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Trimethylaluminium complexes with a multidentate carbosiloxane-type ligand

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Abstract

Trimethylaluminium reacts with the multidentate 1,4-bis(trimethylsiloxy)-3-[methyl-bis(trimethylsiloxy)silyl]but-2-ene ligand, yielding complexes at 1 : 1 and 1 : 2 reactant mole ratios. An exchange of the trimethylaluminium molecule between the oxygen atoms of trimethylsiloxy groups at the carbon atoms ($-CH_2OSiMe_3$) proceeds at room temperature. This exchange is retarded at low temperature when trimethylaluminium is used in an excess ($Me_3Al/-CH_2OSiMe_3$ mole ratio ≥ 1). Free trimethylaluminium appears in the reaction products in addition to complexed trimethylaluminium.

A stable complex is formed at a 1 : 1 reactant mole ratio; it does not decompose at $1 \cdot 10^{-3}$ mmHg up to 40 °C. The oxygen atom O(a) having the smallest steric hindrances is the donor atom in that complex.

Introduction

Complexes of organoaluminium compounds with Lewis bases have been intensively studied. The acidic aluminium atom in organoaluminium compounds reacts readily with basic atoms of oxygen, nitrogen, phosphorus, sulfur etc. of organic compounds, producing donor-acceptor complexes. The course of the reaction and stability of the complex depend mainly on the acidicity of the aluminium atom in the organoaluminium compound and on the basicity of the electron donor atom in the organic compound. In addition to these factors, steric hindrance plays a important role; it may cause a considerable decrease in the stability of the complex or preclude its formation.

Although many studies have been made of complexes of organoaluminium compounds with organic bases, the reactions of multidentate organic compounds with more than one basic centre in a molecule require more detailed elucidation [1].

The purpose of this work was to study the reaction of trimethylaluminium with 1,4-bis(trimethylsiloxy)-3-[methyl-bis(trimethylsiloxy)silyl]but-2-ene, containing four oxygen basic centres and exhibiting large steric hindrances.

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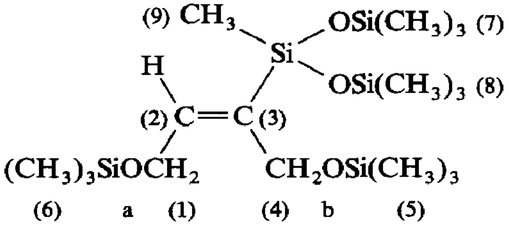
Results and discussion

1,4-bis(trimethylsiloxy)-3-[methyl-bis(trimethylsiloxy)silyl]but-2-ene (**1**) was obtained in reaction 1:

$$(CH_3)_3SiOCH_2C{\equiv}CCH_2OSi(CH_3)_3 + SiHCH_3[OSi(CH_3)_3]_2 \xrightarrow{124-140\,^\circ C} \qquad (1)$$



(**1**)

The method of synthesis of **1** leads exclusively to the *cis*-isomer.

^1H and ^{13}C NMR spectra of **1** are presented in Tables 1 and 2. In the ^1H NMR spectrum of the $OSi(CH_3)_3$ groups [denoted (7) and (8)] recorded at high resolution and at 300 MHz four signals in the form of a narrow multiplet at 0.14 ppm are observed. These are probably caused by the retardment of rotation around the C(3)–Si and Si–O bonds due to the bulkiness of $OSi(CH_3)_3$ groups. The signals of the $OSi(CH_3)_3$ groups [(5) and (6)] are two singlets at 0.21 and 0.22 ppm. The H(1) and H(4) protons of the CH_2 groups give a signal in the form of a narrow multiplet and are practically non-differentiable.

