

Journal of Molecular Catalysis A: Chemical 193 (2003) 207-215



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Study on aminosilane compounds as external electron donors in isospecific propylene polymerization

Hiroyuki Ikeuchi, Takefumi Yano, Shigeru Ikai, Hiroshi Sato, Jun Yamashita

Polymer Research Laboratory, UBE Industries Ltd., 8-1 Goiminamikaigan, Ichihara-shi, Chiba 290-0045, Japan

Received 12 March 2001; received in revised form 30 July 2002; accepted 30 July 2002

Abstract

Propylene polymerization has been studied with a use of MgCl₂ supported titanium solid catalyst in combination with triethylaluminium (TEA) and a monoamino- or diamino-dimethoxysilane as an external electron donor. The aminosilanes having a bulkier amino group, or two amino groups show a tendency to give lower isotacticity and broader molecular weight distribution of polymers obtained. Specifically the aminosilanes with piperidinyl group(s) were found to be highly isospecific external donors. ¹³C and ¹H NMR studies on the mixtures of TEA and di(piperidinyl)dimethoxysilane (DPIP) indicate that TEA forms a Lewis acid/base adduct through the interaction of aluminum and oxygen atom of methoxy group in the silane as have been reported in the case of TEA and di(hydrocarbyl)dimethoxysilanes.

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Keywords: Aminosilane; Isospecific propylene polymerization; Polymerization

1. Introduction

The growing number of industrial applications of polypropylene to structural materials, particularly in the fields of automobiles and electric appliances in a large volume, has been indebted to the efforts for raising the isospecificity of polymerization catalyst systems. The combinations of internal and external electron donors for highly active MgCl₂ supported titanium (solid catalyst) and triethylaluminium (TEA) catalyst systems are of significant importance in the stereocontrol polymerization of polypropylenes. Internal electron donors are supported on the solid catalyst and external electron donors are added in the polymerization stage with TEA. It has been explained that the internal electron donors are displaced from the surface of solid catalyst by the reaction with TEA and external electron donor's complex [1,2]. At an early stage of developing the donors, aromatic mono

acid esters were thought to be excellent for giving highly isotactic polypropylenes [3]. After the combination of a phthalic acid diester and a silane compound as the internal and external electron donors, respectively, has been described in a patent, a quite number of silane compounds has been studied on their performance in propylene polymerization [4–25]. Further studies on the external donors have lead to the discoveries of tetramethylpiperidine [26,27] in place of the silane compounds and 1,3-dimethoxypropane internal donors [28,29] which form highly isospecific catalyst systems without any external donor. Though the silane external donors play an important role in improving isotacticity of polymers, they also influence the catalyst activity, molecular weight and molecular weight distribution of polymers produced [21,26]. Until now, the relationships between the structure of the silane compounds and their polymerization behavior have been discussed in details by Harkonen et al. [5,13,16],

and Harkonen and Seppala [7–10]. It has been generally recognized that hydrocarbon substituents with an appropriate size and an electron density of oxygen atoms for hydrocarbyl–hydrocarbyloxysilanes as external donors are required to produce highly isotactic polypropylenes.

The one category of silane external donors being active and isospecific catalyst component, includes di(hydrocarbyl)dimethoxysilanes in which at least one hydrocarbon group has a secondary or tertiary carbon directly linked to the silicone atom such as *iso*-propyl, *tert*-butyl, cyclopentyl, cyclohexyl, and phenyl groups.

Examples of those di(hydrocarbyl)dimethoxysilanes are di(*iso*-propyl)dimethoxysilane, *tert*-butyl(methyl)dimethoxysilane, cyclohexyl(methyl)dimethoxysilane, di(cyclopentyl)dimethoxysilane, and di(phenyl)dimethoxysilane.

On the other hand, a dihydrocarbyl amino and cyclic amino groups are structurally similar to sec-hydrocarbyl groups in a point that the secondary carbon atom is replaced by the nitrogen atom. The use of a cyclic aminosilane compound as an external donor has appeared first in a patent [30] in which the cyclic amino substituent disclosed is a methyl substituted piperidinyl group. After that, however, no detail study on the catalyst behavior of aminosilane compounds in propylene polymerization has been reported. In this paper, we report the propylene polymerizations with various aminosilane compounds as external electron donors.

