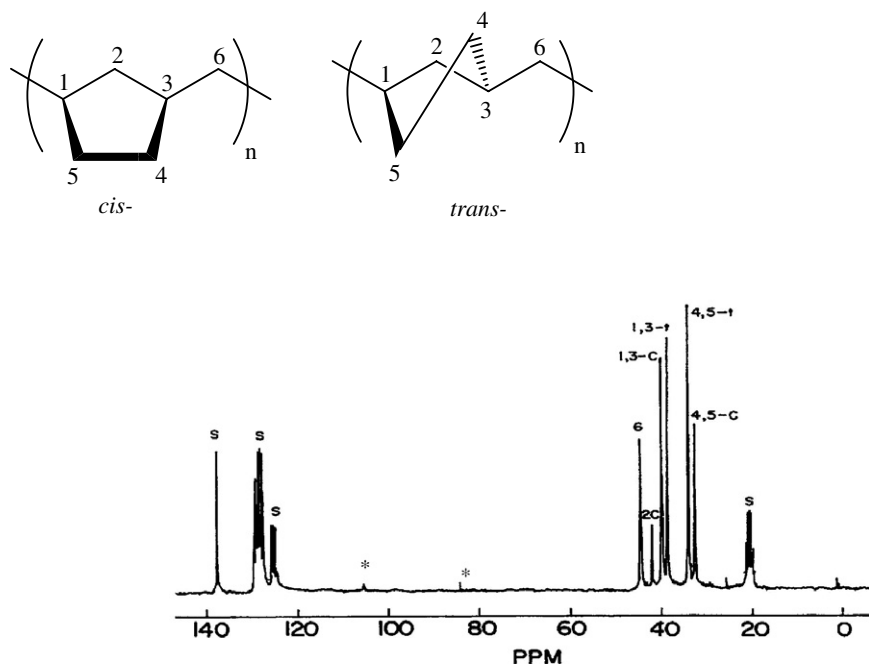
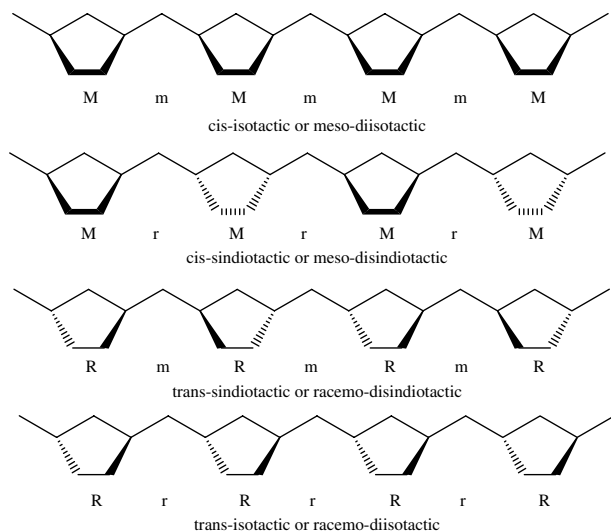


Fig. 1. ¹³C NMR spectrum for PMCP received using the bis-benzamidinate complex **7** as the catalyst (s = solvent, c = *cis*, t = *trans*). Carbons numbered 2 and 6 (*cis* and *trans*) emerge jointly.



The stereochemistry of insertion of the first double bond of the diene into the metal–carbon bond resembles the stereochemistry as found for the polymerization of α -olefins [41], which is strongly dependent on the symmetry of the catalyst [42]. The orientation of the ring closure depends normally on the bulkiness of the ligands, at the metal center, and the polymerization conditions [43].

The percentage of *cis* and *trans* rings for the PMCP was calculated for complexes **4**, **5**, and **7** from the integration ratio between 1,3-*cis* and 1,3-*trans* carbons (Table 1). The obtained ratios were corroborated by the results obtained based on the integration ratio for 4,5-*cis* and 4,5-*trans* carbons.

The physical properties of PMCP strongly depend on the *cis/trans* rings ratio: the larger amount of the *trans* rings, the higher the melting temperature that is observed [44]. It was found that polymers contains more than 60% of *trans* rings are solid with the melting temperature above 180 °C, whereas the polymers with 50–60% of *cis* rings are waxes with melting temperatures below 70 °C. As can be concluded from Table 1, for bis-benzamidate catalysts **4**, **5**, the *cis:trans* rings ratio are very close to 50:50, corroborating with the elastomeric properties of the obtained polymers. For complex **7**, containing the chiral myrtanyl group on the benzamidate ligands, the preference towards the *trans* ring closure (59–69%) was observed.