Table 1

^1H NMR spectra of **1** and of the products of the reactions of **1** with trimethylaluminium at various molar ratios (room temperature, standard C_6D_5H = 7.15 ppm, Varian VRX 300) [a]

	H(1)	H(2)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(CH$_3$Al)
pure 1	4.38m	6.34m	4.37m	0.21m	0.22m	0.14m	0.14m	0.33m	
1/AlMe$_3$ mole ratio									
4:1	4.34m	6.20m	4.28m	0.09m	0.10 0.09 } m	0.10 0.13m	0.15m	0.22 0.21 } d	−0.51m
2:1	4.63 4.61 } m	6.20m	4.33s	0.19m	0.14m	0.22m	0.22m	0.30m	−0.43s
1:1	4.77 4.76 } d	6.18m	4.27d	0.18m	0.10m	0.18m	0.18m	0.26d	−0.35s
1:1 [b]	4.77 4.76 } d	6.20m	4.29s	0.18m	0.11m	0.20m	0.20m	0.28d	−0.35s
1:2	5.03m	6.10m	4.60m	0.19m	0.26m	0.15m	0.15m	0.11m	−0.38m
1:4	5.09m	6.06m	4.75m	0.24m	0.28m	0.13m	0.13m	0.16m	−0.38m
1:8	5.08 5.07 } m	6.05m	4.75 4.76 } m	0.24m	0.28m	0.13m	0.13m	0.13m	−0.38m

[a] For indexes see Eq. 1. [b] The sample was obtained by distilling off (40 °C; $1\cdot10^{-3}$ mmHg; 5 h) the excess of AlMe$_3$ from the 1:4 post-reaction mixture.

Table 2

^{13}C NMR spectra of **1** and of the products of the reactions of **1** with trimethylaluminium at various molar ratios (room temperature, standard C_6H_6 = 128 ppm, Varian VRX 300) [a]

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(CH$_3$Al)
pure **1**	60.89	142.51	139.63	60.51	−0.48	−0.21	2.07	2.07	1.35	–
1/AlMe$_3$ mole ratio										
1 : 1	65.50	141.45	139.18	61.43	−0.51	0.67	2.11	2.11	0.80	−5.70
	67.51		138.58	64.17	−0.13	0.18				
1 : 2	67.46	140.05	138.63	64.52	−0.05	0.15	1.93	1.93	0.88	−5.68
	67.51			64.17	−0.13	0.18				
1 : 2.5	67.46	140.00	138.88	64.52	−0.05	0.15	1.93	1.93	0.88	−5.68

[a] For indexes see Eq. 1.

The ^{13}C NMR spectrum of **1** is presented in Table 2. The carbon atoms of the CH_3 groups C(5) and C(6) give two signals at −0.48 and −0.21 ppm, and C(7,8) appears as one signal at 2.07 ppm. The signals of the double-bonded carbon atoms C(2) and C(3) differ by 2.9 ppm and those of C(1) and C(4) lie near each other.

The reaction of **1** with trimethylaluminium was studied at various reactant mole ratios (Table 1). It was found that a stable donor–acceptor complex is formed at a 1 : 1 reactant mole ratio. This complex does not decompose in a vacuum of $1 \cdot 10^{-3}$ mmHg at 40 °C during long heating. Examination of the ^1H and ^{13}C NMR spectra revealed that the aluminium atom forms a bond with the O(a) atom. The ^1H NMR spectrum of the 1 : 1 complex shows a large downfield shift of the H(1) signal ($\delta = 4.77$) and an upfield shift of the H(2) signal ($\delta = 6.18$) relative to the positions of those signals in **1** ($\delta = 4.38$ and 6.34). The locations of the signals of the other protons remain practically the same (Table 1). The downfield shift of the H(1) signal and the upfield shift of the H(2) signal are caused by the formation of a complex between the aluminium and O(a) oxygen atoms. In the ^{13}C NMR spectrum the downfield shift of the C(1) signal ($\delta = 65.50$) and the small upfield shift of the C(2) signal ($\delta = 141.45$) relative to those of compound **1** ($\delta = 60.89$ and $\delta = 142.51$, respectively) are also found (Table 2). The signal of the methyl groups in $(CH_3)_3Al$ of the 1 : 1 complex appears in the ^1H NMR spectrum at −0.55 ppm and in the ^{13}C NMR spectrum at −5.70 ppm (Tables 1 and 2).

