

THE CHEMISTRY AND STEREOCHEMISTRY OF POLY(*N*-ALKYLIMINOALANES).

XVII *. THE SYNTHESSES OF POLY(*N*-ALKYLIMINOALANES) FROM DIMETHYLAMINO- OR METHOXY-PROPYLAMINES

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(Received November 2nd, 1979)

Summary

3-Dimethylamino-*n*-propylamine, 2-dimethylamino-isopropylamine and 3-methoxy-*n*-propylamine have been used to synthesize poly(*N*-alkyliminoalanes) (PIA) by different routes. These amines yielded PIA with open cage structures, in some cases even under the rather drastic conditions of direct synthesis from aluminum, amine and hydrogen. Reaction between LiAlH_4 and amines gave open cage complexes with LiH.

Introduction

Primary amines usually give poly(*N*-alkyliminoalanes) [2] (PIA) of composition $(\text{HAlNR})_n$, characterized by closed cage molecular structures, independent of the synthesis method. However exceptionally stable open cage tetramer structures, $\text{H}_2\text{Al}(\text{NRAlH})_3\text{NHR}$, were obtained from highly hindered amines, i.e., from *tert*-butylamine [3] and 1-phenyl-ethylamine [4]. Preliminary studies indicated a tendency for some dimethylamino- or methoxy-substituted primary amines to yield PIA with an $\text{H}_{\text{active}}/\text{Al}$ atomic ratio greater than 1, related to the formation of open cage molecular structures. This seemed worthy of further investigation in view of the importance of these molecular features in enhancing the activity of PIA used as polymerization co-catalysts [5] or as reducing agents of organic substrates [6].

* For Part XVI see ref. 1

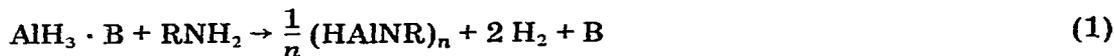
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Results and discussion

Various synthetic methods were examined for the synthesis of poly(*N*-alkyliminoalanes [2]. These methods when applied to dimethylamino- and/or methoxy-propylamines gave the following results.

1. Reaction between AlH_3 complexes and amines

The reaction between $AlH_3 \cdot B$ ($B = \text{ether, THF, trimethylamine}$) and primary amines usually yields a closed cage structure according to equation 1.



The value of n ranges [3] from 4 to 10 (exceptionally [7] 16), depending on the branching of R . Only in the case of *tert*-butylamine [3] and from 1-phenylethylamine [4] did this method give stable open tetrameric cages (equation 2).



The results for the reaction of $AlH_3 \cdot B$ and $(CH_3)_2N(CH_2)_3NH_2$ (3-DMAPA) or

TABLE 1

RESULTS OF THE SYNTHESIS OF POLY(*N*-ALKYLIMINOALANES) FROM AlH_3 COMPLEXES OR $MAIH_4$ ($M = Li, Na$) AND DIMETHYLAMINO- OR METHOXY-PROPYLAMINES

Run	Reagents			Reaction conditions			Reaction product
	AlH_3 complex (mmol)	$MAIH_4$ (mmol)	Amine ^a (mmol)	Solvent (ml)	$T(^{\circ}C)$	time (h)	Yield (g)
1	$AlH_3 \cdot NMe_3$ (25)	—	3-DMAPA (25)	Toluene (80)	25	1.8	2.9 ^b n.d. ^c
2	$(AlH_3)_n \cdot Et_2O$ (60)	—	3-DMAPA (60)	Et_2O (130)	25	18	6.5 ^b
3	$AlH_3 \cdot NMe_3$ (47)	—	3-MOPA (47)	Toluene (140)	25	5	4.8 ^b
4	—	$NaAlH_4$ (20)	3-DMAPA (10)	Toluene (50)	110	20	0.8 ^c
5	—	$LiAlH_4$ (62)	3-DMAPA (58)	Toluene (200)	110	20	4.1 ^c
6	—	$LiAlH_4$ (68)	3-DMAPA (40)	Toluene (150)	110	20	3.2 ^b
7	—	$LiAlH_4$ (68)	2-DMAPA (40)	Toluene (150)	110	30	4.3 ^b

^a 3-DMAPA = $(CH_3)_2N(CH_2)_3NH_2$; 2-DMAPA = $(CH_3)_2NCH_2(CH_2)CHNH_2$; 3-MOPA = $CH_3O(CH_2)_3NH_2$.