The tacticity of PMCP is influenced by the enantioface stereoregularity in the 1,5-hexadiene-insertion step. Regarding the enantioselectivity, the performance of the benzamidate complexes in the polymerization of 1,5-hexadiene is expected to be alike to that encounter in the polymerization of propylene. Hence, the zirconium complex **4** was more stereoselective when compared to complex **5**, in the polymerization of propylene at high pressure [45] and for complex **7**, a highly isotactic polypropylene was obtained (*mmmm* > 99.9%) [36].

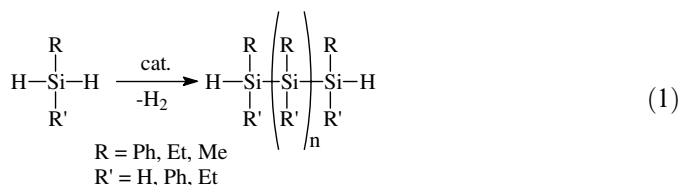
In the NMR analysis towards the tacticity of the PMCP, we have used the same notation as described by Waymouth et al. [20,43]. The capital letters M (*meso*) and R (*racemic*) described the relative stereochemistry within the ring whereas a small cap letters *m* and *r* are used to describe the relative stereochemistry between the closed rings. The small letter *x* denotes either *m* or *r* stereochemistry.

Our results for the tacticity of the obtained polymers are presented in Table 2. The results obtained for the complex Cp_2ZrCl_2 [46], which produces a polymer with no stereoregular control, and the results obtained with the complex (+)-(*S,S*)-(EBTI)ZrBINOL((*S,S*)-1) [15], which produces a highly stereoregular polymer, are presented for comparison. On NMR basis, it was possible to assign and differentiate between RrR and MmM types of rings for the isotactic tetrads, whereas for dissimilar rings RmM, RrM, MrR and MmR, a reliable assignment of the tetrads was not possible.

As can be concluded from Table 2, the polymer produced by complexes **4** and **5**, and the polymer obtained from the chiral complex **7** are totally different as to polymers obtained either by the non-chiral zirconocene or the chiral complex (+)-(*S,S*)-(EBTI)ZrBINOL((*S,S*)-1) [15]. Interestingly, complex **7** produces a cyclic polymer with a high amount of RmR moieties and with almost a total lack MxR and MrM tetrads. The structure of PMCP produced by complexes **4** and **5** are alike, and the amount of the RmR tetrads for these polymers is similar to that obtained with the achiral zirconocene. However, a high content of MmM and MxR tetrads makes these polymers unique. In conclusion, the use of racemic benzamidate or chiral benzamidate group IV complexes allows to produce complementary types of PMCP polymers as compared to other achiral and chiral metallocenes. Important to point out that the ratio between MAO and catalysts are not the same as to the comparison complexes. For the cyclization process, we have found very little effect of the MAO on the polymerization stereoselectivity.

2.4. Dehydrogenative coupling of silanes

The bis-benzamidate complexes **1–2** were found to be active in the polymerization of some mono- and di-substituted silanes (Eq. (1)):



The formation of polysilanes was monitored by ^{29}Si NMR spectroscopy using the INEPTND method in combination with ^1H NMR spectroscopy. As the polymer evolves, the quartet signal of the mono-substituted silane (RSiH_3) is replaced by a triplet signal of the end-group of the formed polymer chain, and a doublet signal of the internal

Table 2
 ^{13}C NMR data for carbons 4 and 5 of PMCP produced by complexes **4**, **5** and **7**

Entry	Catalyst	M:MAO	T ($^{\circ}\text{C}$)	MmM (%)	MrM (%)	RrR + RxM (%)	RmR (%)	MmR + MrR (%)
1	4	1:100	25	26.1	7.0	5.1	37.5	24.3
2	5	1:100	25	24.4	9.4	15.3	33.7	17.2
3	7	1:800	50	30.1	2.4	5.3	61.1	1.1
4	Cp_2ZrCl_2	1:2300	25	10.1	1.8	49.1	34.0	5.0
5	(+)-(S,S)-(EBTI)ZrBINOL((S,S)-1)	1:1200	25	15.1	0.0	53.6	6.6	38.7