At a 1 : 2 mole ratio of **1** to $(CH_3)_3Al$ a bond with the second oxygen atom Al–O(b) is formed in addition to the Al–O(a) bond. The formation of a 1 : 2 complex of **1** with trimethylaluminium causes a downfield shift of the H(4) signal ($\delta = 4.60$) in the ^1H NMR spectrum relative to the position of that signal in the 1 : 1 complex ($\delta = 4.27$) and also causes a downfield shift of the C(4) signal ($\delta = 64.17$) in the ^{13}C NMR spectrum relative to the signal of the 1 : 1 complex ($\delta = 61.43$); these are similar to the downfield shifts of the H(1) and C(1) signals in the 1 : 1 complex in comparison with those of **1**. Moreover, in the region of the CH_2 groups in the ^{13}C NMR spectrum of the 1 : 2 complex several signals appear. These can be explained by the retardation of rotation and the appearance of several rotamers. The downfield shift of the H(1) signal ($\delta = 5.03$) in the 1 : 2 complex relative to that in the 1 : 1 complex ($\delta = 4.77$) in the ^1H NMR spectrum and the downfield shift of the C(1) signal ($\delta = 67.51$) in the 1 : 2 complex relative to the in the 1 : 1 complex ($\delta = 65.50$) in ^{13}C NMR spectrum are also observed. The presence of a single signal of the CH_3Al group in the ^{1}H and ^{13}C NMR spectra indicates a fast exchange of the trimethylaluminium molecule between both oxygen atoms, O(a) and O(b), and free

