

Theoretical investigations on Ziegler–Natta catalysis: models for the cocatalyst components

Eini Puhakka^a, Tuula T. Pakkanen^a, Tapani A. Pakkanen^{a,*}, Eero Iiskola^{b,1}

^a University of Joensuu, Department of Chemistry, PO Box 111, FIN-80101 Joensuu, Finland

^b Neste Oy Chemicals, PO Box 310, FIN-06101 Porvoo, Finland

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Abstract

Theoretical ab-initio methods have been used to study the stability of the Ziegler–Natta cocatalyst complexes, which consist of aluminium trialkyl and silicon alkoxide compounds. The choice of the basis set indicated that the 6-31G* basis set is the best for aluminium-, oxygen- and silicon-containing compounds. Examination of the interaction energies of the complexes showed that the aluminium compounds determine the stability of the cocatalyst complexes. The silicon alkoxides have a slight effect on the interaction energies, which are to some degree dependent on the size and number of the alkoxy groups of the silicon alkoxides.

Keywords: MO calculations; Ziegler–Natta catalysis; Aluminium; Silicon

1. Introduction

The Ziegler–Natta catalysts are used in the polymerization of α -olefins. They originated from Ziegler's catalyst system, which was applied to the polymerization of ethene. In 1954, Natta noticed the significance of this $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$ catalyst system in the polymerization of propylene, when he succeeded in isolating crystalline polypropylene [1]. Since then, the catalyst system, called the Ziegler–Natta catalyst system, has been one of the most widely studied subjects in catalysis.

The development of the commercial Ziegler–Natta catalysts for propene polymerization can be divided into four different stages [2]. The first catalysts, based on Ziegler's and Natta's catalysts, had weak activity and weak selectivity in polymerization. Therefore catalyst residues and amorphous polypropylene had to be removed. However, the removal of the catalyst residues

became unnecessary when the second-generation catalysts with high activity were developed. The selectivity of the catalysts was only typical of the third-generation catalysts, which made the stereospecific polymerization of α -olefins possible. In addition to controlling the activity and selectivity of the catalysts, the morphology of the catalysts can also be mastered by using the fourth-generation catalysts.

The activity and selectivity of the modern MgCl_2 -supported TiCl_4 catalysts with internal electron donors are based on using aluminium alkyl cocatalysts with external electron donors [3–5]. These cocatalyst complexes are present in the environment of the isotactic active titanium centres, making them more stable and more stereospecific. On the contrary, free external electron donors can poison both atactic and isotactic active centers. However, the sterical effects of electron donors lead to a selective deactivation of the active centers. On account of this, the use of electron donors affects the microstructure and the molecular weights of polypropene.

Ziegler–Natta catalysts are now some of the most important in polymerization chemistry, and this has come about mainly through experimental work. However, the development of computers and calculation

* Corresponding author.

¹ Present address: Microchemistry Ltd., PO Box 45, FIN-02151 Espoo, Finland.

methods has made possible the investigations of catalyst systems with ab-initio calculations, which are very useful in examining properties of catalyst systems and the polymerization mechanism on the molecular level.

In ab-initio studies of the Ziegler–Natta catalyst system the subject most often investigated has been the nature of the titanium–alkyl bond in the catalyst compounds [6–13]. In these studies the existence of the agostic interaction [14–16] between the titanium atom and the alkyl group has been proven. This observation is significant, since the polymerization reaction depends on the formation and breaking of the titanium–alkyl bond. The agostic interaction probably has an effect on the activation energy [17–19] of the polymerization reaction.

A good understanding of the most important structural and electronic properties of the Ziegler–Natta catalysts can be derived from previous studies. However, if we want to obtain a more comprehensive description of Ziegler–Natta catalysis, we must also take into account the properties of the cocatalyst components. At the moment, there are only a few theoretical studies [20–28] giving geometrical parameters for a few models of cocatalyst components.