^b Crude product. ^c Crystallization product. ^d Calcd. values for $[HAINC_3H_6N(CH_3)_2]_n$. ^e Calcd. values for $[HAINC_3H_6N(CH_3)_2]_n [H_2AlNHC_3H_6N(CH_3)_2]_n$. ^f Calcd. values for $[HAINC_3H_6OCH_3]_{2n} [H_2AlNHC_3H_6OCH_3]_n$. ^g Calcd. values for $[HAINC_3H_6N(CH_3)_2]_6 \cdot 2 LiH$. ^h XX = crystalline; A = amorphous.

$\text{CH}_3\text{O}(\text{CH}_2)_3\text{NH}_2$ (3-MOPA) are shown in Table 1.

The chemical and physico-chemical properties are consistent with the formation of hexameric $[\text{HAlN}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_6$ (I) from the reaction of $\text{AlH}_3 \cdot \text{N}(\text{CH}_3)_3$ with 3-DMAPA, according to eq. 1. Chemical analyses ($\text{N}/\text{Al} = 2$; $\text{H}_{\text{active}}/\text{Al} = 1$) indicate the formation of closed cage compounds, while mass spectrometry strongly supports the occurrence of the hexameric species. The mass spectrum shows the parent ion at m/e 768, as well as ions $(M - \text{H})^+$ at m/e 767 and $(M - (\text{CH}_2\text{N}(\text{CH}_3)_2))^+$ at m/e 710, as expected from the fragmentation patterns of other PIAs [3]. The ^1H NMR spectrum shows one triplet due to $-\text{CH}_2-\text{N}-\text{Al}$ at τ 6.59. The equivalence of the imino groups is consistent with the formation of a cage skeleton formed by two hexagonal rings $(\text{AlN})_3$ joined by six transverse $\text{Al}-\text{N}$ bonds, as suggested by the fully defined molecular structure of $(\text{HAlNi}-\text{C}_3\text{H}_7)_6$ [8]. In addition one poorly defined $-\text{CH}_2-\text{CH}_2-\text{N}-\text{Al}$ multiplet is found at ca. τ 7.99, and the $-\text{CH}_2-\text{N}(\text{CH}_3)_2$ triplet partially overlaps the singlet at τ 7.74 due to $-\text{N}(\text{CH}_3)_2$ protons. The infrared spectrum in Nujol exhibits one sharp $\nu(\text{Al}-\text{H})$ absorption at 1780 cm^{-1} , i.e. at a lower frequency than those observed (usually 1850 cm^{-1}) for hexameric PIAs from unsubstituted aliphatic amines. In the light of general IR data for aluminum hydride