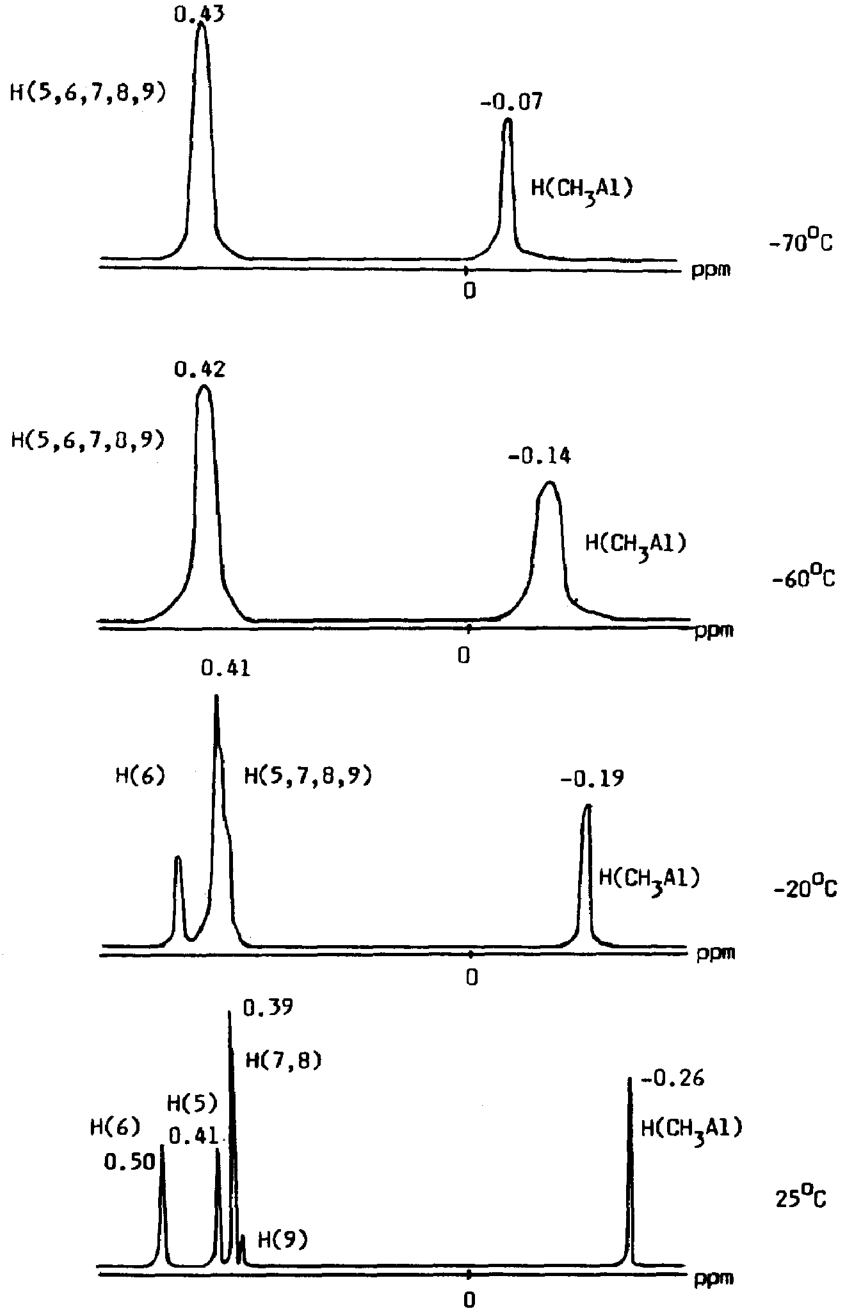


Fig. 1. Variable-temperature ^{1}H NMR spectra of the products of the reaction of 1 with trimethylaluminium at 1 : 1 molar ratio (solvent toluene, standard $C_6D_5CD_2H = 2.34$ ppm, Tesla 587A 80 MHz).

$(CH_3)_3Al$. The 1 : 2 complex is unstable, and $(CH_3)_3Al$ is distilled off at 40 °C under reduced pressure, forming a stable 1 : 1 complex. For more ratios of **1** to $(CH_3)_3Al$ of 1 : 4 and 1 : 8, the proton chemical shifts remain practically unchanged