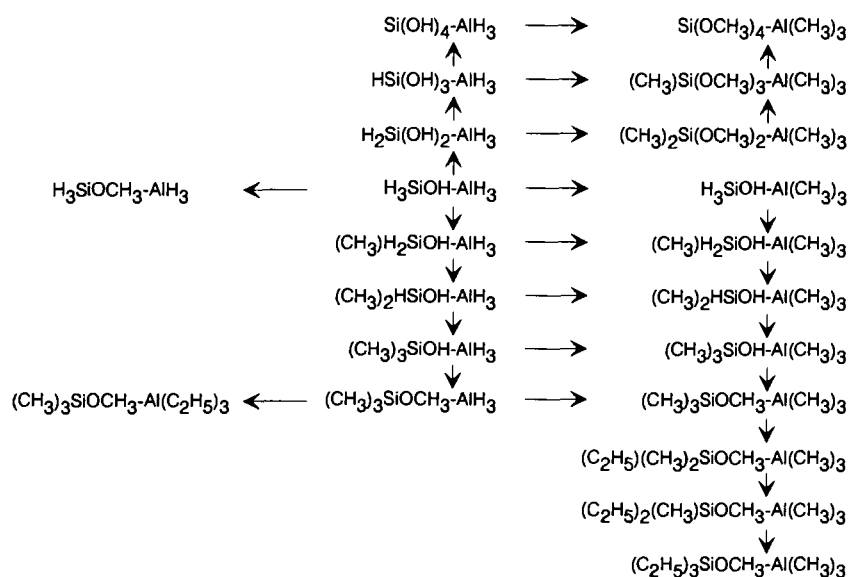
In the present paper we describe an ab-initio study of the Ziegler–Natta cocatalysts. The cocatalysts consist of aluminium alkyl and silicon alkoxide compounds [29]. The most commonly used aluminium alkyls are triethylaluminium and tri-isobutylaluminium. The silicon alkoxide compounds are generally phenylalkoxysilanes, such as phenyltriethoxysilane and diphenyldimethoxysilane. The interaction of the aluminium alkyls with the silicon alkoxides has been studied with ^{13}C and ^{29}Si

NMR spectroscopy [30–32]. These studies have shown that the aluminium alkyl ($\text{Al}(\text{C}_2\text{H}_5)_3$) and the silicon alkoxide ($\text{R}_n\text{Si}(\text{OR}')_{4-n}$, in which $\text{R} = \text{C}_2\text{H}_5$, C_4H_9 or C_6H_5 , $\text{R}' = \text{CH}_3$ or C_2H_5 and $n = 0-3$) form a donor–acceptor complex, which is stable at a 1 : 1 molar ratio. According to the semiempirical study [33] the properties of the silicon alkoxides in the polymerization are more dependent on their structural than electronic factors.

The present study has focused on the interaction between aluminium trialkyls and silicon alkoxides. Because real complexes are quite large, we have used model complexes in our calculations. The models for the aluminium trialkyls have been aluminiumhydride (AlH_3), trimethylaluminium ($\text{Al}(\text{CH}_3)_3$) and triethylaluminium ($\text{Al}(\text{C}_2\text{H}_5)_3$). We have studied complexation of these aluminium compounds with silicon alkoxides with the general formula of $\text{H}_m(\text{CH}_3)_n\text{SiOX}$, $(\text{CH}_3)_m(\text{C}_2\text{H}_5)_n\text{SiOCH}_3$, $\text{H}_m(\text{OH})_n\text{SiOH}$ or $(\text{CH}_3)_m(\text{CH}_3\text{O})_n\text{SiOCH}_3$ ($m = 0-3$, $n = 0-3$, $m + n = 3$ and $\text{X} = \text{H}$ except if $n = 0$, so $\text{X} = \text{H}$ or CH_3).

2. Computational methods

All investigated model cocatalysts complexes (Scheme 1) consisted of two components: the aluminium compound and the silicon alkoxide. These components and complexes were fully geometry optimized using ab-initio calculations, which were carried out with GAUSSIAN 88, GAUSSIAN 90 and GAUSSIAN 92 computer programs [34] at the restricted Hartree–Fock level of theory. The choice of the basis set was performed using



Scheme 1.

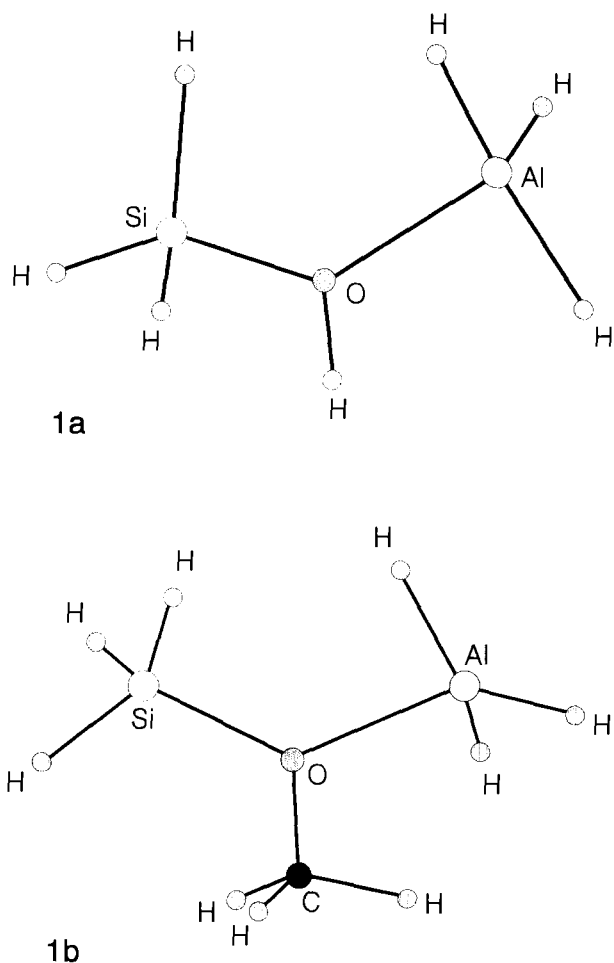


Fig. 1. The AlH_3 complex with (a) silanol and (b) methyl silyl ether.