2. Experimental

2.1. Silane compounds

Di(amino)dimethoxysilanes and hydrocarbyl(amino)dimethoxysilanes were prepared by the reaction of an amidolithium with tetramethoxysilane and hydrocarbyltrimethoxysilane, respectively. For example, the synthesis of di(piperidinyl)dimethoxysilane (DPIP) was carried out as follows.

In a 500-ml flask were placed 80 ml n-heptane, and 19.2 g (0.2 mol) of piperidine. Thereo was dropwise added, from a dropping funnel, 133 ml (0.22 mol) of a *n*-hexane solution of 1.66 M of butyllithium slowly with water-cooling. After the completion of the dropwise addition, the mixture was stirred at room temperature for 1 h. Then, 15.2 g (0.1 mol) of

tetramethoxysilane was dropwise added slowly with water-cooling. After the completion of the dropwise addition, the mixture was stirred at room temperature for 6h. After confirming, by gas chromatography, the formation of a sufficient amount of intended product, the mixture was filtered by a G4 glass filter at room temperature to remove the precipitate. The precipitated solid on the glass filter was washed with each 30 ml of heptane three times. The filtrate was subjected to distillation under reduced pressure to sufficiently vaporize solvent contained in the filtrate, and the resulting liquid was subjected to secondary distillation to recover an intended product, di(piperidinyl)dimethoxysilane. The product had a boiling point of 99.5 °C per 3 mmHg and a purity (by gas chromatography) of 96.8%. The yield of di(piperidinyl)dimethoxysilane was 92.7% based on piperidine fed. The product was identified by elementary analysis and mass spectrometry. The elementary analysis data of the product was C = 55.0 wt.%, H = 9.8 wt.%, N = 10.6 wt.%, respectively (theoretical value: C = 55.8 wt.%, H =10.1 wt.%, N = 10.8 wt.%).

The purities of di(amino)dimethoxysilanes and hydrocarbyl (amino)dimethoxysilanes are listed in the tables together with catalyst performances.

3. Propylene bulk polymerization

Polymerizations were carried out as follows.

To a 2-1 autoclave added *n*-heptane solutions of TEA (2.2 mmol) and a silane compound (0.36 mol), a *n*-heptane slurry of solid catalyst (8 mg), hydrogen gas (3.61), liquefied propylene (1.51). The mixture was stirred for 10 min at 10 °C to perform pre-polymerization. After that, the autoclave was heated to 70 °C within a few minutes to perform main-polymerization for 60 min at 70 °C.

TEA was purchased from TOSOH AKZO Co. The magnesium chloride supported titanium solid catalyst (named THC) having the titanium content of 2.0 wt.% was purchased from TOHO CATALYST CO. LTD.

4. Polymer analysis

Molecular weights (M_n and M_w) were obtained by gel-permeation chromatography analysis on a Waters

150-CV gel-permeation chromatograph equipped with a Shodex AT-806MS column using polystyrene standards sample and *o*-dichlorobenzene as solvent at 145 °C. Isopentad percents (mmmm%) of polymers were determined by ¹³C NMR (100.40 MHz) spectroscopy (JEOL EX-400) for *o*-dichlorobenzene/C₆C₆ (4/1) solutions at 135 °C (scans = 8,000) with TMS as a standard. The ¹³C and ¹H NMR (399.65 MHz) data for the mixtures of a silane compound and TEA were obtained using C₆D₆ or CDCl₃ as a solvent at room temperature.

5. Results and discussion

Until now, aminosilanes have been scarcely studied as external donors for propylene polymerization in contrast with hydrocarbyloxysilanes. Therefore, to investigate the structural influence of amino substituents in hydrocarbyl(amino)dihydrocarbyloxysilanes or di-(amino)dihydrocarbyloxysilanes on catalyst performance is very intriguing, corresponding to hydrocarbon substituents in di(hydrocarbyl)dihydrocarbyloxysilanes.

Table 1 lists the catalyst performances of various amino(alkyl)dimethoxysilanes and di(amino)dimethoxysilanes together with that of di(*iso*-propyl)dimethoxysilane for a comparison purpose. Interestingly, nearly the same polymer isotacticities (mmmm%) were observed for di(*iso*-propyl)dimethoxysilane (DIP) and bis(dimethylamino)dimethoxysilane (Run 1 and 2). The *iso*-propyl group is geometrically similar to dimethylamino group, which has an electron pair on nitrogen atom being potentially capable of interacting with a Lewis acid as TEA. The interaction of an aminosilane with TEA will be discussed later in the present study by ¹³C and ¹H NMR.

