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GEMINAL ORGANODIALUMINIUM COMPOUNDS AND THEIR COMPLEXES WITH AMINES *

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Summary

Hexyne-1 reacts with dialkylaluminium hydride to give the geminal organodialuminium hexane IIa,b in 80 to 85% yield. IIa,b form complexes with amines at molar ratios 1 : 1 as well as 1 : 2. The properties of the amines, especially steric properties, determine whether a complex is formed and at which molar ratio.

Introduction

Several organoaluminium compounds of the general formula $R_2Al—X—AlR_2$ with a heteroatom bridge (X = O [1], S [2], NR [3,4]) have been synthesized and investigated in recent years. In contrast to this, only a few reports can be found on such compounds with a carbon bridge (X = CH_2, CHR). These compounds are very interesting, especially as a theoretical model; because they contain two Lewis acid centres in one molecule. Recently some calculations on the conformation and electron density at the α-C atom have been carried out [5].

Serveral geminal organodialuminium compounds were prepared and the complex formation with several amines was investigated.

Results and discussion

1. *Syntheses of geminal organodialuminium compounds*

As is known from the literature, 1,1-bis(dialkylaluminium)hexane (IIa, b) is

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

formed in a two-step reaction of two moles of dialkylaluminium hydride with one mole of hexyne-1 [6—9]

$$R_2AlH + HC{\equiv}C{-}C_4H_9 \rightarrow \underset{(Ia,b)}{R_2Al{-}CH{=}CH{-}C_4H_9} \qquad (1)$$

$$R_2AlH + \underset{(Ia,b)}{R_2Al{-}CH{=}CH{-}C_4H_9} \rightarrow \underset{(IIa,b)}{(R_2Al)_2CH{-}CH_2{-}C_4H_9} \qquad (2)$$

(a, $R = C_2H_5$; b, $R = i\text{-}C_4H_9$)

These reactions have been investigated for diisobutyl- and diethylaluminium hydrides in order to obtain geminal dialuminium compounds in high yield.

The course of reaction was determined by hydrolysis and deuterolysis. The hexane and 1,1-dideuteriohexane formed demonstrate that 1,1-bis(dialkylaluminium)hexane (IIa, b) is the main product.

$$\underset{(IIa,b)}{(R_2Al)_2CH{-}CH_2{-}C_4H_9} \xrightarrow[-2\,Al^{3+},\,-4\,RH]{6\,H_2O/H^+} H_2CH{-}CH_2{-}C_4H_9 \qquad (3)$$

$$\underset{(IIa,b)}{(R_2Al)_2CH{-}CH_2{-}C_4H_9} \xrightarrow[-2\,Al^{3+},\,-4\,RD]{6\,D_2O/D^+} D_2CH{-}CH_2{-}C_4H_9 \qquad (4)$$

The results presented in Table 1 show that 1,1-bis(diisobutylaluminium)-hexane (IIb) is formed in the reaction of diisobutylaluminium hydride with hexyne-1 in a 80% yield and that a slight excess of the hydride has no influence on the yield of the product. The synthesis of 1,1-bis(diethylaluminium)hexane (IIa) is more complicated because the reaction proceeds more rapidly and it can easily get out of control. The best method for the synthesis seems to be a drop-

TABLE 1

REACTION CONDITIONS AND PRODUCTS OBTAINED BY HYDROLYSIS AND DEUTEROLYSIS OF THE REACTION MIXTURE OF DIISOBUTYLALUMINIUM HYDRIDE AND HEXYNE-1

Run	1	2	3
Molar ratio			
$i\text{-}Bu_2AlH : C_6H_{10}$	2 : 1	2.1 : 1	2.3 : 1
Temperature (°C)	80—85	70	75
Time (h)	4	8.5	3.5
Liquid products of hydrolysis (mol %) [a]			
hexane	85	83	87
hexene-1	7	9	6.8
hexyne-1	—	—	—
C_{10} hydrocarbons	4	6	4.6
C_{12} hydrocarbons	4	2	1.6
Deuterolysis (mol %) [b]			
1,1-dideuteriohexane	92	—	—
1,1,1-trideuteriohexane	8	—	—