STO-3G, STO-3G(*), 3-21G, 3-21G(*), 6-31G, 6-31G* and 6-311G basis sets. The best of the preceding for investigating aluminium, oxygen and silicon containing compounds is the 6-31G* basis set, which was used later in our calculations.

The stability of the complexes was estimated by examining interaction energies, which are released in complex formation. The interaction energy ΔE is calculated using the following equation:

$$\Delta E = E^{R-T} - (E^R + E^T) \quad (1)$$

where E^{R-T} is the total energy of the geometry-optimized complex R-T, E^R is the total energy of the geometry-optimized component R and E^T is the total energy of the geometry-optimized component T [35,36]. The interaction energies are dependent on the order of the basis set superposition error (BSSE), which can be calculated with the counterpoise method [35,36]. The effect of the BSSE on the interaction energies was taken into account with the equation

$$\Delta E^{\text{BSSE}} = \Delta E + \text{BSSE} \quad (2)$$

in which ΔE^{BSSE} is the interaction energy corrected for the BSSE.

3. Results

3.1. Choice of the basis set

The basis set was chosen by optimizing the smallest model cocatalyst complex $\text{H}_3\text{SiOH}-\text{AlH}_3$ and its components H_3SiOH and AlH_3 using STO-3G, STO-3G(*), 3-21G, 3-21G(*), 6-31G, 6-31G* and 6-311G basis sets. Total energies, interaction energies and interaction energies corrected for the BSSE are shown in Table 1.

Examination of these results indicates that lower total energies are obtained using a larger basis set. However, the comparison of the energy values also shows the change of the total energies according to basis sets is insignificant compared with the difference between the interaction energies of the 6-31G and 6-31G* basis sets. The influence of correlation effects has been proved

Table 1

Total energies with different basis sets for AlH_3 (E^R), H_3SiOH (E^T) and $\text{H}_3\text{SiOH}-\text{AlH}_3$ (E^{R-T}), interaction energies ΔE , which are released in the formation of the $\text{H}_3\text{SiOX}-\text{AlH}_3$ ($X = \text{H}$ or CH_3) complex and interaction energies ΔE^{BSSE} corrected for the BSSE

	E^R (au)	E^T (au)	E^{R-T} (au)	ΔE (kJ mol ⁻¹)		ΔE^{BSSE} (kJ mol ⁻¹)	
				X = H	X = CH ₃	X = H	X = CH ₃
STO-3G	-240.7284	-361.7719	-602.5684	-178.7352	-164.7234	-58.3625	-50.9796
STO-3G(*)	-240.7591	-361.8802	-602.7135	-194.6334	-192.6592	-72.9976	-55.9887
3-21G	-242.2841	-364.1806	-606.5250	-158.1689	-156.3937	-114.3895	-117.4728
3-21G(*)	-242.3437	-364.2934	-606.6912	-142.1121	-141.2694	-96.6391	-100.0660
6-31G	-243.5881	-366.0441	-609.6802	-126.1489	-126.8004	-112.8057	-115.2039
6-31G*	-243.6163	-366.1304	-609.7776	-81.3749	-80.1494	-70.9559	-71.4847
	-243.6163 ^a	-366.1283 ^a	-609.7750 ^a	-80.0 ^a		-70.1 ^a	
6-311G	-243.6107	-366.0975	-609.7537	-119.6203	-120.2082	-106.3796	-108.8632

^a [21].

Table 2
Geometrical parameters with different basis sets for H_3SiOX and $\text{H}_3\text{SiOX}-\text{AlH}_3$