Table 1

Comparison of catalyst performance for various mono- and bis-amino silane compounds

Run no.	Silane compounds	Activity	$M_{ m w}$ $ imes$ 10^{-4}	$M_{\rm w}/M_{\rm n}$	mmmm			
	$ \frac{R^{1}R^{2}Si(OCH_{3})_{2}}{R^{1}} \qquad R^{2} $		Boiling temperature (°C per mmHg)	GC purity (%area)	ratio			(%)
1	iso-Propyl	iso-Propyl	86.0/50	98.5	1.00	16.0	5.3	97.4
2	Di(methyl)amino	Di(methyl)amino	85.0/100	98.5	0.83	21.7	6.1	97.3
3	Di(ethyl)amino	Methyl	55.0/21	97.6	0.82	14.2	4.6	97.3
4	Di(ethyl)amino	Ethyl	65.5/20	96.3	0.94	_	-	97.4
5	Di(ethyl)amino	n-Propyl	69.5/15	97.6	0.92	22.1	5.3	97.8
6	Di(ethyl)amino	Di(ethyl)amino	75.0/10	98.1	0.80	12.4	4.7	97.2
7	Di(ethyl)amino	Di(n-propyl)amino	83.0/6	96.1	0.68	9.10	6.2	96.9
8	Di(ethyl)amino	Di(iso-propyl)amino	105.2/13	97.1	0.71	24.2	10.9	95.7
9	Di(n-propyl)amino	Di(n-propyl)amino	86.0/4	97.6	0.54	12.6	6.0	95.1
10	Di(iso-propyl)amino	Methyl	72.0/19	98.1	0.58	16.2	6.4	97.0
11	Di(iso-propyl)amino	Ethyl	77.0/13	96.8	0.84	15.1	8.1	97.2
12	Di(iso-propyl)amino	n-Propyl	66.5/5	96.1	0.79	15.8	9.2	97.3
13	Di(iso-propyl)amino	Di(n-propyl)amino	127.2/14	96.6	0.70	20.0	10.4	95.3
14	Ethyl(phenyl)amino	Methyl	77.1/2	97.1	0.58	21.5	9.1	97.5
15	Ethyl(phenyl)amino	n-Propyl	105.8/3	97.6	0.68	25.1	10.7	97.4
16	Ethyl(phenyl)amino	Ethyl(phenyl)amino	152.5/2	99.8	0.52	12.1	9.9	96.6
17	Ethyl(cyclohexyl)amino	Methyl	75.2/3	96.7	0.55	23.8	8.9	97.5
18	Ethyl(cyclohexyl)amino	n-Propyl	98.2/2	99.7	0.71	23.5	10.7	97.5
19	Ethyl(cyclohexyl)amino	Ethyl(cyclohexyl)amino	144.0/2	99.5	0.56	14.2	8.2	96.6
20	Di(phenyl)amino	Methyl	130.6/2	98.6	0.29	15.2	11.6	94.0
21	bis(Trimethylsilyl)amino	Methyl	94.5/14	98.7	0.95	20.3	12.0	93.7
22	bis(Trimethylsilyl)amino	Ethyl	114.5/15	95.3	0.98	15.1	8.3	91.8
23	bis(Dimethylsilyl)amino	Methyl	56.1/6	93.5	0.84	26.4	11.9	95.7

Polymerization conditions: propylene bulk polymerization; silane compound/TEA (molar ratio) = 1/6; H₂ = 3.61; pre-polymerization = $10 \degree C$, $10 \min$; main-polymerization = $70 \degree C$, $60 \min$.