(–SiHR–) moieties from the growing chain. For bis-substituted substrates, only the doublet signal of the end group can be observed on the ^{29}Si NMR spectrum (a polarization transfer from H to Si is required). In addition, ^{29}Si NMR is useful for the determination of the polysilanes type. Hence, linear polymers have signals between –60 and –70 ppm, whereas cyclic polysilanes have signals in the range of –20 to –30 ppm, and branched polysilanes appeared with signals between 10 and 30 ppm [47]. The conversion or the end of the polymerization was determined by ^1H NMR spectroscopy, using the integration ratio between the Si–H signal of the growing polymer chain and the Si–H signal of the monomer.

Figs. 2 and 3 illustrate the ^1H NMR and ^{29}Si NMR spectra of polysilanes obtained in the polymerization of phenylsilane promoted by the neutral complex **1**.

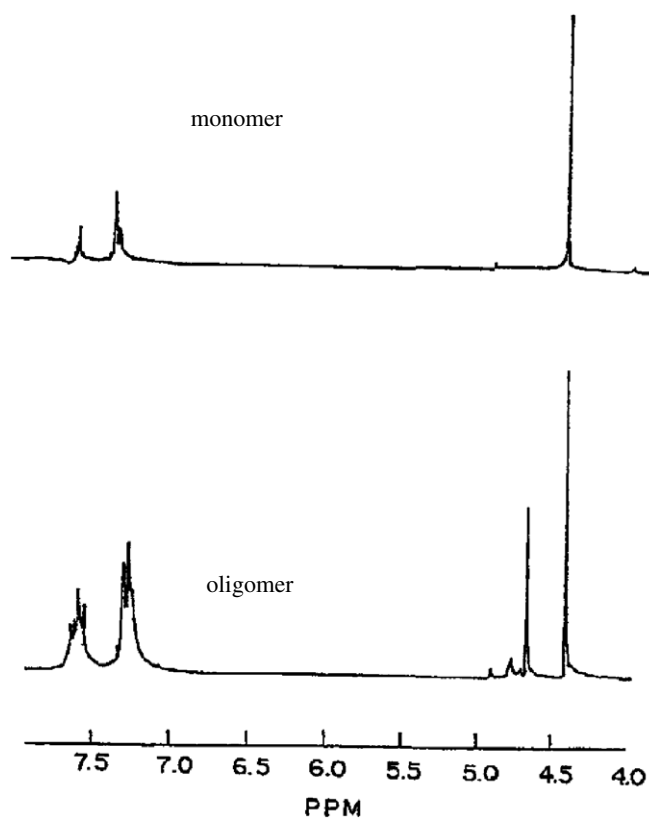


Fig. 2. ^1H NMR spectrum of the monomer and the obtained oligomer in the dehydrogenative coupling of phenylsilane promoted by the neutral complex **1** at 90 $^{\circ}\text{C}$.