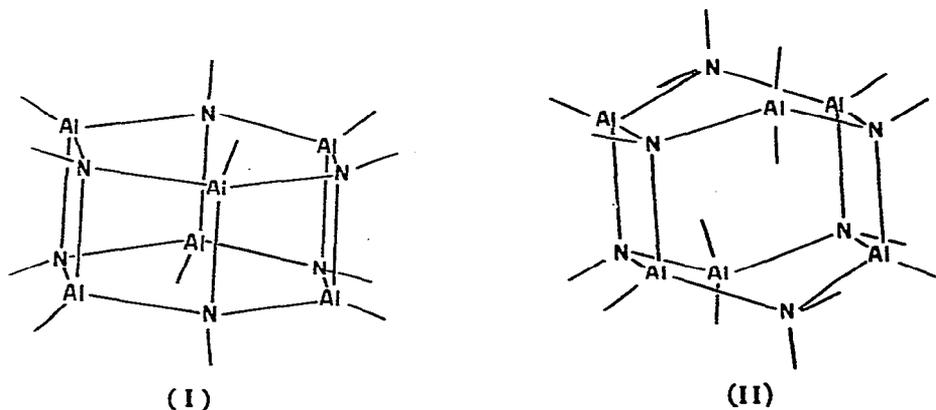
Chemical composition - found (calcd.)						RX powder anal. ^h	$\nu(\text{Al}-\text{H})$ (cm^{-1}) in Nujol	Structure as indicated by physico-chemical data
Al (%)	N (%)	M (%)	H_{act} (meq/g)	M/Al atomic ratio	$\text{H}_{\text{act}}/\text{Al}$ atomic ratio			
19.9	21.3	—	7.39	—	1.0	XX	1870	closed cage hexamer
(21.1)	(21.9)	—	(7.81) ^d	—	(1.0)			
21.0	21.5	—	12.0	—	1.52	XX	1870; 1700	open cage hexamer
(20.9)	(21.7)	—	(11.6) ^e	—	(1.50)			
23.5	12.3	—	11.3	—	1.3	A	1780; 1790	open cage hexamers
(23.3)	(12.1)	—	(11.5) ^f	—	(1.3)			
18.9	20.5	0.5	7.56	0.1	1.08	XX	1780	closed cage hexamer
20.7	22.6	1.8	11.1	0.3	1.4	XX	1780; 1630	predominantly hexamer and its LiH complex
(20.6)	(21.4)	(1.8)	(10.2) ^g	—	—			
21.1	19.6	2.1	10.8	0.4	1.4	XX	1770; 1650	predominantly hexamer and its LiH complex
20.9	20.8	0.7	11.3	0.1	1.46	A	1690	predominantly open tetramer
(20.9)	(21.7)	—	(11.6) ^e	—	—			

derivatives [9], this suggests some coordinative interaction of the $-\text{N}(\text{CH}_3)_2$ groups with the aluminum atoms of the $(\text{AlN})_6$ skeleton. The reaction of aluminum hydride etherate with 3-DMAPA yields hexameric open cage species $[(\text{HAlN}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2)_3(\text{H}_2\text{AlNH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2)_3]$ (II) according to eq. 3.



Chemical analyses ($\text{N}/\text{Al} = 2$; $\text{H}_{\text{active}}/\text{Al} = 1.5$) are consistent with the formation of open cage molecules. The mass spectrum supports the hexameric structure; it is similar to the spectrum observed for I. It must be emphasized that so far mass spectrometry has not been useful in detecting open cage structures, which rearrange to the corresponding closed structures under the measurement conditions. This was verified earlier for open tetrameric PIA from *tert*-butylamine and from 1-phenylethylamine. However the presence of open cage structures is strongly supported by the ^1H NMR spectrum, which shows a multiplicity of signals for the protons of coexisting imino $-\text{CH}_2-\text{N}-\text{Al}$ and amino $-\text{CH}_2-\text{NH}-\text{Al}$ groups and two singlets at τ ca. 7.70 and 7.93 assigned to $-\text{N}(\text{CH}_3)_2$ protons. Two signals for $-\text{N}(\text{CH}_3)_2$ (the starting amine shows one singlet $-\text{N}(\text{CH}_3)_2$ at τ 7.84) were unexpected in the light of the spectra of the PIA from unsubstituted primary amines; ^1H NMR spectra showed no influence of the $(\text{AlN})_n$ skeleton structure on protons more distant than those bonded to α - or β -carbon atoms of the imino groups [10]. The spectrum of II, however, could be explained by some coordinative interaction, especially of $-\text{N}(\text{CH}_3)_2$ groups of the amino units with aluminum atoms. As expected from the observed thermal rearrangement of other open cage PIA, the ^1H NMR gives evidence for the gradual heat-promoted transformation of II into the corresponding closed hexameric species I; the $-\text{CH}_2-\text{N}-\text{Al}$ imino or amino group multiplet and the $-(\text{CH}_3)_2$ protons multiplet gradually are transformed into the triplet at τ 6.59 and the singlet at τ 7.74, respectively, for the closed hexamer I. The IR spectrum of II shows a broad $\nu(\text{Al}-\text{H})$ absorption at 1780 cm^{-1} and a shoulder at a lower frequency.