[a] The amount of hydrocarbons formed during hydrolysis with the exception of isobutane was assumed to be 100% mol. [b] Total amount of deuterated hexanes was assumed to be 100%.

wise addition of hexyne-1 to diethylaluminium hydride at about 60°C. This method avoids rapid increase of the temperature and assures the presence of excess hydride during the reaction which reduces the possibilities of side-reactions (Table 2). The yield of geminal dialuminium compound obtained in this way was about 85%.

The compounds obtained are viscous liquids soluble in hydrocarbons and in methylene chloride. They are not distillable. At low temperatures they become glass-like solids. Our attempts of crystallization from solvents such as pentane and methylene chloride at low temperatures were not successful, and no method of purification was found.

Furthermore, the investigation of the hydrolyzed or deuterolyzed mixtures indicates the formation of small amount of monoaddition products, Ia, b (after hydrolysis hexene-1; eq. 5), dialkylhexyn-1-yl-aluminium, IIIa, b (eq. 6; hexyne-1) and 1,1,1-tris(dialkylaluminium)hexane (eq. 7; 1,1,1-trideuteriohexane).

$$\underset{\text{(Ia,b)}}{R_2Al{-}CH{=}CH{-}C_4H_9} + 3\,H_2O \xrightarrow[-Al^{3+}]{-2\,RH} HCH{=}CH{-}C_4H_9 \tag{5}$$

$$\underset{\text{(IIIa,b)}}{R_2Al{-}C{\equiv}C{-}C_4H_9} + 3\,H_2O \xrightarrow[-Al^{3+}]{-2\,RH} HC{\equiv}C{-}C_4H_9 \tag{6}$$

$$\underset{\text{(IVa,b)}}{(R_2Al)_3C{-}CH_2{-}C_4H_9} + 9\,D_2O \xrightarrow[-3\,Al^{3+}]{-6\,RD} D_3C{-}CH_2{-}C_4H_9 \tag{7}$$

(a, $R = C_2H_5$; b, $R = i\text{-}C_4H_9$)

After hydrolysis of the reaction mixture some long-chained hydrocarbons (C_8 or C_{10}, C_{12}) were also found, which indicates an Al—C addition.

2. *Complexes of geminal organoaluminium compounds with tertiary amines*

One of the characteristic properties of organoaluminium compounds is their ability to form complexes with Lewis bases. Furthermore donor-acceptor complex formation is always a first step in reactions with such compounds as protolytic agents (e.g. alcohols, primary and secondary amines, ketones, aldehydes, nitriles). In order to study the acceptor properties of the geminal dialuminium compounds their complexes with tertiary amines, namely triethylamine, pyridine and *N,N*-diethyl(trimethylsilyl)amine have been investigated.

In the mixtures of triethylamine with 1,1-bis(diethylaluminium)hexane (IIa) or 1,1-bis(diisobutylaluminium)hexane (IIb) the complexes at the molar ratio 1 : 1 were formed:

$$\underset{\text{(IIa,b)}}{(R_2Al)_2C_6H_{12}} + Et_3N \rightarrow \underset{\text{(Va,b)}}{(R_2Al)_2C_6H_{12} \cdot Et_3N} \tag{8}$$

(a, $R = C_2H_5$; b, $R = i\text{-}C_4H_9$)

TABLE 2

REACTION CONDITIONS AND PRODUCTS OBTAINED BY HYDROLYSIS AND DEUTEROLYSIS OF THE REACTION MIXTURE OF DIETHYLALUMINIUM HYDRIDE WITH HEXYNE-1