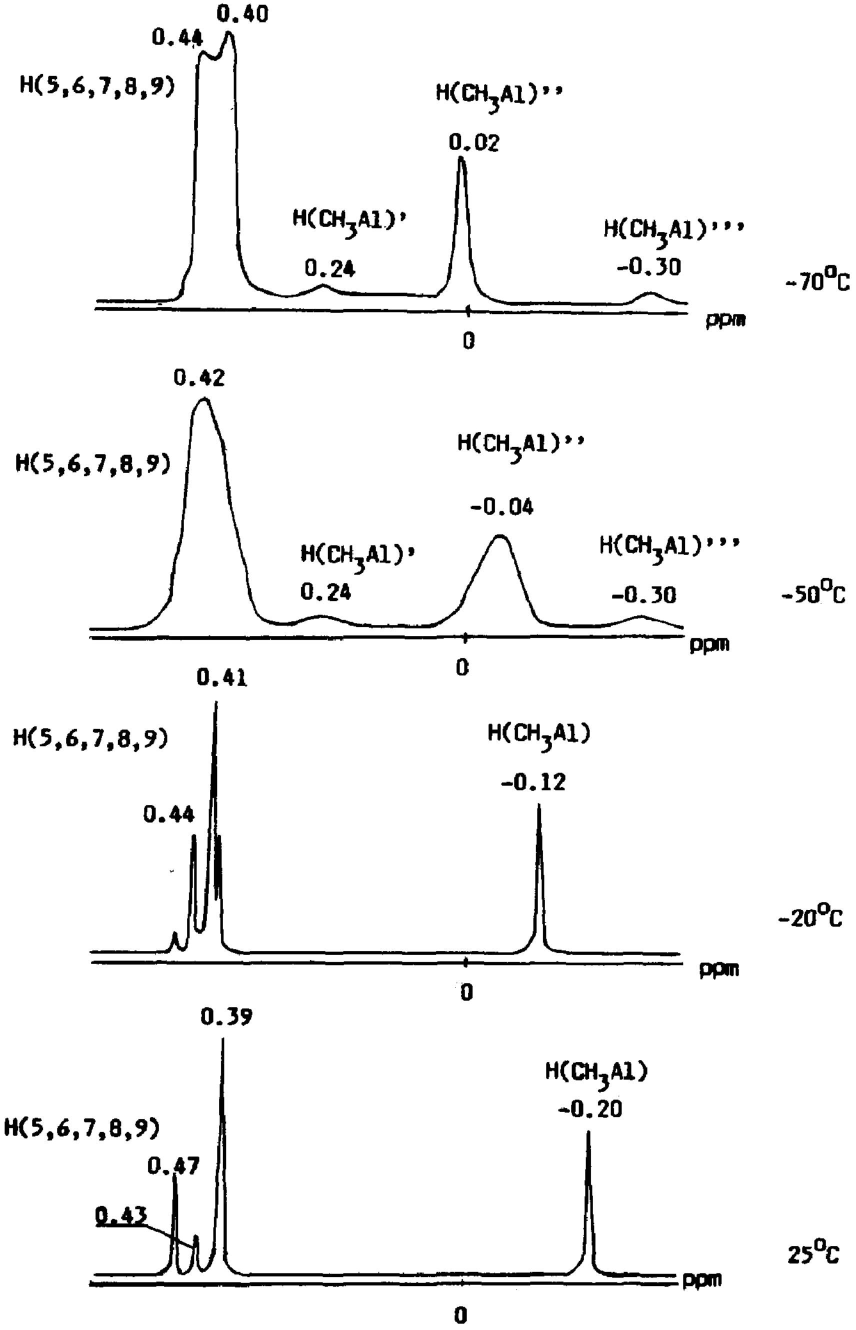


Fig. 2. Variable-temperature ^1H NMR spectra of the products of the reaction of 1 with trimethylaluminium at 1 : 1.75 molar ratio (solvent toluene, standard $C_6D_5CD_2H = 2.34$ ppm, Tesla 587A 80 MHz).

in comparison to those of the 1 : 2 complex (Table 1). This means that the oxygen atoms of the other trimethylsiloxy groups do not form complexes with trimethylaluminium.