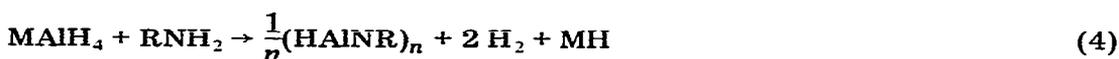
Further information is necessary to provide structural details of II; particularly in view of a possible coordinative interaction of $-\text{N}(\text{CH}_3)_2$ groups with aluminum atoms. However, in the case of tetracoordinate aluminum atoms a reasonable structure for II could have the following $(\text{AlN})_6$ skeleton:



The synthesis of hexameric open cage structures is also supported by the reaction of $\text{AlH}_3 \cdot \text{N}(\text{CH}_3)_3$ and 3-MOPA. The formation of hexameric species was indicated by the mass spectrum, with ions $(M - \text{H})^+$ at m/e 689, plus ions at m/e 659 derived from the molecular ion by loss of one $-\text{CH}_2-\text{CH}_2\text{OCH}_3$ group. The ^1H NMR spectrum shows a complex multiplet in the range τ 6.41–6.84 attributed to $-\text{O}-\text{CH}_3$ and $-\text{O}-\text{CH}_2-$ protons of amino and imino groups. Upon heating, a signal at τ 6.78, assigned to $-\text{O}-\text{CH}_3$ of imino groups, increases as expected for the transformation from open to closed cages. In every case CH_2 signals overlap and are poorly resolved. The IR spectrum in Nujol shows a broad $\nu(\text{Al}-\text{H})$ absorption with a maximum at 1780–1790 cm^{-1} .

2. Reaction between alkali metal alanates and amines

Closed cage PIAs have been shown previously [11] to be formed in the reaction between lithium or sodium alanate and branched unsubstituted primary amines, even in the case of tert-butylamine (equation 4), whereas insoluble undefined products were formed from linear amines.



(M = Li, Na)

The synthesis of hexameric PIA with a closed cage structure I was also carried out by treating NaAlH_4 with 3-DMAPA. In contrast, a complex of a hexameric open cage PIA with LiH was isolated from the reaction of 3-DMAPA and LiAlH_4 , and the formation of a tetrameric open cage structure was found for LiAlH_4 and $(\text{CH}_3)_2\text{NCH}_2(\text{CH}_3)\text{CHNH}_2$ (2-DMAPA); either the alkali metal or the amine affects the nature of the final PIA. In particular the tendency of the more branched amines to yield PIA with simpler $(\text{AlN})_n$ skeleton is confirmed. Evidence for the formation of I is based on the chemical behaviour and physico-chemical data described above. The presence of PIA complexed with LiH in the product from 3-DMAPA and LiAlH_4 is indicated by the mass spectrum, which, in addition to the typical fragments of the hexameric PIA, exhibits less abundant ions $(M + \text{Li})^+$ at m/e 775 and $(M + \text{LiHLi})^+$ at m/e 783. Also the presence of small amounts of a pentamer and its LiH complex is supported by the presence of ions $[M - (\text{CH}_2\text{N}(\text{CH}_3)_2)]^+$ at m/e 582 and at m/e 590 respectively.

A single crystal of the crystalline complex $[\text{HAIN}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_6 \cdot 2 \text{LiH}$ was successfully separated from the reaction mixture; its molecular structure has been fully established by X-ray studies [12].

Independently of the occurrence of the PIA · LiH complex ($\text{Li}/\text{Al} = 0.12$), the formation of open cage structures ($\text{H}_{\text{active}}/\text{Al} = 1.46$) is shown by the chemical composition of the product from LiAlH_4 and 2-DMAPA. Its mass spectrum shows it to be a tetramer with abundant ions at m/e 511 and at m/e 454, attributed to $(M - \text{H})^+$ and to $[M - (\text{CH}_2\text{N}(\text{CH}_3)_2)]^+$ of the $(\text{AlN})_4$ skeleton respectively.