Run	1	2	3	4
Molar ratio				
$Et_2AlH : C_6H_{10}$	2 : 1	2 : 1	2.2 : 1	2 : 1
Method [a]	A	B	B'	C
Solvent	none	benzene	benzene	none
Time (h)	0.25	5	5 + 1	0.5
Temperature (°C)	60	60	60	60
Liquid products of hydrolysis (mol %) [b]				
hexane	80.4	75.5	87.4	89.2
hexene-1	6.5	16.7	2.1	2.1
hexyne-1	7.7	6.2	2.5	6.3
3-methylheptane	2.6	—	1.3	1.2
2-ethylhexene-1	2.8	1.6	6.2	1.2
C_{12} hydrocarbons	—	—	0.5	—
Deuterolysis [c]				
1,1-dideuteriohexane	—	—	—	95
1,1,1-trideuteriohexane	—	—	—	5

[a] Description in the experimental part. [b] The amount of hydrocarbon formed during hydrolysis with the exception of isobutane was assumed to be 100% mol. [c] Total amount of deuterated hexanes was assumed to be 100%.

The excess amine is in dynamic equilibrium with the 1 : 1 complex:

$$(R_2Al)_2C_6H_{12}\cdot Et_3N + Et_3N^* \rightarrow (R_2Al)_2C_6H_{12}\cdot Et_3N^* + Et_3N \qquad (9)$$

(Va,b)

This exchange can be easily observed in ^1H NMR (Table 3). Amine protons give well resolved signals of the free and complexed amine at 45°C (ambient temperature in the NMR apparatus) for the ethyl compound (IIa) (Table 3, line 11) and below +2°C for the isobutyl compound (IIb) (Table 3, line 8). At higher temperatures the exchange rate increases and only averaged signals of amine protons can be observed (Table 3, lines 3, 5). The excess triethylamine can be distilled off under vacuum and the non-volatile residue is identical with that obtained as a mixture at molar ratio 1 : 1 (Table 3, lines 2, 7).

1,1-bis(diethylaluminium)hexane (IIa) or 1,1-bis(diisobutylaluminium)-hexane (IIb) form complexes with pyridine at molar ratios 1 : 1 and 1 : 2.

$$(R_2Al)_2C_6H_{12} + C_5H_5N \rightarrow (R_2Al)_2C_6H_{12}\cdot C_5H_5N \qquad (10)$$

(IIa,b) (VIa,b)
yellow

$$(R_2Al)_2C_6H_{12}\cdot C_5H_5N + C_5H_5N \rightarrow (R_2Al)_2C_6H_{12}\cdot 2\ C_5H_5N \qquad (11)$$

(VIa,b) (VIIa,b)
dark red

(a, $R = C_2H_5$; b, $R = i\text{-}C_4H_9$)

^1H NMR spectra confirm the formation of both complexes (Table 4). The most

TABLE 3

^{1}H NMR SPECTRA OF THE MIXTURES OF TRIETHYLAMINE WITH 1,1-BIS(DIETHYLALUMINIUM)-HEXANE (IIa) OR 1,1-BIS(DIISOBUTYLALUMINIUM)HEXANE (IIb). POSITIONS OF THE MOST CHARACTERISTIC SIGNALS (δ, ppm)

No.	Molar ratio	$\underline{CH_2}$—N	$\underline{CH_3}$—CH_2—N	—$\underline{CH_2}$Al
	Et_3N : $(i\text{-}Bu_2Al)_2C_6H_{12}$			
1	1 : 0	2.49	0.97	—
2	1 : 1	2.79	1.12	—0.07
3	2 : 1 found	2.62	1.04	—0.07
4	2 : 1 calcd. [a]	2.64	1.05	—
5	3.4 : 1 found	2.58	1.03	—0.06
6	3.4 : 1 calcd. [a]	2.56	1.00	—
7	Non-volatile residue [b]	2.82	1.14	—0.06
8	2 : 1 at 2°C	2.81 [c]	1.12	
		2.50	— [d]	—0.08
9	0 : 1	—	—	0.29
	Et_3N : $(Et_2Al)_2C_6H_{12}$			
10	1 : 1	2.81	— [d]	—0.16
11	2 : 1	2.80 [c]	— [d]	—0.16
		2.50		
12	0 : 1	—	—	0.33