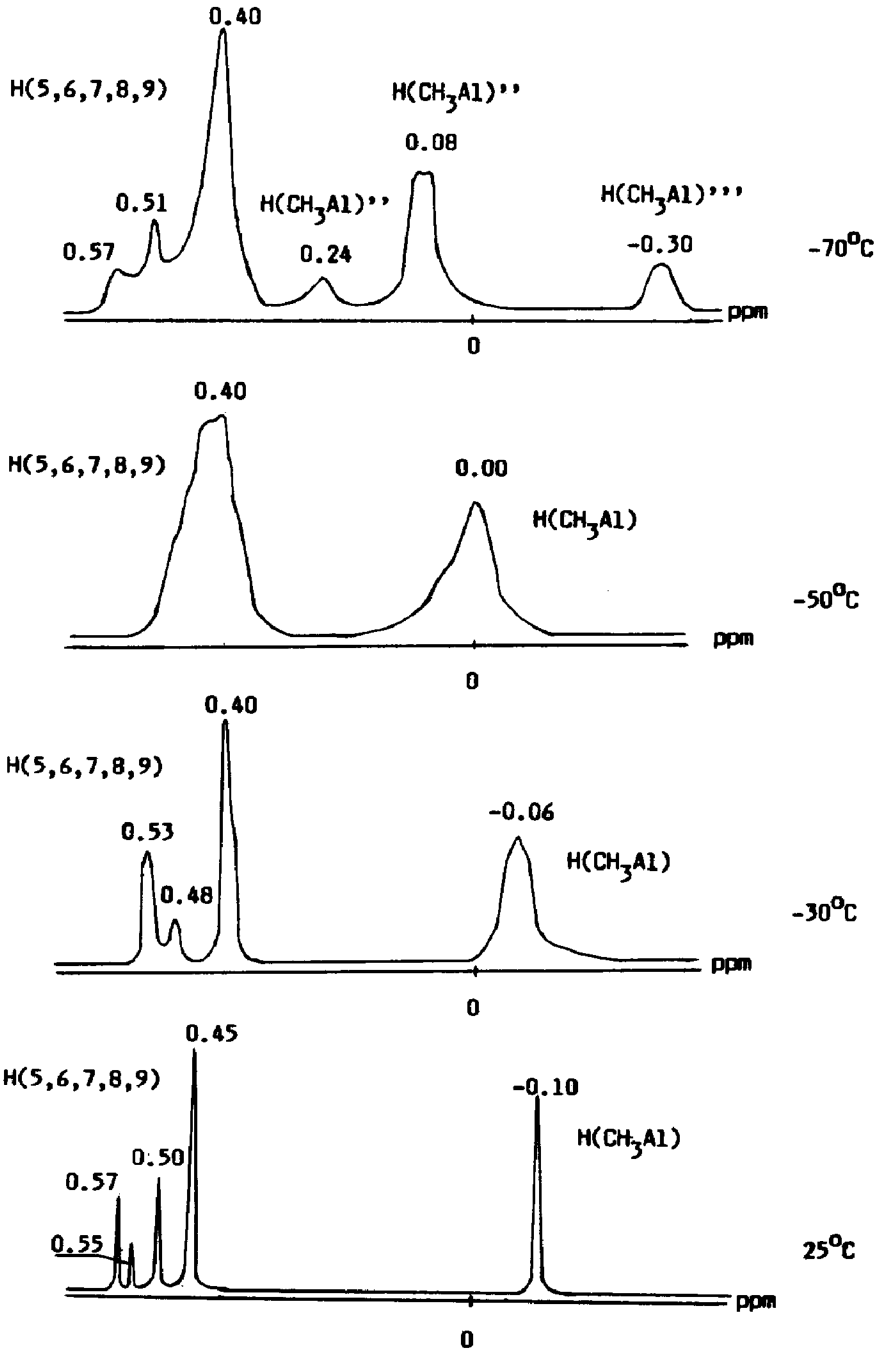


Fig. 3. Variable-temperature ^{1}H NMR spectra of the products of the reaction of 1 with trimethylaluminium at 1 : 3 molar ratio (solvent toluene, standard $C_6D_5CD_2H$ = 2.34 ppm, Tesla 587A 80 MHz).

The signal of the CH_3Al protons of the 1 : 1 complex broadens at −20 °C. At −60 °C the signal is broad, and at −70 °C it becomes narrow again (Fig. 1). This phenomenon can be explained by an exchange of the $(CH_3)_3Al$ molecule between the O(a) and O(b) oxygen atoms. The broadening of the signal results from the slower exchange:

$$1\ O(a)\cdot Al(CH_3)_3 \rightleftharpoons 1\ O(b)\cdot Al(CH_3)_3 \tag{2}$$

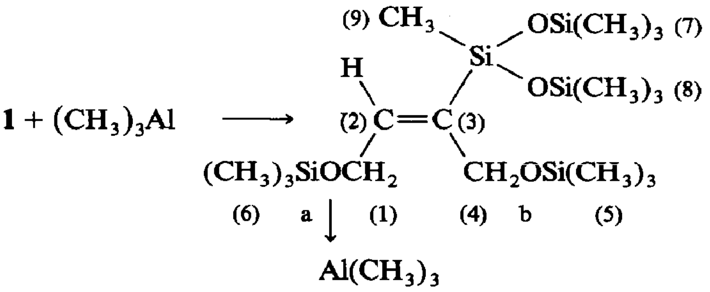
At −70 °C the exchange is probably slow, and the thermodynamically more stable form of the complex with O(a) predominates.

For a $1/Me_3Al = 1/1.75$ mole ratio (Fig. 2) the signal of the CH_3Al protons broadens at −20 °C, and at −50 °C two broad signals of uncomplexed trimethylaluminium [$H(CH_3Al)'$ 0.24 ppm bridging and $H(CH_3Al)'''$ −0.30 ppm terminal methyl groups] appear, in addition to the broad signal of $H(CH_3Al)''$ protons of complexed trimethylaluminium. These data indicate a fast exchange of complexed $(CH_3)_3Al$ between O(a), free trimethylaluminium and O(b).

At a 1 : 3 reactant mole ratio the signals of CH_3Al protons at low temperatures are similar to those at a 1 : 1.75 mole ratio. Only the intensity of the signals of free $(CH_3)_3Al$ is higher (Fig. 3). The measured integration ratio of the signals of H(5,6,7,8,9): $H(CH_3Al)''$: $H(CH_3Al)'''$ (39 : 18.5 : 5.3) is in good agreement with that calculated for the 1 : 2 complex (39 : 18 : 6).