		$r(\text{Si}-\text{O})$ (pm)		$r(\text{O}-\text{X})(\text{pm})$		$r(\text{Al}-\text{O})$	Si-O-X angle		Si-O-Al angle
		Free	Complexed	Free	Complexed	(pm)	(°)	(°)	(°)
3-21G	X = H	167.48	173.58	95.98	96.62	192.22	126.8	119.6	125.0
		167.4 ^a	173.4 ^a	95.9 ^a	96.7 ^a	192.7 ^a	127.8 ^a	119.6 ^a	130.7 ^a
3-21G(*)	X = CH ₃	167.23	172.90	143.01	147.08	191.32	130.4	124.6	121.2
		163.30	170.67	95.86	96.75	193.99	128.9	120.4	123.8
6-31G	X = H	162.99	170.13	143.53	147.94	192.72	132.5	122.9	119.9
		170.33	176.55	94.38	95.10	196.73	131.1	121.1	123.7
6-31G*	X = CH ₃	170.03	175.91	141.95	145.71	195.37	132.6	122.8	120.0
		164.73	169.99	94.62	95.15	203.58	119.0	118.5	131.1
Experimental ^c	X = H	165.4 ^b	170.9 ^b	94.6 ^b	95.1 ^b	203.3 ^b	118.1 ^b	117.7 ^b	131.1 ^b
		163.99	170.11	140.04	143.40	200.74	125.0	122.9	120.0
	X = CH ₃	164.0		141.8			120.6		

^a [25].

^b [21].

^c [37].

to be minor, because the 3-21G(*) basis set predicts the $\text{H}_3\text{SiOH}-\text{AlH}_3$ complex (Fig. 1(a)) to be only 0.86 kJ mol^{-1} more stable at the MP2 level than without taking into account Møller–Plesset treatment.

Comparison of the optimized structures indicates the geometrical parameters of Table 2 change in the formation of the $\text{H}_3\text{SiOH}-\text{AlH}_3$ complex according to basis set in the following way. The bond lengths in H_3SiOH are generally too long if basis sets without polarization functions are used. The Si–O–H bond angle of H_3SiOH and the Al–O bond length of the $\text{H}_3\text{SiOH}-\text{AlH}_3$ complex are strongly dependent on basis sets. The complex formation weakens the Si–O and O–H bonds and decreases the Si–O–H angle as earlier investigations [21,25,37] have also shown. These structural changes of the molecules in the complex formation are smallest in the case of the 6-31G* basis set.

In order to ensure the accuracy of our results and their lack of dependence on the model, we continued the choice of the basis set by optimizing a $\text{H}_3\text{SiOCH}_3-\text{AlH}_3$ complex (Fig. 1(b)) and its components H_3SiOCH_3 and AlH_3 using the same basis sets as earlier. Comparison of the H_3SiOH and H_3SiOCH_3 systems indicated the interaction energies ΔE in both cases depending on basis sets in the same way (Table 1). In addition to this, the geometrical parameters (Table 2) behave similarly in the formation of both the $\text{H}_3\text{SiOCH}_3-\text{AlH}_3$ and the $\text{H}_3\text{SiOH}-\text{AlH}_3$ complexes.

The bond lengths in H_3SiOCH_3 are generally too long if basis sets are used without polarization functions. The Si–O–C bond angle of H_3SiOCH_3 and the Al–O bond length of the $\text{H}_3\text{SiOCH}_3-\text{AlH}_3$ complex are strongly dependent on basis sets. The complex formation weakens the Si–O and C–O bonds and de-

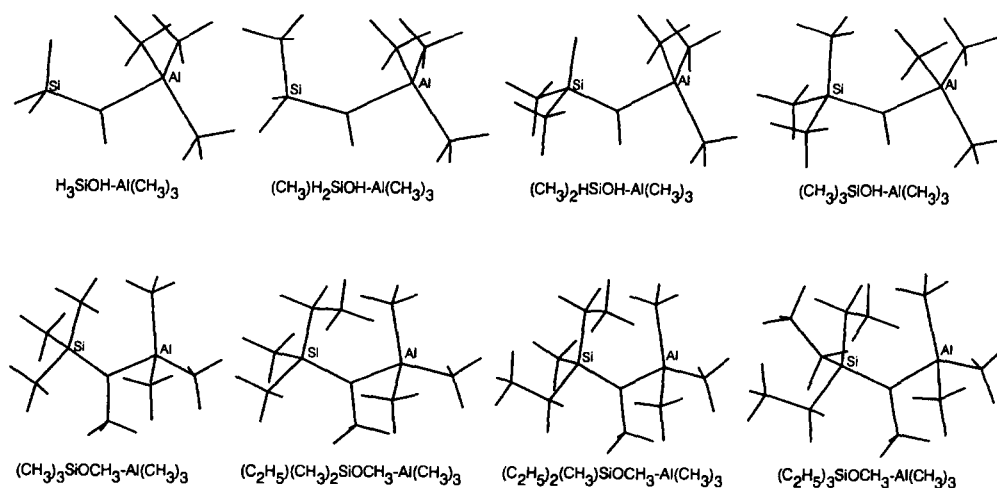


Fig. 2. Complexes of methyl derivatives of silanol and silyl ethers with $\text{Al}(\text{CH}_3)_3$.