[a] Calculated for rapid exchange between excess amine and 1 : 1 complex. [b] Non-volatile residue left after distilling off the excess triethylamine. [c] Splitted signals due to free and complexed amine. [d] Covered by other strong signals.

characteristic feature is the alteration of chemical shifts of the pyridine protons with the molar ratio of reagents. When the molar ratio of organoaluminium compound to pyridine changes from 0.1 to 1 : 1 and then to 1 : 2 the signals of α protons shift to lower field while the signals of β and γ protons

TABLE 4

^{1}H NMR SPECTRA OF THE MIXTURES OF PYRIDINE WITH 1,1-BIS(DIISOBUTYLALUMINIUM)-HEXANE (IIb) OR 1,1-BIS(DIETHYLALUMINIUM)HEXANE (IIa). POSITIONS OF THE MOST CHARACTERISTIC SIGNALS (δ, ppm)

No.	Molar ratio	Pyridine protons			CH_2—Al
		H_α	H_β	H_γ	
	C_5H_5N : $(i\text{-}Bu_2Al)_2C_6H_{12}$				
1	1 : 0	8.62	7.22	7.63	—
2	1 : 1	8.69	7.60	8.06	0.06
3	2 : 1	8.74	7.56	8.01	0.07
4	3 : 1 found	8.69	7.45	7.88	0.07
5	3 : 1 calcd. [a]	8.70	7.45	7.88	8
6	Non-volatile residue [b]	8.73	7.56	8.00	0.07
7	0 : 1	—	—	—	0.29
	C_5H_5N : $(Et_2Al)_2C_6H_{12}$				
8	1 : 1	8.62	7.64	8.08	—0.10
9	2 : 1	8.68	7.51	7.96	—0.07
10	3 : 1 found	8.67	7.42	7.86	—0.06
11	3 : 1 calcd. [a]	8.66	7.41	7.85	—
12	0 : 1	—	—	—	0.33

[a] Calculated for rapid exchange between excess pyridine and 2 : 1 complex. [b] Non-volatile residue left after distilling off the excess pyridine.

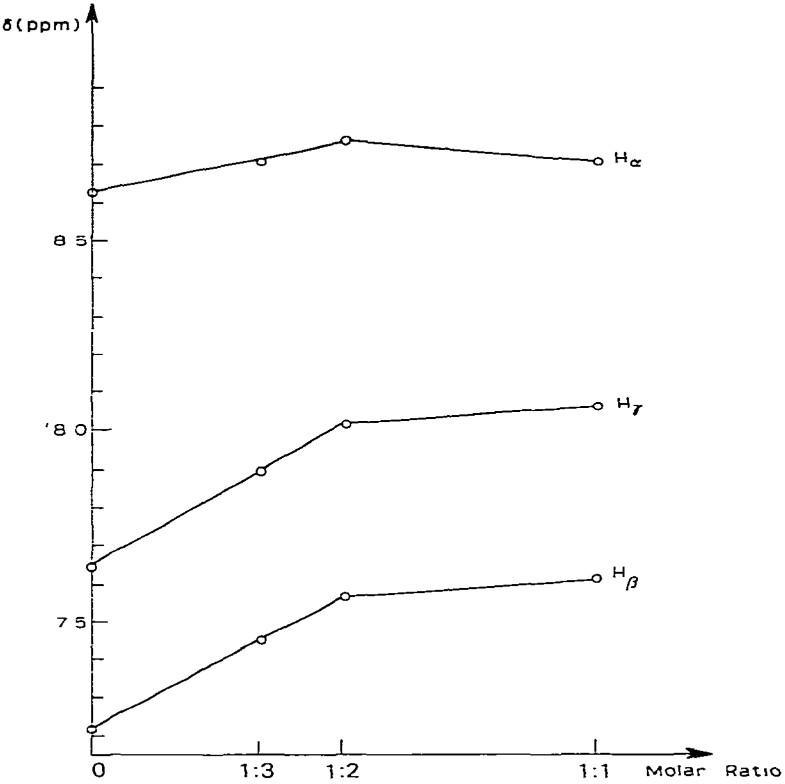

Fig. 1. Changes in the chemical shifts of the pyridine proton signals in its mixtures with 1,1-bis(diisobutylaluminium)hexane with molar ratio of organoaluminium compound to pyridine. (Molar ratio equal to 0 corresponds to pure pyridine.)