The signals of the H(5), H(6), H(7) and H(8) protons in the 1 : 1 and 1 : 2 complexes are observed in the ^1H NMR spectra in the form of narrow multiplets, as in the case of H(7) and H(8) of pure **1**. This means that steric hindrances retard the rotation around the C(1)–C(2), C(3)–C(4), C(3)–Si, C(1)–O and C(4)–O bonds at room temperature.

The accessibility of the oxygen atom for the approach of the aluminium atom is easiest for O(a). This is the reason why complex **2** is stable.

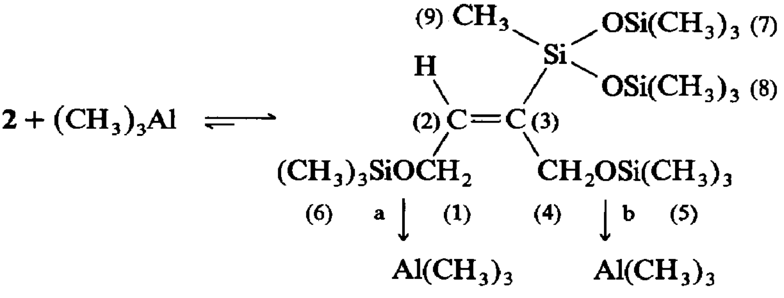


(3)

(2)

Rotation around the C(1)–O(a) bond is still possible, despite the formation of complex **2**, but rotation around the C(1)–C(2) bond is difficult or impossible.

The approach of the $(CH_3)_3Al$ aluminium atom to the O(b) oxygen atom is sterically hindered. The steric hindrance increases after formation of the 1 : 1 complex. Therefore the 1 : 2 complex **3** is unstable, and a fast exchange proceeds in the reaction medium between the complexed and free trimethylaluminium.



(3)

(4)

The steric hindrances around the other oxygen atoms of the OSiMe$_3$ groups (7) and (8) are so large that no complexes are formed with these atoms.

Experimental

1. Reactants

Compound **1** was obtained by the hydrosylilation of 1,4-bis(trimethylsiloxy)but-2-ine with bis(trimethylsiloxy)methylsilane [2].

35 g (0.152 mol) of 1,4-bis(trimethylsiloxy)but-2-ine was placed in a 100 cm^3 three-necked flask and heated to 125 ° C. 4.3 cm^3 of bis(trimethylsiloxy)methylsilane containing 0.07 cm^3 of the catalyst (0.1 *M* solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol) was slowly dropped in. At a certain time a sudden rise of temperature by 7 ° C was noticed, indicating that the reaction had begun. 39.3 cm^3 of bis(trimethylsiloxy)methylsilane containing 0.03 cm^3 of the catalyst was dropped in. Altogether 35.5 g (0.159 mol) of bis(trimethylsiloxy)methylsilane was added to the reaction flask. The temperature of the reaction mixture was maintained within 125–140 ° C and was controlled by dropping in silane and heating the bath. After cooling to room temperature the post-reaction mixture was distilled into fractions, from which that containing **1** was chosen following chromatographic studies. Trimethylaluminium (Aldrich Ch.C) was distilled prior to the reaction.

2. Methods

All operations were carried out in an atmosphere of dried and deoxygenated argon. The complexes used for NMR studies were obtained in such a way that an appropriate amount of **1** was added to an AlMe$_3$ solution in benzene or toluene cooled to 5 ° C.

*3. **1** · AlMe$_3$ complex (1 : 1)*

2.26 g (0.005 mol) of **1** was added to a 10% solution of AlMe$_3$ in benzene cooled to 5 ° C, containing 0.50 g (0.07 mol) of AlMe$_3$. The solvent and excess of AlMe$_3$ were then distilled off during 5 h under a vacuum of $1 \cdot 10^{-3}$ mmHg/40 ° C. The 1 : 1 complex was obtained in the form of a dense, transparent and colourless liquid. Anal. Calcd. for 1 : 1 complex: Me 8.59; Al 5.15; found Me 8.76; Al 5.19. The degree of association calculated on the basis of cryoscopic molecular weight determinations was equal to 1.

4. Spectra

Room-temperature ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer and low-temperature spectra on a Tesla 587 A 80 MHz spectrometer.

References

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