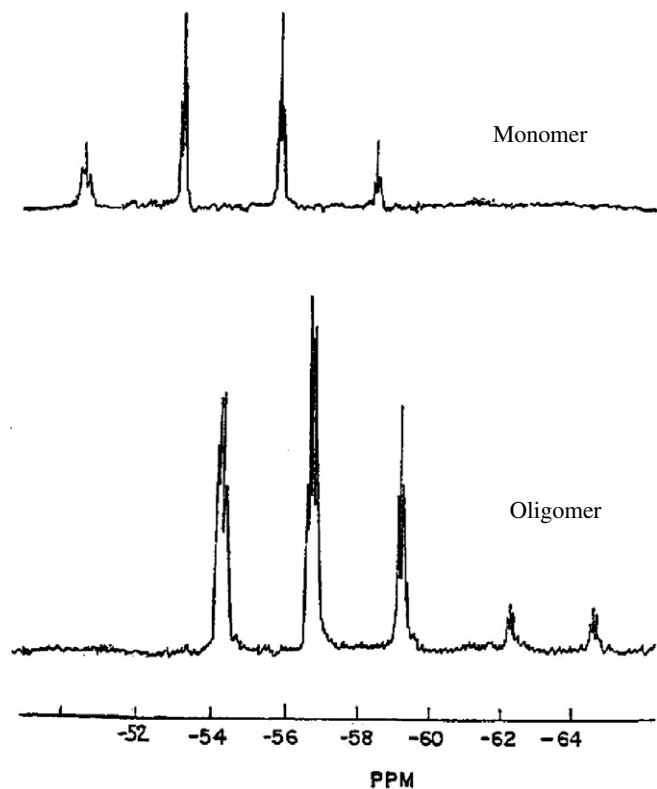


Fig. 3. ^{29}Si NMR spectrum of the monomer and the obtained oligomer in the dehydrogenative coupling of phenylsilane promoted by the neutral complex **1** at 90 $^{\circ}\text{C}$.

Complexes **1** and **2** exhibit low oligomerization activity in toluene at room temperature. However, when the reaction is carried out at 90 $^{\circ}\text{C}$, most of the substrates can be easily oligomerized/polymerized, yielding remarkable conversions (see Table 3).

All the dehydrogenative coupling studies were performed both in NMR sealed J-Young tubes, and in large scales in Schlenk glass reactors to obtain larger quantities of the oligomers/polymers. The resulted compounds were isolated, washed out, and analyzed by GPC (gel permeation chromatography) and multinuclear NMR spectroscopy. The polymerization results are presented in Table 3.

As can be concluded from Table 3, complex **1** is able to polymerize only small and not bulky substrates, such as phenylsilane and diethylsilane to form mixtures of oligomers; whereas the titanium complex **2** is able to polymerize only the smallest phenylsilane to high molecular weight polymer but unexpectedly is unable to oligomerize any

Table 3
Oligomerization/polymerization data for the dehydrogenative coupling of silanes promoted by the neutral complexes **1** and **2**^a

Substrate	Complex	Reaction time (h)	Conversion (%)	Polymerization results							
				Dimer (%)	Trimer (%)	Tetramer (%)	Octamer (%)	Higher fractions			
								%	<i>M_w</i>	MWD	
PhSiH ₃	1	5	91	30	40	30	–	–	–	–	–
Et ₂ SiH ₂	1	4	66	10	10	20	60	–	–	–	
PhSiH ₃	2	5	88	–	–	–	–	70	4800	1.60	
								30	13,500	1.45	

^a Complex **1** (8.8 mmol), Complex **2** (7.7 mmol), 20 mL toluene, 0.1 mol of silane at 90 °C.

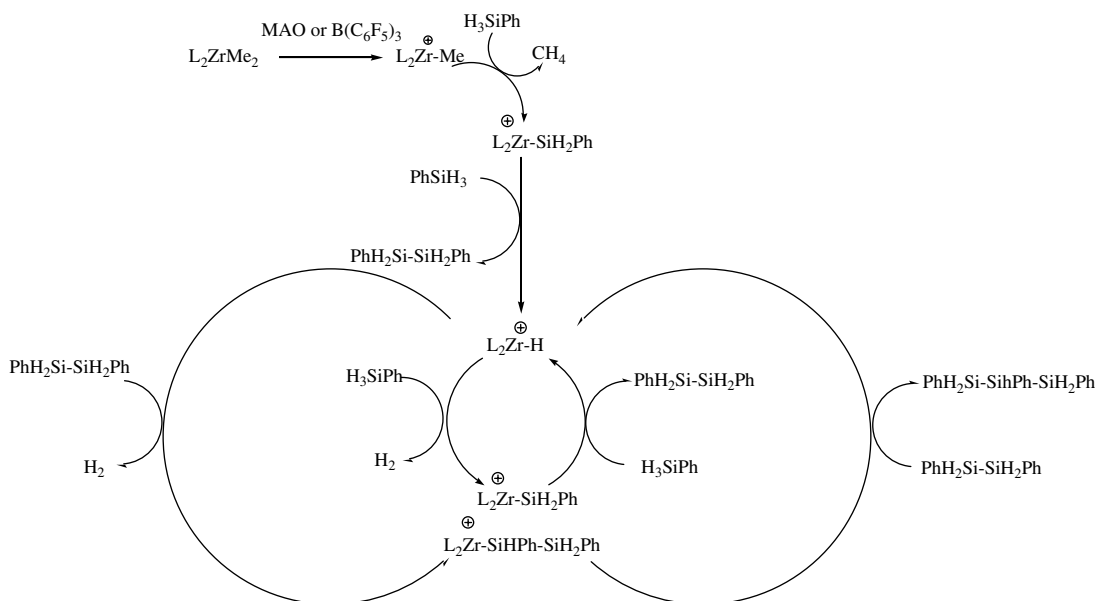
other di-substituted substrates. Interestingly, for both neutral complexes, attempts to polymerize challenging di-substituted monomers like Ph₂SiH₂ or PhMeSiH₂ were unsuccessful. Indication on the sensitivity of this complex towards the steric bulkiness of the substrates is obtained by the fact that complex **2** was able to polymerize phenylsilane but unable to react with diethylsilane or other di-substituted silanes.