shift first to lower and then to the higher field (Table 4). In Fig. 1 the positions of the α, β and γ pyridine proton signals in free compound and in its mixtures with 1,1-bis(diisobutylaluminium)hexane are presented. A characteristic change of the slope at the point corresponding to the 1 : 2 complex is apparent. When excess pyridine is present in the mixture (molar ratio 1 : 3) a rapid exchange between free pyridine and 1 : 2 complex (VIIa, b) takes place and in the ^{1}H NMR spectrum only averaged signals of the pyridine protons are observed (Table 4, lines 4, 5 and 10, 11). The excess pyridine can be distilled off from its mixtures with 1,1-bis(diisobutylaluminium)hexane in vacuum and the non-volatile residue is identical to the 1 : 2 complex (VIIb).

The third amine, *N,N*-diethyl(trimethylsilyl)amine, was chosen with the aim of studying the influence of steric hindrance on complex formation. In this case the methylene protons of the amine in the mixtures with 1,1-bis-(diisobutylaluminium)hexane (IIb) at all investigated molar ratio (1 : 1, 2 : 1, 3 : 1) and in free amine give their signals at the same position ($\delta_{(CH_2-N)}$ = 2.84 ppm). It seems that no complex is formed.

On the basis of the above results it may be said that 1,1-bis(dialkylaluminium)hexane (IIa, b) can form complexes with an electron donor at molar ratios 1 : 1 as well as 1 : 2. It appears that the properties of the donor, especially

TABLE 5

ESTIMATION OF ELECTRONEGATIVITY OF Al ATOMS IN THE ISOBUTYL COMPOUNDS

Compound	Δ	χ (Al)
$(i\text{-Bu}_2\text{Al})_2\text{C}_6\text{H}_{12}$ (IIb)	—0.68	1.58
$i\text{-Bu}_2\text{AlC}_6\text{H}_{13}$	—0.70	1.57
$(i\text{-Bu}_2\text{Al})_2\text{C}_6\text{H}_{12} \cdot \text{C}_5\text{H}_5\text{N}$ (VIb)	—0.82	1.48 [a]
$(i\text{-Bu}_2\text{Al})_2\text{C}_6\text{H}_{12} \cdot 2\ \text{C}_5\text{H}_5\text{N}$ (VIIb)	—0.82	1.48 [a]
$i\text{-Bu}_2\text{AlNEt}_2$	—0.89	1.43
$(i\text{-Bu}_2\text{Al})_2\text{C}_6\text{H}_{12} \cdot \text{NEt}_3$ (Vb)	—1.00	1.35

[a] These results may not reflect true values. The ring current in the pyridine molecules may result in an abnormal deshielding of the methylene protons leading to higher electronegativity of the aluminium atoms.

the steric properties, decide which complex is formed.

Some additional information can be derived from ^{1}H NMR spectra of the investigated compounds. The internal chemical shift, i.e. the difference between signals of methylene and methyl protons of the isobutyl bonded to the aluminium atom, can be used for estimating the electronegativity of aluminium atoms in isobutyl compounds. The equation given by Takeshita [8] $\chi_{(\text{Al})} = 0.73\ \Delta + 2.08$ (where $\Delta = \delta_{(\text{CH}_3)} - \delta_{(\text{CH}_2)}$ for the isobutyl group) was used and the results given in Table 5 were obtained.

It is noteworthy that the electronegativity of the aluminium in 1,1-bis(diisobutylaluminium)hexane (IIb) is nearly the same as in the corresponding diisobutylhexylaluminium. The electronegativity decreases remarkably when 1,1-bis(diisobutylaluminium)hexane (IIb) forms complexes with amines (Vb—VIIb).