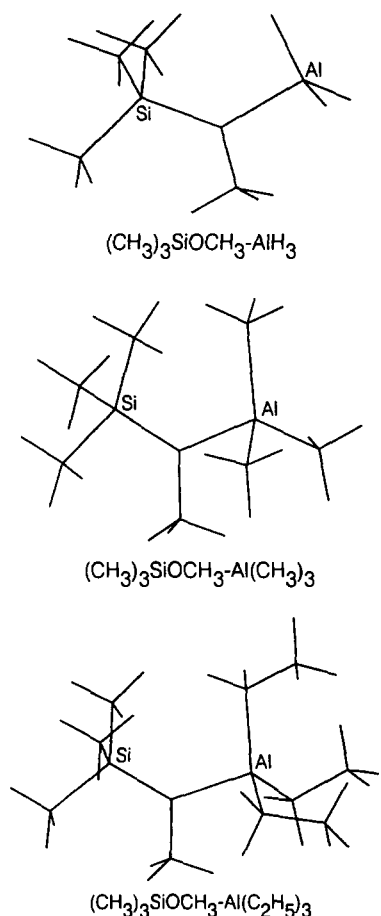


Fig. 3. Complexes of (CH₃)₃SiOCH₃ with AlH₃, Al(CH₃)₃ and Al(C₂H₅)₃.

increases the Si–O–C angle. Further, these structural changes are smallest in the case of the 6-31G* basis set as in the formation of the H₃SiOH–AlH₃ complex. On the basis of these observations we agree with earlier investigations [21,38,39] in affirming that the 6-31G*

basis set is the most suitable for investigating aluminium-, oxygen- and silicon-containing compounds.

This conclusion is also supported by the superposition effects, because the BSSE for the 6-31G* basis set is only 11–13% of the interaction energy. For the 6-31G and 6-311G basis sets the superposition effects are even smaller (9–11% of the interaction energy), but for the other basis sets the superposition effects are considerably larger. For the 3-21G and 3-21G(*) basis sets the BSSE is about 30% of the interaction energy, and for the STO-3G and STO-3G(*) basis sets the BSSE is even 70% of the interaction energy.

3.2. Effect of the alkyl groups

The effect of the alkyl groups on the stability of the cocatalysts complexes was estimated by investigating methyl derivatives of silanol and silyl ethers. The general formula of these compounds is H_m(CH₃)_nSiOH (methyl derivatives of silanol) or (CH₃)_m(C₂H₅)_nSiOCH₃ (silyl ethers), in which $m = 0-3$, $n = 0-3$ and $m + n = 3$. In this study we have investigated complexes, formed from methyl derivatives of silanol or silyl ethers with AlH₃ and Al(CH₃)₃ (Fig. 2). Interaction energies with the 6-31G* basis set and interaction energies corrected for the BSSE are shown in Table 3 and geometrical parameters in Table 4.

Examination of methyl derivatives of silanol indicates AlH₃ forms its most stable complex with (CH₃)₂HSiOH and Al(CH₃)₃ with (CH₃)₃SiOH, if the BSSE is ignored. However, after the interaction energies have been corrected for the BSSE, both AlH₃ and Al(CH₃)₃ seem to form their most stable complex with (CH₃)₃SiOH. The BSSE is 9–13% of the interaction energy in the complexes with AlH₃ and 17–21% of the interaction energy in the complexes with Al(CH₃)₃.

Table 3

Interaction energies with the 6-31G* basis set and interaction energies corrected for the BSSE for methyl derivatives of silanol and silyl ethers with one methoxy group

	ΔE (kJ mol ⁻¹)		ΔE^{BSSE} (kJ mol ⁻¹)	
	X = H	X = CH ₃	X = H	X = CH ₃
H ₃ SiOH–AlX ₃	–81.3749	–63.8110	–70.9559	–51.5276
H ₃ SiOH–AlX ₃	–80.0 ^a		–70.1 ^a	
(CH ₃) ₂ SiOH–AlX ₃	–88.4773	–68.7098	–77.7039	–55.9217
(CH ₃) ₂ HSiOH–AlX ₃	–93.6805	–71.9276	–82.8186	–59.6184
(CH ₃) ₃ SiOH–AlX ₃	–93.1944	–72.8326	–84.6325	–60.6730
(CH ₃) ₃ SiOCH ₃ –AlX ₃	–83.0944	–52.4486	–74.5242	–41.5881
(CH ₃) ₃ SiOCH ₃ –AlX ₃		–45.5713 ^b		–34.4325 ^b
(C ₂ H ₅)X(CH ₃) ₂ SiOCH ₃ –AlX ₃		–52.4483		–40.9196
(C ₂ H ₅)X(CH ₃)SiOCH ₃ –AlX ₃		–51.1334		–40.3393
(C ₂ H ₅) ₃ SiOCH ₃ –AlX ₃		–54.9549		–43.8678

^a [21].