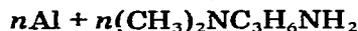
3. Reaction between aluminum and amine

The reaction between aluminum and amine under a pressure of hydrogen provides the more direct route to PIA [13]. It occurs at high temperature, which is

known to favour the formation of closed cage structure [3]. These structures were obtained only from unsubstituted primary amines, according to eq. 5. It is



therefore surprising that open cage structures were obtained from 3-DMAPA and from 2-DMAPA according to eq. 6. As in the direct synthesis of PIA from unsubstituted amines, reaction 6 also is promoted by an activator i.e. NaAlH_4 .



$$n = x + y; z = \frac{x - y}{2}$$

The results reported in Table 2 indicated that the use of toluene rather than ether as a solvent, and branching of the R radical favour the formation of open cage structures. They also confirm that the branching leads to PIA with a simpler AlN) skeleton. All the products were identified from the physico-chemical data described above.

The formation of new tetrameric PIA with open cage structures from 2-DMAPA was also demonstrated by the ^1H NMR data. The ^1H NMR spectrum of product III (Table 2 run 3; Fig. 1. a) shows doublets due to N—CH—(CH₃)— at τ 8.49, 8.48 and 8.26 with relative intensities 2 : 1 : 1. This is consistent with two imino units N—CH(CH₃)— linked to two Al—H groups and to

TABLE 2

RESULTS OF THE DIRECT SYNTHESIS OF POLY(N-ALKYLIMINOALANES) FROM ALUMINUM AND DIMETHYLAMINOPROPYLAMINES

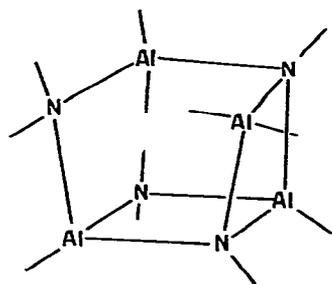
Run	Reagents		NaAlH ₄ (mmol)	Reaction conditions			
	Aluminum (mmol)	Amine ^a (mmol)		Solvent (ml)	T(°C)	P(H ₂) (kg/cm ²)	time (h)
1	140	3-DMAPA (100)	5	Et ₂ O (250)	130	150	16
2	200	3-DMAPA (120)	6	Toluene (300)	145	165	36
3	160	2-DMAPA (90)	4.5	Et ₂ O (300)	100	130	18
4	160	2-DMAPA	4	Toluene (300)	140	160	18

^a 3-DMAPA = 3-dimethylamino-n-propylamine; 2-DMAPA = 2-dimethylamino-isopropylamine. ^b The yield was practically quantitative with respect to amine. ^c Calcd. values for $[\text{HAlNC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_n$.

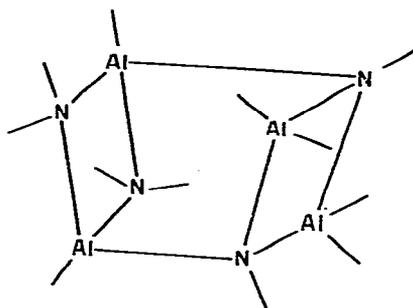
^d Calcd. values for $[\text{HAlNC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_x [\text{H}_2\text{AlNHC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_y$. ^e Calcd. values for $[\text{HAlNC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_n [\text{H}_2\text{AlNHC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_n$. ^f Calcd. values for $[\text{HAlNC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_{3n} [\text{H}_2\text{AlNHC}_3\text{H}_6\text{N}(\text{CH}_3)_2]_n$.