Experimental

All operations were performed in a purified dry nitrogen or argon atmosphere. All reagents were dried and distilled before use.

The NMR spectra were recorded with a Varian A-60A spectrometer at 60 MHz, using 33% solutions of the sample in methylene chloride.

1,1-bis(diisobutylaluminium)hexane (IIb)

Diisobutylaluminium hydride and hexyne-1 were mixed at 0°C at the required molar ratio (Table 1). Then the mixture was allowed to warm up slowly and next it was heated in an oil bath to 70—85°C to complete the reaction. During the reaction no gas evolution was observed. After cooling, the reaction mixture was hydrolyzed or deuterolyzed and the hydrocarbons formed were analysed by GLC—MS. (Results in Table 1.)

1,1-bis(diethylaluminium)hexane (IIa)

In this case the method described above (method A) led to uncontrolled reaction, especially when working in larger scale.

Method B. The solution of 8.6 g of Et_2AlH in 40 cm^3 of benzene was introduced into the reactor. Under stirring, 4.26 g of hexyne was added at about

+5°C. The reaction mixture was then allowed to warm up slowly, and its temperature raised up to 60°C. During this period some gas evolved. The mixture was kept at this temperature for 5 h, and then the solvent was distilled off. The analysis of the reaction mixture showed that the hydroalumination of hexyne-1 had not been completed (Table 2). This reaction could be completed by addding a small amount of diethylaluminium hydride (Method B′, Table 2). It means that some diethylaluminium hydride is used in metalation reactions.

Method C. To 1.63 g of diethylaluminium hydride, which was heated in an oil bath to 60°C, 1.08 ml of hexyne-1 was added dropwise. Then the reaction mixture was kept at 60°C for the next 1/2 h. During the reaction no gas evolution was observed. This method gave the best yield (89%, Table 2).

Hydrolysis

About 200 mg of the investigated geminal organodialuminium compound was dissolved in 0.8 cm^3 of pentane and then 0.2 cm^3 of ether was added. The mixture was cooled and several drops of water were added to the solution. When the evolution of gas ceased, aqueous HCl was added in excess. After hydrolysis, the organic layer was collected, washed and investigated by GLC (Tables 1 and 2).

Deuterolysis

A small sample of the investigated geminal organodialuminium compound was dissolved in benzene and cooled to +6°C. Then 20% DCl in D_2O or 10% D_2SO_4 in D_2O was added dropwise to the solution. The temperature did not exceed +20°C. The organic layer was investigated by GLC-MS (Tables 1 and 2). The complexes with tertiary amines were obtained simply by mixing the weighed amounts of reagents. In some cases geminal dialuminium compound was mixed with an excess of amine and then kept for some hours under vacuum (10^{-1}—10^{-2} mmHg). The nonvolatile residue was then used for spectroscopic investigations.

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References

1 A. Storr, K. Jones and A.W. Laubengayer, J. Amer. Chem. Soc., 90 (1969) 3173.
2 H. Imaeda, T. Hirabayashi, K. Itoh and Y. Ishii, Organometal. Chem. Synth., 1 (1970/1971) 115.
3 K. Gesling, J.D. Smith and D.H.W. Wharmby, J. Chem. Soc. A, (1969) 1738.
4 K. Gesling, G.M. McLaughlin, G.A. Sinn and J.D. Smith, Chem. Commun., (1970) 1617.
5 P. Schönfeld, M. Hollmann, H. Reinheckel, G. Sonnek und D. Jahnke, Z. Chem., 19 (1979) 221.
6 W. Schneider, Dissertation, Aachen, 1962.
7 G. Wilke and H. Müller, Liebigs Ann. Chemie, 629 (1960) 222.
8 T. Takeshita and W.E. Frankle, Tetrahedron. Lett., 56 (1968) 5913.
9 H. Reinheckel, M. Hollmann and D. Jahnke, to be published; M. Hollmann, Dissertation, Berlin, 1977.