Remarkably, the single site complex **1** is able to produce linear dimers, trimers, tetramers and octamers, but not pentamer and hexamers. This fact is similar for metallocene complexes when disilanes are polymerized with higher activity when compare to monosilanes [30]. Hence, a dimer formed in the first polymerization cycle, reacts with the catalyst faster than the monomer to form a trimer. However, the tetramer is formed as the result of the reaction of two dimers and the octamer is formed from two tetramers. The octamer is the thermodynamic sink obtained with the highest conversion presumably due to steric reasons. Regarding complex **2**, which produce a bimodal polymer, it was found recently that the complex disproportionate in a toluene solution forming two different species [45], each of them responsible to produce a different oligosilane fraction.

To overcome the steric hindrance of the mono- and di-substituted silanes, and to increase the catalytic activity of both complexes, we have introduced methylaluminoxane (MAO) and B(C₆F₅)₃ as a co-catalysts to obtain the cationic complexes. Interestingly, for complex **1**, the reaction with MAO produces the cationic complex **4**, and a similar reaction with B(C₆F₅)₃ produces complex **5**. Both complexes exhibit remarkable activities and selectivities for the polymerization of mono- and di-substituted silanes.

The conceptual reasoning of use of a co-catalyst for the formation of a cationic complex is rendered by the fact that the cationic complex has a more coordinative unsaturated geometry, as compared to the neutral complex, and as a result, bulky substrates will be able to approach the active metal center of the complex. In addition, we also expected that a positive charge on the metal will promote silane insertions, inducing better polymerization activities. A plausible mechanism for the formation of the oligomers/polymers is presented in Scheme 2.

The polymerization results for the dehydrogenative coupling of silanes promoted by the cationic complexes **4** and **5** are presented in Table 4. Small silanes were easily polymerized to products contained between 15 and 40 silicon atoms



Scheme 2. Mechanism for the oligomerization of silanes by the cationic benzamidinate complexes (only one catalytic site is presented for clarity).

Table 4
Dehydrogenative coupling of silanes promoted by the cationic complexes **4** and **6** at 90 °C

Substrate	Reaction time (h)	Catalyst	Conversion ^a (%)	Polymerization results			
				Dimer ^b (%)	Trimer ^b (%)	Tetramer ^b (%)	Polymer % ^b M_n M_w MWD
PhSiH ₃	4	4 Zr:Al = 1:50	98	–	–	–	100 2650 4800 1.95
PhSiH ₃	4	6 Zr:B = 1:1	92	3	4	3	90 1700 2400 1.42
Ph ₂ SiH ₂	4	4 Zr:Al = 1:50	67	20	22	58	– – – –
Ph ₂ SiH ₂	4	6 Zr:B = 1:1	70	20	35	45	– – – –
PhMeSiH ₂	4	6 Zr:B = 1:1	62	20	20	40	20 600 1350 2.25
Et ₂ SiH ₂	4	6 Zr:B = 1:1	88	20	–	–	80 3600 5300 1.46

^a Mass% of the total resulting mixture of oligo-/polymers from the started amount of substrate.

^b Mass% of the polymeric fraction from the total amount of the converted product.

in the chain, whereas for bulky silanes, only oligomers were observed. According to the NMR analysis, all the polysilanes and oligosilanes were characterized having a linear structure. It is important to point out, as expected, for similar silanes the cationic complexes were better catalysts than the corresponding neutral complexes.