A group of monoaminosilanes $[R'(R_2N)Si(OCH_3)_2;$ R' is methyl, ethyl, or *n*-propyl group and R is ethyl, iso-propyl, phenyl, cyclohexyl, trimethylsihyl, or dimethylsiliyl group] gave higher mmmm values (more than 95%), except for particular aminosilanes with diphenylamino (Run 20) and bis(trimethylsilyl)amino (Run 21 and 22) substituents. It seems that there exists the most preferable total volume of substituents (R' and R_2N) and the most preferable angle of C-N-C for R₂N to realize catalyst isospecificities of a higher level. The mmmm values for di(amino)dimethoxysilanes $[(R_2N)_2Si(OCH_3)_2]$ seem to decrease with a total volume of the two amino substituents in the following order; $(Me_2N_{-})_2 >$ $(Et_2N-)_2 > (Et_2N-)(n-Pr_2N-) > [Et(cyclohexyl)N-]_2$ = $[Et(Phenyl)N_{-}]_2 \gg (Et_2N_{-})(iso_{-}Pr_2N_{-}) > (iso_{-}Pr_2N_{-}) > (iso_{-}Pr_2N_$ $Pr_2N_{-}(n-Pr_2N_{-}) \ge (n-Pr_2N_{-})_2$. The present results are somewhat fitted by the report [26] that, in the type of R₂Si(OCH₃)₂ donors, a stereocontrol by the donors is achieved in the following order R = Me < n-butyl < iso-butyl = phenyl < iso-propyl. In fact, among the various diaminosilanes, (Me₂N)₂Si(OCH₃)₂ gives the highest isotactic polymer corresponding to DIP.

Distinct relationships have not been found among the catalyst activity, molecular weight, and its distribution for all the external donors. Aminosilanes show lower activities compared to DIP. Larger $M_{\rm w}/M_{\rm n}$ ratios are observed for the diaminosilanes and the mono amino silanes having bulkier amino substituents: ethyl(phenyl)amino (Run 14–16), ethyl(cyclohexyl)amino (Run 17–19), diphenylamino (Run 20), bis(trimethylsilyl)amino (Run 21 and 22), and bis(dimethylsilyl)amino (Run 23) groups. Broadening of molecular weight distribution for some donors would be accounted for by the considerable formation of less isospecific active sites together with isospecific ones. For the donors, [ethyl(phenyl)amino]dimethoxysilane and [ethyl(cyclohexyl)amino]dimethoxysilane, however, the $M_{\rm w}/M_{\rm n}$ ratios are large without reducing polymer isotacticity.

Table 2 shows the catalyst performances of a series of (piperidinyl)dimethoxysilanes, [(piperidinyl)RSi-(OCH₃)₂ and (piperidinyl)₂Si(OCH₃)₂] and some of (cyclohexyl)-dimethoxysilanes [(cyclohexyl)RSi-(OCH₃)₂]. The (piperidinyl)dimethoxysilanes give higher mmmm values compared with the analogous (cyclohexyl)dimethoxysilanes (Runs 24–26 versus Runs 27, 28 and 37), though no substantial differences have been observed for activity and molecular weight. All the donors of a series of (piperidinyl)RSi(OCH₃)₂ have high isospecificity and the values of mmmm are nearly at the same high level (97.3–97.9%) for the substituents from R = methyl to cyclohexyl group.

Table 2	2
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Comparison of catalyst performance for various piperidinyl silane compounds

Run no.	Silane compo	ounds	Activity	$M_{ m w} imes10^{-4}$	$M_{\rm w}/M_{\rm n}$	mmmm		
	$R^1 R^2 Si(OCH_3)_2$		Boiling temperature (°C per mmHg)	GC purity (%area)	ratio			(%)
	R^1 R^2							
24	Cyclohexyl	Methyl	196/760	98.0	0.96	17.3	6.3	96.6
25	Cyclohexyl	Ethyl	-	-	0.80	16.3	4.6	96.7
26	Cyclohexyl	Cyclohexyl	_	_	1.00	26.8	11.2	97.2
27	Piperidinyl	Methyl	77.8/19	97.0	0.65	17.1	6.0	97.6
28	Piperidinyl	Ethyl	91.0/17	97.6	0.79	16.7	6.4	97.8
29	Piperidinyl	n-Propyl	106.6/19	98.7	0.83	16.8	5.2	97.4
30	Piperidinyl	iso-Propyl	77.0/15	96.8	0.89	23.1	7.7	97.9
31	Piperidinyl	n-Butyl	77.0/3	97.9	0.99	12.5	3.9	97.7
32	Piperidinyl	iso-Butyl	71.5/5	97.7	0.75	13.5	4.9	97.6
33	Piperidinyl	tert-butyl	67.0/5	99.2	0.93	18.0	6.2	97.9
34	Piperidinyl	1,1,2-Trimethyl-propyl	85.9/4	99.0	1.00	22.0	10.5	97.3
35	Piperidinyl	Cyclopentyl	97.7/4	96.1	0.81	22.8	8.7	97.9
36	Piperidinyl	Cyclohexyl	101.2/4	97.2	0.58	20.2	8.2	97.5
37	Piperidinyl	Piperidinyl	99.5/3	96.8	1.02	20.2	6.0	98.5

Polymerization conditions: propylene bulk polymerization; silane compound/TEA (molar ratio) = 1/6; H₂ = 3.61; pre-polymerization = $10 \degree C$, $10 \min$; main-polymerization = $70 \degree C$, $60 \min$.