^g XX = crystalline; A = amorphous.

one AlH_2 group, one imino unit linked to three Al-H groups and one amine unit $\text{NH-CH(CH}_3\text{)-}$, as previously found for an open tetramer with a skeleton type IV [3,4]. Furthermore two different $-\text{N(CH}_3\text{)}_2$ singlets at τ 7.48 and 7.71 are observed, with relative intensities 1 : 3. (The amine starting material has one singlet at τ 7.85).



(IV)



(VI)

The ^1H NMR spectrum of product V from 2-DMAPA (Table 2, run 4) in toluene (Fig. 1. b) shows two $-\text{N-CH(CH}_3\text{)-}$ doublets at τ 8.34 and 8.57 and two $-\text{N(CH}_3\text{)}_2$ singlets at τ 7.41 and 7.71. The relative intensities (1 : 1) in both cases suggest the formation of a doubly open PIA. Such a PIA could have a central $(\text{AlN})_4$ skeleton, as does VI in the case of tetracoordinated aluminum. The different chemical shifts of the $-\text{N(CH}_3\text{)}_2$ singlets for the individual products could again be explained by some interaction with the aluminum atoms, but no further details are yet available about the structure of these new PIAs.

When either III or V is heated, three broad ^1H NMR signals arise at τ 6.4 for

Reaction product ^b Chemical Composition - Found (Calcd.)				$\nu(\text{Al-H})$ (cm^{-1}) in Nujol	RX powder analysis ^g	Structure as indicated by physico-chemical data
Al (%)	N (%)	$H_{\text{act.}}$ (meq/g)	$H_{\text{act.}}/\text{Al}$ atomic ratio			
21.2 (21.1)	21.8 (21.9)	8.3 (7.8) ^c	1.06	1780	XX	Closed cage hexamer
19.9 (21.0)	19.8 (21.8)	10.1 (10.4) ^d	1.37	1790	XX	Open cage hexamer
21.3 (21.0)	21.7 (21.8)	10.4 (9.7) ^f	1.32	1750 1650 (sh)	A	Open cage tetramer (III)
20.9 (20.9)	20.6 (21.7)	11.5 (11.6) ^e	1.49	1650 1750 (sh)	A	Open cage tetramer (V)

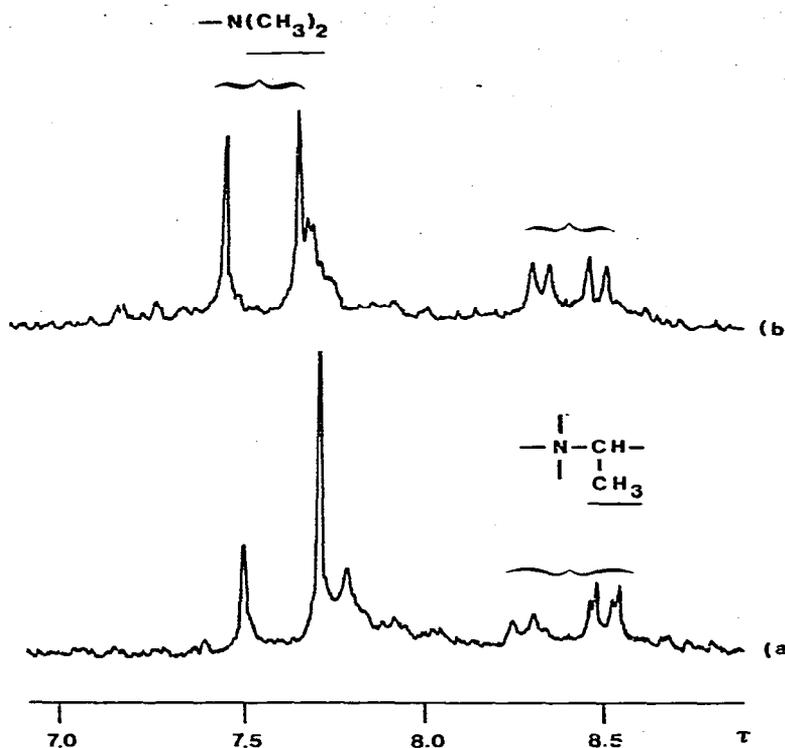


Fig. 1. ^1H NMR spectra of open poly(*N*-alkyliminoalanes) from 2-dimethylamino-iso-propylamine.