^b X = C₂H₅.

Table 4
Geometrical parameters with the 6-31G* basis set for methyl derivatives of silanol and silyl ethers with one methoxy group

	$r(\text{Si-O})$ (pm)		$r(\text{Al-O})$ (pm)		Si-O-Al angle ($^\circ$)	
	X = H	X = CH ₃	X = H	X = CH ₃	X = H	X = CH ₃
H ₃ SiOH-AlX ₃	169.99	169.42	203.58	207.69	131.1	133.2
(CH ₃) ₂ H ₂ SiOH-AlX ₃	171.17	170.43	201.99	206.35	130.3	134.8
(CH ₃) ₂ HSiOH-AlX ₃	172.23	170.95	200.65	205.20	130.8	133.5
(CH ₃) ₃ SiOH-AlX ₃	172.91	171.86	200.28	204.68	131.8	137.4
(CH ₃) ₃ SiOCH ₃ -AlX ₃	172.67	172.13	200.63	206.98	123.3	127.7
(CH ₃) ₃ SiOCH ₃ -AlX ₃		172.26 ^a		207.75 ^a		127.9 ^a
(C ₂ H ₅) ₃ (CH ₃) ₂ SiOCH ₃ -AlX ₃		172.35		206.78		127.2
(C ₂ H ₅) ₂ (CH ₃) ₂ SiOCH ₃ -AlX ₃		172.57		207.09		127.4
(C ₂ H ₅) ₃ SiOCH ₃ -AlX ₃		172.88		206.67		127.2

^a X = C₂H₅.

Comparison of the geometrical parameters shows that the most stable complex has the largest Si-O-Al bond angle and the strongest Al-O bond. On the contrary, the weakest complex has the weakest Al-O bond and the strongest Si-O bond. Further, it is typical of these complexes that one of the O-Al-X (X = H or C) angles is 95.1–99.8° and the corresponding Al-X bond is the longest of the Al-X bonds.

The same kinds of results were also obtained in the investigation of silyl ethers, because Al(CH₃)₃ forms its most stable complex with (C₂H₅)₃SiOCH₃, which is triply substituted like (CH₃)₃SiOH. This result does not depend on the BSSE, which has been estimated to be

20–22% of the interaction energy in these complexes. Examination of the geometrical parameters shows the most stable complex has the strongest Al-O bond and the weakest Si-O bond.

3.3. Effect of the aluminium compounds

Different aluminium compounds were used to see how they affected the stability of cocatalysts complexes. We investigated complexes, which have been formed from (CH₃)₃SiOCH₃ with AlH₃, Al(CH₃)₃ and Al(C₂H₅)₃ (Fig. 3). The interaction energies with the 6-31G* basis set and interaction energies corrected for

Table 5
Interaction energies with the 6-31G* basis set and interaction energies corrected for the BSSE for silanols and silyl ethers

	ΔE (kJ mol ⁻¹)		ΔE^{BSSE} (kJ mol ⁻¹)	
	X = H	X = CH ₃	X = H	X = CH ₃
H ₃ SiOH-AlX ₃	-81.3749		-70.9559	
H ₂ Si(OH) ₂ -AlX ₃	-94.6884		-82.7268	
HSi(OH) ₃ -AlX ₃	-89.8079		-77.9487	
Si(OH) ₄ -AlX ₃	-82.8514		-70.3123	
(CH ₃) ₃ SiOCH ₃ -AlX ₃		-52.4486		-41.5881
(CH ₃) ₂ Si(OCH ₃) ₂ -AlX ₃		-53.1341		-41.8570
(CH ₃)Si(OCH ₃) ₃ -AlX ₃		-55.8513		-43.0414
Si(OCH ₃) ₄ -AlX ₃		-49.6395		-35.6634

Table 6
Geometrical parameters with the 6-31G* basis set for free and complexed silanols (with AlH₃) and silyl ethers (with Al(CH₃)₃)

	$r(\text{Si-O})$ (pm)		$r(\text{O-X})^a$ (pm)		$r(\text{Al-O})$ (pm)	Si-O-X ^a angle ($^\circ$)		Si-O-Al angle ($^\circ$)
	Free	Complexed	Free	Complexed	Complexed	Free	Complexed	Complexed
H ₃ SiOH	164.73	169.99	94.62	95.15	203.58	119.0	118.5	131.1
H ₂ Si(OH) ₂	164.07	170.47	94.57	95.19	202.23	120.0	117.5	123.1
HSi(OH) ₃	163.23	169.62	94.71	95.28	201.25	117.0	115.6	125.1
Si(OH) ₄	162.89	169.21	94.69	95.26	199.93	117.1	115.5	124.3
(CH ₃) ₃ SiOCH ₃	165.37	172.13	139.61	143.22	206.98	127.2	120.0	127.7
(CH ₃) ₂ Si(OCH ₃) ₂	164.56	170.93	139.98	143.80	207.36	126.3	117.5	129.0
(CH ₃)Si(OCH ₃) ₃	162.81	168.99	140.17	144.03	207.76	129.3	120.7	126.6
Si(OCH ₃) ₄	162.27	167.75	140.37	144.19	208.09	126.2	120.4	126.5

^a X = H in silanols and X = C in silyl ethers.