To obtain the optimal time of performance in the dehydrogenative coupling, we have study the progress of the reaction as a function of time, as shown for phenylsilane catalyzed by complex **4** (Fig. 4). Fig. 4 shows that during the first 3 h of the reaction, the chain grows linearly with a monomer insertion rate of 7–8 units/h. After that period, the reaction rate starts to decelerate, due to monomer starvation (the reaction runs to 98% yield, forming 25 monomeric units on the chain).

When comparing under the same reaction conditions the dehydrogenative coupling of phenylsilane with the cationic complexes **4** or **6** (Table 4) and the neutral complex **1** it can be concluded that the former complexes are able to polymerize the silane in better yields (100%) and better molecular weights (compare octamer with 25 monomeric units in

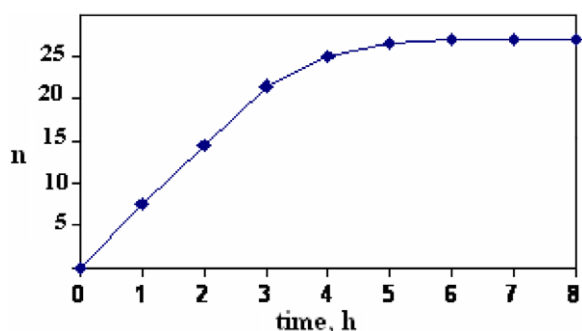


Fig. 4. Polymerization of phenylsilane by complex **4** activated by MAO in toluene at 90 °C. n = the number of monomeric units in the polysilane.

the polymer chain). These cationic complexes were also able to polymerize bulky di-substituted silanes, which have not been observed previously for any other organometallic complex. Regarding the effect of the co-catalysts, we have found no major discrepancies among MAO and the tris(pentafluorophenyl)borane indicating that similar cationic motifs are formed. Our attempts to perform the coupling of silanes with a cationic titanium complex **5** were unsuccessful presumably due to the formation of Ti (III) observed by the reaction of Ti(IV) and MAO [45].

3. Conclusions

Complexes **4**, **5** and **7** were found to be active complexes in the polymerization of 1,5-hexadienes. For the cationic bis-benzamidinate complexes **4** and **5** the *cis* to *trans* ring closure ratio was found to be close to 50:50%. For complex **7**, containing the chiral myrtanyl moiety on the ancillary ligand, a slight preference towards the *trans* closure was observed. Complex **7** produces the polymer with higher amount of MxR tetrad moieties and with almost full absence of MxR and MrM tetrads, as compared to the other chiral zirconium complexes, described in literature. The structure of PMCP produced by complexes **4** or **5** is quite similar. The percentage of RmR tetrads for these polymers is comparable to those obtained with a simple zirconocene. However, a high content of MmM and MxR tetrads makes these polymers different from all types of PMCP described previously.

Complexes **1** and **2** were found to be active in the polymerization of non-bulky phenylsilane. The zirconium complex **1** produced oligomers only, whereas titanium complex **2**, forms a bimodal polymer with 28–88 monomeric units. To our knowledge, this is the longest linear polysilanes-obtained using an organometallic complex. The large

coordinative unsaturation of the cationic complexes **4** and **6** allows the polymerization of bulky mono- and di-substituted silanes. This is the first example in which cationic octahedral group 4 complexes are used for the dehydrogenative coupling of silanes. The degree of polymerization was strongly dependent on the bulkiness of the silane substrates.

4. Experimental

4.1. General procedure

All manipulations with air-sensitive materials were carried out with the rigorous exclusion of oxygen and moisture in a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-6} Torr) line, or in a nitrogen filled 'Vacuum Atmospheres' glove box with a medium capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Deuterated solvents were stored under nitrogen over Na/K alloy. All solvents for vacuum line manipulations were stored in vacuum over Na/K alloy. All silanes (Aldrich) were distilled and dried using a Davison 4 Å molecular sieve, and transferred into calibrated storage tubes connected to high vacuum line. Solid methylalumoxane (MAO) was prepared from a 30% suspension in toluene (Witco) by vacuum evaporation of the solvent at $25^\circ C/10^{-5}$ mm Hg and was stored in the glove box. 1,5-Hexadiene was distilled and dried using a Davison 4 Å molecular sieve.