CH, at τ 7.7 for $-\text{N}(\text{CH}_3)_2$ and at τ 8.5 for $\text{N}-\text{CH}(\text{CH}_3)-$ protons, consistent with the transformation of the open cage into a closed hindered structure.

Experimental

Reagents and solvents

$\text{AlH}_3 \cdot \text{N}(\text{CH}_3)_3$ was prepared from LiAlH_4 (Merck-Schuchardt) and $\text{N}(\text{CH}_3)_3 \cdot \text{HCl}$ according to the method of Ruff and Hawthorne [14]. $\text{AlH}_3 \cdot n\text{Et}_2\text{O}$ and $\text{AlH}_3 \cdot \text{THF}$ were obtained from LiAlH_4 and AlCl_3 in diethyl-ether or tetrahydrofuran [15]. Commercial NaAlH_4 (Metalgesellschaft A.G.) and aluminum (Walter Marx A9T8) were used without further treatment. Pure commercial amines were dried and purified by distillation from Na or from KOH. All solvents were purified and dried by standard methods and all syntheses were carried out under nitrogen, except for the direct syntheses from aluminum, which were performed under a pressure of hydrogen.

Chemical analyses and physico-chemical measurements

Chemical analyses were performed as described in our previous paper [3]. The physico-chemical instruments were also the same, except that a Perkin-Elmer model 157 IR spectrometer was used.

Synthesis of poly(*N*-alkyliminoalanes)

Typical preparations are reported. (a) A solution of 3-dimethylamino-*n*-propylamine (60 mmol) in diethylether (40 ml) was added dropwise to a stirred suspension of aluminum hydride etherate (60 mmol) in diethylether (90 ml) at 25°C. Hydrogen was immediately evolved. The mixture was stirred at 25°C for 18 h, then the solution was filtered to remove traces of insoluble material and evaporated in vacuo. The white solid residue was dried (8 h, 25°C, 1×10^{-3} mmHg) and analyzed (Found: Al, 21.0; N, 21.5%; H_{active} 12.0 meq/g. $C_{30}H_{84}Al_6N_{12}$ calcd.: Al, 20.9; N, 21.7%; H_{active} 11.6 meq/g). The yield was 6.5 g. (b) A solution of 3-dimethylamino-*n*-propylamine (58 mmol) in toluene (60 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (62 mmol) in toluene (140 ml) at room temperature. Hydrogen was immediately evolved. The mixture was refluxed for 20 hours and filtered. After filtration, the solution was concentrated and cooled to 5°C. Crystals then separated were dried (8 h, 25°C, 1×10^{-3} mmHg) and analyzed (Found: Al, 20.7; Li, 1.8; N, 22.6%; H_{active} 11.1 meq/g. $C_{30}H_{80}Al_6Li_2N_{12}$ calcd.: Al, 20.6; Li, 1.8; N, 21.4%; H_{active} 10.2 meq/g). The yield was 4.1 g. (c) A mixture of powdered aluminum (160 mmol), toluene (300 ml), $NaAlH_4$ (4 mmol), and 2-dimethylamino-isopropylamine (90 mmol) was introduced into one liter stainless steel autoclave furnished with an anchor stirrer. The mixture was stirred for 18 h under a pressure of hydrogen (160 kg/cm^2) at 140°C, then the autoclave was allowed to cool to room temperature. The solution was filtered and the solvent was removed by evaporation in vacuo. The solid white residue was dried (10 h, room temp., 1×10^{-3} mmHg) and analyzed (Found Al, 20.9; N, 20.6%; H_{active} 11.5 meq/g. $C_{20}H_{50}Al_4N_8$ calcd.: Al, 20.9; N, 21.7%; H_{active} 11.6 meq/g). The yield was quantitative.

Acknowledgments

The authors thank the Assoreni management for permitting publication of this work.

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