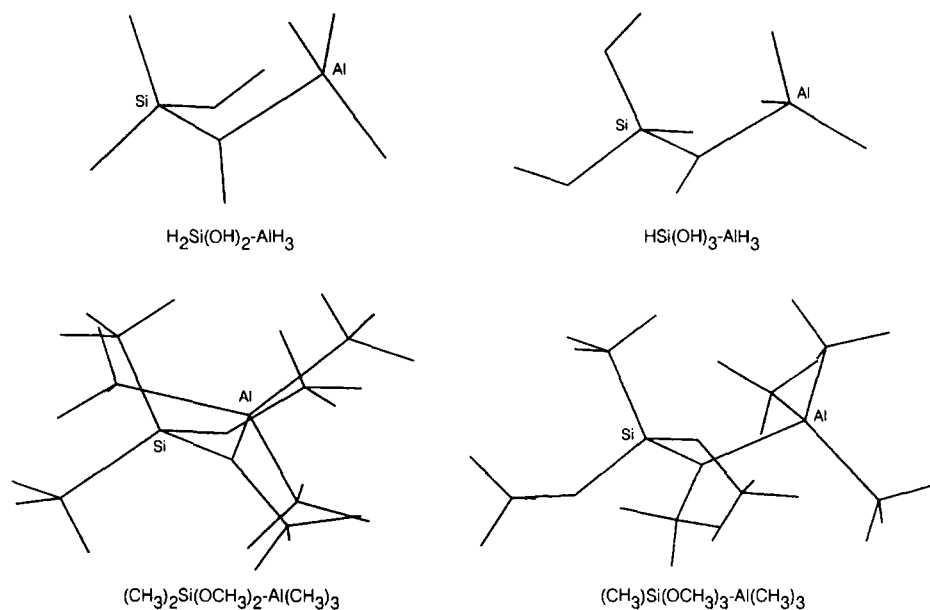


Fig. 4. Complexes of silanols with AlH_3 and silyl ethers with $\text{Al}(\text{CH}_3)_3$.

the BSSE are shown in Table 3 and geometrical parameters in Table 4.

Examination of the geometrical parameters shows the Si–O bond length does not depend to a great extent on the aluminium compound, but the Al–O bond length and the Si–O–Al bond angle do depend somewhat on the aluminium compound. However, the difference in the geometrical parameters between the $(\text{CH}_3)_3\text{SiOCH}_3\text{-AlH}_3$ complex and the $(\text{CH}_3)_3\text{SiOCH}_3\text{-AlX}_3$ ($\text{X} = \text{CH}_3$ or C_2H_5) complexes is not so distinct as the difference in their interaction energies.

3.4. Effect of hydroxy and alkoxy groups

The effect of the hydroxy and alkoxy groups on the stability of the cocatalysts complexes was estimated by investigating silanols and their methyl derivatives (silyl ethers). The general formula of these compounds is $\text{H}_m(\text{OH})_n\text{SiOH}$ (silanol) or $(\text{CH}_3)_m(\text{CH}_3\text{O})_n\text{SiOCH}_3$ (silyl ether), in which $m = 0\text{--}3$, $n = 0\text{--}3$ and $m + n = 3$. In this study we have investigated complexes that have been formed from silanols with AlH_3 and silyl ethers with $\text{Al}(\text{CH}_3)_3$.

Interaction energies with the 6-31G* basis set and interaction energies corrected for the BSSE are shown in Table 5. These values show that the most stable complex of the silanols is $\text{H}_2\text{Si}(\text{OH})_2\text{-AlH}_3$, and the most stable complex of the silyl ethers is $(\text{CH}_3)\text{Si}(\text{OCH}_3)_3\text{-Al}(\text{CH}_3)_3$. These results do not depend on the BSSE, which has been estimated to be 13–15% of the interaction energy in the complexes of the silanols and 21–28% of the interaction energy in the complexes of the silyl ethers.

Geometrical parameters calculated with the 6-31G* basis set are shown in Table 6. Comparison of these parameters indicates that the complex formation weakens the Si–O and O–X bonds and decreases the Si–O–X angle.