Interestingly, di(piperidinyl)dimethoxysilane (Run 37) shows the highest mmmm value (98.5%) among a series of (piperidinyl)dimethoxysilanes, in consistent with the fact that di(cyclohexyl)dimethoxysilane gives also the highest mmmm value relative to other (cyclohexyl)dimethoxysilanes. This indicates that the piperidinyl substituents as well as the cyclohexyl ones play a determinant role in the formation of stereo configuration of active site.

The larger M_w/M_n ratios have been obtained for di(cyclohexyl)dimethoxysilane and the mono-piperidinylsilanes having the second bulkier substituents, 1,1,2-trimethylpropyl (Run 34), cyclopentyl (Run 35), and cyclohexyl (Run 36) groups. From these results, it is incomprehensive that broaden molecular weight distribution was not realized by di(piperidinyl)dimethoxysilane which is structurally similar to di(cyclohexyl) dimethoxysilane.

6. NMR study on the mixture of TEA and aminosilane

The roles of internal and external electron donors have been often discussed in abundant studies on MgCl₂-supported TiCl₄ catalysts for propylene polymerization. Since it is quite difficult to identify experimentally active species of polymerization located



Fig. 1. The ¹³C and ¹H NMR spectra of TEA [34] in CDCl₃.

Fig. 2. The ¹H NMR spectra of DPIP and TEA/DPIP (1/1) complex in CDCl₃.

on a heterogeneous MgCl₂ support, the interaction of the donors with a central titanium atom of the active species is not well-understood. In fact, except for polymerization kinetics, experiments conducted for the assumptions of the role of each catalyst component and polymerization mechanism were the chemical analysis on the reaction mixtures of catalyst components such as a MgCl₂-supported solid catalyst with TEA, and an external donor with TEA. The interaction of TEA and a hydrocarbyloxysilane has been studied mainly by IR, ²⁹Si NMR, ¹³C NMR, and ¹H NMR analysis and a Lewis acid base adduct (Al/Si = 1/1) was identified for the mixture of them at room temperature [31,32]. In the excess of TEA or at a high temperature, the silanes undergo exchange reaction to some extent to give ethyl substituted silanes and hydrocarbyloxy(diethyl)aluminum. Also, it has been known that an internal donor of the supported catalysts



Fig. 3. The ¹³C NMR spectra of DPIP and TEA/DPIP (1/1) complex in CDCl₃.

is stripped off when contacted with TEA or a mixture of TEA and the hydrocarbyloxysilane external donor [33]. From these facts, it is understandable to have the hypothesis that either the silane compounds external donor or the TEA/silane compounds complex plays a role of one of the constituents of the active species.

As shown in the present work, the di(amino)dimethoxysilanes are different from di(hydrocarbyl)dimethoxysilanes in such a respect that the formers would be capable of interacting with TEA as a Lewis acid through the methoxy groups and/or the amino groups. Furthermore, in the case of the di(amino)dimethoxysilanes, the exchange reaction with TEA could occur even at a lower temperature.

Hence, it is quite interesting to study the interaction between TEA and the aminosilanes in order to understand how it functions as an external donor. At first, mixtures of DPIP and TEA in different mole ratios were analyzed by ¹H NMR spectroscopy using C_6D_6 as a solvent, and the three CDCl₃ solutions of di(isopropyl)dimethoxysilane (DIP), DPIP, and [di(isopropyl)di(piperidinyl)]silane (DPIP-DIP) containing TEA in Si/Al (molar ratio) equal to 1, respectively, were measured by ¹³C and ¹H NMR spectrometers.

As the ¹³C and ¹H NMR spectra as shown in Figs. 1–3 show peak numbers and patterns for the mixture of TEA and DPIP are just a sum of the peaks for each of the component, though the peaks shifted to some extent depending upon kinds of the protons for ethyl groups of TEA [34], the piperidinyl rings, and the methoxy groups. The exchange reaction of the ethyl groups of TEA and the piperidinyl rings of DPIP does not seem to have taken place.