The synthesis of the bis-benzamidinate dimethyl complexes of Zr and Ti were performed as described previously [35k].

NMR spectra were recorded on a Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for 1H NMR, ^{13}C NMR and ^{29}Si NMR are referenced to internal solvent resonance, and reported relative to tetramethylsilane.

Melting points were determined on a Differential Scanning Calorimeter (DSC). Three runs (first heating, cooling, second heating) were performed at a heating rate of $10^\circ C/min$ in the temperature range 30–190 $^\circ C$. The second-heating melting peak temperature was taken as a melting point.

GPC measurements were carried out on Water's Alliance 2000 instrument: for polysilanes at $90^\circ C$, using toluene (HPLC) as a mobile phase and Water's Styragel HT columns, and for poly-1,5-hexadienes in trichlorobenzene at $150^\circ C$, using the same type of columns. Molecular weights are referenced to polystyrene standards (Aldrich).

4.2. Polymerization of silanes in NMR tubes

All polymerization experiments with silanes were performed in Teflon valve-sealed tubes. A certain amount of catalyst (and co-catalyst in part of experiments) was weighted in a glove box, and then added to an NMR tube. The closed tube was attached to a high vacuum line

(10^{-6} mmHg), and a certain amount of a dry deuterated solvent was transferred into the tube, to dissolve the catalyst. An exact amount of silane was vacuum-transferred to the frozen tube. The tube was placed into a glycerol/oil bath (according to the reaction temperature), and the reaction was started. Monitoring of the reaction was performed by 1H NMR spectroscopy. At the end of polymerization, the solvent and the non-reacted silane were removed by vacuum transfer to another NMR tube, and the contents of the latter was analyzed by NMR spectroscopy in order to confirm the presence of dimerization product and a non-reacted monomer. The reactions were finally quenched by the addition of water. The resulted polymer (or oligomer) was dissolved in toluene at $90^\circ C$ and the toluene fraction was evaporated, and the resulted poly-/oligosilane was dried in vacuum.

4.3. Large scale polymerization of silanes

Polymerization was carried out in a 50 ml Schlenk vessel equipped with magnetic stirrer. The Schlenk vessel was charged in glove-box by 5 mg of the catalyst. Then the Schlenk vessel was connected to a vacuum line, and 10–15 ml of the dry solvent was added by syringe. After dissolving the catalyst, 10 ml of pure dry silane was added, the Schlenk vessel was placed into the oil bath at $90^\circ C$ and the polymerization started. At the end of polymerization time the reaction was quenched by HCl/methanol (1:1 mixture), and the toluene fraction was isolated. In the case of monosilanes, toluene and dimeric products were transferred to a Schlenk vessel, and the dimeric products were separated by distillation. The solid/oily fraction was dried under vacuum.

4.4. Polymerization of 1,5-hexadiene

Polymerization was carried out in a 50 ml Schlenk vessel equipped with magnetic stirrer. The Schlenk vessel was charged in a glove-box with 5 mg of the catalyst and the calculated amount of MAO. Then the Schlenk vessel was connected to a high vacuum line, and 10–15 ml of dry toluene was added by syringe. After dissolving the catalyst and the formation of the active species, 10 ml of pure dry 1,5-hexadiene was added, and the polymerization started. At the end of the polymerization time, the reaction was quenched by the addition of methanol. Solid polymer was filtered, washed with a large amount of methanol and dried. The toluene fraction was isolated and toluene was removed by vacuum. The toluene soluble polymer was obtained and dried.

4.5. Calculation of the number of monomeric units in the resulted silane oligomer (n)

At the end of reaction, the number of monomeric units in the formed oligomer (n) was calculated as $M_n/106$, where 106 is M_w of one monomeric silane repeating unit. For

every reaction time, n was calculated based on the integration of the corresponding ^1H NMR signal, related to the same integration on the end of reaction: $\text{Int}_i/\text{Int}_n = n_i/n$, where Int_i is an integration on the time I , Int_n is an integration on the end of reaction; n_i is a number of monomeric units at the time “ i ” and n is a number of monomeric units in the obtained oligomer.

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