4. Discussion

The results presented above give us information about the structural and energetical changes in the formation of Ziegler–Natta cocatalyst complexes. Comparison of the geometrical parameters before and after the complex formation indicates that the Si–O and O–X ($\text{X} = \text{H}$ or C) bonds weaken and the Si–O–X bond angle decreases in the formation of the cocatalyst complexes. The basis sets without polarization functions and the basis sets with polarization functions only for aluminium and silicon atoms predict these structural changes of the molecules to be larger than the basis set with polarization functions for the oxygen atom also. In addition to this, the difference between the interaction energies obtained with the basis sets with and without polarization functions for oxygen is significant (Table 1). On the basis of these statements we agree with earlier investigations [21,38,39] that d-type polarization functions are a prerequisite for a correct prediction of properties of compounds containing atoms with lone pairs.

On account of this, the 6-31G* basis set is the best compromise for investigating aluminium-, oxygen- and silicon-containing cocatalysts complexes. This basis set

predicts the Si–O (168–173 pm) and Al–O (200–208 pm) bond lengths of the complexes longer than the previously reported experimental Si–O (167–168 pm) and Al–O (182–187 pm) bond lengths in dimeric $[(\text{CH}_3)_2\text{Al}(\text{OSi}(\text{CH}_3)_3)]_2$ and $[(\text{CH}_3)_2\text{Al}(\text{OSi}(\text{CH}_3)_2(\text{C}_6\text{H}_5))]_2$ compounds with a planar Al_2O_2 ring system [40,41]. However, the Al–O bond lengths do not deviate significantly from the general trend, since the Al–O bond length varies from 178 to 201 pm in anions with $(\text{CH}_3)_3\text{Al–O}$ linkages [42,43].

The stability of cocatalyst complexes depends on both aluminium compounds and silicon alkoxides. However, the effect of the aluminium compounds on the interaction energies is more important than that of the silicon alkoxides, because for example the interaction energy of the $\text{H}_3\text{SiOH–AlH}_3$ complex changes only 1.72 kJ mol^{-1} in replacing H_3SiOH by $(\text{CH}_3)_3\text{SiOCH}_3$, but the change is $17.56 \text{ kJ mol}^{-1}$ in replacing AlH_3 by $\text{Al}(\text{CH}_3)_3$. On account of this, it is assumed that the aluminium compounds determine the order of the interaction energies. In spite of this, the prediction of the geometrical parameters around the oxygen atom, which takes part in the complex formation, can be obtained with a small model complex, since the aluminium compound has only a slight effect on the complex structure around the oxygen atom.

Investigation of silicon alkoxides has been divided into different parts: silanols, alkyl derivatives of silanol and silyl ethers. These investigations have indicated that the interaction energies depend on the degree of substitution and the number of alkoxy groups. Examination of the alkyl derivatives of silanol and silyl ethers with one alkoxy group has shown that the stability of the complexes decreases, when the sterical hindrance of the alkoxy group increases. In particular, this is noticed in replacing the hydroxy group of $(\text{CH}_3)_3\text{SiOH}$ by methoxy group. This calculated result is consistent with earlier investigations [3,5], indicating that the complexing capability of silicon alkoxides is high, when the sterical hindrance of the alkoxy group that takes part in the complex formation is less than that of the other hydrocarbon groups.

Further, according to silanols and silyl ethers the complexing capability of silicon alkoxides is also dependent on the number of alkoxy groups. It is noticed that the complexing capability improves by increasing the number of alkoxy groups. However, in silyl ethers, three alkoxy groups are optimum, if not the sterical hindrance around the oxygen atoms will make the interaction between the silicon alkoxide and the aluminium compound difficult. On the contrary, in silanols, two hydroxy groups are optimum. In spite of this difference between the silanols and silyl ethers, the most stable complexes $(\text{H}_2\text{Si}(\text{OH})_2\text{–AlH}_3$ and $(\text{CH}_3)_3\text{Si}(\text{OCH}_3)_3\text{–Al}(\text{CH}_3)_3$) also have common features. The angle between the geminal Si–O bonds is 110° , and the O–Si–

O–Al torsion angle is about 60° (Fig. 4). In addition to this, the stability of the complexes can be explained by the anomeric effect [44,45]. The effect is noticed in silanols and is also supposed to exist in organosilicon compounds, where the lone pairs of the oxygen atoms can interact with the geminal Si–O σ^* orbitals.

5. Conclusions

Investigation of the Ziegler–Natta cocatalysts has indicated that the size and number of the alkoxy groups of the silicon alkoxides affect the stability of the cocatalyst complexes. The sterical hindrance, especially around the oxygen atom, which takes part in the complex formation, weakens the stability of the complex. In spite of this, silicon alkoxides have only little effect on the interaction energies, because the aluminium compounds determine the order of the interaction energies.

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