The ¹H NMR chemical shift of CH₂Al versus DPIP/TEA (molar ratio) was plotted as shown in Fig. 4 and that for CH₃O and CH₂–N–CH₂ against TEA/DPIP (molar ratio) as shown in Fig. 5. The chemical shifts of TEA and those of DPIP do not vary at Si/Al and Al/Si molar ratios >1. These results indicate that TEA and DPIP forms a complex (1:1) and that the complex exchanges the coordinated TEA or DPIP for free TEA or DPIP at a speed that is faster than the ¹H NMR time scale.

Table 3 summarizes the 13 C and 1 H NMR chemical shifts for DPIP, DIP and DPIP-DIP, before and after complexed with TEA (1:1). Upon the addition of TEA to DIP, the chemical shifts of **CH**₃O moved



Fig. 4. Relationships between DPIP/TEA and $^1\mathrm{H}$ NMR chemical shifts (CH2AI).

quite a great deal as supported by the report that TEA forms a complex with a hydrocarbyloxysilane through the interaction between the hydrocarbyloxy group and aluminum atom.



Fig. 5. Relationships between TEA/DPIP and ${}^{1}H$ NMR chemical shifts (OCH₃ and CH₂N).

Table 3							
Chemical	shifts	of	various	silane	compounds	with	TEA

Silane compounds		Chemical shifts by ¹³ C NMR		Chemical shifts by ¹ H NMR	
		(ppm)	$\delta (+TEA^a)$	(ppm)	$\delta (+TEA^a)$
[(CH ₃) ₂ CH] ₂ Si(OCH ₃) ₂ (DIP)	[(CH ₃) ₂ CH] ₂	17.2	-0.3	1.03	0.08
	[(CH ₃) ₂ CH] ₂	11.2	0.8	1.20	0.04
	$Si(OCH_3)_2$	50.8	2.7	3.56	0.17
$ \begin{pmatrix} H_2C - CH_2 \\ H_2C & N \\ N \end{pmatrix}_2 Si (OCH_3)_2 (DPIP) $	NCH ₂ CH ₂ CH ₂ CH ₂	45.8	0.1	2.89	0.05
	NCH2CH2CH2	27.7	-0.4	1.39	0.10
	NCH ₂ CH ₂ CH ₂	25.5	-0.5	1.54	0.06
DPIP	Si(OCH ₃) ₂	50.2	2.2	3.42	0.15
$\begin{pmatrix} H_2C - CH_2 \\ H_2C & N \\ H_2C - CH_2 \end{pmatrix}_2$ Si [CH(CH_3)_2]_2 (DPIP-DIP)	NCH ₂ CH ₂ CH ₂ CH ₂	47.3	-0.1	2.91	0.00
、 · ·	$NCH_2CH_2CH_2$	27.9	0.0	1.40	0.00
	$NCH_2CH_2CH_2$	25.9	-0.1	1.57	0.00
DPIP-DIP	[(CH ₃) ₂ CH] ₂	17.6	0.0	0.95	0.00
	[(CH ₃) ₂ CH] ₂	12.1	0.0	1.10	0.05

^a Si/Al (molar ratio) = 1; solvent = $CDCl_3$.

Almost no change in the chemical shifts were observed for the mixture of TEA and DPIP-DIP. The interaction between TEA and DPIP-DIP seems to be difficult presumably because of a steric crowding around the Si atom by bulky two *iso*-propyl groups and two piperidinyl groups.

On the other hand, in the case of TEA and DPIP, every chemical shift moved more or less with rather large changes for the CH_3O chemical shifts as observed for the combination of TEA and DIP. This indicates that DPIP also forms a complex with TEA (1:1) through an interaction with the methoxy groups and the aluminum atom. Therefore, no exchange reaction is likely to take place between an ethyl group of TEA and a piperidinyl group of DPIP.

From the data, it can be concluded that the piperidinyl group behaves roughly in the same manner as the hydrocarbyl groups for di(hydrocarbyl)dimethoxysilanes. Additionally, from the fact that DPIP, which is more isospecific as an external donor compared to di(cyclohexyl)dimethoxysilane, has a similar geometrical structure to latter compound, the nitrogen atoms in the aminosilanes could form some interaction with a titanium atom of the active species, bringing up a much severe steric control of propylene insertion.

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